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STRUCTURE-PROPERTY RELATIONSHIPS IN FLUORINATED ORGANIC-ORGANOMETALLIC POLYMERS

BY

XIUGUANG ANDREW GUO ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
FALL, 1994

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F. Cantwell (Chairman)

Michael C. Williams

M. C. Williams (Co-supervisor)

M. Cowie

D. Clive

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DATE: Sept. 28, 1994

谨以此论文献给我望子成龙的双亲、勤劳朴实的齐鲁父老

及含辛茹苦的妻子。

Dedicated to my parents and my wife Joanna

ABSTRACT

A novel diol monomer, $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-tetrafluorobenzenedimethanol, was synthesized by derivatization from 1,2,4,5-tetrafluorobenzene. Four polyesters, one polycarbonate, and two polyurethanes were subsequently prepared from the diol. Each polymer was fully characterized by GPC, NMR, FTIR, and UV-Visible spectroscopies.

Five acrylic esters having different fluorine contents and distributions in their side-groups have been prepared. These monomers were polymerized by AIBN and five polyacrylates were prepared. The polymers were fully characterized by GPC, VPO, DSC, TGA, NMR, FTIR, and UV-Visible spectroscopies. Significant differences in their thermal stabilities were found.

The synthesis and characterization of five novel organonickel-organosilicon copolymers were reported. Two model compounds were prepared and characterized and the polymers were subsequently prepared accordingly. Each polymer was fully characterized by GPC, VPO, NMR, FTIR, and UV-Visible spectroscopies. Observations indicate that introduction of silyl or siloxane units into organonickel main-chains has significantly decreased the backbone rigidity of the polymers. Nine organosilicon derivatives of 1,2,3,5- and 1,2,4,5-tetrafluorobenzene were also prepared. They have been characterized by conventional analytical and spectroscopic means, and one has had its structure confirmed by X-ray crystallography.

Molecular weights of two organonickel polymers have been obtained from GPC traces using both a direct calibration and a universal calibration. The latter method was found more reliable. An iterative data-fitting procedure using GPC and dilute-solution viscosity measurements indicated that these polymers possess a rod-like structure. The GPC behavior of 13 related organonickel oligomers was also examined and found consistent with the polymer performance.

The syntheses of 27 new organometallic azine and thiaazine derivatives of iron were reported. Their analytical and spectroscopic characterizations indicated that in each case the Fp fragments are bonded to the heterocyclic rings by Fe-C σ-bonds. This was confirmed for five representative complexes by the determination of their X-ray crystal structures. The organometallic derivatives of heterocyclic rings might be biologically active.

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LIST OF ABBREVIATIONS AND SYMBOLS

AIBN	2,2'-azobis(2-methylpropionitrile)
ANAL.	analysis
bp	boiling point
br	broad (IR or NMR signals)
BPO	benzoyl peroxide
n-Bu	*n*-butyl ($CH_3CH_2CH_2CH_2$—)
ca.	circa (approximately)
CaH_2	calcium dihydride
cal	calories
Calcd	calculated
CD_2Cl_2	dichloromethane-d_2
$(CD_3)_2SO$	dimethyl sulfoxide-d_6
CH_2Cl_2	dichloromethane
d	doublet (NMR signals)
dL	deciliters (10^{-1} L)
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide ($(CH_3)_2S{=}O$)
$\overline{DP}_n$	number-average degree of polymerization
DSC	Differential Scanning Calorimetry
EA	elemental analysis
EtOH	ethanol (CH_3CH_2OH)
Et_2O	diethyl ether
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
h	hour

Hex	*n*-hexyl ($CH_3CH_2CH_2CH_2CH_2CH_2$—)
HPLC	High Performance Liquid Chromatography
IR	Infrared
LS	Light Scattering
m	medium (IR signals); multiplet (NMR signals)
MDI	methylenedi-1,4-phenyl diisocyanate
Me	methyl (CH_3—)
MeOH	methanol (CH_3OH)
mg	milligrams
min	minutes
mL	milliliters
mmol	millimoles
$\overline{M}_n$	number-average molecular weight
mp	melting point
$\overline{M}$	average molecular weight
$\overline{M}_p$	molecular weight at the peak of GPC traces
$\overline{M}_v$	viscosity-average molecular weight
MW	molecular weight
$\overline{M}_w$	weight-average molecular weight
MWD	molecular weight distribution
m/z	mass to charge ratio in the mass spectrum
$\overline{M}_z$	Z-average molecular weight
N_2	dinitrogen
$Na[Ph_2CO]$	sodium benzophenone ketal
nm	nanometer (10^{-9} m)
NMR	Nuclear Magnetic Resonance
P^+	parent ion in the mass spectrum

PDI	polydispersity index ($\overline{M}_w / \overline{M}_n$)
Ph	phenyl (C_6H_5—)
ppm	parts per million
q	quartet (NMR signals)
R.T.	room temperature (*ca*. 23°C)
s	strong (IR signals); singlet (NMR signals)
sh	shoulder (IR signals)
t	triplet (NMR signals)
TDI	tolylene 2,4-diisocyanate
Tg	glass transition temperature
TGA	Thermal Gravity Analysis
THF	tetrahydrofuran
UV	Ultraviolet
VPO	Vapor Pressure Osmometry
vs	very strong (IR signals)
w	weak (IR signals)
$[\eta]$	intrinsic viscosity
Å	Angstrom
µL	microliters
µm	microns (10^{-6} m)

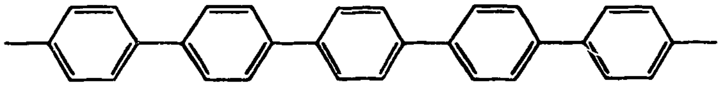
CHAPTER 1

GENERAL INTRODUCTION

Over the last twenty years, there has been extensive interest in the synthesis of organic polymers having delocalized π systems.[1-7] The materials that have been most widely studied are *trans*-polyacetylene, i.e.,

I

and various polyaromatic systems such as poly(*para*-phenylene), **II**, polythiophene, **III**, and polypyrrole, **IV**, i.e.,



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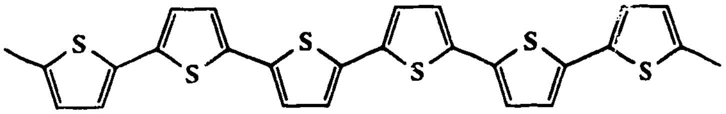

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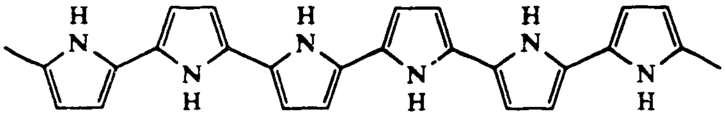
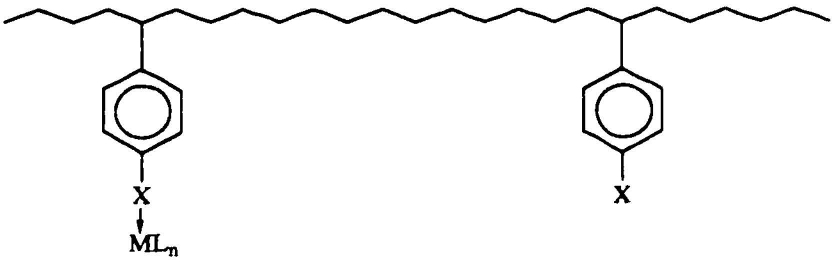


IV

and their derivatives. The delocalization of electron density along the polymer backbone in such species gives them a variety of remarkable physical properties including electrical conductivity, photoconductivity, and non-linear optical behavior. These properties are widely expected to give these materials substantial commercial applications in the near future in a variety of applications where they are thought of either as synthetic metals or as components of unique materials such as solar cells, electronic devices, or high-energy-density batteries. For this reason, they have been the subject of intense scrutiny in academic, military and industrial laboratories.

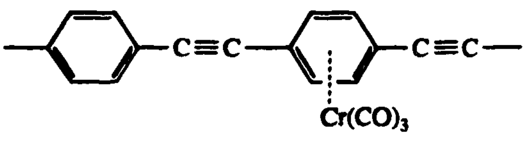
Investigations on transition-metal-containing polymers have been rare but interest has been growing over the last decade.[6,8-18] Most of the work on the synthesis of organometallic polymers can be classified into one of two categories, namely: primarily organic backbone polymers having pendant organometallic fragments and inorganic coordination polymers.

Much of the early work on organometallic polymers concentrated on the synthesis of organometallic polymers in which the metal centers were not an intrinsic part of the polymer backbone.[5,9,12c,19] Thus the "polymer part" of the term organometallic polymer was derived from the organic polymer backbone (generally a polystyrene derivative) while the "organometallic part" was due to the presence of pendant organometallic fragments, e.g.,



V

where X = $-CH=CHR$, $-PR_2$, $-NR_2$, $-SR$, etc. More recently, researchers have also begun to investigate the electrical properties of such species on, for instance, electrode surfaces and of newer polymers in which the polymer backbone contains a delocalized π system,[4,8,12e,19] e.g.,



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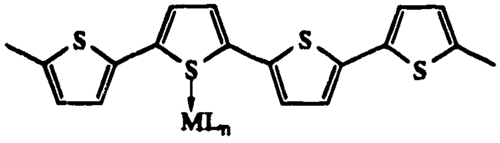
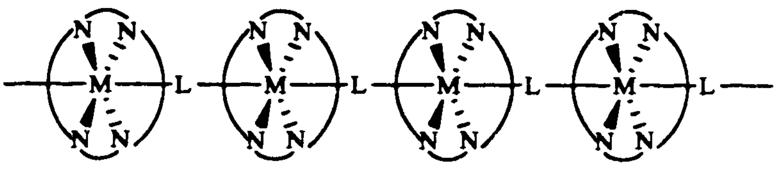


VI

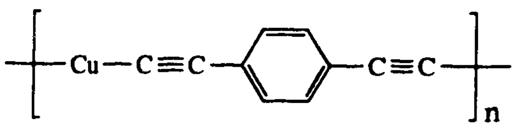
VII

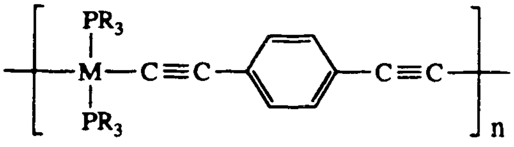
The second approach has been to prepare polymers in which the metal center is an integral part of the polymer backbone.[6,12c,12f,20] To date, almost all of the work reported in this area has involved species that can be classified as inorganic coordination polymers (such as phthalocyanines, porphrins, etc.) and the metal centers are joined either by direct metal-metal bonds or by conventional inorganic ligands in which the metal is bound to the heteroatoms (such as O, N, S, etc.) of the bridging groups, e.g.,



VIII

However, very little work has been reported in which a "true" transition-metal organometallic polymer (that is, one with the metal atoms in the polymer backbone and with the bridging ligands being attached to the metal through metal-carbon covalent bonds) had been prepared. One of the few examples of such species is a series of acetylide-bridged complexes which have been reported for Cu, Ni, Pd and Pt, e.g.,[6,9,21]

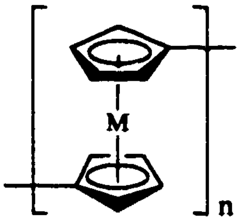




IX

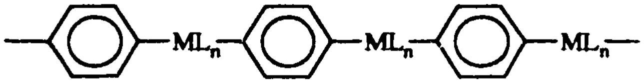
X

where M = Ni, Pd or Pt. Another example is a series of polymetallocenes in which the metal is incorporated into the polymer backbone through metal-carbon π-bonding, e.g.,[22]



XI

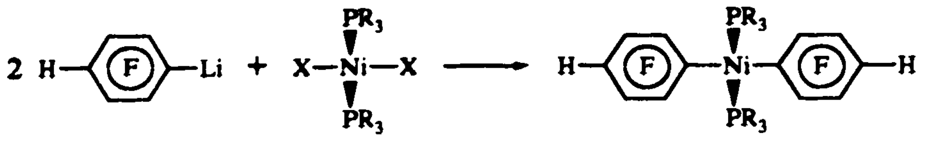
where M = Fe or Ru. To the best of our knowledge, no examples of the synthesis of a transition-metal organometallic polymer have been reported in which the metal centers are joined by aromatic ligands through metal-carbon σ-bonds before our work on arene-bridged organometallic polymers was initiated, e.g.,



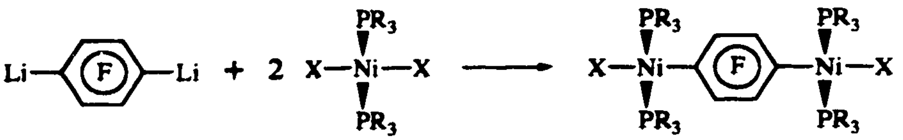
XII

The 1,4-phenylene group in **XII** could, in principle, be replaced by other aromatic fragments. Such species are excellent candidates as electrically conductive polymers. Thus, the central theme of the work in the Hunter group has been the syntheses and characterizations of model compounds and polymers containing transition-metal-(arene) carbon σ-bonds. In this regard, the systematic synthesis and characterization of a variety of arene-bridged organometallic model complexes as well as some polymers have been reported.[13-18]

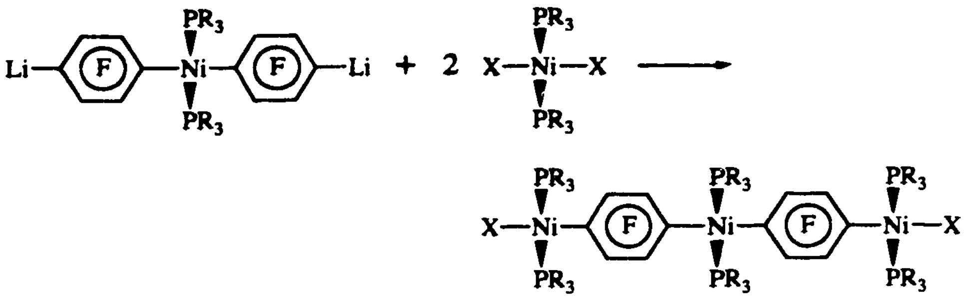
Work on related organic and organometallic materials has naturally tended to be preceded by studies on lower molecular weight species since these are more readily handled, yet they can serve as excellent model compounds for their target higher molecular weight analogs. Typical examples of the syntheses of these model compounds are demonstrated below:



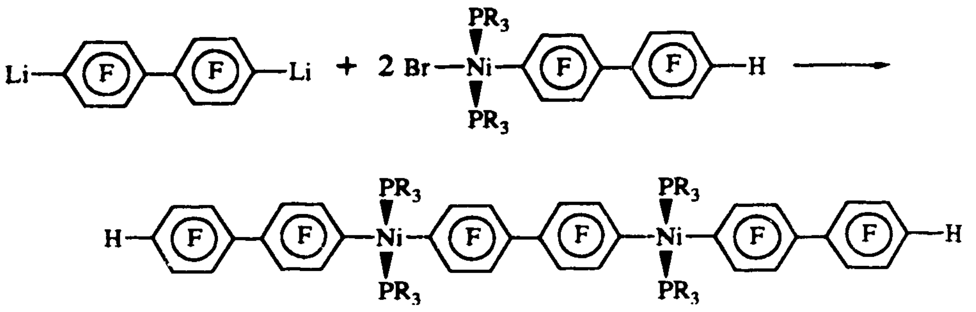
(1.1)



(1.2)

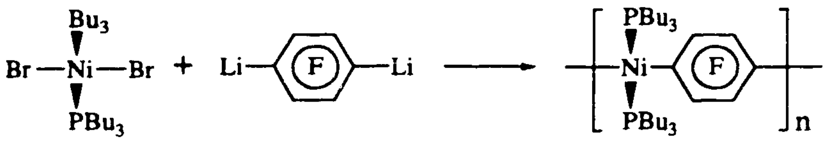


(1.3)

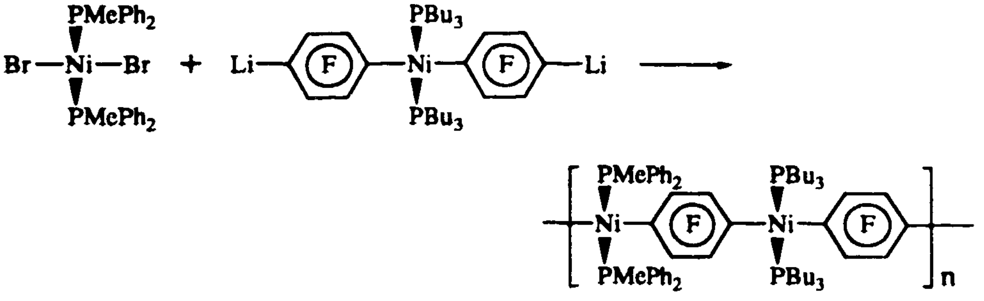


(1.4)

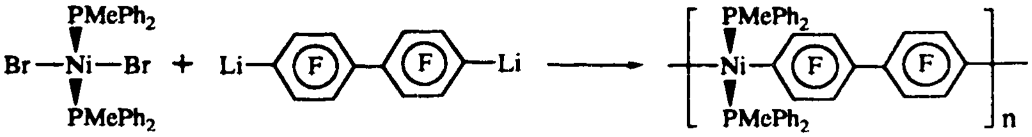
where $PR_3 = PMePh_2$ or PBu_3, and X = Br or Cl. The successful syntheses of these mono-, bi-, and trimetallic model species have paved the way for the preparation of the organometallic polymers containing analogous structures in their repeating units. Thus, such organonickel polymers have been successfully prepared by our group, e.g.,[13,14],



(1.5)



(1.6)

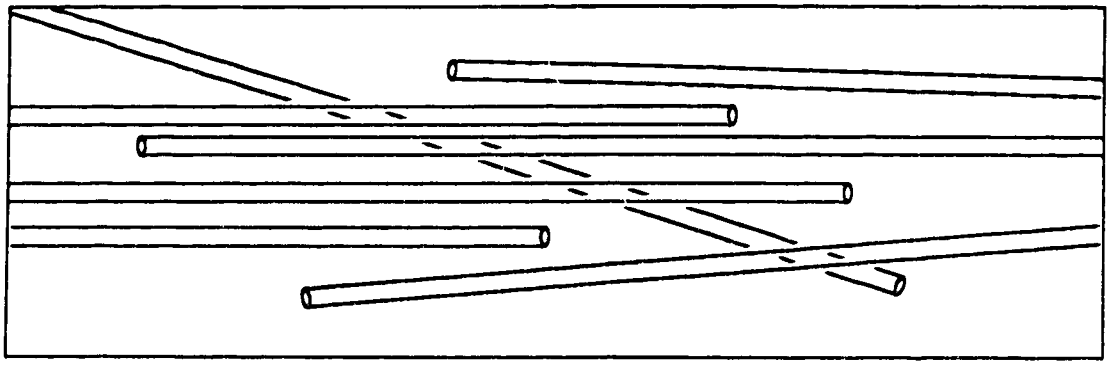


(1.7)

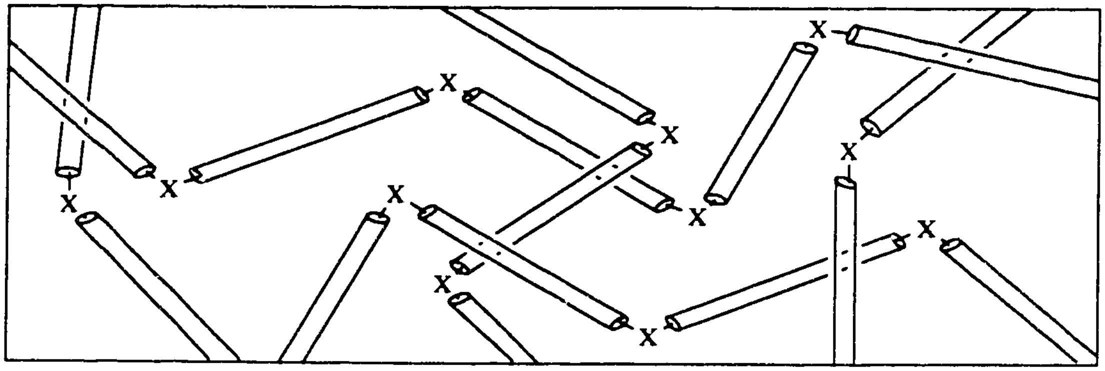
In principle, these syntheses can be extended to other transition metals such as Pd, Pt, Co, Mn, and Fe. In fact, similar oligomeric complexes of Pd have been made by other members of the Hunter group.[14]

These organometallic polymers have a large number of potential applications. They might be expected to be conductors or semiconductors arising from electron delocalization down the polymer backbone as a result of long-range indirect metal-metal interactions via overlap of the *d* orbitals on the metal center and the π^* orbitals on the arenes. These arene-bridged organometallic polymers are normally rigid-rod shaped molecules.[14,18] This will tend to make them relatively highly ordered in the solid state. Hence, oriented samples will likely display some degree of anisotropy in their conductivity behavior and thus might have some potential as one-dimensional electronic materials. Such electronic structures suggest that they might be good candidates to be tested as photoconductors and as non-linear optical materials.

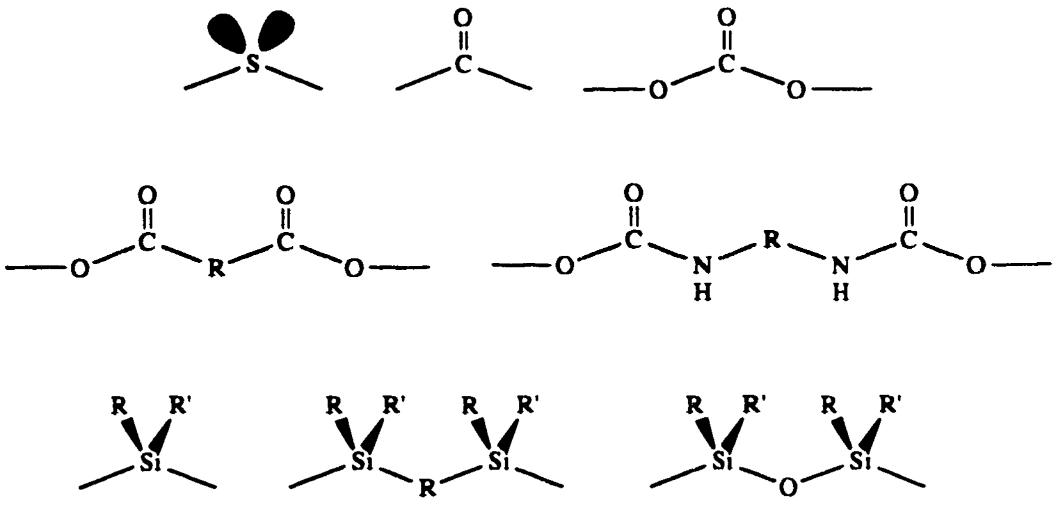
Since rigid-rod molecules typically are highly ordered in the solid state, i.e.,



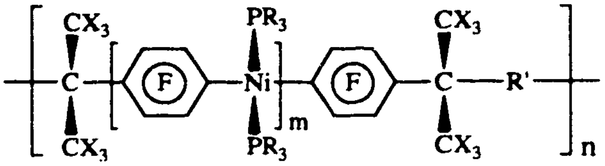
the processability as well as characterizability of the organometallic rigid-rods are expected to suffer. Poly(*para*-phenylene) is a typical example of rigid organic electroactive materials and is insoluble and infusible making it hard to characterize and impossible to process. In fact, some of the organonickel polymers we have synthesized show limited solubilities and undesirable softening or melting behavior (no appreciable change physically until decomposition). The use of ancillary ligands with longer dangling substituents (e.g., P(n-C_4H_9)$_3$) gave some improvement. However, we are also interested in other approaches to overcome the structural rigidity of these organometallic polymers. One of them is to provide flexible "joints" in the rigid-rods, breaking the long highly-ordered rigid-rods into short rigid organometallic segments, i.e.,



Candidates as these "joints" range from inorganic heteroatoms to longer organic flexible chains, e.g.,

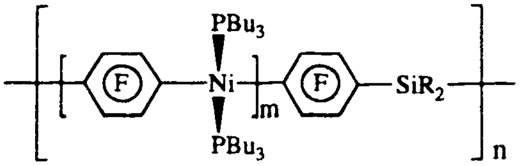


where R, R' = alkyl or aryl. These flexible chains, once incorporated into the rigid organometallic polymers, will dramatically reduce the rigidity of the polymer backbones (rigid as a segment, flexible as a whole!) and therefore impart better tractability on these materials. One example of such polymers is the following:



XIII

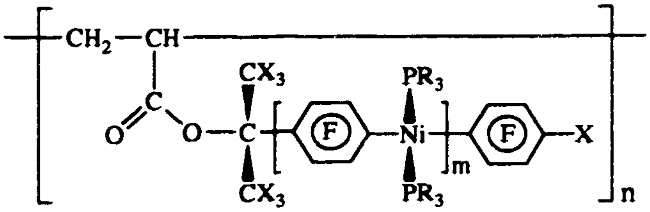
where m = 1 - 10, X = H or F, R = alkyl or aryl, R' = –OC(O)–R–C(O)O–, –OC(O)O–, –OC(O)NH–R–NHC(O)O–, etc. These polymers have rigid organometallic units linked by flexible organic structural units including polyesters, polycarbonates, or polyurethanes.[15,16] Another example is:



XIV

where m = 1 - 10, SiR_2 = $-SiMe_2-$, $-SiMe(Hex)-$, $-SiPh_2-$, $-SiMe_2-O-SiMe_2-$, $-SiMe_2-(CH_2)_6-SiMe_2-$, etc. These polymers have rigid organometallic units joined by flexible organosilicon (silane or siloxane) units.[17] Polysilanes and polysiloxanes are normally elastomeric materials because of the extensive structural flexibility of their repeating units.[23] Therefore, it is understandable that introduction of these silyl or siloxane units into the organometallic polymer main-chains will significantly reduce the backbone rigidity of the resulting polymers. Organometallic polymers with longer rigid chains (e.g., m > 10) can be ideally modified with these kinds of "joints".

Both **XIII** and **XIV** are organometallic polymers in which the rigid transition-metal segments are placed in the main-chains of the polymer. It is also possible to prepare polymers in which the rigid transition-metal segments are placed in the side-chains of a flexible organic polymer backbone, for example,



XV

where m = 1 - 10, X = H or F, R = alkyl or aryl. This polymer is a flexible polyacrylate with the rigid organometallic segments located in the dangling side-chains.[16] The overwhelming flexibility of the polyacrylate backbone (a random coil) will make the resulting polymer highly processable, even with long rigid organometallic segments placed in the side-chains (e.g., m > 10).

The shorter conjugation lengths in the modified organometallic polymers described above may not be a serious concern with respect to their electroactivity. It is well known that the conductivity of many organic polymers plateau at low average oligomerization values (e.g., $\overline{DP}_n \approx 10$ for poly(*para*-phenylene) and $\overline{DP}_n \approx 15$ for *trans*-

polyacetylene). On the other hand, the major limitation in bulk conductivity in many organic polymers is often found to be *inter*-chain, rather than *intra*-chain electron transfer, and it is therefore still unclear how the bulk conductivity will be affected by the degree of oligomerization. Therefore, it is expected that the delocalization down the chains of the organometallic segments in these flexible-as-a-whole polymers may be sufficient to give the polymers intrinsic conductivity values as high as those of the parent rigid-backbone organometallic polymers. In any case, it is well known in the field of organic conductors that high conductivity and high processability are almost always mutually exclusive. Thus, one has to make compromises between these two parameters in most cases.

As a first stage in our work on electroactive organometallic polymers, this thesis has mainly concentrated on studies of more conventional model polymers to identify the optimum conditions required for the successful preparation of the analogous organometallic polymers. Examining the structure-property relationships of these model polymers will be necessary to reveal valuable information in this regard.

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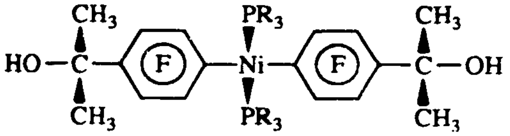
CHAPTER 2

POLYESTERS, POLYCARBONATE, AND POLYURETHANES FROM A NOVEL MONOMER: α,α,α',α'-TETRAMETHYL-1,4-TETRAFLUOROBENZENEDIMETHANOL†

INTRODUCTION

As part of ongoing studies of new electroactive polymeric materials, our group has recently reported a series of novel organometallic oligomers and polymers having $Ni(PMePh_2)_2$ fragments and fluoroaromatic bridging units (e.g., $-1,4-C_6F_4-$ and $-4,4'-C_{12}F_8-$) in the polymer backbones (e.g., $[Ni(PMePh_2)_2]_3(\mu-1,4-C_6F_4)_2Br_2$ and $-[-Ni(PMePh_2)_2(4,4'-C_{12}F_8)-]_n-$).[1,2] We would like to extend these studies by investigating more conventional condensation polymers derived from organometallic monomers[3] such as *trans*-$Ni(PR_3)_2(1,4-C_6F_4CMe_2OH)_2$, **1**.



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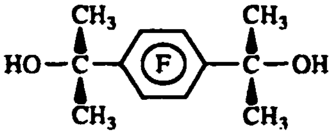
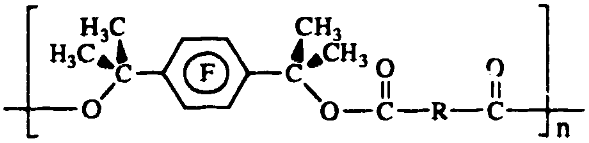
†A version of this chapter has been published. See: X. A. Guo and A. D. Hunter, *J. Polym. Sci.*, Part A: *Polym. Chem.*, **31**, 1431 (1993).

Unfortunately, our early efforts to use this monomer directly in producing polyesters, polycarbonates, and polyurethanes were unsuccessful, probably due to the low nucleophilicity and high steric hindrance of this tertiary alcohol. To identify the origin of this synthetic problem and to find superior routes for such polymerizations, we decided to investigate the chemistry of the most closely related organic monomer, α,α,α',α'-tetramethyl-1,4-tetrafluorobenzenedimethanol, **2**.



2

Since this compound had not previously been reported, we decided to prepare monomer **2** and use it to study the polymerization conditions required to successfully prepare the $-C(CH_3)_2O-C(O)-$, $-C(CH_3)_2O-C(O)-O-$, and $-C(CH_3)_2O-C(O)-NH-$ linkages of polymers having fluoroaromatic bridging units in their backbones. We expect that the complete characterization of such purely organic condensation polymers, i.e.,



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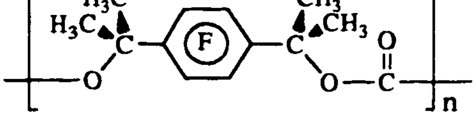

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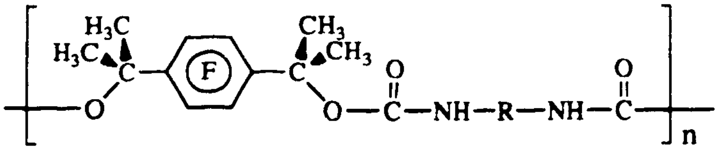

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will also serve as an invaluable aid in the identification of their organometallic analogs (i.e., polymers derived from monomer **1**). Further, comparison of the analogous organic and organometallic condensation polymers should help to elucidate the effects of inserting –Ni(PR$_3$)$_2$– fragments into polymer backbones. In this chapter, we report the convenient preparation and facile purification of diol **2** and the preparation and characterization of several classes of condensation polymers derived from this novel monomer including polyesters, polycarbonates, and polyurethanes.

EXPERIMENTAL SECTION

Materials

1,4-Dibromotetrafluorobenzene, *n*-butyllithium (1.6 M in hexanes), dimethyl adipate, adipoyl dichloride, sebacoyl dichloride, isophthaloyl dichloride, and terephthaloyl dichloride were purchased from Aldrich. Phosgene (20% (1.93 M) in toluene) was purchased from Fluka. Tolylene 2,4-diisocyanate (TDI) and methylenedi-1,4-phenyl diisocyanate (MDI) were purchased from Kodak. All chemicals purchased were of reagent grade and were used without further purification.

Preparation of α,α,α',α'-Tetramethyl-1,4-tetrafluorobenzenedimethanol, 2

The reaction was conducted using conventional techniques for the manipulation of air-sensitive compounds as described previously.[4-7] Thus, anaerobic and anhydrous conditions were maintained by using a prepurified argon or dinitrogen atmosphere employing conventional vacuum line techniques. Diethyl ether was dried and distilled from Na[Ph$_2$CO] and stored under Ar or N$_2$. Reagent acetone was dried and distilled twice from CaSO$_4$ (Drierite) and stored under N$_2$ in the dark. *n*-Butyllithium/hexanes solutions were standardized before use.[8]

1,4-Dibromotetrafluorobenzene (10.0 g, 32.5 mmol) was placed in a 300 mL three-necked flask, followed by introduction of diethyl ether (200 mL). The flask was cooled to -78°C (solid CO_2/acetone bath) and *n*-butyllithium (1.6 M in hexanes, 41.6 mL, 67 mmol) was added dropwise over a period of 15 min. The resulting yellow-white slurry was stirred at -78°C for a further 20 min, and then anhydrous acetone (7.2 mL, 98 mmol) was added dropwise over a period of 5-10 min. Both additions were accompanied by efficient stirring. The resulting white slurry was stirred at -78°C for 15 min and then allowed to warm to ambient temperature (*ca.* 23°C). The subsequent manipulations were performed in air. The slurry was acidified (pH = 4 - 6) and then washed with water until a neutral pH for the aqueous layer was observed. The ether solution was concentrated under vacuum to *ca.* 20 mL and hexanes (200 mL) was added to complete the precipitation. The final white crystalline solid was placed in a filter funnel and washed with copious amount of water, followed by hexanes, and then allowed to air-dry for 2 h. The solid was then redissolved in THF (30 mL), and reprecipitated by the addition of hexanes (300 mL). Product **2** was collected by filtration and air-dried overnight giving a 67% yield (5.8 g). m.p. 157 - 159°C. ^{1}H-NMR (CD_2Cl_2): δ 1.72 (m, 12H), δ 2.74 (s, br, 2H). ^{19}F NMR (CD_2Cl_2): δ -142.01 (s). Low Resolution Mass Spectrum: 266 (P^+), 251 (P^+-CH_3). ANAL. Calcd for $C_{12}H_{14}F_4O_2$: C, 54.14%; H, 5.30%. Found: C, 54.23%; H, 5.39%.

Polymerization

Representative examples of the preparations of the new polyesters, polycarbonate and polyurethanes prepared in this work are given below. Details of yields and characterization data are given in Tables 2.1 to 2.3. All polymerizations were conducted under an atmosphere of dry N_2.

Table 2.1. Yield, Molecular Weight and Softening Range Data

Reactant	Polymer	Yield (%)	VPO Molecular Weight[a]	GPC Molecular Weight[b]		$[\eta]^c$ (dL/g)	Softening Range[d] (°C)
				$\overline{M}_n$	$\overline{M}_w$		
sebacoyl dichloride	**3a**	37	4892	4460	7260	0.11	72 - 96
adipoyl dichloride	**3b**	62	682	1100	1850	0.057	*e*
isophthaloyl dichloride	**3c**	95	1843	1900	3950	0.082	110 - 148
terephthaloyl dichloride	**3d**	95	—	—	—	—	240 - 250
phosgene	**4a**	96	1082	1000	2200	0.055	118 - 196
tolylene-2,4-diisocyanate	**5a**	51	—	—	—	0.057	176 - dec.
methylene-di-p-phenyl diisocyanate	**5b**	89	—	—	—	0.11	290 - dec.

[a] Number-average molecular weight, $\overline{M}_n$.

[b] Polystyrene-equivalent molecular weights.

[c] Measured in THF at 30°C except for **5a** and **5b** where $[\eta]$ is measured in DMF at 30°C.

[d] Range from initiation of softening to complete liquification.

[e] Liquid at room temperature.

Table 2.2. ^{1}H- and ^{19}F-NMR Assignment[a]

Polymer	Primary Structure[b]	^{1}H (ppm)	^{19}F (ppm)
3a	$-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)(CH_2)_8C(O)-]_n-$	2.28 (t, $^3J_{H\text{-}H}$=7.54 Hz, 4H, H_α), 1.80 (s, CH_3), 1.57 (m, 4H, H_β), 1.29 (br, 8H, $H\gamma$ and H_δ)	-141.97 (s, br)
3b	$-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)(CH_2)_4C(O)-]_n-$	2.31 (br, 4H, H_α), 1.80 (s, CH_3), 1.59 (m, 4H, H_β)	-141.92 to -141.99 (br)
3c	$-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)\text{-}1,3\text{-}C_6H_4C(O)-]_n-$	8.60 (m, Ar*H*), 8.20 (m, Ar*H*), 7.54 (m, Ar*H*), 1.97 (s, br, CH_3)	-140.95 to -141.30 (br)
3d	$-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)C_6H_4C(O)-]_n-$ [c]	8.07 (m, Ar*H*), 1.98 (s, br, CH_3)	-139.74 to -141.65 (m)
4a	$-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)-]_n-$	1.78 (s, br, CH_3)	-141.95 (s, br)
5a	$-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)NH\text{-}1,3\text{-}(2\text{-}CH_3)C_6H_3NHC(O)-]_n-$	9.66 (br, N*H*), 8.94 (m, br, N*H*), 8.65 - 7.60 (m, br, Ar*H*), 7.39 - 6.90 (m, Ar*H*), 2.17 (m, br, ArCH_3), 1.84 (s, br, CH_3)	-139.73 to -144.17 (m)
5b	$-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)NHC_6H_4CH_2\text{-}C_6H_4NHC(O)-]_n-$	9.69 (br, N*H*), 8.52 (br, N*H*), 7.32 (m, Ar*H*), 7.06 (m, Ar*H*), 3.76 (m, br, CH_2), 1.83 (s, br, CH_3)	-139.69 to -144.16 (m)

[a] Dichloromethane-d_2 as the solvent except for **5a** and **5b** where dimethyl sulfoxide-d_6 was used as the solvent.

[b] Unspecified phenylenes denote *para* linkages.

[c] Dichloromethane-d_2 soluble portion (trace).

Table 2.3. UV-Visible and Infrared Absorption Data

Polymer	UV Maxima (nm)	IR Frequencies[a] (cm^{-1})			
		C–F	C=O	C–O	N–H
3a	240 (m), 264 (s), 290 (w)	1132	1738	1292	—
3b	246 (s), 260 (s), 290 (w)	1131	1737	1292	—
3c	240 (s), 264 (m), 290 (w)	1135	1726	1251 1293	—
3d	248 (vs), 294 (w)[b]	1101 - 1116 1143	1720	1280	—
4a	240 (m), 264 (vs), 290 (w)	1123	1747	1287	—
5a	250 (vs), 294 (m)[b]	1140	1685 (br)	1228	1536 (br); 3100 - 3600
5b	250 (vs), 294 (m)[b]	1139	1712 (br)	1233	1511 - 1524 1596; 3100 - 3600

[a] Measured as dichloromethane casts except for **3d**, **5a**, and **5b** where the spectra were recorded as KBr pellets.

[b] THF soluble portion (trace).

Polyester from Sebacoyl Dichloride

To a solution of the diol **2** (0.500 g, 1.88 mmol) in THF (40 mL) cooled to 0°C (ice/water bath) was added dropwise *n*-butyllithium (1.6 M in hexanes, 2.46 mL, 3.9 mmol), producing the presumed α,α,α',α'-tetramethyl-1,4-tetrafluorobenzenedimethoxy-dilithium **2Li**. The resulting white slurry was stirred at 0°C for 30 min and then sebacoyl dichloride (0.400 mL, 1.88 mmol) was added dropwise. The clear yellow solution produced was stirred at 0°C for 10 min, then at ambient temperature for 18 h. The solvent was reduced in volume under vacuum to *ca.* 10 mL and the flask was cooled to 0°C, at which point methanolic hydrochloric acid was added and the pH adjusted to 4-6. The mixture was then poured into H_2O (200 mL), warmed to *ca.* 60°C with stirring, and subsequently filtered. The solid was washed with excess water and hexanes (3 × 20 mL) and air-dried overnight, yielding 37% (0.30 g) of pale yellow powder of **3a** ($-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)(CH_2)_8C(O)-]_n-$).

Polycarbonate from Phosgene

A slurry of the dilithium salt of the diol, **2Li** (1.88 mmol), in THF (40 mL) was prepared at 0°C as described above. To this mixture, phosgene (1.93 M in toluene, 1.00 mL, 1.93 mmol) was added dropwise. The resulting yellow solution was stirred at 0°C for 10 min, then at ambient temperature for 18 h. The solution was concentrated under vacuum to *ca.* 10 mL and cooled to 0°C, after which it was poured into water (200 mL) and the pH adjusted to 4-6. The mixture was then warmed to *ca.* 60°C with stirring and subsequently filtered. The final pale yellow powder was washed with excess water and hexanes (2 × 10 mL) and air-dried overnight, giving 96% (0.55 g) yield of **4a** ($-[-OC(CH_3)_2C_6F_4C(CH_3)_2OC(O)-]_n-$).

Polyurethane from MDI

A solution of the diol **2** (0.500 g, 1.88 mmol) in dimethyl sulfoxide (10 mL) and pyridine (1.0 mL, 12 mmol) was placed in a three-necked flask equipped with a magnetic stirrer and an air-condenser. MDI (0.470 g, 1.88 mmol) was added, and the solution was heated to reflux and this temperature was maintained for a further 7 h. The clear viscous brown solution was cooled to ambient temperature and poured into water (400 mL). The mixture was warmed to *ca.* 80°C with stirring and subsequently filtered. The polymer was washed with excess water, followed by hexanes, and air-dried overnight, giving a very fine, tan-colored powder in 89% (0.86 g) yield of **5a** ($\text{–[–OC(CH}_3\text{)}_2\text{C}_6\text{F}_4\text{C(CH}_3\text{)}_2\text{O-C(O)NH-1,3-(4-CH}_3\text{)C}_6\text{H}_3\text{NHC(O)–]}_n\text{–}$).

Attempted Preparation of Polyester from Diol 2 and Sebacoyl Dichloride by Solution Polymerization

To a solution of diol **2** (0.500 g, 1.88 mmol) and pyridine (0.5 mL, 6 mmol) in dichloromethane (50 mL) was added sebacoyl dichloride (0.400 mL, 1.88 mmol) dropwise with stirring. The resulting clear solution was stirred at ambient temperature (*ca.* 23°C) for 10 h, and then refluxed for another 10 h. A sample was taken whose GPC in THF revealed that only low oligomers of the polysebacate were obtained ($\overline{DP}_n \approx 3$).

Attempted Preparation of Polyester from Diol 2 and Sebacoyl Dichloride by Melt Polymerization

The diol **2** (1.00 g, 3.76 mmol) and sebacoyl dichloride (0.800 mL, 3.75 mmol) were placed in a three-necked flask equipped with a N_2 gas inlet extending beneath the reaction mixture and an air-condenser with a gas outlet on top. The mixture was heated to 120°C (silicon-oil bath), at which time the reaction started and a viscous liquid was formed with hydrogen chloride gas smoke filling the flask. A gentle stream of N_2 was applied and the mixture was heated for a few hours during which the temperature of the heating source was gradually raised to 150°C. Deposits of the diol (revealed by its GPC and UV absorption) were observed on the inner wall of the condenser. Heating was stopped when the mixture became colored. GPC showed the polysebacate obtained was only low oligomers ($\overline{DP}_n \approx 3$).

