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SYNTHESIS, REACTIVITY, AND SPECTROSCOPIC STUDIES OF η^5-$C_5H_5(CO)(L)Fe[C(SCH_3)_2]^+$ CARBENE COMPLEXES

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Summary

Irradiation of $Cp(CO)_2Fe[C(SCH_3)_2]^+$ in CH_3CN solution with UV light produces high yields of $Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]^+$; the reaction appears to be general for other $Cp(CO)_2Fe[carbene]^+$ complexes. The CH_3CN ligand of $Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]^+$ is readily displaced by other ligands to form $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ ($L = P(OPh)_3, P(OCH_3)_3, PPh_3, AsPh_3, SbPh_3, CH_3NC, C_5H_5N$) in good yields. Carbon-13 NMR studies of the $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ complexes show a general downfield shift of the C(carbene) Resonance as Fe→C(carbene) π-backbonding is increased by changes in L. Temperature dependent ^1H NMR studies of the S—C(carbene) rotational barrier indicate that S→C(carbene) π-donation decreases as Fe→C(carbene) π-backbonding is increased by changing L. The reactivity of these complexes towards primary and secondary amines to form $Cp(CO)(L)Fe(CNR)^+$ and $Cp(CO)(L)Fe[C(SCH_3)NR_2]^+$ derivatives also decreases as Fe→C(carbene) π-backbonding is increased by varying L.

Introduction

Carbene complexes are of interest because of their importance in stoichiometric [1—4] as well as catalytic [4—6] organic syntheses. In hopes of more fully understanding the chemistry of carbene complexes, we have studied a series of $Cp(CO)_2Fe[C(XR)YR]^+$ ($Cp = \eta^5$-C_5H_5) carbene derivatives and found the reactivity and electronic environment of the carbene carbon to be strongly influenced by the π-donation ability of the heteroatomic groups, XR and YR [7—9]. We now wish to report on the effects of changing L in a series of Cp(CO)-

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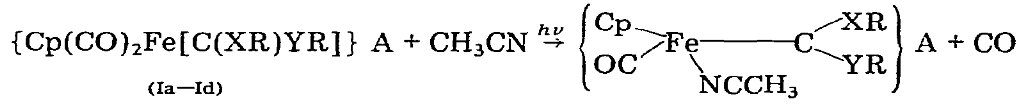
$(L)Fe[C(SCH_3)_2]^+$ carbene complexes on the bonding and reactivity of the carbene ligand.

Results and discussion

Photochemical synthesis of $Cp(CO)(CH_3CN)Fe[C(XR)YR]^+$ complexes. Photolysis of the $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes in acetonitrile solution result in the facile substitution of a CO ligand by CH_3CN to form the complexes $Cp(CO)(CH_3CN)Fe[C(XR)YR]^+$ (IIa—IId) (eq. 1).



$$\{Cp(CO)_2Fe[C(XR)YR]\}\,A + CH_3CN \xrightarrow{h\nu} \left\{\begin{matrix}Cp\\OC\end{matrix}\!>\!Fe(NCCH_3)\!-\!C\!<\!\begin{matrix}XR\\YR\end{matrix}\right\} A + CO \qquad (1)$$

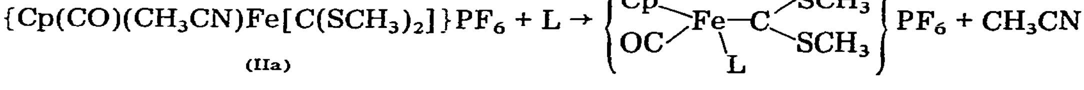
(Ia—Id) (IIa—IId)

(Ia, IIa: XR, YR = SCH_3; A = PF_6^-. IIa, 88%. Ib, IIb: XR, YR = SCH_3; A = $CF_3SO_3^-$. Ic, IIc: XR = OCH_3, YR = SCH_3; A = $CF_3SO_3^-$. IIc, 34%. Id, IId: XR = OCH_3, YR = NH_2; A = $CF_3SO_3^-$).

The photolysis proceeds equally well with 254 or 366 nm ultraviolet irradiation. Complex IIa is obtained in excellent yield as very stable, deep red crystals. The photolysis appears to be a general reaction for $Cp(CO)_2Fe[carbene]^+$ complexes as Ib—Id are also efficiently converted to IIb—IId. However, their $CF_3SO_3^-$ salts are reluctant to crystallize; IIb, IId form red oils, and crystals of IIc are isolated in fairly low yield.

Attempts to prepare complexes with other coordinating solvents have been unsuccessful. The photolysis of Ia in THF leads to slow decomposition of Ia with no evidence for the formation of $Cp(CO)(THF)Fe[C(SCH_3)_2]^+$. The photolysis of Ia in acetone leads to decomposition of Ia and what appears to be very slow formation of $Cp(CO)(acetone)Fe[C(SCH_3)_2]^+$ (ν(CO) ~1970 cm^{-1} in acetone) which could not be isolated.

