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Synthesis and Alkylation of an Iron Phosphane Complex. Crystal and Molecular Structure Determinations for $CpFe(CO)_2\{P(C_6H_5)\{N[Si(CH_3)_3]_2\}\}$ and $CpFe(CO)_2\{P(CH_3)(C_6H_5)\{N[Si(CH_3)_3]_2{}^+\}\}(O_3SCF_3{}^-)$

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The reactions of $NaFe(C_5H_5)(CO)_2$ and $NaFe[(CH_3)_5C_5](CO)_2$ with $(C_6H_5)P(Cl)\{N[Si(CH_3)_3]_2\}$ form iron phosphane compounds $(C_5H_5)Fe(CO)_2\{P(C_6H_5)\{N[Si(CH_3)_3]_2\}\}$ (1) and $[(CH_3)_5C_5]Fe(CO)_2\{P(C_6H_5)\{N[Si(CH_3)_3]_2\}\}$ (2) which have been characterized by spectroscopic methods, and the crystal and molecular structure of 1 has been determined by single-crystal X-ray diffraction analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.871$ (2) Å, $b = 18.231$ (4) Å, $c = 11.561$ (2) Å, $\beta = 95.89$ (2)°, $Z = 4$, $V = 2279.1$ (7) Å^3, and $\rho = 1.30$ g cm^{-3}. Least-squares refinement gave $R_F = 5.5\%$ and $R_{wF} = 5.2\%$ on 2894 unique data with $F > 5\sigma(F)$. The molecular structure contains a $CpFe(CO)_2$ unit bonded to a pyramidal $P(C_6H_5)\{N[Si(CH_3)_3]_2\}$ fragment through a long Fe–P bond distance, 2.338 (1) Å. Reactions of 1 with $(CH_3)_3OBF_4$ and $CH_3O_3SCF_3$ result in methylation of the phosphorus center, and the products have been characterized by spectroscopic methods. The crystal and molecular structure of $(C_5H_5)Fe(CO)_2\{P(CH_3)(C_6H_5)\{N[Si(CH_3)_3]_2\}\}^+(O_3SCF_3{}^-)$ has been determined by single-crystal X-ray diffraction analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.571$ (4) Å, $b = 17.590$ (5) Å, $c = 14.200$ (3) Å, $\beta = 104.91$ (2)°, $Z = 4$, $V = 2792$ (1) Å^3, and $\rho = 1.45$ g cm^{-3}. Least-squares refinement gave $R_F = 9.4\%$ and $R_{wF} = 9.7\%$ on 2966 unique reflections with $F > 5\sigma(F)$. The molecular structure is related to the structure of 1 with the addition of a methyl group on the pyramidal phosphorus center. The addition results in a shorter Fe–P bond distance, Fe–P = 2.263 (3) Å, and P–CH_3 = 1.82 (1) Å.

Introduction

Reactions of halophosphanes, P(X)(Y)Cl, with nucleophilic d^8 metal carbonylates such as $[CpFe(CO)_2{}^-]$ lead to the formation, in most cases, of metallophosphanes, $CpFe(CO)_2[P(X)(Y)]$ in which the phosphorus ligand is terminal and pyramidal.[1-8] One consequence of the structural and electronic features of these reagents is that the phosphorus atom should serve as a site for electrophilic attack. Several reports on the reactivity of selected metallophosphanes have appeared,[2,3,5-8] but few of the resulting compounds have been structurally characterized.[2,5] In our group, we have observed that the compound $CpFe(CO)_2[P(Ph)N(SiMe_3)_2]$[9-11] (1) is attacked by borane (3) and the electron-deficient acetylene $CF_3C{\equiv}CCF_3$ with formation of a ferraphosphaborane, $CpFe(CO)_2[P(BH_3)(Ph)N(SiMe_3)_2]$,[10] and a ferraphosphacyclopentenone, $CpFe(CO)[P(Ph)N(SiMe_3)_2C(CF_3){=}C(CF_3)C(O)]$.[9] We report here on the formation of $CpFe(CO)_2[P(Ph)N(SiMe_3)_2]$ (1) and $Cp^*Fe(CO)_2[P(Ph)N(SiMe_3)_2]$ (2) and on the reactions of 1 with methyl cation sources $(CH_3)_3OBF_4$ and $CH_3SO_3CF_3$ which produce $CpFe(CO)_2[P(CH_3)(Ph)N(SiMe_3)_2{}^+][BF_4{}^-]$ (3) and $CpFe(CO)_2[P(CH_3)(Ph)N(SiMe_3)_2{}^+][SO_3CF_3{}^-]$ (4). The molecular structures of 1 and 4, determined by single-crystal X-ray diffraction techniques, are described and compared.

Experimental Section

General Information. Standard inert atmosphere techniques were used for the manipulations of all reagents and reaction products. Infrared spectra were recorded on a Nicolet FT-IR Model 6000 spectrometer, and the samples were contained in NaCl solution cells. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian FT-80A and GE NT-360 spectrometers. Spectral standards were $(CH_3)_4Si$ (^{13}C, ^1H), $BF_3{\cdot}Et_2O$ (^{11}B), and 85% H_3PO_4 (^{31}P). $Na(C_5H_5)Fe(CO)_2$ was prepared from Na/Hg amalgam reduction of $[(C_5H_5)_2Fe_2(CO)_4]$ in THF,[12] and the solutions were used without isolation. $Na[(CH_3)_5C_5]Fe(CO)_2$ was prepared similarly from $[(CH_3)_5C_5]_2Fe_2(CO)_4$.[13] The phosphane was

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[11] Abbreviations used in the text include the following: Cp, $C_5H_5{}^-$; Cp*, $(CH_3)_5C_5{}^-$; THF, tetrahydrofuran; Me, CH_3; Ph, C_6H_5.