Attempted Preparation of Polyester from 2Na and Sebacoyl Dichloride

The diol **2** (1.00 g, 3.76 mmol) and sodium hydride (60% dispersion, 0.39 g, 9.8 mmol) diluted by THF (50 mL) were placed in a three-necked flask equipped with a magnetic stirrer and an air-condenser. The mixture was refluxed for 2.5 h, and the presumed disodium salt of the diol, **2Na** thus formed.[9] At this point sebacoyl dichloride (0.800 mL, 3.75 mmol) was added dropwise. An exotherm was observed and an orange-yellow voluminous precipitate was formed. The mixture was refluxed for 4 h, then its solvent was replaced by N,N-dimethyl acetamide (30 mL) and refluxed for 10 h. The solvent was reduced in volume by vacuum to *ca.* 10 mL and the flask cooled to room temperature. Methanol (2 mL) was added and stirred for *ca.* 2 min, followed by addition of water (50 mL) and the pH of the mixture was adjusted to pH $\approx$ 4. A sticky dark brown solid was obtained after filtration of the mixture and washing with excess water. The solid was air-dried overnight, giving 62% (1.0 g) yield. GPC showed the polysebacate obtained had $\overline{M}_n$ = 1620, $\overline{M}_w$ = 3580 (relative to polystyrene). This polymer gradually loses its solubility in solvents in days under ambient conditions. Its ^{19}F-NMR spectrum exhibited complicated resonances and differential scanning calorimetry (DSC) showed no clear thermal transformations until decomposition.

^{1}H-NMR Data for the Model Compounds

Dimethyl sebacate (**6a**), (2-methyl-1,3-phenylene)bisdimethyl carbamate (**7a**), (methylene-di-1,4-phenylene)bisdimethyl carbamate (**7b**) were prepared via the reactions with excess anhydrous methanol, of sebacoyl dichloride, TDI, and MDI, respectively. Reactions were achieved by refluxing methanol for 2 - 4 h and the yields were quantitative.

Triethylamine was used as the base in the preparation of **6a**. Dimethyl adipate (**6b**) was used as purchased.

^{1}H-NMR (CD_2Cl_2) for **6a**: δ 2.27(t, $^3J_{H\text{-}H}$ = 7.54 Hz, 4H, H_α), 1.58 (m, 4H, H_β), 1.29 (br, 8H, $H_\gamma$and H_δ).

^{1}H-NMR (CD_2Cl_2) for **6b**: δ 2.27(br, 4H, H_α), 1.58 (m, 4H, H_β).

^{1}H-NMR ($(CD_3)_2SO$) for **7a**: δ 9.53 (s, br, 1H, N*H*), 8.80 (s, br, 1H, N*H*), 7.47 (s, 1H, Ar*H*), 7.15 (dd, 1H, Ar*H*), 7.05 (d, 1H, Ar*H*), 2.10 (s, 3H, ArCH_3).

^{1}H-NMR ($(CD_3)_2SO$) for **7b**: δ 9.53 (s, br, 2H, N*H*), 7.32 (d, 4H, Ar*H*), 7.08 (d, 4H, Ar*H*), 3.77 (s, 2H, CH_2).

Measurements

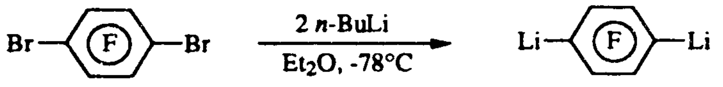
The NMR spectra were recorded on a Bruker AM-400 spectrometer as dichloromethane-d_2 (CD_2Cl_2) or dimethyl sulfoxide-d_6 ($(CD_3)_2SO$) solutions and employing a deuterium solvent lock. The ^{19}F-NMR chemical shifts are reported in parts per million downfield from external $CFCl_3$ and the ^{1}H-NMR chemical shifts downfield from external Me_4Si. The FTIR spectra were recorded on a Nicolet 7199 spectrophotometer. Softening ranges were ascertained by visual methods in unsealed capillaries. Osmometry measurements were made in benzene solutions on a Corona Wescan Vapor Pressure Osmometer by the University of Alberta Microanalytical Services. Gel permeation chromatography was performed on an automated Waters 600E HPLC/GPC system operated at 30.0°C using THF as the eluting solvent at a flow rate of 1.20 mL/min through three Waters HT μ-Styragel columns (10^3 Å, 10^6 Å, and 10 μm linear). Chromatograms and UV-Visible spectra were collected on-line on a Waters 991 Photodiode Array (UV-Visible) detector incorporating a Waters 410 Differential Refractive Index detector. Molecular weight calculations were performed using the Maxima 820 chromatography software (Waters, Dynamic Solutions, Division of Millipore) based on calibration using polystyrene narrow standards. Intrinsic viscosities were measured in

0.05 – 0.1% solutions using an Ubbelohde viscometer in a water bath maintained at 30.00 ± 0.01°C and calculated according to the method described by Solomon and Ciuta.[10]

RESULTS AND DISCUSSION

Preparation of the Diol Monomer

One of the criteria for the practical application of a new bifunctional monomer in condensation polymerizations is that the monomer be readily accessible and of high purity since impurities such as monofunctional species will upset the balance of stoichiometry and prevent the formation of high molecular weight polymers. It is in this context that we report the preparation of the novel diol monomer since it offers the advantage of convenient synthesis and facile purification, and is therefore suitable for preparations of various classes of condensation polymers. Bromine-lithium exchange between one equivalent of 1,4-dibromotetrafluorobenzene and two equivalents of *n*-butyllithium produces 1,4-$C_6F_4Li_2$.[1,2,11-16] When this is followed by derivatization using two equivalents of acetone, the desired diol **2** is produced in high yield and in multigram quantities (Equations 2.1 to 2.3).



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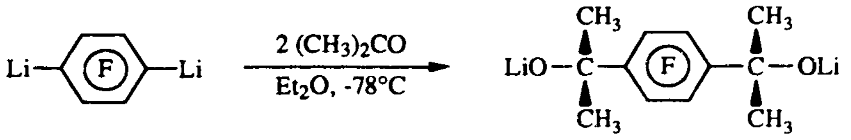

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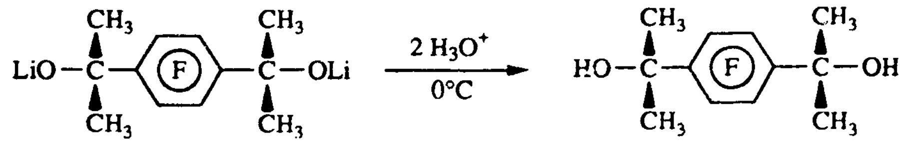


(2.3)

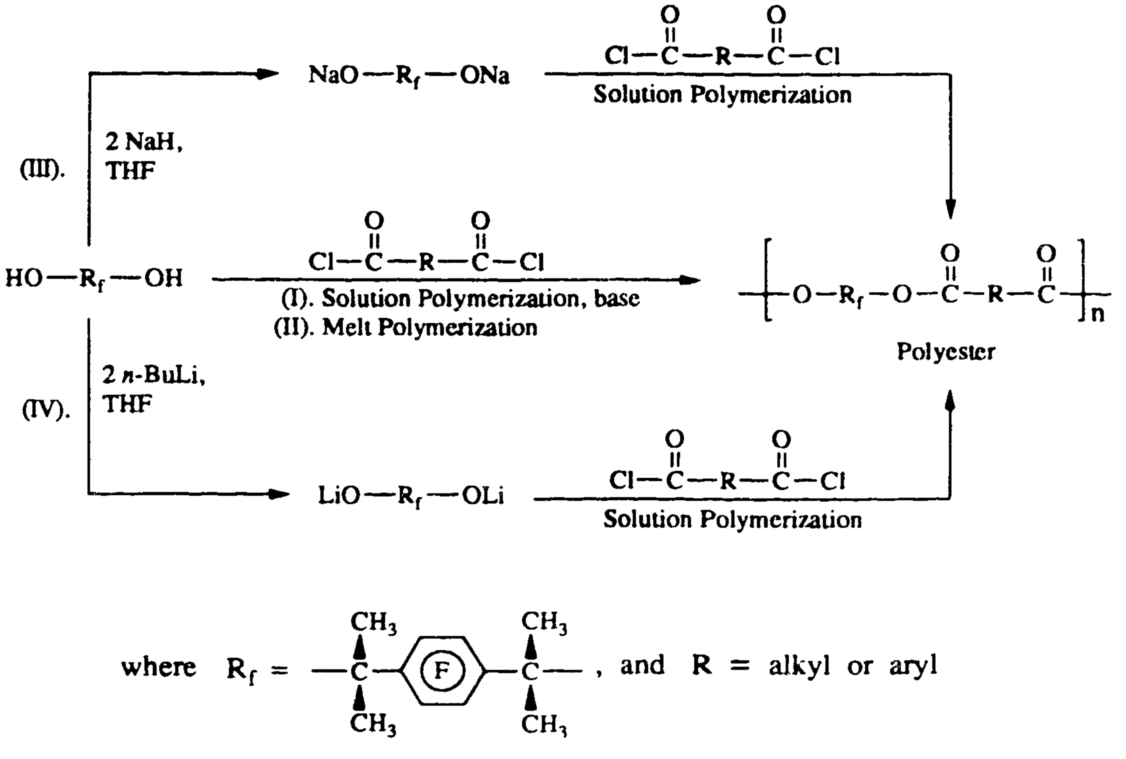
It was found that solvent played a critical role in the synthesis. In particular, an isolated yield of 80% could be achieved when diethyl ether was used as the solvent, while less than 30% was obtained when THF was employed. This is presumably due to the acidity of the α-hydrogen atoms of acetone[17,18] and the greater basicity of the perfluoroaryl dilithium reagent in THF. Elimination of lithium fluoride to form benzyne derivatives during the preparation of the aryl dilithium can occur on scaling up this exothermic reaction.[12-16] This may be avoided or minimized by slow addition of *n*-butyllithium/hexanes solutions. This product is simple to purify and its analytical and spectroscopic data show that it is essentially 100% pure after washing with hexanes and reprecipitation from THF/hexanes (see experimental section), since the monofunctional byproducts and other impurities are very soluble in hexanes while the diol is not. In fact, transparent colorless needle-like crystals can be easily grown from diethyl ether or dichloromethane solutions. The diol is readily soluble in THF, acetone, and ethanol and is moderately soluble in diethyl ether, dichloromethane, and chloroform.

Preparation of Condensation Polymers

Four polyesters, one polycarbonate, and two polyurethanes have been prepared using the novel diol monomer **2** employing modified solution polymerization techniques. These polymers were characterized using vapor pressure osmometry (VPO) and gel permeation chromatography (GPC) for determinations of molecular weights, and ^{1}H- and ^{19}F-NMR, IR, and UV-Visible spectroscopies for determinations of primary structures. These data are listed in Tables 2.1, 2.2, and 2.3. Since it is easier to obtain and interpret the spectroscopic, particularly NMR data, at the relatively low molecular weight level, no attempt was made to maximize the molecular weights of the polymers.

Preparation and Characterization of Polyesters 3a to 3d and Polycarbonate 4a

Four different routes leading from the diol monomer **2** to the polyesters have been attempted (Scheme 2.1). The first route involves the direct polymerization of the diol with diacid chlorides in solution (Schotten-Baumann reactions) using pyridine or triethylamine as the base. Although the mixture was found to be completely soluble in certain solvents such as dichloromethane or chloroform, only low molecular weight oligomers were produced through this procedure even at elevated temperatures. This is probably due to the relatively low nucleophilicity and high steric hindrance expected of the tertiary alcohol. The



Scheme 2.1.

volatility of the diol seems to have prevented the success of melt polymerization due to resultant non-optimal stoichiometry in our open reaction system, while prolonged heating of the reaction mixture above 120°C resulted in decomposition of the oligomers formed. Although conversion to the disodium salt of the diol, **2Na**, was relatively easy to achieve in THF,[9] the reaction mixture remained insoluble in this solvent after addition of diacid chloride even at refluxing temperature, hence, heating in N,N-dimethylacetamide (bp ≈ 165°C) was necessary to effect the further conversion of the oligomers formed in THF into higher molecular weight species. By this procedure, polymers of certain molecular weight were obtained after a few hours of heating. Unfortunately, the products isolated were dark brown colored and decomposed spontaneously in air at ambient temperature, their ^{19}F-NMR spectra were also unexpectedly complicated. Therefore, the above three routes were not investigated further. The fourth route, involving the dilithium salt, **2Li**, however, was found to be successful. It produced a solution that was totally clear upon addition of diacid chlorides into the suspension of **2Li** in THF (except for the case of polyterephthalate whose reaction mixture precipitated out of the solution). Although the conditions for this transformation have not been optimized, the polymerization under the conditions described could be completed in a few hours at ambient temperature and polyesters of acceptable molecular weights were obtained (the MWD curve of polysebacate, **3a**, is displayed in Figure 2.1). Therefore, this route was chosen to prepare the four polyesters reported (i.e., polysebacate, **3a**, polyadipate, **3b**, polyisophthalate, **3c**, and polyterephthalate, **3d**).

Except for the polyterephthalate, **3d**, which is only sparingly soluble, these polyesters are readily soluble in common solvents, such as THF, acetone, dichloromethane, and benzene, which aids in their subsequent characterizations. Interestingly, but not surprisingly, the GPC results for molecular weight measurement are consistent with the osmometry data (Table 2.1), even though the molecular weights reported from GPC are calculated relative to polystyrene. The spectroscopic data for these polymers suggest that they possess the expected primary structures. In particular, the ^{1}H-

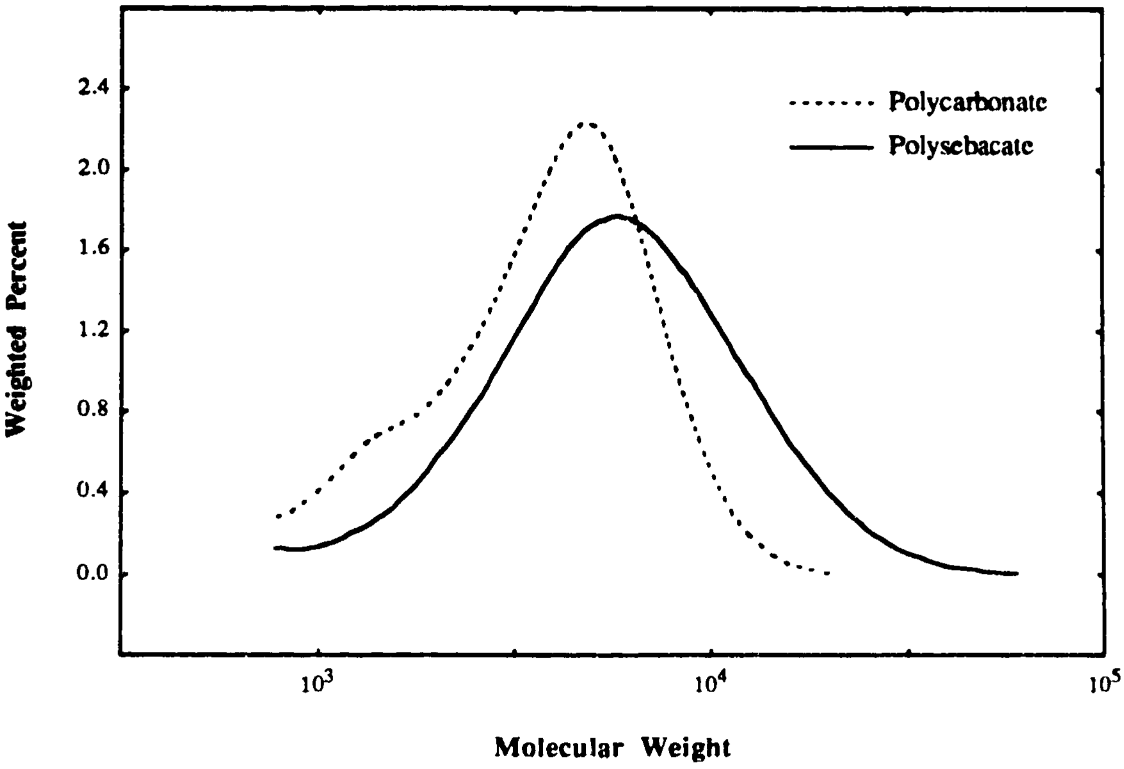
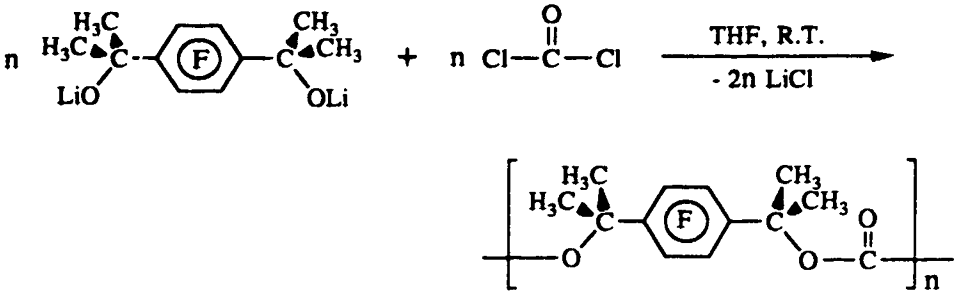


Figure 2.1. MWD Curves of polysebacate (**3a**) and polycarbonate (**4a**)

and ^{19}F-NMR resonances are completely assigned (see Table 2.2) by comparison to some model compounds, although peak broadening was encountered in some cases (presumably due to the polydispersive nature of the polymers). The IR absorptions of the polymers are consistent with the assigned structures, and typical frequencies attributable to C=O, C–O, and C–F listed in Table 2.3 indicate the integrity of "ester" linkages derived from reactions between the diacid chlorides and the diol. The UV absorptions of these polymers are also consistent with this suggestion. Thus, they normally show a strong shoulder absorption between 240 nm and 260 nm (Table 2.3), presumably arising from the arene ring and the carbonyl $\pi \rightarrow \pi^*$ transitions, together with a weak maximum around 290 nm.

The polycarbonate, **4a**, was prepared via the same route as that to the polyesters (Equation 2.4). In fact, the polycarbonate should possess a primary structure similar to that of the polyesters, i.e.,



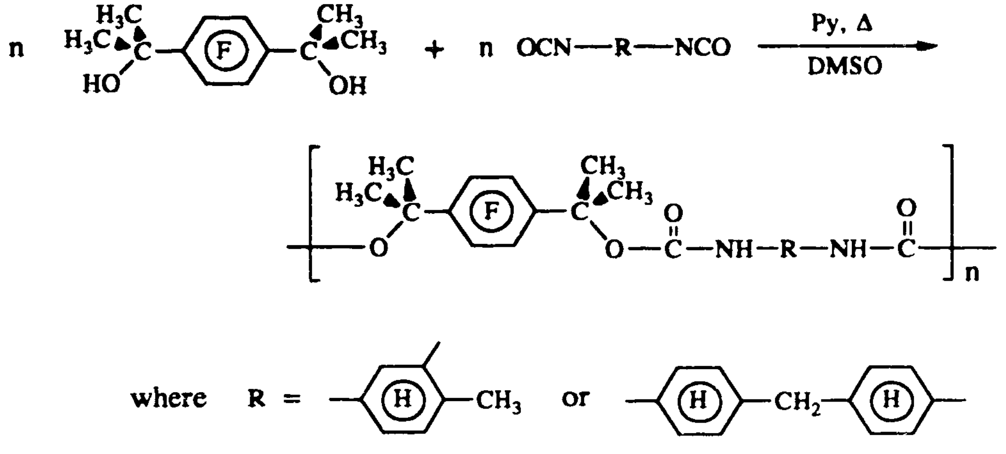
(2.4)

and therefore should be expected to have similar properties. Indeed, its simple ^{1}H- and ^{19}F-NMR data (Table 2.2) revealed the expected structure, the identity of which is further supported by its IR and UV absorptions (Table 2.3). GPC characterization of this polymer was also accomplished and its MWD curve is shown in Figure 2.1. Similar to the polyester analogues, the polycarbonate is readily soluble in most common solvents.

These polyesters and polycarbonate normally soften between ambient temperature and 250°C, low initial temperatures of **3a** to **3c** and **4a** indicate the presence of lower oligomers (Table 2.1). As expected, the polyarylates possess higher softening ranges than the polyalkylates, reflecting the greater chain stiffness or higher crystallinity when aromatics are introduced into the polymer backbone. The polyterephthalate, **3d**, shows the highest and narrowest softening (melting) range (240 - 250°C), suggesting the possibility of very high crystallinity expected for a highly symmetrical backbone. However, we are unable to obtain its molecular weight data because of its poor solubility.

Preparation and Characterization of the Polyurethanes

Considering the possible lower reactivity of the tertiary diol, **2**, Lyman's method for making polyurethanes[19] was modified by incorporating pyridine (a tertiary amine) as the catalyst. As a result, two polyurethanes were successfully made through this convenient solution technique (Equation 2.5). These polyurethanes are essentially insoluble in common solvents such as THF and dichloromethane etc., they are, however, soluble in highly polar solvents such as dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF), and intrinsic viscosities are therefore reported (Table 2.1). In contrast to the polyesters and polycarbonate, the polyurethanes do not show a clear softening range. Rather, they begin to shrink before they decompose. These polymers appear very hard and brittle at ambient temperature.



(2.5)

Dimethyl sulfoxide was used as the solvent to collect the NMR data of the polyurethanes (Table 2.2). In contrast to the NMR spectra of the polyesters and the polycarbonate which are relatively simple, those for the polyurethanes show broader peaks in the ^{1}H-NMR and multiplets in the ^{19}F-NMR spectra. However, with the aid of some model compounds, tentative assignments can be made which suggest the polyurethanes possess the expected primary structures. IR data for these polymers (Table 2.3) are also in accord with this suggestion. Thus, distinctive and strong absorptions attributable to N–H, C–F, and –C(O)–O– groups can be readily identified from the spectra, the amide carbonyl stretching frequencies being considerably lower (by 30 - 50 cm^{-1}) than those of the ester carbonyl. The UV spectra of these polyurethanes show two maxima, namely a strong absorption at 250 nm and a medium absorption at 294 nm.

In conclusion, acetone derivatization of dilithiotetrafluorobenzene afforded a high purity bifunctional monomer which was found to be suitable for the preparation of various classes of condensation polymers. Although in these small scale preparations, relatively low molecular weight polymers were obtained, we expect high polymers would be accessible upon scaling up the reactions. These results suggest improved routes to the analogous organometallic condensation polymers. Work is underway to extend this methodology and to optimize the polymerization conditions which can be applied to the preparation of these polymers.

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CHAPTER 3

PREPARATION AND CHARACTERIZATION OF ACRYLATES AND POLYACRYLATES HAVING VARIABLE FLUORINE CONTENTS AND DISTRIBUTIONS†

INTRODUCTION

We are interested in the relationships between the chemistry of novel organic polymers and their organometallic analogues incorporating transition-metal fragments (e.g., $-1,4-C_6F_4-Ni(PR_3)_2-1,4-C_6F_4-$) and particularly how the organometallic fragments can affect the properties of the polymers. Initially, our studies have focused on the organometallic rigid-rod oligomeric species (e.g., $-[-Ni(PR_3)_2-1,4-C_6F_4-]_n-$).[1-7] We have also reported some more conventional organic condensation polymers (i.e., polyesters, polyurethanes, and a polycarbonate derived from a diol monomer: $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-tetrafluoro-benzenedimethanol).[8-10] These were studied as models for the related organometallic polymers, i.e.,

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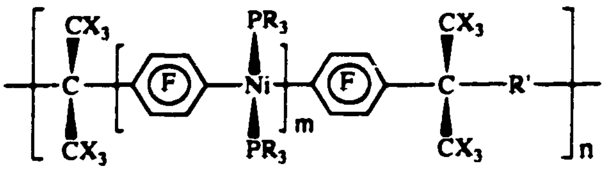
†A version of this chapter has been published. See: X. A. Guo, A. D. Hunter and J. Chen, *J. Polym. Sci.*, Part A: *Polym. Chem.*, 32, 47 (1994).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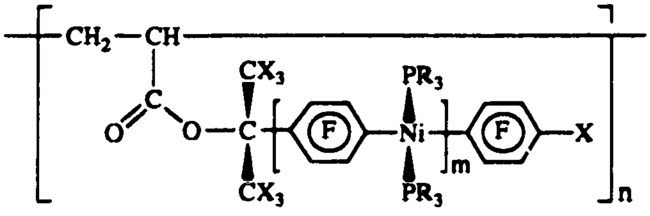
where $m = 1 - 10$, $X = H$ or F, R = alkyl or aryl, $R' = -OC(O)-R-C(O)O-$, $-OC(O)O-$, or $-OC(O)NH-R-NHC(O)O-$, which we are now attempting to prepare. Apart from these condensation polymers incorporating $-Ni(PR_3)_2-$ units into their main-chains, we are also interested in addition polymers incorporating $-Ni(PR_3)_2-$ units into their side-chains, e.g.,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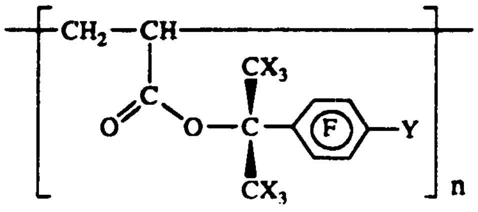
where $m = 1 - 10$, $X = H$ or F, R = alkyl or aryl. As a model study on these currently hypothetical organometallic polymers, we now have extended the methodology we previously developed for the preparation of the polyesters.[8-10] Thus we have prepared a series of analogous organic addition polymers, polyacrylates, i.e.,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where X, Y = H or F. These studies are designed to optimize the conditions for the preparation of the related organometallic addition polymers (i.e., 2 above) using the more readily prepared organic monomers. These organic model polymers were also chosen to have different fluorine contents and distributions in their side-chains which should enable us to systematically explore the effect of these differences on the syntheses and the physical properties of these materials and eventually to choose better target organometallic polymers for the syntheses. In this chapter, we report the preparation and characterization of five such polyacrylates as well as their corresponding acrylic monomers.

EXPERIMENTAL SECTION

Materials

1,2,4,5-Tetrafluorobenzene, *n*-butyllithium (1.6 M or 2.5 M in hexanes), bromopentafluorobenzene, acryloyl chloride, 2-phenyl-2-propanol, 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, 1,1,1,3,3,3-hexafluoroacetone, 2,2'-azobis(2-methylpropionitrile), and methyl acrylate were purchased from Aldrich. These chemicals were of reagent grade and were used without further purification. Acetone was purchased from Anachemia and was dried and distilled twice from Drierite® ($CaSO_4$) and stored under N_2 in the dark.

Preparation of Monomers

All reactions were conducted using conventional techniques for manipulation of air-sensitive compounds as described previously.[11-14] Thus, anaerobic and anhydrous conditions were maintained by using a prepurified argon or dinitrogen atmosphere employing conventional vacuum line techniques. Solvent diethyl ether and tetrahydrofuran were dried and distilled from $Na[Ph_2CO]$ and stored under argon or N_2. *n*-Butyllithium/hexanes solutions were standardized before use.[15] Collected analytical and spectroscopic data for the monomers **4** to **8** (including precursor **4a**) were given in Tables 3.1 and 3.2.

Table 3.1. Collected Data for the Monomers

No.	Structure[a]	Analytical Data				Low-Resolution Mass Spectral Data	b.p.	Yield
		C%		H%				
		Calcd	Found	Calcd	Found	(m/z)	(°C/torr)	(%)
4a	$HC_6F_4C(CH_3)_2OH$	51.93	51.78	3.87	4.22	208 (P^+), 193 (P^+-CH_3)	71-73/4.5	83
4	CH_2=$CHC(O)OC(CH_3)_2C_6F_4H$	54.97	54.95	3.84	3.81	262 (P^+), 191 (P^+-$OC(O)CHCH_2$)	89.5/2.6	58
5	CH_2=$CHC(O)OC(CH_3)_2C_6F_5$	51.44	51.39	3.24	3.28	280 (P^+), 209 (P^+-$OC(O)CHCH_2$)	81-83/2.8	35
6	CH_2=$CHC(O)OC(CF_3)_2C_6F_5$	37.13	36.83	0.78	0.64	388 (P^+), 317 (P^+-$OC(O)CHCH_2$)	81/4.5	92
7	CH_2=$CHC(O)OC(CF_3)_2C_6H_5$	48.34	48.18	2.70	3.08	298 (P^+), 227 (P^+-$OC(O)CHCH_2$)	84.5/3.8	73
8	CH_2=$CHC(O)OC(CH_3)_2C_6H_5$	75.76	75.76	7.42	7.46	190 (P^+), 175 (P^+-CH_3), 119 (P^+-$OC(O)CHCH_2$)	88-89/2.6	51

[a] The C_6F_4 linkage refers to 2,3,5,6-tetrafluorophenylene.

Table 3.2. ^1H- and ^{19}F-NMR (CD_2Cl_2 Solution) Data for the Monomers

No.	Structure[a]	^1H (ppm)	^{19}F (ppm)
4a	$HC_6F_4C(CH_3)_2OH$	7.03 (m, 1H), 2.78 (br, 1H), 1.71 (m, 6H)	-139.96 (m, 2F), -141.42 (m, 2F)
4	$CH_2{=}CHC(O)OC(CH_3)_2C_6F_4H$	7.03 (m, 1H), 6.34 (dd, 1H), 6.10 (dd, 1H), 5.83 (dd, 1H), 1.88 (m, 6H) ($^3J_{trans}$ = 17.4 Hz, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ =1.4 Hz)	-140.03 (m, 2F), -141.19 (m, 2F)
5	$CH_2{=}CHC(O)OC(CH_3)_2C_6F_5$	6.34 (dd, 1H), 6.09 (dd, 1H), 5.83 (dd, 1H), 1.87 (m, 6H) ($^3J_{trans}$ = 17.4 Hz, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ =1.4 Hz)	-140.63 (m, 2F), -157.19 (m, 1F), -163.32 (m, 2F)
6	$CH_2{=}CHC(O)OC(CF_3)_2C_6F_5$	6.61 (dd, 1H), 6.28 (dd, 1H), 6.15 (dd, 1H) ($^3J_{trans}$ = 17.1 Hz, $^3J_{cis}$ = 10.8 Hz, $^2J_{gem}$ =0.65 Hz)	-71.74 (br, 6F), -133.50 (br, s, 1F), -139.94 (br, s, 1F), -149.18 (m, 1F), -160.40 (br, m, 2F)
7	$CH_2{=}CHC(O)OC(CF_3)_2C_6H_5$	7.47 (m, 5H), 6.59 (dd, 1H), 6.30 (dd, 1H), 6.11 (dd, 1H) ($^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.6 Hz)	-70.55 (s)
8	$CH_2{=}CHC(O)OC(CH_3)_2C_6H_5$	7.34 (m, 4H), 7.25 (m, 1H), 6.31 (dd, 1H), 6.12 (dd, 1H), 5.78 (dd, 1H), 1.78 (s, 6H) ($^3J_{trans}$ = 17.3 Hz, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ =1.6 Hz)	—

[a] The C_6F_4 linkage refers to 2,3,5,6-tetrafluorophenylene.

Preparation of 2-2',3',5',6'-Tetrafluorophenyl-2-propyl acrylate, 4

*(1). Preparation of 2-2',3',5',6'-Tetrafluorophenyl-2-propanol, **4a***

Into a 500-mL three-necked flask, was added 1,2,4,5-tetrafluorobenzene (10.1 g, 67.2 mmol) and diethyl ether (300 mL). The flask was cooled to -78°C (solid CO_2/acetone bath) and *n*-butyllithium (1.60 M in hexanes, 42.5 mL, 68.0 mmol) was added dropwise over a period of 10 min. The resulting pale yellow clear solution was stirred at -78°C for 2.5 h and then anhydrous acetone (7.0 mL, 95 mmol) was added dropwise over a period of 5 min. Both additions were accompanied by efficient stirring. The flask was allowed to warm to ambient temperature (*ca.* 23°C), resulting in the formation of a white suspension. The subsequent manipulations were performed in air. The slurry was acidified (pH = 2 - 4) and washed with water until a neutral pH for the aqueous layer was obtained. The ether layer was collected and was combined with subsequent washings (100 mL). The solvent was removed under vacuum and the resulting liquid was vacuum distilled yielding 2-2',3',5',6'-tetrafluorophenyl-2-propanol, **4a**, as a colorless oily liquid, bp. 71 - 73°C/4.5 torr, in 83% yield (11.6 g, 55.9 mmol).

*(2) Preparation of 2-2',3',5',6'-Tetrafluorophenyl-2-propyl acrylate, **4***

A solution of **4a** (10.2 g, 48.9 mmol) in tetrahydrofuran (180 mL) was placed in a 200-mL three-necked flask which was then cooled to 0°C (ice/water bath). *n*-Butyllithium (2.50 M in hexanes, 20.0 mL, 50.0 mmol) was added dropwise with efficient stirring. The bath was removed and the solution stirred at room temperature for 30 min, then cannulated into another flask which contained a solution of excess acryloyl chloride (6.0 mL, 74 mmol) in tetrahydrofuran (20 mL) which had been cooled to 0°C (ice/water bath). The resulting pale-yellow solution was stirred at room temperature for 10 h, then its solvent was removed by vacuum. Diethyl ether (2 × 40 mL) was used to extract the product, and subsequently methanol (50 mL) was added to precipitate a solid byproduct which was separated by filtration and discarded. Vacuum distillation of the final liquid product afforded the desired monomer 2-2',3',5',6'-tetrafluorophenyl-2-propyl acrylate, **4**, as a colorless oily liquid, bp. 84 - 85°C/2.1 torr, in 58% yield (7.5 g, 29 mmol).

Preparation of 1,1,1,3,3,3-Hexafluoro-2-pentafluorophenyl-2-propyl acrylate, 6

A solution of bromopentafluorobenzene (9.78 g, 39.6 mmol) in diethyl ether (200 mL) was placed in a 300-mL three-necked flask, which was subsequently cooled to -78°C (solid CO_2/acetone bath). *n*-Butyllithium (1.60 M in hexanes, 24.5 mL, 39.2 mmol) was added dropwise over a period of 10-15 min. The resulting clear, light orange solution was stirred at -78°C for 30 min, then 1,1,1,3,3,3-hexafluoroacetone (10 g, 60 mmol) was introduced through a needle extending beneath the solution. A cloudy solution was formed, which was kept stirring at -78°C for 1 h, then allowed to warm to ambient temperature (*ca.* 23°C). This resulting clear colorless solution was cannulated into another flask which contained a solution of acryloyl chloride (4.80 mL, 59.1 mmol) in diethyl ether (10 mL) which had been cooled to 0°C (ice/water bath). A white precipitate was formed within 10 min, and the slurry left stirred at room temperature for 10 h. The precipitate was filtered off and the ether solution was collected. The solvent was removed under vacuum and vacuum distillation of the final liquid afforded monomer 1,1,1,3,3,3-hexafluoro-2-pentafluorophenyl-2-propyl acrylate, **6**,[16] as a colorless oily liquid, bp. 81°C/4.5 torr, in 92% yield (14.0 g, 36.1 mmol).

Monomer 2-pentafluorophenyl-2-propyl acrylate, **5**, was prepared in a similar fashion. An oily liquid, bp. 80 - 82°C/3.0 torr, was obtained in 35% yield starting with bromopentafluorobenzene.

Preparation of 1,1,1,3,3,3-Hexafluoro-2-phenyl-2-propyl acrylate, 7

A solution of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (9.79 g, 40.1 mmol) in diethyl ether (180 mL) was placed in a 200-mL three-necked flask and was then cooled to

0°C (ice/water bath). *n*-Butyllithium (1.60 M in hexanes, 25.0 mL, 40.0 mmol) was added dropwise with efficient stirring. The bath was removed and the resulting cloudy solution was stirred at room temperature for 30 min and then cannulated into another flask which contained a solution of acryloyl chloride (5.00 mL, 61.5 mmol) in diethyl ether (20 mL) which had been cooled to 0°C (ice/water bath). A white precipitate was formed and the slurry left stirred at room temperature for 14 h. Subsequent workup, similar to that described for the preparation of monomer **6**, afforded monomer 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propyl acrylate, **7**,[17-19] as a colorless oily liquid, bp. 84.5°C/3.8 torr, in 73% yield (8.74 g, 29.3 mmol).

Monomer 2-phenyl-2-propyl acrylate, **8**, was prepared in a similar fashion. An oily liquid, bp. 88 - 89°C/2.6 torr, was obtained upon vacuum distillation in 51% yield starting with 2-phenyl-2-propanol.

Polymerization

The general methods used for the polymerizations of the five monomers are given below as specific examples. All polymerizations were conducted under an atmosphere of dry N_2. Solvent toluene was distilled over $Na[Ph_2CO]$ and stored under N_2. Details of yields and characterization data for these polymers are listed in Tables 3.3, 3.4, and 3.5.

Solution Polymerization

A solution of monomer **5**, 2-pentafluorophenyl-2-propyl acrylate, (1.00 g, 3.57 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN) (12 mg, 0.073 mmol) dissolved in toluene (1.0-1.5 mL) was placed in a 5-mL vial under N_2. The vial was kept for 36 h in a water bath whose temperature was maintained at 55°C, during which period the solution became more and more viscous, then for a further 3 h at 90°C (oil bath). The solution was cooled to room temperature, diluted with diethyl ether (10 mL) and poured into methanol

Table 3.3. Yield, Molecular Weight and Glass Transition Data for the Polyacrylates

Polymer	Polymerization Technique	Yield (%)	VPO Molecular Weight[a]	GPC Molecular Weight[b] $\overline{M}_n$	GPC Molecular Weight[b] $\overline{M}_w$	[η] (dL/g)	Tg[c] (°C)
poly-H_6-F_4H	bulk	e	4,755	11,406	209,926	0.41	57
poly-H_6-F_4H	solution	96	16,203	29,552	244,466	0.33	53
poly-H_6-F_5	solution	90	26,333	36,926	245,717	0.41	51
poly-F_6-F_5	solution[d]	80	—	—	—	—	83
poly-F_6-F_5	bulk	e	—	—	—	—	117
poly-F_6-H_5	solution	90	20,681	17,907	521,336	0.33	61
poly-H_6-H_5	solution	87	28,108	58,883	247,938	0.50	33

[a] Number-average molecular weight, $\overline{M}_n$.

[b] Polystyrene-equivalent molecular weights.

[c] Taken as the intersection of the extrapolation of the baseline with that of the inflection in the DSC thermogram.

[d] Polymer precipitated out of the solution.

[e] Essentially quantitative conversion of the monomer is observed.

Table 3.4. ^{1}H- and ^{19}F-NMR (CD_2Cl_2 Solution) Data for the Polyacrylates $-[-CH_2CHC(O)OY-]_n-$

Y[a]	Polymer	^{1}H (ppm)	^{19}F (ppm)
$-C(CH_3)_2C_6F_4H$	poly-H_6-F_4H	6.98 (br, Ar*H*), 2.42 (br, H_α), 1.79 (br, CH_3), 1.59 (br, H_β), 1.55 (br, $H_{\beta'}$)	-139.83 (br, 2F), -140.47 (br, 2F)
$-C(CH_3)_2C_6F_5$	poly-H_6-F_5	2.36 (br, H_α), 1.79 (br, CH_3), 1.55 (br, H_β), 1.45 (br, $H_{\beta'}$)	-140.17 (br, 2F), -157.30 (br, 1F), -163.30 (br, 2F)
$-C(CF_3)_2C_6H_5$	poly-F_6-H_5	7.30 (br, m, Ar*H*), 2.86 (br, H_α), 1.88 (br, H_β), 1.56 (br, $H_{\beta'}$)	-70.57 (br, m, 6F)
$-C(CH_3)_2C_6H_5$	poly-H_6-H_5	7.34 (br, 2H, Ar*H*), 7.26 (br, 2H, Ar*H*), 7.17 (br, 1H, Ar*H*), 2.37 (br, H_α), 1.69 (s, br, CH_3), 1.66 (br, H_β), 1.55 (br, $H_{\beta'}$)	—

[a] The C_6F_4 linkage refers to 2,3,5,6-tetrafluorophenylene.

Table 3.5. UV-Visible and Infrared Absorption Data for the Polyacrylates

Polymer	UV Maxima[a] (nm)	ε_{max} (L/mol·cm)	IR Frequencies (cm^{-1})			
			C–F	C=O	C–O	–C_6F_4Y[b]
poly-H_6-F_4H	236 (w), 264 (s)	1.9×10^4	1131	1736	1276	1492
poly-H_6-F_5	240 (m), 260 (s)	3.6×10^4	1132	1736	1260	1492
poly-F_6-F_5	236 (w), 264 (s)[c]	—	1145	1781	1233, 1280	1500
poly-F_6-H_5	240 (m), 260 (s)	2.4×10^4	1133	1734	1273	—
poly-H_6-H_5	240 (m), 260 (s)	2.4×10^4	1133	1734	1273	—

[a] s — strong, m — medium, w — weak.

[b] Frequencies of fluoroarene skeleton vibrations, where Y = H or F.

[c] Tetrahydrofuran soluble portion (trace).

(200 mL). The white precipitate was chopped into small pieces, filtered and air-dried overnight yielding polymer poly-H_6-F_5 (0.90 g, 90%) as a white powder.

Bulk Polymerization

A mixture of monomer **6**, 1,1,1,3,3,3-hexafluoro-2-pentafluorophenyl-2-propyl acrylate, (2.00 g, 5.15 mmol) and AIBN (17 mg, 0.10 mmol) was placed in a 5-mL vial under N_2, which was placed into a water bath whose temperature was maintained at 55°C. A transparent colorless hard object (rod) was obtained (poly-F_6-F_5) after 45 h. The polymer doesn't dissolve in any cold solvents under test: tetrahydrofuran, acetone, dichloromethane, benzene, toluene, and diethyl ether, but swells in hot toluene (80 - 100°C). Preliminary flame (oxygen-acetylene) test indicated that it is self-extinguishing.

NMR Data for the Model Compound

Methyl acrylate was used as purchased. ^{1}H-NMR (CD_2Cl_2) for $CH_{syn}H_{anti}{=}CH_{\alpha}C(O)OCH_3$: δ 6.34 (dd, 1H, H_{anti}), 6.09 (dd, 1H, H_{α}), 5.78 (dd, 1H, H_{syn}), 3.69 (s, 3H, CH_3), $^3J_{trans}$ = 17.4 Hz, $^3J_{cis}$ = 10.4 Hz, and $^2J_{gem}$ = 1.5 Hz.

