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Synthesis and Characterization of Cyclopentadienylfluorophosphine Ligands and Their Borane(3) Complexes

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The reactions of PF_2Br, PF_2Cl, and $PFCl_2$ with thallium(I) salts of cyclopentadiene and methylcyclopentadiene at −78 °C produce the organofluorophosphines η^1-$C_5H_5PF_2$, $(\eta^1$-$C_5H_5)_2PF$, $(\eta^1$-$CH_3C_5H_4)PF_2$, and $(\eta^1$-$CH_3C_5H_4)_2PF$ in high yields. Each ligand combines with B_2H_6; the resulting compounds are classical borane(3) coordination complexes which contain a direct P–B coordinate bond. The ligands and coordination complexes have been characterized by mass, infrared, and ^1H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectrometries, and these data are presented and discussed.

Introduction

Syntheses for a number of η^1-cyclopentadienyl derivatives of nonmetal and metal atoms have been reported in the literature. Many of these cyclopentadienyl compounds have been observed to participate in complex intramolecular rearrangements in the liquid phase, and the fluxional motions of several molecules have been successfully explored by ^1H and ^{13}C NMR techniques.[1] Despite the attention given specifically to the motional properties of nonmetal η^1-cyclopentadienyl compounds, the chemistry of these species has received little attention. As an example, several η^1-C_5H_5 derivatives of group 4A elements have been prepared and extensively characterized by NMR spectroscopy,[2] but a systematic exploration of their reaction chemistry has not been presented. Further, for the case of group 5A elements only one cyclopentadienyl derivative of a halophosphine, η^1-$C_5H_5PF_2$, has been reported.[3] The tris(cyclopentadienyl) derivatives Cp_3As, Cp_3Sb, and Cp_3Bi also have been prepared.[4]

For our purposes group 5A cyclopentadienyl derivatives represent a class of ligands of special interest; the ligands are potentially bifunctional and bidentate. It is expected that the lone electron pair localized on the central phosphorus atom should be available for coordination by classical Lewis acceptors and low-valent transition-metal atoms. Furthermore, the cyclopentadienyl ring may be available for coordination by low-valent transition-metal atoms; the η^1-C_5H_5 might coordinate as a diene or, if the ring is deprotonated, as a η^5-cyclopentadienyl group. It is also conceivable that both the phosphorus and olefin functions could simultaneously coordinate one transition-metal site or bridge two metal sites.

In this paper we report a much improved synthesis for η^1-$C_5H_5PF_2$ and syntheses for the previously unknown ligands $(\eta^1$-$C_5H_5)_2PF$, $(\eta^1$-$CH_3C_5H_4)PF_2$, and $(\eta^1$-$CH_3C_5H_4)_2PF$. These syntheses, for the first time, have permitted convenient studies of the coordination properties of this group of ligands. The coordination chemistry of each ligand toward borane(3) is specifically described here while the coordination chemistry with transition-metal complexes is the subject of another report.[5]

Experimental Section

General Information. Standard high-vacuum synthetic techniques were used for the manipulations of the volatile compounds. Mass spectra were recorded on a DuPont Model 21-491 spectrometer operating at 70 eV with an inlet temperature of 30 °C and a source temperature of 100 °C. All samples were introduced as gases. Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrometer using a 10-cm glass cell fitted with KBr windows. The infrared spectra were calibrated with polystyrene film absorptions and fundamental absorptions in the PF_3 spectrum. The NMR spectra were recorded on a Varian XL-100 NMR spectrometer operating at 25.2 MHz (^{13}C), 32.1 MHz (^{11}B), 40.5 MHz (^{31}P), 94.1 MHz (^{19}F), and 100 MHz (^1H). The data were collected in the pulse mode using a Nicolet TT-100 data system. Samples were contained in sealed 5-mm tubes rigidly placed in a 12-mm tube containing a deuterated lock sample. Spectra standards were $(CH_3)_4Si$ (^{13}C, ^1H), $BF_3\cdot(C_2H_5)_2O$ (^{11}B), 85% H_3PO_4 (^{31}P), and $CFCl_3$ (^{19}F).

Materials. Thallium cyclopentadienide was prepared by a literature method.[6] Methylcyclopentadiene dimer was purified and thermally cracked as described in the literature.[7] Care must be taken to rid the $CH_3C_5H_5$ of C_5H_6; otherwise the thallium reagent is contaminated with C_5H_5Tl. Purity of the $CH_3C_5H_5$ was verified by gas chromatograms of the cracked distillate. The $CH_3C_5H_4Tl$ salt was prepared in a fashion similar to C_5H_5Tl except the filtrations and isolation were performed in a nitrogen-filled drybag. Fluorophosphines F_2PBr,[8] F_2PCl,[8] and $FPCl_2$[9] and diborane(6)[10] were prepared by literature methods.

