Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. 1. Synthesis and Characterization

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The reaction of 1,1′-dilithioferrocene–tetramethylethylenediamine with the respective phosphorus and arsenic dichloride was used in the preparation of (1,1′-ferrocenediyl)phenylphosphine and methylphosphine and (1,1′-ferrocenediyl)phenylarsine. The reactions of these [1]ferrocenophanes are of two types: (a) those which occur with retention of the ferrocenophane system (e.g., those with elemental sulfur, with THF·W(CO)$_5$, and Fe$_2$(CO)$_9$ in THF); (b) those which occur with opening of the ferrocenophane system. Phenyllithium and other RLi react in the latter manner to give 1-phosphino- (or 1-arsino-) 1′-lithioferrocenes whose reactions with several electrophiles were studied. The reaction of 1,1′-dilithioferrocene with diorganotin dichlorides gave 1,1,12,12-tetraalkyl[1.1]stannaferrocenophanes in very low yield, in addition to high yields of polymeric material.

Introduction

The first [1]ferrocenophanes, (1,1′-ferrocenediyl)diphenylsilane and bis(1,1′-ferrocenediyl)silane, were prepared in 1975 by the reaction of 1,1′-dilithioferrocene with diphenyldichlorosilane and silicon tetrachloride, respectively.[1] Since then, other group 4b bridged ferrocenophanes have been prepared.[2,3] Such silicon-bridged [1]ferrocenophanes have been found to be considerably more reactive than the usual organosilicon compounds with four Si–C bonds.[2] It seemed probable that heteroatom groups other than R$_2$Si and R$_2$Ge could be introduced as bridges into [1]ferrocenophanes, and we undertook to prepare some [1]ferrocenophanes with group 5 atom bridges, i.e., RP and RAs.

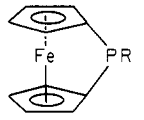
We have reported preliminary results of our work in this area,[4] and we describe here full details of these experiments as well as of further studies. Of particular interest is our discovery of the organolithium-induced ring-opening reactions of the RP- and RAs-bridged [1]ferrocenophanes. We report also concerning our attempts to prepare R$_2$Sn-bridged [1]ferrocenophanes. When the present work was in its later stages, Osborne and co-workers reported independently on the preparation[3] and structure[5] of the PhP-bridged ferrocenophane.

Table I. Electronic Spectral Data for (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$PPh$_2$) and (1,1′-Ferrocenediyl)phenylphosphine and -arsine and Their Derivatives

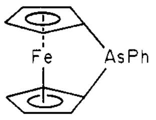
compd	solvent	λ_{max}, nm	ϵ, cm^2/mol
(C$_5$H$_5$)Fe(C$_5$H$_4$)PPh$_2$	CH$_2$Cl$_2$	440	143
Fe(C$_5$H$_4$-)$_2$PPh	hexane	498	408
Fe(C$_5$H$_4$-)$_2$PMe	hexane	498	410
Fe(C$_5$H$_4$-)$_2$AsPh	hexane	494	312
Fe(C$_5$H$_4$-)$_2$P(S)Ph	Et$_2$O	485	(poor solubility)
Fe(C$_5$H$_4$-)$_2$PPh·W(CO)$_5$	CH$_2$Cl$_2$	494	439
Fe(C$_5$H$_4$-)$_2$AsPh·W(CO)$_5$	CH$_2$Cl$_2$	492	330

Results and Discussion

(1,1′-Ferrocenediyl)phenylphosphine, 1, (1,1′-ferrocenediyl)methylphosphine, 2, and (1,1′-ferrocenediyl)phenylarsine, 3, were prepared by the addition of the appropriate RPCl$_2$ or PhAsCl$_2$ in hexane solution to a suspension of 1,1′-dilithioferrocene–tetramethylethylenediamine[6] in hexane at −78 °C and subsequent slow warming of the reaction mixture to room temperature. The product yields were not high, and deviation from the cited reaction conditions gave even lower yields or no ferrocenophane product at all. (1,1′-Ferrocenediyl)phenylphosphine, the compound with which we carried out most of our subsequent studies, was obtained in yields of 35–50% in the form of slightly air-sensitive, brick-red nuggets. The methyl derivative was isolated in 19% yield, and red nuggets of (1,1′-ferrocenediyl)phenylarsine were obtained in 34% yield. All three compounds are soluble in common organic solvents. Upon exposure to air, their solutions deposit a tan solid over a period of several hours. In the solid state they appear to be stable when stored under an inert atmosphere.



1, R = Ph
2, R = Me



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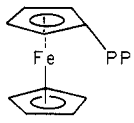

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In order to understand the spectroscopic and some of the chemical properties of 1–3, it is useful to comment briefly on the structure of 1.[5] A generalized [1]ferrocenophane structure is shown in Figure 1. Characteristic parameters are the ring tilt angle α and the deviation of the bridging substituent from the C$_5$ ring plane, β. (In ferrocene the C$_5$ rings are parallel.) In 1, α = 26.7° and β = 32.5°. The C–P–C angle γ = 90.6°.

The electronic spectra of 1–3 and of several derivatives of 1 and 2 in which the [1]ferrocenophane system has been retained are given in Table I. The electronic spectra of ferrocene and unbridged substituted ferrocenes such as 4 show a major absorption band at 440 nm. It has been

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[1] Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27.

[2] Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501.

[3] (a) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345. (b) Osborne, A. G.; Whiteley, R. H.; Hollands, R. E. Proceedings of the Ninth International Conference on Organometallic Chemistry, Dijon, Sept 3–7, 1979; Abstract P14T.

[4] Seyferth, D.; Withers, H. P., Jr. *J. Organomet. Chem.* **1980**, *185*, C1.

[5] Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91.

[6] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.

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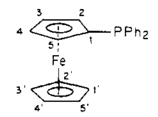
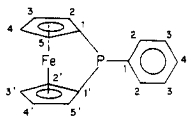
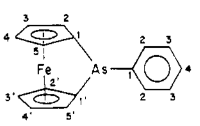
Table II. ^{13}C Chemical Shifts

					
carbon	chem shift[a]	carbon	chem shift[a]	carbon	chem shift[a]
C(1)	76.6 (d, J(C-P) = 8 Hz)	Cp, C(1), C(1')	18.7 (d, J(C-P) = 54 Hz)	Cp, C(1), C(1')	18.3
C(2), C(5)	73.1 (d, J(C-P) = 15 Hz)	C(2)-C(5), C(2')-C(5')	76.6-78.2	C(2)-C(5), C(2')-C(5')	76.5-77.7
C(3), C(4)	70.9 (d, J(C-P) = 4 Hz)	Ph, C(1)	137.8 (d, J(C-P) = 11 Hz)	Ph, C(1)	139.0
C(1')-C(5')	69.3 (s)	C(2)	130.7 (d, J(C-P) = 16 Hz)	C(2)	132.7
phenyl	normal shift values	C(3)	128.9 (d, J(C-P) = 2 Hz)	C(3)	129.1
		C(4)	127.9 (s)	C(4)	127.9

[a] These values were obtained in C_6D_6 solution and are reported in δ_C units ppm downfield from tetramethylsilane using the center line of C_6D_6 as reference at 128 ppm. The NMR spectrometer was operated in the proton-decoupled mode.

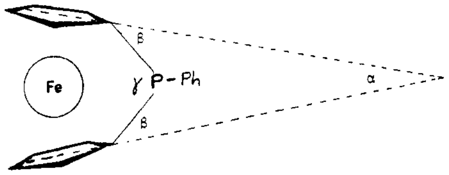


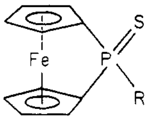
Figure 1. Structure of (1,1'-ferrocenediyl)phenylphosphine.

found that the position and intensity of this band are affected by deviations of the C_5 rings from the parallel configuration.[7] In the spectra of ferrocenophanes with a tilted ring system this band is shifted to lower energy and increases in intensity. The shifts reported for [1]ferrocenophanes are larger than any reported for other [*n*]ferrocenophanes, and such shifts of 40–60 nm to lower energy apppear to be characteristic of this class of substituted ferrocenes.

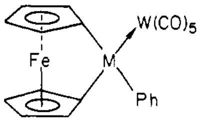
The ^{13}C NMR spectra of **1** and **3** clearly reflect the bond angle distortion (i.e., β) at the ipso-carbon atom of the cyclopentadienyl rings [C(1) and C(1')] to which the bridging PPh or AsPh unit is attached (Table II). The C(1) carbon atom resonance in the ^{13}C NMR spectrum of (diphenylphosphino)ferrocene, **4**, is found at δ_C 76.6 (d, J(C–P) = 8 Hz). In contrast, the C(1) and C(1') resonances in the ^{13}C NMR spectrum of **1** are shifted by 60-ppm upfield to δ_C 18.7, with J(C–P) increased substantially to 54 Hz. A similar upfield shift of the C(1)/C(1') resonances was found for **3**. Such shifts may be indicative of a change from sp^2 hybridization to one approaching sp^3,[8] but there appears to be no quantitative relationship between the magnitude of the shift and any single structural feature.

