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Reactions of η^5-$C_5H_5(CO)_2Fe[C(XR)YR]^+$ Carbene Complexes, Where X and Y Are O, S, Se, and/or NR, with Amines

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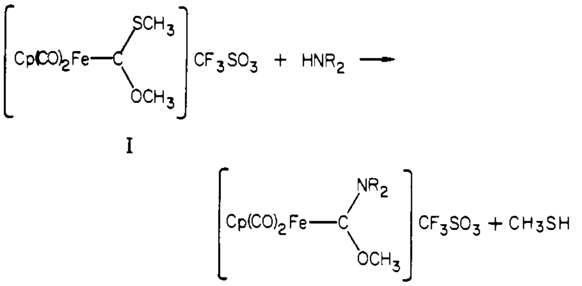
Reactions of $Cp(CO)_2Fe[C(XR)YR]^+$ with amines occur at the carbene ligand when X, Y = O, S, and/or Se and the product distribution is dependent upon the leaving-group abilities of the carbene substituents ($PhSe^- \approx PhS^- > PhO^- > CH_3S^- > CH_3O^-$). When both carbene substituents are good leaving groups ($PhSe^-$, PhS^-, PhO^-, or CH_3S^-), $Cp(CO)_2Fe[C(XR)YR]^+$ reacts with primary amines to give isocyanide complexes, $Cp(CO)_2FeCNR^+$, and with secondary amines to form carbene derivatives, $Cp(CO)_2Fe[C(XR)NR_2]^+$. When only one carbene substituent is a good leaving group, $Cp(CO)_2Fe[C(XR)YR]^+$ yields carbene derivatives, $Cp(CO)_2Fe^+[C(XR)NRR']^+$ ($XR = OCH_3$; R′ = R, H), upon reaction with primary or secondary amines. When both carbene substituents are poor leaving groups (CH_3O^-), a complex mixture of products generally results on reaction with amines. A mechanism involving formation of an ylide intermediate, $Cp(CO)_2Fe[C(XR)(YR)NR_3]^+$, is proposed to account for these results. Spectroscopic studies (IR and ^{13}C NMR) show that N → C(carbene) π donation increases as the basicity of the amine group increases for the $Cp(CO)_2Fe[C(OCH_3)NR_2]^+$ complexes.

Introduction

Transition-metal carbene complexes are of interest as they may be reactive intermediates in several catalytic[2,3] and stoichiometric[3-6] organic reactions. Although there have been numerous reports concerning the preparation of carbene complexes,[3-7] few systematic studies on the reactivity of carbene ligands with two heteroatomic substituents have been reported.[8] The availability of a variety of $Cp(CO)_2Fe[C(XR)YR]^+$ ($Cp = \eta^5$-C_5H_5) carbene complexes, where X and Y are O, S, Se, and/or NR,[8,9] has allowed us to compare the electronic environment of the carbene carbon in these complexes by the use of IR, ^1H NMR, and ^{13}C NMR spectroscopy. We now report on the effect of these various substituents on the electrophilic reactivity of the carbene ligand toward amines. The electronic effects of the heteroatomic carbene substituents are studied further by spectroscopic analysis of the new carbene complexes reported herein.

Results

Reactions of $\{Cp(CO)_2Fe[(SCH_3)OCH_3]\}CF_3SO_3$ (I) with Amines. Complex I reacts readily at room temperature with a variety of amine reagents by exclusive nucleophilic substitution of the CH_3S group to give a series of new aminooxocarbene complexes (eq 1). Complex IId is not obtained pure but is contaminated with IIa due to some ammonia impurity present in the CH_3NH_2(g) used. Complexes IIa-f are all very stable, crystalline solids which are soluble in polar organic solvents.


I

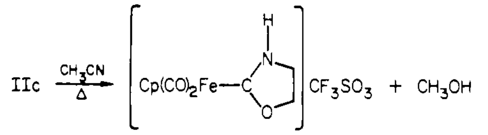
(1)

$HNR_2 = NH_3$ (IIa, 81%)
$= NH_2CH_2Ph$ (IIb, 53%)
$= NH_2(CH_2)_2OH$ (IIc, 68%)
$= NH_2CH_3$ (IId, 50%)
$= NH(CH_3)_2$ (IIe, 68%)
$= \overline{NH(CH_2)_4CH_2}$ (IIf, 60%)

Intramolecular extrusion of CH_3OH may be seen when IIb-d are exposed to elevated temperatures. Partial conversions of IIb,d to the corresponding isocyanide complexes, as identified by their IR spectra,[8] occur when the complexes are heated in the solid state to temperatures (150-165 °C) well above their melting points for a few minutes (eq 2). Evolution

$$\text{IIb,d} \xrightarrow[\Delta]{} \{Cp(CO)_2FeCNR\}CF_3SO_3 + CH_3OH \quad (2)$$
$$R = CH_2Ph\ (\text{IIIb}),\ CH_3\ (\text{IIId})$$

of gas, presumably methanol, is evidenced by slow and continuous bubbling of the melts. Refluxing IIb in CH_3CN, however, produces no isocyanide complex; after 35 h, only starting material is recovered. Complex IIc loses methanol under milder conditions than do IIb,d. Refluxing IIc in acetonitrile for 12 h produces the cyclic aminooxocarbene complex which had been reported earlier as a PF_6^- salt[8] (eq 3).


(3)

IIIc (81%)

Reactions of $\{Cp(CO)_2Fe[C(OCH_3)_2]\}PF_6$ (IV) with Amines. Complex IV seems to react with amines in a manner similar to that of I. However, the yields of aminooxocarbene products are much lower (less than 20%), and several other uncharacterized products are observed. For example, the reaction of IV with benzylamine produces a 17% yield of the PF_6^- salt of IIb and a large quantity of a complex mixture of neutral

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[1] Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Energy Research, Office of Energy Research, Grant WPAS-KC-03-02-01.

[2] (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-103. (b) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. Ibid. **1979**, *17*, 449-92.

[3] Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99-144.

[4] Cardin, D. F.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545-574.