Synthesis of $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ complexes. Photolysis of homogeneous CH_2Cl_2 solutions containing Ia and ligand under an N_2 atmosphere does not appear to produce any of the $Cp(CO)(L)[C(SCH_3)_2]^+$ complexes. However, preformation of the acetonitrile adduct, IIa, followed by its reaction with various ligands at room temperature in CH_2Cl_2 provides a good route to the ligand substituted carbene complexes, IIIa—IIIg (eq. 2).



$$\{Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]\}PF_6 + L \rightarrow \left\{\begin{matrix}Cp\\OC\end{matrix}\!>\!Fe(L)\!-\!C\!<\!\begin{matrix}SCH_3\\SCH_3\end{matrix}\right\} PF_6 + CH_3CN \qquad (2)$$

(IIa) (IIIa—IIIg)

(L = $P(OPh)_3$ (IIIa, 78%); L = $P(OCH_3)_3$ (IIIb, 49%); L = PPh_3 (IIIc, 58%);
L = $AsPh_3$ (IIId, 73%); L = $SbPh_3$ (IIIe, 74%); L = CH_3NC (IIIf, 65%);
L = C_5H_5N (IIIg, 67%))

All of the complexes, IIIa—IIIg, are stable, crystalline solids varying in color from deep red to bright yellow.

Stoichiometry is important in the reaction of IIa with CH_3NC (eq. 2). When slight excesses of CH_3NC are used, varying amounts of the bis(isocyanide) complex, $\{Cp(CH_3NC)_2Fe[C(SCH_3)_2]\}PF_6$ (IV), are also obtained presumably by thermal displacement of the CO ligand of IIIf by the excess of CH_3NC. This complex has not been obtained analytically pure, but it appears to be a stable, deep red, crystalline solid.

The reaction of IIa with $P(CH_2CH_3)_3$ or $P(Ph)_2CH_3$ results in the decomposition of IIa rather than in the formation of the expected ligand substituted carbene complex. These highly nucleophilic phosphines may react with the carbene ligand to form unstable ylide complexes [9,10]. The reaction of IIa with $N(CH_2CH_2)_3N$ also leads to decomposition, possibly for the same reason.

The reaction of IIa with an excess of $\{(CH_3CH_2)_4N\}I$ in CH_2Cl_2 under an N_2 atmosphere for 30 min produces a low yield of a neutral mono-carbonyl complex with spectra consistent with the expected product, $Cp(CO)(I)Fe[C(SCH_3)_2]$ (IR (CH_2Cl_2): 1958s cm^{-1}; ^1H NMR (CS_2): τ 5.44 (s, C_5H_5), 6.85 (s, 2 SCH_3)). However, this complex does not appear to be very stable and crystals have not been obtained. The reaction of IIa with stoichiometric amounts of $\{PhCH_2(CH_3CH_2)_3N\}Cl$ or $\{PPN\}Cl$ under similar conditions for 8 h produces $Cp(CO)_2FeCl$ as the only organometallic product.

TABLE 1

INFRARED SPECTRA OF THE COMPLEXES IN CH_2Cl_2

Complex		ν(CN) (cm^{-1})	ν(CO) (cm^{-1})	k(CO) (mdyn/Å) [a]
$\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ [b]	Ia		2058s, 2017s	16.77
$\{Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]\}PF_6$	IIa	[c]	1997s	16.10
$\{Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]\}CF_3SO_3$	IIb	[c]	1994s	16.06
$\{Cp(CO)(CH_3CN)Fe[C(OCH_3)SCH_3]\}CF_3SO_3$	IIc	[c]	1999s	16.14
$\{Cp(CO)(CH_3CN)Fe[C(OCH_3)NH_2]\}CF_3SO_3$	IId	[c]	1983s	15.88
$\{Cp(CO)[P(OPh)_3]Fe[C(SCH_3)_2]\}PF_6$	IIIa		1985s	15.91
$\{Cp(CO)[P(OCH_3)_3]Fe[C(SCH_3)_2]\}PF_6$	IIIb		1981s	15.85
$\{Cp(CO)(PPh_3)Fe[C(SCH_3)_2]\}PF_6$	IIIc		1970s	15.67
$\{Cp(CO)(AsPh_3)Fe[C(SCH_3)_2]\}PF_6$	IIId		1969s	15.66
$\{Cp(CO)(SbPh_3)Fe[C(SCH_3)_2]\}PF_6$	IIIe		1965s	15.59
$\{Cp(CO)(CH_3NC)Fe[C(SCH_3)_2]\}PF_6$	IIIf	2203m	2001s	16.17
$\{Cp(CO)(C_5H_5N)Fe[C(SCH_3)_2]\}PF_6$	IIIg		1977s	15.78
$\{Cp(CH_3NC)_2Fe[C(SCH_3)_2]\}PF_6$	IV	2187s, 2161s		
$\{Cp(CO)_2Fe(CNCH_2Ph)\}PF_6$ [b]	V	2225m	2082s, 2042s	17.17
$\{Cp(CO)[P(OPh)_3]Fe(CNCH_2Ph)\}PF_6$	VIa	2196m	2023s	16.53
$\{Cp(CO)(PPh_3)Fe(CNCH_2Ph)\}PF_6$	VIc	2180m	1998s	16.12
$\{Cp(CO)(AsPh_3)Fe(CNCH_2Ph)\}PF_6$	VId	2177m	1997s	16.10
$\{Cp(CO)(CH_3NC)Fe(CNCH_2Ph)\}PF_6$	VIf	2225m, 2195s	2027vs	16.59
$\{Cp(CO)_2Fe[C(SCH_3)\overline{N(CH_2)_4CH_2}]\}PF_6$ [b]	VII		2047s, 2002s	16.55
$\{Cp(CO)(CH_3NC)Fe[C(SCH_3)\overline{N(CH_2)_4CH_2}\}PF_6$	VIII	2184m	1986s	15.93
$\{Cp(CO)(CH_3CN)Fe(CNCH_2Ph)\}PF_6$ [d]	IX	2188m	2013s	16.36