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prepared from $PhPCl_2$ and $NaN(SiMe_3)_2$ in Et_2O by a procedure similar to that described for related phosphanes.[14] All solvents were rigorously dried with an appropriate drying agent and degassed. All solvent transfers were accomplished by vacuum distillation.

Preparation of the Complexes. Both complexes, $CpFe(CO)_2[P(Ph)N(SiMe_3)_2]$ (1) and $Cp^*Fe(CO)_2[P(Ph)N(SiMe_3)_2]$ (2), were prepared in an identical fashion, and the procedure for 1 is described in detail. Typically, 3.0 mmol (0.91 g) of $PhPN(SiMe_3)_2(Cl)$ was added through a septum port in a 100-mL Schlenk vessel to a solution of 3.0 mmol of $NaCpFe(CO)_2$ in 50 mL of THF cooled to −78 °C. The mixture was stirred and warmed slowly to 25 °C. The mixture was then refluxed for 3–6 h to ensure complete reaction. The resulting mixture was filtered to remove NaCl, and the THF was removed from the filtrate by vacuum evaporation. The crude residue was extracted with benzene and filtered and the benzene vacuum evaporated from the filtrate. The resulting blood-red microcrystalline solid was obtained in 90% or better yield. The synthesis of both 1 and 2 can be increased to at least 12–15 mmol scale.

Characterization Data. 1: mp 136–138 °C; selected infrared bands (cyclohexane, cm^{-1}) 1985 (s), 1931 (vs), 1793 (vw), 1251 (m), 906 (m), 866 (m), 842 (m), 826 (m), 576 (m); mass spectrum, *m/e* (ion, relative intensity) 445 (M^+, 7), 417 ($M - CO^+$, 47), 389 ($M - 2CO^+$, 78), 372 ($M - O_2C_3H_3^+$, 8), 358 ($M - O_2C_4H_6^+$, 30), 312 ($M - O_2C_8H_5^+$, 22); phosphorus-31 NMR (THF) δ 110; phosphorus-31 NMR (CH_2Cl_2) δ 107; carbon-13 NMR (CH_2Cl_2/CD_2Cl_2) δ 131–125.5 (m, C_6H_5), 88.1 (d, ${}^2J_{CP} = 4.6$ Hz, C_5H_5), 1.9 (CH_3Si); proton NMR (CH_2Cl_2/CD_2Cl_2) δ 7.3 (m, C_6H_5), 4.8 (C_5H_5), 0.09 (CH_3Si). Anal. Calcd for $FePSi_2O_2NC_{19}H_{28}$: C, 51.24; H, 6.34; N, 3.14. Found: C, 51.48; H, 6.23; N, 3.18. 2: mp 118–120 °C; selected infrared bands (cyclohexane, cm^{-1}) 2360 (m), 2335 (w), 1989 (s), 1941 (vs), 1250 (m), 900 (m), 870 (s), 842 (m); mass spectrum, *m/e* (ion, relative intensity) 515 (M^+, 13), 487 ($M - CO^+$, 52), 459 ($M - 2CO^+$, 100), 444 ($M - O_2C_3H_3^+$); phosphorus-31 NMR (THF) δ 153; phosphorus-31 NMR (CH_2Cl_2) δ 151; carbon-13 NMR (CH_2Cl_2/CD_2Cl_2) δ 153.6 (d, ${}^1J_{CP} = 60.6$, C_i), 130.9 (d, ${}^2J_{CP} = 16.9$ Hz, C_o), 125.3 (d, ${}^2J_{CP} = 3.2$ Hz, C_m), 127.3 (C_p), 97.2 (C_5H_5), 9.5 (d, ${}^3J_{CP} = 8.3$ Hz, $C_5(CH_3)_5$), 3.7 (d, ${}^3J_{CP} = 13.1$ Hz, CH_3Si); proton NMR (CH_2Cl_2/CD_2Cl_2) δ 7.3 (m, C_6H_5), 1.8 ($C_5(CH_3)_5$), 0.1 (CH_3Si). Anal. Calcd for $FePSi_2O_2NC_{24}H_{38}$: C, 55.91; H, 7.43; N, 2.72. Found: C, 55.48; H, 7.24; N, 2.96.

Preparation of $\{CpFe(CO)_2[P(CH_3)(C_6H_5)N(SiMe_3)_2^+]\}\{X^-\}$ [$X = BF_4^-$ (3), $F_3CSO_3^-$ (4)]. Trimethyloxonium tetrafluoroborate, Me_3OBF_4 (Aldrich), 0.55 mmol (0.081 g) was dissolved in 30 mL CH_2Cl_2, and this solution was added under nitrogen to 0.55 mmol (.244 g) $CpFe(CO)_2P(Ph)N(SiMe_3)_2$ in 50 mL CH_2Cl_2 cooled to −78 °C. The mixture was warmed slowly to 25 °C and stirred for 12 h. The solution color changed from dark red to pink during this time. The solvent was evaporated, leaving a golden-red microcrystalline solid, 3: yield 100%; mp 122–124 °C; infrared spectrum (CH_2Cl_2, cm^{-1}) 2962 (w), 2032 (vs), 1983 (vs), 1419 (m), 1258 (m), 1095 (s), 931 (m), 887 (m), 859 (m); phosphorus-31 NMR (CH_2Cl_2) δ 105.9; boron-11 NMR (CH_2Cl_2) δ −1.9; carbon-13 NMR (CH_2Cl_2/CD_2Cl_2) δ 141.0 (d, ${}^1J_{CP} = 45$ Hz, C_i), 129–127 (m, $C_{o,m,p}$), 88.5 (C_5H_5), 33.0 (d, ${}^1J_{CP} = 33$ Hz, CH_3P), 5.3 (CH_3Si); proton NMR (CH_2Cl_2/CD_2Cl_2) δ 7.6–7.5 (m, C_6H_5), 5.5 (d, ${}^3J_{HP} = 3.1$ Hz, C_5H_5), 2.6 (d, ${}^2J_{HP} = 8.0$ Hz, CH_3P), 0.3 (CH_3Si). Anal. Calcd for $FePSi_2F_4O_2NBC_{20}H_{31}$: C, 43.89; H, 5.71; N, 2.56. Found: C, 47.84; H, 6.84; N, 2.24.

