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Synthesis of Cyclopentadienyldicarbonyl(dithiocarbene)iron Cations and Their Reactions with Amines

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Dithiocarbene complexes, $Cp(CO)_2Fe[C(SR)SR']^+$, are easily prepared by $R'SO_3F$ alkylation of the dithioester ligand of $Cp(CO)_2FeC(=S)SR$. The dimethyl derivative, $Cp(CO)_2Fe[C(SCH_3)_2]^+$, shows unusual reactivity toward nucleophilic amines to provide a variety of $Cp(CO)_2FeL^+$ derivatives. Primary amines produce isocyanide complexes, $Cp(CO)_2Fe(CNR)^+$; secondary amines give amino–thiocarbene complexes, $Cp(CO)_2Fe[C(NR_2)SCH_3]^+$; diamines, amino alcohols, and amino thiols yield complexes with cyclic carbene ligands, $Cp(CO)_2Fe[CY(CH_2)_nNR']^+$, where Y = NH, O, or S. The novel orthothioformate complex $Cp(CO)_2Fe[C(SCH_3)_3]$ is formed as a byproduct in some of the reactions. Spectral properties of the new complexes are discussed.

Introduction

Transition-metal carbene complexes have become a well-known class of organometallic compounds.[1-4] Only recently, however, have complexes with dithiocarbene ligands, M–C(SR)$_2$, been isolated. Such complexes have been reported for iron,[5] chromium,[6-8] tungsten,[7,8] osmium,[9] and platinum.[10,11] One route used to prepare dithiocarbene complexes has been alkylation of the thione sulfur atom in dithioester complexes, M–C(=S)SR, by CH_3SO_3F or $[Et_3O]BF_4$.[10] In the present paper, we extend this route to the preparation of $Cp(CO)_2Fe–C(SR)_2^+$ ($Cp = \eta^5$-C_5H_5) starting with the iron dithioester complexes $Cp(CO)_2Fe–C(=S)SR$ (R = CH_3,[12] $CH_2C_6H_5$).

Since there are no reports describing reactions of the dithiocarbene ligand itself, it was of interest to examine its reactions for the purpose of preparing novel ligands, as well as establishing general patterns of reactivity of this ligand.

Results and Discussion

Preparation and Characterization of $Cp(CO)_2Fe[C(SR)SR']^+$ Carbene Complexes. Iron dithioester complexes are readily available through the reaction of $Cp(CO)_2Fe^-$ with carbon disulfide and a suitable alkyl halide (eq 1).[12] Short reaction

$$Cp(CO)_2Fe^- \xrightarrow[(2)\ RX]{(1)\ CS_2} \underset{\text{Ia,b}}{Cp(CO)_2Fe—C(=S)SR} + X^- \quad (1)$$

$$RX = CH_3I\ (Ia),\ C_6H_5CH_2Br\ (Ib)$$

times are important since other products have been observed by using longer reaction times.[13] A ruthenium analogue of Ia has been prepared by the same route.[14] The dithioester complexes Ia,b are stable toward air in the solid state, but they decompose slowly when exposed to light.

Alkyl fluorosulfonates readily alkylate the thiocarbonyl sulfur atom of the dithioester ligand to give the corresponding cationic dithiocarbene complexes (eq 2). The yields are

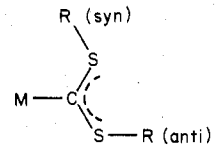
$$\text{Ia,b} \xrightarrow[(2)\ PF_6^-\ \text{exchange}]{(1)\ R'SO_3F} \{Cp(CO)_2Fe[C(SR)SR']\}PF_6 \quad (2)$$

IIa, R = R' = CH_3
IIb, R = CH_3, R' = C_2H_5
IIc, R = $CH_2C_6H_5$, R' = CH_3

generally in the range of 60–70%. Anion exchange is performed as the SO_3F^- salts of IIa–c are less stable and less readily crystallized than the PF_6^- salts. In the solid state the yellow crystalline carbene complexes IIa–c show no noticeable decomposition after several months of exposure to air. Complex IIa is slightly soluble in water; it is also stable toward water at room temperature and can be recovered almost quantitatively from aqueous solutions. The carbenes are soluble in polar solvents such as CH_2Cl_2, CH_3CN, and acetone, slightly soluble in $CHCl_3$ and THF, and insoluble in nonpolar solvents such as hexanes or Et_2O. Solutions of IIa exposed to air at room temperature are stable for several days. This stability differs markedly from that of a related carbene complex with no stabilizing heteroatomic groups, $\{Cp(CO)_2Fe[C(C_6H_5)H]\}PF_6$, solutions of which decompose completely within 1 h under similar conditions.[15]

The IR spectrum of IIa in CH_2Cl_2 shows two ν(CO) absorptions at 2058 and 2017 cm^{-1} with a calculated ν(CO) force constant[16a] of 16.8 mdyn/Å. Comparison of this value with the ν(CO) force constants of 17.6 and 17.1 mdyn/Å found for $\{CpFe(CO)_3\}PF_6$[16b] and $\{Cp(CO)_2FeCNCH_3\}PF_6$,[16b] respectively, indicates that the dithiocarbene ligand has a lower π-acceptor/σ-donor ratio than either the carbonyl or isocyanide ligand, which is consistent with conclusions drawn for other transition-metal carbene complexes.[3] The position of the carbene carbon resonance in the ^{13}C NMR (acetone-d_6) spectrum of IIa occurs at 303 ppm downfield relative to Me_4Si, which is also consistent with previous reports.[3]

