Reactions of $\mathrm{CpFe(CO)_2(=\overline{COCH_2CH_2O})^+}$, $\mathrm{CpFe(CO)_2[=C(SMe)_2]^+}$ and Related Carbene Complexes with Reducing Agents and Nucleophiles. The Structure of $\mathrm{\{CpFe(CO)_2[=C(SMe)_2]\}PF_6}$

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Abstract

The reduction of $\mathrm{CpFe(CO)_2(=\overline{COCH_2CH_2O})^+}$ (**I**) with one equivalent of sodium naphthalenide (NaNp) yields $\mathrm{[CpFe(CO)_2]_2}$ (**II**), CO_2 and C_2H_4. The same reduction of $\mathrm{CpFe(CO)_2[=C(SMe)_2]^+}$ (**X**), however, gives **II**, $\mathrm{CpFe(CO)_2[C(SMe)_3]}$ (**XII**), $\mathrm{\overline{CpFe(CO)[C(S}Me)(SMe)_2]}$ (**XIII**) and $\mathrm{[CpFe(CO)(SMe)]_2}$. Small amounts (0.1 equivalent) of NaNp catalyze reactions of **I** and **X** with phosphines to give a mixture of CO- and carbene-substituted products, $\mathrm{CpFe(CO)(L)(=\overline{COCH_2CH_2O})^+}$, $\mathrm{CpFe(CO)_2(L)^+}$, $\mathrm{CpFe(CO)(L)_2^+}$ and $\mathrm{CpFe(CO)(L)[=C(SMe)_2]^+}$ ($\mathrm{L = PMePh_2}$); a mechanism involving radical intermediates is proposed for the reactions. Complex **I** reacts with anions (I^-, Cl^-, MeO^-, NCS^-, $PhCH_2S^-$) to give the ring-opened alkoxycarbonyl complexes $\mathrm{CpFe(CO)_2[C(=O)OCH_2CH_2X]}$. With oxidizing agents such aa Me_3NO, the dioxycarbene ligand in **I** is converted to ethylene carbonate, $\mathrm{O=\overline{COCH_2CH_2O}}$. An X-ray diffraction study of **X** shows the carbene moiety to be planar with the SMe groups in a syn and anti conformation. The plane of the carbene ligand is oriented 'crosswise' with respect to the CO groups.

Introduction

Transition metal carbene complexes are important in reactions leading to carbon–carbon bond formation in organic synthesis [1] and in metal catalyzed reactions such as polymerization of alkenes [2a], olefin cyclopropanation [2b], Fischer–Tropsch synthesis [2c] and olefin metathesis [3]. Consequently, there is a great deal of interest in their reaction chemistry. The $\mathrm{CpFe(CO)_2(carbene)^+}$ complexes (Cp = η^5-C_5H_5) are one such class of compounds which have received considerable attention in the quest to generate stable, isolable and yet reactive carbene complexes [4–28]. These complexes are of two general types: those with at least one heteroatom, e.g., O, S, N or P, directly bonded to the carbene carbon and those without. The latter type, with alkyl, aryl or hydrogen substituents bonded to the carbene carbon, are generally unstable even at low temperatures. As a result they either decompose giving the transition metal olefin complex along with other products [4, 11, 12] or react with unactivated olefins to form cyclopropanes [7–10, 14, 25]. They also readily undergo addition at the carbene carbon with phosphines and other nucleophiles [4, 5, 11, 12].

In contrast, α-heteroatom carbenes tend to be more stable and often may be isolated at ambient temperature [15–17, 20–22, 24]. The stability of these complexes is attributed to the interaction of the carbene carbon with a lone electron pair on the heteroatom. Coupling of the carbene moiety in these systems to give olefinic products [20, 26] and reactions with olefins to give free cyclopropanes [27] are relatively rare. However, these complexes undergo a variety of other reactions as illustrated by eqns. (1) [15–18], (2) [23], (3) [19, 20] and (4) [6, 9b, 13, 28].

Despite the wide range of reactivity which has been observed for the $\mathrm{CpFe(CO)_2(carbene)^+}$ complexes, there are no reports, to our knowledge, of studies involving reducing agents such as Na-amalgam or sodium naphthalenide. We report in this paper the X-ray-determined structure of $\mathrm{\{CpFe(CO)_2[=C(SMe)_2]\}PF_6}$ and its reactions with reducing agents. Reactions of $\mathrm{[CpFe(CO)_2(=COCH_2CH_2O)]PF_6}$ and other α-heteroatom carbenes are also described.

Experimental

General Procedures

All reactions were carried out under an atmosphere of prepurified N_2 at room temperature using standard inert atmosphere [29] and Schlenk [30] techniques unless otherwise stated. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Hexanes, MeCN and CH_2Cl_2 were distilled from CaH_2 under N_2.

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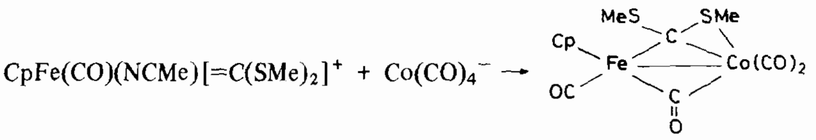
$$CpFe(CO)_2[=C(SMe)_2]^+ \xrightarrow{MeS^-} CpFe(CO)_2[C(SMe)_3]$$

$$\xrightarrow{HNR_2} CpFe(CO)_2[=C(SMe)(NR_2)]^+ + MeSH$$

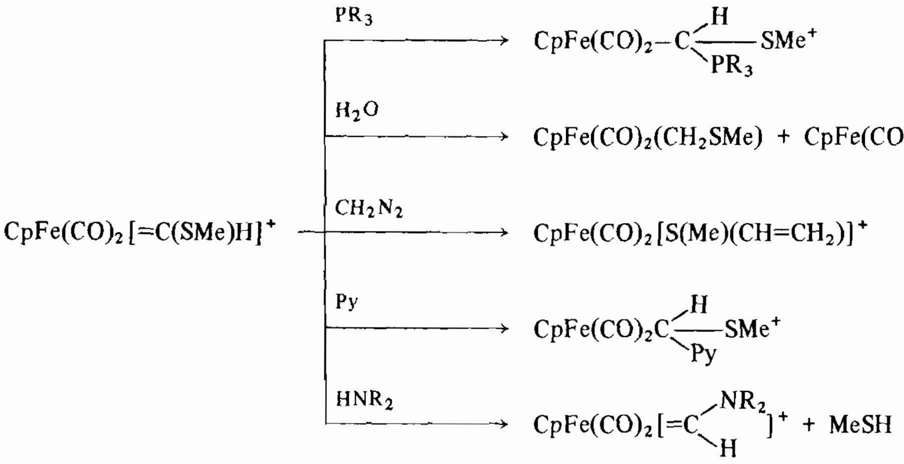
$$\xrightarrow{H_2NMe} CpFe(CO)_2(C{\equiv}N{-}Me)^+ + 2MeSH \qquad (1)$$

$$\xrightarrow{H_2N(CH_2)_nNH_2} CpFe(CO)_2[=\overline{CNH(CH_2)_nNH}]^+ + 2MeSH$$

$$\xrightarrow{H^-} CpFe(CO)_2[C(SMe)_2H]$$



(2)



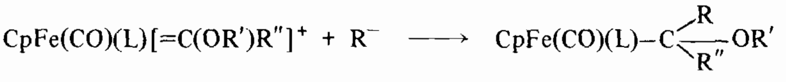
$$CpFe(CO)_2[=C(SMe)H]^+ \xrightarrow{PR_3} CpFe(CO)_2{-}C(H)(PR_3){-}SMe^+$$

$$\xrightarrow{H_2O} CpFe(CO)_2(CH_2SMe) + CpFe(CO)_3^+$$

$$\xrightarrow{CH_2N_2} CpFe(CO)_2[S(Me)(CH{=}CH_2)]^+ \qquad (3)$$

$$\xrightarrow{Py} CpFe(CO)_2C(H)(Py){-}SMe^+$$

$$\xrightarrow{HNR_2} CpFe(CO)_2[=C(NR_2)(H)]^+ + MeSH$$



$$CpFe(CO)(L)[=C(OR')R'']^+ + R^- \longrightarrow CpFe(CO)(L){-}C(R)(R''){-}OR' \qquad (4)$$

$L = CO, PPh_3, P(OPh)_3$

$R^- = H^-, Me^-, Ph^-$; $R' = Me, Et$; $R'' = Me, Et, c\text{-}C_3H_5, CH(Me)_2$.