[a] Ref. 11. [b] Ref. 7. [c] ν(CN) of the CH_3CN ligand not observed. [d] In CH_3CN.

Spectroscopic studies. The IR, ^1H NMR, and ^{13}C NMR data for the complexes discussed herein are presented in Tables 1, 2 and 3, respectively. All $\nu(CO)$ force constants, $k(CO)$, are calculated by the method of Cotton and Kraihanzel [11].

The $k(CO)$ values of the $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ complexes decrease in the order: $CO > CH_3NC > CH_3CN > P(OPh)_3 > P(OCH_3)_3 > C_5H_5N > PPh_3 \approx AsPh_3 > SbPh_3$. With the exceptions of CH_3CN and C_5H_5N, this is the trend established for the decreasing π-acceptor/σ-donor ratios of these ligands [12—18]. The CH_3CN and C_5H_5N ligands are generally regarded as having lower π-acceptor/σ-donor ratios [16—22] than indicated by the $k(CO)$ values of the $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ carbene complexes. As for the $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ complexes, the $k(CO)$ values for the CH_3CN and C_5H_5N derivatives of the related $Cp(CO)_2FeL^+$ complexes [23—26] are also anomalously high. No unequivocal explanation of the apparently anomalous IR data for these iron CH_3CN and C_5H_5N complexes is evident, but one possibility is coupling of the $\nu(CO)$ mode with CH_3CN and C_5H_5N modes which results in unusually high approximate $k(CO)$ values [11,16].

It is also of interest that $\nu(CN)$ for IIIf and IV are 40—50 cm^{-1} less than the corresponding frequencies of $Cp(CO)_2Fe(CNCH_3)^+$ and $Cp(CO)Fe(CNCH_3)_2^+$ [24]. This is a reflection of the lower π-acceptor/σ-donor ratio for the dimethyl(dithio)carbene ligand as compared to CO [7]. A comparison of the $k(CO)$ values of Ia (16.77 mdyn/Å) and $\{Cp(CO)_2Fe(PPh_3)\}PF_6$ (16.74 mdyn/Å) [23]

TABLE 2

^1H NMR SPECTRA OF THE COMPLEXES IN ACETONE-d_6 (τ) [a]

Complex	C_5H_5	SCH_3	Other resonances
Ia [b]	4.43	6.73	
IIa	4.97	6.77	7.56 (CH_3CN)
IIc	4.91	7.37	5.11 (OCH_3), 7.54 (CH_3CN)
IId	5.11		5.92 (OCH_3), 7.60 (CH_3CN)
IIIa	4.85d [c]	6.93	2.63 (m, 3 C_6H_5)
IIIb	4.78d [d]	6.81	6.23 (d, 3 OCH_3) [e]
IIIc	4.81d [f]	6.94	2.42 (m, 3 C_6H_5)
IIId	4.76	6.91	2.51 (m, 3 C_6H_5)
IIIe	4.64	6.88	2.47 (m, 3 C_6H_5)
IIIf	4.80	6.80	6.35 (CH_3NC)
IIIg	4.79	7.01	1.47 (dd, *o*-C_5H_5N), 2.05 (tt, *p*-C_5H_5N), 2.63 (tt, *m*-C_5H_5N)
IV [g]	5.35	6.95	6.56 (2 CH_3NC)
V [b]	4.34		2.66 (C_6H_5), 4.83 (CH_2)
VIa	5.07d [d]		2.58 (m, 4 C_6H_5), 4.83 (d, CH_2) [f]
VIc	4.82d [h]		2.46 ($PhCH_2NC$), 2.64 (m, PPh_3), 5.05 (d, CH_2) [i]
VId [g]	4.98		2.68 (m, 4 C_6H_5), 5.23 (CH_2)
VIf	4.64		2.53 (C_6H_5), 4.80 (CH_2), 6.39 (CH_3NC)
VII [j]	4.45	7.09	5.62 (m, 2 NCH_2), 8.13 (m, 3 CH_2)
VIII [g]	5.07	7.22	5.65 (t, NCH_2), 5.84 (t, NCH_2), 6.56 (CH_3NC), 8.23 (m, 3 CH_2)
IX	4.79		2.53 (C_6H_5), 4.92 (CH_2), 7.61 (CH_3CN)