Synthesis of η^1-$C_5H_5PF_2$ and η^1-$CH_3C_5H_4PF_2$. A 5.0-mmol sample of TlCp or TlMeCp was loaded under nitrogen into a 50-mL Schlenk tube. To the evacuated tube, 5.2 mmol of PF_2Cl or PF_2Br was condensed, and the mixture was allowed to warm to −78 °C. Reaction occurred immediately upon contact of the liquid phosphine and solid thallium salt. To ensure complete reaction the mixture was allowed to remain at −78 °C for 2 h. The volatile products were vacuum distilled through −23, −78, and −196 °C traps. The F_2PCp and $F_2P(MeCp)$ were retained at −78 °C as colorless crystals and as a colorless oil, respectively. The yields were 95–98% based upon the fluorophosphine consumed.

Synthesis of $(\eta^1$-$C_5H_5)_2PF$ and $(\eta^1$-$CH_3C_5H_4)_2PF$. A 5.0-mmol sample of TlCp or TlMeCp was added to a 50-mL Schlenk tube, and the tube was evacuated. A 2.0-mmol sample of $PFCl_2$ was condensed into the tube at −196 °C, and the tube was then warmed to −78 °C. The reactions occurred upon contact of the reagents. After 2 h, the volatile products were vacuum distilled through −23, −78, and −196 °C traps. The phosphines were retained at −78 °C as colorless solids. The yields ranged from 85 to 90% based upon the fluorophosphine consumed.

Synthesis of Borane(3) Complexes. A 2.0-mmol sample of cyclopentadienylphosphine ligand was condensed into a 50-mL Schlenk tube at −196 °C. A 1.2-mmol sample of B_2H_6 was condensed over

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the ligand and the tube was allowed to warm to −23 °C. The mixture was maintained at −23 °C for 5 min, and the volatile products were then distilled through −45, −78, and −196 °C traps. The borane complexes were retained at −45 °C with yields of 80–85% based on the B_2H_6 consumed.

Properties of Ligands and Complexes. Each of the ligands is susceptible to rapid air oxidation, hydrolysis, and thermal decomposition at 23 °C. The major products of these reactions have not been fully determined. The borane(3) complexes are air and moisture sensitive, and they decompose by a complex route involving dissociation and apparent reduction of the olefin function.

1. $CpPF_2$. Mass spectrum[11] [*m/e* (assignment) relative intensity]: 199 ($(C_5H_5)_2PF_2^+$) 5, 134 ($C_5H_5PF_2^+$) 92, 115 ($C_5H_5PF^+$) 16, 69 (PF_2^+) 39, 65 ($C_5H_5^+$) 100, 64 ($C_5H_4^+$) 8, 63 ($C_5H_3^+$) 35, 62 ($C_5H_2^+$) 16, 61 ($C_5H_1^+$) 10, 50 (PF^+) 2, 39 ($C_3H_3^+$) 87, 38 ($C_3H_2^+$) 16, 37 ($C_3H_1^+$) 8. Infrared spectrum (cm^{-1}) (gas): 3130 (sh, w), 3115 (m, sh), 3085 (m), 1658 (w), 1390 (sh, w), 1385 (m), 1298 w, 1290 w, 1222 (w), 1212 w, 1120 (m), 1011 (s), 948 (sh, m), 945 (m), 941 (sh, m), 820 (sh, s), 798 (s), 703 (s), 515 (w), 483 (w), 441 (sh, m), 437 (m), 431 (sh, m). NMR spectra[12] (neat) −40 °C: ^1H, $\delta = 7.02$, 6.52, 4.04 ($J_{HCPF} = 10.5$ Hz); $^{13}C[^1H]$, $\delta = 138.71$ ($J_{CP} = 5$ Hz), 125.65 ($J_{CP} = 11$ Hz), 65.46 ($J_{CP} = 44$ Hz, $J_{CPF} = 6$ Hz); ^{19}F, $\delta = -72.4$ ($J_{FP} = 1183$ Hz, $J_{FPCH} = 10$ Hz); $^{31}P[^1H]$, $\delta = 195$ ($J_{PF} = 1172$ Hz).

