countercations in the solid state, while only one or none is present in solution. In all cases, it is interesting to point out that the frequency of the bridging CO decreases approximately by 100 cm^{-1} for each hydrogen bond formed to this CO group.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this work.

Registry No. $[H_2Et_2][HFe_3(CO)_{11}]$, 56048-18-1; $[H_2(n\text{-}Bu)_2N][HFe_3(CO)_{11}]$, 107011-15-4; $[H_2(i\text{-}Pr)_2N][HFe_3(CO)_{11}]$, 107011-16-5; $[PPN][HFe_3(CO)_{11}]$, 23254-21-9; $[HEt_3N][HFe_3(CO)_{11}]$, 56048-18-1; $K[HFe_3(CO)_{11}]$, 87145-35-5; CO, 630-08-0.

Supplementary Material Available: Table IV, fractional coordinates (×10^4) for the hydrogen atoms of $[H_2(i\text{-}Pr)_2][HFe_3(CO)_{11}]$, and Table V, anisotropic temperature factors of $[H_2(i\text{-}Pr)_2N][HFe_3(CO)_{11}]$ (2 pages); Table VI, observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Reaction of $Fe(\eta^5\text{-}C_5H_4PPh)(\eta^5\text{-}C_5H_4)$ with LiC_5H_5 and $NaFe(CO)_2(\eta^5\text{-}C_5H_5)$. Structures of $\{Fe[(\eta^5\text{-}C_5H_4)_2]P(C_6H_5)\text{-}P\}Fe(H)(\eta^5\text{-}C_5H_5)(CO)$ and $\{(C_6H_5)[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)][Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3C(O))]P\text{-}P,C\}Fe(\eta^5\text{-}C_5H_5)(CO)\cdot CHCl_3$

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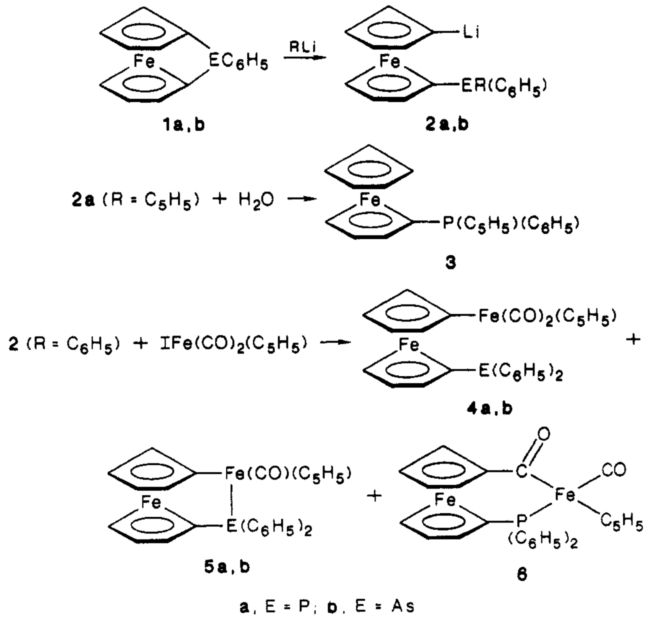
Crystals of $\{Fe[(\eta^5\text{-}C_5H_4)_2]P(C_6H_5)\text{-}P\}Fe(H)(\eta^5\text{-}C_5H_5)(CO)$ (17) are monoclinic, space group $P2_1/c$, with a = 13.521 (2) Å, b = 10.998 (1) Å, c = 13.007 (2) Å, β = 101.375 (7)°, and Z = 4, and crystals of $\{(C_6H_5)[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)][Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3C(O))]P\text{-}P,C\}Fe(\eta^5\text{-}C_5H_5)(CO)\cdot CHCl_3$ (12) are monoclinic, space group $P2_1/c$, with a = 11.878 (1) Å, b = 11.980 (1) Å, c = 22.948 (2) Å, β = 103.743 (7)°, and Z = 4. Both structures were solved by heavy-atom methods and were refined by full-matrix least-squares procedures to R values of 0.048 and 0.045 for 1922 and 3481 reflections, respectively. Compound 17 is a derivative of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ in which a carbonyl group has been replaced by the phosphine $Fe[(\eta^5\text{-}C_5H_4)_2]P(C_6H_5)$. The structure of 12 is related to that of 17 in that the phosphine ligand is a derivative of diferrocenylphenylphosphine in which one of the ferrocene groups is substituted by a –C(O)– group that also constitutes the X group in $(\eta^5\text{-}C_5H_5)Fe(CO)PR_3X$. Bond distances in both structures are similar to those in related molecules. 17 was isolated following treatment of (1,1′-ferrocenediyl)phenylphosphine (1a) with $NaFe(CO)_2(\eta^5\text{-}C_5H_5)$. Cleavage of the [1]ferrocenophane (1a) with LiC_5H_5/TMED affords $FcPPh(C_5H_5)$ (3). Solutions containing 3 and LiC_5H_5 react with $IFe(CO)_2(\eta^5\text{-}C_5H_5)$ to yield separable diastereomers of 12.

Much of our current research has focused on the cleavage reactions of phosphorus- or arsenic-bridged [1]-ferrocenophanes using alkyl- or aryllithium reagents[2,3] (Scheme I). We have also explored the subsequent reaction of the resulting lithium compounds (e.g. **2a**, R = Ph) with appropriate transition-metal derivatives.[4,5] For example, the reaction of $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$ with **2a**, R = Ph, results in the formation of the phosphorus-coordinated compound **5a** as the major reaction product together with smaller amounts of the CO migration product **6a**.[4] The analogous reaction of **2b**, R = Ph, gives only the arsenical **4b** at ambient temperature; however, heating solutions of **4b** results in the formation of **5b**.[6]

Scheme I



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[6] Recent results show that **4b** transforms to **5b** on heating in toluene solution (110 °C). **5b**: ^1H NMR ($CDCl_3$, 270 MHz) δ 3.85 (m, 1), 4.02 (m, 1), 4.16 (m, 1), 4.22 (m, 1), 4.40 (2m, 2), 4.50 (s, 5), 4.63 (m, 1), 4.70 (m, 1), 7.45–7.50 (m, 6), 7.55–7.63 (m, 4); MS (150 °C), m/e 563 (2.93), 562 (M$^+$, 8.68), 535 (12.38), 534 (36.41), 456 (14.11), 414 (28.31), 381 (4.56), 337 (36.91), 305 (66.96), 304 (82.95).

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This paper describes work done in an attempt to extend the scope of the cleavage reaction using reagents that, in principle, would yield products **2** in which the R group attached to phosphorus would be capable of further chemical elaboration, one such group would be η^1-C_5H_5 that could afford a reactive anion and another would be $-Fe(CO)_2(\eta^5\text{-}C_5H_5)$.

We find that the successful reaction of **1a** with lithium cyclopentadienide, followed by hydrolysis, results in the isolation of the anticipated product **3**. Metalation of the $P-C_5H_5$ moiety seems to be facile since **1a** in the presence of C_5H_5Li affords a dianion that in turn reacts with $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$ to give a novel complex whose structure is described. The failure of **1a** to react with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ directly results in the isolation of an iron carbonyl hydride derivative of **1a** whose structure is also described.

Experimental Section

All manipulations were carried out under an argon atmosphere by using standard Schlenk glassware. Solvents were predried and freshly distilled. Commercially available *n*-butyllithium solutions (Aldrich) and cyclopentadienylthallium (Strem) were used. ^{1}H NMR spectra were recorded by using either a Bruker WH-400, Varian XL-300, Bruker WM-270, or Bruker WP-80 instrument. ^{31}P chemical shifts are given relative to $P(OMe)_3$. Mass spectra data were acquired by using a Kratos MS-50 spectrometer (probe temperature 150–200 °C). Microanalyses were performed by Mr. Peter Borda of this department.

Dicarbonylcyclopentadienyliron iodide, (1,1′-ferrocenediyl)phenylphosphine, and 1,1′-dilithioferrocene–tetramethylethylenediamine were prepared by using published procedures.[2,7–9]