Solutions of sodium naphthalenide (NaNp) were prepared by stirring 1:1 molar ratios of sodium metal and naphthalene in THF [31]. These solutions were standardized using a standard potassium hydrogenphthalate solution. The $[N(n\text{-}Bu)_4]PF_6$ was prepared by a published procedure [32].

Diphenylmethylphosphine and PMe_2Ph were obtained from Strem Chemicals and used without further purification. Triphenylphosphine was used as received from SCM Chemicals.

Infrared spectra were obtained using either a Perkin-Elmer 281 or 681 spectrophotometer, and spectra were referenced to the 1944.0 cm^{-1} band of polystyrene. The ^1H and ^{13}C NMR data were recorded on a Nicolet NT-300 MHz spectrometer using Me_4Si as the internal reference. The ^{31}P NMR spectra were obtained on a Bruker WM 300 MHz instrument. The ^{31}P signals which are upfield of the H_3PO_4 external reference are given as negative values. Electron impact mass spectra (EIMS) and GC-MS spectra were obtained on a Finnigan 4000. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained using a Kratos MS-50 spectrometer.

Cyclic voltammograms were recorded with a Bioanalytical System CV-1B cyclic voltagraph in a conventional three electrode cell at 25 °C. A stationary platinum disk (3.1 mm^2) was used as the working electrode, and platinum wire served as the auxiliary electrode. The reference electrode was Ag/AgCl (3.0 M NaCl) and measurements were made in MeCN (0.1 M $[N(n\text{-}Bu)_4]PF_6$). All solutions were deoxygenated by purging with argon and kept under an atmosphere of argon throughout the measurements. Photochemical reactions were carried out with a 254 nm light source in a quartz Schlenk tube equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

The complexes $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ (**I**) [21], $[CpFe(CO)(PPh_3)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIb**) [22], $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (**X**) [16], $Cp_2Fe_2(CO)_2(SMe)_2$ (**XI**) [33], $CpFe(CO)_2[C(SMe)_3]$ (**XII**) [18a], $Cp\overline{(CO)Fe[C(S}Me)(SMe)_2]$ (**XIII**) [18b], $[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$ (**XV**) [22] and $\{CpFe(CO)_2[=C(SMe)(NMe_2)]\}PF_6$ (**XVIII**) [15] were prepared according to literature methods. The complexes $[CpFe(CO)_2(PMePh_2)]PF_6$ (**Va**) [34], $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**) [34] and $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) [22] were prepared by using slight modifications (see below) of the syntheses reported for their PPh_3 analogs.

IR spectra of the complexes are given in Table 1.

Preparation of $[CpFe(CO)_2(PMePh_2)]PF_6$ (Va)

To a stirred acetone (30 ml) solution of $[CpFe(CO)_3]PF_6$ (0.71 g, 2.0 mmol), $PMePh_2$ (0.81 g, 4.0 mmol, 0.75 ml) was added. The mixture was stirred for 15 min, then the volume was reduced to ~5.0 ml under reduced pressure. Addition of Et_2O (80 ml) resulted in the precipitation of a yellow–green solid. The solvent was decanted from the residue which was dissolved in a minimum amount of acetone. Crystallization from acetone/Et_2O gave **Va** (0.97 g) in 93% yield. ^1H NMR(CD_3CN): δ 5.34 (d, J_{PH} = 1.6 Hz, Cp), 2.35 (d, J_{PH} = 10.6 Hz, Me), 7.56 (m, Ph). ^{31}P NMR (CD_3CN): δ 49.91.

Preparation of $[CpFe(CO)(PMePh_2)_2]PF_6$ (IV)

Irradiation of a CH_2Cl_2 (35 ml) solution of **Va** (1.1 g, 2.1 mmol) and $PMePh_2$ (1.2 g, 6.0 mmol, 1.1 ml) with 254 nm light for 4 h led to the formation of **IV**. Crystallization in CH_2Cl_2/hexane at −20 °C gave **IV** (0.98 g) in 70% yield. ^1H NMR (CD_3CN): δ 4.88 (t, J_{PH} = 1.6 Hz, Cp), 1.41 (pseudotriplet, J_{PH} = 4.9 Hz, Me), 7.65–7.02 (m, Ph). ^{31}P NMR (CD_3CN): δ 47.34. *Anal.* Calc. for $C_{32}H_{31}F_6FeOP_3$: C, 55.35; H, 4.50. Found: C, 54.97; H, 4.49%.

Preparation of $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (IIIa)

To a cooled (0 °C) suspension of **Va** (0.39 g, 0.75 mmol), NaBr (0.060 g, 0.60 mmol) and $BrCH_2CH_2OH$ (2 ml) was added ethylene oxide (8 ml). The mixture was stirred for 18 h, and the solvent was removed under reduced pressure. The residue was washed with three 10-ml portions of Et_2O and then extracted with CH_2Cl_2. The extract was filtered through anhydrous $MgSO_4$ on a glass frit. The filtrate was concentrated under vacuum, Et_2O was added and solution allowed to stand at −20 °C overnight resulting in the formation of crystals of **IIIa** (0.36 g) in 86% yield. ^1H NMR (CD_3CN): δ 4.98 (d, J_{PH} = 1.7 Hz, Cp), 4.50 m and 4.21 m (OCH_2), 2.20 (d, J_{PH} = 9.9 Hz, Me), 7.27–7.54 (m, Ph). ^{31}P NMR (CD_3CN): δ 55.69. *Anal.* Calc. for $C_{22}H_{22}F_6FeO_3P_2$: C, 46.67; H, 3.92. Found: C, 46.45; H, 3.81%.

Reduction of $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ (I)

To a stirred THF (40 ml) solution of **I** (0.12 g, 0.31 mmol), 0.30 M NaNp (1.0 ml, 0.30 mmol) was added; the pale yellow solution instantly turned red. After stirring for 1 h the reddish solution became purple. The solvent was removed under reduced pressure. The naphthalene was removed by sublimation into a trap under dynamic vacuum at 25 °C. The remaining purple residue was dissolved in Et_2O and chromatographed on a 1 X 6 cm column of alumina (adsorption, 80–200 mesh). Elution with a 1:1 mixture of hexane/Et_2O, followed by evaporation of the solution to dryness gave $[CpFe(CO)_2]_2$ (**II**) in 70% yield. ^1H NMR ($CDCl_3$): δ 4.76 (s, Cp). ^{13}C NMR (CD_2Cl_2): δ 88.80 (Cp), 215.86 (CO). Mass spec.: 354 (M^+). A GC-MS analysis of the gaseous products formed in this reaction gave the following *m/e*: 44 and 28, 27 and 26. (This reaction was carried out under He.) These peaks correspond to carbon dioxide and ethylene, respectively. In an effort to find out if any intermediates were formed enroute to the formation of **II**, the above reaction was repeated using **I** (0.060 g, 0.15 mmol) and 0.24 ml of 0.58 M NaNp in a 100 ml Schlenk flask connected directly to an IR cell by teflon tubing as described by Gladysz *et al.* [35]. By periodically drawing some of the solution from the reaction vessel into the IR cell, the reaction was monitored. The results are described in 'Results and Discussion'.