A single line at τ 6.73 is observed for the two methyl groups of the carbene ligand in the ^1H NMR (acetone-d_6) spectrum of IIa. This is in contrast with spectra reported for $\{PtCl[C(SEt)_2](PPh_3)_2\}BF_4$,[10] $\{PtI[C(SMe)_2](PPh_3)_2\}I$,[11] and $\{PtI[C(SEt)_2](PPh_3)_2\}I$[11] which show different resonances for the two alkyl groups of the carbene ligands. The inequivalence of the alkyl groups is explained by the presence of syn and anti R groups



caused by restricted rotation around the C(carbene)–S bonds.[10,11] When an acetone-d_6 solution of IIa is cooled to −55

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°C, the methyl groups become nonequivalent, and two sharp singlets at τ 6.87 and 6.53 are observed. When the solution is warmed, the two singlets broaden, become less intense, and finally coalesce at −2.5 °C. As the sample is warmed further, the signal sharpens to the previously observed singlet at τ 6.73. The equivalence of the methyl groups of IIa is presumably due to rapid rotation around the C(carbene)–S bonds. Single resonances for the R and R′ groups in the room-temperature ^{1}H NMR spectra of IIb and IIc suggest that there is rapid rotation in these complexes as well.

Since the coalescence temperature of IIa is lower (−2.5 °C) than that of $Cl(PPh_3)_2Pt[C(SR)_2]^+$ (>30 °C), the rate of rotation around the C(carbene)–S bonds is presumably greater in IIa. This rate difference may be rationalized by suggesting that the $Cl(PPh_3)_2Pt^+$ moiety is more electron withdrawing than $Cp(CO)_2Fe^+$. This would promote more S→C(carbene) π bonding in the Pt complexes, which would restrict rotation around the C(carbene)–S bonds. That the $Cl(PPh_3)_2Pt^+$ group is indeed more electron withdrawing than the $Cp(CO)_2Fe^+$ group is supported by the higher ν(CO) force constant for $\{Cl(PPh_3)_2Pt(CO)\}BF_4$ (18.2 mdyn/Å)[17] than for $\{CpFe(CO)_3\}PF_6$ (17.6 mdyn/Å).[16b] The steric bulk of the two triphenyl phosphine ligands in $Cl(PPh_3)_2Pt[C(SR)_2]^+$ may also be a factor in restricting rotation around the C(carbene)–S bonds in the platinum complexes.

Reactions of $Cp(CO)_2Fe[C(SCH_3)_2]^+$. With Primary Amines. Except for reactions with methylamine and aniline, two products are identified in reactions of IIa with amines. The minor product, usually too little to isolate, is a neutral complex that has been characterized as cyclopentadienyldicarbonyliron trimethylorthothioformate, $Cp(CO)_2Fe[C(SCH_3)_3]$; it is formed in reactions of IIa with certain bases. This neutral complex, with ν(CO) values of 2013 and 1964 cm^{-1} in CH_2Cl_2, is presently under investigation, and an X-ray analysis is in progress, the details of which will be presented in a later report.[18]

In all cases, the major product (55–88%) of the reaction of IIa with a primary amine at room temperature in CH_2Cl_2 is a cationic isocyanide derivative (eq 3). With the exception

$$\text{IIa} + RNH_2 \rightarrow \{Cp(CO)_2Fe(CNR)\}PF_6 + 2HSCH_3 \quad (3)$$

IIIa–i

R = CH_3 (IIIa), *n*-Pr (IIIb), *i*-Pr (IIIc), cyclohexyl (IIId), benzyl (IIIe), C_6H_5 (IIIf), $CH_2CH_2N(CH_3)_2$ (IIIg), $CH(CH_3)C(=O)OCH_3$ (IIIh), $CH_2(CH_2)_2OH$ (IIIi)

of aniline, all of the reactions are usually complete within 1 h. Aniline, a considerably weaker nucleophile, reacts much slower and gives the lowest yield (25%) of the corresponding isocyanide complex. Although no kinetic studies have been carried out on these reactions, the slowness of the aniline reaction suggests that an important step is attack of the amine on the carbene carbon to give an intermediate which subsequently collapses to the product.

In the reaction solutions, these type III complexes undergo further reaction with excess amine to form carbamoyl complexes, Cp(CO)Fe(CNR)[C(=O)NHR], characterized by their ν(CO) absorptions at approximately 2160 and 1950 cm^{-1}.[16b] Upon evaporation of the amine, they revert to III, as described previously.[16b]

The spectral characteristics of IIIa–i are generally very similar. Their IR spectra show three bands: 2192–2242 (m) cm^{-1}, ν(CN); 2079–2085 (s) cm^{-1}, ν(CO); 2037–2046 (s) cm^{-1}, ν(CO). The Cp resonance in their ^{1}H NMR spectra appears at approximately τ 4.25. Exceptions to this are IIIe (τ 4.34), possibly due to shielding effects of the phenyl ring, and IIIf (τ 4.10), most likely due to the weaker donor ability of the isocyanide ligand. Resonances arising from the isocyanide ligands, while consistent with the proposed products, are sometimes broadened or are of unexpected multiplicities due to possible coupling with the nitrogen of the ligand.

