Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. 2. Synthesis of Poly((1,1'-ferrocenediyl)phenylphosphine) Oligomers and Polymers

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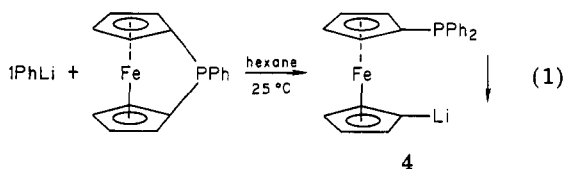
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Received May 3, 1982

The reaction of (1,1'-ferrocenediyl)phenylphosphine with 1 molar equiv of 1-lithio-1'-(diphenylphosphino)ferrocene in THF resulted in the formation of oligomers. After hydrolysis, species of type H $[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]Ph$ (x = 1–5) were obtained which could be separated by preparative-scale high-performance liquid chromatography. Under appropriate conditions (temperature, mode of addition, solvent) the reaction of 1,1'-dilithioferrocene–tetramethylethylenediamine with phenyldichlorophosphine gave low to high molecular weight polymers ($\bar{M}_w$ = 8900–161 000 amu). Both the oligomers and polymers were found to be thermally stable to 350 °C.

Introduction

In part 1 we reported the preparation of (1,1'-ferrocenediyl)phenylphosphine and -methylphosphine (1 and 2) and (1,1'-ferrocenediyl)phenylarsine, 3. Among the reactions of 1 and 3 which we studied were those with organolithium reagents which resulted in opening of the [1]ferrocenophane system, as shown in eq 1 for ferrocen-


ophane 1. Under strictly specified conditions, a good yield of the lithium species 4 could be obtained, and this then was available for further reactions with appropriate electrophiles.[1] However, 4 is an organolithium reagent which also should be capable of reaction with 1 in the sense of eq 1. The product formed in such a 4/1 reaction in turn is an organolithium reagent, so that eventually one might expect to obtain oligomers and possibly even polymers 5, when 4 is generated in the presence of equimolar or even greater amounts of 1. This paper describes the preparation and characterization of such oligomers and polymers.

Results and Discussion

Studies of the reaction of (1,1'-ferrocenediyl)phenylphosphine, 1, with organolithium reagents in ethereal solvents showed that if an equimolar amount or a deficiency of the organolithium reagent is used, the expected oligomerization does take place: many more products than (diphenylphosphino)ferrocene are seen when the reaction mixture, after hydrolytic workup, is examined by thin layer chromatography (TLC). Attempts to obtain a high polymer of type 5 by using catalytic amounts (<10 mol %) of phenyllithium to initiate a ring-opening polymerization of 1 were unsuccessful; only oligomeric material and unreacted 1 were isolated. Apparently, as the ferrocenyl-

lithium reagent 5 grows in length to several (ferrocenediyl)phenylphosphine units, it becomes much less reactive toward attack at 1, due either to steric effects or to insolubility.

An attempt was made to specifically prepare the (ferrocenediyl)phenylphosphine dimer 6 (x = 2) by the route shown in eq 2. Instead, this provided the best synthesis
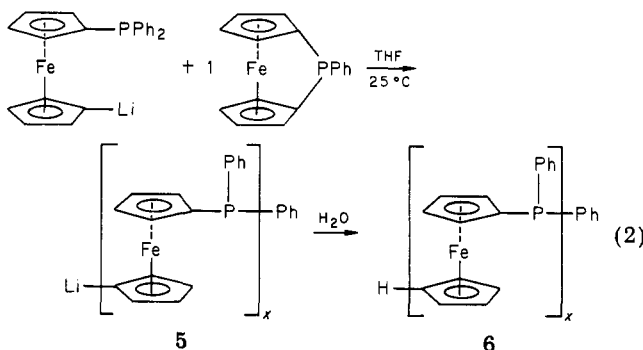
of a mixture of oligomers and a means of obtaining useful quantities of such products. The dimer (x = 2) and the trimer (x = 3) were the major components of the mixture of oligomers. Addition of tetramethylethylenediamine to the reaction mixture at the stage of eq 2 changed the distribution of oligomers only slightly to favor formation of the trimer. The oligomer yield dropped off rapidly after the tetramer, and the pentamer and hexamer were produced in only very small amounts.

High-performance liquid chromatography (HPLC) proved to be very useful in studying the distribution of oligomers and, ultimately, in separating the mixture of oligomers (see Figure 1). Normal-phase chromatography was used, with a mixture of dichloromethane and hexane found to be the best eluent. In this manner oligomers 6 (x = 1–5) were isolated as the pure species and characterized. The oligomers could not be induced to crystallize. They were isolated first as oils from dichloromethane, and these formed glassy solids after high vacuum treatment overnight. Thermal gravimetric analysis (TGA) of these solids showed a slight, broad weight loss from 100 to 200 °C. The volatile material which was evolved was identified

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(1) Seyferth, D.; Withers, H. P., Jr., preceding article in this issue.
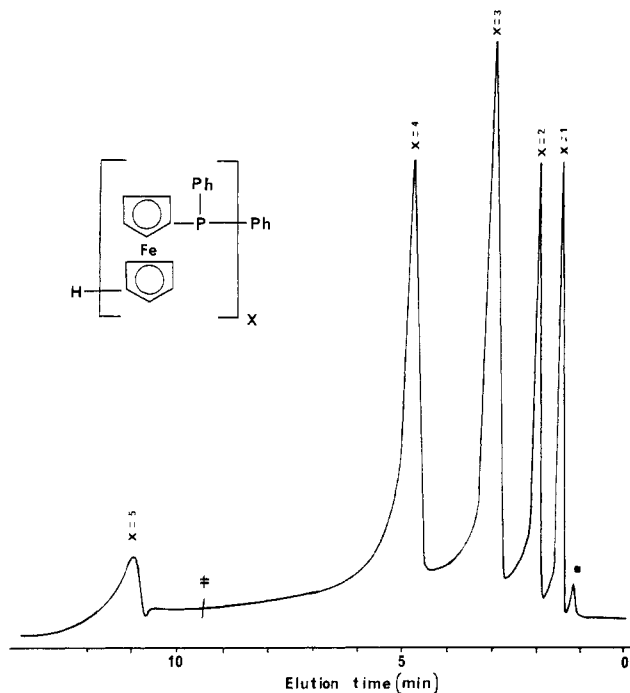
Figure 1. Elution of oligomers **6** (x = 1–5) on a μ-Porasil analytical liquid chromatography column with a 60/40 CH_2Cl_2/hexane eluent (t = 10 min, 99% CH_2Cl_2).