1. Reaction of C_5H_5Li with 1a. Preparation of 3. To a cooled (−70 °C) solution of freshly cracked cyclopentadiene (5 g, ~75 mmol) in THF (100 mL) was added a solution of *n*-butyllithium in hexanes (20 mL of a 1.55 M solution, ~31 mmol). The reaction mixture was warmed to room temperature and then recooled to −20 °C. A solution of **1a** (4.0 g, 13.7 mmol) in the minimum quantity of THF required for complete solution was then added followed by TMED (5.0 g, 43 mmol). The resultant solution was stirred at room temperature for 6–7 days. Small samples (1–2 drops) of the reaction solution were removed for examination by TLC (aerobic conditions, eluting solvent 20/80 diethyl ether/hexanes). The disappearance of the red band due to **1a** and the appearance of a new product band (with slightly lower R_f) were used to monitor the progress of the reaction. This procedure was carried out daily. Once all **1a** had reacted, the solution was cooled (−40 °C) and carefully hydrolyzed (H_2O, 50 mL) or deuteriated (D_2O, 10 mL). After the solution was allowed to warm to room temperature, the reaction mixture was stirred for 1 h. The organic layer was separated [diethyl ether extracts (3 × 20 mL) were used to completely remove the orange product], dried overnight over anhydrous $MgSO_4$, and filtered. The $MgSO_4$ was washed clean with diethyl ether, and the washings were added to the filtrate. The solvent was then removed from the product-containing solution to yield a yellow-orange oil. This oil was then chromatographed on a neutral alumina support (activity grade II). Elution with hexanes removed residual TMED and THF. The orange product band was eluted with diethyl ether. (In cases where the reaction mixture is hydrolyzed before completion, **1a** can be removed by elution with 30/70 diethyl ether/hexanes.) The solvent was removed and the resultant oily solid crystallized from hexanes (−20 °C) to give **3** as orange nodules (>80%). As isolated, **3** always consisted of a mixture of isomers. The ratio of isomers varies from 1:2 to 2:1 in different preparations; however, one spot only is observed on TLC. ^{1}H NMR (400 MHz, $CDCl_3$): δ [3.07 (m), 3.15 (t), ratio 1:1.8, total area 2], 4.13 (2s, approximate ratio 1:1.5, smallest intensity singlet slightly downfield of larger singlet), 4.15–4.20 (2m, 1), 4.23 (2t, 1), 4.35 (2m, 2), [6.47 (m), 6.54 (m), 6.60 (m), 6.61 (m), 6.66 (m), total area 3], [7.20 (m), 7.30 (m), approximate ratio 1:1.6 total intensity 3], 7.38 (m, 2). ^{31}P NMR: δ −28.7 (s, 1.6), −172.83 (s, 1.0). J_{P-H} values obtained for $\{^{31}P\}^1H$: P–Ph, 7.5 Hz; $P-C_5H_5$ (sp^3 carbon), ~1 Hz. Homonuclear 2-D *J*-resolved spectrum (η^1-C_5H_5 region): 3.07 (ddd, *J* = 1.6, 1.6, 0.85 Hz), 3.15 (dd, *J* = 1.9, 0.95 Hz), 6.47 (dd, *J* = 3.4, 0.95 Hz), 6.54 (dd, *J* = 3.4, 1.3 Hz), 6.60 (ddd, *J* = 3.4, 2.3, 0.9 Hz), 6.61 (ddd, *J* = 3.4, 1.8, 0.9 Hz), 6.66 (d, *J* = 1.3, 0.85 Hz). Mass spectrum: *m/e* (relative intensity) 359 (5.01), 358 (M^+, 22.32), 294 (22.21), 293 ($M^+ - C_5H_5$, 100.00), 291 (12.80), 186 (5.37).

Anal. Calcd for $C_{21}H_{14}FeP$: C, 70.42; H, 5.35. Found: C, 70.12; H, 5.43.

Table I. Crystallographic Data[a]

	17	12
formula	$C_{22}H_{19}Fe_2OP$	$C_{33}H_{27}Fe_3O_2P\cdot CHCl_3$
fw	442.06	773.47
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	13.521 (2)	11.878 (1)
b, Å	10.998 (1)	11.980 (1)
c, Å	13.007 (2)	22.948 (2)
α, deg	90	90
β, deg	101.375 (7)	103.743 (7)
γ, deg	90	90
V, Å^3	1896.2 (4)	3171.8 (5)
Z	4	4
D_{calcd}, g/cm^3	1.548	1.620
F(000)	904	1568
μ(Mo Kα), cm^{-1}	16.2	16.9
cryst dimens, mm	0.18 × 0.25 × 0.58	0.22 × 0.23 × 0.40
transmissn factors	0.472–0.785	0.673–0.734
scan type	$\omega-2\theta$	$\omega-2\theta$
scan range, deg in ω	$0.85 + 0.35 \tan\theta$	$0.65 + 0.35 \tan\theta$
scan speed, deg/min	1.06–10.06	1.18–10.06
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
max 2θ, deg	55	55
cryst decay	negligible	negligible
unique reflctns	4332	7252
reflctns with $I \geq 3\sigma(I)$	1922	3481[b]
no. of variables	235	388
R	0.048	0.045
R_w	0.052	0.045
S	1.982	1.504
mean Δ/σ (final cycle)	0.04	0.03
max Δ/σ (final cycle)	0.30	0.20
residual density, e/Å^3	−1.1 to +0.9	−1.3 to +0.5

[a] Temperature, 22 °C; Enraf-Nonius CAD4-F diffractometer; Mo Kα radiation ($\lambda_{K\alpha_1}$ = 0.709 30 and $\lambda_{K\alpha_2}$ = 0.713 59 Å); graphite monochromator; takeoff angle = 2.7°, aperture (2.0 + tan θ) × 4.0 mm at a distance of 173 mm from the crystal; scan range extended by 25% on both sides for background measurement: $\sigma^2(I) = S + 2B + [0.040(S - B)]^2$ (*S* = scan count; *B* = normalized background count); function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$. Values given for *R*, R_w, and *S* are based on those reflections with $I \geq 3\sigma(I)$. [b] 2σ data used for this structure.

2. Reaction of Dilithioferrocene–Tetramethylethylenediamine (8) with $(C_5H_5)(C_6H_5)PCl$ (7). Preparation of 9. A slurry of C_5H_5Tl (4.6 g, ~17 mmol) in diethyl ether (50 mL) was added to a cooled (−70 °C) rapidly stirred solution of $(C_6H_5)PCl_2$ (3.0 g, ~17 mmol) in diethyl ether. The reaction mixture was allowed to warm to room temperature and was stirred for 4 h. The suspension was then filtered and added dropwise to a stirred suspension of dilithioferrocene–tetramethylethylenediamine[9a] (8.0 mmol) in diethyl ether (100 mL). The reaction mixture was stirred overnight. Following hydrolysis (H_2O, 30 mL), the organic layer

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Table II. Final Positional (Fractional, ×10⁴; Fe and P, ×10⁵) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	U_{eq}
{[Fe(C_5H_4)$_2$]P(C_6H_5)-*P*}Fe(H)(C_5H_5)(CO) (**17**)				
Fe(1)	28616 (7)	58986 (8)	46696 (6)	52
Fe(2)	11382 (6)	39963 (8)	18685 (7)	51
P	23633 (11)	41523 (13)	31642 (11)	41
O	2343 (5)	5047 (6)	513 (5)	112
C(1)	3129 (4)	5547 (4)	3253 (4)	41
C(2)	4062 (4)	5669 (5)	3992 (5)	49
C(3)	4109 (5)	6859 (6)	4423 (5)	67
C(4)	3207 (6)	7489 (5)	3975 (5)	69
C(5)	2608 (5)	6705 (5)	3255 (5)	55
C(6)	2108 (4)	4340 (5)	4491 (5)	49
C(7)	2897 (5)	4307 (6)	5432 (5)	64
C(8)	2702 (6)	5234 (8)	6126 (5)	78
C(9)	1816 (6)	5842 (7)	5649 (6)	81
C(10)	1440 (5)	5324 (6)	4657 (5)	64
C(11)	581 (8)	2429 (9)	1077 (11)	109
C(12)	734 (10)	2226 (10)	2116 (15)	143
C(13)	116 (12)	3051 (17)	2500 (10)	139
C(14)	−393 (6)	3701 (9)	1663 (14)	116
C(15)	−91 (8)	3336 (10)	811 (8)	96
C(16)	1826 (6)	4618 (7)	1061 (6)	74
C(17)	3308 (4)	2951 (5)	3321 (5)	48
C(18)	4092 (5)	2995 (6)	2788 (5)	63
C(19)	4796 (6)	2074 (8)	2880 (6)	85
C(20)	4699 (7)	1075 (8)	3484 (8)	95
C(21)	3927 (7)	1006 (6)	4012 (7)	81
C(22)	3206 (5)	1940 (6)	3940 (6)	68
{(C_6H_5)[Fe(C_5H_5)(C_5H_4)][Fe(C_5H_5)(C_5H_3C(O))]P-*P*,*C*}-Fe(C_5H_5)(CO)·$CHCl_3$ (**12**)				
Fe(1)	32344 (6)	41521 (7)	29381 (3)	35
Fe(2)	10843 (7)	66721 (6)	18994 (3)	38
Fe(3)	15843 (7)	23160 (7)	7443 (3)	45
P	26816 (11)	41961 (11)	19598 (5)	32
Cl(1)	2853 (3)	6115 (2)	5051 (1)	147
Cl(2)	2282 (2)	7881 (2)	4196 (1)	129
Cl(3)	4533 (2)	6915 (2)	4455 (1)	130
O(1)	4422 (4)	6254 (4)	2987 (2)	73
O(2)	1504 (3)	5214 (3)	3414 (1)	49
C(1)	3933 (5)	5417 (5)	2963 (2)	47
C(2)	1798 (4)	4957 (4)	2959 (2)	34
C(3)	4109 (5)	2606 (5)	3001 (2)	51
C(4)	4669 (5)	3305 (6)	3476 (3)	60
C(5)	3854 (6)	3563 (6)	3817 (2)	64
C(6)	2812 (5)	3010 (5)	3553 (3)	59
C(7)	2960 (5)	2438 (5)	3043 (2)	51
C(8)	1366 (4)	5008 (4)	1821 (2)	33
C(9)	1017 (4)	5238 (4)	2362 (2)	32
C(10)	−90 (4)	5744 (4)	2203 (2)	41
C(11)	−430 (5)	5828 (5)	1571 (3)	49
C(12)	467 (5)	5364 (4)	1334 (2)	41
C(13)	2570 (5)	7555 (5)	1936 (3)	54
C(14)	2151 (6)	7780 (5)	2444 (3)	63
C(15)	1029 (6)	8224 (5)	2255 (3)	62
C(16)	753 (6)	8295 (5)	1629 (3)	63
C(17)	1700 (6)	7881 (5)	1429 (3)	55
C(18)	2197 (4)	2882 (4)	1602 (2)	32
C(19)	1084 (5)	2404 (5)	1535 (2)	42
C(20)	1113 (6)	1280 (5)	1350 (3)	56
C(21)	2248 (6)	1044 (5)	1318 (3)	59
C(22)	2923 (5)	2020 (5)	1463 (2)	48
C(23)	1348 (8)	3574 (6)	126 (3)	68
C(24)	330 (7)	2974 (10)	79 (3)	94
C(25)	566 (14)	1896 (11)	−56 (4)	138
C(26)	1667 (16)	1791 (11)	−77 (4)	133
C(27)	2173 (7)	2853 (9)	28 (3)	91
C(28)	3690 (5)	4731 (4)	1545 (2)	38
C(29)	3361 (5)	5401 (5)	1042 (2)	52
C(30)	4172 (7)	5744 (6)	738 (3)	68
C(31)	5297 (7)	5418 (6)	917 (3)	74
C(32)	5646 (6)	4775 (6)	1424 (3)	72
C(33)	4849 (5)	4430 (5)	1737 (3)	53
C(34)	3085 (7)	6637 (7)	4389 (3)	91

