Generation, Characterization, and Chemistry of the Methylene Complexes $[Fe(\eta^5\text{-}C_5Me_5)(CO)(L)(=CH_2)]^+$ (L = CO, PPh_3) and the X-ray Crystal Structure of $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2(CH_2PPh_3)]^+BF_4^-$

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The unstable methylene complexes $[Fe(Cp^*)(CO)(L)(=CH_2)]^+X^-$ ($Cp^* = \eta^5\text{-}C_5Me_5$; L = CO (**3**), PPh_3 (**13**)) are generated at −80 °C by the reaction of $H^+BF_4^-$–Et_2O or $Me_3SiOSO_2CF_3$ or CF_3CO_2H in CH_2Cl_2 with the precursor complexes $[Fe(Cp^*)(CO)(L)(CH_2OCH_3)]$ (L = CO (**2**), PPh_3 (**12**)). The ancillary PPh_3 ligand stabilizes the iron–methylene complex so that **13a** is stable up to −10 °C. The methylene unit is aligned with the CO–Fe bond (Scheme III) and is characterized by two distinct broad singlets at δ 16.67 and 15.10 ppm in the ^1H NMR spectrum at −80 °C. These coalesce at −45 °C and give a sharp singlet (δ 15.95 ppm) at −20 °C ($\Delta G^* = 10.9 \pm 0.1$ kcal mol^{-1}). Methylene transfer has been obtained by reaction of **3** with styrene to give phenylcyclopropane and with Ph_3SiH to give Ph_3SiMe. Both reactions occur at −80 °C with 100% chromatographic yield. Thermal decomposition of **3** gives $[Fe(Cp^*)(CO)_3]^+BF_4^-$ (**9**) and $[Fe(Cp^*)(CO)_2(CH_2{=}CH_2)]^+BF_4^-$ (**10**). The unstable methylene complex **2** can be trapped with CF_3CO_2H give mainly $[Fe(Cp^*)(CO)_2(CH_2OCOCF_3)]$ (**7**) and with PPh_3 and $H^+BF_4^-$–Et_2O, which gives $[Fe(Cp^*)(CO)_2(CH_2PPh_3)]^+BF_4^-$ (**4**). The X-ray crystal structure of **4** was obtained and shows a ∠FeCP angle of 118°, larger than the regular sp^3 angle because of the steric repulsion between the Cp* and PPh_3 ligands. Crystals of **4**, $FeC_{31}H_{32}O_2PBF_4$, are orthorhombic, space group $P2_12_12_1$, and have cell constants $a = 13.078$ (2) Å, $b = 14.511$ (5) Å, $c = 17.160$ (4) Å, $V = 3257$ Å^3, and $Z = 4$. A total of 3216 reflections (radiation Mo Kα, $\mu = 7.2$ cm^{-1}) were used in the refinement, resulting in a final R value of 0.093 ($R_w = 0.102$).

Iron–methylene complexes of the type $[Fe(Cp)(L_1)(L_2)(CH_2)]^+$, first generated by Pettit,[2] were stabilized with use of the dppe ligand and characterized by Brookhart et al.[3,4] Being cationic with a late transition metal, they are the most electrophilic methylene complexes. Theoretical studies were in agreement with their low rotation barrier[5] and preferred synclinal and anticlinal conformations,[5] which also explained their high reactivity.[4] For instance, neither $[Fe(Cp)(CO)_2(=CH_2)]^+$ nor $[Fe(Cp)(CO)(PPh_3)(=CH_2)]^+$ could be characterized even at −80 °C, in contrast with $[Fe(Cp)(dppe)(=CH_2)]^+$, because of the high, positive charge on the sterically unprotected methylene carbon:[3]

$$[(Cp)(L_1)(L_2)Fe^+{=}CH_2] \leftrightarrow [(Cp)(L_1)(L_2)Fe{-}CH_2]^+ \quad (1)$$

Disproportionation to iron–ethylene complexes was rationalized by fragmentation of the dimetallacyclobutane $[\overline{Fe{-}CH_2{-}Fe{-}CH_2}]^{2+}$, a mechanism established by Schrock and Sharp for nucleophilic methylenetantalum complexes.[6]

Elegant alkylidene transfer studies[7,8] were performed by Brookhart and recently reviewed.[4] A rich C_1 and C_2 ligand chemistry evolving from the iron–methylene species has been reported by Cutler and recently reviewed.[9]

We have focused our attention on the stabilization of these iron–methylene complexes by the C_5Me_5 ligand (Cp*). Such Cp*-substituted complexes were easily prepared following the disclosure of the synthesis of $[Fe(Cp^*)(CO)_2]^-Na^+$ (Na^+1^-). In a preliminary communication, we reported the syntheses and protonations of $[Fe(Cp^*)(CO)(L)(CH_2OCH_3)]$ (L = CO (**2**), PPh_3 (**12**),[10] generating the methylene complexes $[Fe(Cp^*)(CO)(L)(=CH_2)]^+$ (L = CO (**3**), PPh_3 (**13**)). We now report details of this chemistry as well as the X-ray crystal structure of the PPh_3 adduct of the methylene complex $[Fe(Cp^*)(CO)_2(=CH_2)]^+$ (**3**).