With Secondary Amines. The reaction of IIa with secondary amines is very similar to the aminolysis of $(CO)_5Cr[C(OCH_3)C_6H_5]$.[19] One thiomethoxy group is readily replaced to produce amino–thiocarbene complexes (eq 4). When the

$$\text{IIa} + HNR_2 \rightarrow \{Cp(CO)_2Fe[C(SCH_3)NR_2]\}PF_6 + HSCH_3 \quad (4)$$

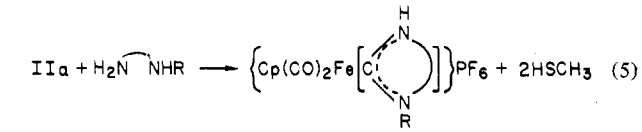
IVa–c

HNR_2 = $HNMe_2$ (IVa), piperidine (IVb), morpholine (IVc)

reaction is run at room temperature in CH_2Cl_2, even with a large excess of secondary amine, the second thiomethoxy group is not replaced. Only sterically small amines such as dimethyl or heterocyclic amines will react in this manner to give carbenes of type IV. Diethyl and higher amines are too bulky and give $Cp(CO)_2Fe[C(SCH_3)_3]$[18] as the only identified organometallic product. Infrared spectral studies indicate that, when reacted with IIa, piperazine, pyrrolidine, and aziridine also form amino–thiocarbene complexes of type IV, but these products were not isolated. A large amount of intractable tar with an IR spectrum characteristic of isocyanide complexes of type III is also formed in the aziridine reaction.

The IR spectra of complexes IVa–c contain strong ν(CO) absorptions at 2046–2047 and 2001–2002 cm^{-1}. These low frequencies, as compared to those of IIa (2058 and 2017 cm^{-1}), reflect the greater ability of nitrogen to donate π-electron density into the carbene carbon atom.[3,20] In the ^{1}H NMR spectra of the complexes, singlets are found at τ 4.40–4.45 and τ 7.04–7.09 for the Cp and SCH_3 groups, respectively. Complex IVa shows nonequivalent amine methyl groups in its room temperature ^{1}H NMR which is consistent with a large N→C(carbene) π interaction.

With Diamines. The reaction of IIa with appropriate diamines at room temperature in CH_2Cl_2 provides a general, high-yield synthesis of cyclic diaminocarbene complexes (eq 5).

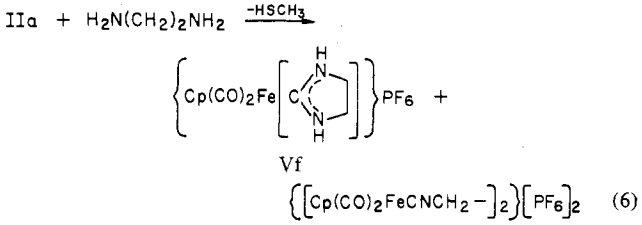


$$\text{IIa} + H_2N\frown NHR \rightarrow \{Cp(CO)_2Fe[C(NHCH_2CH_2NR)]\}PF_6 + 2HSCH_3 \quad (5)$$

Va–e

$H_2N\frown NHR$ = $H_2N(CH_2)_3NH_2$ (Va), *o*-$C_6H_4(NH_2)_2$ (Vb), $H_2NCH(CH_3)CH_2NH_2$ (Vc), $H_2NC(CH_3)_2CH_2NH_2$ (Vd), $H_2N(CH_2)_2NHCH_3$ (Ve)

When IIa is allowed to react with an equimolar amount of ethylenediamine, approximately equal amounts of carbene and isocyanide products are always obtained (eq 6). Analytically



$$\text{IIa} + H_2N(CH_2)_2NH_2 \xrightarrow{-HSCH_3} \{Cp(CO)_2Fe[C(NHCH_2CH_2NH)]\}PF_6 + \quad (6)$$

Vf

$$\{[Cp(CO)_2FeCNCH_2-]_2\}[PF_6]_2$$

VI

pure samples of the binuclear isocyanide complex VI are obtained by fractional crystallization, but Vf obtained in this manner is always contaminated with traces of VI. However, when IIa is allowed to react with 2 equiv of the monotosylate

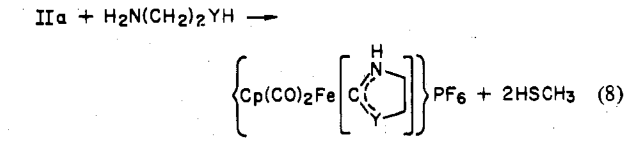
salt of ethylenediamine, pure samples of Vf are obtained (eq 7). It was hoped that $Cp(CO)_2Fe[CN(CH_2)_2NH_3^+]^+$ could

$$IIa + 2H_2N(CH_2)_2NH_3^+Ts^- \rightarrow Vf + 2HSCH_3 + [H_3N(CH_2)_2NH_3]^{2+}Ts^-_2 \quad (7)$$

be isolated as a possible intermediate in this reaction. But when IIa is reacted with 1 equiv of $H_2N(CH_2)_2NH_3^+Ts^-$, only equal amounts of IIa and Vf are obtained; thus, there is no evidence for the isocyanide intermediate.

Infrared spectra of the cyclic diaminocarbene complexes Va–f are quite similar to those of the amino–thiocarbene complexes IVa–c, displaying strong ν(CO) absorptions at 2050–2056 and 2000–2006 cm^{-1}. In their ^1H NMR spectra, protons attached to the nitrogens cannot be observed in any of these complexes; presumably this is due to quadrupolar interactions with the nitrogen atoms.

With Amino Alcohols and Amino Thiols. Both ethanolamine and β-mercaptoethylamine react with IIa at room temperature in a manner similar to diamines to give cyclic carbene complexes (eq 8). However, 3-aminopropanol seems to behave



VIIa,b

Y = O (VIIa), S (VIIb)

simply as a primary amine to give IIIi, $\{Cp(CO)_2Fe[CN(CH_2)_3OH]\}PF_6$, as indicated in eq 3. When IIIi is stirred in CH_2Cl_2 at room temperature for several days, bands at 2058 and 2011 cm^{-1} slowly develop while those of IIIi slowly diminish. This indicates that IIIi may slowly cyclize to give a carbene complex of type VII, but this cyclic carbene has not been isolated. Infrared data (very weak ν(CN) absorptions in spectra of the reaction mixtures) also indicate that the reactions shown in eq 8 may proceed through an isocyanide intermediate analogous to IIIi, but these intermediates have not been isolated.