NaNp-catalyzed Substitution of I

To a THF (20 ml) solution of **I** (0.13 g, 0.33 mmol) and $PMePh_2$ (0.52 g, 2.6 mmol, 0.48 ml), 0.1 equivalent of NaNp (0.11 ml of an 0.34 M solution) was quickly added with stirring. The pale yellow solution immediately became intense yellow. The volume of the solution was quickly reduced to 5 ml under vacuum and hexanes were added with

TABLE 1. Infrared Spectra of Complexes in CH_2Cl_2

Complex	ν(CO) (cm^{-1})
$[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ (**I**)	2070(s), 2024(s)
$Cp_2Fe_2(CO)_4$ (**II**)[a]	2006(m), 1963(s), 1794(s)
$[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**)	1992(s)
$[CpFe(CO)(PPh_3)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIb**)	1994(s)
$[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**)	1968(s, broad)
$[CpFe(CO)_2(PMePh_2)]PF_6$ (**Va**)	2053(s), 2010(s)
$[CpFe(CO)_2(PPh_3)]PF_6$ (**Vb**)	2055(s), 2010(s)
$CpFe(CO)_2[C(=O)OCH_2CH_2Cl]$ (**VIa**)	2037(vs), 1985(vs), 1635(m)
$CpFe(CO)_2(\overline{C(H)OCH_2CH_2O})$ (**VII**)[a]	2026(s), 1970(s)
$O=\overline{COCH_2CH_2O}$ (**VIII**)	1810(s), 1773(m)
$\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (**X**)	2072(s), 2030(s)
$Cp_2Fe_2(CO)_2(SMe)_2$ (**XI**)[a]	1962(s)
$CpFe(CO)_2[C(SMe)_3]$ (**XII**)[a]	2025(s), 2014(m), 1978(s), 1968(m)
$Cp\overline{Fe(CO)[C(S}Me)(SMe)_2]$ (**XIII**)[a]	1949(m), 1938(s)
$\{CpFe(CO)(PMePh_2)[=C(SMe)_2]\}PF_6$ (**XIV**)	1969(s)
$[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$ (**XV**)	2077(s), 2038(s)
$[CpFe(CO)(PMePh_2)(=\overline{CSCH_2CH_2S})]PF_6$ (**XVI**)	1982(s, broad)
$CpFe(CO)_2[\overline{C(SMe)SCH_2CH_2S}]$ (**XVII**)[a]	2030(s), 1976(vs)
$\{CpFe(CO)_2[=C(SMe)(NMe_2)]\}PF_6$ (**XVIII**)	2046(s), 2001(s)
$Cp^*Fe(CO)_2[C(SMe)_3]$ (**XIX**)	2010(s), 1994(w), 1954(vs), 1945(w)
$\{CpRu(CO)_2[=C(SMe)_2]\}PF_6$ (**XX**)	2070(s), 2027(s)
$CpRu(CO)_2[C(SMe)_3]$ (**XXI**)	2040(s), 2032(m), 1984(vs), 1974(ms)
$CpRu(CO)_2[C(SMe)_2(SPh)]$ (**XXII**)[b]	2034(s), 1973(s)
$\{CpRu(CO)(MeCN)[=C(SMe)_2]\}PF_6$ (**XXIII**)[c]	1993(s)

[a] In hexanes solvent. [b] In THF. [c] In CH_3CN.

stirring. This resulted in the precipitation of a yellow solid. The solvent was decanted from the yellow residue which was then washed with two 10-ml portions of Et_2O. The residue was then extracted with CH_2Cl_2 (20 ml) and filtered through anhydrous $MgSO_4$ on a glass frit. After reduction of the filtrate volume to ~4 ml under vacuum, it was layered with 20 ml of Et_2O and stored at −20 °C overnight. After filtering and drying, 0.16 g of a yellow solid was obtained. The ^1H NMR of this solid in CD_3CN indicated that it was composed of $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) and $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**) in 72% and 21% yields, respectively; there was also a trace amount of **Va**. Similar results were obtained using PPh_3 as the phosphine.

*Reaction of **I** with PR_3*

A CH_2Cl_2 (10 ml) solution of **I** (0.050 g, 0.12 mmol) and $PMePh_2$ (0.20 g, 1.0 mmol, 0.19 ml) was stirred for 60 min. The volume of the solvent was reduced to ~2 ml under vacuum, and hexanes (~40 ml) were added with stirring. The solvent was decanted, and the residue was washed with Et_2O and then extracted with CH_2Cl_2. The CH_2Cl_2 solution was filtered through anhydrous $MgSO_4$ on a glass frit. Hexanes were added to precipitate a yellow solid (65 mg). The ^1H NMR spectrum of the solid in CD_3CN indicated the following compounds were present: $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) (73%), $[CpFe(CO)_2(PMePh_2)]PF_6$ (**Va**) (12%) and $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**) (6%). When **I** and $PMePh_2$ were reacted for 18 h, **IV** was isolated as the only product in 85% yield.

The reaction of **I** (0.060 g, 0.15 mmol) and PPh_3 (0.33 g, 1.2 mmol) in CH_2Cl_2 (20 ml) was performed as described above for the analogous $PMePh_2$ reaction. In this case, $[CpFe(CO)_2(PPh_3)]PF_6$ (**Vb**) and $[CpFe(CO)(PPh_3)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIb**) were the only products observed after a 12 h reaction time. No further reaction occurred after 24 h.

*Reaction of $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) and $PMePh_2$*

To a stirred solution of **IIIa** (0.15 g, 0.26 mmol) in CH_2Cl_2 (10 ml) was added $PMePh_2$ (0.050 g, 1.8 mmol, 0.34 ml). After 20 h, the volume of the solvent was reduced to ~5 ml under vacuum, and hexanes (50 ml) were added with stirring. This resulted in the precipitation of a yellow solid. The solvent was decanted from the residue which was then washed with two 10-ml portions of Et_2O. The residue was extracted with two 10-ml portions of CH_2Cl_2 and the extract was filtered through anhydrous $MgSO_4$ on a glass frit. The volume of the CH_2Cl_2 extract was reduced to ~4 ml and then layered with Et_2O (20 ml) and stored at −20 °C overnight. Yellow crystals of **IV** were formed; 0.16 g (87%).

Reaction of I with [PPN] Cl and Other Anions

When a stirred solution of **I** (66 mg, 0.17 mmol) in CH_2Cl_2 (10 ml) was treated with [PPN]Cl (96 mg, 0.17 mmol), the pale yellow solution of **I** instantly became golden. The IR (CH_2Cl_2) spectrum displayed bands at 2037(vs), 1985(vs) and 1635(m) cm^{-1}, suggesting the presence of $CpFe(CO)_2[C(=O)OCH_2CH_2Cl]$ (**VIa**) [^1H NMR (CD_3CN): δ 5.03 (s, Cp), 4.14 (t, $J = 5.6$ Hz, CH_2), 3.64 (t, $J = 5.6$ Hz, CH_2)]. Addition of CF_3SO_3H (15 μl, 0.17 mmol) to this solution resulted in the formation of a pale yellowish powdery suspension. Removal of the solvent under vacuum produced 0.16 g of a yellow solid. ^1H NMR and IR spectra of the solid product showed it to be $[CpFe(CO)_3]CF_3SO_3$ (54 mg, 92%). IR (CH_3CN): 2125(vs), 2073(vs) cm^{-1}. ^1H NMR (CD_3CN): δ 5.77 (s, Cp).

The reaction of **I** (24 mg, 0.060 mmol) and $[N(n\text{-}Bu)_4]I$ (23 mg, 0.060 mmol) in CH_2Cl_2 (10 ml), followed by CF_3SO_3H, yielded very similar results to that of [PPN]Cl. The analogous reactions of **I** with NaOMe (in MeOH), $NaSCH_2Ph$ (in THF) and [PPN]SCN, followed by CF_3SO_3H gave the same types of IR and NMR spectra as observed in the reaction of [PPN]Cl.