Experimental Section

General Data. All reactions were performed under an argon atmosphere with use of Schlenk techniques. Reagent grade

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tetrahydrofuran (THF), diethyl ether, toluene, and pentane were distilled from sodium benzophenone ketyl; acetonitrile and methylene chloride were distilled from P_2O_5. [Fe(Cp*)$(CO)_2$]$_2$ (1) was prepared according to the literature procedure.[11,12] All other chemicals were used as received. Infrared solution spectra were recorded on a Pye Unicam SP 1100 spectrophotometer using 0.1-mm cells with KBr windows and were calibrated with polystyrene film. Proton NMR spectra were obtained with a Varian EM 360 (60 MHz) instrument. FT ^1H (80 MHz), ^{13}C (20.115 MHz), and ^{31}P (32.38 MHz) NMR spectra were recorded on a Bruker WP 80 FT spectrometer by Dr. S. Sinbandhit. All chemical shifts are reported in parts per million (ppm) relative to Me_4Si for ^1H and ^{13}C NMR data and 85% H_3PO_4 for ^{31}P resonances. Mass spectra were recorded on a Varian MAT 311 (70 eV) instrument by Dr. P. Guênot (Centre de Mesures Physiques de l'Ouest, Rennes, France). Gas chromatographic (GC) analyses were obtained with a Delsi GC 121 chromatograph equipped with a Hewlett-Packard 3390 integrator, by using a glass column (length 1.4 m, i.d. 3 mm) packed with Apiezon L (15%) on Chromosorb WAW. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon, France.

Warning! $ClCH_2OCH_3$ is quite volatile and is a potent carcinogen. Reactions must thus be carried out in a well-ventilated hood.

1. Preparation of [Fe(Cp*)$(CO)_2$(CH_2OCH_3)] (2). A Schlenk tube was charged with 5 g (10 mmol) of [Fe(Cp*)$(CO)_2$]$_2$ (1), 115 g of Na/Hg (50 mmol of Na), and 100 mL of THF. The reaction mixture was stirred overnight and filtered; $ClCH_2OCH_3$ (1.5 mL, 20 mmol) was added by syringe. After the mixture was stirred for 1 h, the solvent was evaporated in vacuo. The residue was extracted with pentane (3 × 50 mL). Compound 2 was chromatographed on preparative thick-layer plates (silica gel, pentane/ether, 95/5). A 4.4-g amount (75% yield) of 2 was isolated as an amber oil.[5] ^1H NMR (C_6D_6, δ): 4.44 (s, 2 H, CH_2), 3.30 (s, 3 H, OCH_3), 1.47 (s, 15 H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 218.7 (CO), 95.5 (C_5Me_5), 73.3 (CH_2), 61.3 (OCH_3), 9.2 (C_5Me_5). IR (ν, cm^{-1}, pentane): 2000 (s, ν_{CO}), 1935 (s, ν_{CO}), 1060 (s, ν_{CO}). Anal. Calcd for $C_{14}H_{20}FeO_3$: C, 57.55; H, 6.90; Fe, 19.11. Found: C, 57.21; H, 6.84; Fe, 19.23.

2. Preparation of [Fe(Cp*)$(CO)_2$(CH_2PPh_3)]$^+BF_4^-$ (4). In a Schlenk tube, 292 mg (1 mmol) of [Fe(Cp*)$(CO)_2$(CH_2OCH_3)] (2) and 262 mg (1 mmol) of PPh_3 were dissolved in 20 mL of CH_2Cl_2 at -80 °C; 70 μL (1 mmol) of $H^+BF_4^-$–Et_2O was then added by syringe. After being stirred for 1 h at -80 °C, the reaction mixture was slowly warmed to room temperature. Addition of 100 mL of ether led to precipitation of a yellow powder of 4 (400 mg 66% yield). ^1H NMR (CD_3COCD_3, δ): 7.80 (m, 15 H, PPh_3), 1.87 (s, 15 H, Cp*), 1.60 (d, 2 H, $^2J_{P-H}$ = 14 Hz, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN, δ): 217.4 (d, CO, $^3J_{P-C}$ = 2.9 Hz), 134.7 (d, para Ph, $^4J_{P-C}$ = 2.9 Hz), 134.1 (d, ortho Ph, $^2J_{P-C}$ = 10.3 Hz), 130.6 (d, meta Ph, $^3J_{P-C}$ = 11.7 Hz), 125.5 (d, ipso Ph, $^1J_{P-C}$ = 83.8 Hz), 98.6 (C_5Me_5), 9.4 (C_5Me_5), -13.3 (d, CH_2, $^1J_{P-C}$ = 36.8 Hz). ^{31}P NMR (CD_3CN, δ): 37.2 (t, PPh_3), IR (ν, cm^{-1}, CH_2Cl_2): 2010, 1960 (s, ν_{CO}), 1070 (s, ν_{BF_4}).

3. Preparation of [Fe(Cp*)$(CO)_2$(OSO_2CF_3)] (5). To a CH_2Cl_2 solution of 876 mg (3 mmol) of [Fe(Cp*)$(CO)_2$(CH_2OCH_3)] (2) and 690 μL (6 mmol) of styrene was added, at -80 °C, 580 μL (3 mmol) of $Me_3SiOSO_2CF_3$. The yellow reaction mixture immediately turned deep red. After the mixture was warmed up to room temperature, the solvent was evaporated to dryness. The residue was washed with pentane (2 × 20 mL) and then extracted with 10 mL of toluene. Adding pentane and cooling to -20 °C gave 1.08 g (91% yield) of 5 as red needles. ^1H NMR (CD_2Cl_2, δ): 1.73 (s, Cp*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 212.6 (CO), 119.3 (q, CF_3), 98.2 (C_5Me_5), 9.6 (C_5Me_5). IR (ν, cm^{-1}, CH_2Cl_2): 2060, 2000 (s, ν_{CO}). Mass spectrum (*m/e*): 340.0021 (M^+ - 2CO), calcd for $C_{11}H_{15}F_3FeO_3S$ 340.0043. Anal. Calcd for $C_{13}H_{15}F_3FeO_5S$: C, 39.41; H, 3.81; S, 8.09. Found: C, 39.20; H, 4.02; S, 8.24.