Table I. Characterizing Data for Oligomers 6 (x = 1-5)

| **6,** | | *m/e* | anal. calcd (found) | |
x =	mp, °C	(M⁺)	carbon	hydrogen
1	120–122		known compound[a]	
2	69–75	661	68.71 (68.90)	4.88 (5.39)
3	90–100	954	67.95 (68.27)	4.76 (5.15)
4	95–130	1247	67.44 (67.95)	4.70 (5.15)
5		1539		

[a] Kotz, J. C.; Nivert, C. L. *J. Organomet. Chem.* **1973**, *52*, 387, and ref 10.

as dichloromethane by temperature-programmed mass spectroscopy. The strong affinity for dichloromethane that these materials showed probably is responsible for their somewhat broad melting point ranges (Table I). The observation of parent ions by mass spectroscopy for each of the oligomers (**6**, x = 2–5) and the analytical data are consistent with our assignments of structure. The oligomers of type **6** are air-stable, yellow solids which are quite soluble in ethers, dichloromethane, and chloroform. Their solutions are not stable on exposure to air and begin to show evidence of decomposition after 1 or 2 days. For all oligomers (x = 2–4), no decomposition was observed below 350 °C by TGA.

Details of the ³¹P{¹H} NMR spectra of the (ferrocenediyl)phenylphosphine oligomers and of related ferrocene-derived tertiary phosphines are given in Table II. Compared to the triphenylphosphine ³¹P resonance, one observes an upfield shift upon substitution of a phenyl by a ferrocenyl group. Substituent electronegativity and bond angles are known to be the two major variables in the determination of ³¹P chemical shifts.[2] Since the only structural data which are available[3] show the P–C bond

Table II. 36.2-MHz ³¹P {¹H}NMR Data for Ferrocenylphosphines[a]

compd	δ P(terminal)	δ P(bridging)
oligomer **6**, x = 1	–17.0 (1)	
x = 2	–17.8 (1)	–31.8 (1)
x = 3	–17.6 (1)	–31.5 (1), –32.2 (1)
x = 4	–17.7 (1)	–31.5 (1), –32.2 (br, 2)
x = 5	–17.7 (1)	–31.5 (1), –32.2 (br, 3)
[(η^5-C_5H_5)Fe(η^5-C_5H_4)]$_2$PPh		–30 (1)
[(η^5-$Ph_2PC_5H_4$)-Fe(η^5-C_5H_4)]$_2$PPh	–17.9 (2)	–32.3 (1)
(η^5-$Ph_2PC_5H_4$)$_2$Fe	–17.9 (1)	

[a] Relative intensities in parentheses.
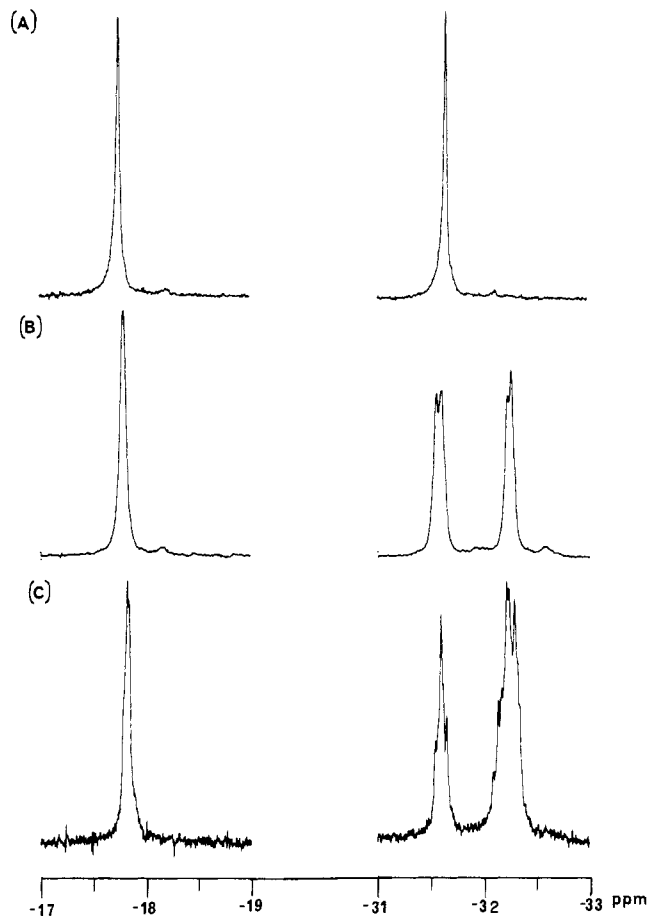
Figure 2. 145.8-MHz ³¹P{¹H} NMR spectra of oligomers **6** (x = 2–4): (A) dimer; (B) trimer; (C) tetramer.

lengths for the phenyl and ferrocenyl substituents to be nearly equal, one is led to predict that the phosphorus cone angle[4] will increase as substitution by ferrocenyl groups occurs. Thus, on the basis of steric considerations alone, a downfield shift would be predicted for ferrocenyl substitution.[2] Since quite the opposite is observed, it is clear that substituent electronegativity is the major contributor to the chemical shifts in this case. Nesmeyanov[5] has shown that ferrocenyl groups are strong electron donors, stronger than the methyl group, in fact. Substitution by the electron-donating ferrocenyl group should result in an increase in shielding and therefore, an upfield shift of the resonance when substituted for phenyl.[2] These observations are

(2) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. "³¹P Nuclear Magnetic Resonance"; Interscience: New York, 1967. Pregosin, P. S.; Kunz, R. W. "³¹P and ¹³C NMR of Transition Metal Complexes"; Springer-Verlag: Berlin, 1979.