The availability of VIIa,b as well as the diaminocarbene Vf allows us to compare the effect of the heteroatoms on the CO groups. The ν(CO) frequencies and force constants[16a] of $\{Cp(CO)_2Fe[\overline{CNHCH_2CH_2NH}]\}PF_6$ (Vf: 2053, 2003 cm^{-1}; 16.61 mdyn/Å), $\{Cp(CO)_2Fe[\overline{CNHCH_2CH_2S}]\}PF_6$ (VIIb: 2059, 2014 cm^{-1}; 16.75 mdyn/Å), and $\{Cp(CO)_2Fe[\overline{CNHCH_2CH_2O}]\}PF_6$ (VIIa: 2063, 2017 cm^{-1}; 16.81 mdyn/Å) increase as the heteroatom is changed from nitrogen to sulfur to oxygen. The same trend is found in comparing carbene complexes where both heteroatoms are changed. This is seen in the following series: $\{Cp(CO)_2Fe[\overline{CNHCH_2CH_2NH}]\}PF_6$ (Vf: 2053, 2003 cm^{-1}; 16.61 mdyn/Å), $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ (2058, 2017 cm^{-1}; 16.77 mdyn/Å), $\{Cp(CO)_2Fe[C(OCH_3)_2]\}PF_6$ (2068, 2020 cm^{-1}; 16.87 mdyn/Å).[22] These results suggest that the carbene ligand becomes a weaker donor ligand as the heteroatoms are changed in the order N > S > O.

With Miscellaneous Reagents. Ammonia reacts readily with IIa in CH_2Cl_2 at room temperature to give the neutral cyanide complex in fair (34%) yield (eq 9). Its spectral characteristics

$$IIa + 2NH_3 \rightarrow \underset{VIII}{Cp(CO)_2Fe(CN)} + NH_4^+ + 2HSCH_3 \quad (9)$$

are identical to those reported for the complex obtained by a different route.[21] Infrared studies indicate that NaN_3 also reacts very rapidly with IIa in CH_3CN at room temperature to give $Cp(CO)_2Fe(CN)$, $Cp(CO)_2FeC(SCH_3)_3$, and other unidentified products.

When cyclohexylphosphine, $C_6H_{11}PH_2$, was allowed to react with IIa in hopes of preparing a complex with the unknown C≡P–R ligand, no such product was obtained. No reaction was observed between IIa and I^-, Cl^-, I_2, HCl, HF, or PPh_3 at room temperature.

Experimental Section

General Information. $Cp(CO)_2FeC(=S)SCH_3$ was prepared as reported previously.[12] Reagent grade chemicals were used without further purification. Tetrahydrofuran (THF) was distilled from $NaK_{2.8}$[23] under N_2 immediately prior to use. Unless otherwise noted, the following procedures did not require the use of an inert atmosphere.

Infrared spectra were recorded on a Perkin-Elmer 237B or 337 spectrometer equipped with an expanded-scale recorder calibrated with gaseous CO. Routine ^1H NMR spectra were recorded on Perkin-Elmer Hitachi R-20B or Varian A-60 spectrometers; temperature-dependent ^1H NMR spectra were recorded on a Varian HA-100 spectrometer. Carbon-13 spectra were run on a Bruker HX-90 FT NMR spectrometer; $Cr(acac)_3$ (~0.1 M) was added to the solutions to reduce data collection time.[24] Tetramethylsilane (Me_4Si) was employed as the internal standard for all NMR spectra. Elemental analyses are given in Table I.

Synthesis of Complexes. $Cp(CO)_2Fe[C(=S)SCH_2C_6H_5]$ (Ib). This complex was prepared from $BrCH_2C_6H_5$ (6.8 mL, 57.2 mmol) and 10.00 g (28.3 mmol) of $[CpFe(CO)_2]_2$ following the procedure[12] used for $Cp(CO)_2Fe[C(=S)SCH_3]$ (Ia). The evaporated reaction mixture was extracted with Et_2O until the extracts were only a faint yellow. The extracts were filtered through Celite and then evaporated to a dark, viscous oil. Repeated fractional crystallization of this oil from hexanes and/or Et_2O at −20 °C afforded 7.23 g (37%) of Ib as dark orange crystals. IR (CH_2Cl_2): 2031 (s), 1982 (s) cm^{-1}. ^1H NMR ($CDCl_3$): τ 2.61 (s, C_6H_5), 5.03 (s, C_5H_5), 5.39 (s, CH_2). Mp 73–75 °C.

$\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ (IIa). The methyl dithioester, Ia (0.50 g, 1.87 mmol), in 20 mL of CH_2Cl_2 was stirred with CH_3SO_3F (0.20 mL, 2.47 mmol) for 1 h. The resulting dark solution was evaporated to a dark oil which was washed with Et_2O. The oil was dissolved in a minimum amount of acetone, placed on an anion-exchange column (Amberlite IRA-400, 35 × 1 cm) in the PF_6^- form, and eluted slowly with acetone. The yellow acetone fraction was collected, concentrated to ~10 mL, and filtered, and hexanes were carefully added such that two layers formed. When the solution was cooled to −20 °C, yellow crystals of IIa precipitated as the hexanes slowly diffused into the CH_2Cl_2 solution. After the crystals were washed with Et_2O and dried under high vacuum, 0.55 g (69%) of IIa was isolated. IR (CH_2Cl_2): 2058 (s), 2017 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.43 (s, C_5H_5), 6.73 (s, 2 CH_3). Mp 163–165 °C.