In a second procedure, trifluoromethanesulfonic acid methyl ester MeO_3SCF_3 (Aldrich, 0.27 mmol, 0.031 mL) was added through a syringe port in a 100-mL Schlenk vessel containing a cold solution (−78 °C) of $CpFe(CO)_2P(Ph)N(SiMe_3)_2$ (0.27 mmol, 0.122 g) in 50 mL of methylcyclohexane. The mixture was allowed to warm to 25 °C and was stirred for 12 h. At room temperature, the mixture contains a yellow-red solution and a yellow-pink solid. The solution was concentrated and filtered, and the collected solid product 4 was washed with hexane. The filtrate produced additional solid product by addition of hexane: yield 90%; mp 142–144 °C; selected infrared bands (CH_2Cl_2, cm^{-1}) 2030 (s), 1982 (s), 1262 (s), 931 (s); phosphorus-31 NMR (CH_2Cl_2) δ 104.7. Anal. Calcd for $FePSi_2SO_5NC_{21}H_{31}$: C, 41.38; H, 5.13; N, 2.30. Found: C, 41.62; H, 5.54; N, 2.42.

Table I. Summary of Crystal and Data Collection Parameters for $CpFe(CO)_2\{P(C_6H_5)\{N[Si(CH_3)_3]_2\}\}$ (1) and $CpFe(CO)_2\{P(CH_3)(C_6H_5)\{N[Si(CH_3)_3]_2^+\}\}(O_3SCF_3^-)$ (4)

	1 (17 °C)	4 (20 °C)
	(A) Crystal Parameters	
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	10.871 (2)	11.571 (4)
b, Å	18.231 (4)	17.590 (5)
c, Å	11.561 (2)	14.200 (3)
β, deg	95.89 (2)	104.91 (2)
V, Å^3	2279.1 (7)	2792 (1)
Z	4	4
M_r	445.47	609.59
ρ(calcd), g cm^{-3}	1.30	1.45
μ(Mo Kα), cm^{-1}	8.60	8.01
$F(000)$	936	1264
	(B) Data Collection	
diffractometer	Syntex P3/F	
radiation	Mo Kα ($\bar{\lambda} = 0.71069$ Å)	
monochromator	highly oriented graphite crystal	
scan speed	6–30 deg min^{-1} (in 2θ)	3–30 deg min^{-1} (in 2θ)
scan range	from $[2\theta(K\alpha_1) - 1.15]°$ to $[2\theta(K\alpha_2) + 1.15]°$	from $[2\theta(K\alpha_1) - 1.15]°$ to $[2\theta(K\alpha_2) + 1.4]°$
2θ limits	$1° \le h,-k,\pm l \le 60°$	$2° \le h,k,\pm l \le 60°$
bkgd counting time/ total scan time	0.5	0.5
stds monitored	3/141 reflections [400, 0$\bar{6}$0, 006], no significant changes	3/141 reflections [600, 05$\bar{1}$, 006]
reflctns collected	7073	8999
unique reflctns	6658	8150
unique data used	2894, $F \ge 5\sigma(F)$	2966, $F \ge 5\sigma(F)$
no. of variables	235	290
GOF	1.525	1.879
R_F	5.5%	9.4%
R_{wF}	5.2%	9.7%
$w = [\sigma(F)^2 + \lvert g\rvert F_o^2]^{-1}$, g =	0.00064	0.00166

Crystal Structure Determinations and Solutions. Single crystals of 1 were obtained from a saturated THF solution at 0 °C. A cubic-shaped block (0.3 mm on an edge) was sealed under argon in a glass capillary. The crystal was centered on a P3/F automated diffractometer, and determinations of the crystal class, the orientation matrix, and unit cell parameters were performed in a standard manner.[15] Axial photographs and a short data set were consistent with a monoclinic space group $P2_1/n$. The data were collected at 17 °C by the θ–2θ technique using Mo Kα radiation, a scintillation counter, and a pulse height analyzer. Details of the data collection are summarized in Table I. The standard reflections showed a small decrease in intensity during data collection; the average intensities of the standards decreased by about 10%. The reflections were scaled accordingly; redundant and equivalent data averaged, corrected for Lorentz and polarization effects, and converted to $|F_o|$ values. A small absorption correction was applied on the basis of Ψ scans: R_{merge} = 1.28% and 1.22% before and after, respectively. The estimated maximum and minimum transmission factors were 0.50 and 0.48.

All calculations were performed on a SHELXTL structure determination system.[16] Neutral atom scattering factors and anomalous dispersion factors were used for all non-hydrogen atoms during the refinements. Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of the anomalous dispersion were included for all non-hydrogen atoms. The function[17] minimized during the

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(15) Programs used for centering reflections, autoindexing, refinement of cell parameters, and axial photographs are those described in: *Nicolet P3/R3 Operations Manual*; Sparks, R. A., Ed.; Syntex Analytical Instruments: Cupertino, CA 1978.