Reactions of $[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$ (XV) with NaSMe

To a stirred THF (20 ml) solution of NaSMe prepared by slowly bubbling MeSH through a suspension NaH (50% in mineral oil, 14 mg, 0.29 mmol), **XV** (0.12 g, 0.28 mmol) was added. The mixture was stirred for 15 min, and the solvent was removed under reduced pressure. The residue was extracted with hexane and the extract was filtered through Celite on a glass frit. Removal of solvent *in vacuo* led to the isolation of $CpFe(CO)_2[\overline{C(SMe)SCH_2CH_2S}]$ (**XVII**) as a yellow solid (0.060 g, 65%). Further purification of **XVII** by column chromatography on alumina led to decomposition. Its elemental analysis was not obtained. ^1H NMR (C_6D_6): δ 4.34 (s, Cp), 3.16 (m, SCH_2), 2.81 (m, SCH_2), 2.21 (s, SMe). Mass spec.: 328 (M^+), 300 ($M^+ - CO$), 272 ($M^+ - 2CO$), 151 {$[\overline{C(SMe)SCH_2CH_2S}]$, base peak}, 121 (CpFe). When **XVII** was treated with 1 eq. $HBF_4 \cdot Et_2O$, **XV** was regenerated quantitatively.

Reaction of I with Me_3NO

To a stirred solution of **I** (0.050 g, 0.13 mmol) in CH_2Cl_2 (20 ml), Me_3NO (0.010 g, 0.20 mmol) was added. An instantaneous color change from pale yellow to red was observed. The IR spectrum taken in CH_2Cl_2 showed bands at 2040(m), 1993(m, sh), 1973(s), 1810(s), and 1773(mw) cm^{-1}. The reddish solution slowly decomposed to give a dark brown residue which showed no IR bands in the carbonyl region. The IR of the supernatant showed bands at 1973(s, broad), 1810(s), 1773(mw) cm^{-1}. The ^1H NMR spectrum of the supernatant showed signals at δ 4.78 and 4.52. The IR bands at 1810 and 1773 cm^{-1} and the NMR signal at 4.52 are characteristic of ethylene carbonate (**VIII**). In an attempt to capture $CpFe(CO)_2^+$ as $CpFe(CO)_2I$, $[Bu_4N]I$ (1 equivalent) was quickly added to the reaction mixture after the Me_3NO addition; however, no $CpFe(CO)_2I$ was detected.

When a suspension of iodosobenzene (0.050 g, 0.25 mmol) and **I** (0.020 g, 0.060 mmol) was stirred for 3 days, ethylene carbonate was the only new product identified.

Similarly, the reaction of **I** (0.020 g, 0.040 mmol) and freshly distilled H_2O (10 drops) in CH_2Cl_2 yielded ethylene carbonate in 7 days.

Reduction of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (X)

The reduction of **X** was achieved by the method used in the reduction of **I**. A solution of **X** (0.040 g, 0.10 mmol) in THF (20 ml) was treated with one equivalent of NaNp in THF. An instantaneous color change from greenish-yellow to dark red was observed. The solvent was removed under reduced pressure, and the residue extracted with hexanes. The extract was filtered through Celite on a glass frit, and the solvent was removed under vacuum. The IR, ^1H and ^{13}C NMR and mass spectra of the resulting reduction residue were obtained. Similar reactions were carried out at 60, 0, −30 and −60 °C. Reactions were also performed at 25 °C on solutions containing (0.080 g, 0.19 mmol), (0.12, 0.29 mmol) and (0.20 g, 0.47 mmol) of **X**. Analysis of the spectroscopic data showed that the hexanes extracts of all the reduction reactions consisted of the following compounds: $Cp_2Fe_2(CO)_4$ (**II**). $Cp_2Fe_2(CO)_2(SMe)_2$ (**XI**) {^1H NMR (CD_2Cl_2): δ 4.35 (Cp), 1.27 (SMe). ^{13}C NMR (CD_2Cl_2): δ 216.69 (CO), 81.24 (Cp), 16.51 (SMe). Mass spec.: 392 (M^+)}. $CpFe(CO)_2[C(SMe)_3]$ (**XII**) {^1H NMR (CD_2Cl_2): δ 4.89 (Cp), 2.24 (SMe). ^{13}C NMR (CD_2Cl_2): δ 89.66 (Cp), 19.27 (SMe), 59.72 [$C(SMe)_3$]. Mass spec.: 348 ($M^+ - SMe$), 153 (base peak, $C(SMe)_3$)}, and $Cp\overline{Fe(CO)[C(S}Me)(SMe)_2$ (**XIII**) {^1H NMR (C_6D_6): δ 4.27 (Cp), 2.22 (6H, SMe), 1.38 (3H, SMe). ^{13}C NMR (C_6D_6): δ 216.03 (CO), 79.94 (Cp), 70.67 [$C(SMe)_3$], 21.51 (coordinated SMe), 20.00 (uncoordinated SMe). Mass spec.: 274 (base peak, $M^+ - CO$)}.

NaNp-catalyzed Substitution of X

This reaction was carried out in the same way as the NaNp-catalyzed substitution of **I** described above starting with **X** (0.20 g, 0.47 mmol) and $PMePh_2$ (0.74 g, 3.7 mmol, 0.69 ml). The ^1H NMR spectrum of the yellow, solid product (0.298 g) confirmed the presence of $[CpFe(CO)(PMePh_2)_2]PF_6$, $[CpFe(CO)_2(PMePh_2)]PF_6$ and $\{CpFe(CO)(PMePh_2)[=C(SMe)_2]\}PF_6$ (**XIV**) in 32%, 48% and 18% yields, respectively. ^1H NMR (CD_3CN) for **XIV**: δ 5.10 (d, J_{PH} = 1.5 Hz, Cp), 2.81 (s, SMe), 2.26 (d, J_{PH} = 9.6 Hz, Me), 7.44–7.23 (m, Ph). This ^1H NMR spectrum is very similar to that of $\{CpFe(CO)(PPh_3)[=C(SMe)_2]\}PF_6$ [15b].

Reaction of X with $PMePh_2$

To a stirred solution of **X** (0.030 g, 0.080 mmol) in CH_2Cl_2 (10 ml), $PMePh_2$ (0.12 g, 0.60 mmol, 0.11 ml) was added. After stirring for 2 h, the solvent was reduced to ~2 ml under vacuum and hexanes (~40 ml) were added with stirring. The solvent was decanted off, and the residue was crystallized from CH_2Cl_2/hexane to give 0.040 g of a brownish-yellow solid. The ^1H NMR spectrum indicated the presence of the following compounds: $[CpFe(CO)(PMePh_2)_2]PF_6$ (64%), $[CpFe(CO)_2(PMePh_2)]PF_6$ (13%), and $\{CpFe(CO)(PMePh_2)[=C(SMe)_2]\}PF_6$ (3.8%).

Reaction of $[CpFe(CO)_2(=\overline{CSCH_2CH_2S})]PF_6$ *(XV) with* $PMePh_2$

A CH_2Cl_2 (10 ml) solution of **XV** (0.030 g, 0.070 mmol) and $PMePh_2$ (0.11 g, 0.54 mmol, 0.10 ml) was stirred for 15 min. The solvent was removed under reduced pressure, and the residue was washed several times with Et_2O. The residue was extracted with CH_2Cl_2 and filtered through anhydrous $MgSO_4$ on a glass frit. The product in the filtrate was crystallized from CH_2Cl_2/hexane affording 0.35 g of $[CpFe(CO)(PMePh_2)(=\overline{CSCH_2CH_2S})]PF_6$ (**XVI**) (85%). ^1H NMR (CD_2Cl_2): δ 5.05 (d, J_{PH} = 1.7 Hz, Cp), 3.72 m and 3.36 m (SCH_2), 2.23 (d, J_{PH} = 10.9 Hz, Me), 7.56–7.25 (m, Ph). Trace amounts of **IV** and **Va** were also produced in this reaction and were not separated from **XVI**.