Table III. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

{[Fe(C_5H_4)$_2$]P(C_6H_5)-*P*}Fe(H)(C_5H_5)(CO) (**17**)			
Fe(1)–C(1)	1.985 (6)	C(1)–C(2)	1.434 (8)
Fe(1)–C(2)	2.010 (6)	C(1)–C(5)	1.456 (7)
Fe(1)–C(3)	2.068 (6)	C(2)–C(3)	1.421 (8)
Fe(1)–C(4)	2.064 (6)	C(3)–C(4)	1.423 (9)
Fe(1)–C(5)	2.010 (6)	C(4)–C(5)	1.407 (8)
Fe(1)–C(6)	1.984 (5)	C(6)–C(7)	1.458 (8)
Fe(1)–C(7)	2.008 (6)	C(6)–C(10)	1.452 (8)
Fe(1)–C(8)	2.081 (7)	C(7)–C(8)	1.420 (9)
Fe(1)–C(9)	2.083 (7)	C(8)–C(9)	1.405 (10)
Fe(1)–C(10)	2.020 (7)	C(9)–C(10)	1.410 (9)
Fe(2)–P	2.124 (2)	C(11)–C(12)	1.34 (2)
Fe(2)–C(11)	2.071 (7)	C(11)–C(15)	1.348 (12)
Fe(2)–C(12)	2.065 (9)	C(12)–C(13)	1.391 (15)
Fe(2)–C(13)	2.028 (10)	C(13)–C(14)	1.37 (2)
Fe(2)–C(14)	2.061 (8)	C(14)–C(15)	1.316 (13)
Fe(2)–C(15)	2.069 (7)	C(17)–C(18)	1.377 (8)
Fe(2)–C(16)	1.680 (9)	C(17)–C(22)	1.396 (8)
P–C(1)	1.841 (5)	C(18)–C(19)	1.378 (9)
P–C(6)	1.837 (6)	C(19)–C(20)	1.372 (11)
P–C(17)	1.821 (6)	C(20)–C(21)	1.360 (12)
O–C(16)	1.190 (8)	C(21)–C(22)	1.406 (9)
Fe(1)–Cp(1)	1.624 (3)	Fe(2)–Cp(3)	1.707 (6)
Fe(1)–Cp(2)	1.632 (3)		
{(C_6H_5)[Fe(C_5H_5)(C_5H_4)][Fe(C_5H_5)(C_5H_3C(O))]P-*P*,*C*}-Fe(C_5H_5)(CO)·$CHCl_3$ (**12**)			
Fe(1)–P	2.1848 (14)	Cl(2)–C(34)	1.768 (8)
Fe(1)–C(1)	1.722 (6)	Cl(3)–C(34)	1.723 (8)
Fe(1)–C(2)	1.970 (5)	O(1)–C(1)	1.153 (6)
Fe(1)–C(3)	2.111 (6)	O(2)–C(2)	1.218 (5)
Fe(1)–C(4)	2.112 (5)	C(2)–C(9)	1.498 (6)
Fe(1)–C(5)	2.099 (5)	C(3)–C(4)	1.410 (8)
Fe(1)–C(6)	2.109 (5)	C(3)–C(7)	1.405 (8)
Fe(1)–C(7)	2.102 (6)	C(4)–C(5)	1.416 (8)
Fe(1)–Cp(1)	1.733 (3)	C(5)–C(6)	1.408 (8)
Fe(2)–C(8)	2.036 (5)	C(6)–C(7)	1.403 (8)
Fe(2)–C(9)	2.031 (5)	C(8)–C(9)	1.427 (6)
Fe(2)–C(10)	2.032 (5)	C(8)–C(12)	1.415 (6)
Fe(2)–C(11)	2.045 (5)	C(9)–C(10)	1.414 (6)
Fe(2)–C(12)	2.056 (5)	C(10)–C(11)	1.415 (7)
Fe(2)–C(13)	2.042 (5)	C(11)–C(12)	1.420 (7)
Fe(2)–C(14)	2.043 (5)	C(13)–C(14)	1.398 (8)
Fe(2)–C(15)	2.038 (6)	C(13)–C(17)	1.415 (8)
Fe(2)–C(16)	2.051 (6)	C(14)–C(15)	1.405 (8)
Fe(2)–C(17)	2.043 (6)	C(15)–C(16)	1.398 (8)
Fe(2)–Cp(2)	1.645 (2)	C(16)–C(17)	1.402 (8)
Fe(2)–Cp(3)	1.658 (3)	C(18)–C(19)	1.415 (7)
Fe(3)–C(18)	2.045 (4)	C(18)–C(22)	1.430 (7)
Fe(3)–C(19)	2.043 (5)	C(19)–C(20)	1.414 (7)
Fe(3)–C(20)	2.038 (6)	C(20)–C(21)	1.396 (8)
Fe(3)–C(21)	2.045 (6)	C(21)–C(22)	1.412 (8)
Fe(3)–C(22)	2.032 (5)	C(23)–C(24)	1.388 (11)
Fe(3)–C(23)	2.043 (6)	C(23)–C(27)	1.364 (10)
Fe(3)–C(24)	2.022 (6)	C(24)–C(25)	1.373 (13)
Fe(3)–C(25)	2.008 (8)	C(25)–C(26)	1.327 (15)
Fe(3)–C(26)	2.012 (8)	C(26)–C(27)	1.404 (15)
Fe(3)–C(27)	2.037 (7)	C(28)–C(29)	1.384 (7)
Fe(3)–Cp(4)	1.649 (2)	C(28)–C(33)	1.389 (7)
Fe(3)–Cp(5)	1.655 (4)	C(29)–C(30)	1.379 (8)
P–C(8)	1.804 (5)	C(30)–C(31)	1.359 (9)
P–C(18)	1.805 (5)	C(31)–C(32)	1.375 (9)
P–C(28)	1.816 (5)	C(32)–C(33)	1.379 (8)
Cl(1)–C(34)	1.725 (7)		

[a] Here and elsewhere Cp refers to the cyclopentadienyl ring centroid.

was separated and dried over anhydrous $MgSO_4$. TLC inspection (eluant, 30/70 diethyl ether/hexanes) of this fraction indicated the presence of several compounds including ferrocene. The two compounds in greatest abundance showed as yellow bands with similar R_f values. These diastereomers of **9**, **a** and **b**, eluted as one band on column chromatography. They are separable by a combination of preparative plate TLC (~100-mg scale) and fractional crystallization (yield ~35% (both isomers)). **9a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (m, 1), 3.13 (m, 2), 3.90–4.35 (m, 8), 6.43–6.75 (m, 6), 7.25–7.40 (m, 10); mass spectrum, m/e (relative intensity) 531 (5.15), 530 (13.71, M^+), 466 (22.09), 465 (70.06, $M^+ - C_6H_5$), 401 (12.05), 400 (34.50, $M^+ - 2C_5H_5$), 323 (4.86, $M^+ - 2C_5H_5 - C_6H_5$), 294 (6.32), 293 (26.06), 292 (8.26), 241 (11.74). **9b**: ^1H NMR (80 MHz, $CDCl_3$) δ [2.90 (m), 3.05 (m), total intensity 4], 3.80–4.30 (m, 8), 6.40–6.70 (m, 6), 7.15–7.30 (m, 10); mass spectrum, m/e (relative intensity) 531 (6.85), 530 (19.20, M^+), 466 (32.36), 465 (100.00), 401 (27.57), 400 (54.37), 358 (4.30), 323 (8.29), 304 (24.16), 293 (40.63), 292 (15.42), 291 (23.32).