Measurements

The NMR spectra were recorded on a Bruker AM-400 spectrometer as dichloromethane-d_2 (CD_2Cl_2) solutions and employing a deuterium solvent lock. The ^{19}F-NMR chemical shifts are reported in parts per million downfield from external $CFCl_3$ and the ^{1}H-NMR chemical shifts downfield from external Me_4Si. The IR spectra were recorded as KBr pallets on a Nicolet 7199 spectrophotometer. The molar extinction coefficients of the polymers were measured as tetrahydrofuran solutions on a Hewlett Packard 8450A Diode Array spectrophotometer and calculated based on the absorbances at the strongest maximum (*ca.* 260 nm) and the $\overline{M}_n$ values from VPO measurements. Glass transition temperatures (Tg) of the polymers were determined by using a TA Instruments

DSC 2910 differential scanning calorimeter (DSC). Samples were run under an N_2 atmosphere at a heating rate of 10°C/min. The second heating thermograms were adopted to remove thermal history.[20] The T_g was taken as the intersection of the extrapolation of the baseline with that of the inflection in the DSC thermogram.[21] Osmometry measurements were made in benzene solutions on a Corona Wescan Vapor Pressure Osmometer (VPO) by the University of Alberta Microanalytical Services. Thermal gravity analyses (TGA) were made on a DuPont 900 Differential Thermal Analyser by this Services and samples were run either under N_2 (Figure 3.1) or in air (Figure 3.2) at a heating rate of 10°C/min, the results of sample weight *versus* temperature were reprocessed and replotted in percent weight loss *versus* temperature. Gel permeation chromatography (GPC) was performed on an automated Waters 600E HPLC/GPC system operated at 30.0°C using tetrahydrofuran as the eluting solvent at a flow rate of 1.20 mL/min through three Waters HT μ-Styragel columns (10^3 Å, 10^6 Å, and 10 μm linear). Chromatograms and UV-Visible spectra were collected on-line on a Waters 991 Photodiode Array (UV-Visible) detector incorporating a Waters 410 Differential Refractive Index detector. Molecular weight calculations were performed using the Maxima 820 chromatography software (Waters, Dynamic Solutions, Division of Millipore) based on calibration using polystyrene narrow standards. Intrinsic viscosities were measured in 0.05 - 0.1% tetrahydrofuran solutions using an Ubbelohde viscometer in a water bath maintained at 30.00 ± 0.01°C and calculated according to the single-point method described by Solomon and Ciuta.[22]

RESULTS AND DISCUSSION

Preparation and Characterization of the Monomers

We have previously reported that acetone derivatization of dilithiotetrafluorobenzene afforded a diol monomer in excellent yield, which was used, upon dilithiation, to react with

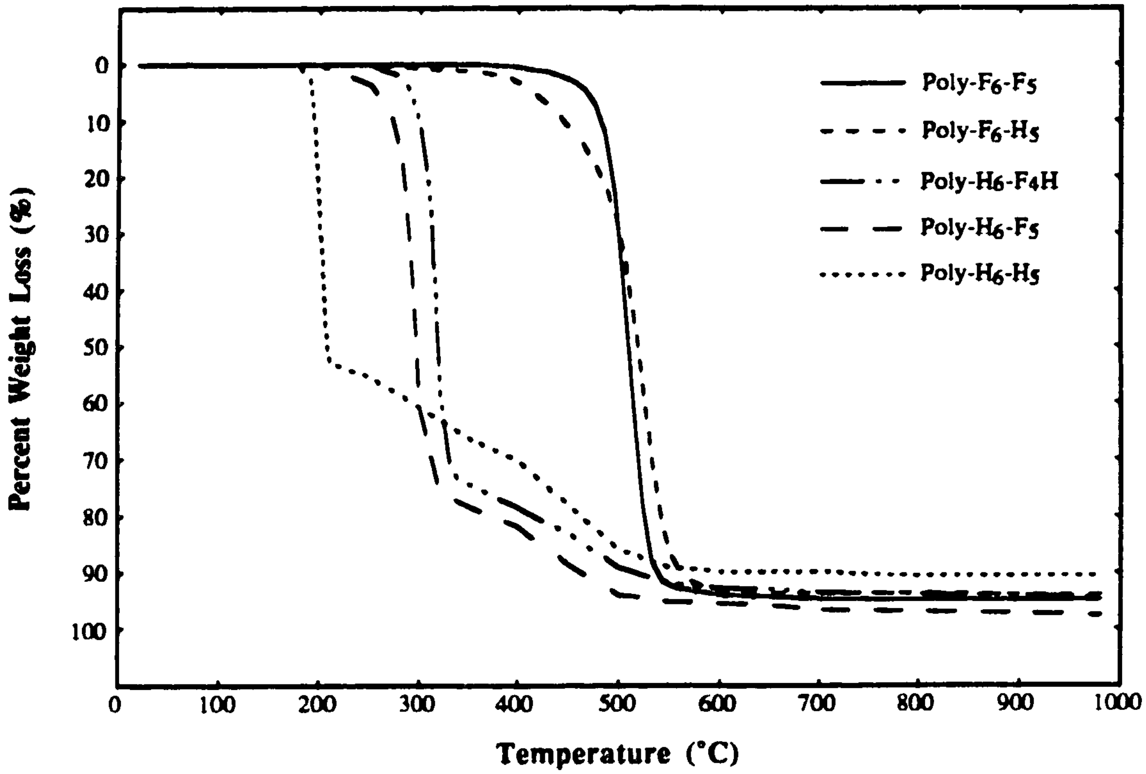


Figure 3.1. TGA Curves of the polyacrylates (under N_2)

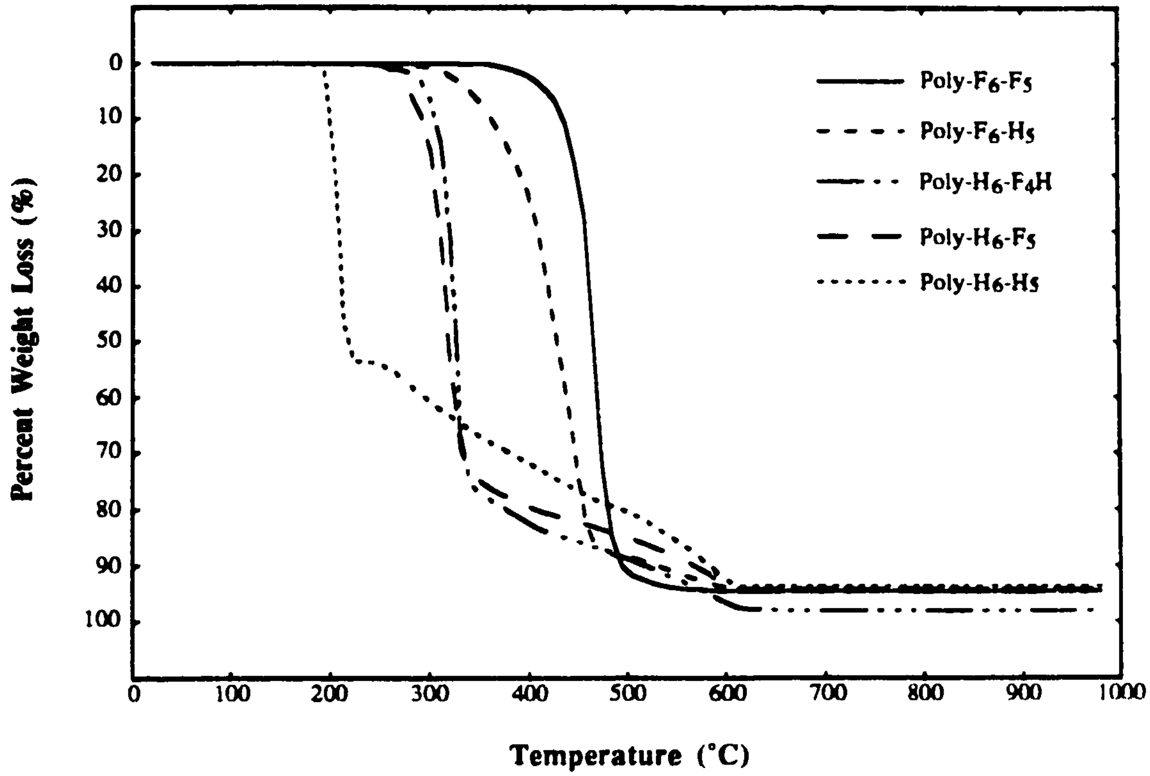
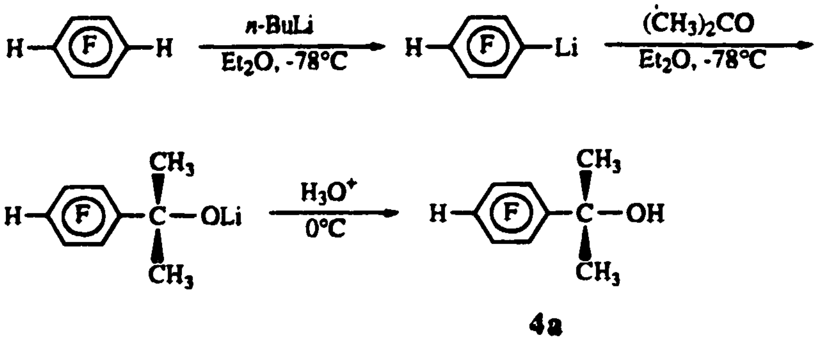


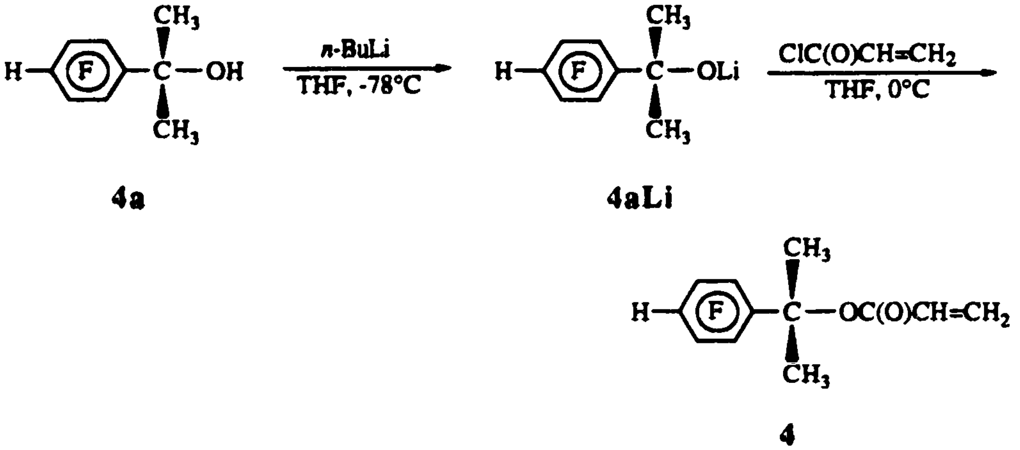
Figure 3.2. TGA Curves of the polyacrylates (in air)

diacid chlorides to produce the polyesters.[8-10] A logical extension of this methodology is to prepare the corresponding monofunctional alcohol from tetrafluorobenzene, i.e.,



(3.1)

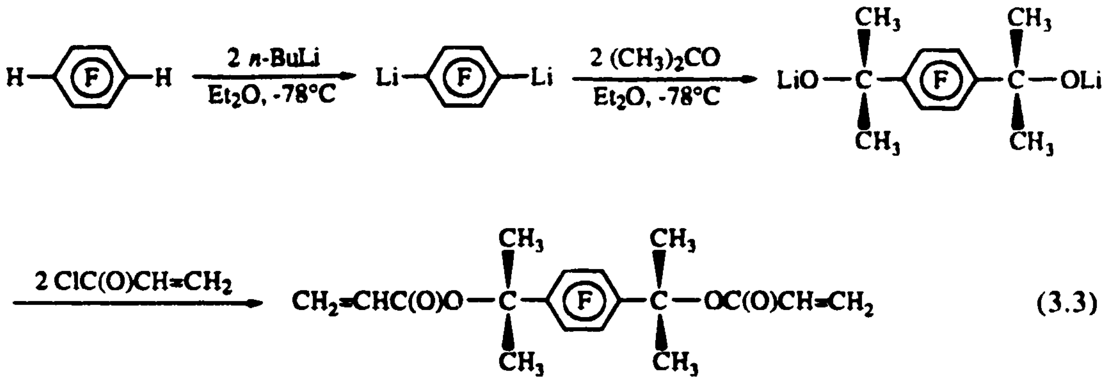
This species is then useful for the preparation of a new vinyl monomer by reaction with acryloyl chloride, i.e.,



(3.2)

This route successfully produced the desired compound **4a** in excellent yield (83%) and monomer **4** in good yield (58%).

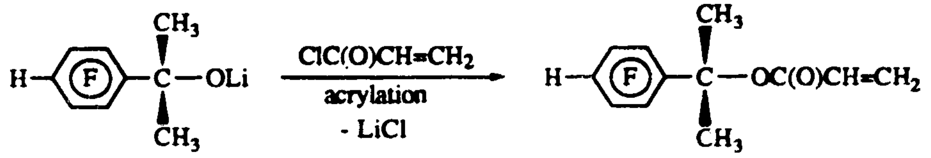
An obvious side-reaction of this mono-derivatization of tetrafluorobenzene is the undesired dilithiation, which upon addition of acetone and subsequent reaction with acryloyl chloride will form a divinyl byproduct, i.e.,



(3.3)

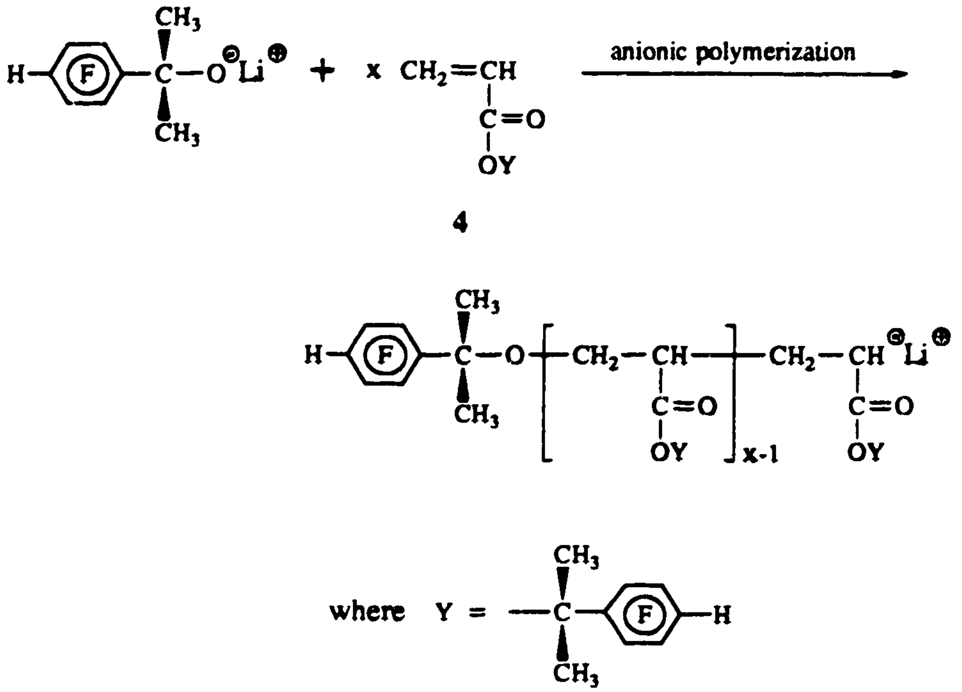
which would be expected to interfere with the preparation and subsequent polymerization of monomer 4 (causing crosslinkages). To avoid this problem, two measures have been taken. The first one is the use of solvent diethyl ether instead of tetrahydrofuran in the preparation of **4a**, since it has been previously demonstrated that dilithiation is minimized in diethyl ether rather than in tetrahydrofuran.[23,24] The second is the isolation of **4a** which can be readily separated from the diol byproduct by means of distillation.

A second problem which we encountered in the monomer synthesis is the polymerization of the monomer in the last step (i.e., of Equation 3.2). We feel that this polymerization is likely to be anionic in nature due to the basicity of the lithium salt of **4a** (i.e., **4aLi** in Equation 3.2) which can be expected to initiate the anionic polymerization of the monomer produced *in situ*, in addition to reacting with the acid chloride, i.e.,



(3.4)

4

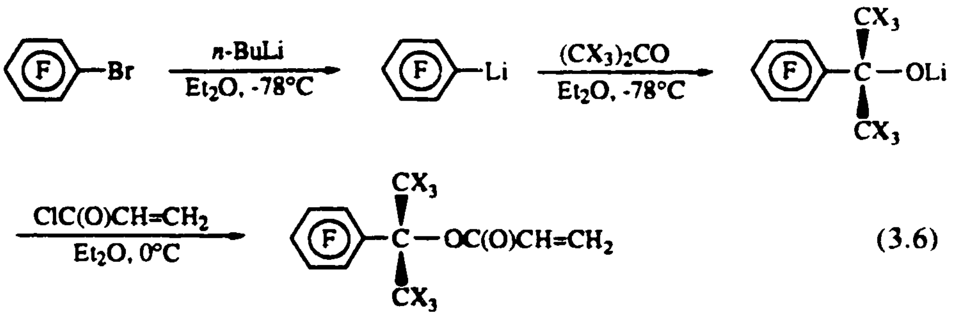


4

(3.5)

This problem cannot be entirely eliminated since the mutual presence of **4** and **4aLi** is unavoidable, but can be minimized if the acid chloride is always kept in excess. This was achieved by altering the order of addition such that addition of **4aLi** is made into excess of acryloyl chloride.

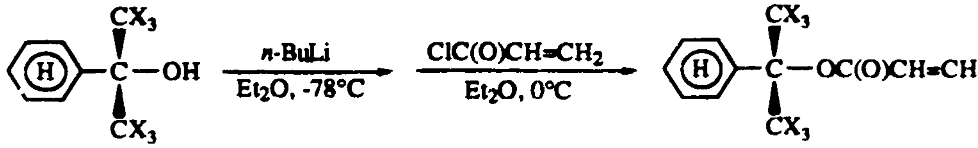
The other monomers were chosen to prepare polymers having different fluorine contents and distributions in their side-chains. This has enabled us to explore the effect of these differences on the physical properties of these materials. Since monomer **5** is prepared from a monolithioarene (C_6F_5Li) derived from bromopentafluorobenzene, which has a substantially lower tendency than does $C_6F_4H_2$ for the formation of bifunctional byproducts, isolation of its corresponding alcohol becomes unnecessary. This suggested to us that a one step synthesis of the vinyl monomers might be more practical and more convenient. This has been proven to be the case for monomers **5** and **6** which were prepared according to the following revised route:



(3.6)

where X = H for monomer **5**, X = F for monomer **6**.

Monomer **6** was produced in excellent overall yield (92%) while monomer **5** was formed in a lower overall yield (35%, mainly due to as yet undetermined side-reactions in the last step). Monomers **7** and **8** were prepared directly from their corresponding alcohols which are commercially available, i.e.,



(3.7)

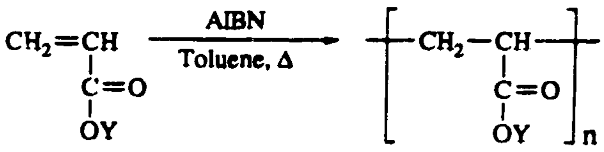
where X = F for monomer **7**, X = H for monomer **8**.

Monomers **6**, **7**, and **8** have been previously reported, however, they were not, or were only partially spectroscopically characterized.[16-19] They, along with monomers **4** and **5**, were identified from their elemental analysis, mass spectral, and multinuclear NMR data (Tables 3.1 and 3.2). Particularly noteworthy are the ^{1}H- and ^{19}F-NMR data. The vinyl protons appear as doublets of doublets at 5.8 - 6.4 ppm for the CH$_3$-substituted compounds (**4**, **5**, and **8**) and are shifted to lower field (by *ca.* 0.3 ppm) for the related compounds having CF$_3$ groups (**6** and **7**). As is seen from Table 3.2, the coupling constants for these vinyl protons are within the normal range (see the NMR data for the model compound methyl acrylate in the experimental section). The ^{19}F-NMR spectra are also a useful tool for identifying the fluorinated monomers. Thus, the fluorines in the CF$_3$

groups usually appear at around -71 ppm and the fluorines on the arene rings from -140 ppm to -163 ppm and are in their usual range.[1,2] These monomers have different fluorine contents varying from 0% (8) to about 54% (6) by weight as well as different fluorine distributions (i.e., substitutions on the arene rings and/or on their adjacent tertiary CX_3 carbons).

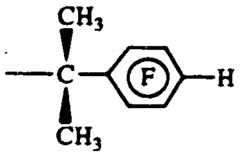
Preparation and Characterization of the Polyacrylates

Since these monomers belong to the vinyl family, they are subject to addition polymerizations with a variety of radical initiators such as 2,2'-azobis(2-methylpropionitrile) (AIBN), benzoyl peroxide (BPO), etc. In this work, we chose AIBN as the initiator since its initiation can be readily effected under mild conditions (40 - 70°C). Each of the polymers was prepared identically so that the effect of the H/F substitutions could be more readily ascertained. As a result, five addition polymers (polyacrylates) were conveniently and successfully prepared using solution techniques, i.e.,



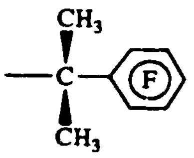
$$CH_2{=}CH(C{=}O)OY \xrightarrow[\text{Toluene, }\Delta]{\text{AIBN}} \left[-CH_2-CH(C{=}O)OY- \right]_n \qquad (3.8)$$

where Y =

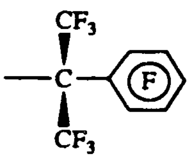


for poly-H_6-F_4H,

Y =

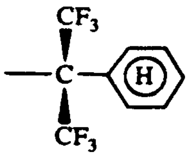


for poly-H_6-F_5, Y =

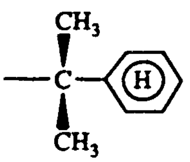


for poly-F_6-F_5,

Y =

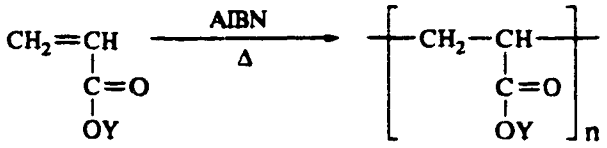


for poly-F_6-H_5, and Y =



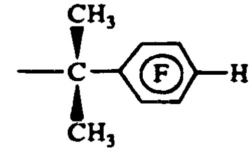
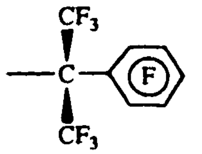
for poly-H_6-H_5

While the primary conversions were achieved readily at 55°C, final conversions of the monomers were effected under forcing conditions (90 - 100°C) to overcome the high viscosities of the reaction solutions. Polymerizations of monomers **4**, **5**, **7**, and **8** in toluene were homogeneous throughout the reaction, while that of monomer **6** was a precipitation polymerization. Except for poly-F_6-F_5, which is essentially insoluble in any solvents tested, these polyacrylates are readily soluble in solvents such as tetrahydrofuran, acetone, dichloromethane, benzene, toluene, and even diethyl ether. Thus, freestanding transparent films of these polymers can be easily cast from these solutions. On the other hand, transparent colorless objects (such as rods) of these polymers can be made through bulk polymerization, i.e.,



$$CH_2{=}CH(C{=}O)OY \xrightarrow[\Delta]{AIBN} \left[CH_2{-}CH(C{=}O)OY \right]_n \qquad (3.9)$$

where

Y =  for poly-H_6-F_4H, and Y =  for poly-F_6-F_5

These objects resemble Plexiglas® in both appearance and in hardness, probably due to their structural similarity, although quantitative measurements have not yet been made. The insolubility of poly-F_6-F_5 prevented elucidation of its molecular weight data by VPO and GPC, and of its microstructure by NMR. However, this insolubility or solvent-resistancy can be a desirable property of this material in certain circumstances such as when used as solvent-resistant containers, coatings, membranes, etc. The high fluorine content (*ca.* 54% by weight) of poly-F_6-F_5 also suggests that this material might act as a flame-retardant. Indeed, preliminary flame test indicated that it is self-extinguishing. The other polymers are completely characterized by VPO, GPC, and NMR because of their high solubilities. As is seen from Table 3.3, molecular weight data from GPC (polystyrene-equivalent values) are in good consistency with those from VPO measurements. Broad molecular weight distributions are observed for all these polyacrylates (prepared by solution techniques), as is expected for radical polymerizations, with maxima around a molecular weight value of 10^5 Daltons (Figure 3.3).

The ^{1}H- and ^{19}F-NMR data for these polymers (Table 3.4) are in excellent agreement with those for the corresponding monomers (Table 3.1). In particular, only small shifts were observed on the ^{19}F-NMR data for these polymers since the fluorines are in their side-chains which are not subject to bond rearrangements during polymerization. The same result can be seen from Table 3.4 for the ^{1}H-NMR resonances of the methyl groups. However, significant differences between the ^{1}H-NMR of the polymers and that of their corresponding monomers were expectedly observed, shown by the disappearance of the unsaturated vinyl proton resonances and emergence of new saturated methylene proton (around 1.5 ppm) and methine proton (around 2.4 ppm) resonances. A low-field shift (0.3 - 0.5 ppm) was observed on these protons for poly-F_6-H_5. These results lead us to conclude that these polymers possess the microstructures expected for olefin addition polymerizations. Their infrared spectroscopic data (Table 3.5) further support this conclusion and exhibit distinctive strong stretching frequencies attributable to C=O, C–O, and C–F groups at 1734 - 1781, 1233 - 1280, and 1131 - 1145 cm^{-1}, respectively. The fluoroarenes (C_6F_4X, X = H or F) in poly-H_6-F_4H, poly-H_6-F_5, and poly-F_6-F_5 also exhibit a very strong skeleton vibration frequency around 1500 cm^{-1}. UV-Visible spectroscopic data for these polymers are also consistent with their proposed structure. Thus, a strong absorption maximum at *ca.* 260 nm (the calculated extinction coefficient is in the order of 10^4 L/mol·cm, see Table 3.5) plus a weak to medium maximum at *ca.* 240 nm are observed.

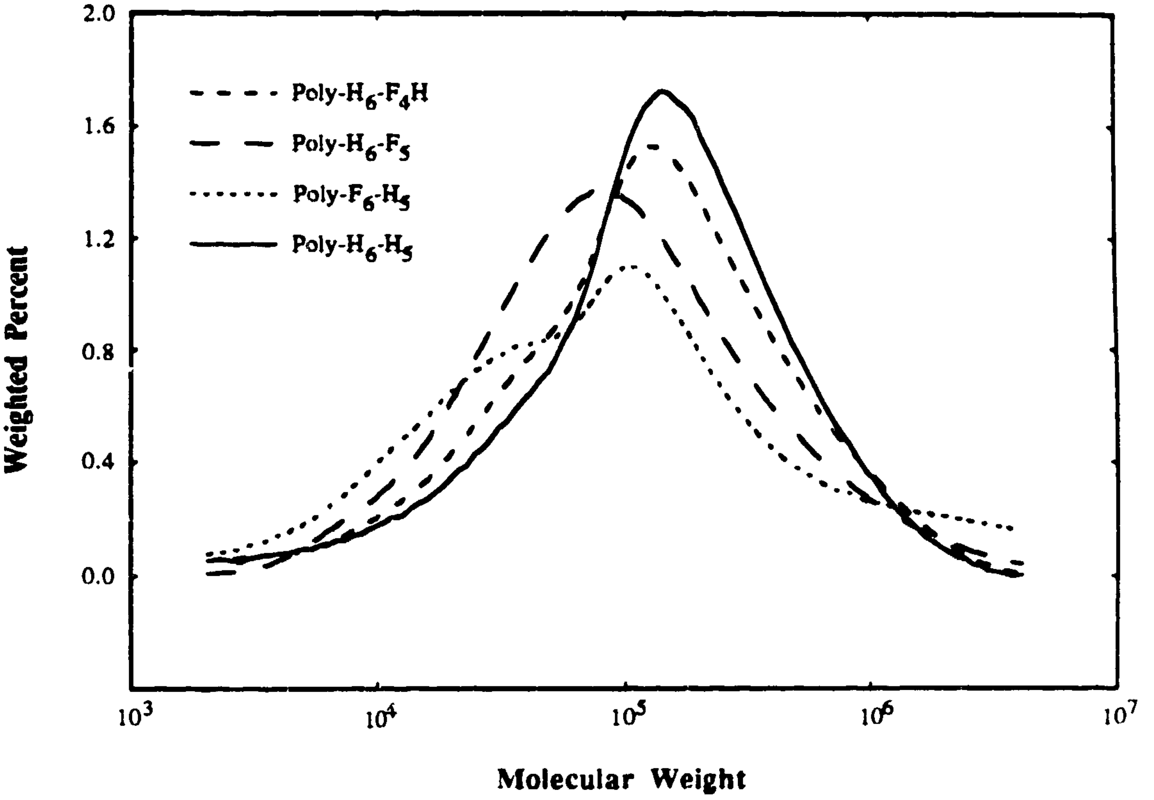


Figure 3.3. Molecular weight distribution curves of the polyacrylates

Morphology studies of these polyacrylates revealed that they are all amorphous materials.[25] The glass transition temperature (Tg) data obtained by DSC measurements were compiled in Table 3.3. We observe different Tg's arising from different fluorine contents and distributions. A general trend is that the fluorinated polymers possess a higher Tg than the non-fluorinated ones (by 20 - 30°C), regardless of whether the substitution of fluorine is to the CX_3 groups or to the arene rings. These polymers soften and flow at temperatures above their Tg's, which indicates that they are readily processable thermoplastics.

Differences in their thermal stabilities with respect to different fluorine contents and distributions in the side-groups of these five polyacrylates (prepared by solution techniques) are clearly shown from their thermal gravity analysis (TGA) results obtained both under N_2 (Figure 3.1) and in air (Figure 3.2). Four conclusions can be drawn: (1). Fluorine substitution does make the polymers thermally more stable. For example, non-fluorine-containing poly-H_6-H_5 starts to decompose at 180°C and loses 50% of its weight at 210°C, while the other fluorine-containing polyacrylates can stay stable until at least 200°C. (2). Substitution of fluorine on the CX_3 groups makes the polymers much more stable, while substitution on the arene ring has much less effect in this regard. For instance, under N_2, the CF_3-substituted polymer, poly-F_6-F_5, does not start to lose weight until 380°C and loses 50% of its weight at 510°C, while the CH_3-substituted polymer, poly-H_6-F_5, starts to decompose at 200°C and loses 50% of its weight at 290°C. This is a more than 200°C difference in their thermal stabilities! On the other hand, comparing poly-F_6-F_5 with poly-F_6-H_5, we see only *ca.* 100°C difference in their initial decomposition temperatures (i.e., 280°C and 380°C, respectively), and they show basically the same overall stability up to *ca.* 550°C. (3). Comparison of their thermal behaviors in air with those under N_2 indicates that the CF_3-substituted polymers decompose at a lower temperature in air than under N_2 due to thermal oxidation. For instance, poly-F_6-H_5 loses 50% of its weight at 520°C under N_2 and 430°C in air, respectively. A 40°C difference is also observed for poly-F_6-F_5. No difference was observed for the other polymers, which indicates that thermal oxidation does not initiate until a specific temperature which is above their decomposition temperatures (*ca.* 300°C in these cases). (4). Poly-F_6-F_5 shows the highest thermal stability in all these five polyacrylates. Specifically, under N_2, it does not start to decompose until 380°C (360°C in air), and loses 50% of its weight at 510°C (470°C in air). This thermal stability, incorporating its solvent-resistance, flame-retardance, and processability (Tg = 83°C), indicates that this material may be of interest in the area of specialty engineering plastics.

In conclusion, five acrylic esters and five polyacrylates having different fluorine contents and distributions in their side-groups have been successfully prepared and these high polymers have potential in practical applications. Significant differences in their thermal stabilities were found with respect to fluorine contents and distributions in these polyacrylates, and the highest stability arises from CF_3 substitutions in the side-chains of the polymers. Extension of this synthetic methodology to prepare the analogous organonickel polyacrylates is currently underway and the syntheses and the properties of these two classes of polymers will be compared.

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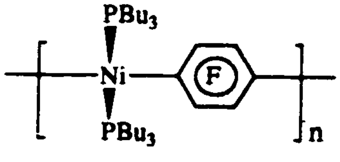
CHAPTER 4

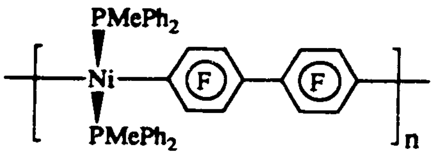
SYNTHESIS AND CHARACTERIZATION OF NOVEL ORGANONICKEL-ORGANOSILICON ALTERNATING COPOLYMERS†

INTRODUCTION

Previous reports from our laboratory have discussed the synthesis by metathesis and the characterization of oligomers and polymers containing $Ni(PBu_3)_2$ or $Ni(PMePh_2)_2$ units having 1,4-tetrafluorophenylene (**I**) or 4,4'-octafluorobiphenylene (**II**) bridges.[1-6]



I



II

These organometallic polymers are materials with potentially interesting mechanical, electrical conductivity, liquid-crystalline, and nonlinear optical properties.[7-14] However,

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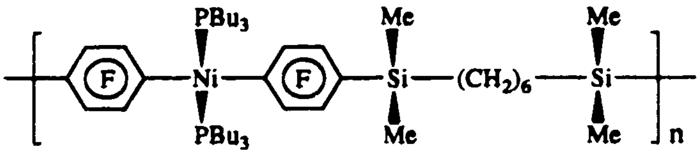
†A version of this chapter has been accepted for publication. See: X. A. Guo, A. D. Hunter and J. Chen, *J. Polym. Sci.*, Part A: *Polym. Chem.* (accepted May 17, 1994).

they are rigid-rods, which do not melt or soften before decomposition,[2,5,15,16] probably due to the severe rigidity of their backbones. It is well established that introduction of silyl or siloxane units into the polymer chains will remarkably reduce the chain stiffness of the resulting polymers. In addition, polymers containing silyl or siloxane units offer a wide range of specialty applications in many diverse fields because of their unique combination of properties.[17] With this in mind, we decided to prepare a series of novel polymers having a repeating unit with alternating nickel and silicon fragments bridged by 1,4-tetrafluorophenylene (i.e., $-1,4\text{-}C_6F_4\text{-}Ni(PR_3)_2\text{-}1,4\text{-}C_6F_4\text{-}SiR_2-$), namely organonickel-organosilicon copolymers derived from condensation or metathesis reactions between an organonickel monomer and a series of organosilicon monomers (i.e., $SiMe_2Cl_2$, $SiMe(Hex)Cl_2$, $SiPh_2Cl_2$, $O(SiMe_2Cl)_2$, and $(CH_2)_6(SiMe_2Cl)_2$), e.g., III:



III

In this chapter, we report the complete results of our synthetic and characterization studies of these novel organonickel-organosilicon copolymers.

EXPERIMENTAL SECTION

Materials

1,2,4,5-tetrafluorobenzene (99+%), *n*-butyllithium (1.6 M and 2.5 M in hexanes), nickel (II) bromide (anhydrous, 99%), tributylphosphine (99%), methyldiphenylphosphine (99%) chlorotrimethylsilane (98%), and dichlorodimethylsilane (99%) were purchased from Aldrich. Diphenyldichlorosilane (97+%), *n*-hexylmethyldichlorosilane (97+%), 1,3-dichlorotetramethyldi-siloxane (97+%) and 1,6-bis(chlorodimethylsilyl)hexane (90%) were purchased from Hüls Petrarch Systems. All of the above chemicals were used without further purification. *n*-Butyllithium was standardized before use.[18]

Unless otherwise stated, all materials and subsequent reactions were performed using standard techniques for the manipulation of air-sensitive materials as described previously.[19-22] Thus, anaerobic and anhydrous conditions were maintained by using a prepurified argon or dinitrogen atmosphere employing vacuum-line techniques. The reagent grade solvents used were purified by distillation under argon and nitrogen from appropriate drying agents: tetrahydrofuran (THF), diethyl ether (Et_2O), and *n*-hexanes from Na/benzophenone, dichloromethane (CH_2Cl_2) from CaH_2. Methanol and ethanol were degassed by nitrogen. Unless specified otherwise, the reactions and any subsequent manipulations described below were effected at ambient temperature (*ca.* 23°C).

The syntheses of $Ni(PBu_3)_2Br_2$, $Ni(PMePh_2)_2Br_2$, and $Ni(PMePh_2)_2(1,4\text{-}C_6F_4H)_2$ have been described previously, as has an alternate preparation of $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$.[1,4,23]

Synthesis of $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$

To a precooled (-78°C) stirred solution of $1,2,4,5\text{-}C_6F_4H_2$ (7.90 mL, 70.8 mmol) in Et_2O (150 mL) was added $^{n}BuLi$ (1.6 M in hexanes, 42.5 mL, 68.0 mmol) over a period of 10 min, resulting in the formation of a clear colorless solution. The mixture was kept for 2 h at -78°C with stirring and was then cannulated into a second flask containing $Ni(PBu_3)_2Br_2$[4,23] (20.0 g, 32.1 mmol) and THF (150 mL) maintained at 0°C. The resulting mixture was stirred for 3 h at 0°C and was then kept overnight at room temperature. A yellow powder started to form 10 min after mixing and eventually developed into a thick yellow suspension. Methanol (2 mL) was added to destroy any residual organolithium reactants which caused the color of the supernatant to change from brown to brownish yellow. The volume of the solvents were reduced by vacuum to *ca.* 30 mL and then methanol (100 mL) was added to complete the precipitation of the product.

The yellow solid was filtered and then recrystallized from THF/hexanes (100 mL/100 mL) in a yield of 93.7% (22.9 g, 30.1 mmol) of $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$.[5] ^{1}H-NMR ($CD_2Cl_2$): δ 6.63 (m, 2H), 1.43 (m, 12H), 1.25 (m, 12H), 1.08 (m, 12H), 0.86 (m, 18H); ^{19}F-NMR (CD_2Cl_2): δ -117.44 (m, 2F), -142.33 (m, 2F); $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 7.64 (s, 2P). ANAL. Calcd for $C_{36}H_{56}F_8NiP_2$: C, 56.78%; H, 7.41%. Found: C, 56.82%; H, 7.44%.

Synthesis of $Ni(PMePh_2)_2(1,4\text{-}C_6F_4SiMe_3)_2$

To a precooled (-20°C, solid CO_2/acetone bath) stirred solution of $Ni(PMePh_2)_2(1,4\text{-}C_6F_4H)_2$ (1.00 g, 1.32 mmol)[1] in THF (50 mL) was added ^{n}BuLi (2.5 M in hexanes, 1.08 mL, 2.71 mmol) over a period of 10 min. The original yellow suspension turned orange, and was stirred for 30 min at -20°C, and the bath was then replaced by an ice/water bath (0°C). 20 min later, $SiMe_3Cl$ (0.340 mL, 2.71 mmol) was added dropwise which caused the orange suspension to turn into a clear green solution after 15 min. This was stirred for 1 h at 0°C and then for another 2 h at room temperature. The volume of the solvent was reduced by vacuum to 5-10 mL and then methanol (20 mL) was added to cause the formation of a powdery precipitate. Subsequently the suspension was taken to dryness *in vacuo*. The product was extracted with CH_2Cl_2 (50 mL) and the resulting solution was subsequently filtered. Removal of the solvent under vacuum resulted in the formation of a yellow powder which was washed with hexanes (3 × 10 mL) and dried *in vacuo* overnight affording $Ni(PMePh_2)_2(1,4\text{-}C_6F_4SiMe_3)_2$ in a yield of 74.8% (0.890 g, 0.987 mmol). ^{1}H-NMR (CD_2Cl_2): δ 7.46 (m, 8H), 7.28 (m, 12H), 1.68 (t, 6H), 0.19 (t, 18H); ^{19}F-NMR (CD_2Cl_2): δ -117.93 (m, 4F), -131.73 (m, 4F); $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 10.62 (s, 2P). ANAL. Calcd for $C_{44}H_{44}F_8NiP_2Si_2$: C, 58.61%; H, 4.92%. Found: C, 58.73%; H, 4.77%.

Synthesis of $Ni(PBu_3)_2(1,4\text{-}C_6F_4SiMe_3)_2$

To a precooled (-15°C, solid CO_2/acetone bath) stirred solution of $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$ (1.9 g, 2.5 mmol) in THF (50 mL) was added ^{n}BuLi (1.6 M in hexanes, 4.6 mL, 7.4 mmol) over a period of 10 min. The original yellow suspension turned into a clear yellow solution which was stirred for 1.5 h at 0°C. $SiMe_3Cl$ (0.73 mL, 5.8 mmol) was then added dropwise and the mixture was stirred for 3 h at 0°C and then for another 20 h at room temperature at which stage the reaction was quenched with methanol (2 mL). The solvent was removed by vacuum and the resulting solid was filtered and washed with water (3 × 10 mL) and methanol (3 × 10 mL). Recrystallization of the product from 95% ethanol (*ca.* 20 mL) afforded $Ni(PBu_3)_2(1,4\text{-}C_6F_4SiMe_3)_2$ as yellow needle-like crystals in a yield of 84% (1.9 g, 2.1 mmol). ^{1}H-NMR (CD_2Cl_2): δ 1.41 (m, 12H), 1.24 (m, 12H), 1.08 (m, 12H), 0.85 (m, 18H), 0.34 (t, 18H); ^{19}F-NMR (CD_2Cl_2): δ -117.79 (m, 4F), -131.71 (m, 4F); ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 7.89 (s, 2P). ANAL. Calcd for $C_{42}H_{72}F_8NiP_2Si_2$: C, 55.69%; H, 8.01%. Found: C, 55.97%; H, 8.06%.

Polymerization

A typical example of the polymerizations is described below. All polymerizations were conducted under an atmosphere of dry N_2, and no effort was made to optimize the yields of the polymers.

To a precooled (0°C) stirred solution of $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$ (2.5 mmol, 1.9 g) in THF (60 mL) was added ^{n}BuLi (1.6 M in hexanes, 3.1 mL, 5.0 mmol) over a period of 15 min. The original yellow suspension turned into a clear yellow solution which was stirred for 1.5 h at 0°C and then $O(SiMe_2Cl)_2$ (0.49 mL, 2.5 mmol) was added dropwise. This mixture was stirred for 3 h at 0°C and then for 2 days at room temperature at which stage the reaction was quenched with methanol (2 mL). The solvent was removed by vacuum resulting in the formation of a yellow viscous liquid which was subsequently washed with water (3 × 20 mL) and methanol (3 × 20 mL) and dried *in vacuo* for 2 days. Polymer **4** was isolated in a yield of 74% (1.6 g) as a soft, orange, and transparent gel-like solid material.

The molecular weight data for these polymers are presented in Table 4.1 and Figure 4.1. The spectroscopic (NMR, FTIR, and UV-Visible) data are listed in Tables 4.2 and 4.3. The glass transition temperatures for polymers **4** and **5** are illustrated in Figure 4.2.

Measurements

Nuclear magnetic resonance spectra were recorded using a Bruker AM-400 spectrometer on dichloromethane-d_2 solutions and employing a deuterated solvent lock. The ^{19}F- and $^{31}P\{^1H\}$-NMR chemical shifts are reported in parts per million downfield from external $CFCl_3$ and 85% H_3PO_4, respectively. The ^1H-NMR chemical shifts are reported in parts per million downfield from external Me_4Si. The IR spectra were recorded as KBr pallets on a Nicolet 7199 spectrophotometer. Elemental analyses was performed by the University of Alberta Microanalytical Services. Glass transition temperatures (Tg) of the polymers were measured using a TA Instruments DSC 2910 differential scanning calorimeter (DSC). Samples were run under a nitrogen atmosphere at a heating rate of 10°C/min. The second heating thermograms were adopted to remove thermal history effects.[24] The Tg was taken as the intersection of the extrapolation of the baseline with that of the inflection in the DSC thermogram.[25] Osmometry measurements were made in benzene solutions on a Corona Wescan Vapor Pressure Osmometer (VPO) by the University of Alberta Microanalytical Services. Gel permeation chromatography (GPC) was performed on an automated Waters 600E HPLC/GPC system operated at 30.0°C using tetrahydrofuran as the eluting solvent at a flow rate of 1.20 mL/min through three Waters HT µ-Styragel columns (10^3 Å, 10^6 Å, and 10 µm linear). Chromatograms and UV-Visible spectra were collected on-line on a Waters model 991 Photodiode Array (UV-Visible) detector incorporating a Waters model 410 Differential Refractive Index detector.