[5] Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487-613.

[6] Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353-372.

[7] Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407-23.

[8] McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231-1235.

[9] McCormick, F. B.; Angelici, R. J. *Inorg. Chem.*, preceding paper in this issue.

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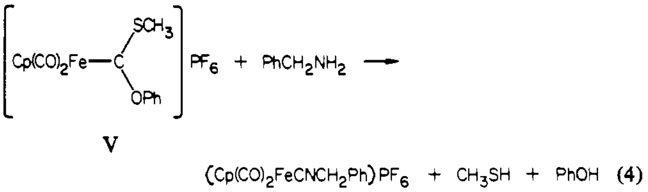
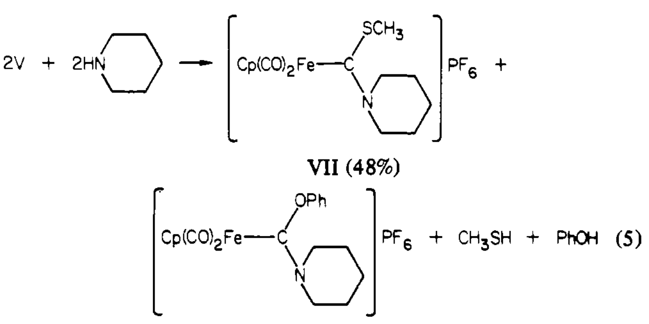
organometallic species which includes $[CpFe(CO)_2]_2$ and $Cp(CO)_2FeC(=O)OCH_3$.[10] The reaction of IV with piperidine forms only trace amounts of the PF_6^- salt of IIf and the same mixture of neutral species. Reacting IV with $(CH_3)_3N$ also produces this complex mixture of neutral species. The IR spectra of all of these reaction solutions show two strong bands, one at 2023–2035 cm^{-1} and the other at 1964–1980 cm^{-1}, as the major absorptions, but upon evaporation the complex mixture of products results.

Reactions of $\{Cp(CO)_2Fe[C(SCH_3)OPh]\}PF_6$ (V) with Amines. Complex V behaves rather differently than I toward amines. With benzylamine at room temperature, complex V yields the isocyanide complex by displacement of both carbene substituents (eq 4). This reaction is similar to that of $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ with primary amines to give isocyanide complexes.[8] With piperidine, a mixture of carbene complexes is obtained (eq 5). Since this mixture has not been separated, the yields are based on the ^1H NMR spectrum of the mixture. Complex VII is identified from its previously reported spectra.[8]



V

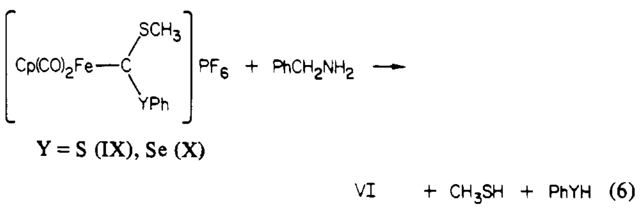
VI (90%)



VII (48%)

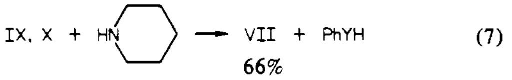
VIII (18%)

Reactions of $\{Cp(CO)_2Fe[C(SCH_3)SPh]\}PF_6$ (IX) and $\{Cp(CO)_2Fe[C(SCH_3)SePh]\}PF_6$ (X) with Amines. Complexes IX and X show almost identical behavior toward amines and yield the same products as found in the reactions of $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$.[8] The reactions of IX and X with benzylamine produce the isocyanide complex VI (eq 6) and with piperidine, the amino-thiocarbene complex, VII, is formed (eq 7). Both IX and X give VII in identical yields, and there is no evidence for nucleophilic substitution of the CH_3S group by piperidine.



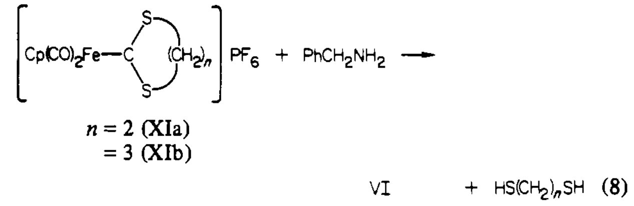
Y = S (IX), Se (X)

56–58%



66%

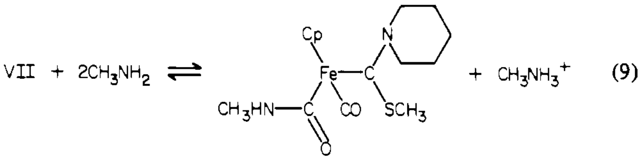
Reactions of $\{Cp(CO)_2Fe[\overline{CS(CH_2)_nS}]\}PF_6$ (n = 2 (XIa), n = 3 (XIb)) with Amines. Both of these complexes react in the same manner as $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ with benzylamine[8] to give the isocyanide derivative VI (eq 8). Complex XIa reacts cleanly to give VI in high yield, while XIb gives a cloudy reaction solution, a low yield of VI, and a large amount of an unstable, neutral species with bands at 2018 (s) and 1967 (s) cm^{-1} in its IR (CH_2Cl_2) spectrum and a Cp resonance at τ 5.22 in its ^1H NMR (CS_2) spectrum. Like $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$, complex XIa reacts with NH_3 to produce the neutral cyano complex $Cp(CO)_2FeCN$.[8] In contrast to $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$,[8] no aminothiocarbene complexes are produced in the reactions of XIa,b with secondary amines. The reactions of XIa with dimethylamine and the reaction of XIb with piperidine both produce new species with ν(CO) at 2027 (s) and 1978 (s) cm^{-1} in CH_2Cl_2; these species are not characterized further as they decompose to $[CpFe(CO)_2]_2$ upon attempted isolation. Similar results are obtained in the reaction of XIa and trimethylamine; a new species, with ν(CO) at 2019 (s) and 1968 (s) in CH_2Cl_2, forms but decomposes readily to $[CpFe(CO)_2]_2$.



n = 2 (XIa)
= 3 (XIb)

85% (from XIa)
32% (from XIb)

Reactions of $\{Cp(CO)_2Fe[C(SCH_3)\overline{N(CH_2)_4CH_2}]\}PF_6$ (VII) with Amines. In an earlier report, we noted that VII did not react with excess piperidine.[8] However, VII does react with some primary amines, but reaction does not occur at the carbene ligand. Reacting VII with excess methylamine produces a new species with one strong, broad absorption at 1909 cm^{-1} in the IR (CH_2Cl_2) spectrum of the reaction solution, but upon evaporation, only starting material is obtained. These observations are consistent with reversible carbamoyl formation (eq 9).[11-13] Similar behavior is seen in the reaction of VII with a large excess of benzylamine, but no reaction is observed between VII and cyclohexylamine, even when a large excess of amine is used.