Anal. Calcd for $C_{32}H_{28}P_2Fe$: C, 72.47; H, 5.32. Found: C, 72.28; H, 5.50.

Three other compounds were isolated in minor quantities. These proved to be **3**, identified by spectral comparison with an authentic sample, **10**, identified by mass spectroscopy (parent ion m/e 478) and by spectral comparison with an authentic sample, and **11**, identified by ^1H NMR and mass spectroscopy. **11**: ^1H NMR ($CDCl_3$, 80 MHz) δ 3.10 (m, 2), 3.94–4.40 [m including singlet (5) at δ 4.11, total area 17], 6.40–6.60 (m, 3), 7.25–7.60 (m, 10); mass spectrum, m/e (relative intensity) 651 (21.6), 650 (55.3, M^+), 586 (35.3), 585 (100.0), 519 (70.4).

3. Reaction of 2a with $IFe(CO)_2(\eta^5\text{-}C_5H_5)$. Preparation of 12. To a cooled (−70 °C) solution of **2a** prepared as described in experiment 1 from 2.0 g of **1a** was added $IFe(CO)_2(\eta^5\text{-}C_5H_5)$ (5.0 g, 16.45 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. TLC examination (eluant, 50/50 diethyl ether/hexane) showed a large number of yellow bands in addition to the red-brown band of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$. The reaction suspension was concentrated to ca. 15 mL and was subjected to column chromatography on neutral alumina (activity grade I). The following fractions were eluted: ferrocene (eluant, 90/10 hexanes/diethyl ether); $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)Fe(CO)_2(\eta^5\text{-}C_5H_5)]$, as an orange band (50/50 hexanes/diethyl ether); **10**, yellow-orange band (20/80 hexanes/diethyl ether); $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$, red-brown band (diethyl ether); and finally a diffuse yellow band containing a compound subsequently identified as **12** (CH_2Cl_2). All compounds eluting prior to **12** were identified initially by ^1H NMR spectroscopy and subsequently by comparison with authentic samples. The solution containing **12** was subjected to a TLC analysis (diethyl ether eluant) that showed the presence of two compounds, one orange **12a** and one yellow-orange **12b** with very similar R_f values. The CH_2Cl_2 solution of **12** was concentrated to ~10 mL and a top layer of hexanes of equal volume added. A mixture of crystalline and powdered **12** was obtained by this procedure (total yield, both isomers, 20% based on **1a**). A second similar crystallization from $CHCl_3$/hexanes yielded a sample that was subsequently used for crystallographic analysis. **12a**: ^1H NMR[10] (400 MHz, $CDCl_3$) δ 3.65 (m, 1), 3.83 (m, 1), 4.04 (s, 5), 4.07 (s, 5), 4.29 (m, 1), 4.35 (m, 1), 4.40 (2s, 5), 4.78 (pt, 1), 4.79 (m, 1), 4.91 (m, 1), 7.53–7.63 (m, 3), 8.17 (dd, 2) ($CHCl_3$ signal observed at δ 7.24, also present CD_2Cl_2). **12b**: ^1H NMR[10] (400 MHz, $CDCl_3$) δ 3.81 (s, 5), 3.89 (m, 1), 4.12 (m, 1), 4.13 (m, 1), 4.22 (m, 2), 4.33 (s, 5), 4.45 (2s, 5), 4.61 (m, 1), 4.78 (pt, 1), 7.44–7.54 (m, 3), 8.14 (pdd, 2). **12** (both isomers): mass spectrum, m/e (relative intensity) 655 (11.83), 654 (28.39, M^+), 626 (8.16, $M^+ - CO$), 599 (37.21), 598 (100.00, $M - 2CO$), 597 (40.81), 596 (83.61), 595 (14.83), 594 (31.81), 530 (23.08), 479 (19.00), 478 (59.07), 452 (22.76), 412 (31.66), 411 (24.03), 410 (48.51).

Anal. Calcd for $C_{33}H_{27}Fe_3O_2P$: C, 60.60; H, 4.19. Found (**12a** + **12b**): C, 59.60; H, 4.34.

4. Attempted Reaction of 1a with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$. Preparation of 17. (a) A solution of **1a** (1.0 g, 3.4 mmol) in the minimum quantity of diethyl ether was added to a stirred solution of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ (6.0 mmol) in THF (30 mL) at 20 °C. Investigation of the reaction mixture by TLC revealed the presence of several compounds with one component, red-orange, in preponderance. After 2 h at 20 °C the stirred reaction mixture was carefully hydrolyzed (H_2O, 20 mL). TLC investigation at this time indicated the presence of only the red-orange compound. The organic layer was separated and the solvent removed under vacuum. The solid product residue was chromatographed on neutral alumina (activity grade I). The red-orange product band was eluted with diethyl ether. The solvent was removed under vacuum and the solid residue was recrystallized from a 1:1 mixture of hexanes/diethyl ether to give deep red needles of product identified as **17** (~40%). This compound can be stored under argon for long periods (>1 year) without apparent decomposition. Infrared: ν_{CO} (cyclohexane) 1939 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ −12.92 (d, 1, J_{P-H} = 76 Hz), 3.96 (m, 1), 4.05 (m, 1), 4.17 (m, 1), 4.19 (m, 1), 4.29 (m, 1), 4.32 (m, 1), 4.45 (s, 5), 4.98 (m, 1), 5.10 (m, 1), 7.16 (b m, 3), 7.71 (b t, 2). $\{^1H\}^{31}P$ NMR: δ 110.5 (s). Mass spectrum: m/e (relative intensity) 443 (11.10), 442 (38.66, M^+), 415 (20.94), 414 (86.38, $M^+ - CO$), 413 (21.09), 412 (36.71), 348 (56.13, $M - CO - H - C_5H_5$), 347 (23.58), 346 (98.30), 304 (41.67), 293 (34.15), 292 (100.00), 291 (77.47).

Anal. Calcd for $C_{22}H_{19}Fe_2OP$: C, 59.78; H, 4.34. Found: C, 59.74; H, 4.32.

(b) The reaction as described in part a was repeated. Samples of the reaction solution were combined with toluene-d_8 and filtered directly into 10-mm NMR tubes. The following ^{31}P data were

Table IV. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

$\{[Fe(C_5H_4)_2]P(C_6H_5)\text{-}P\}Fe(H)(C_5H_5)(CO)$ (**17**)

Cp(1)–Fe(1)–Cp(2)	161.5 (2)	P–C(6)–C(7)	123.0 (4)
P–Fe(2)–Cp(3)	129.6 (2)	P–C(6)–C(10)	117.5 (4)
P–Fe(2)–C(16)	91.3 (2)	C(7)–C(6)–C(10)	105.5 (5)
Cp(3)–Fe(2)–C(16)	130.7 (3)	C(6)–C(7)–C(8)	108.6 (6)
Fe(2)–P–C(1)	117.2 (2)	C(7)–C(8)–C(9)	108.1 (6)
Fe(2)–P–C(6)	119.5 (2)	C(8)–C(9)–C(10)	109.4 (6)
Fe(2)–P–C(17)	116.8 (2)	C(6)–C(10)–C(9)	108.4 (6)
C(1)–P–C(6)	93.2 (2)	Fe(2)–C(11)–C(12)	70.8 (6)
C(1)–P–C(17)	102.9 (3)	Fe(2)–C(11)–C(15)	70.9 (4)
C(6)–P–C(17)	103.5 (3)	C(12)–C(11)–C(15)	110.1 (10)
Fe(1)–C(1)–P	91.0 (2)	C(11)–C(12)–C(13)	105.5 (10)
Fe(1)–C(1)–C(2)	69.9 (3)	C(12)–C(13)–C(14)	107.4 (11)
Fe(1)–C(1)–C(5)	69.5 (3)	C(13)–C(14)–C(15)	108.6 (10)
P–C(1)–C(2)	121.9 (4)	C(11)–C(15)–C(14)	108.4 (10)
P–C(1)–C(5)	117.6 (4)	Fe(2)–C(16)–O	177.7 (7)
C(2)–C(1)–C(5)	106.2 (4)	P–C(17)–C(18)	120.7 (5)
C(1)–C(2)–C(3)	108.4 (5)	P–C(17)–C(22)	119.7 (5)
C(2)–C(3)–C(4)	108.7 (5)	C(18)–C(17)–C(22)	119.5 (6)
C(3)–C(4)–C(5)	108.0 (6)	C(17)–C(18)–C(19)	121.2 (7)
C(1)–C(5)–C(4)	108.8 (5)	C(18)–C(19)–C(20)	119.7 (8)
Fe(1)–C(6)–P	91.1 (2)	C(19)–C(20)–C(21)	120.3 (7)
Fe(1)–C(6)–C(7)	69.4 (3)	C(20)–C(21)–C(22)	121.1 (8)
Fe(1)–C(6)–C(10)	70.1 (3)	C(17)–C(22)–C(21)	118.3 (7)

$\{(C_6H_5)[Fe(C_5H_5)(C_5H_4)][Fe(C_5H_5)(C_5H_3C(O))]P\text{-}P,C\}\text{-}$
$Fe(C_5H_5)(CO)\cdot CHCl_3$ (**12**)