Table 4.1. Molecular Weight Data for the Polymers

Silicon Monomer	Polymer	Yield (%)	[η] (dL/g)	VPO Molecular Weight[a]	GPC Molecular Weight[b]			
					$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_p$	$\overline{M}_w / \overline{M}_n$
$SiMe_2Cl_2$	1	86	0.056	12,530	9,700	15,800	14,500	1.6
$SiMe(Hex)Cl_2$	2	84	0.088	4,260	4,400	7,300	6,500	1.7
$SiPh_2Cl_2$	3	93	0.059	4,360	4,800	8,600	6,600	1.8
$O(SiMe_2Cl)_2$	4	74	0.10	7,970	8,400	13,900	12,400	1.6
$(CH_2)_6(SiMe_2Cl)_2$	5	78	0.12	7,340	7,950	19,700	18,400	2.5

[a] Number-average molecular weight, $\overline{M}_n$.

[b] Polystyrene-equivalent molecular weights.

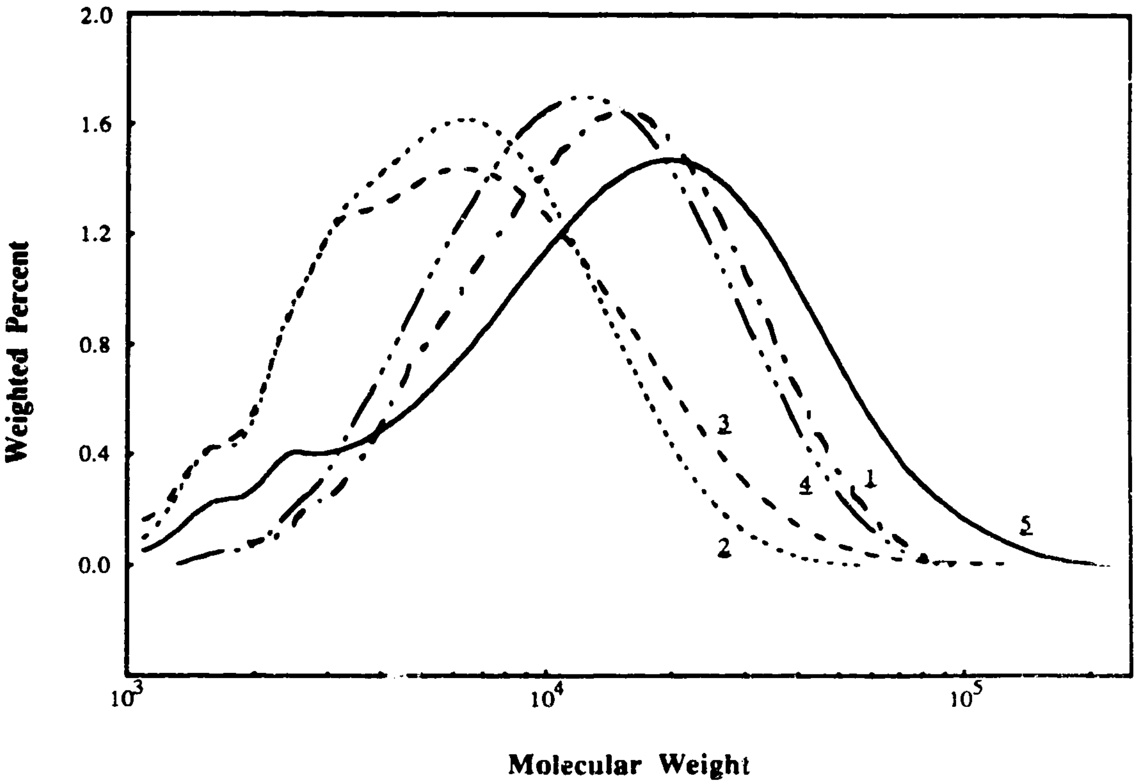


Figure 4.1. Polystyrene equivalent molecular weight distributions of the polymers: (1) polymer **1**; (2) polymer **2**; (3) polymer **3**; (4) polymer **4**; (5) polymer **5**.

Table 4.2. Multinuclear (^1H-, ^{19}F-, and $^{31}P\{^1H\}$-) NMR Data for the Polymers[a]

Polymer	Primary Structure[b]	^1H (ppm)	$^{31}P\{^1H\}$ (ppm)	^{19}F (ppm)
1	$-[-C_6F_4-Ni(PBu_3)_2-C_6F_4-SiMe_2-]_n-$	1.44 (br., 12H), 1.26 (m, 12H), 1.09 (br., 12H), 0.86 (m, 18H), 0.67 (s, 6H)	7.64 (s, 2P)	-117.64 (m, 4F), -131.51 (m, 4F)
2	$-[-C_6F_4-Ni(PBu_3)_2-C_6F_4-SiMe(Hex)-]_n-$	1.44 (br., 12H), 1.35 (br., 4H), 1.26 (m, 12H), 1.21 (br., 4H), 1.09 (br., 12H), 0.85 (m, 23H), 0.66 (br., 3H)	7.60 (s, 2P)	-117.62 (m, 4F), -131.15 (m, 4F)
3	$-[-C_6F_4-Ni(PBu_3)_2-C_6F_4-SiPh_2-]_n-$	7.62 (m, 4H), 7.44 (m, 2H), 7.35 (m, 4H), 1.46 (br., 12H), 1.29 (m, 12H), 1.12 (br., 12H), 0.87 (m, 18H), 0.67 (s, 12H)	7.59 (s, 2P)	-116.84 (m, 4F), -124.62 (m, 4F)
4	$-[-C_6F_4-Ni(PBu_3)_2-C_6F_4-SiMe_2-O-SiMe_2-]_n-$	1.45 (br., 12H), 1.27 (m, 12H), 1.11 (br., 12H), 0.87 (m, 18H), 0.39 (s, 12H)	7.66 (s, 2P)	-117.63 (m, 4F), -132.15 (m, 4F)
5	$-[-C_6F_4-Ni(PBu_3)_2-C_6F_4-SiMe_2-(CH_2)_6-SiMe_2-]_n-$	1.43 (br., 12H), 1.29 (br., 8H), 1.22 (m, 12H), 1.08 (br., 12H), 0.86 (m, 18H), 0.83 (br., 4H), 0.33 (s, 12H)	7.90 (s, 2P)	-117.70 (m, 4F), -131.35 (m, 4F)

[a] Dichloromethane-d_2 as the solvent.

[b] Unspecified phenylenes denote *para* linkages.

Table 4.3. UV-Visible and Infrared Absorption Data for the Polymers

Polymer	UV Maxima (nm)[a]	IR Frequencies[b] (cm^{-1})				
		C–F	–C_6F_4–	Si–CH_3	Si–C_6H_5	Si–O–Si
1	250 (s), 294 (m)	1090	1420, 1406	1254	–	–
2	250 (s), 294 (m)	1091	1418	1256	–	–
3	250 (s), 294 (ms)	1091	1416	–	1109	–
4	250 (s), 290 (w)	1089	1420, 1405	1257	–	1089, 1067
5	250 (s), 290 (w)	1090	1419, 1403	1251	–	–

[a] s — strong, ms — medium strong, m — medium, w — weak.

[b] Measured as dichloromethane casts.

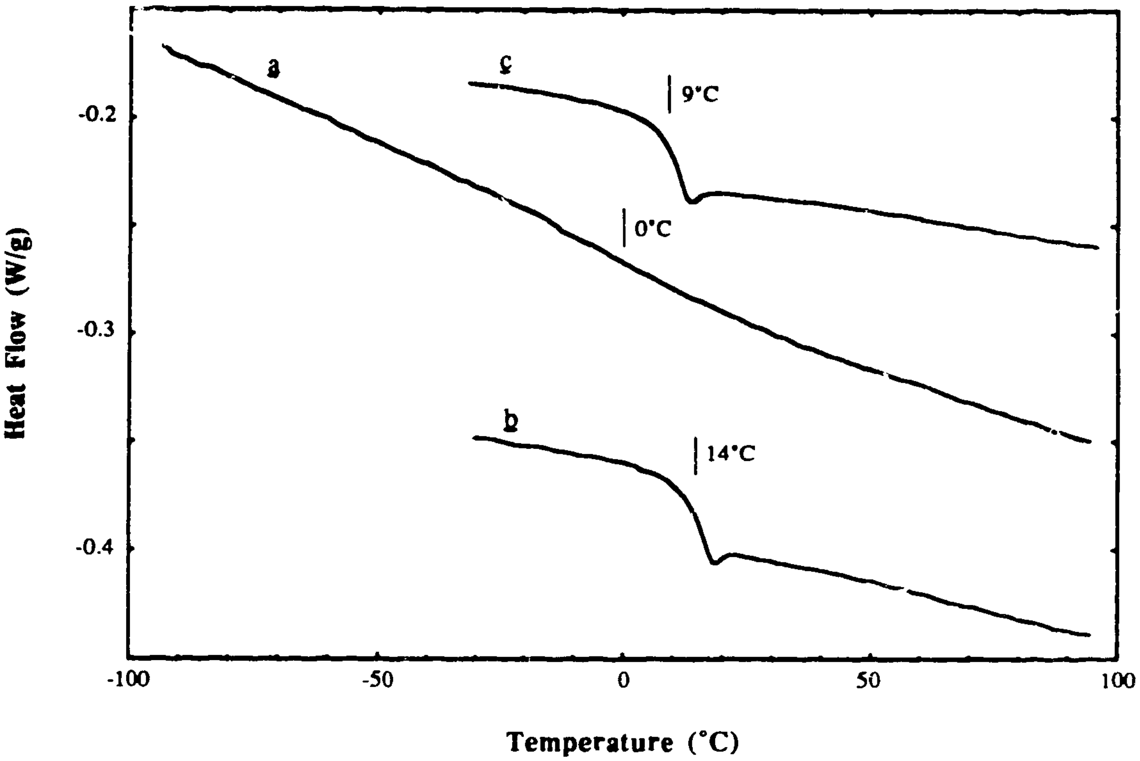


Figure 4.2. Glass transitions of organonickel-organosilicon copolymers *versus* organonickel polymer: (a) organonickel polymer $-[-Ni(PMePh_2)_2-C_6F_4-Ni(PBu_3)_2-C_6F_4-]_n-$ ($\overline{M}_n$ = 12,900, $\overline{M}_w$ = 18,400);[5,16] (b) polymer **4**; (c) polymer **5**.

Molecular weight calculations were performed using the Maxima 820 chromatography software (Waters, Dynamic Solutions, Division of Millipore) based on a calibration using polystyrene narrow standards. Intrinsic viscosities were measured in 0.05–0.1% solutions using an Ubbelohde viscometer in a water bath maintained at 30.00 ± 0.01°C and calculated according to the single-point method described by Solomon and Ciuta.[26]

RESULTS AND DISCUSSION

Preparation of the Monomer

In a previous account, we have stressed that the importance of high purity organometallic monomers is critical to their subsequent condensation polymerizations.[27] The monomer which we used in this preparation of organonickel-organosilicon polymers, $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$, is no exception. Although the preparation of this monomer is, in principal, relatively straightforward, many researchers, including those from this laboratory, have pointed out that to obtain this monomer in high purity and in high yield, special measures have to be taken.[1] In particular, the rate of addition of *n*-butyllithium during the generation of the aryllithium reagent (i.e., $1,4\text{-}C_6F_4HLi$) has to be controlled in order to prevent the formation of the unwanted dilithiation by-product (i.e., $1,4\text{-}C_6F_4Li_2$). The use of an excess of the parent fluoroaryl compound (i.e., $1,4\text{-}C_6F_4H_2$) can also minimize this complication. In this preparation, however, we found that this problem can be minimized more conveniently, or virtually eliminated, simply through utilization of a different solvent system,[6] namely using diethyl ether (Et_2O) instead of tetrahydrofuran (THF) as the solvent for the lithiation of $1,4\text{-}C_6F_4H_2$, i.e.,

$$1,4\text{-}C_6F_4H_2 + n\text{-BuLi} \xrightarrow[-78^\circ C]{Et_2O} 1,4\text{-}C_6F_4HLi \qquad (4.1)$$

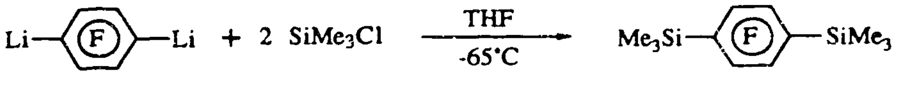
Reines et al. have concluded that the percentage of the dilithiation by-product formed for this reaction was below 1% if using Et_2O as the solvent in place of THF where up to 50% of the by-product can be produced.[28] Solvent Et_2O could also be used for the subsequent metathesis reaction. We chose THF, however, to increase the reaction speed and therefore to avoid other possible side-reactions such as the formation of benzynes, i.e.,[2]

$$Ni(PBu_3)_2Br_2 + 2\ 1,4\text{-}C_6F_4HLi\ (\text{in } Et_2O) \xrightarrow[0^\circ C]{THF} Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2 \qquad (4.2)$$

As a result, the metathesis reaction between $Ni(PBu_3)_2Br_2$ and two equivalents of 1,4-C_6F_4HLi produced the expected product (i.e., $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$) in high isolated yield. Analytical and spectroscopic data also indicated that a compound of essentially 100% purity was obtained. A quantitative reaction is therefore implied.

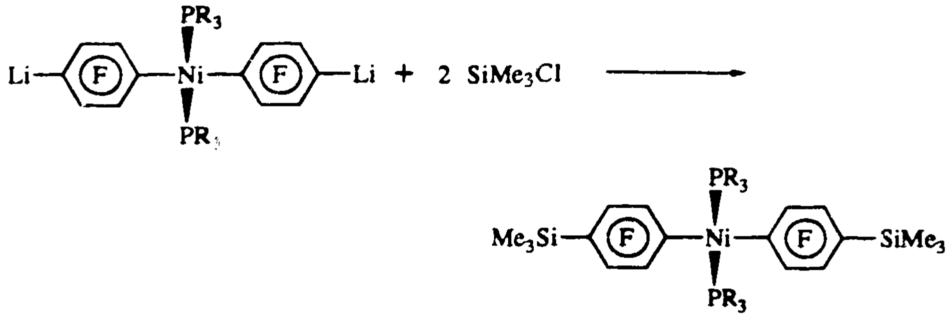
Preparation of the Model Compounds

Before the organonickel-organosilicon copolymers were actually made, we had to establish whether the metathesis reaction between the lithiated nickel compound (i.e., $Ni(PBu_3)_2(1,4\text{-}C_6F_4Li)_2$) and chlorosilanes (*vide infra*) would proceed as postulated. Tamborski et al. have successfully prepared 1,4-bis(trimethylsilyl)tetrafluorobenzene via the metathesis reaction between a dilithiated arene and two equivalents of chlorotrimethylsilane, i.e.,[29,30]



(4.3)

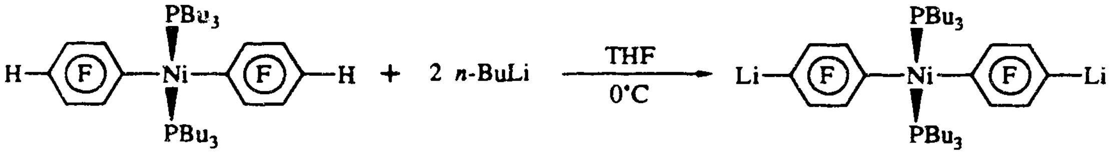
however, no report had previously been made of the preparation of the analogous nickel compounds via the same route:

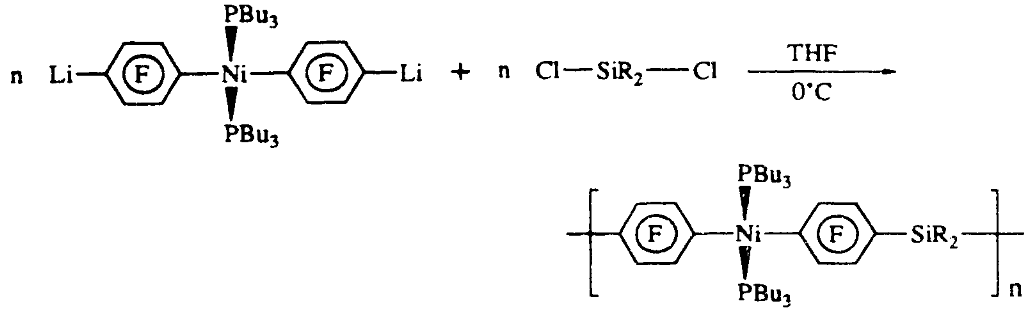

(4.4)

An additional concern which must be addressed for successful condensation polymerizations is that this metathesis reaction must proceed in a very clean fashion to ensure that no side-reactions occur. We have therefore made the attempts to prepare the relevant model compounds for both $PR_3 = PBu_3$ and $PR_3 = PMePh_2$. Both reactions proceeded smoothly, and the corresponding model compounds were obtained via the above route in high yield and in high purity as was indicated by their analytical and spectroscopic (NMR) data. which implied that well-behaved metathesis reactions had taken place. These results unambiguously established the feasibility of our postulated synthetic strategy for the organonickel-organosilicon copolymers.

Preparation of Condensation Polymers

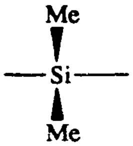
A total of five organonickel-organosilicon alternating copolymers have been successfully prepared using the $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$ monomer and a series of organosilicon chlorides via the metathesis reactions developed in the model studies. The complete scheme for the preparations are illustrated as follows:


(4.5)

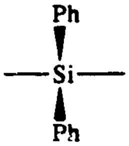


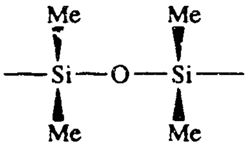
(4.6)

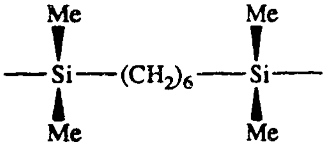
where

$SiR_2 =$  $-\overset{Me}{\underset{Me}{Si}}-$ for polymer **1**;

$SiR_2 =$  $-\overset{Me}{\underset{Hex}{Si}}-$ for polymer **2**;

$SiR_2 =$  $-\overset{Ph}{\underset{Ph}{Si}}-$ for polymer **3**;

$SiR_2 =$  $-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-$ for polymer **4**;

and $SiR_2 =$  $-\overset{Me}{\underset{Me}{Si}}-(CH_2)_6-\overset{Me}{\underset{Me}{Si}}-$ for polymer **5**

The PBu_3-containing polymers, rather than the $PMePh_2$-containing ones, were chosen as the initial targets because the greater solubility of the PBu_3-containing model compound suggested that the PBu_3-containing polymers would be more readily accessible for subsequent characterizations which rely solely on solution techniques. Thus, these polymers were characterized by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC) to determine their molecular weights and by multinuclear (^1H-, ^{19}F-, and $^{31}P\{^1H\}$-) NMR, FTIR, and UV-Visible spectroscopies to determine their repeating unit structures. These data are listed in Tables 4.1, 4.2, and 4.3. Since it is easier to obtain and interpret the spectroscopic, particularly NMR, data at the relatively low molecular weight level, no attempt was made to maximize the molecular weights of the polymers.

As is seen from Table 4.1, the molecular weights of the polymers calculated relative to polystyrene through GPC were consistently in good agreement with the results obtained from VPO. In addition, their molecular weight distributions derived from GPC traces (using polystyrene calibration) displayed polydispersities normal for condensation polymerizations (Figure 4.1), indicating a well-behaved polymerization system. These results are in obvious contrast to those for the analogous organonickel polymers where large discrepancy in between their GPC and their actual molecular weights and wide polydispersities calculated from GPC were usually observed.[5,15,16] These observations, along with the increase in backbone flexibility that introduction of the silyl or siloxane units into the organonickel backbones would be expected to produce,[17,31] suggest that dramatically decreased backbone rigidity of the polymers has occurred to such an extent that the organonickel-organosilicon polymers actually possess a coil-like structure.

All of the five polymers are readily soluble in common organic solvents such as THF, dichloromethane, and benzene. Under ambient conditions, polymers **1** and **3** precipitated as yellow powders from methanol. Polymers **2**, **4**, and **5** were isolated as soft, orange, and transparent gel-like materials. This stands in contrast to the fact that the corresponding organonickel polymers are powdery materials which have much more limited solubilities in organic solvents[2,5,15,16] and is further evidence that introduction of the silyl or siloxane units into the organonickel backbones has remarkably decreased the chain rigidity of the polymers. In fact, the differential scanning calorimetry (DSC) results of the polymers directly reflect this observation. As is depicted in Figure 4.2, polymers **4** and **5** display distinctive Tg transitions, characteristic of polymers having a flexible coil-like structure, near room temperature (Tg = 14°C for polymers **4** and Tg = 9°C for polymer **5**, respectively) while the organonickel analog shows only a very small Tg transition in this temperature range (Tg = *ca.* 0°C) which is not unexpected for a relatively inflexible rod-like polymer where segmental motions of the molecules are so restricted that mainly minor motions from the side-groups (i.e., alkyl or aryl groups in PR_3) contribute to this physical transition.

The multinuclear (^1H-, ^{19}F-, and $^{31}P\{^1H\}$-) NMR spectra of the polymers were qualitatively similar to those of the model compounds (Table 4.2). In particular, compared to the model compound $Ni(PBu_3)_2(1,4\text{-}C_6F_4SiMe_3)_2$, a difference of less than 0.30 ppm (upfield shift except for polymer **5**) was observed for the $^{31}P\{^1H\}$-NMR and some upfield shift (*ca.* 0.4 ppm) occurred for the fluorines which are close to the $SiMe_2OSiMe_2$ unit in polymer **4** while all fluorines in polymer **3** are shifted downfield (*ca.* 1 ppm for the fluorines close to $Ni(PBu_3)_2$ and *ca.* 7 ppm for those adjacent to $SiPh_2$, respectively). The fluorine resonances for all other polymers essentially remain unchanged. This result and those from FTIR and UV-Visible measurements for these polymers are consistent with the polymer repeating units having the structural features illustrated in Equation 4.6.

In conclusion, we have successfully prepared a series of novel organonickel-organosilicon alternating copolymers with molecular weights ranging from 7,300 to 19,700 ($\overline{M}_w$) and normal molecular weight distributions. These polymers appear to behave as relatively flexible coil-like species as would be expected given the introduction of the silyl or siloxane units into the rigid backbones of the organonickel homopolymers. Work is now underway to examine the physical and mechanical properties of these polymers and to compare them to those of the related tetrafluorophenylene bridged organosilicon homopolymers.

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CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF ORGANOSILICON DERIVATIVES OF TETRAFLUOROBENZENE: X-RAY CRYSTAL STRUCTURE OF 1,4-BIS(2',3',5',6'-TETRAFLUOROPHENYLDIMETHYLSILYL)TETRAFLUOROBENZENE†

INTRODUCTION

As an extension of our on-going studies on one-dimensional rigid-rod organometallic polymers (e.g., $-[-Ni(PR_3)_2-1,4\text{-}C_6F_4-]_n-$),[1] we became interested in a new class of polymers incorporating flexible organosilicon entities into the rigid organometallic polymer backbones (i.e., polymers, $-[-1,4\text{-}C_6F_4-Ni(PBu_3)_2-1,4\text{-}C_6F_4-SiR_2-]_n-$, derived from $Ni(PBu_3)_2(1,4\text{-}C_6F_4H)_2$ and SiR_2Cl_2).[2] These organonickel-organosilicon copolymers are expected to offer chemical and physical properties intermediate between those of the corresponding organonickel[1] and organosilicon[3] homopolymers and are therefore interesting in terms of the structure-property relationships of main-chain organometallic polymers.[4] Although organosilicon polymer chemistry is well developed,[3] the particular organosilicon homopolymers (i.e., fluorinated polysilarylenes, e.g., $-[-SiMe_2-(CH_2)_6-SiMe_2-1,4\text{-}C_6F_4-]_n-$) we required for these comparative studies have not been reported and we therefore decided to study their chemistry. Given the complexities incurred in polymerizing such materials to high molecular weights and in characterizing the resultant products, we have found that optimal conditions for the syntheses of model compounds must be established and their detailed characterizations must be carried out before the polymers can be successfully prepared and characterized. We therefore have prepared a series of organosilicon derivatives of tetrafluorobenzene as model compounds through metathesis reactions between organolithium reagents and organosilicon chlorides. In this chapter, we report the complete results of the synthesis and characterization of nine such model compounds, a representative example of which is structurally characterized by X-ray crystallography.

EXPERIMENTAL SECTION

Unless otherwise stated, all materials and subsequent reactions were performed using standard techniques for the manipulation of air-sensitive materials as described previously[5]. Thus, anaerobic and anhydrous conditions were maintained by using a prepurified argon or dinitrogen atmosphere employing vacuum-line techniques. The reagent grade solvents used were purified by distillation under argon and nitrogen from appropriate drying agents: tetrahydrofuran (THF), diethyl ether (Et_2O), and *n*-hexanes from Na/benzophenone. Methanol was deaerated by nitrogen. Unless specified otherwise, the reactions and any subsequent manipulations described below were effected at ambient temperature (*ca.* 23°C). No effort was made to optimize the yield of the product in most of the syntheses.

Nuclear magnetic resonance spectra were recorded using a Bruker AM-400 spectrometer on dichloromethane-d_2 solutions and employ a deuterated solvent lock. The ^1H- and ^{19}F-NMR chemical shifts are reported in parts per million downfield from external Me_4Si and $CFCl_3$, respectively. Elemental analyses were performed by the University of

Alberta Microanalytical Services. Mass spectral data were acquired in the University of Alberta Mass Spectroscopy Laboratory.

Materials

1,2,3,5-tetrafluorobenzene (1,3-$C_6F_4H_2$, 95%), 1,2,4,5-tetrafluorobenzene (1,4-$C_6F_4H_2$, 99+%), *n*-butyllithium (*n*-BuLi, 1.6 M in hexanes), chlorotrimethylsilane ($SiMe_3Cl$, 98%), and dichlorodimethylsilane ($SiMe_2Cl_2$, 99%) were purchased from Aldrich. *n*-Hexylmethyldichloro-silane ($SiMe(Hex)Cl_2$, 97+%), 1,3-dichlorotetramethyl-disiloxane ($O(SiMe_2Cl)_2$, 97+%), and 1,6-bis(chlorodimethylsilyl)hexane ($(CH_2)_6(SiMe_2Cl)_2$, 90%) were purchased from Hüls Petrarch Systems (currently called United Chemicals Technologies, Inc.). All the above chemicals were used without further purification. *n*-Butyllithium was standardized before use[6].

Preparation of 1,3-Bis(trimethylsilyl)tetrafluorobenzene, 1

To a precooled (-78°C) stirred solution of 1,2,3,5-tetrafluorobenzene (1.1 mL, 10 mmol) in Et_2O (70 mL) was added *n*-butyllithium (1.6 M in hexanes, 15 mL, 23 mmol). The solution was stirred at -78°C for 2 h and a colorless solution of 1,3-$C_6F_4Li_2$ was thus formed. $SiMe_3Cl$ (3.2 mL, 25 mmol) was added dropwise and the mixture was stirred at -78°C for 2 h and then at room temperature overnight. The solvent was removed *in vacuo* and the raw product was extracted with hexanes (*ca.* 30 mL). The solution was subsequently filtered and taken to dryness *in vacuo* yielding a white solid, the recrystallization of which from methanol (*ca.* 50 mL) produced 1,3-bis(trimethylsilyl)tetrafluorobenzene ($(\mu$-1,3-$C_6F_4)(SiMe_3)_2$, **1**) in a yield of 55% (1.6 g, 5.5 mmol).

Preparation of 1,4-Bis(trimethylsilyl)tetrafluorobenzene, 2

To a precooled (-78°C) stirred solution of 1,2,4,5-tetrafluorobenzene (1.1 mL, 9.9 mmol) in THF (70 mL) was added *n*-butyllithium (1.6 M in hexanes, 14 mL, 22 mmol). The solution was stirred at -78°C for 30 min and a colorless solution of 1,4-$C_6F_4Li_2$ was thus formed. $SiMe_3Cl$ (3.0 mL, 24 mmol) was then added dropwise. The resulting cloudy mixture was stirred at -78°C for 20 min and then allowed to warm to room temperature, resulting in a clear solution. The solvent was removed *in vacuo* and the raw product was extracted with diethyl ether (*ca.* 50 mL). The solution was subsequently filtered and taken to dryness *in vacuo* yielding a white solid, the recrystallization of which from methanol (*ca.* 50 mL) produced 1,4-bis(trimethylsilyl)tetrafluorobenzene ((μ-1,4-C_6F_4)($SiMe_3$)$_2$, 2) in a yield of 61% (1.8 g, 6.0 mmol).[7]

Preparation of Bis(2,3,4,6-tetrafluorophenyl)dimethylsilane, 3

To a precooled (-78°C) stirred solution of 1,2,3,5-tetrafluorobenzene (6.4 mL, 57 mmol) in Et_2O (100 mL) was added *n*-butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) over a period of 15 min. The solution was stirred at -78°C for 1 h and a colorless solution of 1,3-C_6F_4HLi was thus formed. $SiMe_2Cl_2$ (2.4 mL, 20 mmol) was added dropwise and the mixture was stirred at -78°C for 3 h and then at room temperature overnight. The precipitate (LiCl) was washed off with distilled water (3 × 50 mL) and the ether layer was separated and dried with 4 Å molecular sieves. The solution was taken to dryness *in vacuo* yielding an oily liquid which was distilled under vacuum. The fraction boiling at 85°C/0.65 mmHg was collected, giving bis(2,3,4,6-tetrafluoro-phenyl)dimethylsilane ($SiMe_2$(1,3-C_6F_4H)$_2$, 3) in a yield of 67% (4.8 g, 13 mmol).

Preparation of Bis(2,3,5,6-tetrafluorophenyl)dimethylsilane, 4

To a precooled (-78°C) stirred solution of 1,2,4,5-tetrafluorobenzene (6.4 mL, 57 mmol) in Et_2O (100 mL) was added *n*-butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) over a period of 15 min. The solution was stirred at -78°C for 1 h and a colorless solution of 1,4-C_6F_4HLi was thus formed. $SiMe_2Cl_2$ (2.4 mL, 20 mmol) was added dropwise and the mixture was stirred at -78°C for 5 h and then at room temperature overnight. The precipitate (LiCl) was washed off with distilled water (3 × 50 mL) and the ether layer was separated and dried with 4 Å molecular sieves. The solution was taken to dryness *in vacuo* yielding an oily liquid which was distilled under vacuum. The fraction boiling at 80-82°C/0.27 mmHg was collected, giving bis(2,3,5,6-tetra-fluorophenyl)dimethylsilane ($SiMe_2$(1,4-$C_6F_4H)_2$, **4**) in a yield of 75% (5.4 g, 15 mmol).

Preparation of Bis(2,3,5,6-tetrafluorophenyl)hexylmethylsilane, 5

To a precooled (-78°C) stirred solution of 1,2,4,5-tetrafluorobenzene (6.4 mL, 57 mmol) in Et_2O (80 mL) was added *n*-butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) over a period of 15 min. The solution was stirred at -78°C for 1 h and a colorless solution of 1,4-C_6F_4HLi was thus formed. SiMe(Hex)Cl_2 (4.0 mL, 20 mmol) was added dropwise and the mixture was stirred at -78°C for 5 h and then at room temperature overnight at which stage the reaction was quenched with methanol (5 mL). The precipitate (LiCl) was washed off with distilled water (3 × 20 mL) and the ether layer was separated and dried with 4 Å molecular sieves. The solvent was removed *in vacuo* yielding an oily liquid which was distilled under vacuum. The fraction boiling at 120-122°C/0.25 mmHg was collected, giving bis(2,3,5,6-tetrafluorophenyl)hexylmethylsilane (SiMe(Hex)(1,4-$C_6F_4H)_2$, **5**) in a yield of 41% (3.5 g, 8.2 mmol).

Preparation of 1,3-Bis(2',3',5',6'-tetrafluorophenyl)-tetramethyldisiloxane, 6

To a precooled (-78°C) stirred solution of 1,2,4,5-tetrafluorobenzene (3.0 mL, 27 mmol) in Et_2O (80 mL) was added *n*-butyllithium (1.6 M in hexanes, 13 mL, 20 mmol) over a period of 15 min. The solution was stirred at -78°C for 1 h and a colorless solution of 1,4-C_6F_4HLi was thus formed. $O(SiMe_2Cl)_2$ (2.0 mL, 10 mmol) was added dropwise and the mixture was stirred at -78°C for 5 h and then at room temperature overnight. The precipitate (LiCl) was washed off with distilled water (3 × 20 mL) and the ether layer was separated and dried with 4 Å molecular sieves. The solution was taken to dryness *in vacuo* yielding an oily liquid. Isolation via liquid column chromatography produced 1,3-bis(2',3',5',6'-tetrafluorophenyl)tetramethyldisiloxane ($O(SiMe_2$-1,4-$C_6F_4H)_2$, **6**) in a yield of 37% (3.2 g, 7.3 mmol).

Preparation of 1,6-Bis(2',3',5',6'-tetrafluorophenyldimethylsilyl)hexane, 7

To a precooled (-78°C) stirred solution of 1,2,4,5-tetrafluorobenzene (6.4 mL, 57 mmol) in Et_2O (100 mL) was added *n*-butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) over a period of 15 min. The solution was stirred at -78°C for 1 h and a colorless solution of 1,4-C_6F_4HLi was thus formed. $(CH_2)_6(SiMe_2Cl)_2$ (5.6 mL, 20 mmol) was added dropwise and the mixture was stirred at -78°C for 5 h and then at room temperature overnight. The precipitate (LiCl) was washed off with distilled water (3 × 20 mL) and the ether layer was separated and dried with 4 Å molecular sieves. The solution was taken to dryness *in vacuo* yielding an oily liquid. Isolation via liquid column chromatography produced 1,6-bis(2',3',5',6'-tetrafluorophenyldimethylsilyl)hexane ($(CH_2)_6(SiMe_2$-1,4-$C_6F_4H)_2$, 7) in a yield of 80% (8.0 g, 16 mmol).

Preparation of 1,3-Bis(2',3',4',6'-tetrafluorophenyldimethylsilyl)-tetrafluorobenzene, 8

To a precooled (-78°C) stirred solution of 1,2,3,5-tetrafluorobenzene (3.3 mL, 31 mmol) in THF (60 mL) was added *n*-butyllithium (1.6 M hexanes, 19 mL, 30 mmol) over a period of 10 min. The resulting white slurry was stirred at -78°C for 1 h and $SiMe_2Cl_2$ (1.8 mL, 15 mmol) was then added dropwise. The mixture was stirred at -78°C for 5 h at which stage the reaction was quenched with methanol (5 mL). The solution was taken to dryness *in vacuo* yielding a white solid which was washed with distilled water (3 × 20 mL). Recrystallization of the solid from methanol produced 1,3-bis(2',3',4',6'-tetrafluorophenyldimethylsilyl)tetrafluorobenzene ((μ-1,3-C_6F_4)($SiMe_2$-1,3-C_6F_4H)$_2$, **8**) in a yield of 35% (3.0 g, 5.3 mmol).

Preparation of 1,4-Bis(2',3',5',6'-tetrafluorophenyldimethylsilyl)-tetrafluorobenzene, 9

To a precooled (-78°C) stirred solution of 1,2,4,5-tetrafluorobenzene (6.4 mL, 57 mmol) in THF (80 mL) was added *n*-butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) over a period of 20 min. The resulting white slurry was stirred at -78°C for 1 h and $SiMe_2Cl_2$ (2.4 mL, 20 mmol) was then added dropwise. The mixture was stirred at -78°C for 5 h at which stage the reaction was quenched with methanol (5 mL). The solution was taken to dryness *in vacuo* yielding a white solid which was washed with distilled water (3 × 50 mL) and then with methanol (2 × 10 mL). Recrystallization of the solid from acetone produced 1,4-bis(2',3',5',6'-tetrafluorophenyl-dimethylsilyl)tetrafluorobenzene ((μ-1,4-C_6F_4)($SiMe_2$-1,4-C_6F_4H)$_2$, **9**) in a yield of 26% (2.9 g, 5.2 mmol).

The chemical structures for all nine compounds are depicted in Figure 5.1. The collected analytical data for these compounds are listed in Table 5.1, while the NMR spectroscopic data are presented in Table 5.2. All the compounds prepared above are new except **2**.[7]

X-Ray Crystallographic Characterization of 1,4-Bis(2',3',5',6'-tetrafluorophenyldimethylsilyl)tetrafluorobenzene

Colorless crystals of 1,4-bis(2',3',5',6'-tetrafluorophenyldimethylsilyl)tetrafluorobenzene, **9**, were grown by slow evaporation of a dichloromethane solution and were mounted on glass fibers and optically centered in the X-ray beam on an Enraf-Nonius

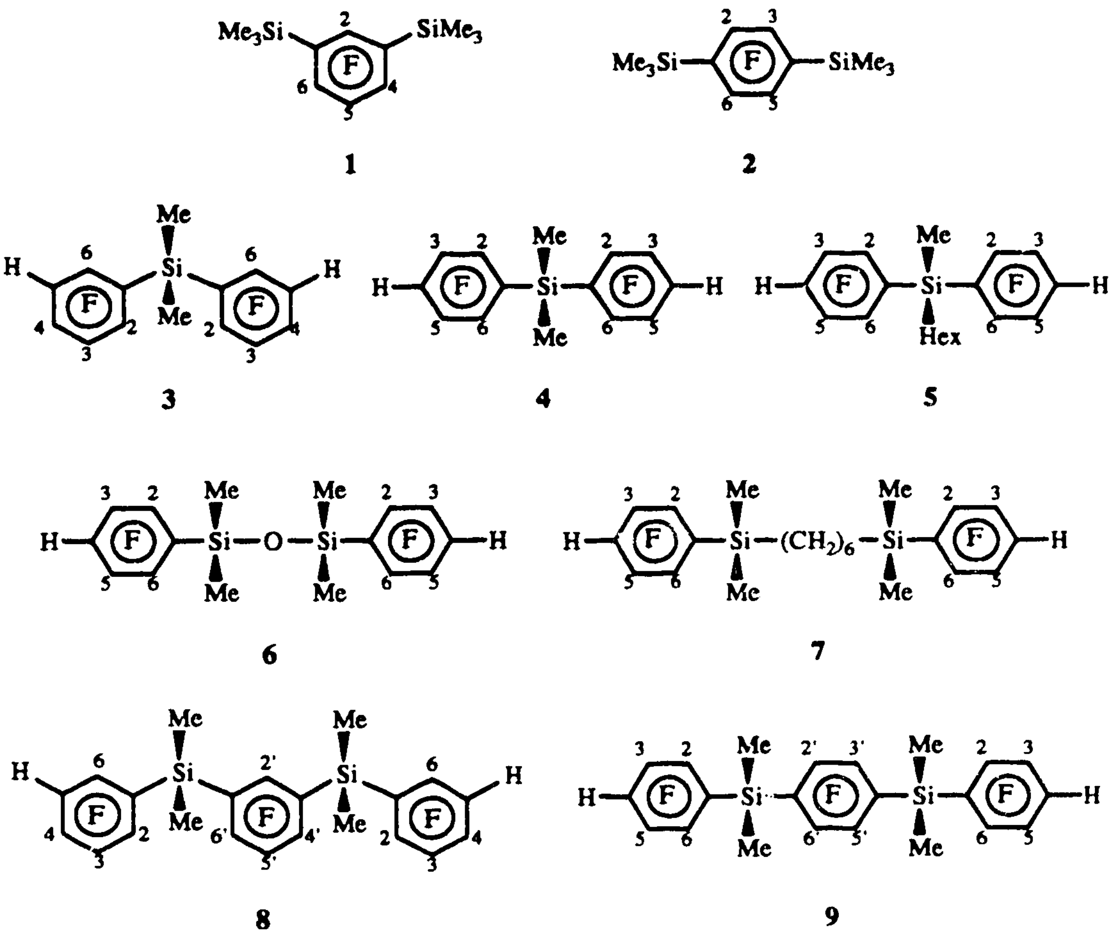

Figure 5.1. Organosilicon derivatives of 1,2,3,5- and 1,2,4,5-tetrafluorobenzene

Table 5.1. Collected Data for the Compounds

Compound	Formula	Analytical Data C% Calcd	Analytical Data C% Found	Analytical Data H% Calcd	Analytical Data H% Found	Low-Resolution Mass Spectral Data (*m/z*)	Yield (%)
1	$C_{12}H_{18}F_4Si_2$	48.96	48.90	6.17	6.29	294 (P^+), 279 (P^+-CH_3)	55
2	$C_{12}H_{18}F_4Si_2$	48.96	48.95	6.17	6.22	294 (P^+), 279 (P^+-CH_3), 73 ($SiMe_3$)	61
3	$C_{14}H_8F_8Si$	47.20	47.48	2.26	2.51	356 (P^+), 341 (P^+-CH_3)	67
4	$C_{14}H_8F_8Si$	47.20	47.24	2.26	2.53	356 (P^+), 341 (P^+-CH_3)	75
5	$C_{19}H_{18}F_8Si$	53.52	53.54	4.25	4.19	426 (P^+), 411 (P^+-CH_3), 341 (P^+-C_6H_{13})	53
6	$C_{16}H_{14}F_8OSi_2$	44.65	44.86	3.28	3.24	430 (P^+), 415 (P^+-CH_3)	37
7	$C_{22}H_{26}F_8Si_2$	53.00	52.98	5.26	5.21	498 (P^+)	80
8	$C_{22}H_{14}F_{12}Si_2$	46.98	47.42	2.51	2.93	562 (P^+)	35
9	$C_{22}H_{14}F_{12}Si_2$	46.98	46.82	2.51	2.80	562 (P^+), 547 (P^+-CH_3)	26

Table 5.2. ^{1}H- and ^{19}F-NMR Assignments for the Compounds

Compound	^{1}H (ppm)	^{19}F (ppm)
1	0.37 (s, 18H)	-86.88 (m, 1F), -120.69 (m, 2F), -168.36 (m, 1F)
2	0.39 (s, 18H)	-132.18 (s, 4F)
3	6.73 (m, 2H), 0.75 (s, 6H)	-101.34 (m, 2F), -121.20 (m, 2F), -130.05 (m, 2F), -166.75 (m, 2F)
4	7.14 (m, 2H), 0.81 (s, 6H)	-128.74 (m, 4F), -139.29 (m, 4F)
5	7.12 (m, 2H), 1.38 (m, 3H), 1.27 (m, 8H), 0.59 (m, 2H), 0.58 (m, 3H)	-128.40 (m, 4F), -139.22 (m, 4F)
6	7.07 (m, 2H), 0.49 (s, 12H)	-129.67 (m, 4F), -139.75 (m, 4F)
7	7.08 (m, 2H), 1.32 (m, 4H), 0.87 (m, 8H), 0.37 (s, 12H)	-128.59 (m, 4F), -139.97 (m, 4F)
8	6.70 (m, 2H), 0.70 (s, 12H)	-87.04 (m, 1F), -101.48 (m, 2F), -118.86 (m, 2F), -121.30 (m, 2F), -130.22 (m, 2F), -166.93 (m, 3F)
9	7.14 (m, 2H), 0.79 (s, 12H)	-128.37 (m, 4F), -128.58 (m, 4F), -139.28 (m, 4F)

CAD-4F automated diffractometer. Data collection and structure solution parameters are given in Table 5.3. The ORTEP plot of the solved structure is presented in Figure 5.3. Data were corrected for Lorentz and polarization effects and also for absorption via the method of Walker and Stuart.[8] Structure solution proceeded in a routine fashion utilizing the MolEN structure solution package.[9,10] All non-hydrogen atoms were treated with anisotropic displacement parameters.