The ^{31}P NMR spectra of **1** and **2** are unexceptional. For **1**, the ^{31}P resonance is found at δ_P 11.5 and for **2** is found at δ_P −13.2. For comparison, δ_P for **4** occurs at −17.1. The mass spectra of **1–3** all showed the molecular ion. For the phosphorus compounds M^+ was the most intense peak in the mass spectrum.

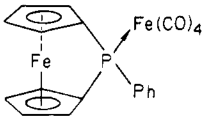
There are two types of reactions of [1]ferrocenophanes **1–3**: (a) those in which the [1]ferrocenophane system is retained in the product and (b) those in which the [1]ferrocenophane bridge is broken to give a 1,1'-disubstituted ferrocene. Reactions which involve donation of the lone electron pair of the group 5 atom in **1–3** are of type a. Thus, reaction with elemental sulfur in benzene solution at room temperature converted **1** to the corresponding fairly air-stable, red-brown phosphine sulfide, **5**, without disruption of the [1]ferrocenophane system, as its electronic spectrum in Table I clearly shows. Also, **1** and **3** can serve as tertiary phosphine and arsine ligands in transition metal carbonyl complexes. The reactions of **1** and **3** with THF·$W(CO)_5$ and of **1** with $Fe_2(CO)_9$ in THF[9] gave stable substitution products **7**, **8** and **9**, respectively, as red, crystalline solids. The ^{31}P NMR spectrum of **7** showed the expected downfield shift of the phosphorus resonance from that of the free ligand to δ_P 25.1, with ^{183}W satellites (J(P–W) = 247 Hz). The observed coupling constant is similar in magnitude to other J(P–W) values reported in the literature.[10] The electronic spectra of **7** and **8** were consistent with the [1]ferrocenophane structure (Table I).



5, R = Ph
6, R = Me



7, M = P
8, M = As



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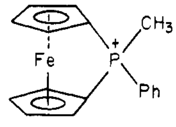

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The isolation of a stable phosphonium salt, **10**, by reaction of **1** with iodomethane was not successful. A reaction in benzene at room temperature proceeded with precipitation of a tan-red solid during a 24-h period. The latter initially was completely soluble in dichloromethane but after a period of minutes began to decompose with deposition of a brown solid, even under an inert atmosphere. An attempt to prepare the Reinecke salt by reaction with $NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$ in methanol failed. A partial characterization of the phosphonium iodide by NMR spectroscopy nevertheless was possible. The ^{31}P NMR spectrum of the reaction solution after the reactants had been mixed showed a single resonance at δ_P 36.0 and the proton NMR spectrum showed the presence of the CH_3 group attached to phosphorus as a doublet at δ 2.8 with J(P–H) = 15 Hz. The decomposition of the phosphonium halide was followed by proton NMR spectroscopy: after 12 h the signals due to this species no longer were present and no new signals had appeared. The nature of the decomposition process remains unknown, but nucleophilic

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(7) Watts, W. E. *Organomet. Chem. Rev., Sect.* A **1967**, *2*, 231.

(8) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

(9) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

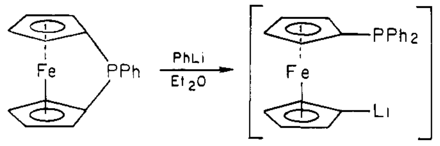
(10) Grim, S. O.; Wheatland, D. A.; MacFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573.

Table III. Substituted Ferrocenes Prepared by Reactions of the Lithium Reagents Derived from (1,1′-Ferrocenediyl)phenylphosphine and -arsine

RLi	reactant	product	mp, °C	yield, %
		A. Reagents Derived from (1,1′-Ferrocenediyl)phenylphosphine/RLi Reactions		
PhLi	H_2O	$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4PPh_2)$	120-123	80
PhLi	Me_3SnCl	$(\eta^5\text{-}C_5H_4SnMe_3)Fe(\eta^5\text{-}C_5H_4PPh_2)$	oil	61
PhLi	Ph_2PCl	$Fe(\eta^5\text{-}C_5H_4PPh_2)_2$	184-185	79
PhLi	Me_3SiCl	$(\eta^5\text{-}C_5H_4SiMe_3)Fe(\eta^5\text{-}C_5H_4PPh_2)$	oil	99
PhLi	Ph_3SnCl	$(\eta^5\text{-}C_5H_4SnPh_3)Fe(\eta^5\text{-}C_5H_4PPh_2)$	152-154	47
MeLi	H_2O	$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4PMePh)$	69-71	29
t-BuLi/hexane	H_2O (S_8)	$(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4P(S)Ph\text{-}t\text{-}Bu]$	132.5-134	47
t-BuLi/Et_2O	H_2O (S_8)	$(\eta\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4P(S)(Ph)CH_2CH_2CMe_3]$	121-122	29
PhLi	Ph_3SiCl	$(\eta^5\text{-}C_5H_4SiPh_3)Fe(\eta^5\text{-}C_5H_4PPh_2)$	157-159.5	43
		B. Reagent Derived from (1,1′-Ferrocenediyl)phenylarsine/PhLi Reaction		
PhLi	H_2O	$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4AsPh_2)$	129-130	73
PhLi	Ph_2PCl	$(\eta^5\text{-}C_5H_4AsPh_2)Fe(\eta^5\text{-}C_5H_4PPh_2)$	164-165.5	53

attack by iodide ion at the phosphonium center to open the strained [1]ferrocenophane system seems a reasonable possibility for the first step.

Nucleophilic attack at the phosphorus atom of tertiary phosphines is rather rare, but we expected that such attack might be successful at the phosphorus atom of the strained RP-bridged [1]ferrocenophanes. Chosen for study was the reaction of 1 with organolithium reagents which are well-known to be potent nucleophiles. We found that the reactions of 1 (and of 3) proceeded as shown in eq 1, that they were of type b in which the ferrocenophane system was opened. These reactions represent a new and useful synthesis of ferrocenyllithium reagents and by means of these reagents access is provided to diverse new mono- and disubstituted ferrocenes.



(1)

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It should be apparent that conversions of the type shown in eq 1 will be very condition dependent since a reaction of an organolithium reagent with a reactive substrate produces a new organolithium reagent. At the later stages of the reaction, the product organolithium species may be expected to compete with the reactant organolithium compound for the reactive substrate, the [1]-ferrocenophane. Two methods were found to deal with this potential complication: (1) addition of the [1]-ferrocenophane to an excess of the organolithium reagent in diethyl ether (soluble system) and (2) slow addition of the [1]ferrocenophane to an equimolar quantity of the organolithium reagent in hexane. The latter procedure is successful because the organolithium compound which is produced (11 in eq 1) is insoluble in hexane and thus its reaction with the ferrocenophane is minimized. This alternate procedure can give product yields of up to 70%, and it is preferred since an excess of the reactant organolithium reagent and of the final substrate is not required. The reactions which were carried out and the products which resulted are listed in Table III. All products are either phosphino- or arsinoferrocenes and, as such, may be of interest as ligands in transition-metal complexes.

In general, the products were isolated as golden yellow, crystalline solids. The ring-opening reaction proceeded most readily with phenyllithium. The reaction of 1 with methyllithium proceeded more slowly. *tert*-Butyllithium reacted more readily with the diethyl ether solvent used in the first experiment to give a new lithium reagent, $Me_3CCH_2CH_2Li$.[11] The latter then reacted with 1. The product formed in this reaction (after hydrolytic workup), $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4P(Ph)CH_2CH_2CMe_3)$, was an oil and was converted to the crystalline phosphine sulfide. This complication was avoided by carrying out the *t*-BuLi/1 reaction in hexane; the product, after hydrolysis and treatment with elemental sulfur, was the expected $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4P(S)(Ph)CMe_3$.

An attempt to extend this [1]ferrocenophane ring-opening chemistry to Grignard reagents was not successful. Phenylmagnesium bromide did not react with 1 in THF at room temperature, and only decomposition to a black powder occurred when such a reaction mixture was heated at reflux for 4 h.

The RLi/[1]ferrocenophane reactions may be carried out in such a way that the subsequent reaction of the product lithium species (11 in eq 1) with as yet unconverted [1]-ferrocenophane is favored. This produces oligomers, and such chemistry will be the subject of the next paper of this series.

It has been reported[3] that attempts to prepare organotin-bridged [1]ferrocenophanes were unsuccessful, only polymeric products (which were only partially characterized) being obtained. We have carried out reactions of 1,1′-dilithioferrocene–tetramethylethylenediamine complex with diethyl- and di-*n*-butyltin dichloride in hexane. A ferrocenophane of type 12 was not obtained. The major product in each reaction was a tan, insoluble, obviously polymer solid. However, in each reaction a low yield of an orange crystalline solid could be isolated. These products were identified as **13a** and **13b** on the basis of their combustion analyses and mass spectra (which showed the molecular ion, M^+). The electronic spectra of **13a** and **13b** showed λ_{max} at 465 nm with ϵ 171 cm^2/mol. This represents a shift to lower energy of about 25 nm from ferrocene and thus may be indicative of some degree of ring tilt. The ^{13}C NMR spectrum of **13a** suggests that only a very small amount of bond distortion at C(1) and C(1′) is occurring since the signal due to these carbon atoms is observed at δ_C 67.7. A crystal structure determination of **13a** or **13b** would be of interest, and we hope to report on the results of such a study at a later date.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen unless otherwise indicated. Air- and/or moisture-sensitive materials were handled either in a Vacuum Atmospheres HE-43 Dri-Lab glovebox or with use of standard Schlenk techniques. Hexane, benzene, toluene, diethyl

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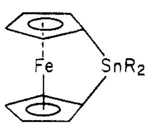
[11] (a) Bartlett, P. D.; Friedman, S.; Stiles, M. *J. Am. Chem. Soc.* **1953**, *75*, 1771. (b) Bartlett, P. D.; Tauber, S. J.; Weber, W. P. *Ibid.* **1969**, *91*, 6362.