$\{Cp(CO)_2Fe[C(SCH_3)SC_2H_5]\}PF_6$ (IIb). This complex was prepared by the same method as IIa. Starting with Ia (0.50 g, 1.87 mmol) and $C_2H_5SO_3F$ (0.25 mL, 2.47 mmol), 0.50 g (60%) of IIb was obtained as fine yellow crystals. IR (CH_2Cl_2): 2060 (s), 2017 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.37 (s, C_5H_5), 6.16 (q, CH_2), 6.69 (s, SCH_3), 8.44 (t, CH_3). Mp 117–119 °C.

$\{Cp(CO)_2Fe[C(SCH_3)SCH_2C_6H_5]\}PF_6$ (IIc). The method used to prepare IIa was also employed for this complex. Starting with Ib (1.00 g, 2.90 mmol) and CH_3SO_3F (0.30 mL, 3.70 mmol) in 40 mL of CH_2Cl_2, 0.93 g (64%) of IIc was obtained as bright yellow crystals. IR (CH_2Cl_2): 2056 (s), 2017 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 2.54 (s, C_6H_5), 4.34 (s, C_5H_5), 4.99 (s, CH_2), 6.63 (s, CH_3). Mp 150 °C dec.

$\{Cp(CO)_2Fe[CNCH_3]\}PF_6$ (IIIa). Methylamine was bubbled through 50 mL of CH_2Cl_2 containing IIa (0.205 g, 0.49 mmol) for 1 h. The bright yellow solution was concentrated to 10 mL, and the product was precipitated by addition of hexanes and cooling to −20 °C. After recrystallization from acetone with hexanes at −20 °C, 0.108 g (62%) of IIIa was isolated as a pale yellow powder. The complex displayed the same physical characteristics as observed for a sample prepared by a different route.[16b]

$\{Cp(CO)_2Fe[CNCH_2CH_2CH_3]\}PF_6$ (IIIb). An 80-mL solution of CH_2Cl_2 containing IIa (0.64 g, 1.49 mmol) and n-propylamine (125 μL, 1.52 mmol) was stirred for 1 h and then evaporated to a dark oil. The oil was washed with Et_2O to remove any neutral species. The residue was crystallized from CH_2Cl_2 with Et_2O at −20 °C to

Table I. Elemental Analyses of the Complexes

complex		% calcd C	% calcd H	% calcd N	% exptl C	% exptl H	% exptl N
$Cp(CO)_2Fe[C(=S)SCH_2C_6H_5]$	Ib	52.34	3.51		52.38	3.58	
$\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$	IIa	28.05	2.59		28.04	2.57	
$\{Cp(CO)_2Fe[C(SCH_3)SC_2H_5]\}PF_6$	IIb	29.88	2.96		29.85	2.97	
$\{Cp(CO)_2Fe[C(SCH_3)SCH_2C_6H_5]\}PF_6$	IIc	38.11	3.00		37.98	2.90	
$\{Cp(CO)_2Fe[CNCH_3]\}PF_6$	IIIa	29.78	2.22	3.86	29.93	2.34	3.91
$\{Cp(CO)_2Fe[CNCH_2CH_2CH_3]\}PF_6$	IIIb	33.79	3.09		33.68	3.28	
$\{Cp(CO)_2Fe[CNCH(CH_3)_2]\}PF_6$	IIIc	33.79	3.09	3.58	33.67	3.03	3.61
$\{Cp(CO)_2Fe[CNC_6H_{11}]\}PF_6$	IIId	39.01	3.74	3.25	38.79	3.72	3.19
$\{Cp(CO)_2Fe[CNCH_2C_6H_5]\}PF_6$	IIIe	41.03	2.75	3.19	41.26	2.80	3.16
$\{Cp(CO)_2Fe[CNC_6H_5]\}PF_6$	IIIf	39.56	2.37	3.30	39.50	2.38	3.30
$\{Cp(CO)_2Fe[CNCH_2CH_2N(CH_3)_2]\}PF_6$	IIIg	34.31	3.60	6.67	34.16	3.60	6.60
$\{Cp(CO)_2Fe[CNCH(CH_3)C(=O)OCH_3]\}PF_6$	IIIh	33.13	2.78	3.22	33.15	2.79	3.21
$\{Cp(CO)_2Fe[CN(CH_2)_3OH]\}PF_6$	IIIi	32.46	2.97	3.44	32.65	3.02	3.43
$\{Cp(CO)_2Fe[C(SCH_3)N(CH_3)_2]\}PF_6$	IVa	31.08	3.32	3.29	31.26	3.42	3.44
$\{Cp(CO)_2Fe[C(SCH_3)\overline{N(CH_2)_4CH_2}]\}PF_6$	IVb	36.15	3.90	3.01	36.26	4.47	3.24
$\{Cp(CO)_2Fe[C(SCH_3)N(CH_2CH_2)_2O]\}PF_6$	IVc	33.42	3.45	3.00	33.51	3.47	2.92
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_3NH}]\}PF_6$	Va	32.54	3.23	6.90	32.03	3.21	6.80
$\{Cp(CO)_2Fe[\overline{CNH(o\text{-}C_6H_4)NH}]\}PF_6$	Vb	38.21	2.52		38.21	2.51	
$\{Cp(CO)_2Fe[\overline{CNHCH(CH_3)CH_2NH}]\}PF_6$	Vc	32.54	3.23	6.90	32.70	3.29	6.86
$\{Cp(CO)_2Fe[\overline{CNHC(CH_3)_2CH_2NH}]\}PF_6$	Vd	34.31	3.60	6.67	33.98	3.58	6.59
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_2NCH_3}]\}PF_6$	Ve	32.54	3.23	6.90	32.81	3.30	6.80
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_2NH}]\}PF_6$	Vf	30.64	2.83	7.15	30.89	2.86	7.08
$\{[Cp(CO)_2FeCNCH_2-]_2\}[PF_6]_2$	VI	29.86	1.95	3.87	29.95	2.01	3.92
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_2O}]\}PF_6$	VIIa	30.56	2.56		30.66	2.67	
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_2S}]\}PF_6$	VIIb	29.36	2.46	3.42	29.36	2.49	3.37

give 0.51 g (87%) of IIIb as light orange-yellow crystals. IR (CH_2Cl_2): 2226 (s), 2081 (vs), 2041 (vs) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.26 (s, C_5H_5), 6.04 (t, CN–CH_2), 8.22 (m, CH_2CH_3), 8.96 (t, CH_3). Mp 118–120 °C.