(16) The SHELXTL package of programs for calculations and plots is described in: *SHELXTL Users Manual, Revision 3*, G. M. Sheldrick, July 1981, Nicolet XRD Corp. SHELXTL uses scattering factors and anomalous dispersion terms taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1968; Vol. IV.

(17) Discrepancy indices are defined as follows: $R_F = [\sum ||F_o| - |F_c||]/\sum |F_o|$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and the goodness of fit GOF = $[w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

Table II. Non-Hydrogen Atom Positional Parameters and Their Esd's for $CpFe(CO)_2\{P(C_6H_5)\{N[Si(CH_3)_3]_2\}\}$

atom	*x/a*	*y/b*	*z/c*
Fe	0.78691 (7)	0.84584 (4)	−0.02465 (6)
P	0.87491 (12)	0.91788 (7)	0.12957 (11)
Si(1)	0.80430 (15)	0.83952 (11)	0.35687 (13)
Si(2)	0.72465 (16)	0.99512 (10)	0.27500 (15)
N(1)	0.8017 (4)	0.9109 (2)	0.2555 (3)
C(1)	0.6521 (6)	0.8377 (4)	0.0451 (5)
O(1)	0.5624 (5)	0.8313 (4)	0.0853 (4)
C(2)	0.8537 (7)	0.7637 (4)	0.0289 (5)
O(2)	0.8952 (7)	0.7082 (3)	0.0548 (5)
C(3)	0.8769 (6)	0.8415 (4)	−0.1760 (5)
C(4)	0.8765 (7)	0.9142 (4)	−0.1364 (5)
C(5)	0.7555 (8)	0.9351 (4)	−0.1382 (5)
C(6)	0.6795 (7)	0.8761 (4)	−0.1797 (5)
C(7)	0.7561 (7)	0.8191 (4)	−0.2025 (5)
C(8)	1.0355 (4)	0.8918 (3)	0.1755 (4)
C(9)	1.1111 (5)	0.8620 (3)	0.0976 (5)
C(10)	1.2370 (5)	0.8550 (3)	0.1266 (6)
C(11)	1.2893 (6)	0.8751 (3)	0.2338 (6)
C(12)	1.2171 (5)	0.9046 (4)	0.3125 (6)
C(13)	1.0923 (5)	0.9130 (3)	0.2839 (5)
C(14)	0.6511 (7)	0.7956 (5)	0.3580 (8)
C(15)	0.9140 (8)	0.7647 (4)	0.3295 (7)
C(16)	0.8512 (9)	0.8746 (6)	0.5060 (6)
C(17)	0.6066 (7)	0.9884 (5)	0.3798 (7)
C(18)	0.6399 (8)	1.0276 (5)	0.1379 (7)
C(19)	0.8384 (8)	1.0648 (4)	0.3313 (8)

Table III. Non-Hydrogen Atom Positional Parameters and Their Esd's for $CpFe(CO)_2\{P(CH_3)(C_6H_5)\{N[Si(CH_3)_3]_2{}^+\}(O_3SCF_3{}^-)$

atom	*x/a*	*y/b*	*z/c*
Fe	0.55703 (13)	0.46647 (9)	0.75177 (10)
C(1)	0.5982 (10)	0.4221 (6)	0.6546 (8)
O(1)	0.6187 (8)	0.3919 (5)	0.5892 (6)
C(2)	0.5070 (11)	0.5510 (8)	0.6834 (9)
O(2)	0.4658 (9)	0.6014 (6)	0.6376 (7)
C(3)	0.4334 (11)	0.4811 (8)	0.8349 (9)
C(4)	0.5325 (10)	0.4433 (7)	0.8904 (8)
C(5)	0.5479 (13)	0.3756 (8)	0.8448 (11)
C(6)	0.4538 (15)	0.3697 (8)	0.7593 (11)
C(7)	0.3826 (11)	0.4364 (10)	0.7515 (9)
P	0.74730 (22)	0.50651 (15)	0.81363 (17)
C(8)	0.7667 (9)	0.5958 (6)	0.8824 (7)
C(9)	0.6740 (10)	0.6272 (6)	0.9128 (8)
C(10)	0.6964 (13)	0.6909 (7)	0.9749 (9)
C(11)	0.8069 (13)	0.7230 (7)	1.0025 (9)
C(12)	0.8972 (12)	0.6926 (7)	0.9684 (9)
C(13)	0.8799 (10)	0.6290 (6)	0.9104 (7)
C(20)	0.8251 (9)	0.4455 (6)	0.9134 (7)
N	0.8303 (7)	0.5127 (4)	0.7325 (5)
Si(1)	0.8176 (3)	0.5911 (2)	0.6493 (2)
C(14)	0.7266 (12)	0.5642 (8)	0.5257 (7)
C(15)	0.7452 (14)	0.6764 (7)	0.6831 (9)
C(16)	0.9688 (11)	0.6240 (8)	0.6458 (9)
Si(2)	0.9348 (3)	0.4392 (2)	0.7238 (2)
C(17)	0.9506 (13)	0.4302 (7)	0.5980 (9)
C(18)	0.8842 (11)	0.3429 (6)	0.7487 (9)
C(19)	1.0824 (10)	0.4595 (7)	0.8087 (10)
S(1)	0.2391 (4)	0.1971 (2)	0.6041 (3)
O(3)	0.3605 (10)	0.2157 (8)	0.6270 (9)
O(4)	0.2140 (13)	0.1182 (6)	0.5955 (8)
O(5)	0.1631 (16)	0.2418 (10)	0.5326 (13)
C(21)	0.1910 (7)	0.2226 (4)	0.7117 (6)