[a] All resonances are singlets unless otherwise indicated. [b] Ref. 7. [c] J(PFeCH) 1.1 Hz. [d] J(PFeCH) 1.2 Hz. [e] J(POCH) 11.5 Hz. [f] J(PFeCH) 1.5 Hz. [g] In CD_3CN. [h] J(PFeCH) 1.6 Hz. [i] J(PFeCH) 1.8 Hz. [j] Ref. 7, NCH_2 resonances have been reassigned.

TABLE 3

^{13}C NMR SPECTRA OF THE COMPLEXES IN CD_3CN (ppm) [a]

Complex	C(carbene)	CO	C_5H_5	SCH_3	Other Resonances
Ia [b]	304.3	210.1	89.2	30.3	
IIa [c]	321.2	216.4	85.0	28.1	136.1 (br, CH_3CN), 4.0 (CH_3CN)
IIc [c]	313.0	215.9	84.9	19.9	69.9 (OCH_3), 4.2 (CH_3CN) [d]
IIIa	310.2d [e]	214.9d [f]	87.5	29.9	151.2 (d) [g], 131.0, 127.0, and 122.0 (3 C_6H_5)
IIIb	314.3d [e]	215.3d [h]	86.9	29.5	54.8 (d, 3 OCH_3) [i]
IIIc	317.7d [j]	218.0d [e]	87.7	29.7	130.8 (m, 3 C_6H_5)
IIId	317.5	217.4	86.1	29.9	133.9, 133.3, 131.7, and 130.3 (3 C_6H_5)
IIIe	316.1	216.4	84.9	30.2	135.9, 132.1, 130.8, and 130.4 (3 C_6H_5)
IIIf	315.8	214.9	86.8	29.6	151.6 (br, CH_3NC), 31.9 (br, CH_3NC)
IIIg	319.6	218.6	88.0	28.0	158.9, 139.5, and 127.1 (C_5H_5N)
IV	325.6		84.3	29.0	159.9 (br, 2 CH_3NC), 31.7 (br, 2 CH_3NC)
VII [k]	237.6	211.4	89.2	26.4	64.9 (NCH_2), 59.5 (NCH_2), 27.7 (NCH_2CH_2), 27.3 (NCH_2CH_2), 24.0 (CH_2)
VIII	248.1	216.7	86.2	25.1	154.5 (br, CH_3NC), 64.5 (NCH_2), 58.3 (NCH_2), 31.9 (br, CH_3NC), 28.2 (NCH_2CH_2), 27.4 (NCH_2CH_2), 24.4 (CH_2)

[a] All resonances are singlets unless otherwise indicated. [b] Ref. 8. [c] In acetone-d_6. [d] CH_3CN resonance not observed. [e] J(PFeC) 29.3 Hz. [f] J(PFeC) 43.0 Hz. [g] J(POC) 9.8 Hz. [h] J(PFeC) 46.9 Hz. [i] J(POC) 7.8 Hz. [j] J(PFeC) 17.6 Hz. [k] Ref. 9.

indicates that the dimethyl(dithio)carbene ligand has a π-acceptor/σ-donor ratio which is very similar to that of the PPh_3 ligand.

It has been shown that the ^{13}C NMR chemical shift of a CO ligand, δ(CO), usually [12,27—30], but not always [31,32], moves to lower field as M→CO π-backbonding increases. For the $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ complexes, the δ(CO) values move to lower field as L is varied in the order: $CO > CH_3NC = P(OPh)_3 > P(OCH_3)_3 > CH_3CN = SbPh_3 > AsPh_3 > PPh_3 > C_5H_5N$. The ^{13}C NMR chemical shifts of the carbene carbons, δ(carbene), move to lower field in the order: $CO > P(OPh)_3 > P(OCH_3)_3 > CH_3NC \approx SbPh_3 > AsPh_3 \approx PPh_3 > C_5H_5N > CH_3CN$. With the exceptions of CH_3CN and the order of $SbPh_3$, $AsPh_3$, and PPh_3, the δ(CO) values follow the expected π-acceptor/σ-donor trend [12—18]. Except for the ordering of $SbPh_3$, $AsPh_3$ and PPh_3, the δ(carbene) values also follow this trend.