$\{Cp(CO)_2Fe[CNCH(CH_3)_2]\}PF_6$ (IIIc). This complex was prepared in the same manner as IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 20 μL (0.23 mmol) of isopropylamine in 20 mL of CH_2Cl_2, 0.064 g (70%) of IIIc was isolated as cream-yellow needles. IR (CH_2Cl_2): 2215 (s), 2082 (vs), 2042 (vs) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.24 (s, C_5H_5), 5.61 (m, CH), 8.51 (doublet of triplets, 2 CH_3). Mp 98–99 °C.

$\{Cp(CO)_2Fe[CNC_6H_{11}]\}PF_6$ (IIId). This derivative was prepared in the same manner as IIIb. From the reaction of IIa (0.25 g, 0.58 mmol) and cyclohexylamine (75 μL, 0.66 mmol) in 50 mL of CH_2Cl_2 for 35 min, 0.182 g (72%) of IIId was isolated as tan needles. IR (CH_2Cl_2): 2212 (s), 2081 (vs), 2042 (vs) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.20 (s, C_5H_5), 5.80 (m, CN–CH), 8.06 and 8.46 (m, 5 CH_2). Mp 135–137 °C.

$\{Cp(CO)_2Fe[CNCH_2C_6H_5]\}PF_6$ (IIIe). This complex was prepared by a route analogous to that used for IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 52 μL (0.47 mmol) of benzylamine in 20 mL of CH_2Cl_2, 0.091 g (88%) of IIIe was obtained as yellow-orange needles. IR (CH_2Cl_2): 2225 (s), 2082 (vs), 2042 (vs) cm^{-1}. ^1H NMR (acetone-d_6): τ 2.66 (s, C_6H_5), 4.34 (s, C_5H_5), 4.83 (s, CH_2). Mp 168–170 °C.

$\{Cp(CO)_2Fe[CNC_6H_5]\}PF_6$ (IIIf). A large excess of aniline (1.0 mL, 11.00 mmol) was stirred with IIa (0.20 g, 0.47 mmol) in 40 mL of CH_2Cl_2 for 4 days. The reaction mixture was then evaporated to an oil and washed with Et_2O. The resulting tar was dissolved in a small volume of CH_2Cl_2 and treated with decolorizing carbon. After filtration, adding Et_2O to the yellow solution and cooling the mixture to −20 °C afforded 0.05 g (25%) of IIIf as pale yellow needles. IR (CH_2Cl_2): 2192 (s), 2085 (s), 2046 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 2.40 (m, C_6H_5), 4.10 (s, C_5H_5). Mp 153–155 °C.

$\{Cp(CO)_2Fe[CNCH_2CH_2N(CH_3)_2]\}PF_6$ (IIIg). This complex was prepared in the same manner as IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 30 μL (0.27 mmol) of *N,N*-dimethylethylenediamine in 20 mL of CH_2Cl_2, 0.05 g (51%) of IIIg was isolated as cream-yellow needles. IR (CH_2Cl_2): 2228 (s), 2082 (vs), 2042 (vs) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.27 (s, C_5H_5), 5.96 (t, CN–CH_2), 7.27 (t, CH_2), 7.68 (s, 2 CH_3). Mp 75–76 °C.

$\{Cp(CO)_2Fe[CNCH(CH_3)C(=O)OCH_3]\}PF_6$ (IIIh). The hydrochloride salt of alanine methyl ester (0.065 g, 0.47 mmol) was suspended as a fine powder in 50 mL of CH_2Cl_2. Ammonia gas was bubbled through the solution for 45 min to generate the soluble amino acid ester and insoluble NH_4Cl. Nitrogen was then bubbled through the solution to purge it of ammonia. After filtration and concentration of the solution to ~20 mL, IIa (0.10 g, 0.23 mmol) was added and stirred for 4 h. The reaction mixture was then evaporated to an oil and washed with Et_2O. Crystallization of the residue from acetone with Et_2O at −20 °C gave 0.063 g (62%) of IIIh as large, bright orange crystals. IR (CH_2Cl_2): 2223 (s), 2083 (vs), 2043 (vs), 1759 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.20 (s, C_5H_5), 4.86 (q, CH), 6.19 (s, OCH_3), 8.26 (d, CH_3). Mp 68–70 °C.

$\{Cp(CO)_2Fe[CN(CH_2)_3OH]\}PF_6$ (IIIi). This complex was prepared in the same manner as IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 20 μL (0.26 mmol) of 3-aminopropanol in 20 mL of CH_2Cl_2 and stirring the mixture for 15 min, we isolated 0.064 g (67%) of IIIi as orange-yellow needles. IR (CH_2Cl_2): 2226 (vs), 2081 (vs), 2040 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.24 (s, C_5H_5), 5.92 (t, $CNCH_2$), 6.26 (t, CH_2O), 8.00 (m, CH_2). Mp 99–101 °C.