least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The solution and refinement of the structure was based on 2894 unique reflections with $F > 5\sigma(F)$. A sharpened Patterson map gave the coordinates of the Fe atom, and a difference Fourier synthesis gave the positions of the other non-hydrogen atoms. Refinement of the positional and individual isotropic thermal parameters for the non-hydrogen atoms gave R = 11.8%. Individual anisotropic thermal parameters were applied, and refinement gave R_F = 6.7%. The hydrogen atoms were included constrained to idealized positions at a fixed distance (0.96 Å) from their parent carbon atom. The $U_{\text{iso's}}$ were set at 1.2 times the last U_{equiv} of the parent carbon atom. The final agreement factors based on 235 parameters were R_F = 5.5% and R_{wF} = 5.2%. A final difference map showed no peak greater than 0.35 e Å^{-3}.

The molecular structure determination for 4 proceeded in a similar fashion with the following specific differences. A pale yellow crystal (0.18 × 0.41 × 0.51 mm), obtained by slow evaporation of a CH_2Cl_2 solution of 4, was sealed in a glass capillary under argon. Data were collected at 20 °C, and details of the data collection are summarized in Table I. The standards monitored showed no signs of crystal decay. The redundant and equivalent reflections were averaged (R_{merge} = 1.5%) and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects. A small absorption correction based on Ψ scans was applied: R = 2.16% and 2.13% before and after, respectively. The estimated maximum and minimum transmission factors were 0.49 and 0.47. A sharpened Patterson map gave a trial position for the Fe atom, and an initial difference map revealed the positions of the P, S, and one Si atom. The next difference map gave the positions of the second Si, N, two carbonyls, and phenyl carbon atoms. The next difference map gave the remaining non-hydrogen atoms in the structure. Isotropic refinement on the non-hydrogen atoms gave R = 13.3%. Anisotropic refinement gave R_F = 9.4%; however, several thermal factors were high for the $F_3CSO_3{}^-$ group. Difference maps yielded only one clear position for each atom although the U's were large. Several constrained refinements were attempted. The best compromise restricted the refinement to reflections observed at the $F > 5\sigma(F)$ level with the fluorine atoms constrained to be in idealized tetrahedral positions about C(21) with a C–F distance of 1.32 Å and S–C–F angles of 109.5°. These atoms were held isotropic in the final refinement. The final refinement with hydrogen atoms calculated on the riding model gave R_F = 9.4% and R_{wF} = 9.7% on 2966 reflections with $F > 5\sigma(F)$. A final difference map showed three peaks (1.58, 1.38, and 1.1 e Å^{-3}) each near the CF_3 group. Tables of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters are available.[18] Non-hydrogen atom positional parameters are listed in Tables II and III.

Results and Discussion

Combination of $PhP(Cl)N(SiMe_3)_2$ with $NaCpFe(CO)_2$ in THF solution results in the formation, in high yield, of a ferraphosphane, $CpFe(CO)_2P(Ph)N(SiMe_3)_2$ (1) as described in eq 1. The corresponding derivative

$$NaCpFe(CO)_2 + PhP(Cl)N(SiMe_3)_2 \rightarrow NaCl + CpFe(CO)_2P(Ph)N(SiMe_3)_2 \quad (1)$$

$[(CH_3)_5C_5]Fe(CO)_2P(Ph)N(SiMe_3)_2$ (2) is obtained in high yield with $NaCp^*Fe(CO)_2$. The compounds are red, crystalline, air-sensitive solids which are indefinitely stable at room temperature in an inert atmosphere.

The mass spectra of 1 and 2 show a parent ion and several expected fragment ions which, together with the elemental analyses, support the proposed compositions. The infrared spectra, obtained from cyclohexane solutions, show two strong carbonyl absorptions: 1, 1985 and 1931 cm^{-1}, and 2, 1989 and 1941 cm^{-1}. These spectra compare favorably, in the carbonyl region, with the spectra for several related ferraphosphanes, $CpFe(CO)_2[P(X)(Y)]$ with $P(X)(Y) = PN(CH_3)CH_2CH_2NCH_3$,[4] 1947 and 1922 cm^{-1}; $P(N\text{-}t\text{-}Bu)PN(H)(t\text{-}Bu)$,[19] 1990 and 1939 cm^{-1}; $P(N\text{-}t\text{-}Bu)P(N\text{-}t\text{-}Bu)(Cl)$,[19] 1995 and 1925 cm^{-1}; $P(CF_3)_2$,[7] 2046 and 2000 cm^{-1}; PPh_2,[7] 2015 and 1966 cm^{-1}; and $P(SiMe_3)_2$, 2020 and 1974 cm^{-1}, and $Cp^*Fe(CO)_2[P(X)(Y)]$ with $P(X)(Y) = PN(CH_3)CH_2CH_2NCH_3$,[4,20] 2002, 1969, 1954,

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[18] Supplementary material.

[19] DuBois, D. A. Ph.D. Thesis, University of New Mexico, 1985.

[20] Some $CpFe(CO)_2P(X)(Y)$ complexes display infrared spectra with four bands in the carbonyl stretching region as a result of rotational isomers.[4]

and 1914 cm^{-1}; P(N-*t*-Bu)P(N-*t*-Bu)(Cl),[19] 1995 and 1925; PPh_2,[8] 2000 and 1953 cm^{-1}; and $P(SiMe_3)_2$,[21] 1990 and 1945 cm^{-1}.