(3) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91: P–C(1) = 1.836 (9) Å; P–C(1′) = 1.849 (10) Å; P–C(6) = 1.825 (9) Å.

(4) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.
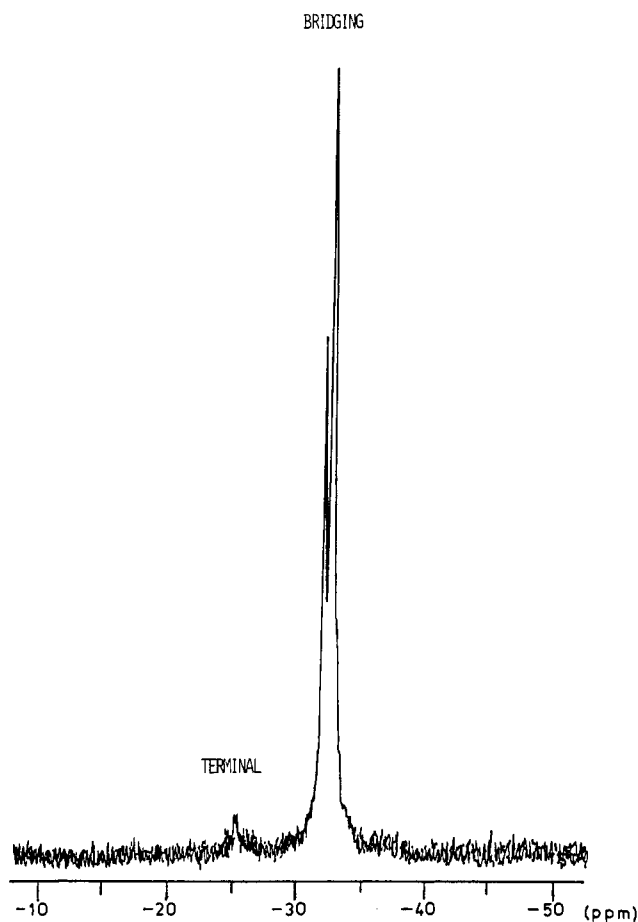
(5) Nesmeyanov, A. N. *Adv. Organomet. Chem.* **1972**, *10*, 1.

Figure 3. 36.2-MHz $^{31}P\{^1H\}$ NMR spectrum of polymer 9 (in CH_2Cl_2) prepared in DME with hydrolytic workup.

consistent with the finding that the resonances of the bridging phosphorus nuclei in the oligomers (6, $x = 2$–4) are upfield (δ_p −31 to −32) of the terminal resonances (δ_p −18).

The oligomers each have $x − 1$ chiral centers. Therefore, since there are $2^{(x-1)}/2$ enantiomeric pairs, $x[2^{(x-1)}/2]$ lines would be observable by NMR spectroscopy. Figure 2 shows the 145.8-MHz $^{31}P\{^1H\}$ NMR spectra for 6 ($x = 2$–4). Note that the line widths for the dimer are such that no J_{PP} ($\sim$1 Hz) is observable. The multiplets which are observed for the bridging phosphorus nuclei in the trimer and tetramer must therefore arise from the enantiomers of each species. The bridging nuclei for the trimer show five of the expected six ABX lines. (It is the low-field x peak which not splitting out). For the tetramer at least 12 lines are observed for the bridging nuclei. It is obvious that overlaps must be occurring.

Polymers of type 7 have been prepared and reported independently by Neuse and Chris[6] and Pittman.[7] In both cases, Lewis acid-catalyzed polycondensation of ferrocene with phenyldichlorophosphine was followed by an oxidation step (eq 3). The reactions were carried out in the melt phase or in solution at temperatures of 80–170 °C. No polymer was obtained with a molecular weight (number average) greater than 6000, and in neither case was an effort made to isolate unoxidized phosphine polymer.

We have found that the reaction between 1,1′-dilithio-ferrocene–tetramethylethylenediamine and phenyldichlorophosphine, which were carried out in hexane produces fair yields of ferrocenophane 1, also may be used to

(3)
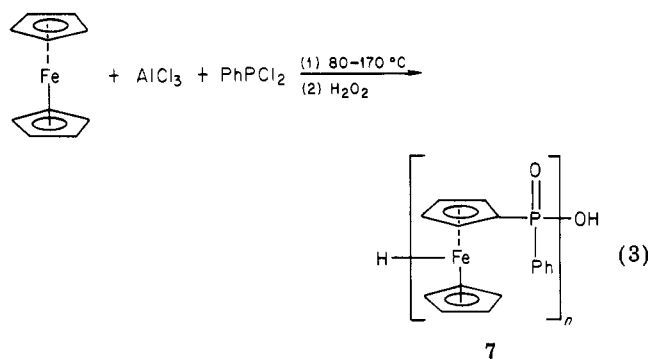
prepare high polymer of type 9 simply by changing the reaction conditions. Even under the optimum conditions for the preparation of the 1:1 PhLi/1 reaction product 4,[1] some polymer is formed. When the 1,1-dilithio-ferrocene/PhPCl$_2$ reaction is carried out at room temperature in hexane, diethyl ether or 1,2-dimethoxyethane (DME) by the slow addition of the lithium reagent to PhPCl$_2$, high polymer is obtained. The initially formed polymer is of type 8 (eq 4). Hydrolytic workup then