2. $MeCpPF_2$. Mass spectrum [*m/e* (assignment) relative intensity]: 149 ($C_6H_7PF_2^+$) 3, 148 ($C_6H_6PF_2^+$) 38, 147 ($C_6H_5PF_2^+$) 1, 134 ($C_5H_4PF_2^+$) 5, 130 ($C_6H_7PF^+$) 1, 129 ($C_6H_6PF^+$) 4, 79 ($C_6H_7^+$) 59, 78 ($C_6H_6^+$) 31, 77 ($C_6H_5^+$) 100, 76 ($C_6H_4^+$) 1, 69 (PF_2^+) 19, 65 ($C_5H_5^+$) 14, 63 ($C_5H_3^+$) 6, 53 ($C_4H_5^+$) 14, 52 ($C_4H_4^+$) 10, 51 ($C_4H_3^+$) 25, 50 ($C_4H_2^+$) 15, 39 ($C_3H_3^+$) 23, 38 ($C_3H_2^+$) 5. Infrared spectrum (cm^{-1}) (gas): 3107 (w), 3070 (w), 3025 (sh, w), 2930 (m), 2875 (w), 1701 (w), 1375 (w), 1022 (m), 863 (s), 800 (s), 760 (m), 713 (m), 598 (w), 438 (w). NMR spectra (neat) −40 °C: ^1H, $\delta = 6.78$, 6.38, 6.09, 3.80 ($J_{HCPF} = 10$ Hz), 2.20, 2.14, 2.10; $^{13}C[^1H]$, $\delta = 150.49$ ($J_{CP} = 4.5$ Hz), 142.30 ($J_{CP} = 2$ Hz), 139.33 ($J_{CP} = 4$ Hz), 126.42 120.3, 68.41 ($J_{CP} = 42$ Hz, $J_{CPF} = 6$ Hz), 65.09 ($J_{CP} = 42$ Hz, $J_{CPF} = 6$ Hz), 16.12, 15.29; ^{19}F, $\delta = -73.7$ ($J_{FP} = 1152$ Hz, $J_{FPCH} = 9$ Hz), −74.4 ($J_{FP} = 1152$ Hz, $J_{FPCH} = 9$ Hz); $^{31}P[^1H]$, $\delta = 194.9$ ($J_{PF} = 1164$ Hz), 195.4 ($J_{PF} = 1164$ Hz).

3. Cp_2PF. Mass spectrum [*m/e* (assignment) relative intensity]: 180 ($C_{10}H_{10}PF^+$)$_2$ 2, 166 ($C_9H_8PF^+$) 9, 165 ($C_9H_7PF^+$) 2, 164 ($C_9H_6PF^+$) 29, 148 ($C_9H_9P^+$) 2, 145 ($C_9H_6P^+$) 3, 129 (?) 21, 109 (?) 4, 85 (?) 3, 81 (?) 5, 80 ($C_2H_6PF^+$) 21, 79 ($C_2H_5PF^+$) 100, 78 ($C_2H_4PF^+$) 43, 77 ($C_2H_3PF^+$) 85, 69 (PF_2^+) 3, 53 ($C_4H_5^+$) 7, 52 ($C_4H_4^+$) 8, 51 ($C_4H_3^+$) 18, 50 (PF^+) 9, 39 ($C_3H_3^+$) 16. Infrared spectrum (cm^{-1}) (gas): 3122 (sh, m), 3100 (m), 3070 (m), 3042 (w), 2910 (m), 1600 (w), 1460 (w), 1445 (w), 890 (w), 860 (m), 845 (sh, m), 800 (s), 756 (m), 710 (m), 592 (w), 532 (w), 523 (w), 430 (m). NMR spectra (neat) −40 °C: ^1H, $\delta = 6.98$, 6.50, 6.11, 3.96, 3.00; $^{13}C[^1H]$, $\delta = 139.23$ ($J_{CP} = 2$ Hz), 128.32 ($J_{CP} = 15$ Hz), 67.25 ($J_{CP} = 46$ Hz, $J_{CPF} = 4$ Hz); ^{19}F, $\delta = -102$ ($J_{FP} = 1119$ Hz, $J_{FPCH} = 6$ Hz); $^{31}P[^1H]$, $\delta = 192$ ($J_{PF} = 1119$ Hz).

4. $(MeCp)_2PF$. Mass spectrum [*m/e* (assignment) relative intensity]: 208 ($C_{12}H_{14}PF^+$) 2, 207 ($C_{12}H_{13}PF^+$) 1, 206 ($C_{12}H_{12}PF^+$) 4, 205 ($C_{12}H_{11}PF^+$) 1, 204 ($C_{12}H_{10}PF^+$) 2, 203 ($C_{12}H_9PF^+$) 1, 202 ($C_{12}H_8PF^+$) 5, 194 ($C_{11}H_{12}PF^+$) 3, 193 ($C_{11}H_{11}PF^+$) 3, 192 ($C_{11}H_{10}PF^+$) 5, 191 ($C_{11}H_9PF^+$) 2, 190 ($C_{11}H_8PF^+$) 7, 187 ($C_{12}H_{12}P^+$) 2, 186 ($C_{12}H_{11}P^+$) 3, 185 ($C_{12}H_{10}P^+$) 5, 130 ($C_6H_7PF^+$) 3, 129 ($C_6H_6PF^+$) 6, 79 ($C_6H_7^+$) 53, 78 ($C_6H_6^+$) 30, 77 ($C_6H_5^+$) 100, 76 ($C_6H_4^+$) 4, 65 ($C_5H_5^+$) 19, 63 ($C_5H_3^+$) 7, 53 ($C_4H_5^+$) 11, 52 ($C_4H_4^+$) 7, 51 ($C_4H_3^+$) 20, 50 ($C_4H_2^+$) 18. NMR spectra (neat) −40 °C: $^{13}C[^1H]$, $\delta = 150.51$ ($J_{CP} = 6.5$ Hz), 142.58 ($J_{CP} = 5$ Hz), $\delta = 128.81$ ($J_{CP} = 12$ Hz), 122.3 ($J_{CP} = 12$ Hz), 66.39 ($J_{CP} = 43$ Hz, $J_{CPF} = 6$ Hz), 15.80; ^{19}F, $\delta = -101.8$ ($J_{FP} = 1107$ Hz), −103.7 ($J_{FP} = 1105$ Hz, $J_{FPCH} = 10$ Hz); $^{31}P[^1H]$, $\delta = 193.3$ ($J_{PF} = 1109$ Hz), 192.3 ($J_{PF} = 1120$ Hz).