Discussion

Mechanism. The results reported here support the formation of a transitory transition metal–ylide complex as suggested earlier for the reactions of $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ with amines.[14] The proposed first step of the reaction between the carbene complex $Cp(CO)_2Fe[C(XR)YR]^+$ (X, Y = O, S, Se) and an amine is nucleophilic attack at the carbene carbon to form an unstable ylide complex which reacts further to give the observed products (eq 10). In the ylide intermediate, the originally sp^2 hybridized carbene carbon becomes sp^3 hybridized, and the positive charge is transferred to the nitrogen atom. Support for such an ylide intermediate may be found

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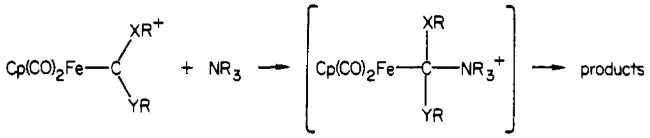
[10] King, R. B.; Bisnette, M. B.; Fronzaglia, A. *J. Organomet. Chem.* **1966**, *5*, 341–356. Busetto, L.; Angelici, R. J. *Inorg. Chim. Acta* **1968**, *2*, 391.

[11] Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335–41.

[12] Angelici, R. J.; Christian, P. A.; Dombek, B. D.; Pfeffer, G. A. *J. Organomet. Chem.* **1974**, *67*, 287–94.

[13] Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754–1758.

[14] McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A., submitted for publication.



(10)

in the isolation of neutral ylide complexes from the reactions of $(CO)_5M[carbene]$ (M = Cr, W) complexes with certain phosphines and tertiary amines.[15,16] A similar, but more complex, mechanism has also been proposed for the reaction of $(CO)_5CrC(OCH_3)Ph$ with primary amines to give aminocarbene complexes, $(CO)_5CrC(NHR)Ph$.[17]

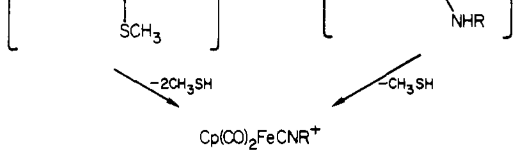
The ability of a $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complex to form an ylide intermediate when reacted with amines should be influenced by the amount of heteroatom π donation into the carbene carbon atom. Thus, in complex VII, the nitrogen atom is sufficiently π donating[9] to reduce the electrophilicity of the carbene carbon to the point that amine attack at the carbene carbon does not occur but rather reaction takes place at a CO ligand to reversibly form carbamoyl complexes (eq 9).[11-13]

The reactivity of the ylide intermediate seems to be controlled largely by the relative leaving-group abilities of the carbene substituents, RX^- and RY^-. Although the leaving groups are considered to be anions, the heteroatoms could be protonated before the groups dissociate. In the absence of mechanistic studies, little can be said about the details of the mechanisms of these reactions. The pK_a values of PhSH (6.50),[18] PhOH (9.99),[19] CH_3SH (10.3),[18] and CH_3OH (15.5)[19] suggest that the order of decreasing leaving-group ability of the corresponding anions should be $PhS^- > PhO^- > CH_3S^- > CH_3O^-$. Our results agree with this trend. The reactions of I, V, IX, and X with piperidine (eq 1, 5, and 7) indicate the order of decreasing leaving-group ability for RX^- and RY^- in the $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes to be $PhSe^- \approx PhS^- > PhO^- > CH_3S^- > CH_3O^-$.

The product distributions observed in the reactions of the various $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes with amines are quite logical considering this trend in leaving-group ability. Complexes V (eq 4), IX, X (eq 6), and $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$,[8] where both carbene substituents are good leaving groups ($PhSe^-$, PhS^-, PhO^-, or CH_3S^-), all react readily with primary amines to yield isocyanide complexes, $Cp(CO)_2FeCNR^+$. With piperidine, the better leaving groups of IX (PhS^-) and X ($PhSe^-$) (eq 7) are replaced exclusively, giving aminocarbene complexes. Complex V (eq 5) reacts with piperidine to give a mixture of aminocarbene complexes resulting from the displacement of either substituent. The somewhat higher yield of the PhO^--displaced product suggests that it is a slightly better leaving group than CH_3S^-. Complex I, in which only one of the carbene substituents (CH_3S^-) is a good leaving group, reacts readily with primary and secondary amines (eq 1) to give aminooxocarbene complexes by displacement of the good leaving group. When both carbene substituents are poor leaving groups (CH_3O^-), as in IV, the reactions with primary and secondary amines give very low yields of aminooxocarbene complexes and a variety of other species, possibly including unstable ylide intermediates (eq 10).

On the basis of the pK_a values[18] of the parent dithiols of the cyclic dithiocarbene complexes XIa,b, $\{Cp(CO)_2Fe[\overline{CS(CH_2)_nS}]\}PF_6$ (n = 2, 3), these carbenes would be expected to react with amines much like $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$.[8] However, only the five-membered ring complex, XIa (eq 8), reacts well with benzylamine to give the corresponding isocyanide derivative, and neither complex forms aminothiocarbene complexes when reacted with secondary amines. These results suggest that the dithio groups in the cyclic carbene complexes have a poorer leaving-group ability than CH_3S^-. This is probably due to the stability of the five- and six-membered ring systems. The higher yield of isocyanide complex from XIa than from XIb (eq 8) may be a consequence of strain in the five-membered ring allowing for easier cleavage of a C–S bond.