P–Fe(1)–C(1)	92.2 (2)	C(10)–C(11)–C(12)	107.9 (4)
P–Fe(1)–C(2)	87.83 (14)	C(8)–C(12)–C(11)	108.0 (4)
P–Fe(1)–Cp(1)	126.4 (1)	C(14)–C(13)–C(17)	107.3 (5)
C(1)–Fe(1)–C(2)	88.9 (2)	C(13)–C(14)–C(15)	108.4 (5)
C(1)–Fe(1)–Cp(1)	127.8 (2)	C(14)–C(15)–C(16)	108.3 (6)
C(2)–Fe(1)–Cp(1)	121.9 (2)	C(15)–C(16)–C(17)	107.7 (6)
Cp(2)–Fe(2)–Cp(3)	177.0 (1)	C(13)–C(17)–C(16)	108.3 (5)
Cp(4)–Fe(3)–Cp(5)	175.9 (2)	P–C(18)–C(19)	126.2 (4)
Fe(1)–P–C(8)	103.4 (2)	P–C(18)–C(22)	126.0 (4)
Fe(1)–P–C(18)	115.61 (15)	C(19)–C(18)–C(22)	106.3 (5)
Fe(1)–P–C(28)	118.2 (2)	C(18)–C(19)–C(20)	109.2 (5)
C(8)–P–C(18)	102.7 (2)	C(19)–C(20)–C(21)	107.5 (5)
C(8)–P–C(28)	111.6 (2)	C(20)–C(21)–C(22)	108.7 (5)
C(18)–P–C(28)	104.4 (2)	C(18)–C(22)–C(21)	108.1 (5)
Fe(1)–C(1)–O(1)	178.5 (5)	C(24)–C(23)–C(27)	107.9 (7)
Fe(1)–C(2)–O(2)	124.8 (4)	C(23)–C(24)–C(25)	106.5 (9)
Fe(1)–C(2)–C(9)	116.1 (3)	C(24)–C(25)–C(26)	110.7 (11)
O(2)–C(2)–C(9)	119.1 (4)	C(25)–C(26)–C(27)	107.0 (10)
C(4)–C(3)–C(7)	108.6 (5)	C(23)–C(27)–C(26)	107.9 (9)
C(3)–C(4)–C(5)	107.4 (5)	P–C(28)–C(29)	123.5 (4)
C(4)–C(5)–C(6)	107.8 (5)	P–C(28)–C(33)	118.0 (4)
C(5)–C(6)–C(7)	108.5 (5)	C(29)–C(28)–C(33)	118.5 (5)
C(3)–C(7)–C(6)	107.7 (5)	C(28)–C(29)–C(30)	120.1 (6)
P–C(8)–C(9)	111.7 (3)	C(29)–C(30)–C(31)	121.1 (6)
P–C(8)–C(12)	139.6 (4)	C(30)–C(31)–C(32)	119.6 (6)
C(9)–C(8)–C(12)	108.0 (4)	C(31)–C(32)–C(33)	120.1 (6)
C(2)–C(9)–C(8)	120.5 (4)	C(28)–C(33)–C(32)	120.5 (5)
C(2)–C(9)–C(10)	131.9 (4)	C(1)–C(34)–Cl(2)	109.7 (5)
C(8)–C(9)–C(10)	107.7 (4)	Cl(1)–C(34)–Cl(3)	111.0 (4)
C(9)–C(10)–C(11)	108.4 (4)	Cl(2)–C(34)–Cl(3)	109.1 (4)

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[10] Abbreviations: pt = pseudotriplet, pdd = pseudodoublet of doublets.

obtained: **1a**, δ 17.1 (s); **17**, δ 110.5 (d); the reaction solution after stirring for 2 h, δ 17.1 (s); the reaction solution after hydrolysis, A, δ 110.5 (d), B, δ 100.8 (s), ratio of A:B = 20:1; a 1:1 mixture of **1a** and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$, δ 17.1 (s).

X-ray Crystallographic Analyses of 12 and 17. Crystallographic data appear in Table I. The final unit-cell parameters were obtained by least-squares on $(2 \sin \theta)/\lambda$ values for 25 reflections (with 2θ = 30–39° for **12** and 24–37° for **17**) measured with Mo $K\alpha_1$ radiation. Data were corrected for absorption by using the Gaussian integration method.[11]

Both structures were solved by coventional heavy-atom methods, the coordinates of the Fe and P atoms being determined from the Patterson function and those of the remaining nonhydrogen atoms from subsequent difference maps. The nonhydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included as fixed contributors in calculated positions (Fe–H = 1.45 Å, C(sp^2)–H = 0.97 Å, and C(sp^3)–H = 0.98 Å). Neutral atom scattering factors and anomalous scattering corrections for Fe, Cl, and P were taken from ref 12.

Final atomic coordinates and equivalent isotropic thermal parameters ($U_{eq} = {}^1/_3$ trace diagonalized U) are given in Table II. Bond lengths, bond angles, and intraannular torsion angles appear in Tables III, IV, and V, respectively. Calculated hydrogen coordinates, anisotropic thermal parameters, torsion angles, and measured and calculated structure factor amplitudes (Tables VI–X) are included as supplementary material.

Results and Discussion

The synthesis of cyclopentadienylphosphines, $PR_n(\eta^1\text{-}C_5H_5)_{3-n}$, is of interest because little is known about this class of compounds, especially the possibility of utilizing the C_5H_5 group for coordination to metals.[13] In principle, cleavage of the [1]ferrocenophane **1a** with C_5H_5Li should afford a route to simple tertiary phosphines of this class such as **3** (Scheme I). This could be the method of preference if ferrocenyl derivatives are needed because of the problem of preparing pure monolithioferrocene[15] for subsequent metathesis reaction with $ClPR_n(\eta^1\text{-}C_5H_5)_{2-n}$. As there is no problem with the preparation of 1,1′-dilithioferrocene,[9] this route should be preferred if 1,1′-disubstituted derivatives are desired (eq 1 and 2).

$$C_5H_5Tl + Cl_2PC_6H_5 \rightarrow ClP(C_6H_5)(C_5H_5) \quad (1)$$

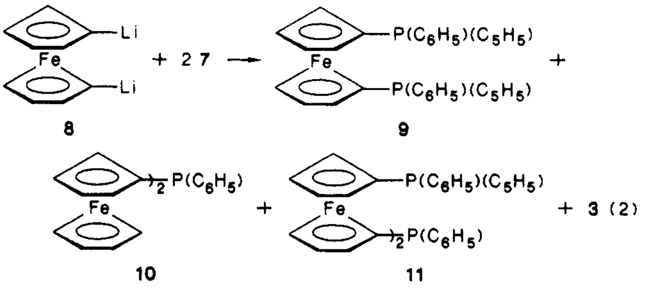
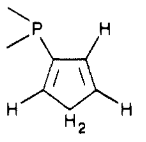


Table V. Intraannular Torsion Angles (deg) with Estimated Standard Deviations in Parentheses for $\{(C_6H_5)[Fe(C_5H_5)(C_5H_4)][Fe(C_5H_5)(C_5H_3C(O))]P\text{-}P,C\}\text{-}Fe(C_5H_5)(CO)\bullet CHCl_3$ (12)

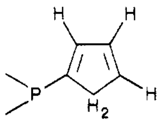
atoms	value, deg
C(2)–Fe(1)–P–C(8)	4.0 (2)
P–C(8)–C(9)–C(2)	8.4 (6)
Fe(1)–C(2)–C(9)–C(8)	−5.0 (6)
P–Fe(1)–C(2)–C(9)	−0.3 (3)
Fe(1)–P–C(8)–C(9)	−7.5 (4)

When the ring cleavage reaction of **1a** with C_5H_5Li is attempted in diethyl ether as solvent, no cleavage products are obtained after 2 days. A slow reaction takes place when the solvent is changed to THF and TMED, tetramethylethylenediamine, is added to enhance the reactivity of the lithium species; TMED also increases its solubility in the reaction medium. The progress of the reaction can be monitored easily by TLC since the ferrocenophane **1a** has a characteristic deep red color. The yield of the orange crystalline product **3**, isolated after hydrolysis, is essentially quantitative (~80% after crystallization).

Although the analytical data for the new derivative confirm its formulation, the ^{1}H NMR spectrum shows some interesting features. The cyclopentadienyl proton resonances exhibit two multiplets in the upfield region (δ 3.1 and 3.2, area ratio 1.5:1), indicating that two isomers are present in solution. This is confirmed by the $\{^1H\}^{31}P$ NMR spectrum that shows two singlets at δ −170 and −172 in the ratio 1: 1.6. Also the ratio of the low-field P–C_5H_5 proton resonances to the high-field resonances is approximately 3:2, indicating that the cyclopentadiene is bound to the phosphorus via sp^2-carbon atoms. This conclusion is confirmed by the $\{^{31}P\}^1H$ NMR spectrum that reveals that the ^{31}P couplings to the olefinic protons range from 2.5 to 5.5 Hz while coupling to the high-field protons is only 1.5 Hz.