5. $CpPF_2{\cdot}BH_3$. Mass spectrum [*m/e* (assignment) relative intensity]:[12] 148 ($C_5H_5PF_2BH_3^+$) 3, 147 ($C_5H_7PF_2B^+$) 3, 146 ($C_5H_6PF_2B^+$) 2, 134 ($C_5H_5PF_2^+$) 85, 115 ($C_5H_5PF^+$) 18, 97 ($C_5H_5P^+$) 3, 96 ($C_5H_4P^+$) 4, 95 ($C_5H_3P^+$) 3, 69 (PF_2^+) 25, 65 (C_5H_5) 100, 64 ($C_5H_4^+$) 5, 63 ($C_5H_3^+$) 17, 62 ($C_5H_2^+$) 6, 50 (PF^+) 14, 41 ($C_3H_5^+$) 6, 40 ($C_3H_4^+$) 15, 39 ($C_3H_3^+$) 68, 38 ($C_3H_2^+$) 11. Infrared spectrum (cm^{-1}) (gas): 3090 (w), 2435 (w), 2402 (sh, w), 1385 (w), 1121 (w), 1013 (m), 946 (w), 820 (sh, s), 807 (s), 795 (s), 702 (s), 535 (w), 525 (w), 438 (m). NMR spectra ($CFCl_3$) −40 °C: ^1H, $\delta = 8.07$, 7.65, 5.24, 2.95; ^{19}F, $\delta = -84.6$ ($J_{FP} = 1184$ Hz, $J_{FPBH} = 22$ Hz, $J_{FPCH} = 10$ Hz); $^{31}P[^1H]$, $\delta = 192.2$ ($J_{PF} = 1160$ Hz); ^{11}B, $\delta = 43.0$ ($J_{BH} = 106$ Hz, $J_{BP} = 50.3$ Hz).

6. $MeCpPF_2{\cdot}BH_3$. Mass spectrum (*m/e* (assignment) relative intensity]:[12] 163 ($C_6H_7PF_2BH_3^+$) 2, 162 ($C_6H_9PF_2B^+$) 4, 161 ($C_6H_8PF_2B^+$) 5, 149 ($C_6H_7PF_2^+$) 7, 148 ($C_6H_6PF_2$) 42, 147 ($C_6H_6PF_2^+$) 3, 134 ($C_5H_4PF_2^+$) 7, 130 ($C_6H_7PF^+$) 2, 129 ($C_6H_6PF^+$) 6, 79 ($C_6H_7^+$) 61, 78 ($C_6H_6^+$) 34, 77 ($C_6H_5^+$) 100, 76 ($C_6H_9^+$) 2, 69 (PF_2^+) 21, 65 ($C_6H_5^+$) 15, 63 ($C_6H_3^+$) 8, 53 ($C_4H_5^+$) 20, 52 ($C_4H_4^+$) 14, 51 ($C_4H_3^+$) 28, 50 ($C_4H_2^+$) 17, 39 ($C_3H_3^+$) 28, 38 ($C_3H_2^+$) 4. Infrared spectrum (cm^{-1}) (gas): 3080 (w), 2985 (w), 2960 (w), 2930 (w), 2880 (w), 2440 (m), 1050 (br, s), 864 (s), 850 (sh, s), 755 (w), 718 (w), 590 (w), 538 (w), 527 (w), 512 (w), 490 (m), 420 (vw). NMR spectra ($CFCl_3$) −40 °C: $^{13}C[^1H]$, $\delta = 151.0$, 147.6, 143.2, 126.5, 120.3, 65.9, 63.7, 16.7, 15.5; ^{19}F, $\delta = -81.9$ ($J_{PF} = 1114$ Hz, $J_{HBPF} = 19$ Hz); $^{31}P[^1H]$, $\delta = 191.8$ ($J_{PF} = 1122$ Hz); ^{11}B, $\delta = 42.5$ ($J_{BH} = 107$ Hz, $J_{BP} = 48$ Hz).

7. $Cp_2PF{\cdot}BH_3$. Mass spectrum [*m/e* (assignment) relative intensity]:[12] 194 ($C_{10}H_{10}PFBH_3^+$) 4, 193 ($C_{10}H_{12}PFB^+$) 2, 180 ($C_{10}H_{10}PF^+$) 4, 166 ($C_9H_8PF^+$) 11, 165 ($C_9H_7PF^+$) 3, 164 ($C_9H_6PF^+$) 32, 148 ($C_9H_9P^+$) 3, 145 ($C_9H_6P^+$) 4, 129 (?) 22, 80 ($C_2H_6PF^+$) 24, 79 ($C_2H_5PF^+$) 100, 78 ($C_2H_4PF^+$) 45, 77 ($C_2H_3PF^+$) 80, 53 ($C_4H_5^+$) 12, 52 ($C_4H_4^+$) 9, 51 ($C_4H_3^+$) 20, 50 (PF^+) 11, 39 ($C_3H_3^+$) 18.