Final fractional atomic coordinates and equivalent isotropic thermal parameters are given in Tables 5.4, 5.5, and 5.6. Tables of structure factors are available from the authors.

RESULTS AND DISCUSSION

Synthetic Strategy

Solvents play an important role in the formation of the fluoroaryllithium reagents,[1,2,11,12] perhaps because the relative reaction rates for the two competing reactions, i.e.,

$$C_6F_4H_2 + n\text{-BuLi} \xrightarrow[\text{-78°C}]{\text{solvent}} C_6F_4HLi \qquad (5.1)$$

$$C_6F_4H_2 + 2\ n\text{-BuLi} \xrightarrow[\text{-78°C}]{\text{solvent}} C_6F_4Li_2 \qquad (5.2)$$

where C_6F_4 = 1,3- or 1,4-C_6F_4

vary as a function of solvent polarity. In our experience, in polar solvents such as THF, both reactions proceed at comparable rates and thus the formation of the dilithio product is unavoidable, even in the attempted synthesis of the monolithio reagent. However, the reaction rate of dilithiation is significantly slower than that of monolithiation in less-polar

Table 5.3. Summary of the Crystal Data and Intensity Collection for Compound 9

Parameter	Compound 9
formula	$C_{22}H_{14}F_{12}Si_2$
formula weight	562.50
crystal dimensions, mm	0.24 × 0.32 × 0.32
space group	$P2_1/c$
crystal system	monoclinic
a, Å	11.577 (2)
b, Å	9.875 (2)
c, Å	10.967 (3)
β, deg	114.85 (2)
V, Å^3	1137.7 (5)
Z	2
calcd density, g cm^{-3}	1.642
diffractometer	Enraf-Nonius CAD-4F
radiation (λ, Å)	Mo K_α (λ = 0.7107 Å)
monochromator	graphite
take-off angle, deg	2.8
detector aperture, mm	$3 + \tan\theta \times 4$
scan type	$\theta - 2\theta$
scan width	$0.8 + 0.35 \tan\theta$
scan rate, deg min^{-1}	8.0
2θ range, deg	$2 < 2\theta < 44$
number of reflections	1576
number of significant reflections	1416
data collection index range	+h,+k,±l
agreement factor R_1, R_2, GOF	0.0537, 0.0564, 1.39
corrections applied	empirical absorption correction

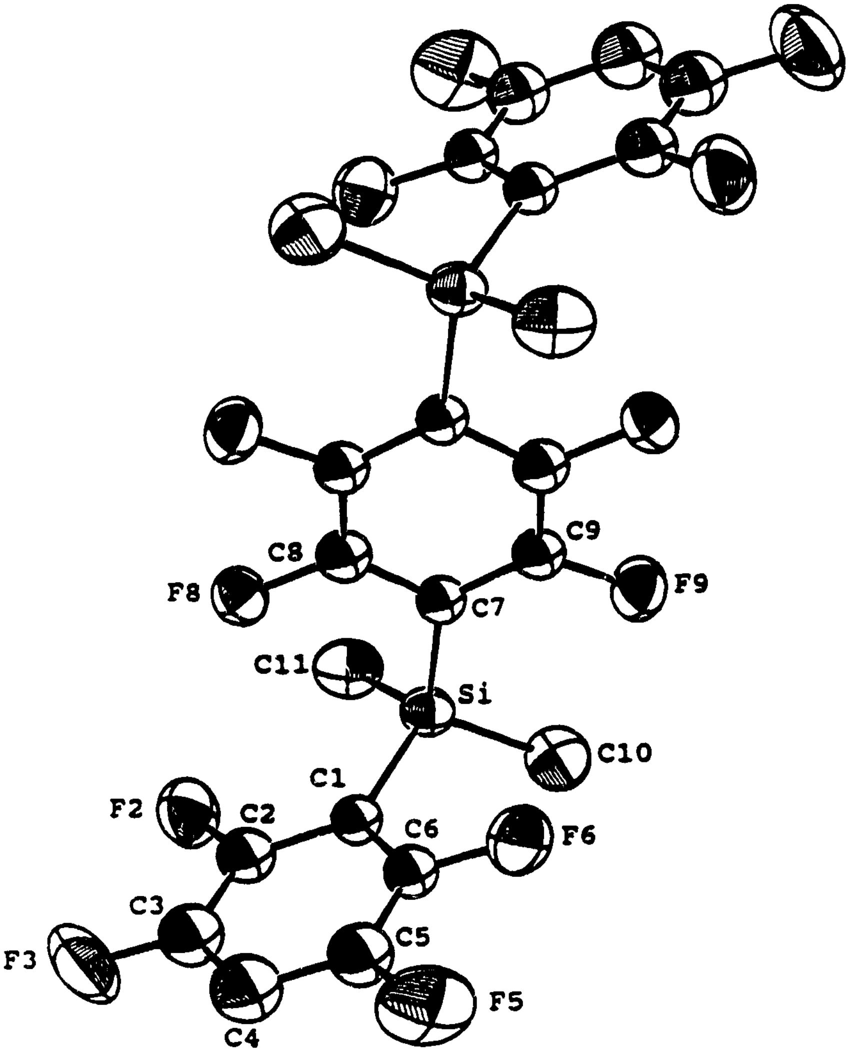

Figure 5.2. ORTEP plot of 1,4-bis(dimethyl-2',3',5',6'-tetrafluorophenylsilyl)tetrafluorobenzene

Table 5.4. Selected Bond Length (Å) for Compound **9**[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Si	C1	1.893 (7)	Si	C7	1.895 (8)
Si	C10	1.847 (8)	Si	C11	1.846 (6)
F2	C2	1.351 (7)	F3	C3	1.339 (9)
F5	C5	1.351 (8)	F6	C6	1.348 (8)
F8	C8	1.358 (8)	F9	C9	1.342 (8)
C1	C2	1.38 (1)	C1	C6	1.382 (8)
C2	C3	1.37 (1)	C3	C4	1.355 (9)
C4	C5	1.36 (1)	C5	C6	1.36 (1)
C7	C8	1.377 (9)	C7	C9	1.365 (9)
C8	C9'	1.395 (9)			

[a] Numbers in parentheses are estimated standards deviations in the least significant digits.

Table 5.5. Selected Bond Angles (°) for Compound 9[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	Si	C7	102.1 (3)	C1	Si	C10	109.4 (3)
C1	Si	C11	113.0 (3)	C7	Si	C10	113.1 (4)
C7	Si	C11	109.3 (3)	C10	Si	C11	109.8 (4)
Si	C1	C2	125.9 (4)	Si	C1	C6	120.2 (5)
C2	C1	C6	113.8 (6)	F2	C2	C1	119.4 (6)
F2	C2	C3	117.3 (6)	C1	C2	C3	123.3 (6)
F3	C3	C2	118.5 (6)	F3	C3	C4	120.6 (7)
C2	C3	C4	120.8 (7)	C3	C4	C5	117.7 (7)
F5	C5	C4	120.9 (7)	F5	C5	C6	118.0 (7)
C4	C5	C6	121.1 (6)	F6	C6	C1	118.6 (6)
F6	C6	C5	118.1 (5)	C1	C6	C5	123.2 (6)
Si	C7	C8	118.2 (5)	Si	C7	C9	126.7 (5)
C8	C7	C9	115.1 (7)	F8	C8	C7	119.7 (7)
F8	C8	C9'	117.0 (7)	C7	C8	C9'	123.3 (7)
F9	C9	C7	120.8 (7)	F9	C9	C8'	117.6 (7)
C7	C9	C8'	121.6 (7)				

[a] Numbers in parentheses are estimated standards deviations in the least significant digits.

Table 5.6. Positional Parameters and Estimated Standard Deviations for Compound 9[a,b]

Atom	x	y	z	B (Å^2)
Si	0.6943 (2)	0.9489 (2)	0.3514 (2)	3.23 (4)
F2	0.6799 (4)	0.6474 (5)	0.2451 (4)	5.8 (1)
F3	0.7929 (5)	0.4286 (5)	0.3772 (5)	7.6 (2)
F5	0.9946 (5)	0.6853 (6)	0.7710 (5)	7.6 (2)
F6	0.8806 (4)	0.9046 (5)	0.6393 (4)	5.0 (1)
F8	0.4810 (3)	0.7777 (4)	0.3498 (4)	4.4 (1)
F9	0.6766 (3)	1.1930 (4)	0.5353 (4)	4.9 (1)
C1	0.7758 (5)	0.7868 (7)	0.4363 (6)	2.8 (1) *
C2	0.7587 (6)	0.6606 (7)	0.3766 (6)	3.5 (1) *
C3	0.8159 (6)	0.5459 (8)	0.4447 (7)	4.4 (2) *
C4	0.8969 (7)	0.5509 (9)	0.5767 (7)	5.0 (2) *
C5	0.9164 (7)	0.6731 (8)	0.6391 (7)	4.3 (2) *
C6	0.8585 (6)	0.7869 (7)	0.5709 (6)	3.2 (1) *
C7	0.5860 (5)	0.9846 (7)	0.4377 (6)	2.8 (1) *
C8	0.4930 (6)	0.8913 (7)	0.4240 (6)	3.2 (1) *
C9	0.5910 (6)	1.0942 (7)	0.5155 (6)	3.0 (1) *
C10	0.8151 (7)	1.0821 (9)	0.3805 (7)	4.8 (2)
C11	0.5971 (7)	0.9285 (9)	0.1693 (7)	4.7 (2)

[a] Numbers in parentheses are estimated standards deviations in the least significant digits.

[b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\,[a^2 \beta_{11} + b^2 \beta_{22} + c^2 \beta_{33} + ab\,(\cos \gamma)\,\beta_{12} + ac\,(\cos \beta)\,\beta_{13} + bc\,(\cos \alpha)\,\beta_{23}]$.

solvent such as Et_2O. Therefore, for the preparation of the monolithio reagent, Et_2O is the solvent of choice. For the preparation of the dilithio reagent, both THF and Et_2O could be used. These differences are clearly reflected in our syntheses where with the appropriate choice of solvents all reactions proceeded smoothly. Thus the desired monolithio or dilithio products were formed in moderate to good yields, except for the preparations of compounds **8** and **9** where complications were unavoidably encountered (*vide infra*).

Synthesis of $C_6F_4(SiMe_3)_2$ (1 and 2)

Compounds **1** and **2** were prepared through reaction 5.3 by the addition of two equivalents of $SiMe_3Cl$ to $C_6F_4Li_2$ prepared through reaction 5.2 in either THF or Et_2O.

$$C_6F_4Li_2 + 2\ SiMe_3Cl \longrightarrow C_6F_4(SiMe_3)_2 \qquad (5.3)$$

where C_6F_4 = 1,3-C_6F_4 for compound **1**; C_6F_4 = 1,4-C_6F_4 for compound **2**

Although compound **2** has been reported previously,[7] we synthesized it to compare its spectroscopic data with those of its *meta*-substituted isomer. As is seen from the data in Tables 5.1 and 5.2, the two isomers have very similar mass spectral and ^1H-NMR data and their ^{19}F-NMR spectra show the differences expected based on their different symmetries. If 1,4-$C_6F_4(SiMe_3)_2$ is compared with its parent compound 1,4-$C_6F_4H_2$,[13] we see that $SiMe_3$ substitution for H leads to a moderate downfield shift (7.89 ppm) for the fluorines in the ^{19}F-NMR. However, compared with 1,3-$C_6F_4H_2$,[14] the fluorines in 1,3-$C_6F_4(SiMe_3)_2$ exhibit large downfield shifts due to silicon substitution. Thus, we can assign compound **1** as follows: δ -86.88, F2 (27.54 ppm downfield of 1,3-$C_6F_4H_2$); -168.36, F5; -120.69, F4/F6 (12.03 ppm downfield of 1,3-$C_6F_4H_2$), with the largest shift being shown in F2.

Synthesis of $SiR_2(C_6F_4H)_2$ (3, 4, 5, 6, and 7)

Compounds **3** to **7** were prepared through reaction 5.4 using C_6F_4HLi prepared in Et_2O[15]. All procedures are identical except for the isolation of the products where either vacuum-distillation or flash-column chromatography can be used to isolate the desired products.

$$2\ C_6F_4HLi + SiR_2Cl_2 \longrightarrow SiR_2(C_6F_4H)_2 \qquad (5.4)$$

where SiR_2 = $SiMe_2$, C_6F_4H = 1,3-C_6F_4H for compound **3**;
SiR_2 = $SiMe_2$, C_6F_4H = 1,4-C_6F_4H for compound **4**;
SiR_2 = SiMe(Hex), C_6F_4H = 1,4-C_6F_4H for compound **5**;
SiR_2 = $SiMe_2$–O–$SiMe_2$, C_6F_4H = 1,4-C_6F_4H for compound **6**;
SiR_2 = $SiMe_2$–$(CH_2)_6$–$SiMe_2$, C_6F_4H = 1,4-C_6F_4H for compound **7**

Based on the assignments for compound **1**, the ^{19}F resonances for compound **3** can be assigned as follows: δ -101.34, F6; -121.25, F2; -166.75, F3; -130.05, F4. Compared with 1,3-$C_6F_4H_2$, both of the two kinds of fluorines *ortho* to Si in compound **3** (i.e., F2 and F6) were shifted further downfield (13.08 ppm and 11.47 ppm, respectively), through which we again see the effect of silicon substitution for hydrogen. Assignments for compounds **4**, **5**, **6**, and **7** are more straight-forward since they are expected to display the same resonance pattern with close chemical shifts, as was observed (a difference of less than 1.3 ppm for either of the two kinds of fluorines).[16] Thus, compound **4** is taken as a representative and assigned as: δ -128.74, F2/F6 (*ortho* to Si); -139.29, F3/F5 (*meta* to Si and *ortho* to H). Compared with 1,4-$C_6F_4H_2$, both of the two kinds of fluorines are shifted downfield (10.40 - 11.67 ppm and 0.10 - 0.85 ppm, respectively), with F2/F6 exhibiting a stronger effect of silicon substitution.

Synthesis of $(\mu\text{-}C_6F_4)(SiMe_2\text{-}C_6F_4H)_2$ (8 and 9)

Compounds 8 and 9 were prepared via the "one-pot" route (reactions 5.5 and 5.6). Reaction 5 was implemented by taking advantage of the polar solvent THF where mixtures of monolithio and dilithio reagents usually coexist.

$$3\ C_6F_4H_2 + 4\ n\text{-BuLi} \xrightarrow[-78^\circ C]{THF} C_6F_4Li_2 + 2\ C_6F_4HLi \qquad (5.5)$$

$$C_6F_4Li_2 + 2\ C_6F_4HLi + SiMe_2Cl_2 \longrightarrow (\mu\text{-}C_6F_4)(SiMe_2\text{–}C_6F_4H)_2 \qquad (5.6)$$

where C_6F_4 = 1,3-C_6F_4 for compound 8; C_6F_4 = 1,4-C_6F_4 for compound 9

The equivalence between $C_6F_4H_2$ and ^{n}BuLi in reaction 5.5 (3:4) is only nominal since in practice an excess $C_6F_4H_2$ is needed to ensure the 2:1 ratio between the monolithiated and the dilithiated products (1:1 produced otherwise[11]). The above route also implies that reaction 5.4 will unavoidably compete with reaction 5.6 thereby producing compounds 3 and 4, respectively, which in fact have been detected (in small amounts) in the mass spectra of the raw products for the preparations of compounds 8 and 9. However, isolation of these two compounds from such byproducts was readily accomplished by recrystallization and both products were prepared in moderate yields. For the ^{19}F-NMR of compound 9, three resonances were observed as expected: δ -139.28, F3/F5 (*ortho* to H); -128.37 and -128.58, F2'/F3'/F5'/F6' and F2/F6. The ambiguity arises from the fact that these two kinds of fluorines are both *ortho* to $SiMe_2$ thus leading to resonances close to each other as was observed. For the ^{19}F-NMR of compound 8, six resonances were observed instead of seven as was expected from Figure 5.1 and the assignments are thus as the following: δ -87.04, F2' (*ortho* to both Si, comparable to F2 in compound 1); -101.48, F6 (comparable to F6 in compound 3); -121.30, F2 (comparable to F2 in 3); -118.86, F4'/F6' (based upon the assignment of F2); -130.22, F4 (comparable to F4 in 3); -166.93, F3 plus F5' (unresolved thus leading to one single resonance instead).

X-Ray Crystal Structure of Compound 9

Compound **9**, (μ-1,4-C_6F_4)($SiMe_2$-1,4-C_6F_4H)$_2$, was structurally characterized by X-ray crystallography. To the best of our knowledge, this is the first example of organosilicon compounds having –$SiMe_2Ar_2$– fragments that have been structurally characterized. The conformation of this compound is best described as a 'chair' as is illustrated in Figure 5.2, with the Si,C1,C4 atoms in one plane (i.e., the Si–C_6F_4H plane), the Si',C1',C4' atoms in a second plane (i.e., the second Si–C_6F_4H plane) which is parallel to the first one, and the Si,C7,C7',Si' atoms in a third plane (i.e., the Si–C_6F_4–Si plane) bisecting the other two at a dihedral angle of 112.3 to 117.6°. Worth mentioning is the entity of Ar–Si–Ar *versus* Me–Si–Me: the former has longer Si–C bonds (1.89 Å *versus* 1.85 Å) and a smaller C–Si–C angle (102° *versus* 110°). The Si atom sits in the center of a distorted tetrahedron, with the other C–Si–C angles ranging from 109° to 113°.

In conclusion, a series of nine organosilicon derivatives of 1,2,3,5- and 1,2,4,5-tetrafluorobenzene have been successfully prepared and fully characterized by analytical and spectroscopic means. One representative compound (**9**) has been structurally characterized by X-ray crystallography. This study has paved the way for the successful syntheses of the analogous organosilicon polymers (i.e., fluorinated polysilarylenes, –[–SiR_2–1,4-C_6F_4–]$_n$–, derived from 1,4-$C_6F_4H_2$ and SiR_2Cl_2). In fact, the analogous organonickel-organosilicon copolymers (i.e., –[–1,4-C_6F_4–Ni(PBu_3)$_2$–1,4-C_6F_4–SiR_2–]$_n$–) have been prepared by following the methodologies defined during these syntheses.[2]

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3. For a wide range of interesting physical properties of the organosilicon compounds and polymers, see: (a) P. Saul, *The Chemistry of Organic Silicon Compounds, part (I) and (II)*, John Wiley & Sons, New York, 1989. (b) A. J. Barry and H. N. Beck, in *Inorganic Polymers*, F. G. A. Stone and W. A. G. Graham, Eds., Academic Press, New York, 1962. Chapter 5. (c) I. Yilgör and J. E. McGrath, in *Advances in Polymer Science*, Springer Verlag, New York, 1988. Vol. 86, Chapter 1. (d) N. Koide and R. W. Lenz, *J. Polym. Sci., Polymer Symposium*, **70**, 91 (1983).
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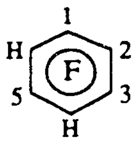
8. (a) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD-4F diffractometer with some local modifications by R. G. Ball. (b) *International Tables for X-ray Crystallography*, Vol. I. Kynoch Press, Birmingham. (c) The computer programs used in this analysis include the Enraf-Nonius *Structure Determination Package. Version 3*, 1985, Delft, The Netherlands, adapted for a SUN Microsystems 3/160 computer, and several locally written programs by R. G. Ball. (d) *International Tables for X-ray Crystallography*, Vol. IV, 1974. Table 2.2B. Kynoch Press, Birmingham. (Present distributor D. Reidel, Dordrecht.). (e) *ibid.*, Table 2.3.1. (f) N. Walker and D. Stuart, *Acta Crystallogr.*, **A39**, 158 (1983).
9. R. Chukwu, A. D. Hunter and B. D. Santarsiero, *Organometallics*, **10**, 2141 (1991).
10. Enquiries concerning the crystallographic results for compound **9** should be directed to S. G. Bott (Department of Chemistry, University of North Texas, Denton, Texas 76203) quoting AH8.
11. S. A. Reines, J. R. Griffith and J. G. O'Reer, *J. Org. Chem.*, **36**, 1209 (1971).
12. (a) X. A. Guo, A. D. Hunter and J. Chen, *J. Polym. Sci.*, Part A: *Polym. Chem.*, **32**, 47 (1994). (b) See chapter 3 of this thesis.
13. ^{19}F-NMR (CD_2Cl_2) for 1,4-$C_6F_4H_2$: δ -140.07 (t, 4F), $^3J_{F\text{-}H}$ = 9.4 Hz.
14. ^{19}F-NMR (CD_2Cl_2) for 1,3-$C_6F_4H_2$: δ -114.42 (dt, 1F), -132.72 (m, 2F), -167.07 (m, 1F). Assignments are as follows: δ -114.42, F5 (*ortho* to both H); -132.72, F1/F3 (*ortho* to one H and *para* to the other); -167.07, F2 (*meta* to both H).



15. Care should be taken to avoid forming an over-concentrated monolithio reagent (C_6F_4HLi) even in Et_2O, since certain amounts of by-products derived from the

dilithiation of $C_6F_4H_2$ (i.e., $C_6F_4Li_2$) were detected in the mass spectra of the raw products for the preparations of compounds **6** and **7**.

16. The fluorines in compound **5** are presumably fluxional (i.e., F2 with F6 and F3 with F5, respectively, see Figure 5.1) since only two resonances instead of four as one postulates otherwise were observed in its ^{19}F-NMR spectra.

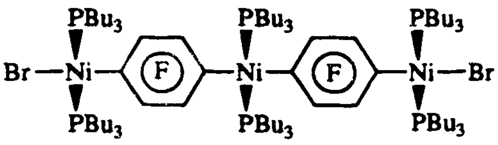
CHAPTER 6

MOLECULAR WEIGHT DETERMINATION AND ESTABLISHMENT OF A ROD-LIKE STRUCTURE FOR ORGANONICKEL POLYMERS

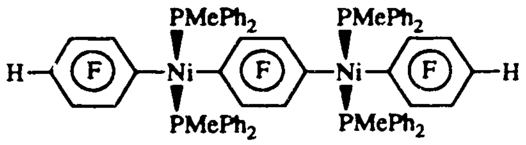
$-[-\mathrm{Ni}(\mathrm{PR}_3)_2-\mathrm{Ar}^{\mathrm{F}}-]_n-$ [†]

INTRODUCTION

Recently, we reported the syntheses of a series of organometallic oligomeric species which were characterized by NMR and elemental analysis and, in some cases, by X-ray crystallography.[1,2] Typical examples, whose structures are illustrated below, are oligomers **1** and **2**:



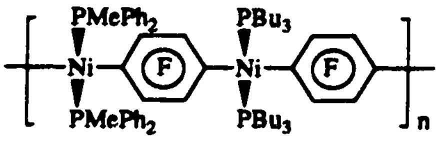
oligomer **1**



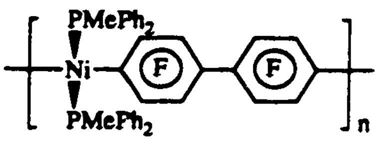
oligomer **2**

[†] A version of this chapter has been accepted for publication. See: X. A. Guo, K. C. Sturge, A. D. Hunter and M. C. Williams, *Macromolecules*, (Sept. 1994).

One of their distinct properties is that they have a rigid-rod structure in the solid state. Evidence from NMR studies also suggests a rod-like configuration for all these oligomeric species in solution. However, a heretofore unanswered question is whether the organometallic polymeric homologues that we recently prepared,[1,2] i.e., polymers I and II,



polymer I



polymer II

also possess a rod-like structure. If they do, then the values for their molecular weight (MW) obtained directly from gel permeation chromatography (GPC) as calibrated with polystyrene standards would be significantly different from their real values, since polystyrene is a typical random coil polymer. It is therefore necessary to ascertain the absolute molecular weight values of our organonickel polymers by different calibration methods. One convenient way to do this is to employ a method of "universal calibration", determining the molecular weights through a combination of GPC traces and viscosity measurements according to an iterative method established by several workers.[3]

Establishing methods for determining the molecular weight distribution (MWD) and associated average values ($\overline{M}$) for rigid-rod organometallic polymers is particularly significant because of the growing importance of these materials in electronics, photonics, and other advanced materials applications.[4] In the only such report known to us, Takahashi et al. prepared Pt-containing rigid-rod polymers and examined their behavior.[5] No effort has been made so far to explore the performance of organonickel-backbone polymers.[6] In this chapter, we report the results of such an investigation and provide additional viscometric evidence of a rod-like structure for the organonickel polymers.

EXPERIMENTAL SECTION

Sample Preparation

The syntheses and characterizations of the oligomeric species have been reported previously, as have the syntheses and characterizations of polymers I and II.[1,2] Samples of polymers for physical measurements were prepared by repeated fractional precipitation from dichloromethane solutions into hexanes or methanol.

Measurements

For the GPC calibrations, 23 monodisperse polystyrene standards were obtained from Showa Denko K. K. (Shodex®) and from Polymer Laboratories Ltd. (Church Stretton, Shropshire, U. K.), covering the MW-range between 580 and 7.1×10^6. They were used to construct the direct calibration curve in tetrahydrofuran (THF) at 30.0°C, given in Figure 6.1. From $[\eta] = K\overline{M}^{\alpha}$ with values of $\alpha = 0.712$ and $K = 1.28 \times 10^{-4}$ dL/g for these polystyrene standards under the same conditions,[7] a "universal" calibration curve in terms of $[\eta(M)]M$ — equivalent to hydrodynamic volume occupied by the polymer — was also established, as shown in Figure 6.1. To facilitate later iterative computations, a sixth-order polynomial was fitted to each calibration curve with standard deviations R = 0.9996 to 0.9999.

For GPC measurements on the organonickel polymers, the polymer (*ca.* 10 mg) was dissolved in 1 mL of THF, and a 100 µL sample of the solution was injected into a Waters model 600E HPLC/GPC system (Waters, Division of Millipore, Mississauga, Ontario) operating at 30.0°C with THF as the eluting solvent. A flow rate of 1.20 mL/min was used with a series of three columns (identified by Waters as 10^3 Å, 10^6 Å, and "10 µm linear" for $M = 5000 - 10^7$). The eluted materials were detected on Waters model 991 Photodiode Array (UV-Visible) and Waters model 410 Differential Refractive Index Detectors. MW calculations for the polymers were performed using both the Maxima 820

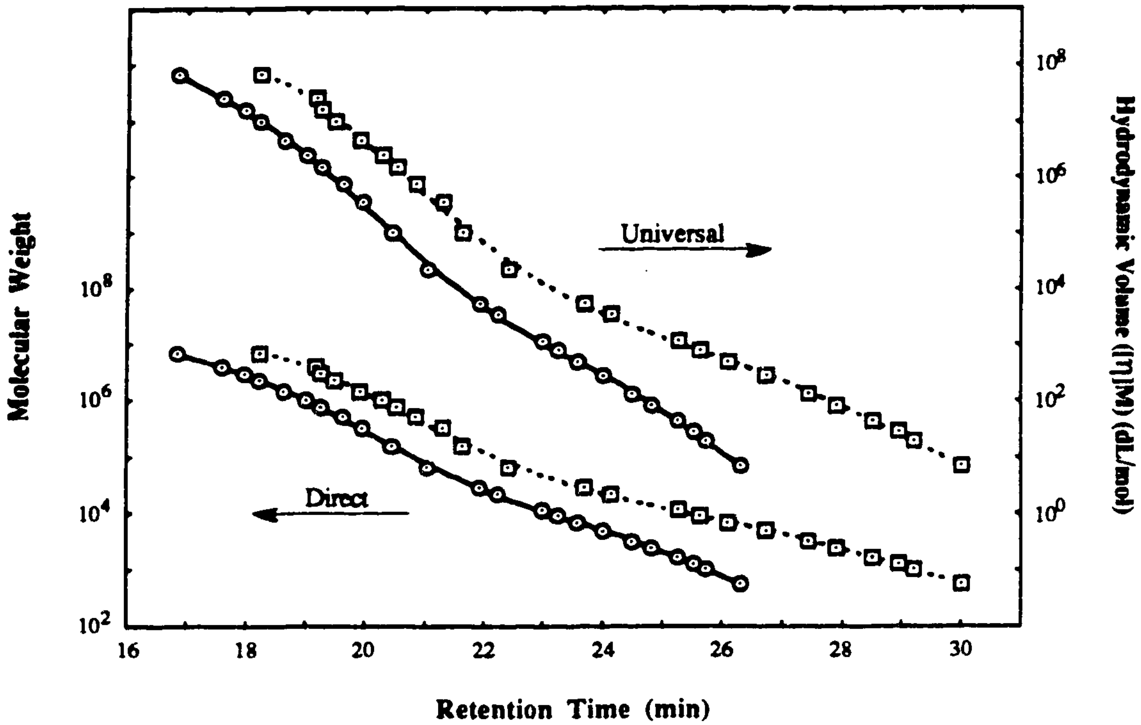


Figure 6.1. Direct calibration (left) and universal calibration (right) curves using monodisperse polystyrene standards: (—o—) 3-column set; (- - ▫ - -) 4-column set. Column flow rates were 1.20 mL/min and 1.40 mL/min, respectively.

chromatography software from Waters and a computer program developed in this laboratory,[8] and the averages of the two values (always close) are tabulated in Table 6.1 for both GPC methods to be discussed here. For GPC measurements on the oligomeric species, resolution was improved in the critical low-MW region by adding to the 3-column assembly a fourth column (labeled 7 × 10^4 Å by Waters). This expanded the range of retention times in the working region (M = 700 - 2600) as shown in Figure 6.1, with the flow rate increased to 1.40 mL/min for convenience.

Viscosities of 0.05 - 0.10% polymer solutions were measured using an Ubbelohde viscometer in a water bath maintained at 30.00 ± 0.01°C. From these data intrinsic viscosity, $[\eta]$, was calculated according to the single-point method described by Solomon and Ciuta;[9] kinetic corrections were furnished where necessary.[10] Light scattering measurements on polymer I in THF were conducted by Wyatt Technology Corporation (Santa Barbara, California) on GPC effluent using a GPC/LS on-line DAWN®F (90°) light scattering detector with a He-Ne laser operating at 633 nm. For the MW calculations, Wyatt employed a *dn/dc* (refractive index dependence on concentration) value of 0.145 mL/g obtained indirectly by integration over the entire refractive index trace and reported here for the first time. From these data, MW averages for polymer I were found to be $\overline{M}_w = 15.6 \times 10^3$, $\overline{M}_n = 12.5 \times 10^3$ ($\overline{M}_w / \overline{M}_n = 1.2$), and $\overline{M}_z = 19.1 \times 10^3$.

RESULTS AND DISCUSSION

GPC Studies on the Oligomeric Species

As models for the organonickel polymers, a series of oligomeric species has been synthesized in this laboratory.[1,2] It is important to examine the GPC behavior of these species before we go to the more complex polymeric systems, as it may reveal valuable information which can be extrapolated to the polymers. Specific chemical factors which can be explored include: (1) the effect of ancillary PR_3 ligands (i.e., $PMePh_2$ *versus*

Table 6.1. Comparison of the GPC Molecular Weight Data[a]

Polymer	Calibration Method	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$	$\overline{M}_v$	$\overline{M}_p$[b]
polymer I	direct	6.8	14.6	2.1	13.0	12.2
	universal	12.9	18.4	1.4	20.2	17.8
polymer II	direct	4.6	78.6	17.1	35.6	5.2
	universal	31.5	110.7	3.5	210.7	31.2

[a] All molecular weight values are in units of 10^3 Daltons.

[b] Molecular weight at the peak of GPC traces.

PBu_3, and mixed PR_3 *versus* uniform $PMePh_2$ or PBu_3) and (2) the effect of fluoroaryl bridging-units (i.e., 1,4-C_6F_4 *versus* 4,4'-$C_{12}F_8$).

GPC traces of 13 samples of the oligomeric species (Table 6.2) were obtained using the 4-column set. A plot of log (M) *versus* retention time is shown in Figure 6.2, along with data for the low-MW polystyrene samples for comparison. We observe that the organonickel oligomers eluted at any given retention time possess a higher MW than the corresponding polystyrene. This is largely because the elements Ni, P, and F in these species are much heavier than the C and H comprising polystyrene. This phenomenon counteracts the geometrical fact that rod-like species should be expected to have a lower MW than coil-like species at a given retention time due to the effectiveness of rod-like rotational hydrodynamic resistance, provided that they have the same chemical composition (which is not the case in our study). Since the GPC retention time of a particular species is determined by its hydrodynamic volume given by $[\eta]M$, a higher MW for the oligomers in Figure 6.2 also implies a lower $[\eta]$ than for polystyrene at the same retention time. The same result is thus expected for the organonickel polymers, as was confirmed by $[\eta]$ measurements for polymers **I** and **II**. By inverting the comments above, we can also expect that Ni-containing oligomeric species possessing the same MW as polystyrene will be eluted at longer retention times (due to their smaller hydrodynamic volumes), as Figure 6.2 confirms. This implies that a GPC direct calibration method using polystyrene standards will significantly underestimate the molecular weights of the organonickel polymers, and therefore will not be adequate to characterize polymers **I** and **II**.

The ancillary PR_3 ligands have a significant effect on the GPC behaviors of their parent species. For example, species belonging to the $Ni(PBu_3)_2$ group (Table 6.2) are shown in Figure 6.2 to elute earlier than those belonging to the $Ni(PMePh_2)_2$ group, for a given MW. This may be rationalized in terms of a larger hydrodynamic volume for the $Ni(PBu_3)_2$ species, since the butyl branches are presumably much more elongated in solution. The effect on GPC behavior of the oligomeric species with mixed ancillary

Table 6.2. GPC Data for the Oligomeric Species

Oligomeric Species[a,b]	No.	MW[c]	Retention Time (min)
$Ni(PMePh_2)_2$ group			
$Ni(PMePh_2)_2(C_6F_4H)Br$	3	688.1	30.37
$Ni(PMePh_2)_2(C_6F_4H)_2$	4	757.3	30.11
$Ni(PMePh_2)_2(C_{12}F_8H)Br$	5	836.2	30.15
$Ni(PMePh_2)_2(C_{12}F_8H)_2$	6	1053.4	29.54
$[Ni(PMePh_2)_2]_2(\mu\text{-}C_6F_4)(C_6F_4H)_2$	2	1364.5	29.40
$[Ni(PMePh_2)_2]_3(\mu\text{-}C_6F_4)_2(C_6F_4H)_2$	7	1971.6	28.92
1,3-$[Ni(PMePh_2)_2]_2$-2-$[Ni(PBu_3)_2](\mu\text{-}C_6F_4)_2(C_6F_4H)_2$	8	1975.8	28.85
$[Ni(PMePh_2)_2]_3(\mu\text{-}C_{12}F_8)_2Br_2$	9	2129.4	28.84
$Ni(PBu_3)_2$ group			
$Ni(PBu_3)_2(C_6F_4H)Br$	10	692.3	29.94
$Ni(PBu_3)_2(C_6F_4H)_2$	11	761.5	29.76
$[Ni(PBu_3)_2]_2(\mu\text{-}C_6F_4)(C_6F_4H)Br$	12	1303.7	29.24
1,3-$[Ni(PBu_3)_2]_2$-2-$[Ni(PMePh_2)_2](\mu\text{-}C_6F_4)_2(C_6F_4H)_2$	13	1980.0	28.64
1,4-$[Ni(PBu_3)_2]_2$-2,3-$[Ni(PMePh_2)_2]_2(\mu\text{-}C_6F_4)_3(C_6F_4H)_2$	14	2587.2	28.28

[a] Unspecified phenylenes denote para linkages.

[b] Separate GPC curves are defined for each group in Figure 6.2.

[c] Values computed from the molecular structures shown in the left-hand column and confirmed by elemental analyses, ^{1}H- and ^{19}F-NMR, and in some cases X-ray crystallography.[1,2]

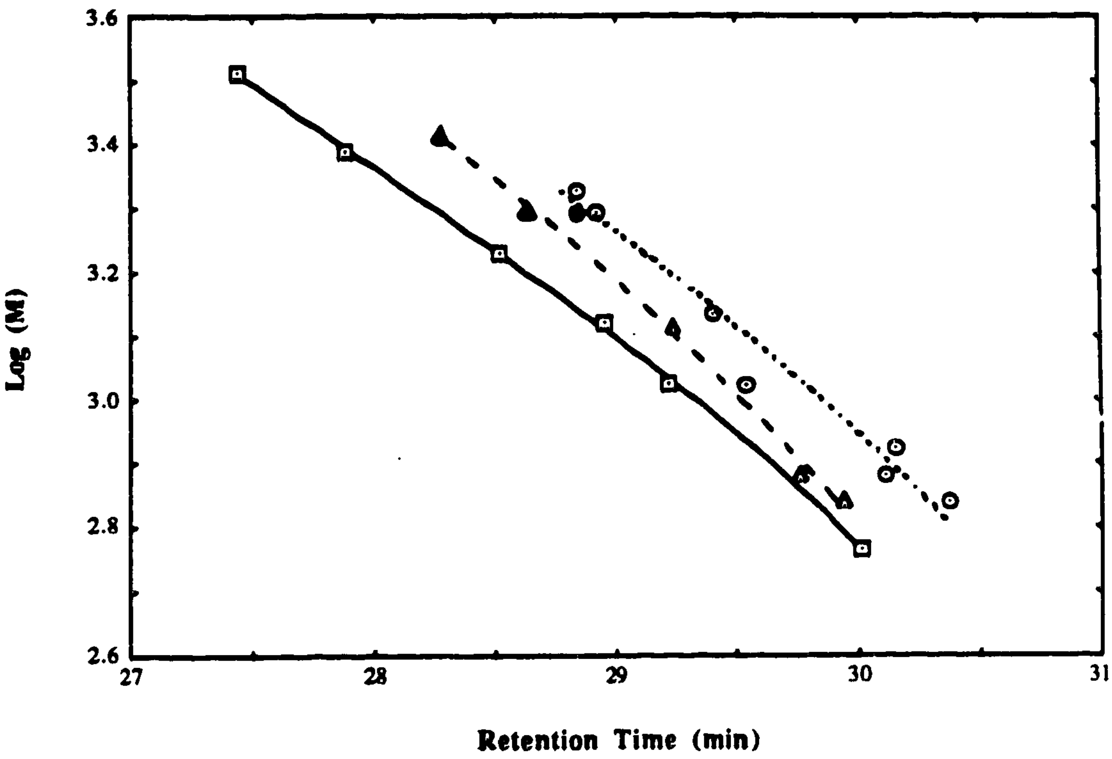


Figure 6.2. GPC behaviors of the organonickel oligomers compared with polystyrene plotted according to Table 6.2: (- - -○- - -) $Ni(PMePh_2)_2$ group; (– -▲- –) $Ni(PBu_3)_2$ group; (—□—) polystyrene standards. Filled symbols designate oligomers with mixed PR_3 ligands, bearing at their ends the ligands characterizing the curve to which they belong.

ligands (i.e., alternating $PMePh_2$ and PBu_3) is somewhat unexpected. One could speculate about whether data would fall onto curves between those established for the $PMePh_2$ and PBu_3 groups, but this proves not to be so. Results in Figure 6.2 indicate that the retention time is independent of the internal composition of these species, and depends only on the nature of the ancillary PR_3 ligands carried by the terminal Ni atoms. For example, tri-Ni species **8**, Table 6.2, carries $PMePh_2$ at the ends, and we see that it falls onto the well-defined $PMePh_2$-group curve in Figure 6.2 despite the presence of PBu_3 ligands on the middle Ni atom. Analogous behavior is exhibited by the tri-Ni and tetra-Ni species **13** and **14**, they clearly belong to the PBu_3-group curve, despite carrying $PMePh_2$ ligands on the middle Ni atoms.

A weak trend for the curves of the two groups of organonickel oligomers (i.e., $Ni(PMePh_2)_2$ and $Ni(PBu_3)_2$ groups in Table 6.2) is that they appear to approach merging at high-MW or short retention time, seen from Figure 6.2. This suggests that the organonickel polymers having either of the PR_3 ligands may behave very similarly as far as GPC measurements are concerned. If so, they might be expected also to have similar $[\eta]$ behavior, meaning close values of α and K. This is indeed demonstrated by the comparison between polymers I and II described in the following discussion. Another conclusion that can be drawn from Figure 6.2 is that the identity of the fluoroaryl bridging-units (1,4-C_6F_4, or 4,4'-$C_{12}F_8$) seems to have no effect on the GPC behavior of their parent species beyond contributing the corresponding mass units to the group curve. Thus these species were treated as being functionally identical when found in the same $Ni(PR_3)_2$ group (e.g., examine the $Ni(PMePh_2)_2$ group in Table 6.2). An extrapolation of this conclusion to the fluoroarene-bridged organonickel polymers means that the nature of the bridging-units may have little or no effect on their α values, which is again reflected in the results of viscosity measurements for polymer I and II.

Relationship Between Solution Viscosity and Molecular Weight

Experience has shown that coil-like polymers such as polystyrene, polybutadiene, and poly(vinyl chloride), whose dilute-solution viscosities are described by the Mark-Houwink equation,

$$[\eta] = K\overline{M}^{\alpha} \tag{6.1}$$

possess α values of 0.5 - 1.0,[11] while rod-like polymers show larger α values ($\alpha > 1.0$). Typical examples of the latter are poly(γ-benzyl-L-glutamate)[12] and poly[trans-bis(tri-*n*-butylphosphine)platinum 1,4-butadynediyl][5] which both have an α value of 1.7.