(4)
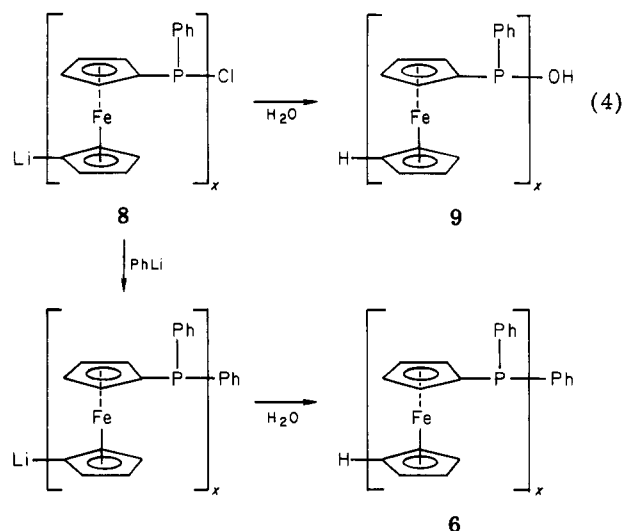
results in the formation of an OH-terminated polymer, 9. On the other hand, treatment of polymer 8 with phenyl-lithium prior to hydrolysis should result in a polymer analogous in all respects to 6 after hydrolysis. Such treatment of polymer 8 was effected several times when the polymer preparation had been carried out in DME. However, ^{31}P NMR spectroscopy indicated that the conversion of P–Cl end groups to P–Ph was not complete. Some phosphinous acid end groups still were observed in the ^{31}P NMR spectra of these polymer samples (resonances at δ_p −25 to −26). The polymers of type 9 are very similar to oligomers 6 in their properties. They are air-stable and thermally stable to temperatures up to 350 °C (by TGA and differential scanning calorimetry), and they are quite soluble in dichloromethane. The ^{31}P NMR spectra of these polymers are very similar to those of the oligomers 6 as may be seen in Figure 3. The relative intensity of the terminal phosphorus resonance is consistent with the presence of polymers which contain primarily bridging phosphine units (δ_p $\sim$−32) and is indicative of a substantial molecular weight.

Molecular weight data obtained by low angle laser light scattering[8] is consistent with the above finding. The

(6) Neuse, E. W.; Chris, G. J. *J. Macromol. Sci., Chem.* **1967**, *3*, 371.
(7) Pittman, C. U., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2927.

(8) Huglin, M. B. "Light Scattering from Polymer Solutions"; Academic Press: New York, 1972.

Table III. Laser Light Scattering M_W Data for Polymers 8

| | reaction | |
solv	temp, °C	M_W
hexane	25	47 000
Et$_2$O	25	161 000
DME[a]	−40	131 000
DME[a]	0	90 000
DME[a]	25	43 500
DME[b]	25	8 900

[a] Phenyl capped (see Experimental Section). [b] Not phenyl capped (see Experimental Section).

weight-average molecular weights obtained in this manner ranged from 8900 to 161 000 g/mol (Table III). Attempts to characterize the apparent molecular weight distributions by size-exclusion chromatography were unsuccessful when dichloromethane was used as eluent with porous glass or when THF was used as eluent with cross-linked semirigid polystyrene gel.

Polymer preparation was studied as a function of solvent and reaction temperature. Table III shows that the molecular weights of the phenylated polymers decrease as the reaction temperature which was used (in DME solution) increases. It is probable that as the temperature increases chain termination via reaction of the organolithium species with the DME solvent[9] becomes more and more important. The highest molecular weight material was prepared by using diethyl ether as solvent and the lowest using DME. Very likely, solubility of the growing polymeric species becomes a problem in hexane solvent, while DME is too reactive toward the organolithium reagent. Diethyl ether appears to combine the desirable properties of good solubility of the growing polymer and low reactivity toward the organolithium function.

In conclusion, it is important to point out that these oligomers and polymers of types 6 and 8, unlike those previously prepared,[6,7] contain tertiary phosphine units in their backbone. These have been demonstrated to have the ability to coordinate to transition-metal complexes. Future publications will describe the reactions of such oligomers and polymers with transition metal species and their applications to catalytic processes.

Experimental Section

General Comments. Any of the general comments of part 1[1] which pertain to the following section are still applicable. Others will be noted here in part 2, which includes the preparation, characterization, and reactivity of the phosphinoferrocene oligomers and polymers.

All reactions were carried out under an atmosphere of prepurified nitrogen unless otherwise indicated. 1,2-Dimethoxyethane (DME) was predried over sodium metal and then distilled under nitrogen from sodium/benzophenone ketyl. Fisher (HPLC grade) or Burdick & Jackson ("distilled in glass") dichloromethane and hexane were used as solvents for high-performance liquid chromatography (HPLC).

Analytical HPLC was carried out on a system consisting of (1) two Waters Associates Model 6000 solvent delivery pumps and a Model 660 solvent programmer set at a constant 65% dichloromethane/35% hexane mixture, (2) an Altex Model 153 analytical UV detector, and (3) a Rheodyne Model 7120 syringe loading sample injector equipped with a 10-μL sample loop for analytical runs or a 2.0-mL sample loop for semiprep analytical runs. Two columns were interchanged on the same system. For noncollecting analytical runs a Waters μ-Porasil, 30 cm × 3.9 mm, column was used with a solvent flow rate of 2.0 mL/min. For

collecting samples from semiprep analytical runs a Waters μ-Porasil, 30 cm × 7.8 mm, column was used with a solvent flow rate of 4–5 mL/min.

Preparative HPLC was carried out on a Waters Prep LC/System 500 liquid chromatograph equipped with a refractive index detector. A single Waters Prep PAK-500 Silica Cartridge, 57 mm × 30 cm, was sufficient for separations. A 65% dichloromethane/35% hexane mixture was used at a flow rate of 0.25 L/min.

Thermogravimetric analysis (TGA) was carried out by using Du Pont 951 and 990 thermogravimetric analyzers programed to heat from 25 to 600 °C at 20° min^{-1} in flowing air at ca. 50 mL min^{-1}. Weight-average molecular weights, $\bar{M}_w$, were determined by using light scattering techniques at various concentrations in dichloromethane with a Chromatics KMX-6 low-angle laser light scattering photometer. Light scattering is an absolute technique; thus no standards were necessary. Weights are reported in atomic mass units (amu).