It has been shown that the barrier to rotation about the C(carbene)—O bond is lowered as the electron density on the carbene carbon is increased by varying the aryl carbene substituent in an extensive series of $(CO)_5CrC(OCH_3)C_6H_5X$ carbene complexes [33]. Temperature dependent ^1H-NMR spectra of the Cp(CO)(L)Fe$[C(SCH_3)_2]^+$ carbene complexes indicate that the barrier to rotation about the C(carbene)—S bonds is sensitive to changes in electron density on the iron atom. At room temperature, Ia, IIa, and IIIa—IIIg all have equivalent SCH_3 groups, but as the temperature is lowered, they become inequivalent because of *syn—anti* isomerization. These complexes are listed in Table 4 in their order

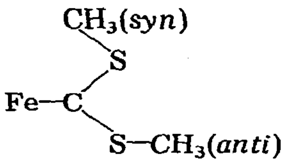


TABLE 4

TEMPERATURE DEPENDENT ^1H NMR SPECTRA OF THE CARBENE COMPLEXES ARISING FROM THE *syn*—*anti* ISOMERIZATION OF THE CARBENE LIGAND (IN ACETONE-d_6)

Complex	L	T_c (°C) [a]	$\Delta G^{\ddagger}$ (kcal/mol) [b]
Ia	CO	−2.5	13.6
IIa	CH_3CN	−28	12.2
IIIf	CH_3NC	−28	12.1
IIIc	PPh_3	−32	11.6
IIId	$AsPh_3$	−48	11.1
IIIb	$P(OCH_3)_3$	−53	11.0
IIIa	$P(OPh)_3$	−67	10.4
IIIe	$SbPh_3$	−60	10.3
IIIg	C_5H_5N	−71	10.1

[a] ±2°C. [b] ±0.2 kcal/mol.

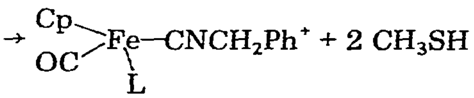
of decreasing free energies of activation, $\Delta G^{\ddagger}$ (calculated from the coalescence temperatures and peak widths at half height using the Eyring equation [34]), for this isomerization. The greatest source of error [34] in the determination of these approximate values is the accuracy of the coalescence temperatures. While the differences in some of the $\Delta G^{\ddagger}$ values appear to be within experimental error, they generally follow the established trend [12—18] for the π-acceptor/σ-donor ratios of the ligands. The higher barriers to rotation of PPh_3 and $AsPh_3$ complexes as compared to those of $P(OCH_3)_3$ and $P(OPh)_3$ is unexpected; the bulkiness [35] of the PPh_3 and $AsPh_3$ ligands may increase the barriers to rotation in these complexes. There is no obvious reason for the unusually high barrier to rotation in the CH_3CN complex.

Reactions of the Cp(CO)(L)Fe[C(SCH₃)₂]⁺ carbene complexes with amines. Increased Fe→C(carbene) π-backbonding resulting from variations in the π-acceptor/σ-donor ratios of the ligands, L, is manifested in the reactivities of Ia and IIIa, IIId, IIIf. Complexes Ia and IIIa, IIId, IIIf all react at room temperature with benzylamine to give isocyanide derivatives (eq. 4), but only Ia and IIIf react with piperidine to form amino-thiocarbene complexes (eq. 5).

$$Cp(CO)(L)Fe[C(SCH_3)_2]^+ + PhCH_2NH_2$$

(Ia, IIIa, IIId, IIIf)

(4)

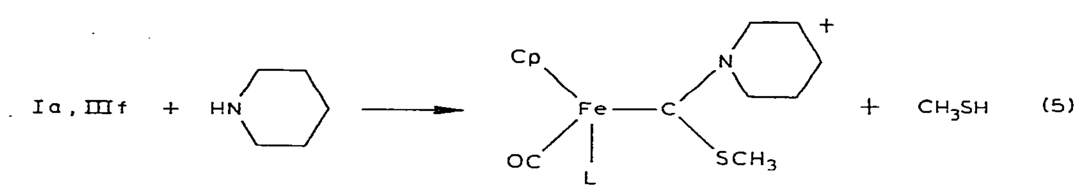


$$\rightarrow Cp(OC)(L)Fe{-}CNCH_2Ph^+ + 2\,CH_3SH$$

(V, VIa, VId, VIf)

(L = CO (Ia → V, 88%); L = $P(OPh)_3$ (IIIa → VIa, 87%); L = $AsPh_3$ (IIId → VId, 57%); L = CH_3NC (IIIf → VIf, 58%))

The phosphine complex, IIIc, also reacts with benzylamine to yield the corresponding isocyanide complex, VIIc, but it has not been fully characterized. Stoichiometry is important in the reaction of IIIf with primary amines (eq. 4). If too large an excess of amine is used, the bis(isocyanide) complex, VIf, which forms will react further to produce diaminocarbene complexes by addition of amine across a C≡N bond [24,36,37].