Several workers have proposed a convenient iterative method to determine the parameters α and K in Equation 6.1 from GPC traces and $[\eta]$ measurements on polymer samples of the same type but different MW in the same solvent and temperature.[3] Suppose one takes two samples ($\underline{1}$ and $\underline{2}$) with different molecular weight distributions (MWD), measures $[\eta]_1$ and $[\eta]_2$, and uses the GPC traces to find MWD_1 and MWD_2 in terms of their respective sets of weight fractions W_{1i} and W_{2i}. Then, applying Equation 6.1 to each fraction gives:

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\Sigma_i W_{1i} J_i^{\alpha/(\alpha+1)}}{\Sigma_i W_{2i} J_i^{\alpha/(\alpha+1)}} \tag{6.2}$$

where $J_i = J_i(M_i) = [\eta]_i M_i$ is the *hydrodynamic volume* of the i-th species. If α is taken to be a constant, we will designate by α_{12} the value obtained by an iterative process on the ($\underline{1}$ + $\underline{2}$)-pair of samples, as shown in Equation 6.2. Then K_{12} can be found using either $[\eta]_1$ or $[\eta]_2$ according to Equation 6.3:

$$[\eta] = K^{1/(\alpha+1)} \Sigma_i W_i J_i^{\alpha/(\alpha+1)} \tag{6.3}$$

This analysis is facilitated by noting that J_i values for Equation 6.2 and Equation 6.3 can be directly obtained from the universal calibration curve (Figure 6.1) constructed using polystyrene standards, since this curve is considered independent of the polymer architecture (coil-like, linear, branched or star, and rod-like polymers).[13]

Three samples of polymer I (Ia, Ib, and Ic) having different MWD's were chosen, and their GPC traces and intrinsic viscosities ($[\eta] = 0.184$, 0.118, and 0.0487 dL/g for samples Ia, Ib, and Ic, respectively) were measured. Subsequently, parameter α for polymer I was calculated using Equation 6.2 for three sets of combinations of two samples (Ia + Ib, Ia + Ic, and Ib + Ic); through iteration, values $\alpha = 1.6$, 1.5, and 1.5 were obtained, respectively, and thus an average value, $\overline{\alpha}_1$, of 1.5. Parameter $\overline{K}_1$ was obtained using Equation 6.3 and $\overline{\alpha}_1$, giving 3.0×10^{-8} dL/g. The same procedure applied to polymer II yielded $\overline{\alpha}_2 = 1.5$ and $\overline{K}_2 = 1.7 \times 10^{-9}$ dL/g. The value $\overline{\alpha} = 1.5$ for both polymers suggests that these organonickel structures behave as rigid rods in solution. Calculations were also made of $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_v$ for both polymers using $\overline{\alpha}$ and $\overline{K}$ values obtained above,[3] and these are listed in Table 6.1 (along with $\overline{M}_p$) as the "universal calibration" values. For polymer I, they are consistent with the results from direct measurements by light scattering (see Experimental).[14,15]

Dependence of Solution Viscosity on Solvents

The intrinsic viscosities of coil-like polymers are strongly dependent on the nature of the solvents. A maximum in $[\eta]$ is observed for such polymers in the best solvent and smaller values in poor solvents. For rod-like polymers, $[\eta]$ is essentially independent of the solubility parameters (δ) of the solvents.[5,16] We have therefore explored the solvent-dependence of $[\eta]$ for polymer I. Seven solvents having δ values ranging from 8.9 to 10.0 $(\text{cal/mL})^{1/2}$ were used to acquire the $[\eta]$'s for the polymer, with results shown in Figure 6.3 along with typical examples of coil-like and rod-like polymers quoted from other sources. We observe that, whereas coil-like polystyrene exhibits the expected bell-shaped

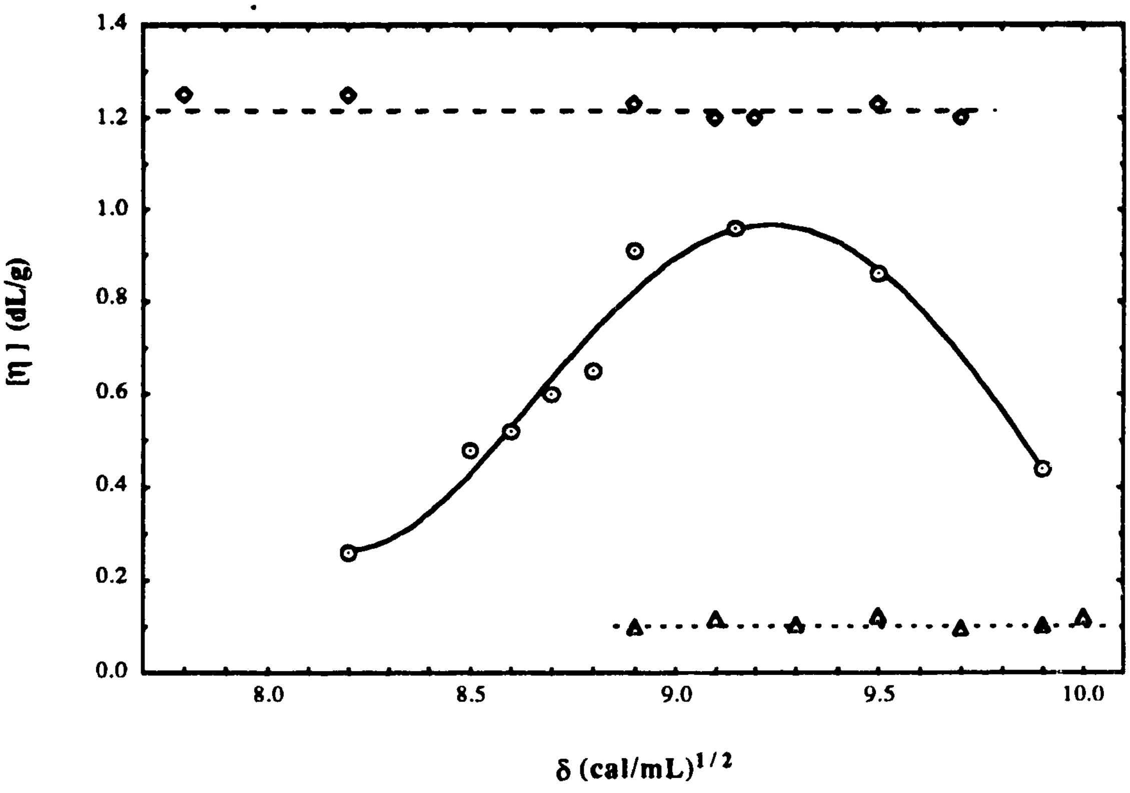


Figure 6.3. Intrinsic viscosity [η] *versus* solubility parameter (δ): (—○—) polystyrene according to reference 16; (– ◇– -) organoplatinum rigid-rod: poly[trans-bis(tri-*n*-butylphosphine)platinum 1,4-butadynediyl] according to reference 5; (- - ▲- - -) polymer I in the following solvents (δ): toluene (8.9), THF (9.1), chloroform (9.3), chlorobenzene (9.5), dichloromethane (9.7), bromobenzene (9.9), and *o*-dichlorobenzene (10.0).

curve within this δ range,[16] polymer I displays little change in [η] (scatter of *ca.* 0.11 dL/g). This resembles the behavior of another organometallic rod-like polymer: poly[trans-bis(tri-*n*-butylphosphine)-platinum 1,4-butadynediyl].[5] The limited solubility of the polymer precluded attempts to explore an even wider range of solvent δ values. This independence of [η] with respect to solvent power for polymer I confirms that it possesses a rod-like structure in solution. We were unable to explore a similar relationship for polymer II due to its very limited solubilities, but its chemical structure is sufficiently similar to that of polymer I that we expect it is rod-like, as is suggested by its α value derived above.

Comparison of Two GPC Methods for Molecular Weight Determination

$\overline{M}$ values for polymers I and II presented in Table 6.1 emerged from MWD curves obtained from GPC data using both the direct calibration method and the universal method. These two MWD curves are shown in Figure 6.4 for both polymers, demonstrating substantial differences between the two polymers as obtained from either calibration scheme. For polymer I, use of the more accurate universal calibration leads to a narrowing of the MWD display as the low-MW tail is shifted to higher MW and the high-MW portion is relatively unaffected. For polymer II, the universal method demonstrates that the whole MWD is shifted about a full order of magnitude higher than suggested by the direct method, with considerable narrowing as well. Corresponding to these method-related MWD differences, there are also significant differences between the $\overline{M}$ values calculated from them, especially for polymer II: much smaller values (up to one order of magnitude) are obtained through the unreliable direct method. As with the oligomers, this can be attributed primarily to the fact that polystyrene possesses a low-mass repeating unit, in contrast to organonickel polymers I and II which have high-mass units. It seems that a direct polystyrene calibration for $\overline{M}$ determination for metal-containing polymers in general are likely to suffer from similar effects.

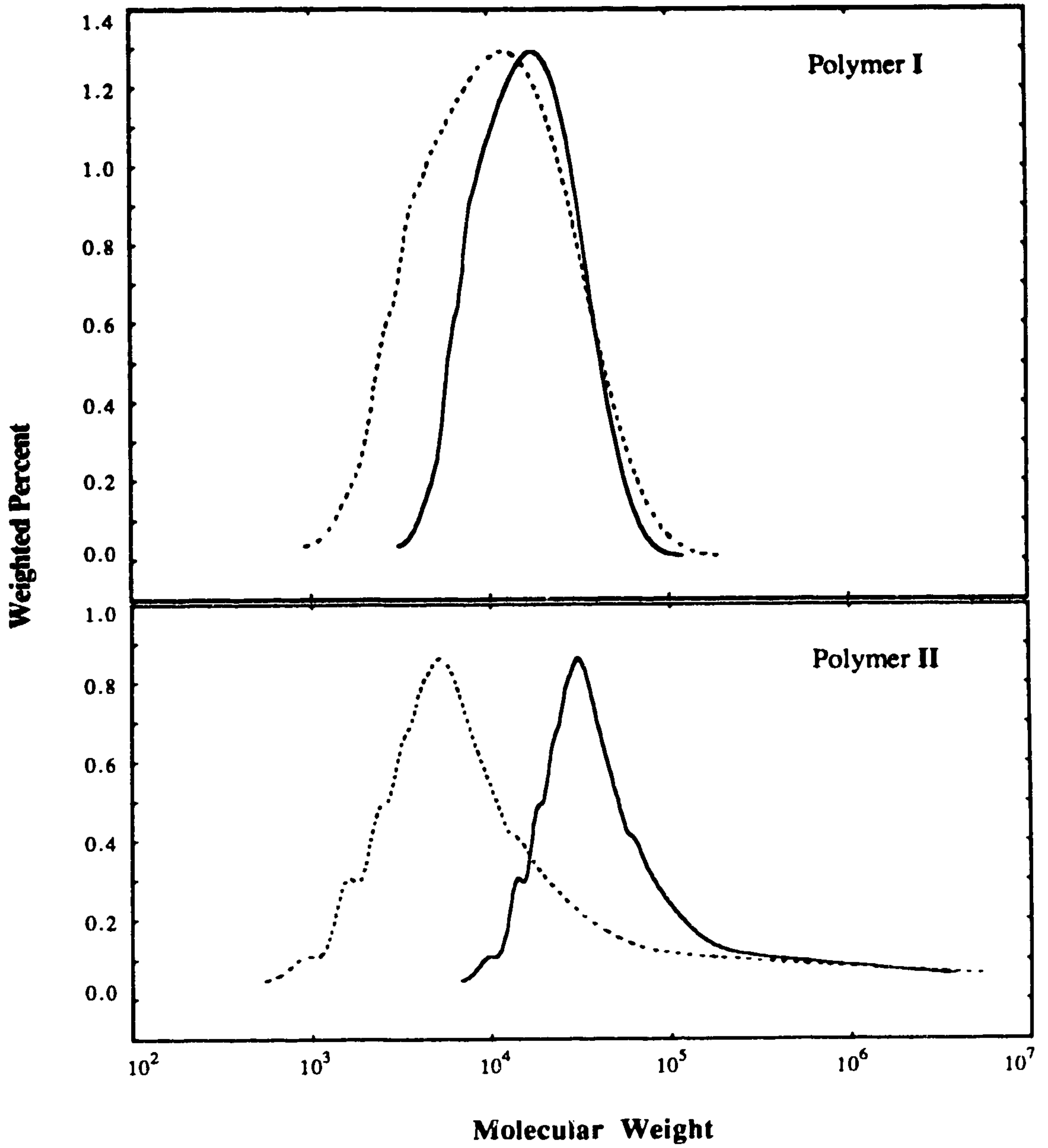


Figure 6.4. MWD curves of the polymers ascertained by the two calibration methods: (-------) direct method; (———) universal method.

It is worth emphasizing one important difference between the relative values of $\overline{M}_w$ and $\overline{M}_v$ for the two different classes of polymers. For coil-like polymers such as polystyrene, one finds by independent experiments that $\alpha < 1$ and that $\overline{M}_v < \overline{M}_w$. It can also be shown that $\overline{M}_v < \overline{M}_w$ is a mathematical consequence of $\alpha < 1$.[17] However, the analogous mathematical prediction when $\alpha > 1$ (as is established for polymers I and II) gives $\overline{M}_v > \overline{M}_w$, so any GPC calibration that fails to produce this result from GPC data is inadequate. Table 6.1 shows that the direct GPC calibration method fails this test and the universal method passes. In effect, the direct method produces the wrong result because its use implies that rod-like molecules behave hydrodynamically as if they were flexible coils.

Finally, values of α and K obtained by iteration for the organonickel polymers can be compared to those reported by Takahashi et al. for a related organoplatinum rod-like polymer, poly[trans-bis(tri-*n*-butylphosphine)platinum 1,4-butadynediyl].[5] They obtained $\overline{\alpha} = 1.7$ and $\overline{K} = 6.5 \times 10^{-9}$ dL/g for the organoplatinum polymer by the same approach, in the same range as the values obtained for our two organonickel polymers.

In conclusion, we have examined the GPC and viscometric behavior of two organonickel polymers and have established their rod-like structure. We are extending our current study to investigate the MW dependence of the viscometric parameters for these rigid-rod polymers, and a detailed report will appear elsewhere.[18]

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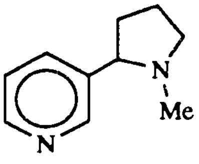
CHAPTER 7

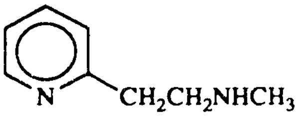
SYNTHESIS, SPECTROSCOPIC, AND STRUCTURAL CHARACTERIZATION OF AZINE AND THIAAZINE DERIVATIVES HAVING $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ SUBSTITUENTS: MOLECULES WHICH ARE STRUCTURALLY RELATED TO BIOLOGICALLY ACTIVE MATERIALS[1,2,†]

INTRODUCTION

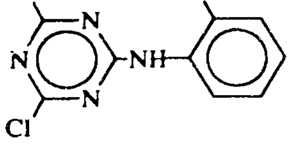
During our earlier studies of polymetallic complexes and polymers having aryl and azinyl bridges,[1-3] we became interested in the relationship between heterocyclic compounds having transition-metal substituents and similar species having only main-group substituents (e.g., F, R, OR and NR_2). Our interest in these heterocyclic species was piqued by the high biological activities that have been demonstrated for many members of the latter class of compounds, e.g.,



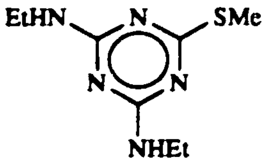
Nicotine



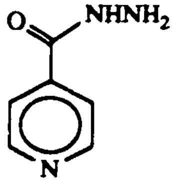
Betahistine



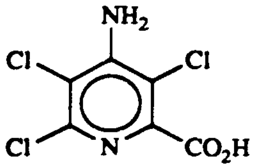
Dyrene



Simatryne



Isoniazid



Picrolam

in pharmaceutical and agricultural chemical applications.[4] Previous studies of transition-metal derivatives of heterocyclic compounds in such applications have mainly focused on coordination complexes as drugs and chemotherapeutic agents.[5] However, the biological activities of heterocyclic compounds having conventional metal-carbonyl substituents have not been widely studied, especially for these applications. Iron is naturally present at high levels in humans and is known to have very low mammalian toxicity compared to other transition metals.[6] Organometallic complexes of iron are therefore likely to be more acceptable, from a regulatory and legal perspective, than are derivatives of most other transition metals in pharmaceutical and/or agricultural chemical applications. In addition, our model studies of simple Fp-aryl and Fp-azinyl complexes (where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) indicated that: (a) they have excellent thermal, air, and moisture stabilities which would be advantageous in any eventual practical applications, (b) Fp and conventional organic substituents such as NHR have similar *net* effects on the electron density of the aromatic rings but that the distribution of electron density on the ring is different (i.e., the Fp group transfers enhanced electron density onto the σ-skeleton but less electron density onto the π-framework), and (c) the Fp group is substantially more sterically bulky than are conventional organic substituents.[3b-3h,7] To evaluate how these difference would affect the biological activities of heterocyclic molecules, we decided to prepare and characterize a series of Fp-azinyl complexes having structural similarities to known biologically active heterocyclic compounds such as those illustrated above. The synthetic studies were also designed to indicate the generality and functional group limitations of these metathetical syntheses and to produce new organometallic azines which might also be of interest as novel ligands in their own right.

In this chapter, the complete results of our synthetic and characterization studies are presented including the X-ray crystallographic analyses of five representative complexes. The results of the biological screening tests on these new compounds will be presented in a later publication.

EXPERIMENTAL SECTION

Unless otherwise noted, all reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. General procedures routinely employed in these laboratories have been described in detail previously.[3b,3g,8] The chemicals used were of reagent grade or comparable purity and where necessary were purified before use and had their purity ascertained by elemental analyses and/or other suitable methods.[8] Solvents used were dried and deaerated by standard procedures and stored under N_2 or Ar.[3b,3c,3g,8] Unless specified otherwise, the chemical reactions described below were effected at ambient temperatures. The Fp_2, and FpI (where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) used in these syntheses were prepared and purified by standard procedures.[9] The heterocyclic starting materials for these syntheses were purchased from the Aldrich chemical company or were supplied by the Ishihara Corporation (USA)[10a] or by DowElanco.[10b] Infrared spectra were recorded on a Pye Unicam PU9522 infrared spectrophotometer calibrated with the 1601 cm^{-1} band of polystyrene. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker WH-300 spectrometer while ^{19}F-NMR spectra were recorded on a Bruker WH-400 spectrometer with reference to the deuterium signal of the solvent employed. The ^1H- and ^{13}C-NMR chemical shifts are reported in parts per million downfield from external Me_4Si and the ^{19}F-NMR chemical shifts are reported in parts per million downfield from external $CFCl_3$. These spectra were recorded with the assistance of the staff of the departmental NMR laboratory while the mass spectra were recorded by the staff of the departmental mass-spectral laboratory.[3b,3g]

Preparation of the New Heterocyclic Complexes of Fp

All of these reactions were performed in a similar manner.[11] The procedure for the synthesis of 2-[(η^5-cyclopentadienyl)irondicarbonyl]-4-chloro-6-(1'-methyl-2'-pyrrolyl)-s-triazine, **24**, is described in detail as a representative example.

An excess of solid sodium amalgam (20.0 g, 20.0 mmol Na)[3b] was placed in a 200 mL three-necked flask equipped with a side arm and the flask was thoroughly flushed with dinitrogen. The amalgam was liquefied by addition of a few drops of mercury and then THF (75 mL) and Fp_2 (1.56 g, 4.4 mmol) were added. The resultant dark red solution was stirred vigorously for 45 min to produce an orange solution containing NaFp. The excess amalgam was then drained through the side arm on the reaction flask. A solution of the substrate, 2,4-dichloro-6-(1'-methyl-2-pyrrolyl)-s-triazine, **24'** (2.00 g, 8.7 mmol), in THF (50 mL) was prepared in a 300 mL flask, to which a Celite-containing (2 × 3 cm) medium porosity fritted funnel had been attached, and was cooled to *ca.* -78°C (solid CO_2/acetone bath). The NaFp solution was then filtered through the funnel into the substrate solution and the funnel was washed with THF (2 × 10 mL). The resulting orange solution was stirred at *ca.* -78°C for 1 h and then the cooling source was removed and the solution was allowed to warm up to ambient temperature. The reaction mixture was stirred until its IR spectrum indicated the complete consumption of NaFp (in this case 4 days) and it was then taken to dryness *in vacuo* and to the resulting solid was added CH_2Cl_2 (*ca.* 7 mL). The desired product was isolated by column chromatography using Florisil as the support and CH_2Cl_2 as eluent. The first band eluted was yellow and had carbonyl bands at 2016 and 1954 cm^{-1}. Its low resolution mass spectrum indicated that Fp-CH_3[9c] was the only carbonyl containing compound present and it was therefore discarded. The second band eluted was dark red and was identified by its infrared spectrum as Fp_2 before being discarded. The third band eluted was light brown and was removed from the column with THF. The resulting solution was dried *in vacuo*, redissolved in CH_2Cl_2 and filtered through Florisil, and then was dried *in vacuo* for 24 h to yield 51% (1.62 g, 4.4 mmol) of a light brown powder, 2-[(η^5-cyclopentadienyl)irondicarbonyl]-4-chloro-6-(1'-methyl-2-pyrrolyl)-s-triazine, **24**.

The other new organometallic products, **1** to **23** and **25**, were prepared similarly by reaction of NaFp with the appropriate chlorine substituted heterocyclic starting materials, **1'** to **23'** and **25'** (i.e., 2-chloro-5-trifluoromethylpyridine, **1'**, 2,6-dichloro-4-trifluoromethylpyridine, **2'**, 2-chloro-4,5-bis(trifluoromethyl)pyridine, **3'**, 2-chloro-4,6-bis(trifluoromethyl)pyridine, **4'**, 4-chloro-2,6-bis(trifluoromethyl)pyridine, **5'**, 2-chloro-5-carbomethoxypyridine, **6'**, 2-chloropyrimidine, **7'**, 4-chloro-2-methylmecaptopyrimidine, **8'**, 4-chloro-2-methylmercapto-6-methylpyrimidine, **9'**, 4-chloro-2-methylmercapto-5-carboethoxypyrimidine, **10'**, 4,6-dichloro-2-methylmercapto-5-phenylpyrimidine, **11'**, 4-chloro-2-methylmercapto-6-aminopyrimidine, **12'**, 4-chloro-2-amino-6-methylpyrimidine, **13'**, 4,6-dichloro-2-aminopyrimidine, **14'**, 4,6-dichloro-5-aminopyrimidine, **15'**, 2,4-dichloro-5-(1',4'-dichlorodiphenylmethyl)-6-methylpyrimidine, **16'**, 4-chloro-2,6-dimethoxypyrimidine, **17'**, 4,5-dichloro-3(2H)pyridazone, **18'**, 4,5-dichloro-2-phenyl-3(2H)pyridazone, **19'**, 3-chloro-6-(4'-chlorophenyl)pyridazine, **20'**, 3,6-dichloro-4-(1'-methylcyclopropyl)pyridazine, **21'**, 2,4-dichloro-6-(2'-chloroanilino)-s-triazine, **22'**, 2-chloro-4,6-bisethylamino-s-triazine, **23'**, and 2-chloro-6-methoxybenzothiazole, **25'**, respectively). In each case, the starting material has a chlorine atom in the position in which the Fp group ends up in the product. The identities, yields,[12] analytical, mass spectral, IR and NMR data for these complexes are recorded in Tables 7.1 and 7.2.

The reaction of three reagents (i.e., 3,6-dichloro-4-(2'-chloro-1',1'-dimethylethyl)-pyridazine, **26'**, 2,4,6-trichloro-5-pyrimadinecarbonitrile, **27'**, and 4-benzylmercapto-3,6-dichloropyridazine, **28'**) with NaFp under conditions similar to those described above, produced mixtures of organometallic products that were not successfully separated by column chromatography and/or fractional crystallization. In addition, because of the number of products present, insufficient spectroscopic evidence was obtained on any of them to unambiguously characterize their isomeric structures. However, comparison of the observed IR, mass spectral and NMR data to that for related well characterized species allows the tentative assignments of the structures presented in the text.

The impure product obtained from reagent **26'** exhibited the following spectroscopic properties: low-resolution mass spectrum: *m/z* 352, 324 (P^+-nCO, n = 1, 2); IR ν_{CO} (CH_2Cl_2): 2031 (s) and 1973 (s) cm^{-1}, (hexanes) 2033 (m), 1977 (m), and 1967 (w) cm^{-1}; ^1H-NMR ($(CD_3)_2SO$): δ 5.32 (7%), 5.23 (100%), 5.21 (7%), 5.18 (18%), and 5.14 (32%) (C_5H_5, where the % figure in bracket refers to the approximate percentage of the peak height compared to the height of the strongest peak between 5.35 and 5.10 ppm) and many resonances between 9.5 and 1.0 ppm (azine ring and substituent hydrogens); ^{13}C-NMR ($(CD_3)_2SO$): δ 215.26 and 214.70 (Fe-*C*O), 188.05 (Fp-C(*ipso*)), 88.05 (20%), 86.60 (10%), 86.45 (100%), and 85.42 (4%) (C_5H_5, where the % figure in bracket refers to the approximate percentage of the peak height compared to the height of the strongest peak between 90 and 80 ppm), and numerous unassigned peaks between 160 and 15 ppm (azine ring and substituent carbons).

The reaction for **27'** was carried out using both one and two equivalents of NaFp. When this reaction was carried out using one equivalent of NaFp, the impure product contained predominantly the monometallic species. ANAL. Calcd for $C_{12}H_5Cl_2FeN_3O_2$: C, 41.19%; H, 1.44%; N, 12.01%. Found: C, 40.44%; H, 1.74%; N, 10.66%. Low-resolution mass spectrum: *m/z* 349, 321, 293 (P^+-nCO, n = 0 - 2); IR ν_{CO} (CH_2Cl_2): 2036 (s) and 1987 (s) cm^{-1}. When this reaction was carried out using two equivalents of NaFp, an impure product containing predominantly the bimetallic species was obtained. ANAL. Calcd for $C_{19}H_{10}ClFe_2N_3O_4$: C, 46.44%; H, 2.05%; N, 8.55%; Cl, 7.21%. Found: C, 46.19%; H, 2.72%; N, 7.49%; Cl, 7.54%. Low-resolution mass spectrum: *m/z* 463, 435, 407, 379 (P^+-nCO, n = 1 - 4); IR ν_{CO} (CH_2Cl_2): 2034 (s) and 1987 (s)

Table 7.1. Yields, Analytical, Mass-Spectral and Infrared Data

		Analytical Data						Low-resolution	
Complex (Fp = (η^5-C_5H_5)Fe(CO)$_2$-)		C%		H%		N%		Mass Spectral	Infrared Data ν_{CO}
	Yield (%)	Calcd	Found	Calcd	Found	Calcd	Found	Data P$^+$, m/z [a]	(CH_2Cl_2, cm^{-1}) [b]
2-Fp-4-CF_3-6-Cl-pyridine, **2**	83	43.68	43.72	1.97	1.94	3.92	3.87	357[c]	2031 (s), 1978 (s)
2-Fp-4,5-$(CF_3)_2$-pyridine, **3**	43	43.01	42.78	1.80	1.94	3.58	3.56	391	2033 (s), 1979 (s)
2-Fp-4,6-$(CF_3)_2$-pyridine, **4**	73	43.01	42.77	1.80	1.66	3.58	3.54	391	2033 (s), 1978 (s)
4-Fp-2,6-$(CF_3)_2$-pyridine, **5**	29	43.01	42.77	1.80	1.72	3.58	3.40	391	2034 (s), 1985 (s)
Methyl 6-Fp-nicotinate, **6**[d]	43	53.71	53.09	3.54	3.66	4.47	4.32	285[e]	2026 (s), 1968 (s)
2-Fp-pyrimidine, **7**	27	51.65	51.25	3.15	3.15	10.94	10.85	256	2029 (s), 1976 (s)
2-SMe-4-Fp-pyrimidine, **8**	85	47.70	47.71	3.34	3.29	9.27	8.91	302	2026 (s), 1968 (s)[f]
2-SMe-4-Fp-5-CO_2Et-pyrimidine, **10**[d]	70	48.14	47.42	3.77	3.91	7.49	7.80	374	2030 (s), 1978 (s)
2-SMe-4-Fp-5-Ph-6-Cl-pyrimidine, **11**	60	52.38	51.97	3.17	3.17	6.79	6.45	384[e]	2030 (s), 1978 (s)
2-SMe-4-Fp-6-NH_2-pyrimidine, **12**	50	45.45	45.41	3.50	3.94	13.25	13.25	289[e]	2026 (s), 1970 (s)
2-NH_2-4-Fp-6-Cl-pyrimidine, **14**	80	43.24	43.45	2.64	2.66	13.75	13.60	277[e]	2030 (s), 1977 (s)
4-Fp-5-NH_2-6-Cl-pyrimidine, **15**	60	43.24	43.18	2.64	2.67	13.75	13.50	277[e]	2030 (s), 1977 (s)
$C_{25}H_{17}Cl_3FeN_2O_2$, **16**[g]	45	55.64	55.84	3.18	3.30	5.19	4.89	482[h]	2032 (s), 1983 (s)
2,6-$(OMe)_2$-4-Fp-pyrimidine, **17**	51	49.39	48.98	3.82	3.88	8.86	8.51	288[e]	2026 (s), 1973 (s)
4-Fp-5-Cl-3-(2H)-pyridezone, **18**[d]	17	43.11	41.88	2.30	2.63	9.13	9.49	278[e]	2035 (s), 1984 (s)
$C_{17}H_{11}ClFeN_2O_3$, **19**[g]	48	53.37	53.38	2.90	3.00	7.32	7.34	354[e]	2034 (s), 1983 (s)
3-Fp-6-(*p*-C_6H_4Cl)-pyridazine, **20**	30	55.70	56.10	3.02	3.13	7.64	7.58	338[e]	2028 (s), 1974 (s)
3-Fp-5-(1'-Me-cyclopropyl)-6-Cl-pyridazine, **21**	79	52.28	52.20	3.67	3.75	7.83	8.00	344	2032 (s), 1977 (s)
2-Fp-4-Cl-6-(*o*-Cl-anilino)-s-triazine, **22**[d]	20	46.08	47.03	2.42	2.58	13.42	13.37	389[i]	2036 (s), 1986 (s)
2-Fp-4,6-(ethylamino)$_2$-s-triazine, **23**[d]	15	49.00	49.57	4.99	5.49	20.41	21.51	315[e]	2025 (s), 1969 (s)
2-Fp-4-Cl-6-(1-Me-pyrolyl)-s-triazine, **24**	51	48.75	49.03	3.00	3.25	15.16	14.88	342[e]	2034 (s), 1986 (s)

[a] Probe temperature 150-280°C. Assignments involve the most abundant naturally occurring isotopes (e.g., ^{35}Cl, ^{56}Fe). All ions displayed peak patterns attributable to the expected isotopomers of the complexes.

[b] Abbreviations w (weak), m (medium), s (strong), sh (shoulder), v (very), br (broad).

[c] When this product was synthesized in the presence of an excess of NaFp, a second set of low-resolution mass spectral peaks (m/z 499 - 28n (n = 0 - 2, 4; i.e., P^+-nCO)) attributable to 2,6-Fp_2-4-CF_3-pyrimidine were observed at low intensities.

[d] This complex was characterized spectroscopically but was not obtained in an analytically pure form, see text.

[e] No parent ion observed in the low resolution mass spectrum, heaviest ion observed as P^+-CO.

[f] Recorded in THF.

[g] Product is a mixture of isomers, see text.

[h] No parent ion observed in the low resolution mass spectrum, heaviest ion observed as P^+-2CO.

[i] Fast atom bombardment mass spectrum, P^+ -CO+H.

Table 7.2. ^{1}H-, ^{13}C- and ^{19}F-NMR Data (δ in ppm, $(CD_3)_2SO$)

Complex^a	^{1}H-NMR^b		^{13}C-NMR^b (Hz)				
				Azine			
	Cp	Azine and Substituents	Cp	X-C	H-C	Substituent-C	Fe-CO
1^{c,d}	5.15 (5H)	8.55 (1H) 7.65 (1H) 7.28 (1H)		^{e}	143.54 140.06 126.11	^{e}	215.34
2	5.25 (s, 5H)	7.67 (s, 1H) 7.17 (s, 1H) [-63.17 (s, 3F)]	87.00	194.07 (C2) 148.50 (C6) 133.80 (C4, q, $^2J_{CF} = 32$)	133.55 (C3, $^3J_{CF} = 2.5$) 112.11 (C5, $^3J_{CF} = 3.6$)	122.55 (q, $^1J_{CF} = 273$)	215.08
3	5.27 (s, 5H)	8.81 (s, 1H) 7.90 (s, 1H) [-57.83 (q, 3F, J=12)] [-60.25 (q, 3F)]	87.14	203.62 (C2) 126.18 (C4, q, $^2J_{CF} = 33$) 113.57 (C5, q, $^2J_{CF} = 32$)	145.26 (C6, q, $^3J_{CF} = 6$) 135.01 (C3, q, $^3J_{CF} = 5$)	123.60 (q, $^1J_{CF} = 272$) 122.19 (q, $^1J_{CF} = 275$)	214.91
4	5.25 (s, 5H)	7.96 (s, 1H) 7.45 (s, 1H) [-63.34 (s, 3F)] [-67.11 (s, 3F)]	87.07	194.63 (C2) 146.16 (C6, q, $^2J_{CF} = 33$) 131.87 (C4, q, $^2J_{CF} = 32$)	137.31 (C3) 109.16 (C5)	122.79 (q, $^1J_{CF} = 274$) 121.28 (q, $^1J_{CF} = 275$)	214.98
5	5.30 (s, 5H)	8.19 (s, 2H) [-66.30 (3, 6F)]	87.26	180.14 (C4) 141.46 (C2/6, q, $^2J_{CF} = 33$)	139.49 (C3/5)	121.58 (q, $^1J_{CF} = 275$)	214.89
6^d	5.25 (s, 5H)	8.74 (1H) 7.66 (1H) 7.47 (1H) 3.83 (OCH_3)	86.94	198.05(C2)	147.62 140.41 129.70	51.75 (OCH_3)	215.62
7	5.09 (s, 5H)	8.18 (d, H4/6, J = 5) 6.84 (t, H5)	87.51	203.67 (C2)	154.11 (C4/6) 115.65 (C5)	-	216.04
8	5.18 (s, 5H)	7.54 (d, 1H, J=4) 7.26 (d, 1H) 2.42 (S, SCH_3)	86.99	205.66 (C4) 166.65 (C2)	147.67 (C6) 135.29 (C5)	13.30(SCH_3)	215.11
9	5.18(s, 5H)	7.16 (s, 1H) 2.42 (s, SCH_3) 2.09 (s, CH_3)	86.99	203.86 (C4) 165.92 (C2) 157.15 (C6)	134.53(C5)	22.51(CH_3) 13.28(SCH_3)	215.35

10	5.08 (s, 5H)	8.07 (s, 1H) 4.24 (OCH_2CH_3) 2.47 (SCH_3) 1.30 (OCH_2CH_3)	87.10	209.21 (C4)	151.14 (C6)	60.71 (OCH_2CH_3) 13.92 (OCH_2CH_3) 13.40 (SCH_3)	214.56
11	4.82 (s, 5H)	7.46 (m, 3H) 7.29 (d, 2H) 2.51 (s, SCH_3)	86.97	210.00 (C4) 163.84 154.50 143.46 140.33	-	130.60 (2C) 128.26 (2C) 127.80 (1C) 13.70 (SCH3)	214.54
12^d	5.14 (s, 5H)	6.34 (s, 1H) 6.05 (NH_2) 2.40 (SCH_3)	86.80	194.60 (C4) *e*	118.05 (C5)	13.03 (SCH_3)	215.93
13	5.08 (s, 5H)	6.61 (s, 1H) 5.82 (NH_2) 1.94 (CH_3)	86.80	199.76 (C4) 159.66 157.47	128.30 (C5)	22.46 (CH_3)	215.88
14^d	5.15 (s, 5H)	6.78 (1H) 6.48 (NH_2)	86.87	205.62 (C4) 159.44 153.81	124.98 (C5)	-	215.76
15	5.16 (s, 5H)	8.20 (s, 1H) 6.20 (NH_2)	*e*	*e*	*e*	-	*e*
16^f	5.20 (s, 5H)	7.67 (d, 1H, J=2) 7.2-7.4 (m, 4H) 7.03 (d, 2H, J=7) 6.86 (d, 1H, J=8) 5.97 (s, 1H, C-*H*) 1.94 (s, 3H, CH_3)	87.34	202.24 *e*	*e*	*e* 47.53 (CH) 23.82 (CH_3)	215.17
17^d	5.14 (s, 5H)	6.64 (s, 1H) 3.84 (s, OCH_3) 3.73 (s, OCH_3)	86.87	202.68 (C4) 165.33 159.88	117.33 (C5)	53.57 (OCH_3) 52.43 (OCH_3)	215.47
18^g	5.14 (s, 5H)	12.28 (s, N*H*) 7.47 (s, C*H*)	86.44	*e*	133.95 (C6)	-	214.47
19^h	5.20 (s, 5H)	7.3-7.7 (m)	86.57	*e*	134.09 (C6)	-	216.04
20	5.24 (s, 5H)	8.06 (d, 2H, J=8.8) 7.65 (d, 1H, J=8.8) 7.54 (d, 2H) 7.44 (d, 1H)	86.76	187.91 (C3) 152.30 (C6)	142.49 (C4) 118.71 (C5)	135.87 133.84 128.75 (*C*-H) 127.64 (*C*-H)	215.48

21	5.24 (s, 5H)	7.48 (s, 1H, C*H*) 1.28 (s, 3H, $C\mathit{H}_3$) 0.79 (s, 2H, $C\mathit{H}_2$) 0.74 (s, 2H, $C\mathit{H}_2$)	86.77	188.34 (C3) 155.31 (C6) 138.09 (C5)	143.79 (C4)	[e]	215.93
22	5.19 (s, 5H)	9.48 (s, 1H, N*H*) 7.59 (br, m, 1H) 7.51 (dd, 1H, J=7.8, 1.5) 7.34 (ddd, 1H, J=7.8, 7.8, 1.5) 7.24 (ddd, 1H, J=7.8, 7.8, 1.8)	87.61	162.52 (C2) [e]	-	129.42 (CH) 127.81 (CH) 127.18 (CH) 126.93 (CH) [e]	214.38
23[d]	5.06 (s, 5H)	3.22 (m, 4H) 1.05 (m, 6H)	87.09	164.82 (C2) [e]	-	34.43 (CH_2CH_3) 14.87 (CH_2CH_3)	215.98
24	5.29 (s, 5H)	7.13 (m, 2H) 6.15 (m, 6H) 4.02 (s, $C\mathit{H}_3$)	87.59	162.83 158.35	-	225.61 131.57 (CH) 118.32 (CH) 108.46 (CH) 37.79 (CH_3)	214.23
25[i]	5.35 (s, 5H)	7.60 (d, 1H, J=8.8) 7.35 (d, 1H, J=2.6) 6.84 (dd, 2H, J=8.8, 2.6) 3.75 (s, 3H, $OC\mathit{H}_3$)	86.91	182.01 [e]	119.32 112.44 103.19	55.40 (OCH_3)	214.06

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[a] Where Fp = (η^5-C_5H_5)Fe$(CO)_2$ and Cp = η^5-C_5H_5.

[b] ^{1}H-NMR were measured at 300.135 MHz and ^{13}C-NMR were measured at 75.469 MHz unless otherwise specified. Values recorded in square brackets are the ^{19}F-NMR chemical shifts and coupling constants of the CF_3 derivatives (measured at 376.504 MHz).

[c] This complex was obtained in low yield as an oil. Low-resolution mass spectrum *m/z* 323 (P^+). IR ν_{CO} (CH_2Cl_2) 2028 (s), 1973 (s) cm^{-1}.

[d] Due to line broadening in the ^{1}H-NMR spectrum of the sample used, the multiplicities of these lines were not established.

[e] The positions of some of these resonances could not be unambiguously established under the usual conditions.

[f] The minor isomer has Cp resonances at 5.03 ppm in the ^{1}H-NMR and 86.61 ppm in the ^{13}C-NMR and has two signals *attributable* to carbonyl ligands at 214.37 and 213.33 ppm in the ^{13}C-NMR. The isomer ratio is *ca.* 3:1.

[g] The minor isomer that was lost upon chromatography had a similar ^{1}H-NMR spectrum 12.57 (s, ^{1}H, N*H*), 7.88 (s, 1H, C*H*) and 5.28 (s, 5H, $C_5\mathit{H}_5$) ppm, and in the ^{13}C-NMR C_5H_5 was observed at 87.05 ppm.

[h] The minor isomer has Fp resonances at 214.02 (*C*O) and 87.09 (C_5H_5) ppm in the ^{13}C-NMR and at 5.35 ($C_5\mathit{H}_5$) ppm in the ^{1}H-NMR, and is present in a *ca.* 1:5 ratio with the major isomer.

[i] This complex was obtained in 10% yield. Low-resolution mass spectrum *m/z* 341 (P^+). IR ν_{CO} (CH_2Cl_2) 2038 (s), 1988 (s) cm^{-1}.

cm^{-1}. For the mixed isomers: ^1H-NMR ($(CD_3)_2SO$): δ 5.76 (3%), 5.34 (100%), 5.31 (38%), and 5.24 (5%) ($C_5\textit{H}_5$, where the % figure in bracket refers to the approximate percentage of the peak height compared to the height of the strongest peak between 6 and 5 ppm); ^{13}C-NMR ($(CD_3)_2SO$): δ 212.72, 212.59 and 211.80 (Fe-*C*O), 87.18 (60%), 86.61 (100%), 86.50 (15%), 86.39 (15%) and 85.00 (44%) ($\textit{C}_5H_5$, where the % figure in bracket refers to the approximate percentage of the peak height compared to the height of the strongest peak between 90 and 80 ppm).

IR spectroscopic monitoring indicates that the reaction of NaFp with reagent **28'** produces Fp-CH_2Ph (identified by its characteristic spectral properties)[9c] as the major (*ca.* 50%) organometallic product (IR ν_{CO} (CH_2Cl_2): 2004 (s) and 1949 (s) cm^{-1}, (hexanes) 2010 (s) and 1960 (s) cm^{-1}; Low-resolution mass spectrum: *m/z* 268, 240, 212 (P^+-nCO, n = 0 - 3)). In addition, at least two other organometallic products were present in the reaction mixture. The other major product (*ca.* 45%) in the reaction mixture was a relatively electron poor azine derivative having lower solubility in hexanes, $C_{11}H_6Cl_2FeN_2O_2$: IR ν_{CO} (CH_2Cl_2): 2038 (s) and 1989 (s) cm^{-1}, (hexanes) 2041 (w) and 1996 (w) cm^{-1}; Low-resolution mass spectrum: *m/z* 324, 296, 268 (P^+-nCO, n = 0 - 3, assignments confirmed by high resolution mass spectra); ^1H-NMR ($(CD_3)_2SO$): δ 8.03 (s, 1H, C(5)*H*) and 5.32 (s, 5H, $C_5\textit{H}_5$); ^{13}C-NMR ($(CD_3)_2SO$): δ 213.71 (Fe*C*O), 147.02 (*C*(5)H), and 87.26 ($\textit{C}_5H_5$), and one or more electron rich and hexanes soluble azine derivative(s) which are present in substantially lower yield (<5%), probably as one or two isomers of $C_{18}H_{13}ClFeN_2O_2S$ (IR ν_{CO} (hexanes): 2031 (w) and 1985 (w) cm^{-1}). ^1H-NMR ($(CD_3)_2SO$): δ 5.18 ($C_5\textit{H}_5$); ^{13}C-NMR ($(CD_3)_2SO$): δ 214.19 (Fe*C*O) and 86.80 ($\textit{C}_5H_5$).

The reactions of 2-chloro-5-carboethoxy-1H-benzimidazole, **29'**, 4-carboethoxy-6-chloro-5-cyano-2-methyl-3-nitropyridine, **30'**, 5-bromopyrimidine, **31'**, and 3-chloro-s-triazolo<3,4-B>benzothiazole, **32'**, with NaFp under conditions similar to those described above, failed to produce any new isolable heterocyclic derivatives of Fp. Rather, spectroscopic evidence for the quantitative formation of Fp_2 was observed by IR spectroscopy.