^{1}H NMR spectra were recorded at 60 MHz on a Varian T-60 or Hitachi Perkin-Elmer R-24B spectrometer and at 250 MHz on a Bruker WK-250 spectrometer. ^{31}P and ^{13}C NMR spectra were recorded on a Bruker HFX-90 or JEOL FX-90Q spectrometer operating at 36.2 and 22.6 MHz, respectively. The high-field ^{31}P NMR spectra were obtained at 145.8 MHz on a Bruker WM-360 spectrometer. The ^{31}P chemical shifts are reported in δp units, ppm downfield from 85% aqueous H$_3$PO$_4$ using external triphenylphosphine (in the same solvent as the sample) as the referenced signal at −6 ppm. Infrared spectra were obtained by using a Perkin-Elmer 457A double-beam grating spectrophotomer. Mass spectra were recorded on a Varian MAT-44 mass spectrometer operating at 70 eV. The temperature programmed mass spectral data was collected by using a Hewlett-Packard GC/MS Model 5985 outfitted with a temperature-programmed direct insertion probe.

Reaction of 1-Lithio-1′-(diphenylphosphino)ferrocene with (1,1′-Ferrocenediyl)phenylphosphine To Give Oligomers. The following procedure has been found to give the best yield and distribution of oligomers.

Following the general procedure for the preparation of 1-lithio-1′-(diphenylphosphino)ferrocene in the absence of an excess of PhLi,[1] a reaction was carried out between 2.50 g (8.56 mmol) of (1,1′-ferrocenediyl)phenylphosphine dissolved in 70 mL of hexane and 12.8 mL (8.56 mmol) of 0.67 M PhLi in diethyl ether (with 15 mL of hexane added to the flask). The addition of the ferrocenophane to the PhLi proceeded over 1.75 h, and upon completion, the mixture was stirred an additional 2 h at room temperature. The 1-lithio-1′-(diphenylphosphino)ferrocene thus formed was dissolved in 40 mL of THF and 1.29 mL (8.56 mmol) of TMEDA was added by syringe. A 2.50-g (9.56-mmol) sample of (1,1′-ferrocenediyl)phenylphosphine dissolved in 50 mL of THF was added to the ferrocenyllithium reagent slowly during 1 h at room temperature, and the resulting brick-colored solution was stirred overnight at room temperature. The solution was hydrolyzed to the "dry end point" with saturated aqueous NH$_4$Cl solution. This produced a yellow-brown solution, which was filtered. The solvent was removed from the filtrate on a rotary evaporator to give a brown oil. The oil was prepurified by filtration chromatography eluting with dichloromethane. This removed a single yellow fraction, which upon removal of the solvent, yielded 5.36 g of a mixture of oligomers 6 as an oily, sticky solid. TLC studies of the oligomer mixture indicated the presence of as many as five or six yellow fractions separable with a dichloromethane/pentane mixture as the eluent. Preparative HPLC was used to separate the oligomers for their individual characterization. Samples for elemental analysis were purified by using semiprep analytical HPLC of the oligomers isolated by preparative HPLC. The following fractions were isolated (listed in order of their elution) and identified as oligomers of type 6 on the basis of the listed data. (All the oligomers were air-stable as solids over a period of months and in solution over a period of several hours.)

(1) 0.878 g (2.37 mmol, 28% based on available lithium reagent from PhLi charged) of 1-(diphenylphosphino)ferrocene, (η^5-C$_5$H$_4$PPh$_2$)Fe(η^5-C$_5$H$_5$), mp 120–122 °C, identified by comparison of its melting point and ^{1}H-NMR spectrum with that of an authentic sample): TGA, 83.2% total weight loss at 300, 370, 390, 400, 420, 490 °C.

(9) Schöllkopf, U. "Houben-Weyl Methoden der Organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1970; Vol. XIII/1, pp 93–94.

(2) 1.43 g (2.16 mmol, 25% of possible 8.56 mmol) of a glassy, yellow, noncrystalline solid, identified as oligomer 6 (x = 2), mp 69–75 °C, on the basis of the following data: IR (CDCl$_3$) 3055 (m), 2953 (m), 1584 (w), 1476 (w), 1436 (s), 1411 (w), 1386 (w), 1362 (w), 1306 (w), 1247 (s), 1228 (w), 1180 (vs), 1160 (sh), 1103 (m), 1030 (s), 997 (w), 886 (w), 857 (vs), 822 (m), 681 (m), 630 (m), 562 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.80–5.00 (m, 17 H, Cp), 7.16–8.12 (m, 15 H, Ph); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ_p –17.8 (s, 1 P, PPh$_2$), –31.8 (s, 1 P, PFcPh); ^{31}P{^{1}H} NMR (high resolution, C$_6$D$_6$) δ_p –17.9 (d, J(P–P') = 1.1 Hz, 1 P, PPh$_2$), –32.0 (d, J(P–P') = 1.1 Hz, 1 P, PFcPh); mass spectrum, m/e 661 (M$^+$ – H, 1.3), 292 (FcPPh + H, 4.6); TGA, 63.7% total weight loss at 400, 430, 480, 585 °C. Anal. Calcd for C$_{38}$H$_{32}$Fe$_2$P$_2$ (662.34): C, 68.90; H, 4.88. Found: C, 68.71; H, 5.39.

(3) 0.951 g (1.00 mmol, 23% of possible 4.28 mmol) of a glassy, yellow, noncrystalline solid, identified as oligomer 6 (x = 3), mp 90–100 °C, on the basis of the following data: IR (CDCl$_3$) 3053 (m), 2951 (m), 1584 (w), 1475 (w), 1433 (s), 1411 (w), 1383 (w), 1360 (w), 1306 (w), 1248 (m), 1179 (vs), 1158 (s), 1103 (m), 1026 (s), 997 (w), 881 (m), 858 (s), 823 (m), 682 (s), 640 (m), 561 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.75–4.91 (m, 25 H, Cp), 7.21–8.00 (m, 20 H, Ph). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) δ_p –17.6 (s, 1 P, PPh$_2$), –31.5 (s, 1 P, P(Ph)), –32.2 (s, 1 P, PFcPh); mass spectrum, m/e 954 (M$^+$, 4.9), 369 (FcPPh$_2$, 10.4). TGA, 59.3% total weight loss at 390, 510, 570 °C. Anal. Calcd for C$_{54}$H$_{45}$Fe$_3$P$_3$ (954.45): C, 67.95; H, 4.76. Found: C, 68.27; H, 5.15.