The ^1H and $^{13}C\{^1H\}$ NMR spectra have been completely assigned, and they are consistent with the proposed formulations of the complexes.[22] The ^{31}P NMR chemical shifts for ferraphosphane complexes are strongly dependent on the electronic character of the phosphorus substituent groups and on the cyclic or acyclic structure of the phosphane.[2,4,19] In addition, where data are available for identical P(X)(Y) groups, the ^{31}P shift for a $Cp^*Fe(CO)_2$ compound usually appears downfield of the shift for the related $CpFe(CO)_2$ compound. Examples of the latter observation include $CpFe(CO)_2PN(CH_3)CH_2CH_2NCH_3$, δ 258,[4] and $Cp^*Fe(CO)_2PN(CH_3)CH_2CH_2NCH_3$, δ 287,[4] $CpFe(CO)_2P(SiMe_3)_2$, δ −265,[21] and $Cp^*Fe(CO)_2P(SiMe_3)_2$, δ −216.8.[8] That the shifts are highly dependent upon substituent groups may also be seen in the following data: $Cp^*Fe(CO)_2P(X)(Y)$,[2] X = Y = Ph, δ 40.5; X = Cl, Y = Ph, δ 121.3; X = Cl, Y = *t*-Bu, δ 323.3; X = Cl, Y = Me, δ 148.4; X = Cl, Y = NMe_2, δ 379.1, and X = Y = Cl, δ 478.7. Unfortunately, no simple predictive trends emerge from these data. The ^{31}P chemical shifts for **1**, δ 110 (THF) and 107 (CH_2Cl_2), and **2**, δ 153 (THF) and 151 (CH_2Cl_2), are found to display the expected order for a $CpFe(CO)_2$ and $Cp^*Fe(CO)_2$ pair, and both resonances fall within the very wide range of resonance positions found in related ferraphosphanes.

Previous to this study, Malisch and co-workers had reported the addition of methyl iodide to $Cp^*Fe(CO)_2PPh_2$,[2] $Cp^*Fe(CO)_2P(Cl)(t\text{-}Bu)$,[2] and $CpM(CO)_3POC(CH_3)_2C(CH_3)_2O$[5] (M = Cr, Mo, W) with the formation of metallophosphonium salts. Initial studies of the reactions of **1** with methyl iodide in CH_2Cl_2 gave a phosphonium salt, but also several unidentified products. This led us to examine reactions of **1** with Me_3OBF_4 and $MeSO_3CF_3$ which produce the respective ferraphosphonium salts $\{CpFe(CO)_2[P(Me)(Ph)N(SiMe_3)_2]^+\}(BF_4^-)$ (**3**) and $\{CpFe(CO)_2[P(Me)(Ph)N(SiMe_3)_2]^+\}(SO_3CF_3^-)$ (**4**) in quantitative yield. The spectroscopic data for **3** and **4** are nearly identical, and they can be compared with data for **1**. For example, the infrared spectrum for **4** in CH_2Cl_2 shows two carbonyl bands at 2030 and 1982 cm^{-1}, and these are shifted significantly up frequency from the carbonyl bands in **1**. This trend is consistent with strong electron withdrawal from the iron center. A similar shift was reported by Malisch upon MeI addition to $Cp^*Fe(CO)_2PPh_2$: ν_{CO} 2029 and 1987 cm^{-1}.

The ^{31}P NMR spectra for **3** and **4** show resonances at δ 105.9, and 104.7, respectively. These resonances are shifted only slightly (Δ − 1.1[23] and Δ − 2.3) from the resonance for **1**. Very different ^{31}P shifts are found for MeI addition to $Cp^*Fe(CO)_2PPh_2$ (δ 47.38, Δ + 7.68) and $Cp^*Fe(CO)_2P(Cl)(t\text{-}Bu)$ (δ 180.6, Δ − 142.7). The coordination shift for a related phosphine to phosphonium salt transformation, (*i*-Pr)N(H)PPh_2 + MeI, is Δ − 4.01.[24] A full set of ^{11}B, $^{13}C\{^1H\}$, and ^1H NMR data were collected for **3**, and no unusual features were observed. Of particular interest, the $^{13}C\{^1H\}$ resonance for the phosphonium methyl group appears as a doublet, δ 33.0 (J_{CP} = 33 Hz), and it is downfield of methyl group resonances in several phosphonium salts [$P(CH_3)R_3^+$], δ 4–18 (J_{CP} = 50–75 Hz).[24,25]

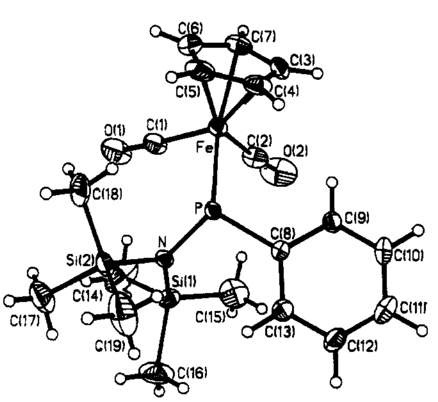

Figure 1. Molecular geometry and atom-labeling scheme for $CpFe(CO)_2\{P(C_6H_5)\{N[Si(CH_3)_3]_2\}\}$ (30% thermal ellipsoids).