$\{Cp(CO)_2Fe[C(SCH_3)N(CH_3)_2]\}PF_6$ (IVa). Dimethylamine was bubbled through 20 mL of CH_2Cl_2 containing IIa (0.10 g, 0.23 mmol) for 10 min, and the solution was stirred for an additional 30 min. After evaporation of the solution to dryness and washing of the solid with Et_2O, the residue was crystallized from acetone with Et_2O at −20 °C to give 0.044 g (44%) of IVa as fine yellow crystals. IR (CH_2Cl_2): 2046 (s), 2001 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.40 (s, C_5H_5), 5.98 (s, NCH_3), 6.24 (s, NCH_3), 7.04 (s, SCH_3). Mp 190 °C dec.

$\{Cp(CO)_2Fe[C(SCH_3)\overline{N(CH_2)_4CH_2}]\}PF_6$ (IVb). This complex was prepared in a manner analogous to that used for IIIb. From 0.20 g (0.47 mmol) of IIa and 93 μL (0.94 mmol) of piperidine in 40 mL of CH_2Cl_2 with stirring for 2 h, 0.15 g (69%) of IVb was obtained as a yellow powder. IR (CH_2Cl_2): 2047 (s), 2002 (s) cm^{-1}. ^1H NMR (acetone-d_6): τ 4.45 (s, C_5H_5), 5.63, 6.60, and 8.13 (m, N-

$(CH_2)_4CH_2$), 7.09 (s, CH_3). Mp 153–155 °C.

{Cp(CO)$_2$Fe[C(SCH$_3$)N(CH$_2$CH$_2$)$_2$O]}PF$_6$ (IVc). This derivative was prepared in the same manner as IIIb. The reaction of IIa (0.10 g, 0.23 mmol) and morpholine (50 μL, 0.58 mmol) in 20 mL of CH_2Cl_2 for 3 h yielded 0.069 g (64%) of IVc as yellow needles. IR (CH_2Cl_2): 2047 (s), 2001 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.42 (s, C_5H_5), 5.54 and 6.06 (m, $N(CH_2CH_2)_2O$), 7.06 (s, CH_3). Mp 185–187 °C dec.

{Cp(CO)$_2$Fe[CNH(CH$_2$)$_3$NH]}PF$_6$ (Va). A solution of 30 mL of CH_2Cl_2 containing IIa (0.50 g, 1.17 mmol) was added dropwise with stirring to 50 mL of CH_2Cl_2 containing 1,3-diaminopropane (100 μL, 1.20 mmol) over a period of 30 min. The reaction mixture was stirred for an additional 40 min, evaporated to an oil, and washed with Et_2O. The residue was crystallized from CH_2Cl_2 with Et_2O at −20 °C to give 0.314 g (66%) of Va as cream-yellow needles. IR (CH_2Cl_2): 2051 (s), 2000 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.62 (s, C_5H_5), 6.60 (t, 2 CH_2), 8.00 (m, CH_2). Mp 204 °C.

{Cp(CO)$_2$Fe[CNH(*o*-C$_6$H$_4$)NH]}PF$_6$ (Vb). An inert (N_2) atmosphere and N_2-saturated solvents were used in this synthesis. A solution of 20 mL of CH_2Cl_2 containing IIa (0.10 g, 0.23 mmol) and *o*-diaminobenzene (0.05 g, 0.46 mmol) was stirred in a Schlenk tube for 3 days. The dark reaction mixture was evaporated to an oil and chromatographed on a Celite/CH_2Cl_2 column (50 × 2 cm). A pink band separated from extensive bright blue trailings of unknown composition. The pink band was collected and treated with decolorizing carbon to give a pale yellow solution after filtration. The addition of hexanes to the filtrate (after concentration) and cooling of the solution to −20 °C gave 0.022 g (21%) of Vb as pale yellow needles. IR (CH_2Cl_2): 2056 (s), 2006 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 2.50 (AA′BB′, C_6H_4), 4.51 (s, C_5H_5). Mp 230–233 °C.

{Cp(CO)$_2$Fe[CNHCH(CH$_3$)CH$_2$NH]}PF$_6$ (Vc). This complex was prepared in the same manner as Va. The reaction of 0.10 g (0.23 mmol) of IIa and 21 μL (0.25 mmol) of 1,2-diaminopropane gave 0.081 g (85%) of Vc as yellow crystals. IR (CH_2Cl_2): 2055 (s), 2004 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.58 (s, C_5H_5), 5.60 and 6.70 (m, CH_2CH), 8.69 (d, CH_3). Mp 177–179 °C.

{Cp(CO)$_2$Fe[CNHC(CH$_3$)$_2$CH$_2$NH]}PF$_6$ (Vd). By use of the method for the preparation of IIIb, 0.20 g (0.47 mmol) of IIb and 60 μL (0.48 mmol) of 2-methyl-1,2-diaminopropane were reacted in 40 mL of CH_2Cl_2 while stirring for 40 min. Yellow needles (0.172 g, 88%) of Vd were isolated. IR (CH_2Cl_2): 2050 (s), 2001 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.59 (s, C_5H_5), 6.44 (s, CH_2), 8.61 (s, 2 CH_3). Mp 246 °C dec.

{Cp(CO)$_2$Fe[CNH(CH$_2$)$_2$NCH$_3$]}PF$_6$ (Ve). This complex was prepared in the same manner as IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 21 μL (0.24 mmol) of *N*-methylethylenediamine in 20 mL of CH_2Cl_2 and stirring the mixture for 20 min, we isolated 0.063 g (66%) of Ve as yellow crystals. IR (CH_2Cl_2): 2052 (s), 2004 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.52 (s, C_5H_5), 6.19 (s, 2 CH_2), 6.68 (s, CH_3). Mp 178–180 °C.