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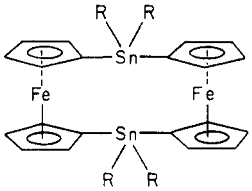

13a, R = Et
b, R = *n*-Bu

ether, and tetrahydrofuran (THF) were purified by distillation from potassium or sodium benzophenone ketyl under a nitrogen atmosphere. All other solvents were of reagent grade and were used without further purification unless oxygen-free solvent was needed; then the solvent was purged with nitrogen for ca. 15 min. For the more air-stable compounds thin-layer chromatography (TLC) could be used to monitor the progress of the reaction being studied (Eastman or J. T. Baker silica gel plates), and filtration chromatography could be used to isolate the desired product by using silicic acid as the support (Mallinckrodt reagent, 100 mesh). The colors of the compounds made visualization of the chromatographs straightforward.

1,1′-Dilithioferrocene–tetramethylethylenediamine was prepared according to the published procedure of Davison and coworkers[6] and stored in the glovebox. Ferrocene (Strem) and *n*-butyllithium (Alfa/Ventron, solution in hexane) were obtained from commercial sources and used as received. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA, Aldrich) was distilled from barium oxide under nitrogen. Phenyldichlorophosphine (Alfa/Ventron) and methyldichlorophosphine (Ethyl Corp.) were distilled at reduced pressure and atmospheric pressure, respectively, under a nitrogen atmosphere immediately prior to use. Phenyldichloroarsine was prepared by the method of Michaelis[12] and distilled at reduced pressure prior to use (bp 102–103 °C at 4 mm (lit.[12] 249 °C at 760 mm)). Phenyllithium was prepared according to the published procedure[13] as a solution in diethyl ether. Phenyllithium, methyllithium (Alfa/Ventron, solution in ether), and *tert*-butyllithium (Alfa/Ventron, solution in *n*-pentane) were all assayed prior to use according to the double titration method of Gilman.[14] All other specific reagents were prepared and/or purified prior to use as indicated and referenced in the detailed experimental procedure of each reaction.

Proton nuclear magnetic resonance spectra were recorded at 60 MHz on a Varian Assoc. T-60 or Hitachi Perkin-Elmer R-24B spectrometer and at 250 MHz on a Brüker WK-250 spectrometer operating in the Fourier transform mode. Chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane. Phosphorus-31 NMR spectra were recorded on either a Brüker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system or on a JEOL FX-90Q spectrometer both operating at 36.2 MHz in the Fourier transform mode. The ^{31}P chemical shifts are reported in δ_P units, parts per million downfield from 85% aqueous H_3PO_4 using external triphenylphosphine (in the same solvent as the sample) as the referenced signal at −6 ppm. Carbon-13 NMR spectra were recorded on a JEOL FX-90Q spectrometer operating at 22.4 MHz in the Fourier transform mode. Infrared spectra were obtained by using a Perkin-Elmer 457A double-beam grating spectrophotomer. Solution samples were contained in 0.1-mm path length sodium chloride solution cells. Mass spectra were recorded on a Varian MAT-44 mass spectrometer operating at 70 eV. Samples were submitted in sealed evacuated vials when necessary. Electronic spectra were recorded on a Cary 17 instrument in nitrogen-purged 1.0 mm solution cells. Melting points were determined by using analytically pure samples, which were sealed in evacuated or nitrogen-filled capillaries, on a Büchi melting point apparatus and are uncorrected.

General Procedure for the Preparation of Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes and Tin-Bridged [1.1]Ferrocenophanes. A 300-mL three-necked, Morton flask was charged with the appropriate amount of 1,1′-dilithioferrocene–tetramethylethylenediamine in the glovebox. The flask was fitted with a gas inlet tube and two noair stoppers and then was removed from the glovebox and attached to a Schlenk manifold. The no-air stopper of the middle neck was replaced with a mechanical stirring unit against a counterflow of nitrogen. Hexane (ca. 200 mL) was cannulated into the flask and the yellow slurry cooled to −78 °C while being stirred.

Meanwhile, a flame-dried, nitrogen-purged, 50-mL one-necked round-bottom flask was charged with the appropriate amount of phosphine, arsine, or tin dichloride. To this was added 25 mL of hexane, and the solution was cooled to −78 °C. This solution was then cannulated into the flask containing the dilithioferrocene/hexane slurry, and the resulting mixture was stirred vigorously while it was allowing to warm slowly. In all cases but the tin dichloride reactions a red color began to appear above 0 °C. At the point where the red color reached its greatest intensity (usually near room temperature) the stirring was stopped and the orange-tan solid settled to the bottom of the flask fairly rapidly. In the tin dichloride reactions no color change was observed and the reaction mixture was stirred at room temperature overnight. The remaining workup was analogous. The reaction mixture was treated with 5–10 mL of saturated aqueous NH_4Cl solution. The "dry endpoint" was difficult to determine. The mixture was filtered under nitrogen, and the solvent was removed in vacuo. The resulting residue was placed under vacuum (0.03 mm) overnight and then extracted under nitrogen with hexane until the extracts were colorless. The extracts were combined, concentrated in vacuo, and cooled to −30 °C under nitrogen to yield crystalline material. During recrystallization of the phosphine- and arsine-bridged [1]ferrocenophanes a small amount of yellow precipitate formed which was not soluble in hexane. It was not characterized. Analytical samples were recrystallized three times prior to analysis.

A. Reaction of 1,1′-Dilithioferrocene–Tetramethylethylenediamine with Phenyldichlorophosphine. Following the general procedure, a reaction was carried out between 1,1′-dilithioferrocene–tetramethylethylenediamine (6.00 g, 18.9 mmol) and $PhPCl_2$ (2.58 mL, 19.0 mmol). Recrystallization from hexane at −30 °C yielded 2.12 g (7.2 mmol, 38%) of moderately air-sensitive, brick-red nuggets. The product must be stored under nitrogen but could be handled in air for weighing and transfer purposes. It was identified as (1,1′-ferrocenediyl)phenylphosphine: mp 100–102 °C; IR (CH_2Cl_2) 3070 (w), 3040 (w), 2955 (w), 1584 (m), 1481 (m), 1430 (w), 1379 (m), 1321 (w), 1292 (w), 1186 (m), 1117 (s), 1069 (w), 1031 (s), 1019 (s), 880 (m), 854 (m), 812 (s), 662 (w) cm^{-1}; ^1H NMR (toluene-d_8) δ 4.55 (m, 2 H, Cp), 4.27 (m, 6 H, Cp), 7.22 (m, 3 H, Ph), 7.60 (m, 2 H, Ph); $^{31}P\{^1H\}$ NMR (C_6D_6) δ_P +11.5 (s); UV-vis (hexane) λ 498 (ϵ 408 cm^2 mol^{-1}), 415 nm (sh, 123); mass spectrum, *m/e* (relative intensity) 292 (M^+, 100). Anal. Calcd for $C_{16}H_{13}FeP$ (292.11); C, 65.78; H, 4.49. Found: C, 66.02; H, 4.57.

B. Reaction of 1,1′-Dilithioferrocene–Tetramethylethylenediamine with Methyldichlorophosphine. Following the general procedure a reaction was carried out between 1,1′-dilithioferrocene–tetramethylethylenediamine (5.00 g, 15.8 mmol) and $MePCl_2$ (1.44 mL, 16.0 mmol). The red color, indicating product formation, occurred between 10 and 20 °C and is a somewhat subtle change. Recrystallization from hexane at −30 °C yielded 0.68 g (3.0 mmol, 19%) of moderately air-sensitive, brick-red flakes identified as (1,1′-ferrocenediyl)methylphosphine: mp 70–72 °C dec; Ir (CH_2Cl_2) 3091 (w), 3038 (w), 2961 (w), 2918 (w), 1405 (w), 1378 (m), 1287 (m), 1185 (m), 1128 (s), 1105 (m), 1031 (m), 1028 (s), 884 (s), 852 (m), 811 (s), 660 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 1.38 (d, 3 H, J(P–H) = 6 Hz, CH_3), 4.28 (m, 6 H, Cp), 4.41 (m, 2 H, Cp); $^{31}P\{^1H\}$ NMR (C_6H_6) δ_P −13.2 (s); UV-Vis (hexane) λ 498 (ϵ 410 cm^2 mol^{-1}), 404 (sh, (108), 315 nm (sh, (486); mass spectrum, *m/e* (relative intensity) 230 (M^+, 100), 215 ($M^+ - CH_3$, 20.5). Anal. Calcd for $C_{11}H_{11}FeP$ (230.04); C, 57.43; H, 4.83. Found: C, 57.39; H, 4.78.