X-Ray Crystal Structures Determinations for Complexes 2, 4, 5, 7, and 21

Crystals suitable for X-ray examination were grown from CH_2Cl_2/hexanes at -15°C. They were mounted on glass fibers and optically centered in the X-ray beam on an Enraf-Nonius CAD4 automated diffractometer for 2-[(η^5-Cyclopentadienyl)irondicarbonyl]-4-trifluoromethyl-6-chloropyridine, **2**, 2-[(η^5-Cyclopentadienyl)irondicarbonyl]-4,6-bistrifluoromethylpyridine, **4**, 4-[(η^5-Cyclopentadienyl)irondicarbonyl]-2,6-bistrifluoromethylpyridine, **5**, and 2-[(η^5-Cyclopentadienyl)irondicarbonyl]pyrimidine, **7**, and on a Rigaku AFC6R automated diffractometer for 3-[(η^5-Cyclopentadienyl)irondicarbonyl]-5-(1'-methylcyclopropyl)-6-chloropyridazine, **21**.[13,14] Data collection and structure solution parameters are given in Table 7.3. Data were corrected for Lorentz and polarization effects and also for absorption via the method of Walker and Stuart.[14c] Structure solution proceeded in a routine fashion for all 5 compounds utilizing the MOLEN structure solution package[13] for compounds **2**, **4**, **5**, and **7** and the TEXSAN[14a] structure solution package for complex **21**. All non-hydrogen atoms were treated with anisotropic displacement parameters and all hydrogen atoms were geometrically generated and included in the model as "riding" on the attached atom (d_{C-H} = 0.95 Å) with isotropic displacement parameters constrained to be 1.2 times that of the attached atom. Disorder was observed in the CF_3 groups of complexes **4** and **5** and in the (η^5-C_5H_5) group of complex **5**. It was treated by first refining the site occupancies with the thermal parameters fixed and then refining the displacement parameters with the site occupancies fixed.

Final fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 7.4 for compounds **2**, **4**, **5**, **7**, and **21**. Tables of Structure Factor Amplitudes (93 pages) are available from the authors.

Table 7.3. Summary of Crystal Data and Intensity Collection for the Complexes

Parameter	Complex 2	Complex 4	Complex 5	Complex 7	Complex 21
formula	$C_{13}H_7ClF_3FeNO_2$	$C_{14}H_7F_6FeNO_2$	$C_{14}H_7F_6FeNO_2$	$C_{11}H_8FeN_2O_2$	$C_{15}H_{13}ClFeN_2O_2$
formula weight	357.50	391.05	391.05	256.05	344.58
crystal dimensions, mm	0.5 × 0.6 × 0.65	0.5 × 0.65 × 0.8	0.21 × 0.23 × 0.72	0.3 × 0.5 × 0.6	0.20 × 0.25 × 0.35
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	Pbca	$Pca2_1$
crystal syst	triclinic	triclinic	monoclinic	orthorhombic	orthorhombic
a, Å	10.1549 (7)	7.806 (1)	10.5424 (5)	7.1348 (3)	13.804 (2)
b, Å	10.393 (1)	9.299 (1)	10.6685 (5)	12.2752 (7)	10.202 (2)
c, Å	14.202 (1)	10.680 (2)	13.8800 (9)	24.414 (2)	10.559 (2)
α, deg	98.042 (7)	78.20 (1)	-	-	-
β, deg	98.613 (6)	84.25 (1)	104.439 (5)	-	-
γ, deg	107.639 (6)	83.75 (2)	-	-	-
V, Å^3	1384.7 (5)	752 (2)	1511.8 (4)	2138.2 (2)	1486.9 (7)
Z	4	2	4	8	4
calcd density, g cm^{-3}	1.715	1.727	1.718	1.591	1.539
abs coeff, cm^{-1}	13.17	10.73	10.67	13.92	11.97
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Rigaku AFC6R
radiation	Mo K_α (λ = 0.7107Å)	Mo K_α (λ = 0.7107Å)	Mo K_α (λ = 0.7107Å)	Mo K_α (λ = 0.7107Å)	Mo K_α (λ = 0.7107Å)
monochromator/filter	incident beam, graphite crystal	incident beam, graphite crystal	incident beam, graphite crystal	incident beam, graphite crystal	incident beam, graphite crystal
take-off angle, deg	2.8	2.8	2.8	2.8	6.0
detector aperture, mm	3.00 + tan θ horiz x 4.0 vert	3.00 + tan θ horiz x 4.0 vert	3.00 + tan θ horiz x 4.0 vert	3.00 + tan θ horiz x 4.0 vert	6.0 x 6.0 vert
crystal-to-detector distance, mm	205	205	205	205	400
scan type	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$
scan width	0.80 + .35 tan θ	0.80 + .35 tan θ	0.80 + .35 tan θ	0.80 + .35 tan θ	1.31 + .30 tan θ
scan rate, deg min-1	0.67 → 89	0.67 → 89	0.67 → 89	0.67 → 89	32.0
2θ range, deg	$2 < 2\theta < 44$	$2 < 2\theta < 44$	$2 < 2\theta < 44$	$2 < 2\theta < 44$	$3 < 2\theta < 56.1$
data collection index range	+h, ±k, ±l	+h, ±k, ±l	+h, +k, ±l	+h, +k, +l	+h, +k, +l
number of reflections	3369	1845	2090	1556	2085
number of significant reflections in refinement	2722 ($F > 6\sigma(F)$)	1715 ($F > 6\sigma(F)$)	1550 ($F > 6\sigma(F)$)	1007 ($F > 6\sigma(F)$)	1298 ($I > 2\sigma_I$)
observations/variables ratio	2722/320	1715/245	1550/201	1007/145	1298/190
agreement factor R_1, R_2, GOF	0.0454, 0.0462, 1.29	0.0512, 0.0531, 1.3	0.052, 0.050, 1.687	0.0278, 0.0276, 0.91	0.033, 0.027, 1.44
corrections applied	empirical absorption correction	empirical absorption correction	empirical absorption correction	empirical absorption correction	empirical absorption correction

Table 7.4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters[a,b]

Complex **2**[c]

Atom	*x*	*y*	*z*	*B* (Å^2)
Fe1	0.14775 (6)	-0.01523 (7)	0.66681 (6)	3.51 (2)
Fe2	0.32529 (6)	0.55830 (8)	0.37491 (6)	3.35 (2)
Cl1	0.2022 (2)	-0.4861 (2)	0.7664 (1)	5.84 (4)
Cl2	0.4826 (2)	0.6753 (4)	0.0402 (2)	11.92 (9)
F51	0.7159 (4)	-0.1313 (6)	0.8532 (5)	12.5 (2)
F52	0.6569 (5)	0.011 (1)	0.9379 (5)	16.0 (3)
F53	0.7060 (4)	0.0416 (7)	0.8057 (6)	15.0 (2)
F251	-0.0162 (5)	0.2998 (8)	-0.0709 (4)	11.8 (2)
F252	0.0226 (5)	0.1649 (6)	0.0080 (6)	12.7 (2)
F253	-0.0971 (4)	0.2820 (7)	0.0508 (4)	12.9 (2)
O7	-0.0310 (4)	-0.2636 (5)	0.5305 (4)	5.5 (1)
O8	0.3296 (4)	0.0588 (5)	0.5307 (4)	6.4 (1)
O27	0.6269 (3)	0.6287 (5)	0.3847 (3)	5.4 (1)
O28	0.2979 (4)	0.2732 (4)	0.3742 (4)	5.8 (1)
N2	0.2075 (3)	-0.2493 (4)	0.7242 (3)	3.59 (8) *
N22	0.3850 (4)	0.5945 (5)	0.1882 (4)	5.0 (1) *
C1	0.2667 (4)	-0.1168 (5)	0.7220 (4)	3.6 (1) *
C3	0.2867 (5)	-0.3147 (6)	0.7644 (4)	4.1 (1) *
C4	0.4291 (5)	-0.2565 (6)	0.8047 (5)	4.6 (1) *
C5	0.4890 (5)	-0.1235 (6)	0.8032 (5)	4.4 (1) *
C6	0.4115 (5)	-0.0481 (6)	0.7616 (5)	4.3 (1) *
C7	0.0391 (4)	-0.1666 (6)	0.5850 (4)	4.1 (1)
C8	0.2577 (5)	0.0303 (6)	0.5849 (5)	4.4 (1)
C11	0.2077 (5)	0.1737 (6)	0.7627 (5)	4.6 (1)
C12	0.0984 (5)	0.1679 (6)	0.6861 (5)	4.9 (1)
C13	-0.0198 (5)	0.0557 (6)	0.6889 (5)	5.3 (2)
C14	0.0164 (5)	-0.0058 (6)	0.7669 (5)	5.3 (1)
C15	0.1577 (5)	0.0681 (6)	0.8123 (5)	5.1 (1)
C21	0.2893 (4)	0.5161 (6)	0.2327 (4)	3.7 (1) *

C23	0.3567 (6)	0.5687 (8)	0.0925 (6)	6.2 (1) *
C24	0.2394 (6)	0.4724 (8)	0.0315 (6)	6.3 (2) *
C25	0.1436 (5)	0.3948 (6)	0.0772 (5)	4.5 (1) *
C26	0.1685 (5)	0.4169 (6)	0.1763 (5)	4.2 (1) *
C27	0.5083 (5)	0.6025 (6)	0.3806 (4)	3.7 (1)
C28	0.3069 (4)	0.3848 (6)	0.3754 (4)	4.1 (1)
C31	0.2300 (5)	0.5871 (6)	0.4944 (4)	4.7 (1)
C32	0.1319 (4)	0.5641 (6)	0.4060 (5)	4.9 (1)
C33	0.1839 (5)	0.6692 (6)	0.3564 (5)	5.0 (1)
C34	0.3151 (5)	0.7563 (6)	0.4115 (5)	5.3 (2)
C35	0.3422 (5)	0.7062 (6)	0.4972 (5)	5.1 (1)
C51	0.6419 (5)	-0.0473 (9)	0.8509 (6)	8.0 (2)
C251	0.0138 (6)	0.2844 (7)	0.0196 (5)	5.9 (2)

Complex 4[c]

Atom	*x*	*y*	*z*	*B* (Å^2)
Fe	0.7718 (1)	0.41100 (9)	0.74888 (7)	3.33 (2)
F31	0.617 (1)	-0.183 (1)	0.900 (1)	12.3 (3)
F31a	0.673 (1)	-0.233 (1)	0.899 (1)	8.1 (3)
F32	0.857 (1)	-0.3004 (7)	0.965 (1)	11.6 (3)
F32a	0.879 (1)	-0.283 (1)	0.998 (1)	10.9 (3)
F33	0.736 (1)	-0.1390 (8)	1.0650 (7)	9.7 (2)
F33a	0.672 (2)	-0.140 (1)	1.044 (1)	11.2 (4)
F51	1.3009 (8)	-0.1364 (6)	0.6328 (6)	6.0 (2)
F52	1.3777 (9)	0.065 (1)	0.6638 (9)	10.7 (3)
F53	1.2010 (9)	0.0428 (8)	0.4933 (6)	7.2 (2)
F51a	1.350 (1)	0.099 (1)	0.6013 (9)	5.9 (2) *
F52a	1.228 (4)	-0.109 (3)	0.569 (3)	10.1 (7) *
F53a	1.348 (3)	-0.109 (2)	0.692 (2)	6.9 (5) *
O7	0.6962 (7)	0.3814 (5)	1.0231 (4)	6.2 (1)

O8	1.1028 (5)	0.5209 (5)	0.7532 (5)	6.0 (1)
N2	0.7918 (8)	0.0916 (6)	0.8551 (6)	6.1 (1)
C1	0.8767 (7)	0.2045 (6)	0.7692 (5)	3.6 (1)
C3	0.8634 (8)	-0.0536 (6)	0.8624 (6)	4.2 (1)
C4	1.0118 (8)	-0.0862 (6)	0.7892 (6)	4.7 (1)
C5	1.0813 (8)	0.0318 (7)	0.7101 (6)	4.6 (1)
C6	1.0188 (6)	0.1710 (5)	0.6991 (5)	2.6 (1)
C7	0.7255 (7)	0.3926 (6)	0.9160 (5)	4.0 (1)
C8	0.9739 (7)	0.4760 (6)	0.7518 (5)	3.8 (1)
C11	0.526 (1)	0.512 (1)	0.706 (1)	4.7 (2) *
C11a	0.505 (2)	0.411 (2)	0.713 (1)	4.0 (3) *
C12a	0.615 (2)	0.338 (1)	0.623 (1)	3.3 (3) *
C12	0.545 (1)	0.387 (1)	0.671 (1)	5.0 (2) *
C13a	0.737 (2)	0.436 (1)	0.551 (1)	2.6 (2) *
C13	0.671 (1)	0.388 (1)	0.581 (1)	5.3 (2) *
C14	0.740 (1)	0.525 (1)	0.5594 (9)	4.1 (2) *
C14a	0.708 (2)	0.587 (2)	0.595 (2)	6.1 (4) *
C15	0.643 (1)	0.602 (1)	0.6426 (9)	4.0 (2) *
C15a	0.553 (2)	0.566 (2)	0.704 (1)	4.0 (3) *
C31	0.7715 (9)	-0.1750 (8)	0.9509 (7)	6.0 (2) *
C51	1.246 (1)	0.0032 (9)	0.6215 (8)	7.1 (2) *

Complex 5^c

Atom	x	y	z	B (Å^2)
Fe	0.18550 (7)	0.23977 (8)	0.10371 (6)	3.15 (2)
F31a	0.5938 (6)	0.3324 (7)	-0.1475 (5)	8.4 (2)
F32a	0.6576 (5)	0.3274 (8)	0.0169 (4)	9.1 (2)
F33a	0.6930 (5)	0.1694 (8)	-0.0681 (6)	9.5 (2)
F51a	0.1542 (6)	-0.0653 (6)	-0.2193 (4)	9.0 (2)
F52a	0.240 (1)	0.0503 (8)	-0.3113 (5)	11.9 (3)
F53a	0.3491 (9)	-0.0998 (8)	-0.2241 (7)	13.6 (3)
F31b	0.696 (2)	0.201 (2)	-0.003 (1)	10.2 (5) *
F32b	0.609 (2)	0.386 (2)	-0.027 (1)	10.3 (5) *
F33b	0.635 (1)	0.286 (1)	-0.1379 (8)	5.9 (3) *
F51b	0.257 (2)	-0.114 (2)	-0.196 (1)	10.8 (5) *
F52b	0.126 (2)	0.030 (2)	-0.270 (1)	9.9 (4) *
F53b	0.308 (1)	-0.003 (1)	-0.2928 (9)	6.8 (3) *
O7	0.4162 (5)	0.2212 (6)	0.2673 (4)	7.2 (1)
O8	0.1050 (5)	-0.0158 (4)	0.1253 (4)	6.6 (1)
N4	0.4279 (5)	293 (5)	-0.1364 (4)	4.5 (1) *
C1	0.2872 (5)	0.1890 (5)	0.0081 (4)	3.3 (1) *
C2	0.4096 (6)	0.2387 (6)	0.0103 (4)	4.0 (1) *
C3	0.4725 (6)	0.2065 (6)	-0.0619 (4)	4.2 (1) *
C5	0.3113 (6)	0.0819 (6)	-0.1382 (4)	4.2 (1) *
C6	0.2395 (6)	0.1086 (6)	-0.0709 (4)	4.0 (1) *
C7	0.3247 (6)	0.2296 (6)	0.2022 (4)	4.4 (1)
C8	0.1369 (6)	0.0837 (6)	0.1166 (4)	4.0 (1)
C11	0.0086 (7)	0.3061 (7)	0.0159 (5)	5.1 (2)
C12	0.0050 (6)	0.3142 (6)	0.1149 (5)	4.9 (2)
C13	0.1024 (7)	0.3903 (6)	0.1639 (5)	5.2 (2)
C14	0.1717 (7)	0.4343 (6)	0.0957 (6)	5.9 (2)
C15	0.1093 (7)	0.3821 (7)	0.0015 (5)	5.9 (2)
C31	0.6081 (7)	0.2622 (8)	-0.0601 (6)	6.7 (2) *
C51	0.2577 (8)	-0.0081 (9)	-0.2241 (6)	7.2 (2) *

Complex 7[c]

Atom	*x*	*y*	*z*	*B* (Å^2)
Fe	0.32888 (8)	0.17421 (4)	0.59439 (2)	3.02 (1)
O7	0.6226 (4)	0.0238 (3)	0.5647 (1)	5.67 (8)
O8	0.5928 (5)	0.3358 (3)	0.6322 (1)	6.60 (9)
N2	0.2990 (5)	0.1753 (3)	0.7107 (1)	4.22 (8)
N6	0.3182 (5)	-0.0003 (3)	0.6717 (1)	4.36 (8)
C1	0.3182 (5)	0.1079 (3)	0.6675 (1)	3.09 (8)
C3	0.2771 (7)	0.1278 (4)	0.7598 (2)	5.0 (1)
C4	0.2742 (7)	0.0190 (4)	0.7676 (2)	4.7 (1)
C5	0.2954 (7)	-0.0432 (4)	0.7217 (2)	5.2 (1)
C7	0.5047 (6)	0.0837 (3)	0.5765 (2)	3.59 (9)
C8	0.4864 (6)	0.2712 (3)	0.6180 (2)	3.84 (9)
C11	0.1874 (8)	0.2781 (4)	0.5410 (2)	6.2 (1)
C12	0.1936 (7)	0.1783 (5)	0.5187 (2)	6.2 (1)
C13	0.1027 (7)	0.1063 (4)	0.5530 (2)	5.9 (1)
C14	0.0370 (6)	0.1647 (4)	0.5965 (2)	5.7 (1)
C15	0.0898 (7)	0.2708 (4)	0.5905 (2)	6.1 (1)

Complex 21[d]

Atom	x	y	z	U_{eq}
Fe	0.60285 (4)	0.09716 (6)	0	2.38 (2)
Cl	0.95201 (8)	0.50875 (12)	-0.0009 (3)	3.63 (5)
O1	0.5437 (3)	0.2540 (4)	0.2186 (5)	5.8 (3)
O2	0.7229 (3)	-0.0808 (4)	0.1494 (5)	6.2 (3)
N8	0.7856 (3)	0.2102 (4)	0.0618 (4)	3.1 (2)
N9	0.8596 (3)	0.2991 (4)	0.0617 (4)	2.9 (2)
C1	0.5663 (4)	0.1929 (6)	0.1350 (6)	3.7 (3)
C2	0.6774 (4)	-0.0073 (6)	0.0944 (6)	3.6 (3)
C3	0.5842 (4)	0.0864 (5)	-0.1930 (5)	3.2 (3)
C4	0.5048 (4)	0.1491 (6)	-0.1384 (6)	3.8 (3)
C5	0.4598 (4)	0.0625 (7)	-0.0546 (6)	4.4 (3)
C6	0.5106 (5)	-0.0549 (6)	-0.0576 (6)	4.3 (3)
C7	0.5879 (4)	-0.0398 (5)	-0.1426 (6)	3.6 (3)
C8	0.7102 (3)	0.2254 (4)	-0.0150 (7)	2.3 (2)
C9	0.8543 (3)	0.4003 (5)	-0.0128 (7)	2.2 (2)
C10	0.7785 (3)	0.4281 (4)	-0.0985 (5)	2.0 (2)
C11	0.7067 (3)	0.3354 (4)	-0.0976 (5)	2.2 (2)
C12	0.7769 (3)	0.5476 (4)	-0.1805 (5)	2.2 (2)
C13	0.8457 (4)	0.5447 (6)	-0.2909 (5)	3.4 (3)
C14	0.7595 (4)	0.6766 (5)	-0.1167 (6)	3.2 (2)
C15	0.6822 (4)	0.6162 (5)	-0.1980 (6)	3.5 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

[b] Starred atoms were refined isotropically.

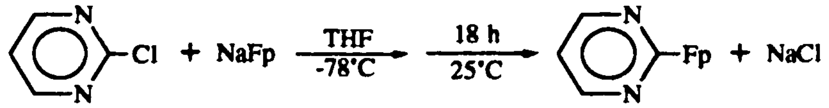
[c] Anisotropically refined atoms are given as B (Å^2), the equivalent isotropic displacement parameters, defined as: (4/3) $[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

[d] Anisotropically refined atoms are given as Ueq, defined as: $U_{eq} = \frac{1}{3}\Sigma_{i=1}^{3} r_i^2$, and r_i are the root-mean-square amplitudes of displacement.

RESULTS AND DISCUSSION

Synthesis of the Complexes

The primary goal of these synthetic studies was to determine the generality and functional group limitations to the metathetical syntheses of Fp-azinyl complexes by preparing new organometallic complexes having close structural similarities to commercially important compounds.[11] Thus, chlorine substituted heterocyclic substrates were chosen having a variety of aromatic cores, substitution geometries, and functional groups (e.g., R, Ar, CF_3, CN, NO_2, OR, SR, F, Cl, NH_2, NHR, and =O) with widely varying steric and electronic requirements. These reactions produced a representative series of new products (Figure 7.1) by the *formal* nucleophilic displacement[15] of a chloride substituent from a haloazine or halothiaazine precursor, e.g.,



(7.1)

(where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$). For organic nucleophiles, such reactions are known to be generally very fast and it is therefore not surprising that for the very strong organometallic Fp^- nucleophile[3g,3h,16,17] these reactions have generally gone to completion upon warming of the reaction solution to ambient temperature. In the reactions leading to some of the new complexes, however, we noticed a considerable decrease in the overall rate of substitution (these reactions taking 2 to 7 days at ambient temperature to proceed to completion). For reactions leading to compounds **18**, **22** and **23** we attribute this decrease in rate to competing proton abstraction reactions,[18] *vide infra*, while for **6**, **10**, **18** and **22** to **25** one contribution to the decreased rate may be the very low solubilities of the precursor azines and thiazines in the reaction medium. The azines used in these studies followed the general trends in reactivity towards Fp^- established for such compounds with

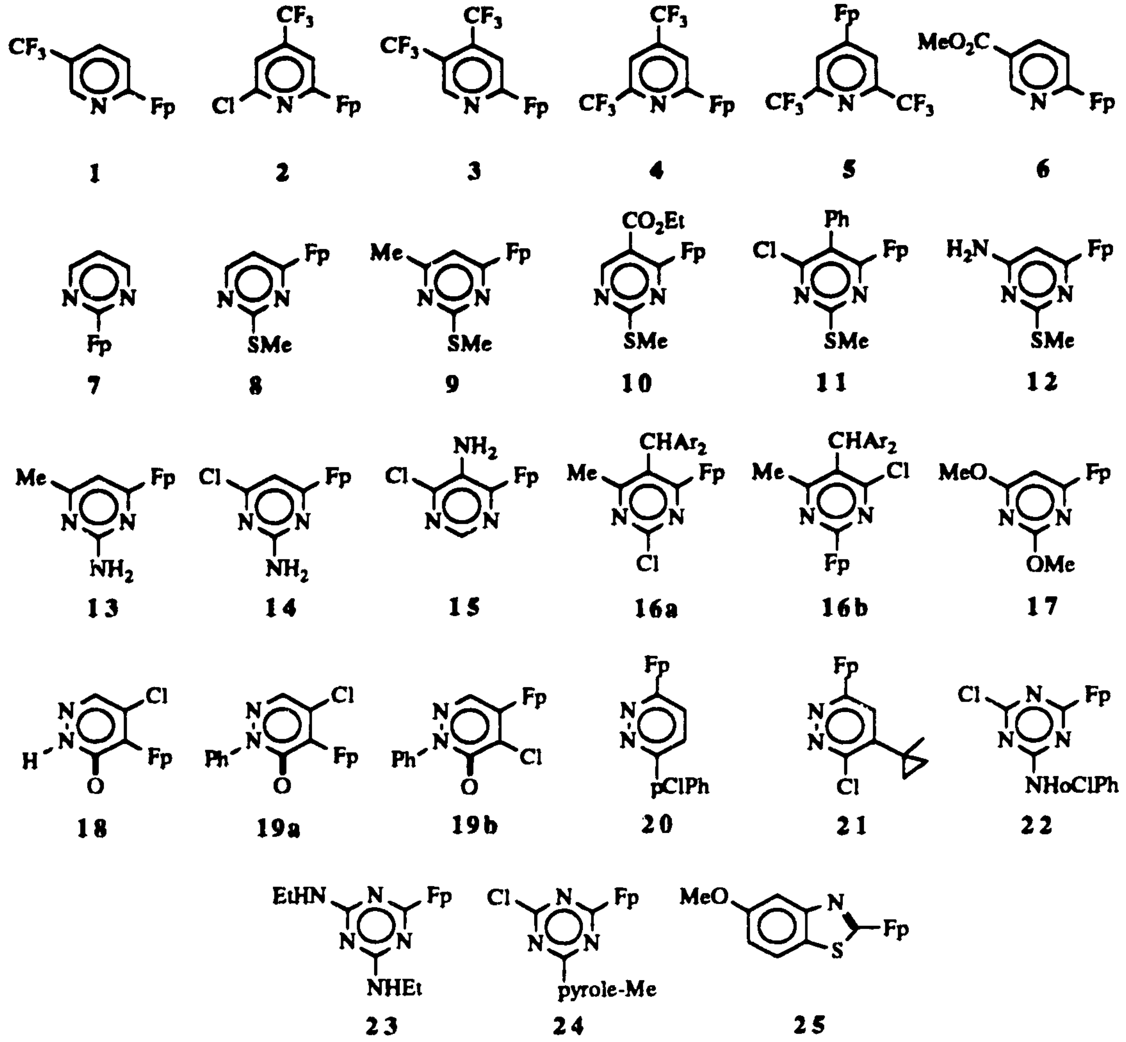
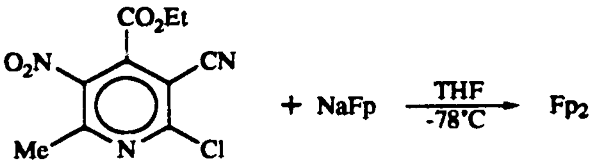


Figure 7.1. Structures of the new organometallic products (where Fp = (η^5-C_5H_5)-$Fe(CO)_2$, oClPh = 2-C_6H_4Cl, pClPh = 4-C_6H_4Cl, $CHAr_2$ = CHPh(2,4-$C_6H_3Cl_2$) and pyrole-Me = N-methylpyrolyl).

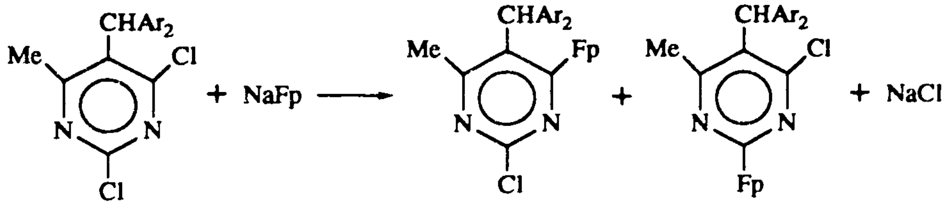
organic nucleophiles.[15] Hence, substitution was more facile for halopyrimidines than for halopyridines, and the greater the number of electron withdrawing groups the ring possesses, the more facile the substitution process is.[3g] Thus, the synthesis of the pyrimidine compounds (i.e., **7** to **17**) were generally more facile than they were for the pyridine complexes (i.e., **1** to **6**). Interestingly, the presence of main-group substituents on the ring that are strongly π-donating but σ-withdrawing (e.g., OMe, NH_2) does not appear to deactivate the precursor azines, whereas σ-donor groups like CH_3 do. However, if too many electron withdrawing groups are bonded to the azine, e.g.,



(7.2)

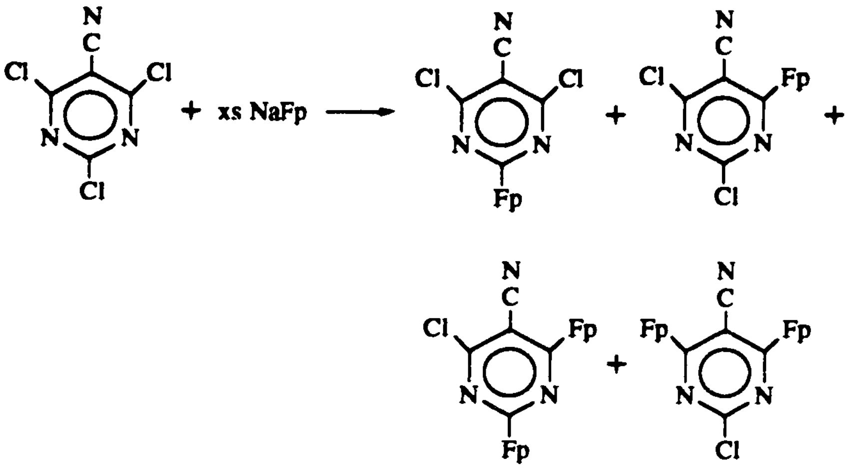
then electron transfer, to give Fp_2 as the exclusive organometallic product,[3b,3c,3e,3g,3h] rather than the desired substitution reaction becomes the dominant reaction pathway.

We have previously reported[3g] the marked regiospecificity of the reactions between the strong Fp^- nucleophile[16] and simple pyridines and pyrimidines. In the current studies, we have observed that the presence of sterically bulky groups or strong electron withdrawing groups at the 5-position of pyrimidines could alter the preferred sites of attack. Thus, the presence of a sterically bulky diarylmethyl group in **16'** leads to *formal* nucleophilic attack at both the 2- and 4-positions, yielding a 1:2 mixture of isomers in product **16**, i.e.,



(7.3)

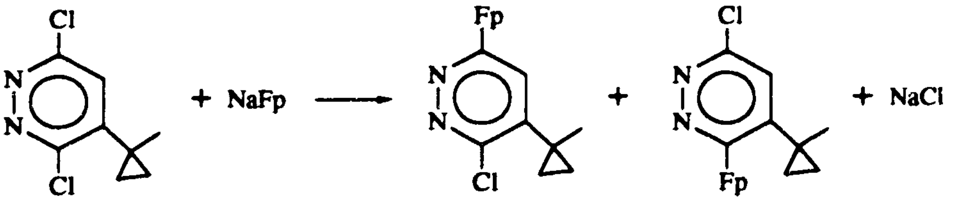
(where $CHAr_2$ = $CHPh(2,4\text{-}C_6H_3Cl_2)$) rather than the completely regioselective attack at the 4 position observed for related polychloropyrimidines lacking this bulky substituent in the 5 position.[3g] Presumably, this occurs because steric congestion around the 4 position from the very bulky $CHAr_2$ group makes substitution at the 2 position *relatively* favorable. Likewise, the reaction between one molar equivalent of NaFp with one equivalent of 2,4,6-trichloro-5-pyrimidine carbonitrile, **27'**, led to the formation of several new organometallic products, i.e.,



(7.4)

In this case, the more facile substitution is probably due to the additional electron withdrawal from the azine ring by the nitrile group. Unfortunately, the separation and characterization of this mixture of isomeric products was not successful and we are therefore unable, at this time, to unambiguously establish their isomer ratios or exact identities. In reaction 7.1, *formal* nucleophilic attack at the 2 position does occur if the molecule lacks alternative sites for nucleophilic reactions but that the reaction then takes days at ambient temperature, rather than the minutes at -78°C required for reactions leading to substitution at the 4 position (e.g., in the substitution reaction for 2,4-dichloropyrimidines),[3g] to go to completion. Thus, these substitution reactions using NaFp are both more selective than those of organic nucleophiles such as OR^-, NR_2^- and SR^- and the preferred site of attack is different (e.g., under some conditions the organic nucleophiles react preferentially at the 2 position). This is surprising because Fp is the stronger nucleophile (and therefore would be expected to show lower selectivity) and combined with the observation that the relative yield of Fp_2 increases as the oxidizing ability of the azine increases suggest that these *formal* nucleophilic substitution reactions involving Fp^- may actually be proceeding via single electron transfer followed by radical coupling.

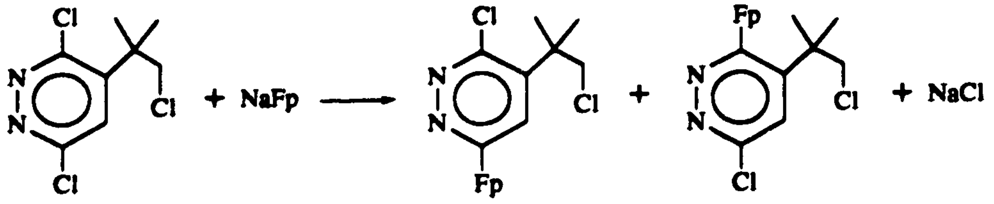
The reactions leading to the formation of the pyridazine complexes are less regiospecific, likely because there is little electronic difference between the 3 and 6 positions. Apart from compound **20**, for which only one isomeric product is possible, all of the other pyridazine complexes were formed as mixtures of isomers with the preferred position of attack apparently being under steric control. For example, the presence of the 1'-methyl-cyclopropyl group in the 4-position, which tends to enhance attack *ortho* to itself,[15] did not prevent the near exclusive synthesis of the 3,5,6 isomer (i.e., **21**) over the 3, 4, 6 isomer, i.e.,



21

(7.5)

Indeed, only a trace amount of a second organometallic product, which might be due to substitution ortho to the 1'-methyl-cyclopropyl group, was observed. The analogous reaction using a related reagent having the even more bulky $C(CH_3)_2(CH_2Cl)$ group in the 4-position resulted in the formation of a product which seems to contain a mixture of two isomers in a 4:1 ratio, i.e.,[19]

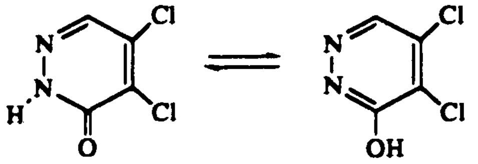


(7.6)

26a **26b**

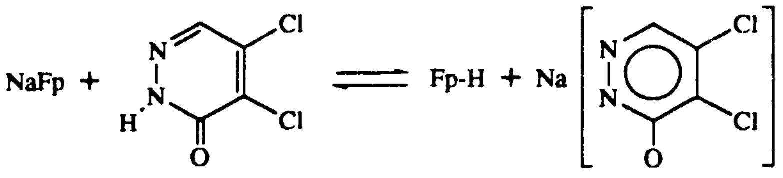
Interestingly, no spectroscopic evidence was observed for the alkyl substitution product which might have been expected from this reaction.

For pyridazinone reagents, the presence of the carbonyl group further activates the C-Cl bonds of the pyridazinone rings,[20] with the substitution at the ortho-carbon atom being favored. This process is aided by the possibility of enol formation, i.e.,[20]



(7.7)

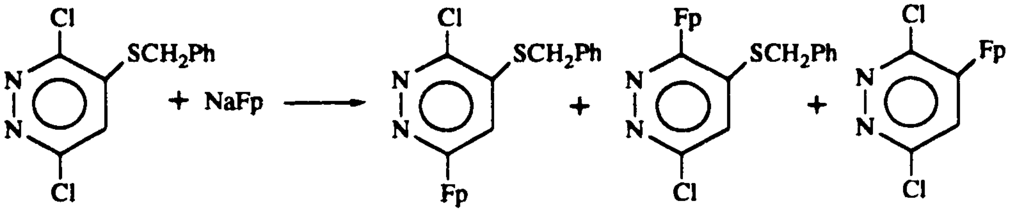
and the substitution reaction would therefore be expected to be less favorable for the 2-phenyl pyridazinone derivative which can not undergo this enolization process. Thus, less regiospecificity is expected in the formation of compounds **19a** and **19b** than for **18**. This is entirely consistent with our observations, in which product **19** is obtained as a 5:1 mixture of isomers while product **18** contains only one isomer. The organometallic nucleophile also appears to be a sufficiently strong base to deprotonate pyridazinones, e.g.,[20]



(7.8)

since Fp-H appears to be present in these solutions (ν_{CO}, = 1952, 2012 cm^{-1} in THF)[21] leading to a competition between the abstraction and substitution reactions. Thus, the reaction to prepare complex **18** takes about 5 days to go to completion while the same process takes only a few hours (with minimal formation of Fp$_2$ dimer) for reagent **19'**. The competition between the acid/base and nucleophilic substitution processes can be eliminated in reactions involving main-group nucleophiles by addition of Na$_2$CO$_3$ to the reaction mixture.[20] Unfortunately, the addition of Na$_2$CO$_3$ had no similar beneficial effect on our organometallic systems (e.g., reaction 7.8).

In the reaction between the Fp$^-$ anion and 4-benzylmercapto-3,6-dichloropyridazine, **28'**, the expected products from nucleophilic attack at the C4 and C6 position of the azine ring (i.e., **28a** and **28b**), represented only a minor portion of the yield. The major products result from the cleavage of the pyridazine-S-benzyl linkages at the pyridazine-S and the S-benzyl bond giving complexes **28c** and **28d**, respectively, in similar yields, e.g.,[23]



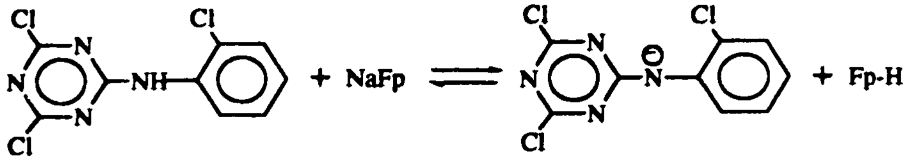
28a **28b** **28c**

+ Fp-CH$_2$Ph (7.9)

28d

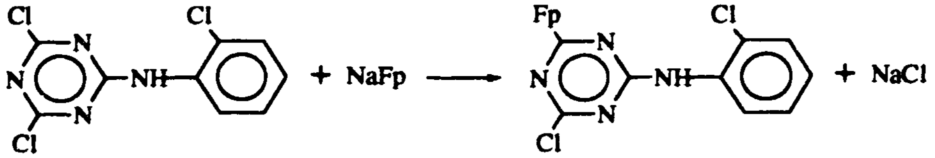
Interestingly, such a cleavage in the methyl-S linkages was not observed for reagents **8'** to **12'** or for the other methylmercapto substituted derivatives studied previously.[3g,3h] However, in the reaction of NaFp leading to **24**, FpMe was identified as one of the products, presumably being formed in a related N-Me cleavage reaction.

On the basis of the observed activation of the ring towards nucleophilic attack on substitution of a CH group in pyridines with an N group in pyrimidines, one would predict that the reactions leading to s-triazine compounds **22-24** would be very facile.[17] Unfortunately, competing reactions (i.e., proton abstraction from the NHR substituents for **22'** and **23'** and methyl abstraction for **24'**) are also observed in these syntheses, e.g.,



(7.10)

$$2\ FpH \longrightarrow Fp_2 + H_2 \qquad (7.11)$$

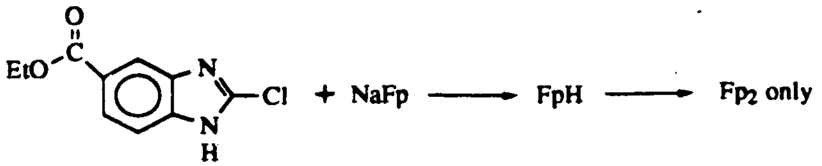


(7.12)

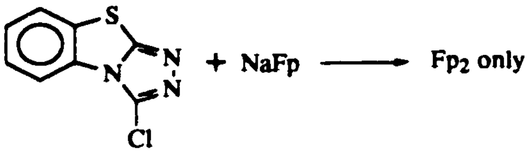
Moreover, **22'** and **23'** have low solubilities in THF and these reactions are very slow, taking between 4 to 5 days to go to completion and are accompanied by the formation of large amounts of the ubiquitous Fp_2 dimer. As in reaction 7.8, addition of Na_2CO_3 had no apparent effect on the rate or outcomes of these reactions.

A halide substituted at the 2-position of a thiazole ring has been shown to be susceptible to nucleophilic displacement. This process is expected to be enhanced by fusing a benzene ring to the thiazole ring,[24] and indeed, the 2-chlorobenzothiazole has been shown to be 100 times more susceptible than is 2-chloroquinoline towards nucleophilic attack.[25] On the other hand, the imidazoles are known to be relatively unreactive, requiring very forcing conditions and the presence of powerful electron withdrawing groups such as NO_2 to go to completion.[25] Our observations with the Fp[25] nucleophile, i.e.,

(7.13)



(7.14)



(7.15)

are consistent with these expectations which, for organic nucleophiles, have been attributed to the ability of the sulfur to use its d-orbitals in bonding and thus to provide additional stabilization to the intermediate formed during nucleophilic substitution.[25]

Characterization of the Complexes

All of these air and water stable yellow to tan colored heteroaromatic complexes (Figure 7.1) are soluble in polar organic solvents such as CH_2Cl_2 and most are also slightly soluble in water. Complexes **12** to **14**, which have NH_2 substituents capable of strong hydrogen bonding interactions, are particularly water soluble. All of the new complexes were characterized by conventional analytical, mass spectral, infrared, and ^{13}C- and ^{1}H- (and ^{19}F- where applicable) NMR methods, and these data are summarized in Tables 7.1 and 7.2. The infrared spectra in the carbonyl region of all these complexes show the expected symmetric and antisymmetric stretches[26] at $2025 < \nu_{CO}$ (CH_2Cl_2) < 2038 cm^{-1} and $1968 < \nu_{CO}$ (CH_2Cl_2) < 1988 cm^{-1}, respectively. The ^{1}H- and ^{13}C-NMR signals due to the cyclopentadienyl rings (i.e., $\delta \approx 5.3$ ppm for ^{1}H and ≈ 87 ppm for ^{13}C) and the carbonyl ligands (i.e., $\delta \approx 215$ ppm for ^{13}C) are in the expected regions[3,9c] indicating that the Fp substituents in these complexes retain their three-legged piano stool structures.[27] For the complexes shown in Figure 7.1, the isomeric identities could generally be unambiguously assigned using their ^{13}C-NMR spectra, which were compared to those for the heterocyclic starting materials and related organometallic complexes and by consideration of the characteristic effects of the Fp and organic substituents on the azine ring chemical shifts.[3,28-30] The ^{19}F-NMR spectra of complexes 1 to 5 (Table 7.2) also display the expected multiplicities. For representative examples (**2**, **4**, **5**, **7**, and **21**), these structural assignments have been confirmed by crystallographic analyses.