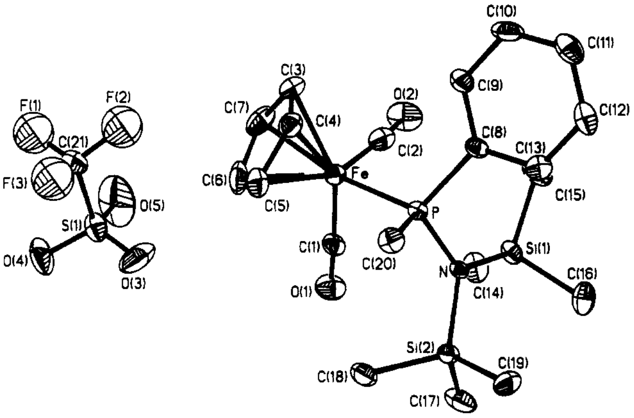

Figure 2. Molecular geometry and atom-labeling scheme for $CpFe(CO)_2\{P(CH_3)(C_6H_5)\{N[Si(CH_3)_3]_2\}^+\}(O_3SCF_3^-)$ (30% thermal ellipsoids).

Table IV. Selected Bond Distances and Angles for $CpFe(CO)_2\{P(C_6H_5)\{N[Si(CH_3)_3]_2\}$

	Distances (Å)		
Fe–P	2.338 (1)	P–N	1.734 (4)
Fe–C(1)	1.751 (7)	P–C(8)	1.834 (5)
Fe–C(2)	1.749 (7)	Si(1)–N	1.749 (4)
Fe–C(Cp)$_{av}$	2.102 (6)	Si(2)–N	1.775 (5)
C(1)–O(1)	1.128 (9)	Si(1)–C$_{av}$	1.856 (8)
C(2)–O(2)	1.136 (9)	Si(2)–C$_{av}$	1.850 (8)
C–C(phenyl)$_{av}$	1.378 (10)	C–C(Cp)$_{av}$	1.386 (10)
	Angles (deg)		
Fe–P–N	114.3 (1)	C(1)–Fe–C(2)	95.8 (3)
Fe–P–C(8)	112.2 (2)	C(1)–Fe–P	89.6 (2)
C(8)–P–N	104.1 (2)	C(2)–Fe–P	95.1 (2)
P–N–Si(1)	129.8 (3)	Fe–C(1)–O(1)	176.7 (6)
P–N–Si(2)	107.8 (2)	Fe–C(2)–O(2)	174.4 (6)
Si(1)–N–Si(2)	122.3 (2)	C–C–C(Cp)$_{av}$	108.0 (6)
C–C–C(phenyl)$_{av}$	119.9 (6)		

The molecular structures of **1** and **4** have been determined by single-crystal X-ray diffraction techniques, and comparison of the structural parameters is informative. Views of the molecules are shown in Figures 1 and 2, and selected bond distances and angles are summarized in Tables IV and V. The structures of **1** and **4** are, as expected, closely related. The structure of **4** confirms that CH_3^+ addition occurs at the phosphorus site of **1**, and the

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[21] Schäfer, H. *Z. Anorg. Allg. Chem.* **1980**, *467*, 105.

[22] All expected ^{13}C and ^1H resonances were detected except as noted here. Compound **2** displays a weak carbon-13 doublet at δ 153.6 ($^1J_{CP}$ = 60.6 Hz) which is assigned to the *ipso* carbon of the phenyl ring. A similar resonance in compound **1** was not resolved. In neither case were the resonances for the CO ligands detected, although no effort was made to vary and optimize the observe excitation parameters.

[23] The delta, Δ, is defined as a shift difference $\delta(3) - \delta(1)$ or $\delta(4) - \delta(1)$.

[24] Cowley, A. H.; Cushner, M.; Fild, M.; Gibson, J. A. *Inorg. Chem.* **1975**, *14*, 1851.

[25] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981.

Table V. Selected Bond Distances and Angles for $CpFe(CO)_2\{P(CH_3)(C_6H_5)\{N[Si(CH_3)_3]_2\}^+\}(O_3SCF_3^-)$

	Distances (Å)		
Fe–P	2.263 (3)	P–N	1.682 (9)
Fe–C(1)	1.755 (12)	P–C(20)	1.820 (10)
Fe–C(2)	1.788 (13)	P–C(8)	1.832 (10)
Fe–C(Cp)$_{av}$	2.093 (15)	Si(1)–N	1.798 (8)
C(1)–O(1)	1.146 (15)	Si(2)–N	1.795 (8)
C(2)–O(2)	1.130 (17)	Si(1)–C$_{av}$	1.852 (14)
C–C(phenyl)$_{av}$	1.379 (20)	Si(2)–C$_{av}$	1.853 (15)
S(1)–O$_{av}$	1.405 (17)	C–C(Cp)$_{av}$	1.405 (9)
S(1)–C(21)	1.812 (10)		
	Angles (deg)		
Fe–P–N	115.1 (3)	C(1)–Fe–C(2)	93.3 (6)
Fe–P–C(8)	116.6 (3)	C(1)–Fe–P	90.6 (4)
Fe–P–C(20)	110.8 (4)	C(2)–Fe–P	95.7 (4)
C(8)–P–N	107.3 (4)	Fe–C(1)–O(1)	176.3 (10)
C(8)–P–C(20)	97.0 (4)	Fe–C(2)–O(2)	173.9 (11)
N–P–C(20)	108.4 (5)	C–C–C(Cp)$_{av}$	108.0 (12)
P–N–Si(1)	122.3 (5)	C–C–C(phenyl)$_{av}$	120.0 (12)
P–N–Si(2)	121.0 (4)		
Si(1)–N–Si(2)	116.7 (5)		