8. $(MeCp)_2PF{\cdot}BH_3$. Mass spectrum [*m/e* (assignment) relative intensity]:[12] 222 ($C_{12}H_{14}PFBH_3^+$) 2, 221 ($C_{12}H_{16}PFB^+$) 4, 208 ($C_{12}H_{14}PF^+$) 1, 207 ($C_{12}H_{13}PF^+$) 1, 206 ($C_{12}H_{12}PF^+$) 3, 194 ($C_{11}H_{12}PF^+$) 2, 192 ($C_{11}H_{10}PF^+$) 3, 190 ($C_{11}H_8PF^+$) 4, 187 ($C_{12}H_{12}P^+$) 3, 185 ($C_{12}H_{10}P^+$) 4, 130 ($C_6H_7PF^+$) 4, 129 ($C_6H_6PF^+$) 5, 79 ($C_6H_7^+$) 47, 78 ($C_6H_6^+$) 24, 77 ($C_6H_5^+$) 100, 76 ($C_6H_4^+$) 5, 65 ($C_5H_5^+$) 17, 63 ($C_5H_3^+$) 5, 53 ($C_4H_5^+$) 7, 51 ($C_4H_3^+$) 18, 50 ($C_4H_2^+$) 12.

Results and Discussion

Ligands. The combination of the thallium salts of cyclopentadiene and methylcyclopentadiene with PF_2Br, PF_2Cl, and $PFCl_2$ at −78 °C in the absence of a solvent results in the formation of the organofluorophosphines $F_2P(\eta^1\text{-}C_5H_5)$, $F_2P(\eta^1\text{-}C_5H_4CH_3)$, $PF(\eta^1\text{-}C_5H_5)_2$, and $FP(\eta^1\text{-}C_5H_4CH_3)_2$[14] in high yields. The syntheses are summarized by eq 1 and 2.

$$F_2PCl,\ F_2PBr + TlC_5H_4X \xrightarrow{-78\ ^\circ C} \underset{\mathbf{1}\ \text{and}\ \mathbf{2}}{F_2P(\eta^1\text{-}C_5H_4X)} + TlCl,\ TlBr \quad (1)$$

$$FPCl_2 + 2TlC_5H_4X \xrightarrow{-78\ ^\circ C} \underset{\mathbf{3}\ \text{and}\ \mathbf{4}}{FP(\eta^1\text{-}C_5H_4X)_2} + 2TlCl \quad (2)$$

$$X = H \text{ in } \mathbf{1} \text{ and } \mathbf{3};\ X = CH_3 \text{ in } \mathbf{2} \text{ and } \mathbf{4}$$

Each of the ligands is observed to be air, moisture, and temperature sensitive. The thermal decomposition half-lives of the ligands at 25 °C range from about 6 h to 1 day with the methylcyclopentadienyl derivatives **2** and **4** being noticeably less stable. The mode of decomposition is complex and the products have not been fully elucidated. Mass, infrared, and ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopic data have been used to characterize the ligands, and the collective data provide for tentative assignments of the molecular structures.

The mass spectrum of each ligand shows a parent molecular ion and a fragmentation pattern typical of fluorophosphines[15] and cyclopentadienyl complexes.[4,15] The most thermally stable ligand, $CpPF_2$, **1**, displays an intense parent ion peak (relative intensity 92) while the remaining ligands provide parent ion peaks with low intensities (relative intensities 4–2). This observation is reproducible at several inlet pressures, but a full understanding of the parent ion intensities will require more detailed mass spectrometric analysis at varying ionization energies and inlet conditions. With $CpPF_2$ it is also observed that at relatively high source pressure (~10^{-4} torr) and high ionization energy (70 eV) a weak molecular ion at *m/e* 199 (relative intensity 5) appears which corresponds to $(C_5H_5)_2PF_2^+$. This observation suggests that $CpPF_2$ is susceptible to complex, thermally activated chemistry which may involve dimerization of the Cp ring via an ion molecule reaction.[16] For the remaining three ligands mass spectrometric conditions have not yet been found which permit the observation of ions of greater mass than the parent ion.