C. Reaction of 1,1′-Dilithioferrocene–Tetramethylethylenediamine with Phenyldichloroarsine. Following the general procedure a reaction was carried out between 1,1′-dilithioferrocene-tetramethylethylenediamine (5.00 g, 15.8 mmol) and $PhAsCl_2$ (2.20 mL, 16.5 mmol). Recrystallization from hexane at −30 °C yielded 1.77 g (5.3 mmol, 34%) of slightly air-sensitive, brick-red nuggets identified as (1,1′-ferrocenediyl)phenylarsine:

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(12) Michaelis, A. *Ber. Dtsch. Chem.* Ges. **1875**, *8*, 1316.

(13) Jones, R. G.; Gilman, H. *Org. React.* **1951**, *6*, 339.

(14) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.

mp 107.5–109 °C; IR (CCl_4) 3095 (vw), 3070 (w), 3059 (vw), 3012 (vw), 2999 (vw), 2955 (w), 2925 (w), 2860 (w), 1576 (w), 1480 (m), 1432 (m), 1378 (w), 1299 (w), 1187 (m), 1147 (w), 1122 (s), 1079 (w), 1064 (w), 1027 (s), 1014 (s), 1000 (vw), 910 (w), 886 (w), 871 (m), 846 (w), 699 (s), 675 (w), 639 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 4.33 (m, 6 H, Cp), 4.52 (m, 2 H, Cp), 7.10 (m, 3 H, Ph), 7.55 (m, 2 H, Ph); UV–vis (hexane) λ 494 (ϵ 312 cm^2 mol^{-1}), 408 nm (sh, 117); mass spectrum, *m/e* (relative intensity) 337 (M^+, 2.2), 260 (M^+ – Ph, 2.4). Anal. Calcd for $C_{16}H_{13}AsFe$ (336.06): C, 57.18; H, 3.91. Found: C, 57.10; H, 4.09.

D. Reaction of 1,1′-Dilithioferrocene–Tetramethylethylenediamine with Diethyltin Dichloride. Following the general procedure, a reaction was carried out between 1,1′-dilithioferrocene–tetramethylethylenediamine (5.00 g, 15.8 mmol) and Et_2SnCl_2 (4.00 g, 16.1 mmol, M&T Chemicals, recrystallized from hexane). During the course of reaction no color change was observed and the mixture was stirred vigorously at room temperature overnight. The stirring was stopped, and the tan-yellow precipitate settled to the bottom leaving an orange-yellow hexane layer. TLC (25% dichloromethane/75% hexane mixture) indicated an orange band eluting with a similar R_f as ferrocene, but the color was too orange for it to be ferrocene. Workup was continued as described in the General Procedure. The golden solid obtained from the recrystallization step was further purified by filtration chromatography, eluting with a 25% dichloromethane/75% hexane mixture. The major band, upon removal of the solvent, gave 0.46 g of a golden solid. Recrystallization from hexane at –30 °C yielded 0.35 g (0.5 mmol, 6%) of air-stable, gold nuggets identified as 1,1,12,12-tetraethyl[1.1]stannaferrocenophane: mp 189–190 °C; ^1H NMR ($CDCl_3$) δ 0.37–1.93 (m, 10 H, Et including ^{117}Sn and ^{119}Sn satellites), 4.13 (t, 4 H, J = 1.8 Hz, Cp), 4.36 (t, 4 H, J = 1.8 Hz, Cp); ^{13}C NMR (C_6D_6) δ_C 4.3 (CH_3), 11.2 (CH_2), 67.7 (C(1), ipso C), 70.7 (C(2)), 75.0 (C(3)) (proton decoupled); UV–vis (CH_2Cl_2) λ 465 (ϵ 171 cm^2 mol^{-1}), 330 nm (92); mass spectrum, *m/e* (relative intensity) 722 (M^+, 21.9%), 693 (M^+ – Et, 45.9), 661 (M^+ – 2Et, 43.2), 635 (M^+ – 3Et, 24.0), 606 (M^+ – 4Et, 69.2), for mass range of *m/e* 800–400. Anal. Calcd for $C_{28}H_{36}Fe_2Sn_2$ (721.72): C, 46.59; H, 5.04. Found: C, 46.63; H, 5.02.

E. Reaction of 1,1′-Dilithioferrocene–Tetramethylethylenediamine with Di-*n*-butyltin Dichloride. Following the general procedure and the procedure described in the previous experiment, a reaction was carried out between 1,1-dilithioferrocene–tetramethylethylenediamine (4.00 g, 12.6 mmol) and n-Bu_2SnCl_2 (3.95 g, 13.0 mmol, M&T Chemicals, recrystallized from hexane). The reaction mixture was stirred for 2 h at room temperature, and no color change was observed. The workup was as before. Filtration chromatography (15% dichloromethane/85% hexane) removed an orange band which gave 0.46 g of a golden solid upon removal of the solvent. Subsequent recrystallization from hexane at –30 °C yielded 0.204 g (0.2 mmol, 3%) of golden nuggets identified as 1,1,12,12-tetra-*n*-butyl[1.1]stannaferrocenophane: mp 140–141 °C; ^1H NMR ($CDCl_3$) δ 0.73–1.60 (m, 18 H, Bu including ^{117}Sn and ^{119}Sn satellites), 4.15 (t, 4 H, J = 1.8 Hz, Cp), 4.37 (t, 4 H, J = 1.8 Hz, Cp); UV–vis (CH_2Cl_2) λ 465 (ϵ 174 cm^2 mol^{-1}), 332 nm (90); mass spectrum, *m/e* (relative intensity) 834 (M^+, 31.9), 777 (M^+ – 1Bu, 100.0), 663 (M^+ – 3Bu, 37.5), 606 (M^+ – 4Bu, 47.2), 486 (M^+ – 4Bu – Sn, 26.8), for mass range of *m/e* 850–400. Anal. Calcd for $C_{36}H_{52}Fe_2Sn_2$ (833.96): C, 51.84; H, 6.30. Found: C, 51.91; H, 6.23.

A similar reaction was performed by using 1,2-dimethoxyethane instead of hexane as the solvent but only the tin–ferrocene polymer was produced. No [1.1]stannaferrocenophane was isolated.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Sulfur. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir bar, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and two no-air stoppers was flame-dried under a nitrogen purge and then charged with 0.10 g (3.1 mmol) of sulfur (J. T. Baker, sublimed grade). A solution of (1,1′-ferrocenediyl)phenylphosphine (0.30 g, 1.0 mmol) in benzene (20 mL) was prepared under nitrogen and cannulated into the flask containing the sulfur. After 15 min of stirring at room temperature, the color of the reaction mixture was red-brown (a very subtle change) and TLC (pentane) indicated no starting phosphine remained, only an orange band eluting with dichloromethane. The solvent was removed in vacuo to give a red-brown solid, and the excess of sulfur was removed by sublimation at ca. 40 °C and 0.03 mmHg. Recrystallization of the red-brown solid from toluene at –10 °C yielded 0.13 g (0.4 mmol, 40%) of moderately air-stable red-brown microcrystals identified as (1,1′-ferrocenediyl)phenylphosphine sulfide: mp > 280 °C (slowly turns black); IR (CH_2Cl_2) 3079 (w), 3038 (w), 2965 (w), 1481 (w), 1435 (w), 1382 (m), 1332 (w), 1308 (vw), 1296 (m), 1190 (m), 1125 (s), 1069 (w), 1032 (m), 1019 (s), 1000 (w), 884 (m), 861 (w), 820 (s), 659 (w), 598 (w) cm^{-1}. ^1H NMR (C_6D_6 δ 3.57 (m, 2 H, Cp), 4.02–4.27 (m, 4 H, Cp), 4.88 (m, 2 H, Cp), 7.01 (m, 3 H, Ph), 7.68 (m, 2 H, Ph), mass spectrum, *m/e* (relative intensity) 324 (M^+, 39.7), 291 (M^+ – SH, 10.6). Anal. Calcd for $C_{16}H_{13}FePS$ (324.17): C, 59.28; H, 4.05. Found: C, 59.17; H, 4.10.