3a



3b

Cyclopentadiene derivatives containing the P–$(CH_2)_nC_5H_5$ (n = 0–2) group have been studied by a number of workers,[14,16] and only one, $F_2PC_5H_5$, has been found to be fluxional.[16] The reported ^{1}H and ^{31}P NMR spectra of the nonfluxional compounds are similar to those obtained for **3**, and the existence of isomers of similar structure to **3a** and **3b** seems well-established. The evidence, particularly a two-dimensional NMR study (2-D J),[17] indicates that **3a** is most likely to be the isomer of **3** present in greater abundance. Variable-temperature NMR spectra (−90 to +100 °C) reveal no fluxional behavior; only slight variations in chemical shifts are observed.

The deep red complex L_2PdCl_2 (L = **3**) is easily prepared. The ^{1}H NMR spectrum of this[18] shows that the η^1-C_5H_5 groups are not involved in bonding to the metal and that the isomer ratio of **3a**:**3b** remains unchanged on complexation.

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(11) The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson; AGNOST, absorption corrections, by J. A. Ibers.

(12) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, 1979; Vol. IV.

(13) Some complexes of the ligands $R_2P(CH_2)_n(\eta^1\text{-}C_5H_5)$ (n > 1) are known[14] in which the C_5H_5 group is η^5-bonded to a transition metal.

(14) (a) Mathey, F.; Lampin, J. D. *Tetrahedron* **1975**, *31*, 2685. (b) Mathey, F.; Lampin, J. D. *J. Organomet. Chem.* **1977**, *128*, 287. (c) Charrier, C.; Mathey, F. *Tetrahedron Lett.* **1978**, 2407. (d) Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1979**, *120*, C41. (e) Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Inorg. Chem.* **1983**, *22*, 3475.

(15) The synthesis of *pure* monolithioferrocene, free from the dilithio compound, normally requires the synthesis of a monosubstituted ferrocene precursor, e.g., (chloromercurio)- or bromoferrocene.

(16) Bentham, J. E.; Ebsworth, E. A. V.; Moretto, H.; Rankin, D. W. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 640.

(17) Recorded by using the Varian XL-300 spectrometer and standard commercial programs.

(18) L_2PdCl_2 (L = 3): ^{1}H NMR ($CDCl_3$) δ 4.30 (m, 2), 4.42 (m, 2), 4.48, 4.49 (2 × s, 10), 4.50 (m, 2), 5.09 (m, 2), 6.53 (m, 2), 6.70 (m, 2), 6.77 (m, 2), 7.36 (m, 6), 7.70 (m, 4).

Mathey and Lampin[14] have prepared several cyclopentadienylphosphines by the reaction of chlorophosphines with cyclopentadienylthallium. For example, the reaction of 2 molar equiv of C_5H_5Tl with Cl_2PPh affords $(C_5H_5)_2PPh$ as an air-sensitive liquid. In the present investigation, in order to synthesize the previously unreported $ClPPh(C_5H_5)$ (7), a similar procedure was used, but the dichlorophosphine was treated with 1 molar equiv of TlC_5H_5 (eq 1). The chlorophosphine was not isolated, but a solution containing **7** (2 molar equiv) was treated immediately with dilithioferrocene–tetramethylethylenediamine (**8**) to give **9** as the major reaction product. This new bis(tertiary phosphine) is isolated as a mixture of diastereomers that are separable by preparative-plate TLC. These isomers give similar NMR spectra of the expected pattern that confirms their formulation as do the other analytical and spectroscopic results. Thus the mass spectrum of **9** shows a clear parent ion (*m/e* 530) with subsequent loss of C_5H_5 groups [*m/e* 465 (most intense peak) and 400]. Less intense peaks occur at *m/e* 323 ($M^+ - 2C_5H_5 - C_6H_5$) and 293 ($M^+ - 2C_5H_5 - PC_6H_5 + H$). The ^1H NMR spectrum of **9** in the η^1-C_5H_5 regions is almost identical with that observed for **3**. Presumably the same options regarding bonding apply as in **3a** and **3b**.

Three byproducts (in addition to ferrocene) are observed during the synthesis of **9**. The first is identified as **3** by comparison with an authentic sample. The second is the known diferrocenylphenylphosphine (**10**)[19] identified initially by mass spectroscopy and confirmed by a TLC comparison with an authentic sample. The third is identified as **11** by NMR and mass spectroscopy.[20]

Both compounds **3** and **9** are highly air-sensitive in solution; however, they can be stored as crystalline solids for prolonged periods in the absence of oxygen, without apparent decomposition.

The mass spectrum of **3** shows a clear parent ion at *m/e* 359 with the most prominent peak corresponding to loss of a C_5H_5 group. The spectrum of deuteriated **3**, formed by quenching the intermediate lithio species **2a**, R = C_5H_5, with D_2O following cleavage of **1a** with excess LiC_5H_5, has a parent ion at *m/e* 361 with the most abundant peak corresponding to a loss of a C_5H_4D group. Thus, in the presence of excess LiC_5H_5, **3** appears to exit, at least partially, as a dianion with lithiation occurring at both the "free" cyclopentadienyl ring as in **2** and at the η^1-C_5H_5 ring on phosphorus. The NMR spectrum of deuteriated **3** thus formed shows new sets of η^1-C_5H_5 resonances in addition to those originally observed in **3**, confirming that substitution of D on the η^1-C_5H_5 group does indeed partially occur.

To further develop the chemistry of these systems, the ring cleavage reaction of **1a** was carried out by using excess cyclopentadienyllithium/TMED and the resulting solution, presumably containing the dianion of **3**, **13** (Scheme II), was treated with $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$. It was anticipated that reaction would occur either on the ferrocenyl ring or on the P-bound cyclopentadienyl ring (or both). Thus products analogous to **5**, with EPh_2 replaced by $PPh(C_5H_5)$, could be expected, or they could be more elaborate.

In practice, TLC examination of the reaction solution indicates that no major product is formed. Column chromatographic separation of the reaction mixture gives the following products in order of elution: ferrocene, $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)Fe(CO)_2(\eta^5\text{-}C_5H_5)]$, $C_6H_5P[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]_2$, $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$, and finally a compound subsequently identified as **12**. Ferrocene is presumably formed by direct reaction of C_5H_5Li with $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$. The iron dimer, a persistent byproduct in all reactions of this type, is presumably formed by radical coupling.

As isolated, **12** is a mixture of two isomers (total yield 20%) that can be separated by fractional crystallization. The mass spectrum of each isomer is identical and shows a parent ion at *m/e* 524 corresponding to the formula $Fe_3C_{33}H_2PO_2$. The ^1H NMR spectrum shows the presence of three unsubstituted η^5-C_5H_5 rings. Clearly a reaction analogous to that shown in Scheme I does not occur. The structure of one isomer of **12** was further investigated by X-ray crystallography; it has the composition $\{(C_6H_5)[(C_5H_5)Fe(C_5H_4)][(C_5H_5)Fe(C_5H_3C(O))]P\text{-}P,C\}Fe(C_5H_5)(CO)\cdot CHCl_3$ and the structure shown in Figure 1. The other isomer is presumably a diastereomer which has a different orientation of the groups on Fe(1). The structure of **12** consists of complex molecules, each hydrogen bonded to one $CHCl_3$ molecule via a strong C–H···O hydrogen bond [C(34)–H(34)···O(2): H···O = 2.17 Å, C···O = 3.073(7) Å, and C–H···O = 153°] to form the basic structural unit. These moieties are associated by weak interactions C(22)–H(22)···O(1)$(1 - x, y - {}^1/_2, {}^1/_2 - z)$ [H···O = 2.46 Å, C···O = 3.238 (7) Å, and C–H···O = 137°] and C(26)–H(26)···Cl(1)$(x, {}^1/_2 - y, z - {}^1/_2)$ [H···Cl = 2.83 Å, C···Cl = 3.74 (1) Å, and C–H···Cl = 157°] to form spirals of complex molecules extending along *b* that are in turn bridged along *c* by solvent molecules. This structure is related to **17** (Figure 2) in that the phosphine ligand is a derivative of diferrocenylphenylphosphine in which one of the ferrocene groups is substituted by a –C(O)– group that also constitutes the X group in $(\eta^5\text{-}C_5H_5)Fe(CO)PR_3X$. Some of the common features will be discussed below.

The C(18)–C(22) cyclopentadienyl and the phenyl rings in **12** are slightly, but significantly, nonplanar (maximum deviations from the mean plane are 0.012 (6) and 0.018 (7) Å, respectively). The remaining cyclopentadienyl rings are planar within experimental error. The five-membered chelate ring has a flattened C(8)-envelope conformation with C(8) displaced 0.089 (5) Å from the mean plane of Fe(1), O(2), C(2), and C(9). The ferrocene moieties are essentially eclipsed [stagger angles: 3.1 (4)° about Fe(2) and 7.7 (6)° about Fe(3)].

The P–Ph and P–Cp distances are not significantly different and are the same as found in $Ru(CO)_4P[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]_3$[21] (1.804 (7), 1.802 (7), and 1.813 (8) Å). The angles at P vary considerably from the tetrahedral value ranging from 102.7 (2)° for C(8)–P–C(18) to 118.2 (2)° for Fe(1)–P–C(28). This is probably due to both the strained ring system and the bulky ligands. The C(9)–C(2) and C(2)–O(2) distances of 1.498 (6) and 1.218 (5) Å, respectively, are similar to those reported[22] [1.472 (22) and 1.215 (21) Å] for the *six*-membered ring of $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}\overline{C_5H_3C(O)CH_2CHMeCH_2}\text{-}1,2)$. Thus the H bonding apparently has little effect. The acyl derivative $(\eta^5\text{-}C_5H_5)Fe(dppe)C(O)Ph$ (dppe = $Ph_2PCH_2CH_2PPh_2$) is reported to have an elongated CO distance of 1.23 Å and a shortened Fe–COPh distance of 1.93 Å[23] supposedly due to conjugation with the iron atom. In the light of the present result this CO distance is probably not unusual

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[19] Kotz, J. C.; Nivert, C. L. *J. Organomet. Chem.* **1973**, *52*, 387.