(VII, VIII)

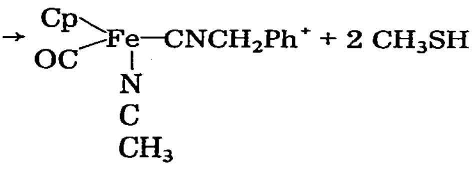
L = CO (VII, 69%) [7] ; L = CH_3NC (VIII, 73%)

To determine the relative reactivities of these $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ complexes, equimolar amounts of two of the complexes were placed in CH_2Cl_2 or CH_3CN solutions, and the reactions with excess (2—5 fold) benzylamine were monitored by IR spectroscopy. Although overlap of the ν(CN) and ν(CO) bands between the complexes precluded the determination of accurate reaction rates, the observation of bands due to the slower reacting carbene complex remaining after the faster reacting carbene complex had been consumed establishes the following order of decreasing rates of reaction with changes in L: $CO > CH_3NC > P(OPh)_3 > AsPh_3$. This is also the order of decreasing π-acceptor/σ-donor ratios for these ligands [12—18], which suggests that electron-donor L groups increase electron density on the carbene carbon and reduce its rate of reaction with the nucleophilic amine. The lower electron donor properties of CO and CH_3NC account for the fact that Ia and IIIf react with piperidine (eq. 5), while IIIa and IIId do not. The reactivity of CO ligands towards nucleophiles has also been shown to decrease as M→CO π-backbonding increases [24,38,39].

The acetonitrile complex, IIa, which has unexpected IR, ^{13}C NMR, and temperature dependent ^1H NMR spectra, also displays rather unusual reactivity patterns. It reacts very slowly (24 h) with a ten-fold excess of benzylamine in CH_2Cl_2 to give a very low yield, by IR, of the corresponding isocyanide complex (eq. 6).

$Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]^+ + PhCH_2NH_2 \rightarrow$

(IIa)



$$\rightarrow Cp(OC)(CH_3CN)Fe{-}CNCH_2Ph^+ + 2\ CH_3SH \qquad (6)$$

(IX)

The only reaction observed between IIa and one equivalent of piperidine in CH_3CN is slow decomposition of IIa. These results are not unexpected, based on the assumed high electron donor ability of CH_3CN. This contrasts, however, with the rapid reaction of IIa with one equivalent of benzylamine in CH_3CN solution (eq. 6). Within two minutes of adding the amine, the IR spectrum of the reaction solution shows no bands for IIa, but rather absorption bands corresponding to IX and a band at 1985s cm^{-1} are observed. The band at 1985 cm^{-1}

gradually disappears as the bands for IX grow in intensity. After approximately one hour, only IX is present. Complex IX is a yellow oil which is isolated in low (29%) yield and is characterized by its IR and ^{1}H NMR spectra (Tables 1 and 2). The band at 1985 cm^{-1} could correspond to $\mathrm{Cp(CO)(PhCH_2NH_2)Fe[C(SCH_3)_2]^+}$ or $\mathrm{Cp(CO)(CH_3CN)Fe[C(SCH_3)NHCH_2Ph]^+}$. Reactions of other $\mathrm{Cp(CO)(L)Fe[C(SCH_3)_2]^+}$ derivatives with amines do not show this solvent dependence, and the unique characteristics of $\mathrm{Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]^+}$ are not presently understood.

Experimental

General information. Reagent grade chemicals were used without further purification; $\mathrm{\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6}$ (Ia) [7], $\mathrm{\{Cp(CO)_2Fe[C(SCH_3)_2]\}CF_3SO_3}$ (Ib) [8], $\mathrm{\{Cp(CO)_2Fe[C(OCH_3)SCH_3]\}CF_3SO_3}$ (Ic) [8], $\mathrm{\{Cp(CO)_2Fe[C(OCH_3)NH_2]\}CF_3SO_3}$ (Id) [9], $\mathrm{\{Cp(CO)_2Fe(CNCH_2Ph)\}PF_6}$ (V) [7], and $\mathrm{\{Cp(CO)_2Fe[C(SCH_3)\overline{N(CH_2)_4CH_2}]\}PF_6}$ (VII) [7] were prepared as reported previously. All irradiations were performed at 254 nm in borosilicate glassware equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, Mass. The irradiations and subsequent $\mathrm{CH_3CN}$ displacement reactions were carried out under an $\mathrm{N_2}$ atmosphere using solvents which were dried over $\mathrm{CaSO_4}$ and purged with $\mathrm{N_2}$, although these precautions did not appear to be necessary. These precautions were not used for the reactions of $\mathrm{Cp(CO)(L)Fe[C(SCH_3)_2]^+}$ with amines which were all run at room temperature. Infrared spectra were recorded on a Perkin—Elmer 281 spectrophotometer. All NMR studies were performed on a Jeol FX-90Q spectrometer; $\mathrm{Cr(acac)_3}$ (~0.1 *M*) was added to the ^{13}C samples to reduce data collection time [40]. Tetramethylsilane (TMS) was employed as the internal standard for all NMR spectra.