A similar reaction was carried out between (1,1′-ferrocenediyl)methylphosphine (0.23 g, 1.0 mmol) and sulfur (0.10 g, 3.0 mmol) in 20 mL of benzene for 30 min. Recrystallization from a toluene/hexane mixture at –30 °C yielded 0.08 g (0.3 mmol, 30%) of moderately air-stable, red-brown microcrystals identified as (1,1′-ferrocenediyl)methylphospnine sulfide: mp > 250 °C (slowly turns black); ^1H NMR (C_6D_6) δ 1.48 (d, J_{P-H} = 14 Hz, 3 H, CH_3), 3.64 (m, 2 H, Cp), 4.15 (m, 4 H, Cp), 4.68 (m, 2 H, Cp); mass spectrum, *m/e* (relative intensity) 262 (M^+, 100), 247 (M^+ – CH_3, 54.2). Anal. Calcd for $C_{11}H_{11}FePS$ (262.10): C, 50.40; H, 4.24. Found: C, 50.09; H, 4.25.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Pentacarbonyl(tetrahydrofuran)tungsten. A 300-mL three-necked, round-bottomed Pyrex flask equipped with a magnetic stir bar, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and two no-air stoppers was flame-dried under a nitrogen purge and then charged with 0.70 g (2.0 mmol) of $W(CO)_6$ (Pressure Chem. Co., as received) and ca. 200 mL of THF. Nitrogen was bubbled through the mixture as it was stirred and irradiated with a 140-W Hanovia high-pressure mercury lamp. After several minutes, all of the $W(CO)_6$ had dissolved and the solution became yellow. The irradiation was maintained for 4 h at the end of which time the solution was a dark yellow-orange.

The irradiation was stopped, and a solution of (1,1′-ferrocenediyl)phenylphosphine (0.30 g, 1.0 mmol) in 20 mL of THF was cannulated into the flask. The red-orange solution was stirred at room temperature for 4 h until TLC indicated that no more starting phosphine remained. The solvent was removed in vacuo to give a red solid. The product was purified by filtration chromatography (20% dichloromethane/80% pentane mixture) which eluted a red orange band. Removal of the solvent and subsequent recrystallization from a 50% dichloromethane/50% pentane mixture at –30 °C yielded 0.18 g (0.3 mmol, 30%) of air-stable red nuggets identified as pentacarbonyl[1,1′-ferrocenediyl)phenylphosphine)tungsten: mp > 180 °C (slowly turns brown); Ir (CH_2Cl_2) 3050 (m), 2988 (m), 1190 (m), 1155 (w), 1121 (m), 1109 (m), 1072 (w), 1060 (w), 1038 (m), 1023 (m), 1001 (w), 938 (w), 892 (m), 854 (w), 820 (m), 660 (w), 599 (w), 573 (w)cm^{-1}; terminal carbonyl region, 2069 (s), 2051 (w), 1981 (w), 1939 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 4.38 (m, 2 H, Cp), 4.57 (m, 4 H, Cp), 4.82 (m, 2 H, Cp), 7.35–8.21 (m, 5 H, Ph); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ_P +25.1 (s with ^{183}W satellites, J(P–W = 247 Hz); UV–vis (CH_2Cl_2) λ 494 nm (ϵ 439 cm^2 mol^{-1}); mass spectrum, *m/e* (relative intensity) 616 (M^+, 10.8), 532 (M^+ – 3CO, 4.1), 504 (M^+ – 4CO, 12.0), 476 (M^+ – 5CO, 41.0), 419 (M^+ – 5CO – Fe, 28.1). Anal. Calcd for $C_{21}H_{13}FeO_5PW$ (616.01): C, 40.94; H, 2.13. Found: C, 40.61; H, 2.15.

Reaction of (1,1′-Ferrocenediyl)phenylarsine with Pentacarbonyl(tetrahydrofuran)tungsten. Following the procedure outlined in the previous experiment for the phosphorus analogue, a reaction was carried out between (1,1′-ferrocenediyl)phenylarsine (0.34 g, 1.0 mmol) and $(THF)W(CO)_6$ formed from 1.41 g (4.0 mmol) of $W(CO)_6$. The product was purified by filtration chromatography (20% dichloromethane/80% pentane mixture) which eluted an orange-red band. Removal of the solvent and subsequent recrystallization from a 30% dichloromethane/70% pentane mixture at –30 °C yielded 0.34 g (0.5 mmol, 51%) of air-stable, red prisms identified as pentacarbonyl[1,1′-ferrocenediyl)phenylarsine]tungsten: mp 174.5–175.5 °C dec; IR (CH_2Cl_2) 3075 (w), 1481 (w), 1435 (vw), 1379 (w), 1330 (vw), 1299 (w), 1189 (m), 1114 (m), 1084 (w), 1056 (vw), 1032 (m), 1017 (s), 1000 (m), 938 (w), 874 (w), 850 (vw), 816 (s), 645 (vw), 597 (m), 573 (s) cm^{-1}; terminal carbonyl region, 2080 (s), 1985 (w), 1945 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.30 (m, 2 H, Cp), 4.44 (m, 4 H, Cp), 4.70 (m, 2 H, Cp), 7.32–7.66 (m, 5 H, Ph); UV–vis (CH$_2$Cl$_2$) λ 492 nm (ε 330 cm^2 mol^{-1}); mass spectrum, *m/e* (relative intensity) 660 (M$^+$, 70.6), 518 (M$^+$ − 5CO, 100.0), for mass range of *m/e* 680–500. Anal. Calcd for $C_{21}H_{13}AsFeO_5W$ (659.96): C, 38.22; H, 1.99. Found: C, 38.16; H, 2.00.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Tetracarbonyl(tetrahydrofuran)iron. A 100-mL three-necked, round-bottomed flask was charged with 1.45 g (4.0 mmol) of $Fe_2(CO)_9$ (Strem Chem. Co., as received) in the glovebox. The flask was fitted with a magnetic stir bar, a gas inlet tube, and two no-air stoppers, then removed from the glovebox, and placed on a Schlenk manifold. The flask was flushed with carbon monoxide (Matheson, research purity) for 5 min, and then 25 mL of THF was added by syringe. This gave a brown mixture in which not all of the $Fe_2(CO)_9$ had dissolved. The mixture was stirred under a carbon monoxide atmosphere at room temperature for 30 min after which time a solution of (1,1′-ferrocenediyl)phenylphosphine (0.3 g, 1.0 mmol) in 10 mL of THF was cannulated into the $Fe_2(CO)_9$/THF mixture. There was no noticeable color change, and TLC indicated the reaction to be complete after 3 h of stirring at room temperature. The mixture was filtered under nitrogen and the solvent removed in vacuo to give a glossy brown semisolid.

The product was purified by filtration chromatography eluting with a nitrogen-purged 15% dichloromethane/85% pentane mixture. The first band eluted was green and not identified (probably $Fe_3(CO)_{12}$). The second band eluted was red-orange and subsequent recrystallization from a toluene/hexane mixture under nitrogen yielded 0.21 g (0.5 mmol, 45%) of moderately air-sensitive, red microcrystals identified as tetracarbonyl[(1,1′-ferrocenediyl)phenylphosphine]iron: mp 137–139 °C; IR (CH$_2$Cl$_2$) 3090 (w), 3033 (w), 2920 (w), 1572 (w), 1483 (m), 1435 (w), 1385 (m), 1331 (w), 1309 (vw), 1294 (m), 1189 (s), 1121 (s), 1107 (s), 1071 (w), 1060 (w), 1039 (m), 1023 (s), 1000 (w), 884 (m), 856 (m), 820 (s), 618 (s) cm^{-1}; terminal carbonyl region (CCl$_4$), 2058 (s), 1980 (vs), 1941 (vs) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 3.72 (m, 2 H, Cp), 3.88–3.98 (m, 4 H, Cp), 4.85 (m, 2 H, Cp), 6.98 (m, 3 H, Ph), 7.52 (m, 2 H, Ph); mass spectrum, *m/e* (relative intensity) 460 (M$^+$, 0.6), 432 (M$^+$ − CO, 3.5), 404 (M$^+$ − 2CO, 1.2), 376 (M$^+$ − 3CO, 4.6), 348 (M$^+$ − 4CO, 62.1), 292 (M$^+$ − 4CO − Fe, 22.1). Anal. Calcd for $C_{20}H_{13}Fe_2O_4P$ (460.00): C, 52.22; H, 2.85. Found: C, 52.36; H, 2.91.

Attempted Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Iodomethane. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir bar, a gas inlet tube leading to a Schlenk manifold, and two no-air stoppers was charged with 0.500 g (1.71 mmol) of (1,1′-ferrocenediyl)phenylphosphine, evacuated, and refilled with nitrogen. Benzene (30 mL) and iodomethane (1.0 mL, 17.1 mmol, Eastman, as received) were added by syringe. The red solution was stirred at room temperature for 24 h, after which time a pink precipitate had deposited, leaving a nearly colorless benzene layer. The precipitate was filtered under nitrogen, washed with 3 × 15-mL portions of benzene, and dried in vacuo to yield 0.550 g (1.27 mmol, 74%) of a tan-orange powder.

Attempts to fully characterize this powder proved difficult due to its apparent instability in solution. It was insoluble in hexane, benzene, THF, and ethyl acetate and slightly soluble in acetone. It was soluble in CH$_2$Cl$_2$, CHCl$_3$, and MeOH, but after initially dissolving it began to deposit a tan precipitate, all done with the exclusion of air. Attempts to prepare the Reinecke salt from $NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$ in MeOH proved unsuccessful; only a small amount of a pink precipitate formed which was insoluble in all solvents. To test whether the iodide anion might be attacking the ferrocenophane ring as in the nucleophilic ring-opening reactions, a reaction was carried out between 0.300 g (1.03 mmol) of (1,1′-ferrocenediyl)phenylphosphine and 0.150 g (1.00 mmol) of NaI in 35 mL of acetone at room temperature. No reaction occurred, and the starting phosphine was recovered in 90% yield.