Preparation of $Cp^*Fe(CO)_2[C(SMe)_3]$ *(XIX)*

Compound **XIX** was prepared as described for **XII** [18a] starting with 0.026 g (0.62 mmol) of 57% NaH in mineral oil and 0.13 g (0.26 mmol) of $\{Cp^*Fe(CO)_2[=C(SMe)_2]\}PF_6$ [18c] in THF (40 ml). The THF was removed under reduced pressure after stirring for 2 h and the residue extracted with hexanes. Compound **XIX** was isolated from the hexanes solution upon removal of the solvent as yellow platelets (0.097 g, 92%). ^1H NMR (C_6D_6): δ 1.53 (15H, C_5Me_5), 2.20 (9H, SMe). ^{13}C NMR (C_6D_6): δ 96.73 (C_5Me_5), 218.40 (CO), 58.89 [$C(SMe)_3$], 18.68 (SMe), 9.26 (C_5Me_5). Mass spec.: 400 (M^+), 372 (M^+ – CO), 353 (M^+ – SMe), 344 (M^+ – 2CO), 153 {base peak, $[C(SMe)_3]$}. *Anal.* Calc. for $C_{16}H_{22}FeO_2S_3$: C, 48.02; H, 6.04. Found: C, 48.11; H, 6.20%.

Synthesis of $\{CpRu(CO)_2[=C(SMe)_2]\}PF_6$ *(XX)*

To a stirred solution of $CpRu(CO)_2[C(S)SMe]$ [23c] (0.85 g) in CH_2Cl_2 (20 ml) cooled to 0 °C, CH_3SO_3F (0.24 ml) was added. Stirring was continued for 1 h after which KPF_6 (~2.0 g) was added and the mixture stirred for an additional 30 min. The mixture was treated with excess hexanes to precipitate products. The solvent was removed and the residue was then washed with three 20-ml portions of Et_2O. The residue was extracted with CH_2Cl_2 (20 ml) and filtered through Celite on a glass frit. The extract was layered with hexanes and stored at –20 °C for 3 days. **XX** (0.092 g, 72%) was obtained as a yellow crystalline solid. ^1H NMR (CD_2Cl_2): δ 5.64 (Cp), 3.08 (6H, SMe). ^{13}C NMR (CD_2Cl_2): δ 89.95 (Cp), 194.62 (CO), 283.39 [$C(SMe)_2$], 30.79 (SMe). *Anal.* Calc. for $C_{10}H_{11}F_6O_2PS_2Ru$: C, 25.37; H, 2.34; S, 13.55. Found: C, 25.58; H, 2.57; S, 13.70%.

Reduction of $\{CpRu(CO)_2[=C(SMe)_2]\}PF_6$

Sodium naphthalenide (0.18 ml of 0.34 M solution, 0.060 mmol) was added to a stirred THF (10 ml) solution of $\{CpRu(CO)_2[=C(SMe)_2]\}PF_6$ (0.030 g, 0.060 mmol). The color of the solution changed instantly from gold to red. The mixture was allowed to stir for 30 min and the solvent removed *in vacuo*. The residue was first extracted with hexanes and then with Et_2O. The hexane extract contained $CpRu(CO)_2[C(SMe)_3]$ (**XXI**), {^1H NMR (C_6D_6): δ 4.64 (Cp), 2.18 (9H, SMe). ^{13}C NMR (C_6D_6): δ 92.16 (Cp), 200.82 (CO), 53.56 [$C(SMe)_3$], 19.10 (SMe). Mass spec.: 376 (M^+), 361 (M^+ – Me), 348 (M^+ – CO), 320 (M^+ – 2CO), 153 [(base peak), $C(SMe)_3$]} and $[CpRu(CO)(SMe)]_2$ [36a] {Mass spec.: 483 (M^+), 468 (M^+ – Me), 456 (M^+ – CO), 428 (M^+ – 2CO)}. The Et_2O extract was mainly $[CpRu(CO)_2]_2$ [36b] {Mass spec.: 446 (M^+), 390 (M^+ – 2CO), 362 (M^+ – 3CO), 334 (M^+ – 4CO), 223 [$CpRu(CO)_2$, ($\frac{1}{2}M^+$)], 195 ($\frac{1}{2}M^+$ – CO), 167 ($\frac{1}{2}M^+$ – 2CO)}.

Preparation of $CpRu(CO)_2[C(SMe)_3]$ *(XXI)*

Sodium hydride (0.026 g, 0.62 mmol), 57% in mineral oil, was washed with three 10-ml portions of hexanes and dried *in vacuo*. It was then dissolved in THF (40 ml) and MeSH slowly bubbled through the solution until H_2 evolution ceased [18a]. To this stirred solution, **XX** (0.21 g, 0.44 mmol) was added. The solvent was removed *in vacuo* after stirring for 30 min, and the residue was extracted with Et_2O and filtered through Celite on a glass frit. Removal of solvent led to the isolation of **XXI** (0.14 g, 84%) as a light yellow powder. *Anal.* Calc. for $C_{11}H_{14}O_2S_3Ru$: C, 35.18; H, 3.76; S, 25.62. Found: C, 35.12; H, 3.61; S, 25.36%.

Preparation of $CpRu(CO)_2[C(SMe)_2(SPh)]$ (XXII)

Sodium hydride (0.014 g, 0.26 mmol), 57% in mineral oil, was placed in a 100 ml Schlenk flask and washed with three 10-ml portions of hexanes. The residue was dried *in vacuo* and dissolved in THF (40 ml). To this stirred solution was added PhSH (25 μl, 0.24 mmol). **XX** (0.097 g, 0.20 mmol) was added after 30 min and stirring continued for 15 min. The solvent was removed *in vacuo* and the residue extracted with Et_2O; the extract was filtered through Celite on a glass frit. Hexanes were added to the extract and the mixture concentrated and stored at −20 °C for 3 days. Tiny yellow needle-like crystals of **XXII** (0.050 g, 60%) were isolated. ^1H NMR $[(CD_3)_2CO]$: δ 5.50 (Cp), 1.84 (6H, SMe), 7.31 (m, 5H, SPh). ^{13}C NMR (CD_2Cl_2): δ 91.72 (Cp), 200.52 (CO), 57.49 [*C*(SMe)$_2$(SPh)], 19.00 (SMe), 138.36, 136.77, 134.76 (SPh). Mass spec.: 438 (M^+), 423 (M^+ − Me), 215 [C(SMe)$_2$(SPh)]. *Anal.* Calc. for $C_{16}H_{16}O_2S_3Ru$: C, 43.92; H, 3.69; S, 21.98. Found: C, 43.52; H, 3.72; S, 22.02%.

Synthesis of $\{CpRu(CO)(MeCN)[=C(SMe)_2]\}PF_6$ (XXIII)

Compound **XXIII** was prepared by irradiation of **XX** (0.11 g, 0.24 mmol) in MeCN (30 ml) for 2 h. The solvent was removed *in vacuo* and the residue washed with several portions of Et_2O. The residue was then extracted with CH_2Cl_2 (25 ml) and filtered through Celite on a glass frit. The extract was reduced in volume to ~10 ml *in vacuo*, layered with hexanes and stored at −20 °C. **XXIII** (0.083 g, 81%) was isolated as a red crystalline solid. ^1H NMR (CD_3CN): δ 5.24 (Cp), 3.02 (6H, SMe), 2.34 (3H, MeCN). *Anal.* Calc. for $C_{11}H_{14}F_6NOPS_2Ru$: C, 27.16; H, 2.90. Found: C, 27.25; H, 2.86%.

Structure Determination

A single crystal with approximate dimensions of 0.20 × 0.10 × 0.05 mm was mounted on a glass fiber and subsequently placed on a goniometer head. Ten reflections ($10.5 < 2\theta < 34°$) were centered on a SYNTEX P2$_1$ four-circle diffractometer and indexed using an automatic indexing program (BLIND) [37]; the results indicated a centered monoclinic space group. A total of 6119 reflections (2 octants of data) were collected using an ω-step scan technique within a 2θ sphere of 50° and corrected for Lorentz–polarization effects. Since the absorption coefficient was comparatively low, an absorption correction was not applied. Independent reflections (760) with $I \geqslant 3\sigma(I)$ were retained for use in subsequent calculations. The estimated variance in each intensity was calculated by $\sigma(I)^2 = C_T + C_B + (0.03\, C_T)^2 + (0.03\, C_B)^2$, where C_T and C_B represent the total background counts, respectively, and the factor 0.03 is an estimate of non-statistical errors.