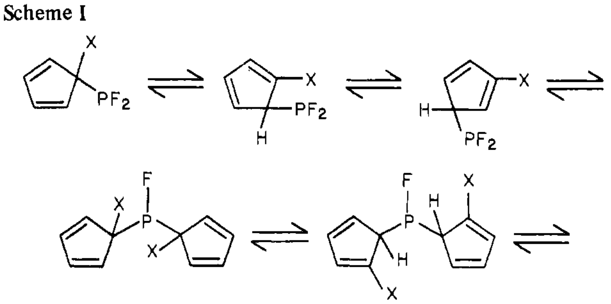
The gas-phase infrared spectra of the ligands support the conclusion that the cyclopentadienyl rings are η^1 coordinated with respect to the phosphorus atom. Davison and Rakita[2] have analyzed the local symmetry requirements for η^1- and η^5-Cp rings in the C–H stretching region; the representation for η^5 is $\Gamma_{\nu(\mathrm{C-H})} = \mathrm{A}_1 + \mathrm{E}_1 + \mathrm{E}_2$ and for η^1 it is $\Gamma_{\nu(\mathrm{C-H})} = 3\ \mathrm{A}' + 2\ \mathrm{A}''$. For the η^5 coordination example only two modes are predicted to be infrared active ($\mathrm{A}_1 + \mathrm{E}_1$) and the A_1 mode is expected to be weak. With η^1 coordination all five modes in the C–H stretching region are infrared active, and four modes associated with the olefinic C–H groups should appear in the region of 3000 cm^{-1}. For the fluorophosphine ligands described here at least three bands are resolved in the 3000-cm^{-1} region, and these can be tentatively assigned to the olefinic C–H stretches. The bands are not sharp, and the expected fourth band may be present but unresolved in **1**, **2**, and **4**. The P–F stretching mode is easily identified in the 800–700-cm^{-1} region for each compound.

The NMR spectra of the ligands are rich, and they provide conclusive structural assignments for each molecule. The $^{31}\mathrm{P}[^1\mathrm{H}]$ spectrum of **1** at −40 °C consists of a triplet centered at 195 ppm (downfield of $\mathrm{H_3PO_4}$) with $J_{\mathrm{PF}} = 1172$ Hz while the spectrum of **3** at −40 °C consists of a doublet centered at 192 ppm with $J_{\mathrm{PF}} = 1119$ Hz. The chemical shifts fall in the region expected for triply connected fluorophosphines,[17,18] and the coupling patterns clearly verify the fluorine atom connectivities to phosphorus. Temperature variations in the range −60 to 0 °C show no significant changes in these phosphorus spectra. The $^{31}\mathrm{P}[^1\mathrm{H}]$ spectrum of the methylcyclopentadienyl derivative **2** at −40 °C shows *two* triplets centered at 194.9 ppm ($J_{\mathrm{PF}} = 1164$ Hz) and 195.4 ppm ($J_{\mathrm{PF}} = 1164$ Hz). The ligand **4** at −40 °C shows *two* doublets centered at 193.3 ppm ($J_{\mathrm{PF}} = 1109$ Hz) and 192.3 ppm ($J_{\mathrm{PF}} = 1120$ Hz). The area ratios at −40 °C for the two triplets and the two doublets are nearly equal to 1 with the downfield member being slightly less intense for both ligands. The relative intensities are a function of temperature in the range −60 to 0 °C with the downfield member decreasing in intensity by about 30% in this temperature range.[19]

The $^{19}\mathrm{F}[^1\mathrm{H}]$ spectrum of **1** at −40 °C consists of a doublet centered at −72.4 ppm (upfield of $\mathrm{CFCl_3}$) with $J_{\mathrm{FP}} = 1183$ Hz. Restoration of proton coupling splits each member of the doublet into a doublet with $J_{\mathrm{FPCH}} = 10$ Hz. The $^{19}\mathrm{F}[^1\mathrm{H}]$ spectrum of **3** at −40 °C shows a doublet centered at −102 ppm with $J_{\mathrm{FP}} = 1119$ Hz. Proton coupling splits each member of the large doublet into a doublet with $J_{\mathrm{FPCH}} = 6$ Hz. Temperature variations in the range −60 to 0 °C leave these spectra unaffected. The $^{19}\mathrm{F}[^1\mathrm{H}]$ spectrum of **2** contains *two* doublets centered at −73.7 ppm ($J_{\mathrm{FP}} = 1152$ Hz) and −74.4 ppm ($J_{\mathrm{FP}} = 1152$ Hz). Proton coupling results in the further splitting of each doublet into doublets with $J_{\mathrm{FPCH}} = 9$ Hz. The spectral intensities are temperature dependent in the region −60 to 0 °C with the low-field doublet less intense at all temperatures and decreasing in relative intensity with decreasing temperature. The $^{19}\mathrm{F}[^1\mathrm{H}]$ spectrum of **4** at −40 °C consists of *two* doublets centered at −101.8 ppm ($J_{\mathrm{FP}} = 1107$ Hz) and −103.7 ppm ($J_{\mathrm{FP}} = 1105$ Hz). Proton coupling produces further doublet splitting; $J_{\mathrm{FPCH}} = 10$ Hz. This fluorine spectrum is temperature dependent in a fashion similar to that of **2**. The $^{19}\mathrm{F}$ chemical shifts for **1**, **2**, **3**, and **4** fall in the expected regions for $\mathrm{F_2PR}$ and $\mathrm{FPR_2}$ compounds: $\delta(\mathrm{CH_3PF_2}) = -92.9$, $\delta(\mathrm{C_6H_5PF_2}) = -92.3$, $\delta((\mathrm{CH_3})_2\mathrm{PF}) = -195.5$.[17]