The tan-orange powder was partially characterized by the following data: IR (CDCl$_3$) 3042 (m), 2954 (w), 2875 (m), 1584 (w), 1481 (w), 1433 (m), 1386 (m), 1302 (sh), 1292 (m), 1259 (w), 1182 (s), 1122 (sh), 1111 (s), 1021 (s), 993 (w), 867 (m), 816 (m), 778 (w), 680 (m), 631 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.85 (d, J_{H-P} = 15 Hz, 3 H, Me), 4.45 (m, 2 H, Cp), 4.88 (m, 4 H, Cp), 5.75 (m, 2 H, Cp), 7.58–8.36 (m, 5 H, Ph); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ_P +36.0 (s).

General Procedure for the Reaction of (1,1′-Ferrocenediyl)phenylphosphine or -arsine with an Excess of Organolithium Reagent Followed by the Reaction with Electrophilic Reagents. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, a gas inlet tube leading to a Schlenk manifold, a pressure-equalizing dropping funnel, and two no-air stoppers was evacuated, flame-dried, and refilled with nitrogen. The flask was charged with a 10–15-fold excess of the appropriate organolithium reagent and 20 mL of diethyl ether by syringe. Separately, a solution of (1,1′-ferrocenediyl)phenylphosphine or -arsine in 20 mL of diethyl ether was prepared under nitrogen and then added to the dropping funnel by cannula. This red solution was added dropwise to the lithium reagent at room temperature over a 30-min period. Upon completion of the addition, the reaction mixture was a golden brown color and was stirred for an additional 30 min at room temperature. The reaction mixture was then cooled to 0 °C, and the appropriate electrophilic reagent and 10 mL of diethyl ether (except when the reagent was water) were added to the dropping funnel by syringe. The resulting solution was added dropwise to the ferrocenyllithium reagent during 10 min. The reaction mixture was now golden yellow and was stirred for an additional 10 min at room temperature.

The workup consisted of filtering the reaction mixture and removing the solvent on a rotary evaporator. The product was further purified by using filtration chromatography and recrystallization when possible. In some cases the phosphine was converted to the phosphine sulfide so that a crystalline solid could be obtained to facilitate characterization. The details are given in each experiment. All the products were air-stable, both as solids and in solution.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Phenyllithium and Subsequent Reaction with Water. Following the general procedure, a reaction was carried out between 0.30 g (1.0 mmol) of (1,1′-ferrocenediyl)phenylphosphine and 15.0 mL (15.0 mmol) of 1.0 M PhLi in diethyl ether. The ferrocenyllithium reagent thus formed was hydrolyzed to the "dry end point" with saturated aqueous NH$_4$Cl solution. Separation of the desired product was achieved by using filtration chromatography, eluting with a 40% dichloromethane/60% pentane mixture. A yellow band was removed which, upon evaporation of the solvent on a rotary evaporator and subsequent recrystallization from hexane at −30 °C, yielded 0.29 g (0.8 mmol, 80%) of golden yellow prisms identified as 1-(diphenylphosphino)ferrocene, $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_5)$, mp 120–123 °C (lit.[15] 122–124 °C), by comparison of its IR and NMR spectra with those of the previously prepared compound found in the literature.[15] Its electronic and ^{31}P NMR spectra were recorded: UV–vis (CH$_2$Cl$_2$) λ 440 nm (ε 143 cm^2 mol^{-1}); ^{31}P{^{1}H} NMR (CDCl$_3$) δ_P −17.1 (s).

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Phenyllithium and Subsequent Reaction with Chlorodiphenylphosphine. Following the general procedure, a reaction was carried out between 0.30 g (1.0 mmol) of (1,1′-ferrocenediyl)phenylphosphine and 15.0 mL (15.0 mmol) of 1.0 M PhLi in diethyl ether. The ferrocenyllithium reagent thus formed was allowed to react with 2.78 mL (15.0 mmol) of Ph$_2$PCl (Alfa/Ventron, distilled in vacuo). The desired product was isolated by using filtration chromatography eluting with a 50% dichloromethane/50% pentane mixture. A yellow band eluted which, upon removal of the solvent and subsequent recrystallization from a 35% benzene/65% hexane mixture at −10 °C, yielded 0.45 g (0.8 mmol, 79%) of golden yellow rods identified as 1,1′-bis(diphenylphosphino)ferrocene, $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$; mp 184–185 °C (lit.[6] 183–184 °C), by comparison of its NMR and IR spectra with those reported in the literature.[6] Its mass spectrum showed the molecular ion at *m/e* 554 (3.3): ^{31}P{^{1}H} NMR (CDCl$_3$) δ_P −17.9 (s).

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Phenyllithium and Subsequent Reaction with Chlorotrimethylsilane. Following the general procedure, a reaction was

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[15] Sollott, G. P.; Mertwoy, H. E.; Portnoy, S.; Snead, J. L. *J. Org. Chem.* **1963**, *28*, 1090.

carried out between 0.30 g (1.0 mmol) of (1,1′-ferrocenediyl)phenylphosphine and 10.0 mL (10.0 mmol) of 1.0 M PhLi in diethyl ether. The ferrocenyllithium reagent thus formed was allowed to react with 1.9 mL (15.0 mmol) of Me_3SiCl (Alfa/Ventron, distilled under nitrogen). The desired product was isolated by using filtration chromatography eluting with a 20% dichloromethane/80% pentane mixture to give a golden brown oil upon removal of the solvent. Filtration chromatography was repeated on the oil eluting with a 10% dichloromethane/90% pentane mixture to yield 0.45 g (1.0 mmol, 99%) of a golden brown oil identified as analytically pure 1-(diphenylphosphino)-1′-(trimethylsily)ferrocene, $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SiMe_3)$: ^1H NMR ($CDCl_3$) δ 0.36 (s, 9 H, Me), 4.18 (m, 4 H, Cp), 4.30 (t, 2 H, Cp, J = 10 Hz), 4.44 (t, 2 H, Cp, J = 10 Hz), 7.28–7.45 (m, 10 H, Ph); mass spectrum, m/e (relative intensity) 442 (M^+, 2.0), 370 ($M^+ - SiMe_3$, 2.4), 365 (M^+ − Ph, 2.4), 293 (M^+ − 2Ph, 5.3). Anal. Calcd for $C_{25}H_{27}FePSi$ (442.43): C, 67.86; H, 6.16. Found: C, 68.00; H, 6.29.

Reaction of (1,1′-Ferrocenediyl)phenylarsine with Phenyllithium and Subsequent Reaction with Water. Following the general procedure, a reaction was carried out between 0.35 g (1.1 mmol) of (1,1′-ferrocenediyl)phenylarsine and 7.6 mL (11.0 mmol) of 1.4 M PhLi in diethyl ether. The ferrocenyllithium reagent thus formed was hydrolyzed with saturated aqueous NH_4Cl solution to the "dry end point". The product was isolated by using filtration chromatography (20% dichloromethane/80% pentane) and subsequent recrystallization from a dichloromethane/pentane mixture afforded 0.32 g (0.8 mmol, 73%) of golden prisms identified as 1-(diphenylarsino)ferrocene, $(\eta^5\text{-}C_5H_4AsPh_2)Fe(\eta^5\text{-}C_5H_5)$: mp 129–130 °C; ^1H NMR ($CDCl_3$) δ 4.08 (s, 7 H, Cp), 4.28 (t, 2 H, J = 2 Hz, Cp), 7.17–7.47 (m, 10 H, Ph); mass spectrum, m/e (relative intensity) 414 (M^+, 3.4), 337 (M^+ − Ph, 5.0), 262 (M^+ PhAs, 10.0). Anal. Calcd for $C_{22}H_{19}AsFe$ (414.18): C, 63.79; H, 4.63. Found: C, 63.84; H, 4.66.