The position of the iron atom in the unit cell was obtained from an analysis of the Patterson map. The remaining non-hydrogen atoms were located from successive structure factor and electron density map calculations. The crystal data and atomic and thermal parameters for the non-hydrogen atoms are given in Tables 2 and 3, respectively. The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by a combination of block matrix/full matrix least-squares calculations [38]. The positional parameters of the hydrogen atoms were calculated and included but were not varied during the refinement; they were all given a fixed isotropic temperature factor of 6.0 Å^2. The conventional residual index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.080; the function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. The PF_6^- was found to be disordered and undoubtedly contributed to the somewhat higher residual index, and the smaller number of observed reflections than expected, and relatively large errors in the distances and angles.

Results and Discussion

Structure of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (X)

A perspective view of **X** showing the numbering scheme and thermal elipsoids is given in Fig. 1. The positional parameters, and selected angles and distances are listed in Tables 3 and 4, respectively.

TABLE 2. Crystal Data for $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (X)

Compound	$\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$
Formula	$C_{10}H_{11}F_6FeO_2PS_2$
Formula weight	428.15
Crystal system	monoclinic
Space group	*C*2/*c*
a (Å)	32.91(1)
b (Å)	6.790(3)
c (Å)	14.509(4)
β (°)	105.48(3)
V (Å^3)	3124(2)
Z	8
μ(Mo Kα) (cm^{-1})	13.83
ρ (calc.) (g/cm^3)	1.82
Temperature (°C)	20
Diffractometer	SYNTEX P2$_1$
Monochromator	oriented graphite
Radiation	Mo Kα (λ = 0.71069 Å)
Reflections measured	hkl, $hk\bar{l}$ (6119 reflections)
Scan type	ω-step scan
Independent reflections observed ($I > 3\sigma I$)	760
Min, max, 2θ (°)	0°, 50°
Max. no. parameters refined	115
R (conventional)	0.080
R_w	0.084

TABLE 3. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Thermal Parameters[a] ($A^2 \times 10^3$) for $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (**X**)

Atom	x	y	z	$\bar{u}$
Fe	6071(1)	644(6)	373(3)	32
S68	6832(2)	−1052(10)	1880(5)	37
S67	6762(2)	−2665(12)	43(5)	45
O9	6455(6)	3868(30)	1614(14)	77
O10	6256(6)	2508(33)	−1285(13)	70
C1	5473(10)	−29(61)	−459(22)	76
C2	5446(8)	1400(51)	182(39)	115
C3	5600(8)	662(69)	1104(24)	80
C4	5728(8)	−1252(50)	1006(28)	76
C5	5666(10)	−1770(54)	616(35)	108
C6	6585(5)	−1102(33)	713(15)	20
C7	6466(9)	−2430(43)	−1181(16)	51
C8	7271(8)	−2681(45)	2019(16)	47
C9	6318(10)	2521(48)	1116(23)	69
C10	6195(8)	1717(39)	−635(23)	47
P4[b]	2500	2500	5000	37
P5[c]	5000	−5035(18)	−2500	59
F41	2306(4)	768(25)	4290(9)	55
F42	2749(5)	938(24)	5753(11)	63
F43	2106(4)	2338(28)	5451(11)	64
F51[c]	5000	−2652(49)	−2500	114
F52[c]	5000	−7418(50)	−2500	114
F53	4564(6)	−5021(29)	−2905(13)	114
F54	4955(6)	−5015(30)	−1443(14)	114

[a] $\bar{u} = \frac{1}{3}\Sigma U_{ii} \times 10^3$ where the temperature factors are defined as $\exp(-2\pi^2\Sigma h_i h_j a_i^* a_j^* U_{ij})$. [b] Occupies special position d in the space group $C2/c$ with atomic multiplicity of 0.50. [c] Occupies special position e with atomic multiplicity of 0.50.

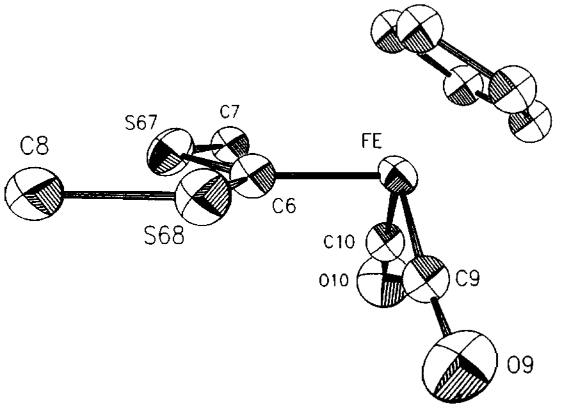


Fig. 1. ORTEP diagram of $CpFe(CO)_2[=C(SMe)_2]^+$ (**X**) showing the orientation of the carbene ligand.

TABLE 4. Selected Bond Distances (A) and Angles (°) for $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (**X**)

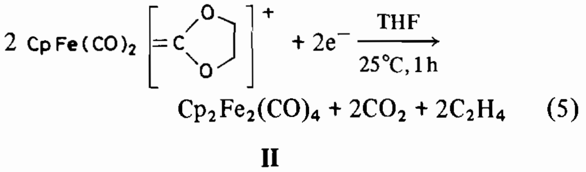
Fe–C1	2.07(3)	C6–Fe–C9	93(1)
Fe–C2	2.07(3)	C6–Fe–C10	94.7(9)
Fe–C3	2.10(3)	C9–Fe–C10	92(1)
Fe–C4	2.08(3)	C6–S68–C8	105(1)
Fe–C5	2.08(4)	C6–S67–C7	110(1)
Fe–C6	2.02(2)	Fe–C6–S68	113(1)
Fe–C9	1.73(3)	Fe–C6–S67	130(1)
Fe–C10	1.78(3)	S68–C6–S67	117(1)
S67–C6	1.65(2)	Fe–C9–O9	175(2)
S68–C6	1.67(2)	Fe–C9–O10	176(2)
S67–C7	1.79(2)		
S68–C8	1.78(3)		
C9–O9	1.18(4)		
C10–O10	1.15(4)		

The iron in **X** is in a slightly distorted octahedral geometry with the cyclopentadienyl ring occupying one face. The L–Fe–L angles 94.7°, 92.1°, and 93.1° for the carbene and two CO ligands are similar to those found in $[CpFe(CO)_2(CS)]PF_6$ [39], $CpFe(CO)_2[C(PPh_3)(=CHPh)]BF_4$ [40] and $CpFe(CO)_2[=\overline{CC(CH_3)S(O)OC}H_2]$ [41] which also have the piano stool geometry. The Fe–C(carbene) bond distance 2.02(2) Å is somewhat longer than Fe=C bond lengths (1.91–2.00 Å) in other Fe–carbene complexes such as $\{CpFe(CO)_2[=C(H)(SPh)]\}PF_6$ [42b], $\{CpFe(CO)_2[=C(Me)(SMe)]\}PF_6$ [42b], $[CpFe(CO)_2(C_7H_6)]PF_6$ [42c] and $[CpFe(CO)_2(C_{11}H_{18})]PF_6$ [42c] but shorter than typical Fe–C(sp^3) bonds (2.08–2.10 Å) [42]. This suggests relatively weak π-bonding between Fe and the carbene carbon; on the other hand, there is significant π-bonding between the carbene carbon and the sulfur atoms. This is evident from the C6–S67 and C6–S68 distances (1.65 and 1.67 Å, respectively), which are much shorter than known S–C(alkyl) distances (range: 1.80–1.84) [42], and the S67–C7 and S68–C8 distances (1.79 Å) in **X**. Pi-bonding between the carbene carbon and the sulfur atoms was previously proposed based on the inequivalence of the methyl groups (C7 and C8) in the carbene ligand in ^1H and ^{13}C NMR spectra of the complex [15]. The ambient temperature solution ^1H NMR spectrum of **X** shows a single line for the two methyl groups; however, on cooling to −55 °C two sharp singlets are observed. The two singlets coalesce upon warming at −2.5 °C [15]. In other thiocarbene complexes such as $\{PtCl[=C(SEt)_2](PPh_3)_2\}$, $\{PtI[=C(SMe)_2](PPh_3)_2\}I$ and $\{PtI[=C(SEt)_2](PPh_3)_2\}I$ [43], NMR studies also indicate the presence of syn and anti R groups, as in **X**. The dithiomethyl carbene ligand in **X** is essentially planar with the plane of the carbene moiety 90° (Fig. 1) from that predicted by frontier orbital arguments for the simplest carbene ($:CH_2$) [44] and observed in $Cp_2Ta(CH_3)(=CH_2)$ and $Cp_2Ta(CH_2Ph)[=C(H)Ph]$ [45a, b], $CpMn(CO)_2[=C(F)Ph]$ [45c], $CpFe(CO)_2[=C(H)Ph]^+$ [7, 9] and $CpFe(CO)_2[=C(H)SPh]^+$ [42b]. Similar deviations from the so-called 'upright' orientation for the carbene moiety have been observed in CpM-