4. Reaction of 3 with $C_6H_5CH{=}CH_2$. $Me_3SiOSO_2CF_3$ (96 μL, 0.50 mmol) was added to a stirred solution of 146 mg (0.50 mmol) of [Fe(Cp*)$(CO)_2$(CH_2OCH_3)] (2) and 115 μL (1 mmol) of styrene in 10 mL of CH_2Cl_2 at -80 °C, which was then allowed to warm up to room temperature over 2 h. GC analysis of the solution (CH_2Cl_2 as internal standard) indicated a 100% yield of phenylcyclopropane, which was identified by comparison with an authentic sample. The workup as in subsection 3 gave 135 mg (68% yield) of compound 5.

5. Reaction of 3 with Ph_3SiH. A CH_2Cl_2 solution of 73 mg (0.25 mmol) of 2 and 120 mg (0.50 mmol) of Ph_3SiH was cooled to -80 °C and treated with 48 μL (0.25 mmol) of $Me_3SiOSO_2CF_3$. The reaction mixture was slowly warmed to room temperature. Analysis of the solution by GC showed a 100% yield of Ph_3SiMe. After workup as in subsection 3, 70 mg (70% yield) of 5 was isolated.

6. Preparation of [Fe(Cp*)$(CO)_2$(CH_3CN)]$^+CF_3SO_3^-$ (6). In a Schlenk tube, 115 mg (0.30 mmol) of [Fe(Cp*)$(CO)_2$(OSO_2CF_3)] (5) was dissolved in 10 mL of CH_3CN. The red solution gradually turned yellow. The solvent was then evaporated in vacuo and the residue extracted with CH_2Cl_2. The solution was concentrated, and addition of an excess of diethyl ether provided 80 mg (63% yield) of 6 as yellow microcrystals. The structure of 6 was assigned on the basis of the similarity of its spectroscopic data with those of the PF_6^- analogue.[12] ^1H NMR (CD_3CN, δ): 2.30 (s, 3 H, CH_3CN), 1.84 (s, 15 H, Cp*). IR (ν, cm^{-1}, CH_2Cl_2): 2060, 2020 (s, ν_{CO}). Anal. Calcd for $C_{15}H_{18}F_3FeNO_5S$: C, 41.20; H, 4.15; N, 3.20; S, 7.33. Found: C, 40.97; H, 4.23; N, 3.06; S, 7.34.

7. Decomposition of [Fe(Cp*)$(CO)_2$(=CH_2)]$^+BF_4^-$ (3): NMR Evidence of [Fe(Cp*)$(CO)_2$($CH_2{=}CH_2$)]$^+BF_4^-$ (10). To a vigorously stirred CH_2Cl_2 solution at -80 °C containing 140 μL (1 mmol) of $H^+BF_4^-$–Et_2O was added dropwise a solution of 292 mg (1 mmol) of [Fe(Cp*)$(CO)_2$(CH_2OCH_3)] (2) in 5 mL of CH_2Cl_2. The reaction mixture was then warmed up to room temperature, and the solvent was removed in vacuo. The red residue was dissolved in CD_2Cl_2. ^1H NMR analysis of the solution showed the presence of [Fe(Cp*)$(CO)_3$]$^+BF_4^-$ (9; δ(Cp*) 2.04)[12] and [Fe(Cp*)$(CO)_2$($CH_2{=}CH_2$)]$^+BF_4^-$, (10; δ(Cp*) 1.90, δ(C_2H_4) 3.17). A Cp* signal at 1.74 ppm appeared simultaneously. This unidentified compound was assumed to be a solvent or counterion coordinated with [Fe(Cp*)$(CO)_2$]$^+$. Integration of the respective Cp* signals indicated a ratio of 14/29/57. The ethylene complex has been identified by comparison with the NMR data of the PF_6^- analogue prepared independently.[13]

8. Preparation of [Fe(Cp*)$(CO)_2$(CH_2OCOCF_3)] (7) and [Fe(Cp*)$(CO)_2$($OCOCF_3$)] (8). A CH_2Cl_2 solution of 1.17 g (4 mmol) of [Fe(Cp*)$(CO)_2$(CH_2OCH_3)] (2) was cooled to -80 °C and treated with 0.31 mL (4 mmol) of CF_3CO_2H. The reaction mixture was warmed to room temperature, and the solvent was removed in vacuo. After extraction of the residue with ether, compounds 7 and 8 were separated on preparative thick-layer chromatography plates (silica gel, 50/50 pentane–ether). This procedure gave 756 mg (51% yield) of 7 as a yellow oil and 250 mg (17% yield) of 8 as red microcrystals. [Fe(Cp*)$(CO)_2$(CH_2OCOCF_3)] (7): ^1H NMR (C_6D_6, δ) 5.07 (s, 2 H, CH_2), 1.37 (s, 15 H, Cp*); $^{13}C\{^1H\}$ NMR (C_6D_6, δ) 219.7 (CO), 156.9 (q, $^2J_{C-F}$ = 40.3 Hz, $OCOCF_3$), 114.6 (q, $^1J_{C-F}$ = 287 Hz, CF_3), 94.8 (C_5Me_5), 68.8 (CH_2), 7.4 (C_5Me_5); IR (ν, cm^{-1}, pentane) 2020, 1960 (s, ν_{CO}), 1780 (s, $\nu_{C=O}$); mass spectrum (*m/e*) 318.0505 (M^+ - 2CO), calcd for $C_{13}H_{17}F_3FeO_2$ 318.0529. Fe(Cp*)$(CO)_2$($OCOCF_3$) (8): ^1H NMR (C_6D_6, δ) 1.24 (s, Cp*); $^{13}C\{^1H\}$ NMR (C_6D_6, δ) 214.0 (CO), 163.4 (q, $^2J_{C-F}$ = 34 Hz, $OCOCF_3$), 114.9 (q, $^1J_{C-F}$ = 290 Hz, CF_3), 97.6 (C_5Me_5), 9.5 (C_5Me_5); IR (ν, cm^{-1}, CH_2Cl_2) 2040, 1990 (s, ν_{CO}), 1690 (s, $\nu_{C=O}$); mass spectrum (*m/e*) 332.0317 (M^+ - CO), calcd for $C_{13}H_{15}F_3FeO_3$ 332.0322. Anal. Calcd for $C_{14}H_{15}F_3FeO_4$: C, 46.69; H, 4.20. Found: C, 46.57; H, 4.26.