The reactions of $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ with primary amines to give isocyanide complexes[8] could go by either concerted loss of two CH_3SH molecules from the ylide intermediate or by stepwise loss of CH_3SH via a transitory aminothiocarbene complex (eq 11). The formation of aminooxocarbene complexes in the reactions of I with primary amines (eq 1) and their thermal conversion to isocyanide complexes (eq 2) support the stepwise mechanism but do not exclude the concerted pathway. The relative ease with which IIc is converted to IIIc (eq 3), as compared to the conversions of IIb,d to IIIb,d (eq 2), indicates that the ring closure does not proceed through an isocyanide intermediate. These results suggest that the reactions of $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ with diamines, amino alcohols, and amino thiols[8] may also proceed through a carbene intermediate (eq 12) rather than an isocyanide intermediate, $Cp(CO)_2FeCN\frown YH^+$, where Y = O, S, NR, or NH.



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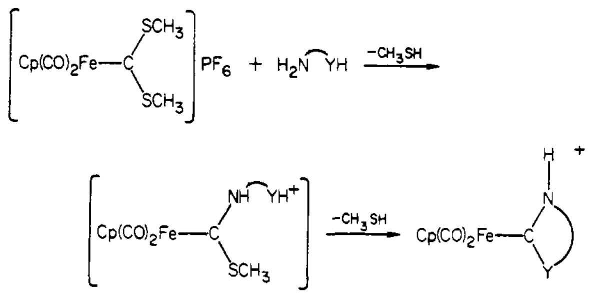

(12)

Y = O, S, NR, or NH

Spectroscopic Analysis. Spectroscopic data for the new complexes are shown in Tables I–III, and the ν(CO) force constants, k(CO), discussed are calculated by the method of Cotton and Kraihanzel.[20]

We have shown that no correlation exists between k(CO) and the ^{13}C NMR chemical shift of the CO ligands, δ(CO), for $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes,[9] and the aminooxocarbene complexes reported herein show the same lack of correlation. In fact, their δ(CO) values are fairly constant, varying over a 0.7-ppm range. As observed for other $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes,[9] the amino-

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(15) Kreissl, F. R.; Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 643, 644.

(16) Fischer, H. *J. Organomet. Chem.* **1979**, *170*, 309–317 and references therein.

(17) Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367–389.

(18) Crampton, M. R. In "The Chemistry of the Thiol Group"; Patai, S., Ed.; Wiley: New York, 1974; Vol. I, pp 379–415.

(19) Rochester, C. H. In "The Chemistry of the Hydroxyl Group"; Patai, S., Ed.; Wiley: New York, 1971; Vol. I, pp 327–92.

(20) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432–4438.

Table I. Infrared Spectra of the Complexes in CH_2Cl_2

complex	ν(CO),[a] cm^{-1}	k(CO),[b] mdyn/Å
$\{Cp(CO)_2Fe[C(OCH_3)NH_2]\}CF_3SO_3$ (IIa)	2059, 2012	16.73
$\{Cp(CO)_2Fe[C(OCH_3)NHCH_2Ph]\}CF_3SO_3$ (IIb)	2058, 2006	16.68
$\{Cp(CO)_2Fe[C(OCH_3)NH(CH_2)_2OH]\}CF_3SO_3$ (IIc)	2058, 2006	16.68
$\{Cp(CO)_2Fe[C(OCH_3)NHCH_3]\}CF_3SO_3$ (IId)	2056, 2005	16.65
$\{Cp(CO)_2Fe[C(OCH_3)N(CH_3)_2]\}CF_3SO_3$ (IIe)	2048, 2001	16.55
$\{Cp(CO)_2Fe[C(OCH_3)N(CH_2)_4CH_2]\}CF_3SO_3$ (IIf)	2048, 2002	16.56
$\{Cp(CO)_2Fe[CO(CH_2)_2NH]\}CF_3SO_3$ (IIIc)	2062, 2017	16.80
$\{Cp(CO)_2Fe[C(SCH_3)N(CH_2)_4CH_2]\}PF_6$ (VII)[c]	2047, 2002	16.55
$\{Cp(CO)_2Fe[C(OPh)N(CH_2)_4CH_2]\}PF_6$ (VIII)[d]	2048, 2005	16.59

[a] All absorptions are strong. [b] Reference 20. [c] Reference 8. [d] In mixture, predominantly VII.

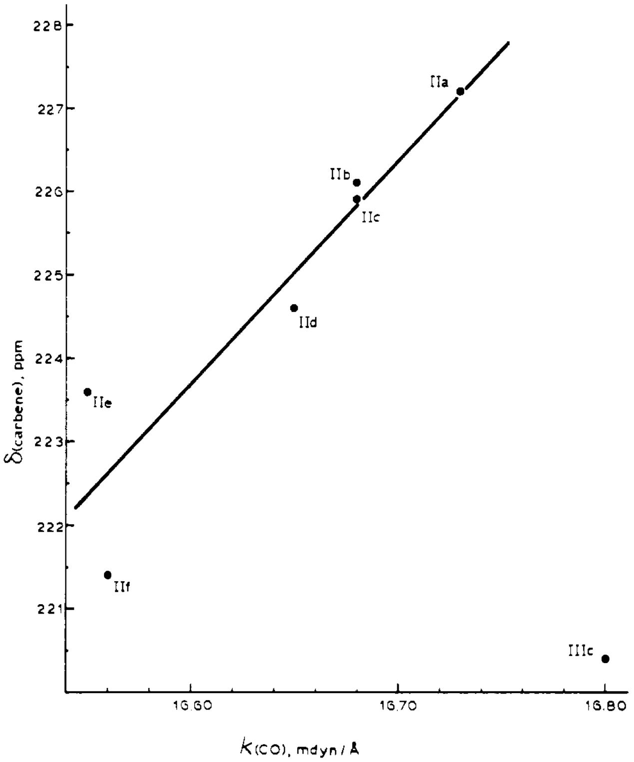

Figure 1. Plot of δ(carbene) vs. k(CO) for the aminooxocarbene complexes.

oxocarbene complexes, as a group, do fit reasonably well the reported correlation between k(CO) and δ(CO) for $Cp(CO)_2FeX$[21] and $Cp(CO)_2FeL^+$[22] derivatives. According to that correlation, the aminooxocarbene complexes generally have δ(CO) values which are slightly (0.0–1.5 ppm) more shielded than would be predicted from their k(CO) values.