(4) 0.654 g (0.52 mmol, 18% of possible 2.85 mmol) of a glassy, yellow, noncrystalline solid, identified as oligomer 6 (x = 4), mp 95–130 °C, on the basis of the following data: ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) δ_p –17.7 (s, 1 P, PPh$_2$), –31.5 (s, 1 P, P(Ph)), 32.2 (br s, 2 P, PFcPh); mass spectrum, molecular ion, M$^+$, observed at 1247 (calcd 1246.56) (this mass spectrum was obtained by the M.I.T. Mass Spectrometry Facility); TGA, 62.2% total weight loss at 415, 440, 470, 570 °C. Anal. Calcd. for C$_{70}$H$_{58}$Fe$_4$P$_4$ (1246.56): C, 67.44; H, 4.70. Found: C, 67.95; H, 5.15.

(5) Less than 0.10 g of a mixture of oligomer 6 (x = 5 and x = 6). Approximately 50 mg of oligomer 6 (x = 5) was separated from this mixture by using semiprep analytical HPLC and identified by its ^{31}P{^{1}H} NMR spectrum and mass spectrum as follows: ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ_p –17.7 (s, 1 P, PPh$_2$), –31.5 (s, 1 P, P(Ph)), –32.1 (s, 3 P, PFcPh); mass spectrum, m/e molecular ion, M$^+$, observed at 1539 (calcd 1538.67). This mass spectrum was obtained by the M.I.T. Mass Spectrometry Facility.

Reaction of 1-Lithio-1'-(diphenylphosphino)ferrocene with Phenyldichlorophosphine. Following the general procedure for the preparation of 1-lithio-1'-(diphenylphosphino)-ferrocene in the absence of an excess of PhLi,[1] a reaction was carried out between 1.00 g (3.4 mmol) of (1,1'-ferrocenediyl)-phenylphosphine and 6.25 mL (5.0 mmol) of 0.8 M PhLi in diethyl ether. The ferrocenyllithium reagent thus formed was dissolved in 30 mL of THF, and 0.34 mL (2.5 mmol) of PhPCl$_2$ was added by syringe at room temperature. The solution turned from golden brown to golden yellow. It was heated at reflux for 30 min and then allowed to cool and stir at room temperature for 3 h. The solvent was removed on a rotary evaporator, and filtration chromatography (30% dichloromethane/70% pentane) removed a faint yellow band first and then the major yellow band. Removal of the solvent on a rotary evaporator yielded 0.543 g (0.6 mmol, 35%) of a glassy, yellow, noncrystalline solid identified as bis-(1'-(diphenylphosphino)ferrocenyl)phenylphosphine, [(η^5-Ph$_2$PC$_5$H$_4$)Fe(η^5-C$_5$H$_4$)]$_2$PPh: ^{1}H NMR (CDCl$_3$) δ 3.82–4.27 (m, 16 H, Cp), 7.20–7.41 (m, 25 H, Ph); ^{31}P{^{1}H} NMR (CDCl$_3$) δ_p –17.9 (s, 2 P, –PPh$_2$), –32.3 (s, 1 P, P(Ph)); mass spectrum, m/e 846 (M$^+$, 54.2%). Anal. Calcd for C$_{50}$H$_{41}$Fe$_2$P$_3$ (846.52): C, 70.94; H, 4.89. Found: C, 71.43; H, 5.35.

Reaction of 1,1'-Dilithioferrocene–Tetramethylethylene-diamine with Phenyldichlorophosphine in Hexane. A 300-mL three-necked, Morton flask was charged with 5.17 g (16.3 mmol) of 1,1'-dilithioferrocene–tetramethylethylenediamine in the glovebox and then fitted with a mechanical stirring unit, a pressure-equalizing dropping funnel, a gas inlet tube, and a no-air stopper. The apparatus was removed from the glovebox and connected to a Schlenk manifold. Hereafter, this will be referred to as the standard apparatus. Hexane (ca. 200 mL) was added to the dilithioferrocene under nitrogen by cannula. PhPCl$_2$ (2.04 mL, 15.0 mmol) and hexane (60 mL) were added to the funnel

by syringe. This solution was added dropwise over 1 h to the vigorously stirred dilithioferrocene/hexane slurry at room temperature. The resulting tan-orange mixture was stirred overnight at room temperature. The mixture now was red in color, indicative of (1,1'-ferrocenediyl)phenylphosphine. The reaction mixture was treated with 10 mL of water and stirred for 30 min. It was then filtered in air and the tan solid washed with 2 × 50 mL portions of hexane. The red filtrate was discarded. The tan solid was extracted with 100 mL of dichloromethane under nitrogen. The extract was dried over MgSO$_4$ and filtered and the solvent removed in vacuo to give 1.87 g (43% conversion) of a glassy, brown solid. Further purification of the polymer was afforded by precipitation of a dichloromethane solution of the polymer into a large volume of rapidly stirring pentane. This gave a very fluffy, tan solid. A more easily handled material could be obtained by dissolving the polymer in dichloromethane and removing the dichloromethane at reduced pressure to yield a brown, glassy, brittle solid. The solid was identified as poly((1,1'-ferrocenediyl)phenylphosphine), H[–(C$_5$H$_4$)Fe(C$_5$H$_4$PPh)–]$_x$OH 9: IR(CH$_2$Cl$_2$) 3080 (br m), 2979 (w), 1483 (m), 1438 (m), 1387 (w), 1311 (w), 1196 (m), 1166 (s), 1110 (m), 1099 (m), 1073 (w), 1060 (w), 1032 (s), 1005 (w), 892 (w), 833 (vs), 635 (w) cm^{-1}; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) δ_p –29.1 (m, end group P atoms), –33.3 (m, internal P atoms); TGA, 55.8% total weight loss at 390, 510, 600 °C; DSC, exotherm at 405 °C of 0.7 J; $\bar{M}_w$ = 47000 amu.