9. Preparation of [Fe(Cp*)(CO)(PPh_3)(CH_2OCH_3)] (12). A solution of 560 mg (1.90 mmol) of [Fe(Cp*)$(CO)_2$(CH_2OCH_3)] (2) and 524 mg (2 mmol) of PPh_3 in toluene (200 mL) was photolyzed with a 450-W medium-pressure mercury lamp for 2 h. The solvent was evaporated in vacuo, and the crude product was

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extracted with pentane. The solution was concentrated and cooled to −20 °C; 460 mg (46% yield) of **12** was isolated as red microcrystals. ^1H NMR (C_6D_6, δ): 7.75–7.05 (m, 15 H, PPh_3), 4.06–3.74 (AB q, 2 H, CH_2), 3.05 (s, 3 H, OCH_3), 1.52 (s, 15 H, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 223.9 (d, CO, $^2J_{P-C}$ = 28.1 Hz), 137.1 (d, ipso Ph, $^1J_{P-C}$ = 36.6 Hz), 134.7 (d, ortho Ph, $^2J_{P-C}$ = 9.8 Hz), 129.1 (d, para Ph, $^4J_{P-C}$ = 7.3 Hz), 127.9 (d, meta Ph, $^3J_{P-C}$ = 9.8 Hz), 92.8 (C_5Me_5), 73.9 (d, CH_2, $^1J_{P-C}$ = 20.7 Hz), 63.5 (OCH_3), 9.6 (C_5Me_5). IR (ν, cm^{-1}, pentane): 1900 (s, ν_{CO}), 1060 (s, ν_{CO}). Anal. Calcd for $C_{31}H_{35}FeO_2P$: C, 70.73; H, 6.70. Found: C, 70.43; H, 6.44.

10. Generation and NMR Characterization of [Fe(Cp*)(CO)(PPh$_3$)(=CH$_2$)]$^+$X$^-$ (13a, X = CF$_3$SO$_3^-$; 13b, X = CF$_3$CO$_2^-$). A solution of 10 mg (19 μmol) of [Fe(Cp*)(CO)(PPh_3)(CH_2OCH_3)] (**12**) in 0.50 mL of CD_2Cl_2 in a 5-mm NMR tube was degassed with argon and cooled to −80 °C. The addition of a slight excess of $Me_3SiOSO_2CF_3$ or CF_3CO_2H led to the immediate formation of a deep red solution. Low-temperature 80-MHz ^1H NMR spectrum (CD_2Cl_2, $CHDCl_2$ internal reference δ 5.30, δ, −80 °C): 16.67 (br s, 1 H, $=CH_2$), 15.10 (br s, 1 H, $=CH_2$), 7.47 (m, 15 H, PPh_3), 1.47 (s, 15 H, Cp*). The methylene resonances coalesce at −45 °C (k = 269 s^{-1}) and sharpen at −20 °C, giving rise to a signal at δ 15.95 (2 H). Decomposition of **13** was not observed up to −10 °C. $\Delta G^{\ddagger}$ = 10.9 ± 0.1 kcal mol^{-1}.

The 20.115-MHz ^{13}C NMR spectrum of **13b** was recorded at −80 °C for a sample prepared from 300 mg (0.57 mmol) of [Fe(Cp*)(CO)(PPh_3)(CH_2OCH_3)] (**12**) and 120 μL (0.62 mmol) of $Me_3SiOSO_2CF_3$ in 4 mL of CD_2Cl_2 at −80 °C in a standard 10-mm NMR tube. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, CD_2Cl_2 internal standard δ 53.8, δ, −80 °C): 351.2 (CH_2, d, $^2J_{P-C}$ = 23.6 Hz), 215.3 (CO, d, $^2J_{P-C}$ = 31.5 Hz), 134.5–128.8 (Ph), 106.5 (C_5Me_5), 9.5 (C_5Me_5).

11. X-ray Analysis of 4. A suitable single crystal of **4** was selected and placed on an Enraf-Nonius CAD-4 diffractometer. The cell parameters and orientation matrix were refined with use of 25 reflections within the 2θ range 26–28°. The data were collected in one unique octant with use of the ω–2θ scan mode and a variable scan rate of 2–10° min^{-1} in ω. The scan width was 0.8 + 0.35 tan θ. Two standard reflections were measured every 3600 s of X-ray exposure. However, no significant decay was observed. The space group $P2_12_12_1$ was defined uniquely on the basis of systematic absences, and the structure was solved by Patterson methods. Full-matrix least-squares refinement resulted in the location of all the non-hydrogen atoms in the structure. One molecule of CH_2Cl_2 per asymmetric unit was found to be cocrystallized with complex **4**. The tetrafluoroborate anion was partially disordered. The four best fluorine positions were chosen and refined isotropically. A weighting scheme was incorporated into the refinement such that $w = 4F_o^2/(\sigma_{\text{counting}} + (0.08F_o^2)^2)$. The somewhat high residual density of 0.9 (1) e $Å^{-3}$ near the fluorine positions is due to the BF_4^- disorder problem. All computations were carried out on a Microwax II computer using the Enraf-Nonius SDP/VAX program package.

Results and Discussion

The starting point of this chemistry is the easy reduction of the dimer $[Fe(Cp^*)(CO)_2]_2$ (**1**) by Na/Hg in THF at 20 °C to give $[Fe(Cp^*)(CO)_2]^-Na^+$ (Na^+1^-).[10] Subsequently, Cp* derivatives containing Fe–carbon bonds can be made by reaction of 1^- with alkyl halides. For instance, the reaction with $ClCH_2OCH_3$ cleanly gives the air-stable complex [Fe(Cp*)(CO)$_2$(CH_2OCH_3)] (**2**) isolated in 75% yield after chromatography. The anion K^+1^- was also made before this study by reduction of the dimer with a K mirror.[12] Several other groups have also reported Fp* complexes[14b,15] (Fp* = Fe(Cp*)(CO)$_2$).