general orientation of the substituents on the iron atom in both compounds is similar. The structure of 1 is related to the structure of $Cp^*Fe(CO)_2PN(CH_3)CH_2CH_2NCH_3$.[4] The iron atom in 1 is bonded to a planar η^5-Cp ring with Fe–C(ring)$_{av}$ = 2.102 (6) Å and C–C(Cp)$_{av}$ = 1.386 (10) Å. In addition, the iron atom is bonded to two terminal carbonyl ligands with Fe—CO$_{av}$ = 1.750 (7) Å and C≡O$_{av}$ = 1.132 (9) Å, and the Fe—C≡O bond axis is nearly linear, Fe—C≡O(av) = 175.5°. The distances are comparable to the distances in $Cp^*Fe(CO)_2PN(CH_3)CH_2CH_2NCH_3$, Fe—C(ring)$_{av}$ = 2.136 (8) Å, C—C(Cp)$_{av}$ = 1.409 (11) Å, Fe—CO$_{av}$ = 1.731 (7) Å and C≡O$_{av}$ = 1.158 (8) Å, and in $CpFe(CO)_2P(CF_3)_2$, Fe—C(ring)$_{av}$ = 2.097 (7) Å, C–C(Cp)$_{av}$ = 1.402 (9) Å, Fe—CO$_{av}$ = 1.768 (6) Å, and C≡O$_{av}$ = 1.138 (8) Å. Within the accuracy of the structure determination for 4, the related structural parameters are not drastically altered by addition of the electrophilic CH_3^+ group: Fe—C(ring)$_{av}$ = 2.093 (15) Å, C—C(Cp)$_{av}$ = 1.405 (9) Å, Fe—CO$_{av}$ = 1.771 (13) Å, and C≡O$_{av}$ = 1.138 (17) Å. The Fe–CO distances do show a qualitative trend toward increasing length with increasing estimated positive charge at the phosphorus atom.[26]

The structural parameters of the phosphane, $FeP(Ph)N(SiMe_3)_2$, and phosphonium, $FeP(CH_3)(Ph)N(SiMe_3)_2^+$, fragments more clearly reveal the effect of CH_3^+ addition. The Fe–P distance in 1, 2.338 (1) Å, is identical with the distance in $Cp^*Fe(CO)_2PN(CH_3)CH_2CH_2NCH_3$, 2.340 (2) Å, and the phosphorus atom in each case is pyramidal (sum of the bond angles about phosphorus in 1, 330.6°). The addition of the CH_3^+ group in 4 provides a tetrahedral phosphorus site. The sum of equivalent bond angles (339.0°) indicates that the CH_3^+ group extracts electron density from the phosphorus atom, thereby opening the other phosphorus-substituent group angles. The Fe–P distance in 4, 2.263 (3) Å, is significantly shorter than in 1. This is also consistent with electron withdrawal from the phosphorus atom and enhanced Fe–P σ bonding in 4. Further confirmation of this electron-flow pattern may be found in comparing the Fe–P distances in 1 and 4 with the Fe–P distances in $CpFe(CO)_2P(CF_3)_2$, 2.265 (3) Å, and $Cp^*Fe(CO)_2P(BH_3)(Ph)_2$, 2.296 Å.[2]

The P–N bond distance in 1, 1.734 (4) Å, is longer than the average P–N distance in $CpFe(CO)_2PN(CH_3)CH_2CH_2NCH_3$, 1.701 (6) Å, and this is consistent with a smaller degree of P–N π overlap in 1. This is anticipated since the two silicon atoms would be expected to compete effectively for π bonding with nitrogen. Indeed, the nitrogen atom is planar and the Si–N$_{av}$ distance is 1.762 (5) Å.[27] This geometry is similar to the condition found in $(H_3Si)_2NPF_2$, and the average Si–N distance is 1.755 (4) Å. The P–N distance in 4, 1.682 (9) Å, is shorter than the distance in 1 and, once more, this trend is consistent with anticipated increased positive charge on the phosphorus atom and better P–N overlap in 4. Correspondingly, the Si–N$_{av}$ bond distance 1.796 Å is slightly longer than in 1. The P–C(8) (phenyl ipso carbon) distances in 1, 1.834 (5) Å, and 4, 1.832 (10) Å are identical, and CH_3^+ addition apparently has no effect on this subunit of the molecule.

The ease of preparation, purification, and crystallization of 1 and 2 make these complexes ideal reagents for surveying the chemistry of d^8 metallophosphanes. We have previously reported the addition of borane(3) to 1,[10] and X-ray crystal structure analysis confirmed the formation of a Lewis acid–base complex, $CpFe(CO)_2P(BH_3)(Ph)N(SiMe_3)_2$. That complex was also found to undergo CO loss and BH_3 addition across the Fe–P under mild conditions. In the present case, CH_3^+ addition to the phosphorus lone pair in 1 was also confirmed by single-crystal X-ray diffraction analysis. However, the subsequent metallophosphonium salts 3 and 4 were not observed to undergo CO loss or CH_3 migration across the Fe–P bond. Further studies of the reaction chemistry of 1 and 2 are in progress.

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Registry No. 1, 103192-37-6; 2, 114184-45-1; 3, 114184-47-3; 4, 114184-48-4; $PhPN(SiMe_3)_2(Cl)$, 84174-75-4; $NaCpFe(CO)_2$, 12152-20-4; $NaCp^*Fe(CO)_2$, 52409-74-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positional parameters, and bond distances and angles (12 pages); listings of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

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[26] On the basis of qualitative substituent group electronegativities, the phosphorus partial positive charge should increase in the order $PN(CH_3)CH_2CH_2NCH_3 < P(Ph)N(SiMe_3)_2 < P(CF_3)_2 < P(CH_3)(Ph)N(SiMe_3)_2^+$.

[27] A rationale for the large difference in Si–N distances, 1.749 (4) and 1.775 (5) Å, is not obvious.