Reaction of (1,1′-Ferrocenediyl)phenylarsine with Phenyllithium and Subsequent Reaction with Chlorodiphenylphosphine. Following the general procedure, a reaction was carried out between 0.35 g (1.1 mmol) of (1,1′-ferrocenediyl)phenylarsine and 6.9 mL (10.0 mmol) of 1.4 M PhLi in diethyl ether. The resulting ferrocenyllithium reagent was allowed to react with 1.85 mL (10.0 mmol) of Ph_2PCl (Alfa/Ventron, distilled in vacuo). The product was isolated by using filtration chromatography (50% dichloromethane/50% pentane mixture), affording a yellow fraction which, upon removal of the solvent and subsequent recrystallization from a 10% benzene/90% hexane mixture at −30 °C, yielded 0.32 g (0.53 mmol, 53%) of golden nuggets identified at 1-(diphenylarsino)-1′-(diphenylphosphino)ferrocene, $(\eta^5\text{-}C_5H_4AsPh_2)Fe(\eta^5\text{-}C_5H_4PPh_2)$: mp 164–165.5 °C; ^1H NMR ($CDCl_3$) δ 3.85–4.03 (m, 4 H, Cp), 4.12–4.22 (m, 4 H, Cp), 7.10–7.37 (m, 20 H, Ph); mass spectrum, m/e (relative intensity) 599 (M^+, 100.0), for mass range m/e 610–520. Anal. Calcd for $C_{34}H_{28}AsFeP$ (598.36): C, 68.24; H, 4.73. Found: C, 67.96; H, 4.76.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Methyllithium and Subsequent Reaction with Water. Following the general procedure, a reaction was carried out between 0.30 g (1.0 mmol) of (1,1′-ferrocenediyl)phenylphosphine and 10.0 mL (15.0 mmol) of 1.5 M MeLi in diethyl ether. Upon completion of the addition of the phosphine to the MeLi, the reaction mixture was stirred at room temperature for 2 h. The ferrocenyllithium reagent thus formed was hdyrolyzed to the "dry end point" with saturated aqueous NH_4Cl solution. TLC showed as many as five yellow fractions eluting with a 20% dichloromethane/80% pentane mixture. The first (major) fraction was isolated by using filtration chromatography with the same eluent. Removal of the solvent and subsequent recrystallization from hexane at −30 °C yielded 0.08 g (0.3 mmol, 29%) of yellow-orange needles identified as 1-(methylphenylphosphino)ferrocene, $(\eta^5\text{-}C_5H_4PPhMe)Fe(\eta^5\text{-}C_5H_5)$: mp 69–71 °C; ^1H NMR ($CDCl_3$) δ 1.58 (d, 3 H, J(P–H) = 4 Hz, CH_3), 4.20 (s, 5 H, Cp), 4.25–4.37 (m, 4 H, Cp), 7.18–7.47 (m, 5 H, Ph); mass spectrum, m/e (relative intensity) 308 (M^+, 66.0), 293 ($M^+ - CH_3$, 98.7). Anal. Calcd for $C_{17}H_{17}FeP$ (308.16): C, 66.25; H, 5.57. Found: C, 65.98; H, 5.56.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with *tert*-Butyllithium in Diethyl Ether and Subsequent Reaction with Water. Following the general procedure, a reaction was carried out between 0.500 g (1.7 mmol) of (1,1′-ferrocenediyl)phenylphosphine and 2.60 mL (5.0 mmol) of 1.92 M *t*-BuLi in *n*-hexane. When the addition was completed the reaction mixture was stirred for 1 h and then was hydrolyzed to the "dry end point" with saturated aqueous NH_4Cl solution. The filtered golden solution was evaporated to dryness in vacuo to give a golden brown oil. The oil was dissolved in 30 mL of oxygen-free absolute ethanol and treated with 0.064 g (2.0 mmol) of sulfur (J.T. Baker) under nitrogen at reflux overnight. TLC indicated two fractions eluting with a 35% dichloromethane/65% pentane mixture. The cooled reaction mixture was filtered and the solvent removed on a rotary evaporator. Filtration chromatography using the same eluent removed the first band which was minor and was not identified. The second fraction to be eluted was evaporated to dryness to give 0.363 g of an orange oil. Dissolution in hexane and cooling to −30 °C afforded two types of crystals: (1) flaky yellow needles and (2) dense yellow clusters (by far the major portion). The latter were separated by hand. The flaky yellow needles were not further characterized. Recrystallization of the dense yellow clusters from hexane at −30 °C yielded 0.200 g (0.5 mmol, 29%) of yellow needles identified as (2-*tert*-butylethyl)phenylferrocenylphosphine sulfide, $[\eta^5\text{-}C_5H_4P(S)Ph(CH_2CH_2CMe_3)]Fe(\eta^5\text{-}C_5H_5)$: mp 121–122 °C; 60-MHz ^1H NMR ($CDCl_3$) δ 0.88 (s, 9 H, *t*-Bu), 1.1–2.5 (m, 4 H, CH_2CH_2), 4.20 (s, 5 H, Cp), 4.42 (m, 3 H, Cp), 4.67 (m, 1 H, Cp), 7.37–8.17 (m, 5 H, Ph); 250-MHz ^1H NMR ($CDCl_3$) δ 0.87 (s, 9 H, *t*-Bu), 1.17–1.33 (m, ^1H CH_2CH_2) 1.60–1.76 (m, 1 H, CH_2CH_2), 2.11–2.29 (m, 2 H, CH_2CH_2), 4.19 (s, 5 H, Cp), 4.36 (m, 1 H, Cp), 4.41 (m, 1 H, Cp), 4.45 (m, 1 H, Cp), 4.65 (m, 1 H, Cp), 7.45–7.50 (m, 3 H, Ph), 7.87–7.96 (m, 2 H, Ph) (see Figure 1); mass spectrum, m/e (relative intensity) 410 (M^+, 1.3), 326 ($M^+ - CH_2CH_2CMe_3$, 1.1), 293 ($M^+ - CH_2CH_2CMe_3$ − S, 1.5), 186 (ferrocene, 24.9). Anal. Calcd for $C_{22}H_{27}FePS$ (410.37): C, 64.39; H, 6.64. Found: C, 64.12; H, 6.64.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with *tert*-Butyllithium in Hexane and Subsequent Reaction with Water. Following the general procedure, except where noted, a reaction was carried out between 0.500 g (1.7 mmol) of (1,1′-ferrocenediyl)phenylphosphine dissolved in 30 mL of hexane and 1.02 mL (2.0 mmol) of 1.95 M *t*-BuLi in *n*-hexane with an additional 10 mL of hexane added. Upon completion of the addition, the reaction mixture was stirred at room temperature overnight. This resulted in a brownish precipitate and an orange-red solution. This mixture was hydrolyzed to the "dry end point" with saturated aqueous NH_4Cl solution. The filtered reaction mixture was evaporated to dryness in vacuo, and the resulting brown oil was dissolved in 20 mL of oxygen-free benzene and treated with 0.064 g (2.0 mmol) of sulfur (J.T. Baker) under nitrogen at reflux for 3.5 h. The cooled reaction mixture was filtered and the solvent removed on a rotary evaporator to give a brown-yellow oil. The product was isolated by using filtration chromatography. Elution with a 50% dichloromethane/50% hexane mixture removed first a faint yellow fraction, which was not identified, and then the major yellow fraction eluted. Removal of the solvent on a rotary evaporator and subsequent recrystallization of the golden solid from hexane at 5 °C yielded 0.300 g (0.8 mmol, 47%) of golden rods identified as *tert*-butylphenylferrocenylphosphine sulfide, $[\eta^5\text{-}C_5H_4P(S)Ph\text{-}t\text{-}Bu]Fe(\eta^5\text{-}C_5H_5)$: mp 132.5–134 °C; ^1H NMR ($CDCl_3$) δ 1.12 (d, J(P–H) = 17 Hz, 9 H, *t*-Bu), 3.90 (s, 5 H, Cp), 4.40 (m, 3 H, Cp), 4.93 (m, 1 H, Cp), 7.32–8.38 (m, 5 H, Ph); mass spectrum, m/e (relative intensity) 382 (M^+, 37.8), 350 (M^+ − S, 0.9), 325 (M^+ − *t*-Bu, 68.3), 293 (M^+ − S − *t*-Bu, 29.0). Anal. Calcd for $C_{20}H_{23}FePS$ (382.31): C, 62.83; H, 6.08. Found: C, 62.79; H, 6.04.

General Procedure for the Reaction of (1,1′-Ferrocenediyl)phenylphosphine with 1 Equiv of Phenyllithium Followed by the Reaction with Electrophilic Reagents. The following procedure has been found, after many experiments, to give the best yield of 1-lithio-1′-(diphenylphosphino)ferrocene without an excess of phenyllithium present and without the occurrence of oligomerization.

A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir bar, a pressure equalizing dropping funnel, a gas inlet tube leading to a Schlenk manifold, and no-air stoppers was evacuated, flame-dried, and refilled with nitrogen. Meanwhile, in a separate flask under nitrogen, the appropriate amount of

(1,1′-ferrocenediyl)phenylphosphine was dissolved in hexane. A small amount of tan-insoluble material always resulted, so the mixture was filtered under nitrogen and then cannulated into the dropping funnel. An equivalent or slight excess of phenyllithium in diethyl ether was added to the flask by syringe. The ferrocenophane/hexane solution was added dropwise to the phenyllithium during 45–60 min. As the addition proceeded, a tan-yellow precipitate formed while the solution became golden brown. At the end of the addition a substantial amount of precipitate was present. The mixture was stirred for an additional hour, and then the solvent was removed in vacuo to give a tan-yellow solid. This solid then was dissolved in diethyl ether or THF and allowed to react with the appropriate electrophilic reagent by addition of the reagent, dissolved in the same solvent, through the dropping funnel during 10 min. The reaction mixture was stirred at room temperature overnight or heated to reflux for not longer than 30 min, then filtered, and evaporated to dryness on a rotary evaporator. Further purification was afforded by using filtration chromatography eluting with the appropriate solvent system. All the products were air-stable, both as solids or in solution.