Scheme I. Generation of the Methylene Complex [Fe(Cp*)(CO)$_2$(=CH$_2$)]$^+$BF$_4^-$ (3)

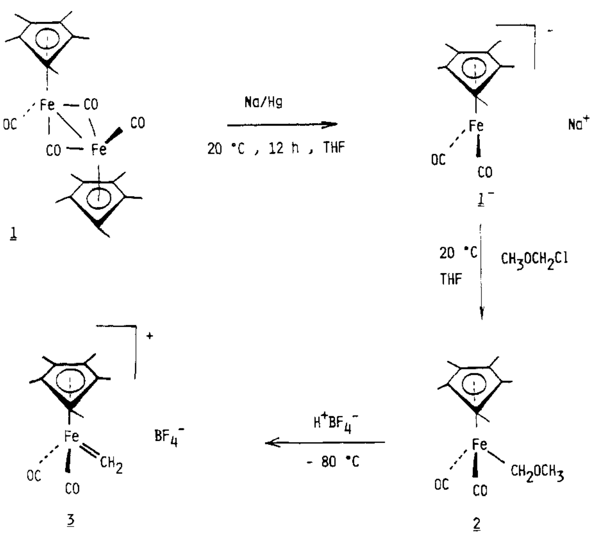

Table I. Crystallographic Data Collection Parameters for Complex 4

mol formula	$C_{31}H_{32}FeO_2PBF_4$
fw	683.2
cryst color	pale orange
cryst dimens, mm	0.35 × 0.30 × 0.40
cryst habit	prism
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
cell params	
a, Å	13.078 (2)
b, Å	14.511 (5)
c, Å	17.160 (4)
V, $Å^3$	3257
Z	4
d(calcd), g cm^{-3}	1.39
radiation	graphite-monochromated Mo radiation, λ = 0.71069 Å
range of data collected	(000) → (15,17,20)
2θ range, deg	3 < 2θ < 50
total no. of rflns	3216
no. of unique data used	2167
criteria for inclusion	$F_o > \sigma F_o$
T, K	297 (1)
μ(Mo Kα), cm^{-1}	7.2
abs cor	not applied
R	0.093
R_w	0.102
highest peak of resid electron dens, e $Å^{-3}$	0.9 (due to poorly refined F positions)
no. of params varied	288

Table II. Selected Bond Distances (Å) for 4[a]

Fe–C1	1.75 (1)	Fe–C7	2.12 (1)
Fe–C2	1.73 (1)	Fe–C8	2.14 (1)
Fe–C3	2.11 (1)	P–C3	1.78 (1)
Fe–C4	2.13 (1)	P–C11	1.79 (1)
Fe–C5	2.12 (1)	P–C21	1.79 (1)
Fe–C6	2.10 (1)	P–C31	1.79 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

As its Cp analogue, complex **2** is a precursor to methyleneiron complexes. The methylene complex [Fe(Cp*)(CO)$_2$(=CH_2)]$^+BF_4^-$ (**3**) can be generated at −80 °C by protonation of **2** with use of $H^+BF_4^-$–Et_2O or by methoxide abstraction with use of $Me_3SiOSO_2CF_3$ (Scheme I). If the protonation reaction is performed in the presence of PPh_3 at −80 °C, the yellow phosphonium salt [Fe(Cp*)(CO)$_2$(CH_2PPh_3)]$^+BF_4^-$ (**4**) is obtained (66% yield) as a result of attack of PPh_3 on the electrophilic methylene ligand.[16a]

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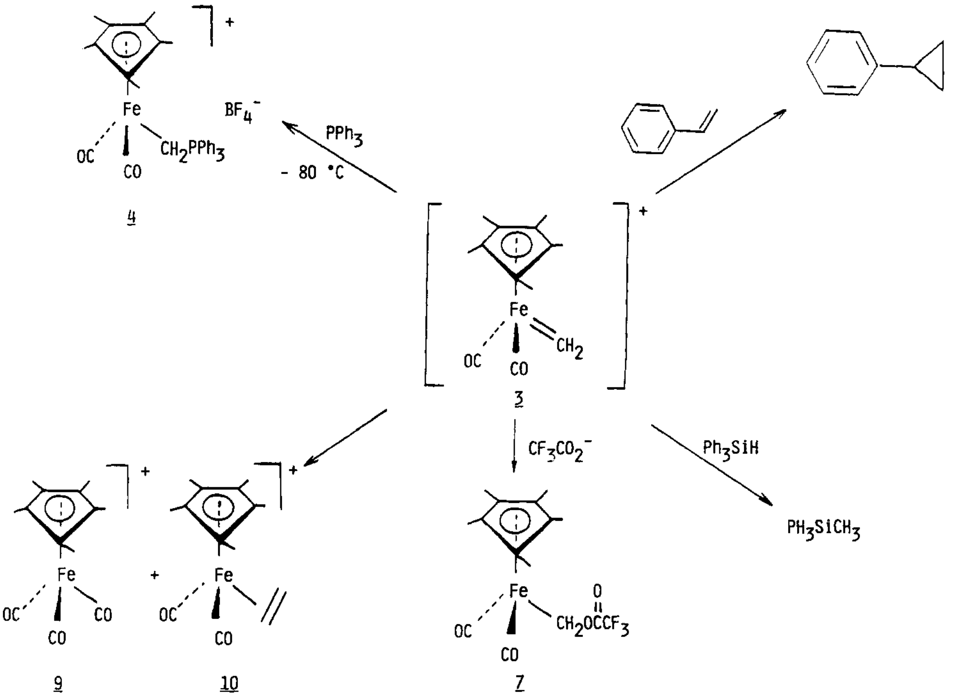
Scheme II. Methylene Transfer and Trapping Reactions from the Methylene Complex [Fe(Cp*)$(CO)_2$(=CH_2)]$^+$ (3^+) Generated from 2 with Use of the Electrophiles $H^+BF_4^-$ (PPh_3), CF_3CO_2H ($CF_3CO_2^-$), $Me_3SiOSO_2CF_3$ (Styrene and Ph_3SiH)[a]



[a] In the last case, [Fp(OSO_2CF_3)] (5) was formed. All the reactions were carried out at -80 °C followed by warming to 20 °C. For details, see the text.