X-Ray Crystal Structures of Complexes 2, 4, 5, 7, and 21

To confirm the structures assigned to these complexes on the basis of spectroscopic data, to provide information on the effect of azine structure on Fp-azine conformations, and to provide structural information for the molecular modeling of the interactions between the potentially biologically active species and protein molecules, we have determined the X-ray crystal structures of five representative complexes. These structure determinations proceeded routinely in each case (Table 7.3) and confirmed that the substitution geometries around the azine ring proposed on the basis of the spectroscopic data (Figures 7.2 to 7.7). Most revealingly, the structure of complex **21** indicated that the Fp substituent was σ-bonded to the less sterically crowded position on the pyridazine ring *meta*-substituted to the methylcyclopropyl group. Each of the Fp substituents have similar three-legged piano stool structures with normal Fe-(η^5-C_5H_5), Fe-CO, and FeC-O linkages (Table 7.5).[1,3a,3c,3g,3h,31,32] The Fe-azine distances in these complexes (i.e., $d_{Fe\text{-}C}$ = 1.977 (6), 1.960 (6), 1.982 (5), 1.978 (6), 1.964 (4), and 1.982 (4) Å) are also similar to those reported earlier for related complexes having *formal* Fe-C(sp^2) single bonds (1.94 to 2.03 Å).[1,3a,3c,3g,3h,31-33] The structures of the azine rings in each of the complexes was not substantially distorted by Fp substitution but the steric environments around the rings were substantially altered. In particular, it is clear that the Fp groups are much more bulky

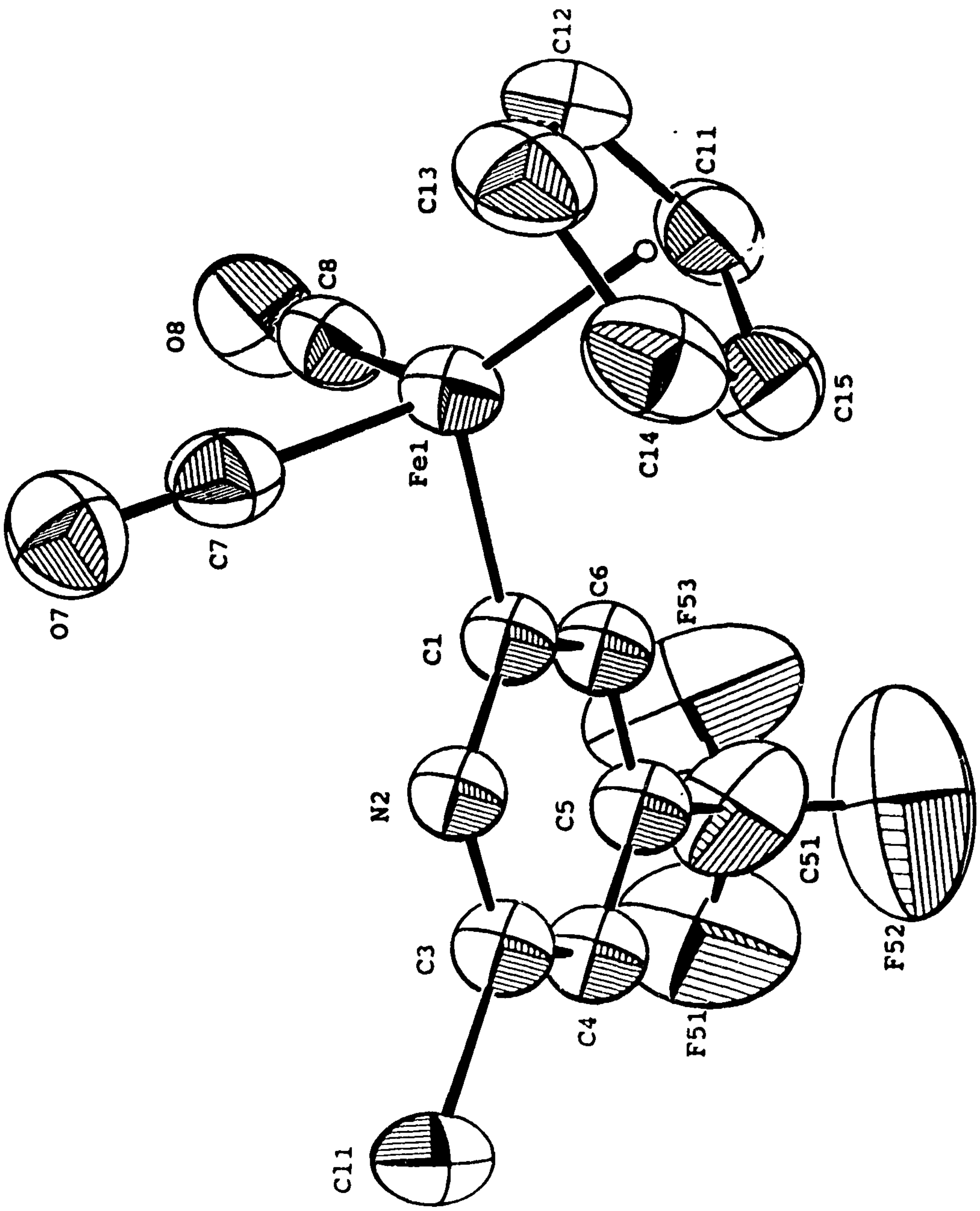


Figure 7.2. ORTEP Plot of one of the independent molecules in the unit cell of complex 2, perspective view.

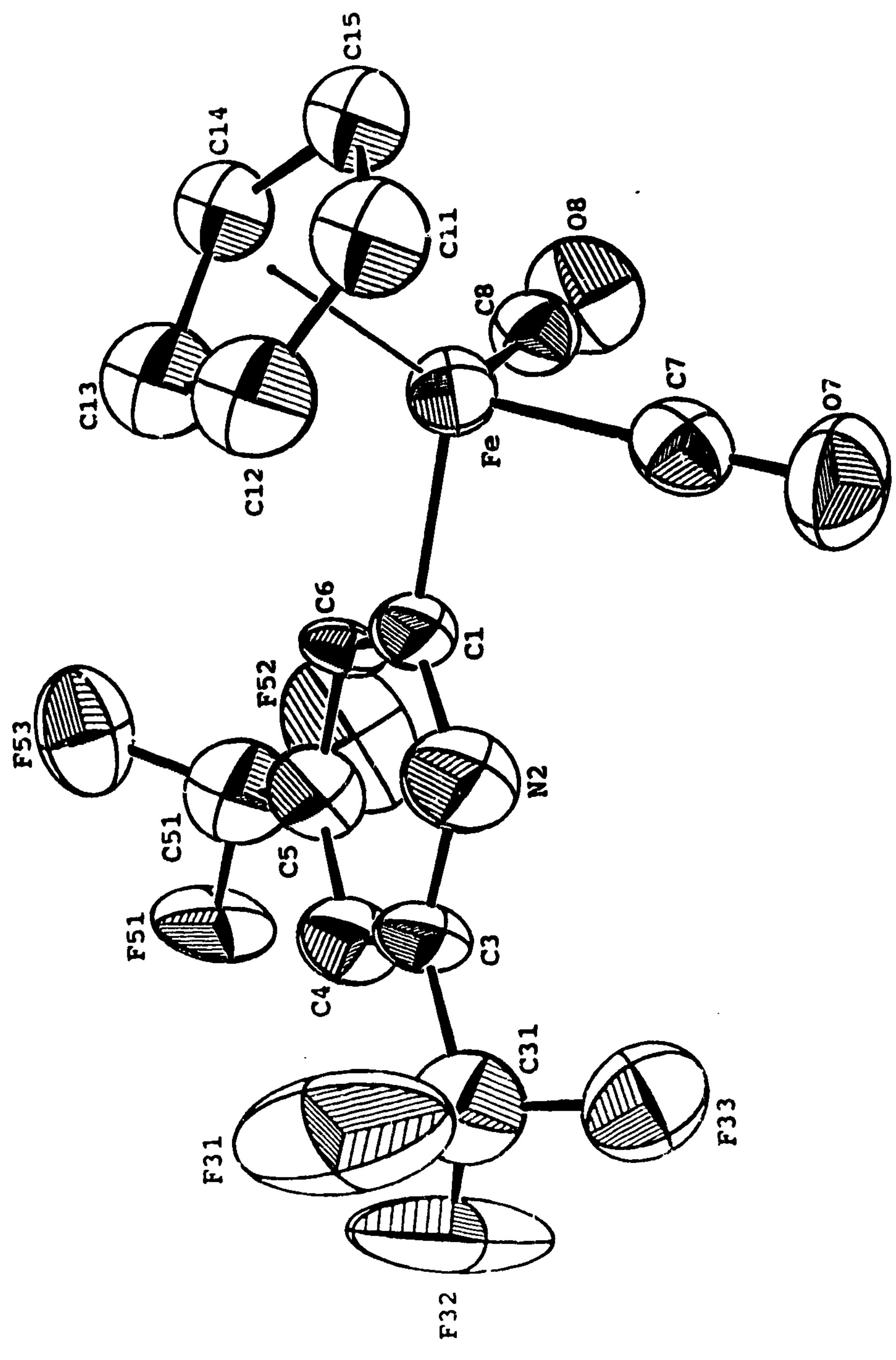


Figure 7.3. ORTEP Plot of complex 4, perspective view.

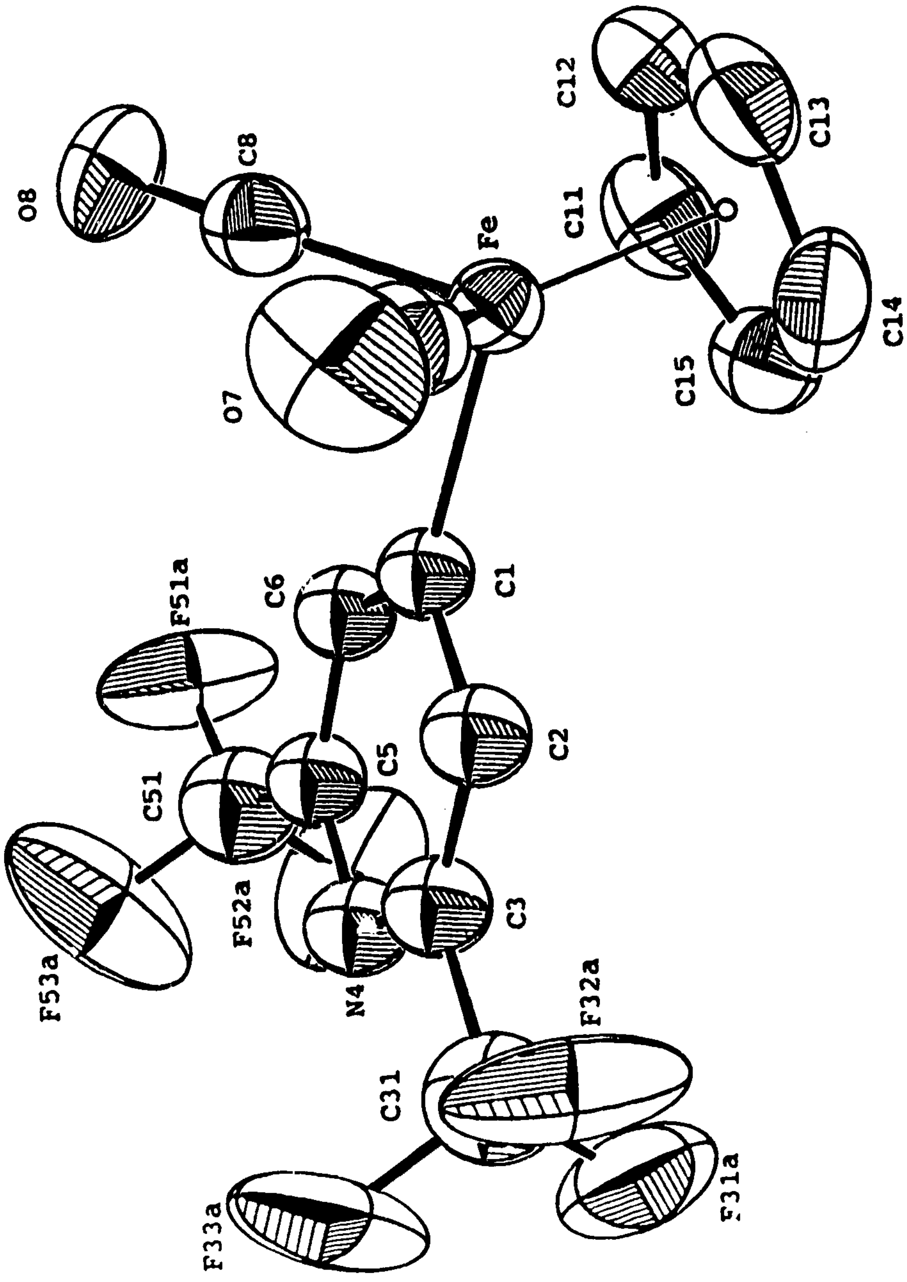


Figure 7.4. ORTEP Plot of complex 5, perspective view.

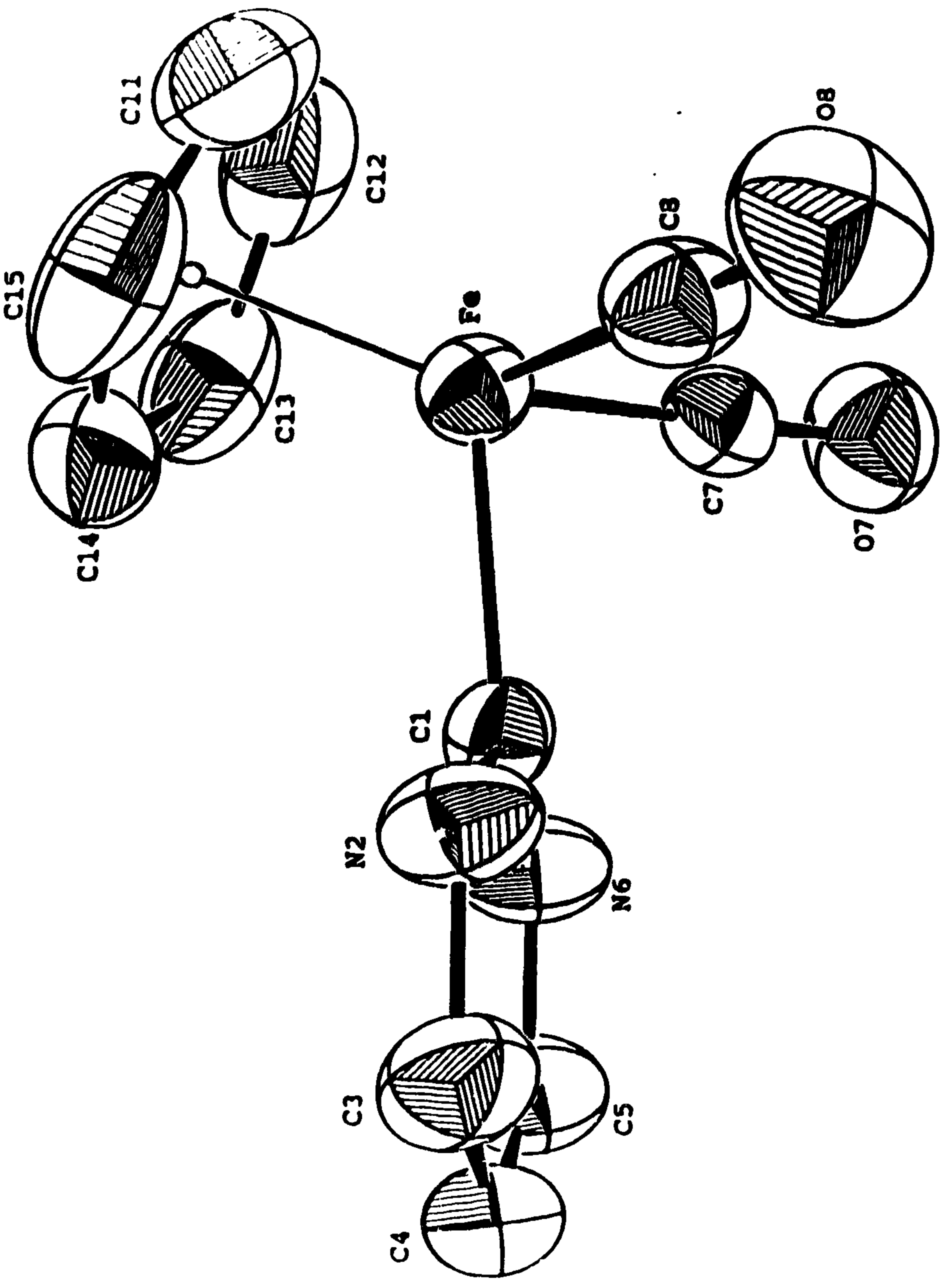


Figure 7.5. ORTEP Plot of complex 7, perspective view.

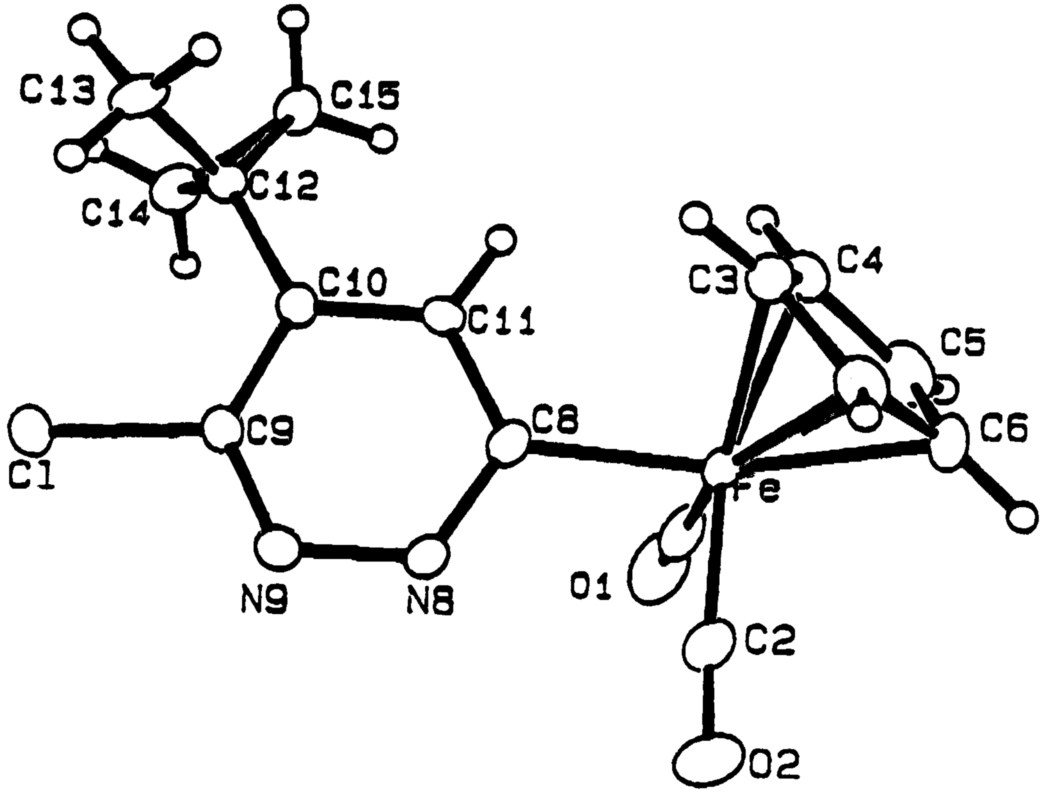


Figure 7.6. ORTEP Plot of complex 21, perspective view.

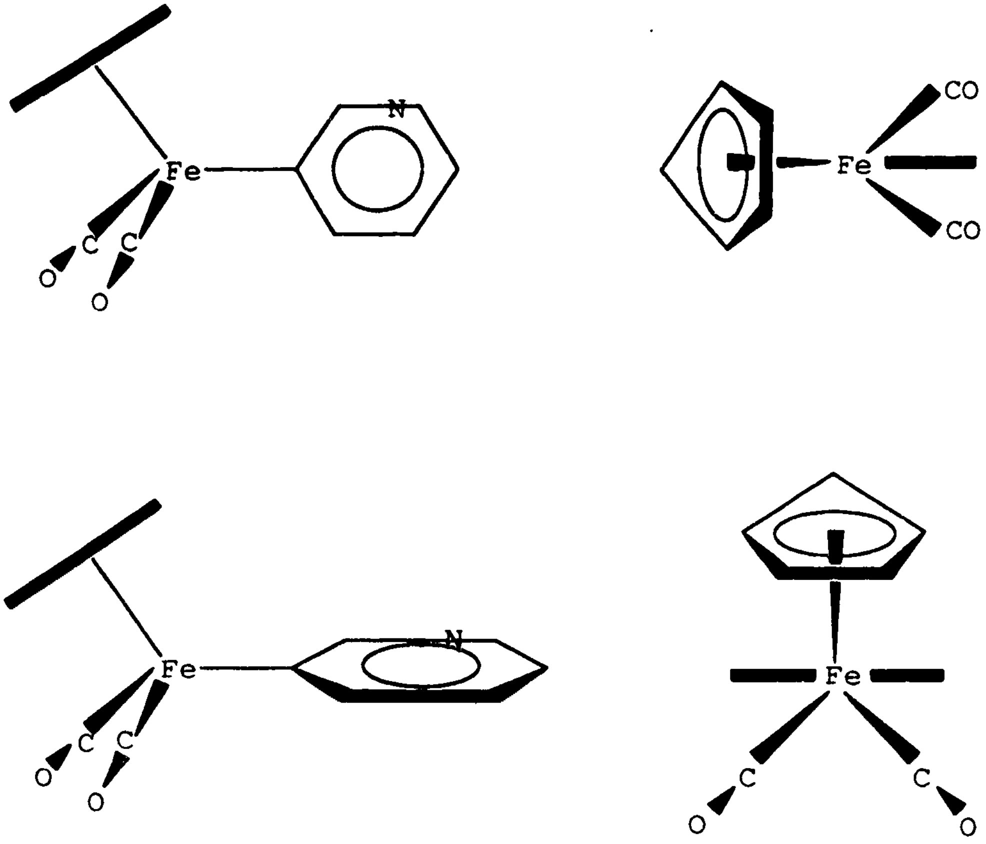


Figure 7.7. Relative orientations of the Fp-azine groups: (7a, top) ϕ = 0° for the conformations predicted to optimize the electronic interactions of π-symmetry and (7b, bottom) ϕ = 90° for the conformations predicted to minimize adverse steric interactions.

Table 7.5. Selected Bond Lengths (Å) and Angles (°)[a]

Complex 2

Fe1-Ce	1.7229 (7)	Fe1-C7	1.759 (5)	C7-O7	1.142 (6)
Fe2-Ce	1.7248 (7)	Fe2-C27	1.760 (5)	C27-O27	1.142 (6)
Fe1-C1	1.977 (6)	Fe1-C8	1.745 (6)	C8-O8	1.147 (8)
Fe2-C21	1.960 (6)	Fe2-C28	1.757 (6)	C28-O28	1.133 (8)
C1-N2	1.333 (7)	Cl1-C3	1.733 (6)	C51-C5	1.512 (7)
C21-N22	1.363 (7)	Cl2-C23	1.751 (8)	C251-C25	1.490 (7)
C4-C5	1.335 (9)	N2-C3	1.318 (8)	C3-C4	1.382 (6)
C24-C25	1.37 (1)	N22-C23	1.32 (1)	C23-C24	1.377 (8)
C5-C6	1.396 (9)	C1-C6	1.412 (6)		
C25-C26	1.366 (9)	C21-C26	1.384 (6)		
Fe1-C7-O7	178.6 (6)	Fe1-C8-O8	179.3 (5)	C7-Fe1-C8	92.1 (3)
Fe2-C27-O27	178.6 (6)	Fe2-C28-O28	178.0 (5)	C27-Fe2-C28	92.1 (2)
Fe1-C1-N2	119.2 (3)	Fe1-C1-C6	120.2 (4)	N2-C1-C6	120.6 (5)
Fe2-C21-N22	117.5 (3)	Fe2-C21-C26	123.2 (4)	N22-C21-C26	119.1 (5)

Complex 4

Fe-Ce	1.7591 (8)	Fe-C7	1.762 (6)	C7-O7	1.129 (7)
Fe-C1	1.982 (5)	Fe-C8	1.754 (6)	C8-O8	1.134 (8)
C1-N2	1.421 (7)	C31-C3	1.512 (9)	C51-C5	1.55 (1)
C4-C5	1.368 (8)	N2-C3	1.394 (8)	C3-C4	1.373 (8)
C5-C6	1.319 (7)	C1-C6	1.319 (7)		
Fe-C7-O7	179.7 (9)	Fe-C8-O8	178.6 (5)	C7-Fe-C8	93.2 (3)
Fe-C1-N2	119.2 (4)	Fe-C1-C6	120.5 (4)	N2-C1-C6	120.3 (5)

Complex **5**

Fe-Ce	1.7248 (8)	Fe-C7	1.742 (5)	C7-O7	1.150 (7)
Fe-C1	1.978 (6)	Fe-C8	1.765 (7)	C8-O8	1.128 (8)
C1-C2	1.389 (8)	C31-C3	1.54 (1)	C51-C5	1.53 (1)
N4-C5	1.323 (8)	C2-C3	1.376 (9)	C3-N4	1.314 (8)
C5-C6	1.37 (1)	C1-C6	1.384 (8)		

Fe-C7-O7	179.1 (6)	Fe-C8-O8	179.3 (6)	C7-Fe-C8	94.1 (3)
Fe-C1-C2	122.5 (4)	Fe-C1-C6	123.4 (4)	C2-C1-C6	114.0 (6)

Complex **7**

Fe-Ce	1.7268 (5)	Fe-C7	1.732 (4)	C7-O7	1.154 (5)
Fe-C1	1.964 (4)	Fe-C8	1.736 (4)	C8-O8	1.150 (5)
C3-C4	1.349 (6)	C1-N2	1.346 (5)	N2-C3	1.343 (5)
C1-N6	1.333 (5)	C4-C5	1.366 (6)	C5-N6	1.339 (5)

Fe-C7-O7	179.6 (4)	Fe-C8-O8	178.1 (4)	C7-Fe-C8	93.1 (2)
Fe-C1-N2	117.5 (3)	Fe-C1-N6	118.8 (3)	N2-C1-N6	123.6 (3)

Complex 21

Fe-Ce	1.6999	Fe-C1	1.800 (7)	C1-O1	1.125 (7)
Fe-C8	1.982 (4)	Fe-C2	1.786 (6)	C2-O2	1.138 (6)
N9-C9	1.300 (7)	C8-N8	1.329 (6)	N8-N9	1.365 (5)
C8-C11	1.423 (7)	C9-C10	1.413 (7)	C10-C11	1.370 (6)
C10-C12	1.495 (6)				
Fe-C1-O1	179.2 (6)	Fe-C2-O2	175.3 (6)	C1-Fe-C2	92.5 (3)
Fe-C8-N8	117.4 (4)	Fe-C8-C11	123.0 (4)	N8-C8-C11	119.5 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit. Fe-Ce is the distance from Fe to the centroid of the cyclopentadienyl ligand.

conventional organic substituents (e.g., R, Cl, OR, NR_2) and that steric constraints are therefore likely to play a greater role in determining their binding coefficients to proteins. Since Fp and NR_2 groups have similar net electronic influences on azine rings, *vide supra*,[3] the primary affect of substituting a Fp group for groups such as NR_2 is likely to be steric.[34] Indeed, the preliminary results of biological screening tests on these molecules indicate that some Fp-azine derivatives do exhibit significant and interesting biological activities as fungicides, herbicides, and/or as insecticides.[35]

An additional chemically interesting feature of the X-ray crystal structures are the Fe-azine conformations (Figures 7.2 to 7.6). As we have found for related arene and azine complexes,[1,3a,3c,3g,3h,24] the orientations observed in the solid state are the opposite of those predicted on the basis of molecular orbital arguments.[36] Thus, the twist angle, ϕ (Figure 7.7), between the pseudo mirror planes of the Fp group and the plane of each azine ring is essentially 90° for the more symmetrically substituted azine complexes, **4**, **5**, and **7** (88°, 88°, and 90°, respectively), as they are for the related symmetric species (i.e., Fp-C_6F_5, 1,4-$C_6F_4Fp_2$, and 4-C_5F_4NFp).[3h] For the less symmetrically substituted azine complexes, **2**, and **21**, these twist angles are somewhat larger (102° and 145°) as they are for the unsymmetrically substituted pyrimidine complex 4,6-Fp_2-2-SMe-pyrimidine.[3g] Thus, we believe that the origin of this twisting is steric which is in accord with the results of elementary molecular modeling studies, for which a minimum in adverse steric interactions between the aromatic rings and the cyclopentadienyl rings is observed at twist angle of *ca.* 90°.[38]

In conclusions, the reactions between NaFp and the 32 representative substituted heteroaromatic complexes described in this work were generally successful at producing new heterocyclic complexes and these syntheses are quite regioselective for a wide variety of azine rings, substitution geometries and substituents and that this synthetic method is viable for all but the most sterically demanding and electron poor azines. It was shown that these metathesis reactions can often be carried out in spite of the presence of substituents on the ring having acidic protons which might have been expected to interfere. However, in some cases the Fp$^-$ nucleophile reacts with other substituents on the ring (e.g., N-Me and S-CH_2Ph) rather than with the chloride substituents on the aromatic ring. The structures of many of these Fp derivatives of heterocyclic molecules are similar to various biological molecules and to known biologically active materials in the fields of pharmaceutical and agricultural chemicals. Their chemical and structural properties suggest to us that the Fp substituents can, in terms of biological activities, be considered as very sterically bulky electron donor groups. Indeed, preliminary results on the herbicidal, fungicidal and insecticidal properties of some of these molecules are encouraging and we are continuing our studies of these materials to determine how Fp substituents modify such biological activities. Finally, in the future, we hope to employ the organometallic azines and thiaazines as novel ligands (i.e., the presence of multiple Lewis base sites on the azine rings and relatively labile carbonyl ligands on the iron centers are likely to give them interesting coordination behaviors) and as reagents in new iron mediated heterocycle syntheses.

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33. For Fp-carbene complexes having *formal* Fe=C double bonds, the bond distances range from 1.91 to 2.00 Å see, for example: (a) E. J. O'Connor and P. Helquist, *J. Am. Chem. Soc.*, **104**, 1869 (1982). (b) H. Adams, N. A. Bailey, M. Grayson, C. Ridgway, A. J. Smith, P. Taylor, M. J. Winter and C. E. Housecroft, *Organometallics*, **9**, 2621 (1990), and references cited therein.

34. The absence of strong hydrogen bonding by the Fp substituents may also influence their binding.

35. These biological screening tests are being carried out at DowElanco and the complete results, and their chemical interpretation, will be published in a separate manuscript.

36. Molecular orbital calculations on related molecules[37] predict that the Fe to azine donor π-symmetry interactions will be maximized when $\phi = 0^\circ$ (i.e., the pseudo mirror plane of Fp and the plane of the azine are coplanar).

37. For further discussion of this effect or calculations on related systems, see references 4 and 7 and, for example: (a) B. E. R. Schilling, R. Hoffmann and J. W. Faller, *J. Am. Chem. Soc.*, **101**, 592 (1979). (b) J. I. Seeman and S. G. Davies, *J. Am.*

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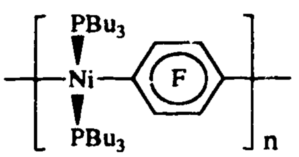
38. These calculations were carried out using the program Chem 3D$^+$ from Cambridge Scientific Computing, using the crystallographically derived internal coordinates.

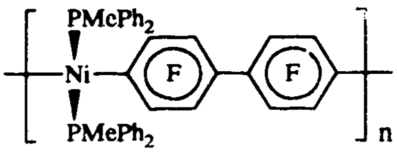
CHAPTER 8

GENERAL DISCUSSIONS

Previous studies in the Hunter group have focused on organometallic polymers having typically a rigid-rod backbone of arene-bridged $Ni(PR_3)_2$, e.g., **I** and **II**,

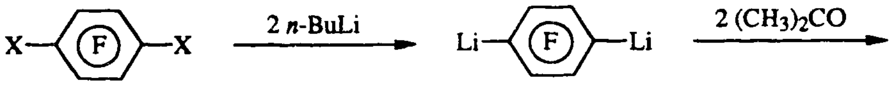


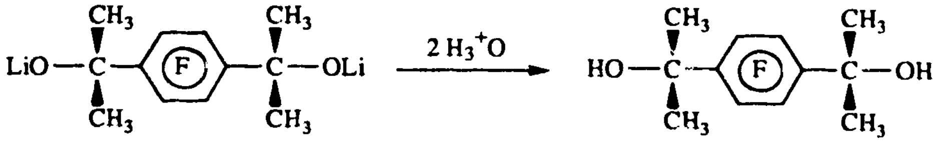
I



II

I started the model studies on modified organonickel electroactive polymers with the investigation of α,α,α',α'-tetramethyl-1,4-tetrafluorobenzenedimethanol (**III**), a bifunctional monomer which can polymerize into a series of condensation polymers.[1] This monomer was synthesized in high yield through the addition of acetone to 1,4-dilithiotetrafluorobenzene (**IV**) which was derived from 1,4-dibromotetrafluorobenzene or 1,2,4,5-tetrafluorobenzene, as is outlined in Scheme 8.1:

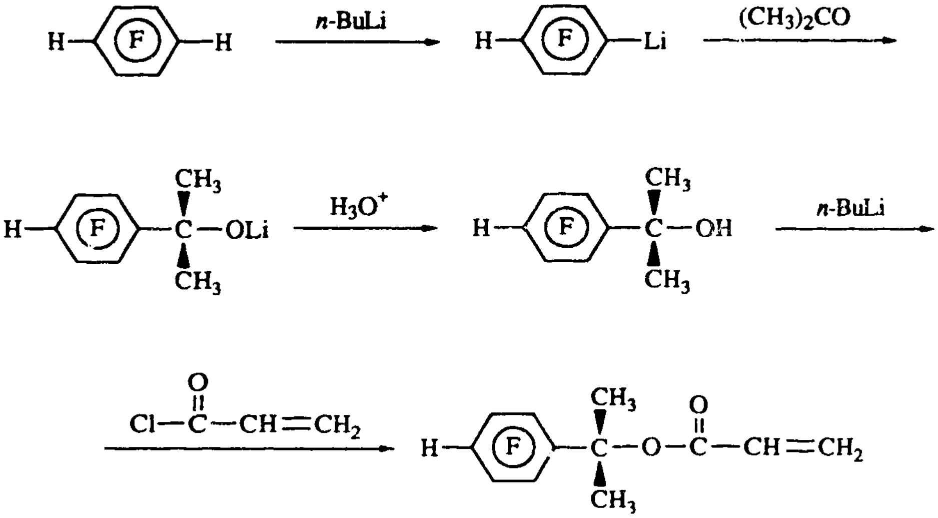




IV III

Scheme 8.1.

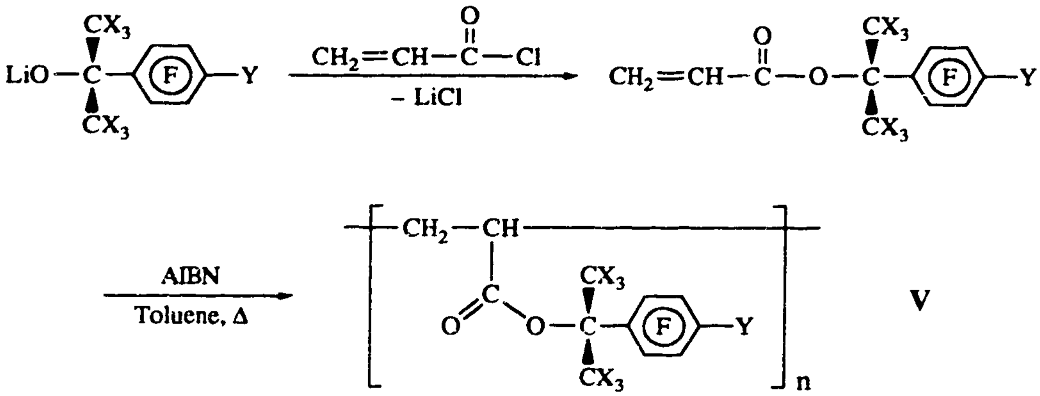
where X = Br or H. It can readily be purified from monolithio byproducts by washing it with hexanes. This implied that monolithio products, if such were desired, could also be easily separated from the dilithio product. This indication became a very useful strategy in the subsequent syntheses of some monofunctional acrylate monomers[2] derived from the monolithiation of 1,2,4,5-tetrafluorobenzene where bifunctional products tend to cause complications and thus have to be removed (Scheme 8.2). In the synthesis of these related



Scheme 8.2.

acrylate monomers, it was also discovered that solvents play an important role in the formation of the fluoroaryllithio products.[1-5] For the preparation of the monolithio product, a less-polar solvent such as Et_2O is desirable, while for the preparation of the dilithio product, a polar solvent such as THF is preferred. This strategy was further extended to the subsequent preparations of organosilicon compounds and organonickel-organosilicon polymers.[4,5]

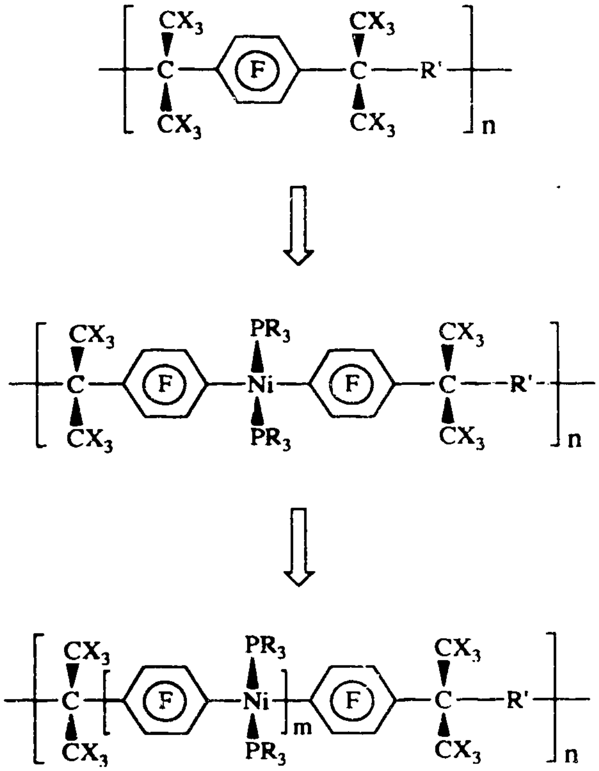
The discovery that the dilithium salt (IV) of diol III was totally soluble in THF and reacted very rapidly with organic diacid chlorides to form the desired condensation polymers[1] was very important in that it not only secured the successful preparation of the corresponding polyesters and polycarbonate, but it has also made it possible to extend the methodology to the syntheses of the monomers of the polyacrylates, e.g.,[2]



Scheme 8.3.

where X, Y = H or F.

The conventional condensation polymers (VI) of diol III are models of organometallic polymers having monomeric organonickel units (VII) such as $-1,4\text{-}C_6F_4-Ni(PR_3)_2-1,4\text{-}C_6F_4-$. These, in turn, are models for modified organometallic backbone polymers (VIII) having flexible linking groups and longer rigid-rod organometallic segments $-[-1,4\text{-}C_6F_4-Ni(PR_3)_2-]_m-1,4\text{-}C_6F_4-$, i.e.,



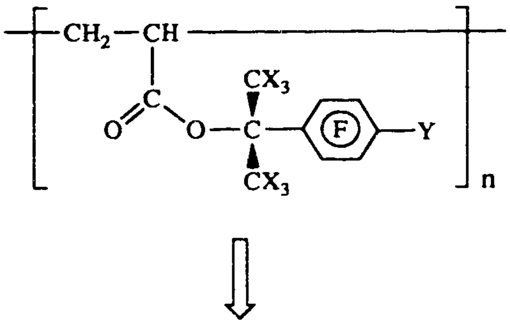
VI

VII

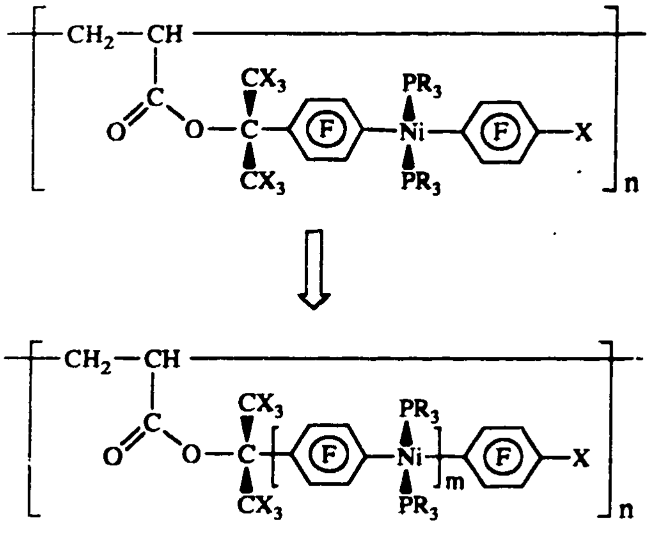
VIII

Scheme 8.4.

where m = 1 - 10, X = H or F, R = alkyl or aryl, R' = –OC(O)–R–C(O)O–, –OC(O)O–, –OC(O)NH–R–NHC(O)O–, etc. Likewise, our study on fluorinated polyacrylates (i.e., V) is leading towards rigid organometallic side-chain polymers with a flexible organic polymer backbone (**IX** and **X**), i.e.,



V



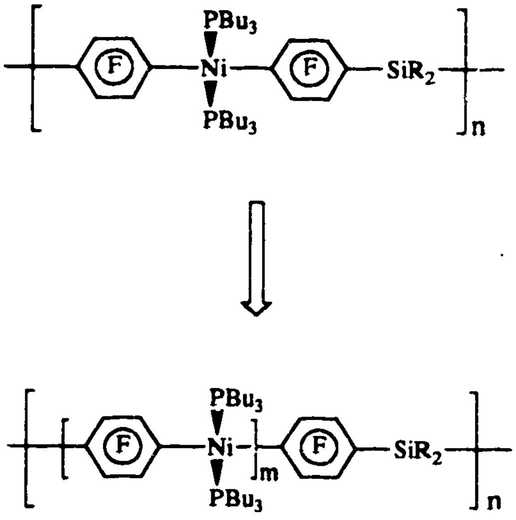
IX

X

Scheme 8.5.

where m = 1 - 10, X = H or F, R = alkyl or aryl. It should be appreciable that **VI** (**V**), **VII** (**IX**) and **VIII** (**X**) are homologous in nature (i.e., with different m value). Our work on these organic polymers has enabled us to successfully identify the optimal conditions required for the synthesis of the target organometallic polymers.

I have also started model studies on organosilicon-modified organometallic polymers that are conceptually related to **VII** and **VIII**. Nine organosilicon model compounds were prepared and these syntheses indicated that the analogous organonickel-organosilicon polymers should be readily preparable through the same types of condensation reactions involving dilithioarenes and silicon dichlorides.[5] On the basis of these studies, the organonickel-organosilicon polymers (**XI**) were successfully prepared and observations indicate that introduction of silyl or siloxane units into organonickel main-chains has significantly decreased the backbone rigidity of the polymers.[4] It therefore seems very likely that organosilicon modification to the organometallic polymers should be useful especially to those polymers with longer rigid segments (**XII**):



XI

XII

Scheme 8.6.

where m = 1 - 10, SiR_2 = $-SiMe_2-$, $-SiMe(Hex)-$, $-SiPh_2-$, $-SiMe_2-O-SiMe_2-$, $-SiMe_2-(CH_2)_6-SiMe_2-$, etc.

We have established the rigid-rod characteristics for the organonickel polymers through GPC and viscometric measurements. This investigation is important not only for the characterization of our family of organonickel polymers but it should also be informative to the entire inorganic polymer community. It indicated that GPC characterization for all of these types of organometallic polymers is better carried out by using a universal calibration procedure rather than by comparing directly to polystyrene.

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