The mass, infrared, and $^{19}\mathrm{F}$ and $^{31}\mathrm{P}$ NMR spectra verify the existence of the $\mathrm{F_2PR}$ and $\mathrm{FPR_2}$ ligands (R = Cp and MeCp). The infrared and NMR data suggest that in each case the cyclopentadienyl rings are bound to the phosphorus in a η^1 fashion as evidenced by the number of olefinic C–H stretching modes and the observation of a relatively constant coupling value for $J_{\mathrm{FPCH}} = 6$–10 Hz. The integrity of this coupling with varying temperature, the temperature dependence of intensities in **2** and **4**, and the observation of two fluorine and two phosphorus environments in $\mathrm{F_2P(MeCp)}$ and $\mathrm{FP(MeCp)_2}$ at low temperature suggest that each molecule is nonrigid. This conclusion is verified by $^{13}\mathrm{C}$ and $^1\mathrm{H}$ data discussed below for each of **1**–**4**. The nonrigid nature of these ligands is presumed at this point to involve interconversions between idealized chemically distinct species such as shown in Scheme I.

Scheme I



The $^{13}\mathrm{C}[^1\mathrm{H}]$ spectrum of **1** at −40 °C shows a doublet at 138.71 ppm ($J_{\mathrm{CP}} = 5$ Hz), a doublet at 125.65 ppm ($J_{\mathrm{CP}} = 11$ Hz), and a doublet at 65.46 ppm ($J_{\mathrm{CP}} = 44$ Hz), each member of which is split into a triplet ($J_{\mathrm{CPF}} = 6$ Hz). Proton coupling results in the splitting of the two downfield resonances into doublets, $J_{\mathrm{CH}} = 169$ Hz and $J_{\mathrm{CH}} = 176$ Hz, respectively. This spectral pattern is unchanged between −10 and −60 °C. Above −10 °C, each resonance noticeably broadens and complete collapse of the three-resonance-line spectrum occurs near +40 °C. The temperature-dependent behavior is reversible. The $^{13}\mathrm{C}[^1\mathrm{H}]$ spectrum of **3** at −40 °C consists of a doublet at 139.23 ppm ($J_{\mathrm{CP}} = 2$ Hz), a doublet at 128.32 ppm ($J_{\mathrm{CP}} = 15$ Hz), and a doublet at 67.25 ppm ($J_{\mathrm{CP}} = 45$ Hz), each member of which is split into a doublet ($J_{\mathrm{CPF}} = 7$ Hz). The general temperature dependence displayed by this molecule is similar to that found for **1**.

The $^{13}\mathrm{C}[^1\mathrm{H}]$ spectrum of **2** at −40 °C shows a spectrum which is essentially the same in spectral features as $(\mathrm{CH_3})_3\mathrm{Ge}(\mathrm{CH_3C_5H_4})$;[1b] however, only seven of the eight olefinic carbon resonances have been fully resolved. J_{CP} coupling is imposed on the carbon bound directly to phosphorus. The spectrum is temperature sensitive, and details of the temperature-dependent spectra have not yet been fully resolved. The $\mathrm{C}^{13}[^1\mathrm{H}]$ spectrum of **4** at −40 °C shows a doublet at 150.51 ppm ($J_{\mathrm{CP}} = 6$ Hz), a doublet at 142.58 ppm ($J_{\mathrm{CP}} = 5$ Hz), a doublet at 128.81 ppm ($J_{\mathrm{CP}} = 12$ Hz), a doublet at 122.3 ppm ($J_{\mathrm{CP}} = 12$ Hz), a doublet at 66.39 ppm ($J_{\mathrm{CP}} = 43$ Hz), each member of which is split into a doublet $J_{\mathrm{CPF}} = 6$ Hz, and a singlet at 15.80 ppm. This spectrum also is temperature dependent.

The $^1\mathrm{H}$ spectra of these compounds are complicated, and they resemble spectra obtained for a variety of group 4A cyclopentadienyl and methylcyclopentadienyl compounds.[2,20–23] The complexity introduced by P–H and P–F coupling as yet as has not been successfully simulated. It is appropriate to point out that each spectrum is of the general AA′BB′X type and the temperature dependence of the pattern is much like that displayed by $(\mathrm{CH_3})_3\mathrm{Si}(\mathrm{C_5H_4CH_3})$[23] and $(\mathrm{CH_3})_3\mathrm{Si}(\mathrm{C_5H_5})$.[2]

Although a complete interpretation of the complex $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra is not presently available, the partial interpretation and observed temperature dependence–line-shape behavior suggest that these molecules are nonrigid as concluded from the phosphorus and fluorine NMR data. The mechanism which operates in the permutation of the Cp and MeCp rings must be intramolecular in kind, and it probably involves a series of 1,2 shifts as predicted for $(CH_3)_3SiCp$[1,2] and $(CH_3)_3SiCpMe$.[1,23]