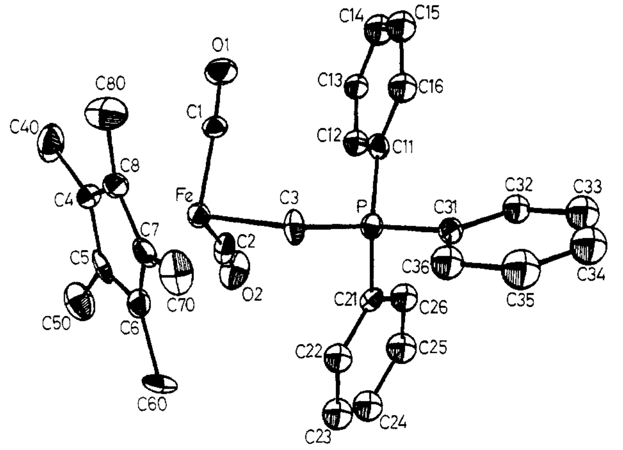


Figure 1. ORTEP view of the X-ray structure of complex 4.

Complex 4 shows a doublet at δ 1.60 ppm for the methylene protons ($^2J_{P-H}$ = 14 Hz) in the ^1H NMR spectrum, a doublet at δ -13.3 ppm ($^1J_{P-C}$ = 36.8 Hz) in the ^{13}C NMR spectrum, and a triplet at δ 37.2 ppm in the ^{31}P NMR spectrum. Crystals of 4 were grown by slow evaporation of an acetonitrile solution at 20 °C, and the X-ray structure was obtained. An ORTEP diagram of 4 is shown in Figure 1, and salient data are given in Tables I-III. An unusual feature is the FeC_3P angle reaching 118°, larger than the expected value for a sp^3 carbon. This increased angle is attributed to the steric bulk of the PPh_3 ligand. The ylide complex [$(CO)_4FeCH_2PPh_3$] has been reported by Des Abbayes et al.[14a] Its crystal structure shows a tetragonal carbon with some steric interaction of the carbonyl ligands and phenyl groups (∠FeCP = 118.6°). The Cp*-Fe distance is as in other known complexes. An early example is that of [FeCp*$(CO)_2OSO_2F$] reported by Brookhart.[14b]

Table III. Selected Bond Angles (deg) for 4[a]

C1–Fe–C2	97.4 (7)	C4–Fe–C5	38.3 (6)
C1–Fe–C3	92.9 (6)	C4–Fe–C6	65.9 (4)
C1–Fe–C1	91.5 (5)	C4–Fe–C7	65.0 (4)
C1–Fe–C5	124.5 (6)	C4–Fe–C8	40.4 (6)
C1–Fe–C6	155.4 (5)	C5–Fe–C6	40.1 (6)
C1–Fe–C7	123.2 (5)	C5–Fe–C7	65.7 (6)
C1—Fe–C8	91.4 (5)	C5–Fe–C8	65.8 (6)
C2–Fe–C3	99.3 (5)	C6–Fe–C7	39.5 (5)
C2–Fe–C4	112.8 (5)	C6–Fe–C8	65.3 (5)
C2–Fe–C5	87.7 (6)	C7–Fe–C8	37.2 (5)
C2–Fe–C6	100.3 (7)	C3–P–C11	111.7 (6)
C2–Fe–C7	138.9 (7)	C3–P–C21	110.0 (6)
C2–Fe–C8	152.3 (6)	C3–P–C31	109.6 (6)
C3–Fe–C4	146.7 (5)	C11–P–C21	112.5 (6)
C3–Fe–C5	140.8 (5)	C11–P–C31	105.4 (6)
C3–Fe–C6	100.9 (5)	C21–P–C31	107.4 (6)
C3–Fe–C7	85.3 (5)	Fe–C3–P	118.1 (7)
C3–Fe–C8	106.5 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Other methylene transfer reactions were observed (Scheme II). In the presence of styrene, complex 2 reacts with $Me_3SiOSO_2CF_3$ in CH_2Cl_2 at -80 °C to give a 100% yield of phenylcyclopropane (by gas chromatography), a classical reaction already reported[2] with the parent complex [Fe(Cp)$(CO)_2$(=CH_2)]$^+$. In this reaction the iron complex [Fp*(OSO_2CF_3)] (5)[14b] was isolated in 91% yield. In the presence of Ph_3SiH, complex 2 reacts with $Me_3SiOSO_2CF_3$ in CH_2Cl_2 at -80 °C to give Ph_3SiMe in 100% yield (by gas chromatography). Complex 5 was also isolated in 70% yield in this reaction. When a solution of 5 in CH_3CN was stirred, smooth replacement of the $OSO_2CF_3^-$ ligand by CH_3CN occurred, giving [Fp*(CH_3CN)]$^+OSO_2CF_3^-$ (6). This exchange shows the weakness of the Fe-O bond in 5.

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(16) (a) The phosphonium salts [FeCp(CO)(PPh_3)CH_2PR_3]$^+$ were recently reported. They were prepared by reaction of phosphines with FeCp(CO)(PPh_3)CH_2Cl: Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Am. Chem. Soc.* **1987**, *109*, 5711. (b) Studabaker, W. B.; Brookhart, M. *J. Organomet. Chem.* **1986**, *310*, C39.