[20] **11** is presumably formed from the reaction of 2 molar equiv of **8** with 2 molar equiv of **7** and 1 molar equiv of $Cl_2PC_6H_5$.

[21] Einstein, F. W. B.; Willis, A. J., personal communication.

[22] Lecomte, C.; Dusausoy, Y.; Protas, J.; Gutheron, B.; Broussier, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1504.

[23] Felkin, H.; Meunier, B.; Pascard, C.; Prange, T. *J. Organomet. Chem.* **1977**, *135*, 361.

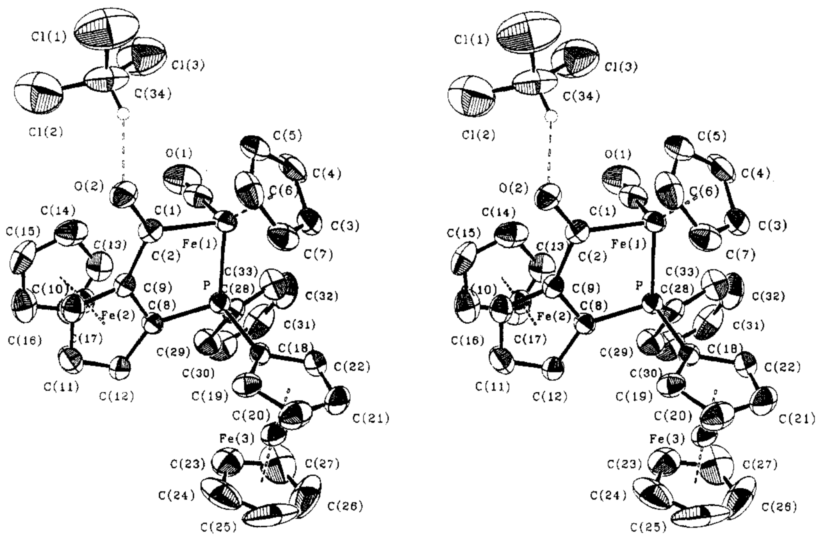


Figure 1. Stereoview of the structure of **12**.

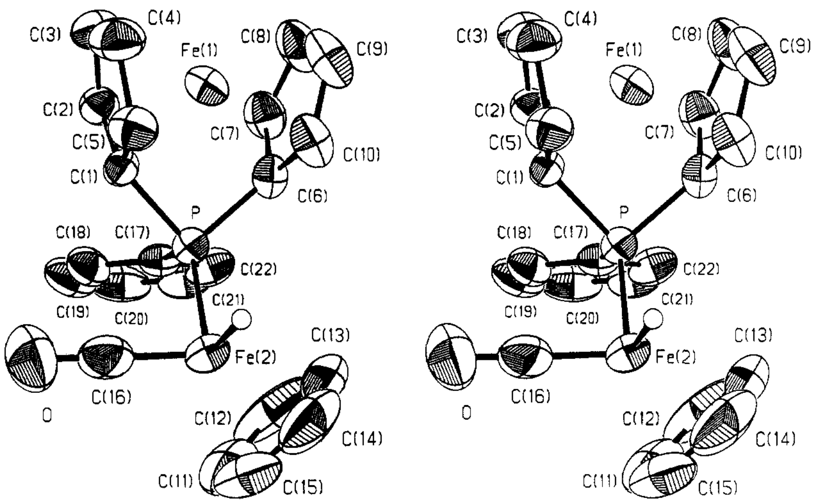
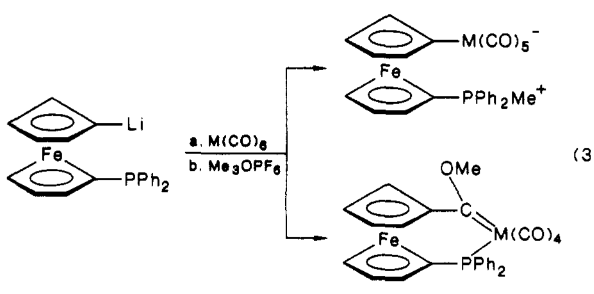


Figure 2. Stereoview of the structure of **17**.

although the Fe–acyl distance in **12** is longer, and normal, at 1.970 (5) Å.[24]

The reactions that give rise to **12** presumably have their origin in an anion derived from the P–C_5H_5 ring since this seems to be the only way in which a 1,2-disubstituted ring could be formed. Reaction of **2a** should yield only 1,1′-disubstituted ferrocene derivatives.[4,5] Scheme II shows a possible reaction sequence starting from the dianion **13**, whose existence is discussed above. The reactions in Scheme I, especially the formation of **6a**, provide precedent for the formation of **14** and **15**. It is a moot point whether the charge on **15** results from **14** or reaction with LiC_5H_5. It is interesting to note that the second ferrocene fragment in **12** is assembled during the reaction and that the "original" one is unaffected by the transformation. Labeling studies and further synthetic work will be necessary to establish the details of Scheme II.

The closest analogue to **12** in terms of ferrocene chemistry appears to be **16** formed from **2** as indicated in eq 3.[5] Casey and co-workers have isolated similar chelated systems based on the ring metal–carbene–donor.[27]



(3)

16a,b

a, M = Cr; **b**, M = W

As mentioned in the Introduction the reaction of **1a** with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ was also investigated. When the reaction mixture is monitored by TLC, the complete disappearance of **1a** on addition of the sodium salt seems to be indicated. This is accompanied by the formation of a new yellow-orange product. It was deemed possible that

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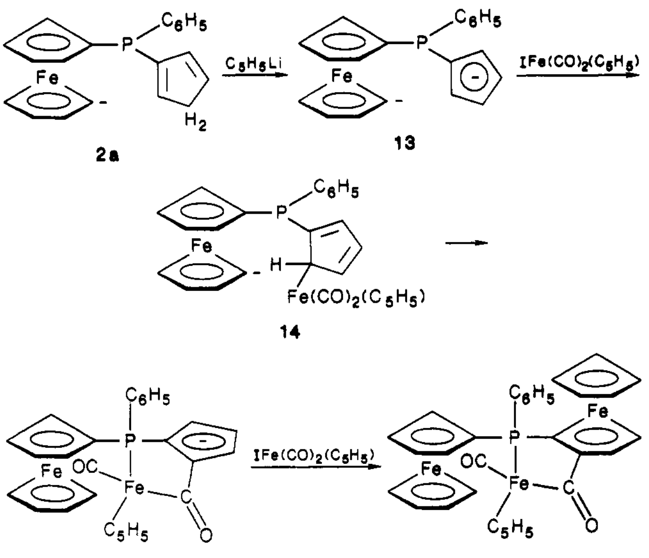
[24] The mean CO distance in $Fe(\eta^5\text{-}C_5H_4COCH_3)_2$ is 1.218 (1) Å, and the C–C_5H_4 distance is 1.471 (3) Å.[25] The corresponding values for $Fe(C_5H_5)(C_5H_4COC_6H_5)$ are 1.225 (2) and 1.467 (3) Å.[26]

[25] Palenik, G. J. *Inorg. Chem.* **1970**, *9*, 2424.

[26] Butler, I. R.; Cullen, W. R.; Rettig, S. J., unpublished results.

[27] E.g.: Casey, C. P.; Vollendorf, N. W.; Haller, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 3754.

Scheme II



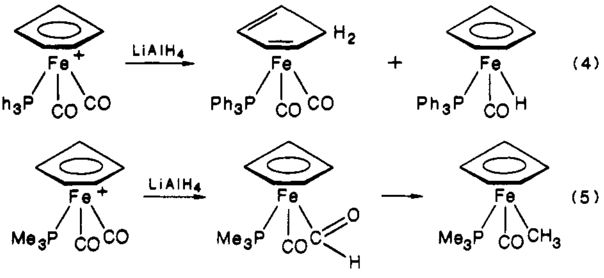
$Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ would react with **1a** according to Scheme I; however, the microanalytical and spectroscopic data of the major isolated product (following hydrolysis and chromatographic workup) do not fit the formulation for likely simple cleavage products. The infrared spectrum suggests the presence of only one Fe–CO group; thus, a phosphido-bridged dimer such as $(CO)(\eta^5\text{-}C_5H_5)Fe[\mu\text{-}P(C_6H_5)(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]_2Fe(CO)(\eta^5\text{-}C_5H_5)$ seems to be indicated. This formulation fits the analytical data but does not agree with the mass spectrum that shows only a monomer. Clues to the correct structure **17**, which is shown in detail in Figure 2 and discussed below, come from the color of the product, which is deep red-orange, characteristic of a [1]ferrocenophane, and the presence of a doublet in the ^1H NMR spectrum at δ −12.92 (J_{P-H} = 76 Hz, singlet on phosphorus decoupling), indicating the presence of a metal hydride.