Borane(3) Complexes. Each of the ligands combines with diborane(6) with the resulting formation of a borane(3) complex. These reactions are summarized by eq 3 and 4. The

$$F_2P(\eta^1\text{-}C_5H_4X) + {}^1/_2B_2H_6 \xrightarrow{-23\ °C} F_2P(\eta^1\text{-}C_5H_4X)(BH_3) \tag{3}$$

$$FP(\eta^1\text{-}C_5H_4X)_2 + {}^1/_2B_2H_6 \xrightarrow{-23\ °C} FP(\eta^1\text{-}C_5H_4X)_2(BH_3) \tag{4}$$

$X = H$ in **5** and **7**; $X = CH_3$ in **6** and **8**

borane(3) complexes are unstable with respect to air, moisture, and thermal decomposition. Above 0 °C the complexes rapidly dissociate and decompose via a complex mechanism which appears to involve the reduction of the cyclopentadiene ring as evidenced by small yields of organoboranes of the type $(C_5H_6)_2B_2H_2$ (detected by mass spectrometry). Complexes **5** and **6** have been identified by mass, infrared, and NMR data, while **7** and **8** have been identified only by their mass spectra. The further characterization of **7** and **8** has been hampered by the low stability of the complexes.

The mass spectra of **5–8** show parent ions of low intensity at *m/e* 148 (3), 163 (2), 194 (4), and 222 (2), respectively, and the fragmentation patterns are similar to the patterns displayed by the free ligands. The infrared spectra of **5** and **6** resemble the free-ligand spectra with the important additional characteristic B–H stretching vibrations at 2435 and 2402 cm^{-1} in **5** and 2440 cm^{-1} in **6** and the B–P stretching vibrations at 535 cm^{-1} in **5** and 538 cm^{-1} in **6**.

The ^{19}F NMR spectrum at −40 °C for **5** shows a resonance centered at −84.6 ppm which is split into a doublet ($J_{FP} = 1184$ Hz) with each member split into a quartet ($J_{FPBH} = 22$ Hz) and a doublet ($J_{FPCH} = 10$ Hz). The ^{19}F NMR spectrum at −40 °C for **6** shows a resonance at −81.9 ppm which is split into a doublet ($J_{FP} = 1114$ Hz) and quartet ($J_{FPBH} = 19$ Hz). The ^{11}B NMR spectrum at −40 °C for **5** has a resonance at 43.0 ppm (upfield of $BF_3 \cdot OEt_2$) which is split into a quartet ($J_{BH} = 106$ Hz) of doublets ($J_{BP} = 50$ Hz). The spectrum of **6** shows a resonance centered at 42.5 ppm, with $J_{BH} = 107$ Hz and $J_{BP} = 48$ Hz.

The characterization data are consistent with the formation of borane(3) complexes of the ligands with boron–phosphorus coordinate bonds. The chemical shifts and coupling constants observed are similar to those reported for related fluorophosphine–borane complexes.[24,25] The magnitude of the B–P coupling constant might be used here, in context with earlier correlations of J_{BP} with coordinate bond strength,[24] to predict relatively stable $CpPF_2BH_3$ and $MeCpPF_2BH_3$ coordinate bonds. In fact, just the opposite is qualitatively indicated by the complexes' facile decomposition.

In conclusion we find that, in contrast to previous work,[3] there is a simple route to cyclopentadienyl derivatives of fluorophosphines. The new synthesis, for the first time, has permitted the exploration of the coordination chemistry of these ligands, and that coordination chemistry with borane(3) has been described here. Coordination chemistry will be described subsequently for a variety of transition-metal systems. In addition, the nonrigid structural rearrangements exhibited by these ligands and first recognized by Rankin and co-workers[2] are complex. A full analysis of the NMR dynamics will eventually lead to a more complete understanding of the general problem of Cp ring permutations in η^1-bound ring systems.

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Registry No. F_2PCp, 36917-22-3; $F_2P(MeCp)$, 68367-25-9; $FP(Cp)_2$, 68367-26-0; $FP(MeCp)_2$, 68367-27-1; $CpPF_2 \cdot BH_3$, 68367-28-2; $MeCpPF_2 \cdot BH_3$, 68367-29-3; $Cp_2PF \cdot BH_3$, 68367-30-6; $(MeCp)_2PF \cdot BH_3$, 68367-31-7; TlCp, 34822-90-7; TlMeCp, 34034-67-8; PF_2Cl, 14335-40-1; PF_2Br, 15597-40-7; $PFCl_2$, 15597-63-4; B_2H_6, 19287-45-7.

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(12) The standard sign convention for chemical shifts was used throughout: a downfield shift from the reference signal is a positive δ.

(13) Except for the parent ion, all ions containing the boron atom are assigned by total molecular composition without any implications about the number of hydrogen atoms on carbon vs. boron.

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