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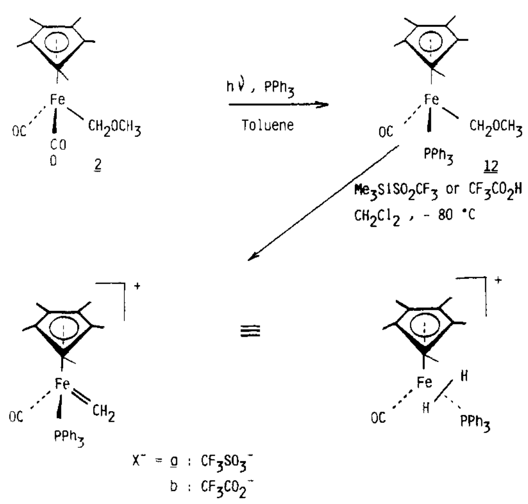
Scheme III



Trapping of the electrophilic methylene ligand of **3** without detachment from iron (Scheme II) is not specific for phosphines. For example, the parent system can be trapped by sulfides.[8,18] Reaction of **2** with CF_3CO_2H gives a 51% yield of $[Fp^*(CH_2OCOCF_3)]$ (**7**). Also obtained in this reaction is a smaller amount of $[Fp^*(OCOCF_3)]$ (**8**; 17% yield), which results from the loss of the methylene ligand.

Although the methylene complex **3** could be characterized spectroscopically,[13] it is not stable above −40 °C. Thus, protonation of **1** with use of $H^+BF_4^-$ in Et_2O, in the absence of a trapping reagent, followed by warming to 20 °C gives a mixture of $[Fp^*(CO)]^+BF_4^-$ (**9**),[12] $[Fp^*(CH_2{=}CH_2)]^+BF_4^-$ (**10**), and a third product, which could be $[Fp^*(OEt_2)]^+BF_4^-$ (**11**).[19] The formation of these three products arises from the decomposition of **3**. The dimetallacycle mechanism[6] indeed leads to the formation of ethylene (or its cationic Fp* complex **10**, eq 2 and 3)[9] and the free 16-electron fragment $[Fp^*]^+$, which can trap a Et_2O solvent molecule as ligand (eq 4)[19] or CO, which results from the decomposition of some $[Fp^*]^+$ (eq 5 and 6).

$$[\mathrm{Fp^*(CH_2)}]^+ \rightarrow [\overline{\mathrm{Fp^*(CH_2)Fp^*(CH_2)}}]^{2+} \qquad (2)$$

$$[\overline{\mathrm{Fp^*(CH_2)Fp^*(CH_2)}}]^{2+} \rightarrow \underset{\mathbf{10}^+}{[\mathrm{Fp^*(CH_2{=}CH_2)}]^+} + [\mathrm{Fp^*}]^+ \qquad (3)$$

$$[\mathrm{Fp^*}]^+ + \mathrm{Et_2O} \rightarrow \underset{\mathbf{11}^+}{[\mathrm{Fp^*(OEt_2)}]^+} \qquad (4)$$

$$[\mathrm{Fp^*}]^+ \rightarrow \mathrm{CO} + [\mathrm{Fe(Cp^*)(CO)}]^+ \qquad (5)$$

$$[\mathrm{Fp^*}]^+ + \mathrm{CO} \rightarrow \underset{\mathbf{9}^+}{[\mathrm{Fp^*CO}]^+} \qquad (6)$$

The iron–methylene complex could be considerably stabilized by replacement of a carbonyl ligand with triphenylphosphine. Photolysis of the precursor **2** with use of UV light in toluene results in the desired ligand exchange (46% yield) and gives $[Fe(Cp^*)(CO)(PPh_3)(CH_2OCH_3)]$ (**12**) as a red, microcrystalline complex. Efforts to replace both carbonyls by PPh_3 or dppe were unsuccessful.[20] Reaction of $Me_3SiOSO_2CF_3$ or CF_3CO_2H with **12** in CH_2Cl_2 at −80 °C generated the deep red methylene complex $[Fe(Cp^*)(CO)(PPh_3)({=}CH_2)]^+X^-$ (**13a**, $X = CF_3SO_3^-$; **13b**, $X = CF_3CO_2^-$) (Scheme III). At −80 °C, the methylene carbon appears at δ 351 ppm in the ^{13}C NMR spectrum and the two methylene protons appear as two broad singlets in the 80-MHz ^1H NMR spectrum at δ 16.67 and 15.10 ppm. Coalescence of these bands is observed at −45 °C, and at higher temperature (−20 °C), the methylene resonance becomes sharp (δ 15.95 ppm). This behavior is typical for iron–methylene complexes. The −80 °C ^1H NMR spectrum is consistent with the preferred methylene orientation[17] in which the CH_2 plane is aligned with the CO–Fe bond as shown in Scheme III. The calculated $\Delta G^‡$ value for the rotation of the methylene is 10.9 ± 0.1 kcal mol^{-1} (45.16 kJ mol^{-1}). This value is very close to the one reported by Brookhart[3] for $[Fe(Cp)(dppe)({=}CH_2)]^+$ (10.4 ± 0.1 kcal mol^{-1}), whereas Hoffmann[5] calculated a lower value (6.2 kcal mol^{-1}) for Pettit's parent compound $[Fe(Cp)(CO)_2({=}CH_2)]^+$. The back-bonding is greater in the latter compound, lowering the order of the Fe–CH_2 bond, so that all these $\Delta G^‡$ values are consistent with one another. The deep red complex **13** decomposes above −10 °C and could not be isolated in the solid state.