The structure of **17** consists of discrete molecules separated by normal van der Waals' distances, the shortest intermolecular distance being $H(2)\cdots H(2)(1-x, 1-y, 1-z) = 2.24$ Å. The cyclopentadienyl and phenyl rings are all planar to within experimental error.

Like **12**, Figure 1, the molecule belongs to a large class of compounds of formula $(\eta^5\text{-}C_5H_5)FeL^1L^2X$, where L^1 and L^2 are two-electron donors and X is a formal one-electron donor such as H, SnR_3, C(O)R, or an alkyl group. Generally they have the "three-legged piano stool" six-coordinate structure,[28] and the present examples are no exception. The unique features of **17** are the presence of the metal hydride and the intact [1]ferrocenophane ligand. Unfortunately the position of the hydride ligand is not well-defined in the present structure, although there is little doubt about its presence. Only a few structural determinations have been made on compounds with Fe–H bonds,[29,30] and the hydride has been located in only two.[30]

Coordination of the ferrocenophane to iron has no significant effect on the bond lengths of the free ligand. There is only a slight effect on the angles. For example, the angles at phosphorus, C(17)–P–C(10), C(1)–P–C(6), and C(12)–P–C(6), have respectively the following values [complex (free ligand[8b])] 103.5 (3)° (101.1 (2)°), 93.2 (2)° (90.7 (2)°), and 103.5 (3)° (103.1 (2)°) as expected for an increase in coordination number. The opening of the C(1)–P–C(6) angle is accompanied by a similar movement of the Cp–Fe–Cp angle which has the value 161.5 (2)° in the complex and 159.8° in the free ligand.[8b,31] The nature of the ligand ensures that the angles involving Fe and P are greater than tetrahedral, e.g. Fe–P–C(6) at 119.5 (2)°. The Fe–P distance in **17** at 2.124 (2) Å is shorter than that found in related molecules of the $CpFe(CO)PR_3X$ type.[32] This may be due to the presence of the hydride ligand since the Fe–P distance found for $H_2Fe[PPh(OEt)_2]_4$ ranges from 2.119 (2) to 2.151 (2) Å.[30a] The Fe–CO distance is also at the shorter end of the range at 1.680 (9) Å; the C–O distance is normal.[32-35]

Compound **17** can be regarded as a derivative of the little known hydride $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$[36] in which a carbonyl group has been replaced by the phosphine **1a**. The spectroscopic and analytical results are entirely consistent with the solid-state structure. A ^1H NMR study of the reactants and products indicates that **17** is not formed until after the hydrolysis step that would produce $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ from $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$. Thus, a simple carbonyl displacement reaction is all that is needed to produce **17**. This is not without precedent since Baird and coworkers[36] have reported that $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ reacts easily with $PPhMe_2$ in this way. A similar reaction must take place on the TLC plate, i.e., hydrolysis followed by substitution, to account for the apparent formation of **17** on first treating **1a** with $NaFe(CO)_2(\eta^5\text{-}C_5H_5)$. Davies and co-workers[37] have prepared an analogue of **17** by reducing cations such as $Fe(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)^+$ with $LiAlH_4$ (eq 4 and 5) although the product obtained in a given instance is dependent on the phosphine.



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(31) Data that are useful for comparison with other ferrocenophanes are listed (the symbols are defined in ref 8b): Fe(1)–Cp(1), 1.624 (3) Å; Fe(1)–Cp(2), 1.633 (3) Å; Cp(1)–Fe(1)–Cp(2), 161.5 (2)°; $C(1)\cdots C(6)$, 2.672 (7) Å; $Fe(1)\cdots P$, 2.731 (2) Å; C(1)–P–C(6) [= θ], 93.2 (2)°; α, 25.4 (3)°, β, 33.9 (3).

(32) E.g.: (a) Einstein, F. W. B.; Restivo, R. *Inorg. Chim. Acta* **1971**, *5*, 501. (b) Churchill, M. R.; Chang, S. W.-Y. N. *J. Am. Chem. Soc.* **1973**, *95*, 5931. (c) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619. (d) Miles, S. L.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7278. (e) Chou, C.-K.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271.

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(35) In **12** the $(\eta^5\text{-}C_5H_5)Fe(CO)PR_3X$ fragment is part of a ring. Here both Fe–P and Fe–CO distances are longer at 2.1848 (14) and 1.722 (6) Å, respectively. The Cp(2)–Fe(2) distance in **17** is also shorter than usual at 1.706 (2) Å; the bench mark value of 1.737 (3) Å is reported for $(\eta^5\text{-}C_5H_5)Fe(CO)_2\overline{CMeCH_2C(CN)_2C(CN)_2CH_2}$[32b] although the same distance is 1.71 (3) Å in $(\eta^5\text{-}C_5H_5)f_6FosSnMe_3$.[36a]

(36) Fergusson, G. B.; Sanderson, L. J.; Shackleton, T. A.; Baird, M. C. *Inorg. Chim. Acta* **1984**, *83*, L45.

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The structure of **17** is the first to be determined in which a [1]ferrocenophane acts as a ligand although a number of derivatives of **1a** are known, e.g. $Fe(CO)_4L$,[2] $Cr(CO)_5L$,[2] and L_2PdCl_2.[38]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support in the form of grants to W.R.C. and the UBC crystal structure service. We also thank Dr. J. Trotter for the use of X-ray equipment, the UBC computing center for funds, and Dr. N. R. Jagannathan for running the 2-D NMR spectrum of **3**.

Supplementary Material Available: Tables of calculated hydrogen coordinates, anisotropic thermal parameters, and torsion angles (Tables VI–VIII) (8 pages); observed and calculated structure factor amplitudes (Tables IX and X) (51 pages). Ordering information is given on any current masthead page.

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Communications

Relative Rate Constants for the Reactions of Methylphenylsilylene[1]

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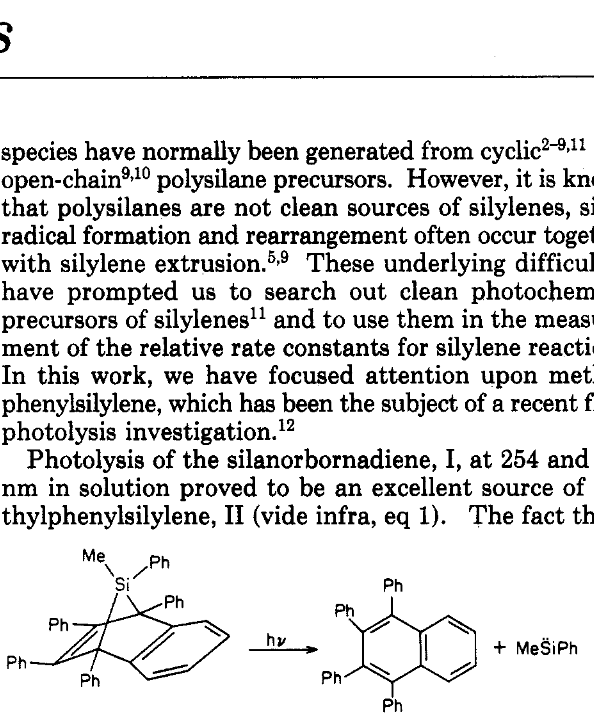
Summary: Photolysis of 1,4,5,6-tetraphenyl-2,3-benzo-7-methyl-7-phenyl-7-silanorbornadiene (I) in benzene–cyclohexane solutions gave methylphenylsilylene (II) that was efficiently scavenged by ethanol, triethylsilane, and 2,3-dimethyl-1,3-butadiene (III) with the following relative rate constants $k_{EtOH}/k_{Et_3SiH} = 4.8$ and $k_{III}/k_{Et_3SiH} = 3.0$ at 298 K. Methylphenylsilylene did not appear to react rapidly with oxygen. The results conflict with those of a recent flash photolysis study.

The chemistry of silylenes has been the subject of considerable interest in recent years.[2–11] These transient species have normally been generated from cyclic[2–9,11] and open-chain[9,10] polysilane precursors. However, it is known that polysilanes are not clean sources of silylenes, since radical formation and rearrangement often occur together with silylene extrusion.[5,9] These underlying difficulties have prompted us to search out clean photochemical precursors of silylenes[11] and to use them in the measurement of the relative rate constants for silylene reactions. In this work, we have focused attention upon methylphenylsilylene, which has been the subject of a recent flash photolysis investigation.[12]

Photolysis of the silanorbornadiene, I, at 254 and 350 nm in solution proved to be an excellent source of methylphenylsilylene, II (vide infra, eq 1). The fact that I can be photolyzed over a wide range of wavelengths, in order to generate methylphenylsilylene, gives it a unique advantage as a precursor, since wavelengths can be chosen to avoid the photolysis of coreagents.



(1)

I

II

Photolysis of I in benzene–cyclohexane mixtures containing ethanol, triethylsilane, or 2,3-dimethyl-1,3-butadiene, III, gave the products shown in Scheme I. These were identified by their GC/mass spectra and were quantified by GC using authentic samples as calibrants wherever possible. The overall yields of products con-

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[1] Issued as NRCC Publication No. 27348.

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