In contrast to the wide variety of carbene complexes studied previously,[9] the more limited group of aminooxocarbene complexes display a fairly good correlation between k(CO) and the ^{13}C NMR chemical shift of the carbene carbon, δ(carbene) (Figure 1). The aminooxocarbene derivatives also have a much narrower range of δ(carbene) values (~7 ppm) than found in the previous study (~130 ppm).[9] Complex IIIc is the only exception to this correlation (Figure 1), and its anomalous behavior may be a consequence of the five-membered ring carbene system. We have previously postulated that the strain in five-membered ring carbene ligands may cause less effective heteroatom → C(carbene) π donation than would normally be expected.[9]

Table II. ^1H NMR Spectra of the Complexes in Acetone-d_6 (τ)

complex	NH[a]	C_5H_5[b]	OCH_3[b]	other resonances
IIa	0.10, 0.82	4.54	5.92	
IIb	−0.23	4.46	5.73	2.64 (s, C_6H_5), 5.37 (d, CH_2)[c]
IIc	0.37	4.45	5.75	5.97 (t, OH), 6.38 (m, 2 CH_2)
IId	0.30	4.45	5.74	7.03 (d, CH_3)[d]
IIe		4.36	5.75	6.38 (s, NCH_3), 6.73 (s, NCH_3)
IIf		4.36	5.75	5.87 (t, NCH_2), 6.06 (t, NCH_2), 8.28 (m, 3 CH_2)
IIIc	*e*	4.45		5.20 and 6.11 (AA'BB', 2 CH_2)
VII[f]		4.45		5.63 (m, 2 NCH_2), 7.09 (s, SCH_3), 8.13 (m, 3 CH_2)
VIII[g]		4.59		2.63 (m, C_6H_5), 5.68 (m, 2 NCH_2), 8.13 (m, 3 CH_2)

[a] All resonances are very broad singlets. [b] All resonances are singlets. [c] $J_{HNCH} = 5.9$ Hz. [d] $J_{HNCH} = 4.6$ Hz. [e] NH resonance not observed. [f] Reference 8, NCH_2 resonances have been reassigned. [g] In mixture, predominantly VII.

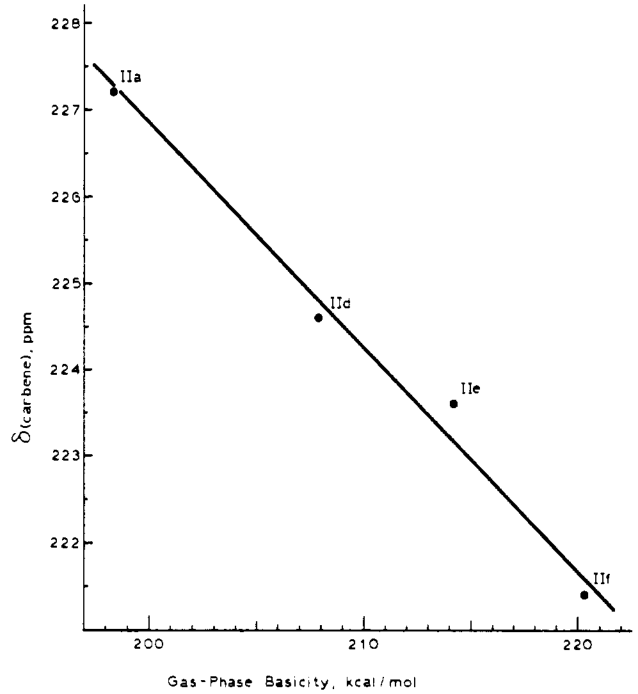

Figure 2. Plot of δ(carbene) vs. the gas-phase basicity of the amine substituent for the aminooxocarbene complexes.

For the acyclic aminooxocarbene complexes, there is also a fair correlation between δ(carbene) and the solution basicities[23] of the amine substituents. The correlation of δ(carbene)

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(21) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406–3408.

(22) Bancroft, G. M.; Butler, K. D.; Manzer, L. E.; Shaver, A.; Ward, J. E. H. *Can. J. Chem.* **1974**, *52*, 782–787.

(23) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; International Union of Pure and Applied Chemistry; Butterworths: London, 1965.

Table III. ^{13}C NMR Spectra of the Complexes in Acetone-d_6 (ppm)^a

complex	C(carbene)	CO	C_5H_5	OCH_3	other resonances
IIa	227.2	211.9	87.9	59.5	
IIb	226.1	211.5	88.4	63.9	137.6, 129.4, 128.9 and 128.4 (C_6H_5), 49.3 (CH_2)
IIc	225.9	211.6	88.3	63.8	60.1 (OCH_2), 48.5 (NCH_2)
IId	224.6	211.5	88.1	63.7	31.8 (NCH_3)
IIe	223.6	211.7	88.9	63.4	46.6 (NCH_3), 40.9 (NCH_3)
IIf^b	221.4	211.6	88.7	63.4	56.6 (NCH_2), 50.1 (NCH_2), 27.3, 26.7, and 24.7 (3 CH_2)
IIIc	220.4	211.2	88.0		73.3 (OCH_2), 46.2 (NCH_2)
VII^b	237.6	211.4	89.2		64.9 (NCH_2), 59.5 (NCH_2), 27.7, 27.3, and 24.0 (3 CH_2), 26.4 (SCH_3)

^{a} All resonances are singlets. ^{b} In CD_3CN.

with the gas-phase basicities[24-26] of the amine substituents is even better (Figure 2). A similar correlation has been observed for a series of $(CO)_5CrC(NR_2)CH_3$ (NR_2 = $NHCH_3$, NH(i-pr), $N(CH_3)_2$) complexes.[27] Thus, as the basicity of the amine substituent increases, the carbene carbon becomes more shielded due to increased N → C(carbene) π donation. This trend is exactly that which would be predicted.[9]

The trends observed previously in δ(carbene) values for the $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes, where X and Y are O, S, Se, or NR, as X and Y were varied,[9] may be extended by the observation that the carbene carbon resonates between 220 and 230 ppm in the ^{13}C NMR spectra of the aminooxocarbene complexes.