It is noteworthy that the trifluoroacetate salt of the methylene complex **13b** is ionic whereas the dicarbonyl analogue **7** is covalent. This is easily checked by ^1H NMR spectroscopy. The methylene protons are found at δ 5.07 ppm in **7** and at δ 15.95 ppm in **13**. The ionization of the C–O bond is favored by the decrease of the positive charge on the methylene carbon in **13**. The influence of the replacement of carbonyls by phosphine ligands on such ionization of the C–O bond was already shown by Pettit[21] in the acids $FeCp(CO)_2COOH$, $FeCp(CO)(PPh_3)COOH$, and $[FeCp(CO)(dppe)]^+OH^-$.

Concluding Remarks

(1) The methylene complex **3** is a useful reagent for methylene transfer reactions under mild conditions and for the synthesis of organometallic fragments Fe–CH_2–X (X = O, P, etc.). Complex **2** is easier to handle than the parent complex $[FpCH_2OCH_3]$.

(2) Stabilization by permethylation of the Cp ligand is roughly equivalent to replacing a CO ligand by PPh_3 regarding (i) the stability of iron–methylene complexes and (ii) the rotational barrier about the iron–carbon bond.

(3) The methylene complexes **3** and **13** compare with other known electrophilic methylene complexes of Fe,[4,9] Ru,[16] Re,[17] Mo,[7e,18] and W.[7e]

(4) The methylene complex **3** was trapped by PPh_3 to give a phosphonium salt, the X-ray crystal structure of which shows a ∠FeCP angle of 118°.

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Supplementary Material Available: Tables of positional parameters and their estimated standard deviations, complete listings of bond distances and angles, refined displacement parameter expressions, and root-mean-square amplitudes of thermal vibration for 4 (9 pages); a listing of observed and calculated structure factors for 4 (11 pages). Ordering information is given on any current masthead page.

Reaction of CH_2O with $[Co(PMe_3)_4]X$ ($X = PF_6$ and BPh_4). Structural Characterization of $[Co(CO)(PMe_3)_4]PF_6$ and the Nonstoichiometric Complex $[CoH_{2-2x}(CO)_x(PMe_3)_4]BPh_4$

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$[Co(PMe_3)_4]PF_6$ reacts with formaldehyde to form $[Co(CO)(PMe_3)_4]PF_6$, which is shown by X-ray diffraction ($P2_1/n$, $a = 11.280$, b 14.948, $c = 14.088$ Å, $\beta = 90.69°$, $Z = 4$, $R = 0.029$) to contain trigonal-bipyramidal cations with CO in the *equatorial* position. From $[Co(PMe_3)_4]BPh_4$, $[Co(CO)(PMe_3)_4]BPh_4$ is formed in low yield. The major product is crystallographically characterized ($P2_1$, $a = 15.985$, $b = 12.512$, $c = 20.410$ Å, $\beta = 111.76$ (3)°, $Z = 4$, $R = 0.048$) and found to contain the cis-octahedral Co(III) dihydrido species $[CoH_2(PMe_3)_4]^+$ and the Co(I) cation $[Co(CO)(PMe_3)_4]^+$ with CO in the *axial* position. These two ions are disordered over the cationic sites in the crystal. The presence of these species in the nonstoichiometric material is also indicated by infrared and NMR data on the compound and its ^2H- and ^{13}C-labeled derivatives.

Introduction

The synthesis and decomposition mechanisms of d^8 metal complexes containing formyl groups, hydroxymethyl groups, carbon monoxide, or formyl-derived methyl groups still attract considerable attention in connection with the role of such species as intermediates in carbon monoxide hydrogenation promoted by homogeneous or heterogeneous catalysts.[1-3] Studies conducted by Thorn et al. on the reaction of CH_2O with cationic $[M(PMe_3)_4]X$ compounds have led to the preparation of the first cationic formyl compound $[MH(CHO)(PMe_3)_4]X$ with M = Ir, but only the carbonyl species has been obtained for M = Rh.[2] With ruthenium and osmium, Roper et al. have isolated molecular formaldehyde and formyl complexes.[4,5] Nickel(0)-phosphine $Ni(PR_3)_4$ complexes have been found to promote the decomposition of formaldehyde into CO and H_2 with formation of $Ni(CO)(PR_3)_3$.[6] No reactions have been performed so far on the cobalt analogues, but for hydroformylation, modifying the $Co_2(CO)_8$ catalyst by addition of phosphines of small cone angle increased the proportion of formate obtained.[7] We felt that the basic coordination chemistry of the cobalt system toward CH_2O had to be examined in greater detail. We wish to report our results on the reaction of CH_2O with $[Co(PMe_3)_4]X$ for $X = PF_6$ and BPh_4. Interestingly, the chemistry of this system was found to be dependent on the counterion used, and it allowed us to observe both the axial-CO and equatorial-CO forms of the trigonal-bipyramidal $[Co(CO)(PMe_3)_4]^+$ ion.

Experimental Section

Materials and Methods. Solvent distillation and all other operations were carried out under argon by using standard Schlenk techniques. Tetrahydrofuran was distilled over Na/benzophenone just before use. Methanol and acetonitrile were distilled over molecular sieves. All solvents were degassed by three freeze–thaw cycles. Trimethylphosphine[8] and $CoBr(PMe_3)_3$[9] were prepared by literature methods. Paraformaldehyde and aqueous formaldehyde (stabilized with 10% methanol) were used without further purification. [^{2}H]- and [^{13}C]paraformaldehyde (CEA) were used as received.

Elemental analyses were done by M. Magna (CNRS, Toulouse) for C and H and by the Service Central de Microanalyse du CNRS (Lyon) for the remaining elements.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer as Nujol mulls prepared in the glovebox. The ^1H and ^{31}P NMR spectra were recorded at low temperature on a Bruker WH-90 spectrometer with THF-d_8 or CD_2Cl_2 as solvents. Chemical shifts were referenced to residual solvent signals for ^1H NMR (CD_2Cl_2, δ_H 5.33; THF-d_8, δ_H 1.90, 3.80) and to external

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