$(CO)_2$(carbene) (M = Mn, Re) [46] and other CpFe$(CO)_2$(carbene)$^+$ complexes [42b, c]. The 'crosswise' or 'orthogonal' conformation of the carbene moiety in $CpFe(CO)_2[=C(Me)SMe]^+$ [42b] was rationalized on the basis of nonbonded interactions between the Cp ligand and either of the two substituents on the carbene center. The long Fe–C6 distance in **X** suggests Fe-to-carbene pi bonding is relatively weak, and it is likely that steric or possibly crystal packing forces determine the orientation of the carbene ligand.

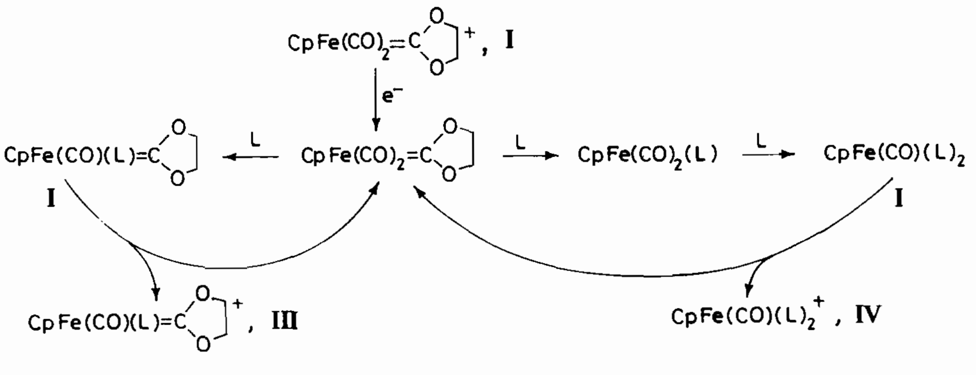
Reactions of $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ *(I)*

Reducing agents such as sodium amalgam and sodium naphthalenide react immediately with **I** to give **II** (70%), CO_2 and ethylene (eqn. (5)). The formation of **II** was established by comparing its infrared and ^{1}H NMR spectra with those of the authentic compound. The presence of CO_2 and ethylene was established by GC-MS. It is apparent from reactions monitored by IR spectroscopy at 25 and 0 °C that the reduction leading to the formation of the products indicated in eqn. (5) goes through some intermediate(s), the exact nature of which is (are) not known. They appear to be fairly long-lived as evident from the IR bands observed at 2035(ms), 2008(ms), 1975(s) and 1950(s) cm^{-1} which appear within the first minute of reaction and gradually diminish over a period of 60 min as bands corresponding to the final product **II** appear. An examination of the NaNp reduction product within 5 min after reduction at 4 K showed it to be ESR silent. The non-existence of a long-lived odd electron product is further supported by the CV of **I**, which show an irreversible reduction wave. Though **II** is obtained in good yield, it is clear from its CV that it is not the initial product of the reduction. Also, coupling of the cyclic dioxocarbene unit to give the alkoxyolefin, $\overline{OCH_2CH_2OC}{=}\overline{COCH_2CH_2O}$, similar to what has been observed by Bianchini and coworkers [26] in the formation of tetrathiafulvalene from a cyclic dithiocarbene, does not occur presumably because the fragmentation of the cyclic dioxycarbene intermediate to give CO_2 and ethylene is faster [47]. Work done by Borden *et al.* [48] suggests that the fragmentation of the cyclic dioxocarbene to CO_2 and ethylene proceeds via a diradical intermediate.

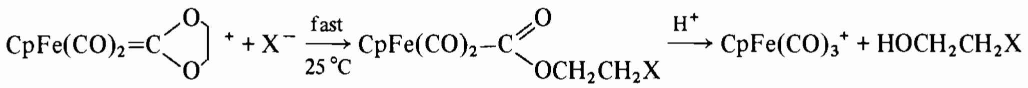


$$2\,CpFe(CO)_2\left[=\overline{COCH_2CH_2O}\right]^+ + 2e^- \xrightarrow[25^\circ C,\,1h]{THF} \underset{\textbf{II}}{Cp_2Fe_2(CO)_4} + 2CO_2 + 2C_2H_4 \quad (5)$$

If **I** is only partially reduced using 0.1 equivalent of NaNp in the presence of PPh_3 and $PMePh_2$, [CpFe(CO)(L)(=$\overline{COCH_2CH_2O}$)]PF_6 (72%), [CpFe(CO)(L)$_2$]PF_6 (21%) and trace amounts of [CpFe$(CO)_2$(L)]PF_6 (L = $PMePh_2$) are formed instantaneously. The reactions presumably proceed by an electron-catalyzed process (Scheme 1). Carbene metal radical complexes such as $Fe(CO)_3[=\overline{CN(Me)CH_2CH_2N(Me)}]_2^{+\cdot}$ [49a], $(CO)_5Cr{-}C(OMe)Ph$ [49b] and $Cr(CO)_4[=\overline{CN(Et)CH_2CH_2N(Et)}]_2^{+\cdot}$ [49c] have been reported in the literature. It is, therefore, reasonable to postulate a radical intermediate in the reaction described in Scheme 1. Reductive CO substitution reactions of this kind have been reported both in cases where the radical intermediate is unstable and where it is stable enough to be characterized spectroscopically [50, 51]. It is presumed, in view of what is known from the reduction of **I**, that the cyclic dioxo-carbene liberated in the formation of **IV** decomposes to CO_2 and ethylene. The proposed scheme is supported by the reaction of CpFe$(CO)_2$($PMePh_2$)$^+$ (**Va**) with $PMePh_2$ in the presence of catalytic quantities of NaNp (0.1 eq.), which leads to the substitution of an additional phosphine in **Va** to give **IV**. Further support for Scheme 1 is provided by the reactions of **III** and **IV** with $PMePh_2$ in the presence of NaNp (0.1 eq.) which do not lead to further substituted products.



Scheme 1.



I **VI**

(6)

$X^- = I^-, Cl^-, MeO^-, NCS^-, PhCH_2S^-$

Reaction of **I** with various anions (eqn. (6)) leads to the formation of an ester as a result of the opening of the carbene ring via an attack at one of the methylene carbons. These esters, which have only been characterized by IR and ^1H NMR spectroscopy, are unstable and readily decompose in solution to give $[CpFe(CO)_2]_2$ (**II**) [52]. However, if the ester formed (eqn. (6)) is immediately treated with CF_3SO_3H, $CpFe(CO)_3^+$ is isolated in 92% yield (X = Cl) [53]. Unlike **I**, $\{CpFe(CO)_2[=\overline{CSCH_2CH_2S}]\}PF_6$ (**XV**) does not react with (PPN)I in CH_2Cl_2 at 25 °C but does react with NaSMe to give $CpFe(CO)_2[\overline{C(SMe)SCH_2CH_2S}]$. In the presence of hydrides such as $LiAlH_4$ and $Li[Al(t\text{-}BuO)_3H]$, **XV** slowly decomposes whereas **I** reacts to give a mixture of unstable products, probably $CpFe(CO)_2[\overline{C(H)OCH_2CH_2O}]$ (**VII**) and $CpFe(CO)_2C(O)CH_2CH_3$.