The ^{1}H NMR spectra of the new aminooxocarbene complexes (Table II) are all quite similar. The amine hydrogens may be seen below τ 1.00 as very broad resonances. Coupling of the amine protons with the amine alkyl substitutents is seen in the splitting of the alkyl protons in IIb,d. That the doublets are not due to syn–anti isomerization of the carbene ligands is shown by the observation of singlets for the alkyl groups and the disappearance of the NH resonances upon addition of D_2O to the ^{1}H NMR samples of IIb,d. Restricted rotation about the C(carbene)–N bonds is shown by separate signals for the α-amino substituents of IIe,f. One set of resonances for the amine substituents of IIb,d may be interpreted as indicating one preferred configuration about the N–C(carbene) bond.

Experimental Section

General Information. Reagent grade chemicals were used without further purification and $\{Cp(CO)_2Fe[C(SCH_3)OCH_3]\}CF_3SO_3$ (I),[9] $\{Cp(CO)_2Fe[C(OCH_3)_2]\}PF_6$ (IV),[28] $\{Cp(CO)_2Fe[C(SCH_3)OPh]\}PF_6$ (V),[9] $\{Cp(CO)_2Fe[C(SCH_3)SPh]\}PF_6$ (IX),[9] $\{Cp(CO)_2Fe[C(SCH_3)SePh]\}PF_6$ (X),[9] $Cp(CO)_2Fe[CS(CH_2)_2S]\}PF_6$ (XIa),[9] $Cp(CO)_2Fe[CS(CH_2)_3S]\}PF_6$ (XIb),[9] and $Cp(CO)_2Fe[C(SCH_3)N(CH_2)_4CH_2]\}PF_6$ (VII)[8] were prepared as reported previously. Routine ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer; $Cr(acac)_3$ (~0.1 M) was added to the ^{13}C samples to reduce data collection time.[29] Tetramethylsilane (Me_4Si) was employed as the internal standard for all NMR spectra. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer.

Preparation of Aminooxocarbene Complexes. $\{Cp(CO)_2Fe[C(OCH_3)NH_2]\}CF_3SO_3$ (IIa). Complex I (0.090 g, 0.21 mmol) was dissolved in 15 mL of CH_3CN, and 400 μL of CH_3CN saturated with NH_3(g) was added in 25-μL increments to the stirred solution over a 2-h period. The reaction was allowed to stir for an additional 30 min and was then evaporated to dryness. The resulting residue was washed with Et_2O and crystallized from CH_2Cl_2 with Et_2O at −20 °C to give 0.068 g (81%) of IIa as large yellow crystals, mp 119–121 °C. Anal. Calcd for $C_{10}H_{10}F_3FeNO_6S$: C, 31.19; H, 2.62; N, 3.64. Found: C, 30.89; H, 2.47; N, 3.67.

$\{Cp(CO)_2Fe[C(OCH_3)NHCH_2Ph]\}CF_3SO_3$ (IIb). A 15-mL solution of CH_2Cl_2 containing I (0.10 g, 0.24 mmol) and $PhCH_2NH_2$ (56 μL, 0.51 mmol) was stirred for 30 min. The solution was then evaporated to an orange oil which was washed with Et_2O. Crystallization of the oil from CH_2Cl_2 with Et_2O at −20 °C afforded 0.061 g (53%) of IIb as yellow crystals, mp 118–122 °C. Anal. Calcd for $C_{17}H_{16}F_3FeNO_6S$: C, 42.97; H, 3.39; N, 2.95. Found: C, 42.77; H, 3.38; N, 2.97.

$\{Cp(CO)_2Fe[C(OCH_3)NH(CH_2)_2OH]\}CF_3SO_3$ (IIc). This complex was prepared by the same method as IIb. From the reaction of I (0.10 g, 0.24 mmol) and β-aminoethanol (15 μL, 0.25 mmol), 0.070 g (68%) of IIc was isolated as yellow needles, mp 124–128 °C. Anal. Calcd for $C_{12}H_{14}F_3FeNO_7S$: C, 33.59; H, 3.29; N, 3.26. Found: C, 33.29; H, 3.04; N, 3.24.

$\{Cp(CO)_2Fe[C(OCH_3)NHCH_3]\}CF_3SO_3$ (IId). Complex I (0.10 g, 0.24 mmol) was dissolved in CH_2Cl_2, and a slow stream of CH_3NH_2(g) was passed through the stirred solution for 30 min. The solution was then evaporated to dryness, and the yellow residue was washed with Et_2O. Crystallization of this residue from CH_2Cl_2 with Et_2O at −20 °C yielded 0.067 g of a mixture of IId and IIa (50 and 20%, respectively, from ^{1}H NMR) as small yellow crystals, mp 128–134 °C.

$\{Cp(CO)_2Fe[C(OCH_3)N(CH_3)_2]\}CF_3SO_3$ (IIe). This complex was prepared in the same manner as IId. Starting with 0.10 g (0.24 mmol) of I and $(CH_3)_2NH$(g), 0.067 g (68%) of IIe was obtained as small yellow needles, mp 174–178 °C dec. Anal. Calcd for $C_{12}H_{14}F_3FeNO_6S$: C, 34.89; H, 3.42; N, 3.39. Found: C, 34.82; H, 3.39; N, 3.41.