Hydrolysis (using saturated aqueous NH_4Cl) of 1-lithio-1′-(diphenylphosphino)ferrocene, generated by this procedure, repeatedly gave 1-diphenylphosphinoferrocene in 70% yields.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Phenyllithium in Hexane and Subsequent Reaction with Trimethyltin Bromide. Following the general procedure, a reaction was carried out between 0.500 g (1.71 mmol) of (1,1′-ferrocenediyl)phenylphosphine (in 30 mL of hexane) and 5.26 mL (4.0 mmol) of 0.76 M PhLi in diethyl ether. The 1-lithio-1′-(diphenylphosphino)ferrocene thus formed was dissolved in 20 mL of THF and allowed to react with 0.975 g (4.0 mmol) of Me_3SnBr dissolved in 30 mL of THF. Upon addition of the Me_3SnBr, the golden solution turned yellow and was stirred for 1 h at room temperature, then heated at reflux for 15 min, and finally allowed to cool and stir overnight.

The solvent was removed on a rotary evaporator, affording a brown oil. The desired product was isolated by using filtration chromatography eluting with a 20% dichloromethane/80% pentane mixture, collecting the first major yellow fraction. This gave a golden yellow oil which was rechromatographed in the same manner to give 0.557 g (1.04 mmol, 61%) of a golden yellow oil identified as 1-(diphenylphosphino)-1′-(trimethystannyl)ferrocene, $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SnMe_3)$.

(The sample which passed elemental analysis was further purified by using a Waters Analytical high-performance liquid-chromatography system and a Waters μ-Porasil semi-prep (7.8 mm × 30 cm) HPLC column eluting with a 50% dichloromethane/50% hexane mixture at a flow rate of 5.0 mL/min, courtesy of Dow Chemical Co.): ^1H NMR ($CDCl_3$) δ 0.23 (s with 117/119 Sn satellites, $J(Sn–H) = 58$ Hz, 9 H, CH_3), 3.91 (t, $J = 1.8$ Hz, 2 H, Cp), 4.00 (t, $J = 1.8$ Hz, 2 H, Cp), 4.13 (t, $J = 1.8$ Hz, 2 H, Cp), 4.22 (t, $J = 1.8$ Hz, 2 H, Cp), 7.03–7.39 (m, 15 H, Ph); mass spectrum, *m/e* 533 (M^+, 24), 518 ($M^+ - Me$, 98), 488 ($M^+ - 3\ Me$, 29), 369 ($M^+ - SnMe_3$, 66), 292 ($M^+ - SnMe_3 - Ph$, 30), 184 ($M^+ - SnMe_3 - PPh_2$, 58). Anal. Calcd for $C_{25}H_{27}FePSn$ (533.03): C, 56.33; H, 5.12. Found: C, 56.75: H, 5.15.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Phenyllithium in Hexane and Subsequent Reaction with Triphenyltin Chloride. Following the general procedure, a reaction was carried out between 0.500 g (1.71 mmol) of (1,1′-ferrocenediyl)phenylphosphine (in 35 mL of hexane) and 2.5 mL (1.85 mmol) of 0.74 M PhLi in diethyl ether. The resulting ferrocenyllithium reagent was dissolved in 25 mL of THF and allowed to react with 1.156 g (3.0 mmol) of Ph_3SnCl (Alfa/Ventron, recrystallized from hexane) dissolved in 10 mL of THF. The resulting golden yellow solution was stirred overnight at room temperature and then filtered and the solvent removed on a rotary evaporator. The remaining golden brown oil was subjected to filtration chromatography eluting first with a 20% dichloromethane/pentane mixture to remove a faint yellow band and then with a 50% dichloromethane/50% pentane mixture to remove the desired fraction. Removal of the solvent and subsequent recrystallization from hexane at −8 °C yielded a fine white precipitate which was filtered; further cooling of the filtrate to −30 °C afforded 0.574 g (0.8 mmol, 47%) of golden orange nuggets identified as 1-(diphenylphosphino)-1′-(triphenylstannyl)ferrocene, $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SnPh_3)$: mp 152–154 °C; ^1H NMR ($CDCl_3$) δ 3.97 (t, $J = 2.0$ Hz, 2 H, Cp), 4.07 (*t*, $J = 2.0$ Hz, 2 H, Cp), 4.15 (t, $J = 2.0$ Hz, 2 H, Cp), 4.32 (t, $J = 2.0$ Hz, 2 H, Cp), 7.18–7.72 (m, 25 H, Ph). Anal. Calcd for $C_{40}H_{33}FePSn$ (719.24): C, 66.79; H, 4.63. Found: C, 66.84; H, 4.83.

Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Phenyllithium in Hexane and Subsequent Reaction with Chlorotriphenylsilane. Following the general procedure, a reaction was carried out between 0.500 g (1.71 mmol) of (1,1′-ferrocenediyl)phenylphosphine (in 35 mL of hexane) and 5.26 mL (4.0 mmol) of 0.76 M PhLi in diethyl ether. The resulting ferrocenyllithium reagent was dissolved in 20 mL of THF and allowed to react with 1.18 g (4.0 mmol) of Ph_3SiCl (Alfa/Ventron, recrystallized from hexane under nitrogen) dissolved in 30 mL of THF. The reaction mixture was stirred for 3 h at room temperature, then heated at reflux for 45 min, and finally allowed to cool and stir at room temperature overnight.

The solvent was removed on a rotary evaporator, and subsequent filtration chromatography, eluting with a 20% dichloromethane/80% pentane mixture, isolated a major yellow fraction. Removal of the solvent, followed by two consecutive recrystallizations from a dichloromethane/hexane mixture by slow evaporation of the dichloromethane at room temperature, afforded 0.468 g (0.74 mmol, 43%) of golden orange nuggets identified as 1-(diphenylphosphino)-1′-(triphenylsilyl)ferrocene $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SiPh_3)$: mp 157–159.5 °C; ^1H NMR ($CDCl_3$) δ 3.92 (m, 4 H, Cp), 4.12 (m, 2 H, Cp), 4.25 (m, 2 H, Cp), 7.15–7.58 (m, 25 H, Ph); mass spectrum, *m/e* 629 (M^+, 7.7), 369 ($M^+ - SiPh_3$, 4.0), 259 ($SiPh_3$, 16.6). Anal. Calcd for $C_{40}H_{33}FePSi$ (628.64): C, 76.42; H, 5.30. Found: C, 75.86; H, 5.29.

Attempted Reaction of (1,1′-Ferrocenediyl)phenylphosphine with Phenylmagnesium Bromide. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir bar, a pressure-equalizing dropping funnel, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and a no-air stopper was evacuated and flame-dried, and then refilled with nitrogen. The flask was charged with 0.073 g (3.0 mmol) of magnesium (Alfa/Ventron, M4N grade) and purged with nitrogen. THF (10 mL) and bromobenzene (0.33 mL, 3.1 mmol, Aldrich, distilled under nitrogen) were added to the flask by syringe. When the formation of the PhMgBr was complete (all the Mg had been consumed), a solution of 0.292 g (1.0 mmol) of (1,1′-ferrocenediyl)phenylphosphine in 20 mL of THF was cannulated into the dropping funnel and then added dropwise to the PhMgBr solution over a 30-min period. No color change was observed, and TLC indicated only starting material. The reaction mixture was heated at reflux for 4 h. During this time the reaction mixture darkened and TLC indicated only a very faint yellow band eluting in pentane and a large amount of immobile black-brown material. Further workup was not pursued.

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Registry No. 1, 72954-06-4; **2**, 72954-07-5; **3**, 72954-08-6; **4**, 12098-17-8; **5**, 72954-09-7; **6**, 73203-08-4; **7**, 73203-07-3; **8**, 72954-10-0; **9**, 72954-11-1; **11**, 82311-95-3; **13a**, 82312-06-9; **13b**, 82312-07-0; $PhPCl_2$, 644-97-3; $MePCl_2$, 676-83-5; $PhAsCl_2$, 696-28-6; Et_2SnCl_2, 866-55-7; *n*-Bu_2SnCl2, 683-18-1; THF·W$(CO)_5$, 36477-75-5; Ph_2PCl, 1079-66-9; $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$, 12150-46-8; Me_3SiCl, 75-77-4; $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SiMe_3)$, 72954-12-2; $(\eta^5\text{-}C_5H_4AsPh_2)Fe(\eta^5\text{-}C_5H_5)$, 12156-01-3; $(\eta^5\text{-}C_5H_4AsPh_2)Fe(\eta^5\text{-}C_5H_4PPh_2)$, 73203-06-2; $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_5)$, 12098-17-8; $[\eta^5\text{-}C_5H_4P(S)Ph(CH_2CH_2CMe_3)]Fe(\eta^5\text{-}C_5H_5)$, 82312-08-1; $[\eta^5\text{-}C_5H_4P(S)Ph\text{-}t\text{-}Bu]Fe(\eta^5\text{-}C_5H_5)$, 82312-09-2; Me_3SnBr, 1066-44-0; $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SnMe_3)$, 72954-23-5; Ph_3SnCl, 379-52-2; $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SnPh_3)$, 82312-10-5; Ph_3SiCl, 76-86-8; $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4SiPh_3)$, 82312-11-6; TMEDA, 33272-09-2; tetracarbonyl(tetrahydrofuran)iron, 52268-67-4; phenylmagnesium bromide, 100-58-3.