With Me_3NO, **I** reacts instantaneously to give ethylene carbonate $O{=}\overline{COCH_2CH_2O}$ (**VIII**) and unidentified organometallic compounds. Iodosobenzene (C_6H_5IO) undergoes a similar reaction to give **VIII**; however, this reaction is very slow and no evidence for a carbonyl containing organometallic product was seen. Ethylene carbonate is also generated by the reaction of **I** and H_2O at an extremely slow rate.

The reaction of **I** with phosphines at ambient temperature results in the formation of $[CpFe(CO)(L)(=\overline{COCH_2CH_2O})]PF_6$ (73%), $[CpFe(CO)_2(L)]PF_6$ (12%) and $[CpFe(CO)(L)_2]PF_6$ (6%) in 1 h (L = $PMePh_2$), at a much slower rate than the NaNp-catalyzed reaction (Scheme 1). A complete conversion of **IIIa** to **IV** is observed in 24 h. With PPh_3, $[CpFe(CO)(L)(\overline{OCH_2CH_2O})]PF_6$ and $[CpFe(CO)_2(L)]PF_6$ are the only products formed from **I**, and no further reaction is observed in 24 h. A GC-MS analysis of the vapor phase of the reaction of **IIIa** and $PMePh_2$ showed it to contain CO_2, CO and ethylene. Though reactions monitored by ^1H NMR and ^{31}P NMR indicate the presence of some intermediates, it has not been possible to elucidate the reaction path.

Reactions of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ *(X)*

$$\underset{\textbf{X}}{CpFe(CO)_2[=C(SMe)_2]^+} + e^- \longrightarrow$$

$$\underset{\textbf{II}}{Cp_2Fe_2(CO)_4} + \underset{\textbf{XI}}{Cp_2Fe_2(CO)_2(SMe)_2}$$

$$+ \underset{\textbf{XII}}{CpFe(CO)_2[C(SMe)_3]} + \underset{\textbf{XIII}}{Cp\overline{Fe(CO)[C(S}Me)(SMe)_2]} \qquad (7)$$

In contrast to the reduction of **I**, the instantaneous reaction of $CpFe(CO)_2[=C(SMe)_2]^+$ with sodium naphthalenide leads to the formation of **II** (19%), **XI** (5%), **XII** (37%) and **XIII** (39%) with some decomposition to insoluble materials. Compounds **II**, **XI**, **XII** and **XIII** have been reported previously [18, 34, 54] and were identified here by their IR, MS and NMR spectra. Although no spectroscopic evidence exists for the radical '$CpFe(CO)_2[=C(SMe)_2]$' as the initial product in the reduction (eqn. (7)), its intermediacy can be used to explain the formation of the observed reduction products. The $Cp_2Fe_2(CO)_4$ probably results from the direct decomposition of the radical intermediate with loss of the carbene[:$C(SMe)_2$]. The formation of **XII** may occur by MeS· transfer from one '$CpFe(CO)_2[=C(SMe)_2]$' radical to another because it is the favored product when high concentrations of **X** ($\geqslant 2.4 \times 10^{-2}$ M) and lower temperatures ($\leqslant 0$ °C) are used. Fast addition of NaNp tends to favor the formation of **XIII** probably because it leads to a high concentration of '$CpFe(CO)_2[=C(SMe)_2]$' in which a CO is readily displaced by THF. Reaction of this THF adduct with MeS· present in solution apparently results in the formation of **XIII**. This postulate is supported by the reduction of $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ with NaNp in the presence of MeSSMe which leads to the formation of **XIII** in 70% yield. While it may be argued that the NaNp reacts with MeSSMe to generate MeS^- which reacts with $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ to yield **XIII**, it is important to note that the reaction of NaSMe and $\{CpFe(CO)(MeCN)[=C(SMe)_2]\}PF_6$ gives **XIII** in only 30% yield [18b], which suggests the MeSSMe reaction proceeds predominately through a reduced MeCN complex.

In contrast to the complex reduction of **X** in eqn. (7), a 0.1 eq. of NaNp instantly catalyzes the reaction of **X** with $PMePh_2$ to form the phosphine substitution products $CpFe(CO)(PMePh_2)[=C(SMe)_2]^+$ (**XIV**, 17.8%), $[CpFe(CO)_2(PMePh_2)]^+$ (**Va**, 32.3%) and $[CpFe(CO)(PMePh_2)_2]PF_6$ (**IV**, 48.5%). The NaNp-catalyzed reaction can be envisaged as occurring via radical intermediates similar to those proposed for phosphine substitution in **I** (Scheme 1). However, the major product in the NaNp-catalyzed phosphine substitution in **I** is $[CpFe(CO)(PMePh_2)(=\overline{COCH_2CH_2O})]PF_6$ (**IIIa**) whereas **IV** and **Va** are the major products in **X**. The reaction of **X** with $PMePh_2$ in the absence of NaNp at 25 °C takes nearly 2 h resulting in the following product distribution: **XIV** (3.8%), **Va** (13%) and **IV** (64%).

Reactions of Other $CpFe(CO)_2(carbene)^+$ and $CpRu(CO)_2(carbene)^+$ Complexes

Reduction of $\{CpFe(CO)_2[=\overline{CSCH_2CH_2S}]\}PF_6$ (**XV**) with NaNp in THF leads predominately to decomposition with formation of a small quantity of **II** and other unidentified products; this compares with the 70% yield of **II** obtained in the reduction of **I** (eqn. (5)). The reaction of **XV** with $PMePh_2$ at 25 °C over a period of 15 min, leads to the formation of $\{CpFe(CO)(PMePh_2)[=\overline{CSCH_2CH_2S}]\}PF_6$ (**XVI**) in 85% yield.

The $\{CpFe(CO)_2[=C(SMe)(NMe_2)\}PF_6$ complex does not react with $PMePh_2$ at 25 °C; in the presence of NaNp, it slowly decomposes with the formation of a small quantity of **II** and other unidentified compounds.

Reaction of $\{Cp^*Fe(CO)_2[=C(SMe)_2]\}PF_6$ with NaSMe at 25 °C leads to the formation of $Cp^*Fe(CO)_2[C(SMe)_3]$ (**XIX**). Compound **XIX** has IR and NMR properties similar to those of $CpFe(CO)_2[C(SMe)_3]$ [18a].

Reduction of $\{CpRu(CO)_2[=C(SMe)_2]\}PF_6$ (**XX**) with NaNp in THF occurs instantly to give $[CpRu(CO)_2]_2$, $[CpRu(CO)(SMe)]_2$ and $CpRu(CO)_2[C(SMe)_3]$. There is no evidence for the formation of $Cp(CO)\overline{Ru[C(S}Me)(SMe)_2]$ in this reaction. Compound **XX** also reacts with NaSMe and NaSPh to give $CpRu(CO)_2[C(SMe)_3]$ and $CpRu(CO)_2[C(SMe)_2(SPh)]$, respectively.

Conclusions

The α-heteroatom carbenes **I**, **X**, **XV**, **XX** examined in this paper are all readily reduced by NaNp to give unstable primary products which undergo rapid decomposition. The $[CpFe(CO)_2(=\overline{COCH_2CH_2O})]PF_6$ (**I**) product decomposes cleanly to give **II**, CO_2 and ethylene. In contrast, its sulfur analog, **XV**, yields mainly insoluble sulfides and only small quantities of **II**, but no CS_2. The reduction of $\{CpFe(CO)_2[=C(SMe)_2]\}PF_6$ (**X**) gives a mixture of products: **XI**, **XII**, **XIII** and **II**. Both **I** and **X** undergo phosphine substitution which is catalyzed by NaNp.

Supplementary Material

Listings of structure factors, hydrogen atom positions, and bond distances and angles for the Cp and PF_6^- groups (8 pages) are available from the authors on request.

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