$\{Cp(CO)_2Fe[C(OCH_3)N(CH_2)_2CH_2]\}CF_3SO_3$ (IIf). This complex was prepared by the method used for IIb. The reaction of I (0.10 g, 0.24 mmol) and piperidine (48 μL, 0.48 mmol) produced 0.065 g (60%) of IIf as large yellow-orange crystals, mp 141–143 °C. Anal. Calcd for $C_{15}H_{18}F_3FeNO_6S$: C, 39.75; H, 4.00; N, 3.09. Found: C, 39.58; H, 3.98; N, 3.07.

Thermal Behavior of IIc. Complex IIc (0.040 g, 0.093 mmol) was dissolved in 25 mL of CH_3CN (dried over $CaSO_4$ and N_2 saturated), and the solution was refluxed under an N_2 atmosphere for 12 h. The yellow solution was then evaporated to dryness, and the residue was washed with Et_2O. The yellow residue was crystallized from CH_2Cl_2 with Et_2O at −20 °C to give 0.030 g (81%) of $\{Cp(CO)_2Fe[CO(CH_2)_2NH]\}CF_3SO_3$ (IIIc) as pale yellow needles, mp 118 °C. Anal. Calcd for $C_{11}H_{10}F_3FeNO_6S$: C, 33.28; H, 2.54; N, 3.53. Found: C, 33.50; H, 2.34; N, 3.63.

Reaction of $\{Cp(CO)_2Fe[C(SCH_3)OPh]\}PF_6$ (V) with Benzylamine. This reaction was carried out by using the procedure used to prepare IIb. The reaction of V (0.012 g, 0.025 mmol) and $PhCH_2NH_2$ (6.0 μL, 0.055 mmol) thus yielded 0.010 g (90%) of $\{Cp(CO)_2FeCNCH_2Ph\}PF_6$[8] (VI) as yellow needles.

Reaction of V with Piperidine. The procedure used was the same as for the preparation of IIb. Starting with V (0.030 g, 0.063 mmol) and piperidine (13 μL, 0.13 mmol), 0.020 g of a mixture of $\{Cp(CO)_2Fe[C(SCH_3)N(CH_2)_4CH_2]\}PF_6$[8] (VII) and $Cp(CO)_2Fe[C(OPh)N(CH_2)_4CH_2]\}PF_6$ (VIII) (48 and 18%, respectively, from ^{1}H NMR) was isolated as a yellow powder.

Reaction of $\{Cp(CO)_2Fe[C(SCH_3)SPh]\}PF_6$ (IX) with Benzylamine. The procedure used for the preparation of IIb was employed here.

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[24] Bowers, M. T.; Aue, D. H.; Webb, H. M.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4314, 4315.

[25] Arnett, E. M.; Jones, F. M., III; Taagepera, M.; Henderson, W. G.; Beauchamp, J. L.; Holtz, D.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 4724–4726.

[26] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1972**, *94*, 4726–4728.

[27] Ciappenelli, D. J.; Cotton, F. A.; Kruczynski, L. *J. Organomet. Chem.* **1973**, *50*, 171–174.

[28] Quick, M. H.; Angelici, R. J. *J. Organomet. Chem.* **1978**, *160*, 231–239.

[29] Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456, 457.

The reaction of IX (0.030 g, 0.061 mmol) and $PhCH_2NH_2$ (14 μL, 0.13 mmol) afforded 0.015 g (56%) of VI[8] as yellow needles.

Reaction of IX with Piperidine. This reaction was carried out by using the method used to prepare IIb. From the reaction of IX (0.040 g, 0.082 mmol) and piperidine (16 μL, 0.16 mmol), 0.025 g (66%) of VII[8] was isolated as small yellow needles.

Reaction of $\{Cp(CO)_2Fe[C(SCH_3)SePh]\}PF_6$ (X) with Benzylamine. The method used to prepare IIb was also used in this reaction. Starting with X (0.024 g, 0.044 mmol) and $PhCH_2NH_2$ (10 μL, 0.092 mmol), 0.011 g (58%) of VI[8] was obtained as yellow needles.

Reaction of X with Piperidine. The reaction of X (0.028 g, 0.052 mmol) with piperidine (11 μL, 0.11 mmol), under the same conditions as used in the preparation of IIb, yielded 0.016 g (66%) of VII[8] as small yellow needles.

Reaction of $\{Cp(CO)_2Fe[\overline{CS(CH_2)_2S}]\}PF_6$ (XIa) with Benzylamine. This reaction was carried out by using the same procedure as used for IIb. The reaction of XIa (0.025 g, 0.059 mmol) with $PhCH_2NH_2$ (13 μL, 0.12 mmol) afforded 0.022 g (85%) of VI[8] as yellow needles.

Reaction of $\{Cp(CO)_2Fe[\overline{CS(CH_2)_3S}]\}PF_6$ (XIb) with Benzylamine. A solution of 15 mL of CH_2Cl_2 containing XIb (0.025 g, 0.057 mmol) and $PhCH_2NH_2$ (13 μL, 0.12 mmol) was stirred for 1 h. The resulting cloudy yellow solution was evaporated to dryness, and the residue was washed with Et_2O to remove an unidentified, neutral, yellow species. The remaining residue was then crystallized from CH_2Cl_2 with Et_2O at −20 °C to give 8.0 mg (32%) of VI[8] as yellow needles.

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Registry No. I, 76136-33-9; IIa, 76136-49-7; IIb, 76136-51-1; IIb (PF_6 salt), 76136-65-7; IIc, 76136-53-3; IId, 76136-55-5; IIe, 76136-57-7; IIf, 76136-59-9; IIIc, 76136-60-2; IV, 68868-37-1; V, 76136-30-6; VI, 69532-23-6; VII, 69532-34-9; VIII, 76136-62-4; IX, 76136-32-8; X, 76136-64-6; XIa, 76136-38-4; XIb, 76136-40-8.