Reaction of 1,1'-Dilithioferrocene–Tetramethylethylene-diamine with Phenyldichlorophosphine in DME. The standard apparatus was charged with 5.00 g (15.8 mmol) of 1,1'-dilithioferrocene–tetramethylethylenediamine as before and connected to a Schlenk manifold. DME (ca. 150 mL) was added by cannula to give an orange solution. PhPCl$_2$ (2.04 mL, 15.0 mmol) was dissolved in 60 mL of DME in the dropping funnel and was added over a 1-h period to the stirred dilithioferrocene/DME solution at room temperature. The resulting yellow-orange solution was stirred overnight. The color did not changed, and the reaction mixture was treated with 10 mL of water and stirred for 30 min. It was then filtered in air and the solvent removed on a rotary evaporator. The resulting brown oil was dissolved in 100 mL of dichloromethane, dried over MgSO$_4$, and concentrated to ca. 35 mL on a rotary evaporator. The concentrate was poured into a large volume (ca. 900 mL) of rapidly stirring pentane (as described previously) to precipitate a fluffy, tan solid. The precipitation was repeated to yield 2.51 g (57% conversion) of polymer identified as poly((1,1'-ferrocenediyl)phenylphosphine), 9, on the basis of the following data: IR (CH$_2$Cl$_2$) 3080 (br m), 2973 (vw), 1585 (vw), 1480 (m), 1436 (m), 1385 (w), 1309 (w), 1195 (m), 1164 (s), 1109 (m), 1097 (m), 1071 (w), 1058 (w), 1031 (s), 1002 (w), 920 (vw), 890 (w), 867 (sh), 833 (vs), 633 (w) cm^{-1}; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) Figure 3, δ_p –25.5 (s, end group P atoms), –31.6 (s, internal P atoms), –32.1 ppm (s, internal P atoms); TGA, 55.2% total weight loss at 385, 500, 605 °C; $\bar{M}_w$ = 8900 amu.

Reaction of 1,1'-Dilithioferrocene–Tetramethylethylene-diamine with Phenyldichlorophosphine in Diethyl Ether. The standard apparatus was charged with 5.00 g (15.8 mmol) of 1,1'-dilithioferrocene–tetramethylethylenediamine and ca. 200 mL of diethyl ether to give an orange slurry. PhPCl$_2$ (2.00 mL, 14.7 mmol) was dissolved in 60 mL of diethyl ether in the dropping funnel and added to the slurry over a 1-h period. The resulting red-orange mixture was stirred overnight, and the red color was still visible. The mixture was treated with 10 mL of water, as in previous experiments, and filtered and the tan solid washed with 2 × 50 mL of hexane. Further treatment and purification of the tan solid was analogous to that described in the previous experiment done in hexane. This afforded 1.35 g (31% conversion) of polymer identified as poly((1,1'-ferrocenediyl)phenylphosphine), 9: IR (CH$_2$Cl$_2$) 3080 (m), 3050 (m), 2970 (w), 1588 (w), 1482 (m), 1437 (m), 1420 (sh), 1388 (m), 1363 (w), 1311 (m), 1195 (m), 1165 (s), 1110 (w), 1099 (w), 1072 (w), 1060 (w), 1031 (s), 1005 (w), 915 (m), 890 (w), 868 (sh), 835 (vs), 632 (w) cm^{-1}; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) δ_p –25.9 (m, end group P atoms), –32.5 (m, internal P atoms); TGA, 49.2% total weight loss at 360, 420, 470, 490, 610 °C; $\bar{M}_w$ = 161000 amu.

The filtrate from the above reaction was evaporated to dryness on a rotary evaporator to give an oily red solid. Filtration chromatography of this solid eluting with a 30% dichloromethane/70% pentane mixture removed three fractions which

were isolated and identified as the following (in order of their elution) on the basis of the data presented.

(1) 0.574 g (3.1 mmol, 20%) of ferrocene: mp 171–173 °C; ^{1}H NMR (CDCl$_3$) δ 4.09 (s).

(2) 0.242 g (0.5 mmol, 6%) of diferrocenylphenylphosphine, [(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)–]PPh: mp 188–190 °C (lit.[10] 191–193 °C); ^{1}H NMR (CDCl$_3$) δ 3.88–4.30 (m, 8 H, Cp), 4.04 (s, 10 H, Cp), 7.24–7.58 (m, 5 H, Ph); mass spectrum, *m/e* 478 (M$^+$, 42.6).

(3) 0.735 g (17% conversion) of oligomers **6** as a fluffy, glassy, yellow solid: IR (CH$_2$Cl$_2$) 3100 (m), 3080 (m), 3050 (m), 2968 (w), 1586 (w), 1482 (m), 1436 (m), 1412 (w), 1386 (m), 1310 (w), 1195 (m), 1164 (s), 1110 (m), 1098 (w), 1071 (w), 1059 (w), 1031 (s), 1004 (w), 913 (s), 890 (sh), 865 (w), 830 (vs), 635 (w) cm^{-1}.

Reaction of 1,1′-Dilithioferrocene–Tetramethylethylene-diamine with Phenyldichlorophosphine in DME at –40, 0, and 25 °C and Subsequent Reaction with Phenyllithium. The standard procedure used for all three temperatures is as follows.