Preparation of the complexes. $\mathrm{\{Cp(CO)(CH_3CN)Fe[C(SCH_3)_2]\}PF_6}$ *(IIa).* A 35 ml solution of $\mathrm{CH_3CN}$ containing Ia (0.10 g, 0.23 mmol) was irradiated at 254 nm until the ν(CO) bands of Ia had disappeared (1—2 h). During this time, gas evolution was apparent, and the solution gradually changed color from bright yellow to red. The solution was then evaporated to a red oil which was washed with $\mathrm{Et_2O}$. This oil was crystallized from $\mathrm{CH_2Cl_2}$ with $\mathrm{Et_2O}$ at —20°C to give 0.091 g (88%) of IIa as dark red crystals. M.p. 121—124°C dec. Anal. Found: C, 30.06; H, 3.26; N, 3.10. $\mathrm{C_{11}H_{14}F_6FeNOPS_2}$ calcd.: C, 29.95; H, 3.20; N, 3.17%.

$\mathrm{\{Cp(CO)(CH_3CN)Fe[C(OCH_3)SCH_3]\}CF_3SO_3}$ *(IIc).* This complex was prepared by the method used for IIa. Thus, the irradiation of Ic (0.060 g, 0.14 mmol) for 1 h afforded 0.021 g (34%) of IIc as red needles. M.p. 81—83°C. Anal. Found: C, 33.29; H, 3.25; N, 3.13. $\mathrm{C_{12}H_{14}F_3FeNO_5S_2}$ calcd.: C, 33.58; H, 3.29; N, 3.26%.

$\mathrm{\{Cp(CO)[P(OPh)_3]Fe[C(SCH_3)_2]\}PF_6}$ *(IIIa).* Crude IIa, generated from 0.500 g (1.13 mmol) of Ia, was dissolved in 20 ml of $\mathrm{CH_2Cl_2}$ containing $\mathrm{P(OPh)_3}$ (350 μl, 1.34 mmol), and the solution was stirred for 6 h at room temperature. The resulting yellow-brown solution was then evaporated to dryness, and the yellow residue was washed with $\mathrm{Et_2O}$. Crystallization of this residue from acetone with $\mathrm{Et_2O}$ at —20°C yielded 0.63 g (78%) of IIIa as dark yellow crystals.

M.p. 133—135°C. Anal. Found: C, 45.25; H, 3.65. $C_{27}H_{26}F_6FeO_4P_2S_2$ calcd.: C, 45.65; H, 3.69%.

{Cp(CO)[P(OCH$_3$)$_3$]Fe[C(SCH$_3$)$_2$]}PF$_6$ (IIIb). Trimethylphosphite (28 μl, 0.24 mmol) was stirred at room temperature with crude IIa, generated from Ia (0.10 g, 0.23 mmol), in 20 ml of CH_2Cl_2 for 5 h. The red solution was then evaporated to an oil which was washed with Et_2O and crystallized from CH_2Cl_2 with Et_2O at —20°C. The yield of IIIb, as orange crystals, was 0.060 g (49%). M.p. 195°C dec. Anal. Found: C, 27.56; H, 3.80. $C_{12}H_{10}F_6FeO_4P_2S_2$ calcd.: C, 27.50; H, 3.85%.

{Cp(CO)(PPh$_3$)Fe[C(SCH$_3$)$_2$]}PF$_6$ (IIIc). This complex was prepared by the same method as for IIIb. The reaction of PPh_3 (0.061 g, 0.23 mmol) and IIa, from 0.10 g (0.23 mmol) of Ia, afforded 0.089 g (58%) of IIIc as bright orange crystals after several recrystallizations from CH_2Cl_2 with Et_2O at —20°C to remove an unidentified black tar and a tan phosphorus-containing species. M.p. 205°C dec. Anal. Found: C, 48.70; H, 3.99. $C_{27}H_{26}F_6FeOP_2S_2$ calcd.: C, 48.96; H, 3.96%.