{Cp(CO)$_2$Fe[CNH(CH$_2$)$_2$NH]}PF$_6$ (Vf). The monotosylate salt of ethylenediamine was prepared by dissolving ethylenediamine (36 μL, 0.54 mmol) and *p*-toluenesulfonic acid monohydrate (0.1028 g, 0.54 mmol) in 20 mL of CH_3CN containing enough CH_3OH to give a clear solution. Complex IIa (0.10 g, 0.23 mmol) was then added and the solution stirred for 2 h. The cloudy reaction mixture was evaporated to dryness, washed with Et_2O, and extracted with CH_2Cl_2. Addition of Et_2O to the CH_2Cl_2 extracts followed by cooling of the mixture to −20 °C gave 0.049 g (54%) of Vf as pale yellow crystals. IR (CH_2Cl_2): 2053 (s), 2003 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.56 (s, C_5H_5), 6.22 (s, 2 CH_2). Mp 183–185 °C.

{[Cp(CO)$_2$FeCNCH$_2$−]$_2$}[PF$_6$]$_2$ (VI). A solution of 10 mL of CH_2Cl_2 containing ethylenediamine (16 μL, 0.24 mmol) was added dropwise with stirring to 10 mL of CH_2Cl_2 containing IIa (0.20 g, 0.47 mmol) over a period of 30 min. A precipitate slowly formed, and the reaction mixture was allowed to stir for an additional 45 min. The precipitate was collected by filtration and recrystallized from acetone with Et_2O at −20 °C to give 0.070 g (41%) of VI as a tan powder. IR (CH_3CN): 2211 (m), 2084 (s), 2037 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.21 (s, 2 C_5H_5), 5.49 (s, 2 CH_2). Mp 254 °C dec.

{Cp(CO)$_2$Fe[CNH(CH$_2$)$_2$O]}PF$_6$ (VIIa). This was prepared in the same manner as IIIb. Starting with 0.20 g (0.47 mmol) of IIa and 29 μL (0.48 mmol) of β-aminoethanol in 40 mL of CH_2Cl_2 and stirring the mixture for 15 min, we obtained 0.133 g (73%) of VIIa as cream-yellow needles. IR (CH_2Cl_2): 2063 (s), 2017 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.52 (s, C_5H_5), 5.20 and 6.10 (AA′BB′, 2 CH_2). Mp 154–157 °C.

{Cp(CO)$_2$Fe[CNH(CH$_2$)$_2$S]}PF$_6$ (VIIb). This was prepared by the same method as used for IIIh. The free amino thiol was generated from β-aminoethanethiol hydrochloride (0.08 g, 0.70 mmol) and stirred with IIa (0.10 g, 0.23 mmol) for 50 min to give 0.046 g (48%) of VIIb as yellow crystals. IR (CH_2Cl_2): 2059 (s), 2014 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 4.52 (s, C_5H_5), 5.64 and 6.50 (AA′BB′, 2 CH_2). Mp 168–170 °C.

{Cp(CO)$_2$Fe(CN)} (VIII). Ammonia gas was bubbled through 15 mL of CH_2Cl_2 containing IIa (0.21 g, 0.49 mmol) for 1 h. The solution was filtered and concentrated to 5 mL. Upon addition of 10 mL of a 50:50 pentane/Et_2O mixture and cooling of the solution to −20 °C, 0.034 g (34%) of VIII was isolated as yellow needles. Its physical properties were identical with those reported previously.[21]

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Registry No. Ia, 59654-63-6; Ib, 69532-09-8; IIa, 69532-11-2; IIb, 69532-13-4; IIc, 69532-15-6; IIIa, 56943-25-0; IIIb, 69532-17-8; IIIc, 69532-19-0; IIId, 69532-21-4; IIIe, 69532-23-6; IIIf, 69532-24-7; IIIg, 69532-26-9; IIIh, 69532-28-1; IIIi, 69532-30-5; IVa, 69532-32-7; IVb, 69532-34-9; IVc, 69532-36-1; Va, 69532-38-3; Vb, 69532-40-7; Vc, 69532-42-9; Vd, 69532-44-1; Ve, 69532-46-3; Vf, 69532-48-5; VI, 69532-50-9; VIIa, 69532-52-1; VIIb, 69532-54-3; VIII, 12152-37-3; $Cp(CO)_2Fe[C(SCH_3)_3]$, 69532-55-4; $[CpFe(CO)_2]_2$, 12154-95-9; $BrCH_2C_6H_5$, 100-39-0; CS_2, 75-15-0; CH_3SO_3F, 421-20-5; $C_2H_5SO_3F$, 371-69-7; CH_3NH_2, 74-89-5; *n*-$PrNH_2$, 107-10-8; *i*-$PrNH_2$, 75-31-0; cyclohexyl-NH_2, 108-91-8; benzyl-NH_2, 100-46-9; $C_6H_5NH_2$, 62-53-3; $NH_2CH_2CH_2N(CH_3)_2$, 108-00-9; $NH_2CH(CH_3)C(=O)OCH_3$·HCl, 2491-20-5; $NH_2CH_2(CH_2)_3OH$, 156-87-6; $HNMe_2$, 124-40-3; piperidine, 110-89-4; morpholine, 110-91-8; $H_2N(CH_2)_3NH_2$, 109-76-2; *o*-$C_6H_4(NH_2)_2$, 95-54-5; $H_2NCH(CH_3)CH_2NH_2$, 78-90-0; $H_2NC(CH_3)_2CH_2NH_2$, 811-93-8; $H_2N(CH_2)_2NHCH_3$, 109-81-9; $H_2N(CH_2)_2NH_2$, 107-15-3; $H_2N(CH_2)_2NH_3^+Ts^-$, 14034-59-4; $H_2N(CH_2)_2OH$, 141-43-5; $H_2N(CH_2)_2SH$·HCl, 156-57-0; NH_3, 7664-41-7.

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