A 300-mL three-necked, round-bottomed flask was charged with 2.00 g (6.3 mmol) of dilithioferrocene and then equipped with a magnetic stir-bar, a pressure-equalizing dropping funnel, a gas inlet tube, and two no-air stoppers in the glovebox. The apparatus was connected to a Schlenk manifold, and 75 mL of DME was added to give an orange solution. A solution of PhPCl$_2$ (0.855 mL, 6.3 mmol) in 50 mL of DME was added to the dilithio-ferrocene/DME solution, which was maintained at the appropriate temperature, over a 1.25–1.5-h period. The reaction mixture was stirred an additional hour at the same temperature and then at room temperature for 2 h. The reaction mixture was then cooled to 0 °C, 10 mL (7.6 mmol) of 0.76 M PhLi in diethyl ether was added, and the mixture was then stirred for 45 min at 0 °C. The mixture was hydrolyzed to the "dry end point" with sat. aq. NH$_4$Cl solution. MgSO$_4$ was added to ensure drying, and the mixture was filtered, followed by removal of the solvent on a rotary evaporator to give a brown oil. The precipitation method described previously was used to purify the polymer. The results of each temperature run and characterization of the polymers is listed as follows.

(10) Sollott, G. P.; Mertwoy, H. E.; Portnoy, S.; Snead, J. L. *J. Org. Chem.* **1963,** *28,* 1090.

(11) Measurements made at the University of Michigan NMR facilities funded under NSF Grant CHE-7909108.

A. Reaction at 25 °C: 1.256 g (68% conversion) of polymer; IR (CH$_2$Cl$_2$) 3078 (m), 3048 (m), 2965 (w), 1480 (m), 1435 (m), 1417 (w), 1384 (m), 1308 (m), 1257 (w), 1191 (s), 1162 (vs), 1108 (m), 1095 (m), 1070 (m), 1058 (w), 1030 (vs), 1002 (m), 887 (w), 832 (vs), 688 (w), 630 (m) cm^{-1}; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) δ_p –25.1 (m, P(Ph)OH), –31.7 (m, internal P atoms), –32.3 (m, internal P atoms).

B. Reaction at 0 °C: 1.269 g (69% conversion) of polymer; IR (CH$_2$Cl$_2$) 3078 (m), 3048 (m), 2965 (w), 1480 (m), 1435 (m), 1417 (w), 1384 (m), 1308 (m), 1257 (w), 1191 (s), 1163 (vs), 1108 (m), 1095 (m), 1070 (m), 1058 (w), 1030 (vs), 1002 (m), 887 (w), 832 (vs), 688 (w), 630 (m) cm^{-1}; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) δ_p –25.2 (m, P(Ph)OH), –32.3 (m, internal P atoms).

C. Reaction at –40 °C: 1.307 g (71% conversion) of polymer; IR (CH$_2$Cl$_2$) 3078 (m), 3048 (m), 2965 (w), 1480 (m), 1435 (m), 1417 (w), 1384 (m), 1308 (m), 1257 (w), 1191 (s), 1162 (vs), 1108 (m), 1095 (m), 1070 (m), 1058 (w), 1020 (vs), 1002 (m), 887 (w), 832 (vs), 688 (w), 630 (m) cm^{-1}; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$) δ_p –26.2 (m, P(Ph)OH), –32.4 (m, internal P atoms).

The molecular weights, M_w, of the polymers obtained in experiments A, B, and C were 43 500, 90 000 and 131 000 amu, respectively.

Registry No. 6 x = 2, 82311-92-0; **6** x = 3, 82311-93-1; **6** x = 4, 82322-77-8; **6** x = 5, 82311-94-2; (1,1′-ferrocenediyl)phenylphosphine, 72954-06-4; 1-lithio-1′-(diphenylphosphino)ferrocene, 82311-95-3; phenyldichlorophosphine, 644-97-3; bis(1′-(diphenylphosphino)-ferrocenyl)phenylphosphine, 82311-96-4; (1,1′-dilithioferrocene)(di-chlorophenyl)phosphine copolymer, 82322-78-9.

Hexamethylsilirane. 3. Dimethylsilylene-Transfer Chemistry[1]

Dietmar Seyferth,* Dennis C. Annarelli, and Don P. Duncan

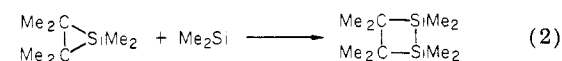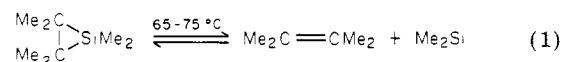*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Received April 15, 1982

The thermolysis of hexamethylsilirane at ca. 65–75 °C results in the extrusion of trappable dimethylsilylene. Dimethylsilylene generated in this manner inserted into the Si–H bonds of organosilicon hydrides and into the Si–O bonds of methoxysilanes, hexamethylcyclotrisiloxane, and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane, and it added to the C=C bonds of various olefins to yield new siliranes. Evidence is presented which indicates that such Me$_2$Si addition to the C=C bond occurs stereospecifically with retention of configuration.

Introduction

In previous papers we have described the preparation and properties of hexamethylsilirane, its mode of thermal decomposition, and some of its reactions with simple reagents in which the SiC$_2$ ring is opened.[2,3] As noted in

(1) Preliminary communications: Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975,** *97,* 7162; Seyferth, D.; Annarelli, D. C. *J. Organomet. Chem.* **1976,** *117,* C51.

(2) Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan, D. P. *J. Organomet. Chem.* **1980,** *201,* 179.

(3) Seyferth, D.; Annarelli, D. C.; Shannon, M. L.; Escudie, J.; Duncan, D. P. *J. Organomet. Chem.* **1982,** *225,* 177.

part 1,[2] hexamethylsilirane decomposes thermally by extrusion of dimethylsilylene (eq 1). The process is rever-

$$\underset{Me_2C}{\overset{Me_2C}{\diagdown}}SiMe_2 \xrightleftharpoons{65-75\ °C} Me_2C=CMe_2 + Me_2Si \qquad (1)$$

$$\underset{Me_2C}{\overset{Me_2C}{\diagdown}}SiMe_2 + Me_2Si \longrightarrow \underset{Me_2C-SiMe_2}{\overset{Me_2C-SiMe_2}{\mid\quad\mid}} \qquad (2)$$

sible, but there are two irreversible pathways which involve consumption of dimethylsilylene: its polymerization to form poly(dimethylsilylene) and its reaction with as yet