{Cp(CO)(AsPh$_3$)Fe[C(SCH$_3$)$_2$]}PF$_6$ (IIId). The method used to prepare IIIb was also used for this complex. A 73% yield (0.12 g) of IIId was obtained from the reaction of IIa, from 0.10 g (0.23 mmol) of Ia, and $AsPh_3$ (0.071 g, 0.23 mmol). M.p. 180—184°C dec. Anal. Found: C, 45.98; H, 3.67. $C_{27}H_{26}AsF_6FeOPS_2$ calcd.: C, 45.91; H, 3.71%.

{Cp(CO)(SbPh$_3$)Fe[C(SCH$_3$)$_2$]}PF$_6$ (IIIe). This derivative was prepared by the method used for IIIb. The reaction of IIa, generated from Ia (0.10 g, 0.23 mmol), and $SbPh_3$ (0.082 g, 0.23 mmol) afforded 0.13 g (74%) of IIIe as red needles. M.p. 165°C dec. Anal. Found: C, 43.19; H, 3.77. $C_{27}H_{26}F_6FeOPS_2Sb$ calcd.: C, 43.06; H, 3.48%.

{Cp(CO)(CH$_3$NC)Fe[C(SCH$_3$)$_2$]}PF$_6$ (IIIf). The reaction of CH_3NC (13.5 μl, 0.230 mmol) and IIa, prepared from 0.10 g (0.23 mmol) of Ia, by the method used for IIIb afforded 0.065 g (65%) of IIIf as orange-red crystals. M.p. 128—130°C. Anal. Found: C, 29.89; H, 3.29; N, 3.53. $C_{11}H_{14}F_6FeNOPS_2$ calcd.: C, 29.95; H, 3.20; N, 3.17%.

{Cp(CO)(C$_5$H$_5$N)Fe[C(SCH$_3$)$_2$]}PF$_6$ (IIIg). This complex was prepared by the route used for IIIb. Starting with pyridine (19 μl, 0.23 mmol) and IIa, from Ia (0.10 g, 0.23 mmol), 0.075 g (67%) of IIIg was isolated as dark red crystals. M.p. 112—115°C dec. Anal. Found: C, 35.04; H, 3.37; N, 2.87. $C_{14}H_{16}F_6FeNOS_2P$ calcd.: C, 35.09; H, 3.37; N, 2.92%.

{Cp(CO)[P(OPh)$_3$]Fe(CNCH$_2$Ph)}PF$_6$ (VIa). Complex IIIa (0.10 g, 0.14 mmol) was stirred with $PhCH_2NH_2$ (30 μl, 0.27 mmol) in 20 ml of CH_3CN for 9 h. The yellow solution was then evaporated to dryness, and the residue was washed with hexanes. Crystallization of the residue from CH_2Cl_2 with Et_2O at —20°C yielded 0.088 g (87%) of VIa as yellow crystals. M.p. 126—128°C. Anal. Found: C, 52.90; H, 3.79; N, 1.90, $C_{32}H_{27}F_6FeNO_4P_2$ calcd.: C, 53.28; H, 3.77; N, 1.94%.

{Cp(CO)(AsPh$_3$)Fe[CNCH$_2$Ph]}PF$_6$ (VId). Benzylamine (62 μl, 0.57 mmol) and IIId (0.040 g, 0.057 mmol) were stirred in 10 ml of CH_3CN for 18 h. The solution was then evaporated to a yellow oil which was washed with hexanes. The oil was crystallized from CH_2Cl_2 with Et_2O at —20°C to give 0.023 g (57%) of VId as small yellow crystals. M.p. 293—295°C. Anal. Found: C, 53.39; H,

3.80; N, 1.88. $C_{32}H_{27}AsF_6FeNOP$ calcd.: C, 53.58; H, 3.79; N, 1.95%.

{Cp(CO)(CH₃NC)Fe(CNCH₂Ph)}PF₆ (VIf). A solution of 20 ml of CH_3CN containing IIIf (0.10 g, 0.23 mmol) and $PhCH_2NH_2$ (27 μl, 0.25 mmol) was stirred for 4 h. The yellow solution was then evaporated to a yellow oil which could not be induced to crystallize. The yield of VIf was approximately 0.060 g (58%). It was characterized by its infrared and ^1H NMR spectra (Tables 1 and 2).

$\{Cp(CO)(CH_3NC)Fe[C(SCH_3)\overline{N(CH_2)_4CH_2}]\}PF_6$ *(VIII).* Complex IIIf (0.10 g 0.23 mmol) was stirred with piperidine (225 μl, 2.27 mmol) in 20 ml of CH_3CN for 6 h. The resulting yellow solution was evaporated to an oil which was washed with hexanes. The oil was crystallized from CH_2Cl_2 with Et_2O at −20°C to afford 0.079 g (73%) of VIII as irregular, glass-like, yellow crystals. M.p. 75–78°C. Anal. Found: C, 37.31; H, 4.45; N, 5.60. $C_{15}H_{21}F_6FeN_2OPS$ calcd.: C, 37.67; H, 4.43; N, 5.86%.

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