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Substitution and S-Alkylation Reactions of Thiocarbonyl-Bridged $Cp_2Fe_2(CO)_3CS$

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In refluxing CH_3CN, $Cp_2Fe_2(CO)_3CS$ reacts with PEt_3, PMe_2Ph, $PMePh_2$, and $P(OMe)_3$ to give the monosubstituted derivatives $Cp_2Fe_2(CO)_2(PR_3)CS$, in which the CS group remains in the bridging position, as it does in all of the complexes described in this report. The reaction of MeNC with $Cp_2Fe_2(CO)_3CS$ in refluxing THF or cyclohexane gives $Cp_2Fe_2(CO)_2(MeNC)CS$ which exists predominantly as an isomer in which the MeNC is terminal. There is, however, spectroscopic evidence for a less abundant isomer in which the MeNC is bridging. The bissubstituted complex $Cp_2Fe_2(CO)(MeNC)_2CS$ may be obtained by refluxing $Cp_2Fe_2(CO)_3CS$ and MeNC in acetonitrile. This complex has been partially separated chromatographically into a major isomer, in which one MeNC is bridging and the other is terminal, and a minor bis-terminal MeNC isomer. The bridging thiocarbonyl sulfur atom of $CpFe_2(CO)_3CS$ may be alkylated at room temperature by reaction with alkyl iodides, benzyl bromide, allyl bromide, $MeOSO_2F$, and Et_3O^+ to give the $Cp_2Fe_2(CO)_3CSR^+$ complexes. The methyl derivative $Cp_2Fe_2(CO)_3CSMe^+$ reacts readily with ligands PEt_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$, and MeNC to give the CO-substituted products $Cp_2Fe_2(CO)_2(L)CSMe^+$. Both alkylation and substitution occur when $Cp_2Fe_2(CO)_3CS$ is refluxed in acetonitrile with MeI and NaI to give $Cp_2Fe_2(CO)_2(I)(CSMe)$. Only the CS-alkylated product $Cp_2Fe_2(CO)_2(MeNC)CSMe^+$ is obtained from the reaction of $Cp_2Fe_2(CO)_2(MeNC)CS$ with $MeOSO_2F$ or MeI. The bissubstituted complex $Cp_2Fe_2(CO)(MeNC)_2CS$ reacts with MeI to yield the CS-alkylated compound $Cp_2Fe_2(CO)(MeNC)_2CSMe^+$ in which both of the MeNC groups are terminal. With the stronger alkylating $MeOSO_2F$, this complex gives the dimethylated product $Cp_2Fe_2(CO)(MeNC)(Me_2NC)CSMe^{2+}$, in which both alkylated groups are bridging. All of the complexes are characterized by their IR and ^1H and ^{13}C NMR spectra, which give evidence of isomers in which the Cp rings are cis or trans to each other across the Fe–Fe bond. Mechanisms for the interconversion of several of the isomers are discussed.

Introduction

Recent research on metal thiocarbonyl complexes has led to the isolation of several compounds with bridging CS ligands.[1-5] One of these compounds is $Cp_2Fe_2(CO)_3CS$ (Cp = η^5-C_5H_5), which is a thiocarbonyl analogue of the well-known carbonyl complex $[CpFe(CO)_2]_2$. We have previously reported[5] the preparation of $Cp_2Fe_2(CO)_3CS$ and its reactions which result in cleavage of the Fe–Fe bond. In this paper, we discuss reactions leading to the alkylation of the bridging thiocarbonyl sulfur atom and reactions involving substitution of CO by other ligands.

Experimental Section

General Procedures. All reactions were conducted under prepurified N_2, with use of Schlenk ware (or similar apparatus) and standard inert-atmosphere techniques. Reactions were carried out at room temperature unless stated otherwise. Many compounds were conveniently isolated by a "slow evaporation" technique; in this method, the compound to be crystallized was dissolved in a suitable solvent, a higher boiling solvent in which the compound was less soluble was added, and the solution was evaporated to a small volume under reduced pressure (50–60 torr) at room temperature with a rotary evaporator. Exchange of PF_6^- for other anions was accomplished on a 10 × 25 cm column of Amberlite IRA-400 resin in acetone. Molar conductivities were determined in nitromethane solutions at 25 °C with use of an Industrial Instruments RC-16B2 conductivity bridge.

Infrared spectra were recorded on a Perkin-Elmer 337 or 237B instrument; NaCl cells with a 1-mm path length were used for most spectra. Band positions were determined with use of CO gas (CO region) and polystyrene (CS region) as references and are believed accurate to within 2 cm^{-1}. Proton NMR spectra were obtained with a Varian A-60 spectrometer; variable-temperature ^1H NMR spectra were run on a Varian HA-100 instrument. All ^{13}C NMR spectra were recorded on a Bruker HX-90 FT-NMR spectrometer; $Cr(acac)_3$ was added to the samples to reduce data collection time.[6] Tetramethylsilane was used as the internal reference for all NMR spectra.

Elemental analyses were performed by Galbraith Laboratories; analytical data are given below for representative compounds.

Solvents and Reagents. Tetrahydrofuran (THF) was distilled from $NaK_{2.8}$ under N_2 immediately before use. Nitromethane for conductivity measurements was dried over P_4O_{10}, fractionally distilled twice under N_2, and stored over type 4A molecular sieves under N_2.

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(1) Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. *J. Organomet. Chem.* **1976**, *114*, C49.
(2) Efraty, A.; Arneri, R.; Huang, M. H. A. *J. Am. Chem. Soc.* **1976**, *98*, 639. Efraty, A.; Arneri, R.; Ruda, W. A. *Inorg. Chem.* **1977**, *16*, 3124.
(3) Wnuk, T. A.; Angelici, R. J. *Inorg. Chem.* **1977**, *16*, 1173.
(4) Wagner, R. E.; Jacobson, R. A.; Angelici, R. J.; Quick, M. H. *J. Organomet. Chem.* **1978**, *148*, C35.
(5) Quick, M. H.; Angelici, R. J. *J. Organomet. Chem.* **1978**, *160*, 231.
(6) Gansow, O. A.; Burke, A. R.; Lamar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.