and dried under vacuum. Recrystallization of the precipitate from THF afforded 6.74 g (53.9%) of **3**. The ^{1}H NMR spectrum of **3** was identical with that of samples prepared via oxidation by Ag^+ or protonolysis by $HN(^nBu)_3^+$ reagents.

Preparation of [$Cp_2Zr(Ph)(THF)$][BPh_4] (6) from $Cp_2Zr(Ph)(CH_2Ph)$. A slurry of $Cp_2Zr(CH_2Ph)(Ph)$ (0.489 g, 1.26 mmol) and [Cp'_2Fe][BPh_4] (2.02 g, 3.78 mmol) in THF (15 mL) was prepared at -78 °C. The blue reaction mixture was warmed to 23 °C and stirred for 4 h, producing an orange slurry. The slurry was stirred overnight and then evaporated to dryness under vacuum. The resulting solid was washed with toluene to remove Cp'_2Fe and recrystallized from THF (-30 °C), yielding 0.32 g (36%) of bright yellow **6**. A sample of **6** that analyzed acceptably was prepared via recrystallization from CH_2Cl_2/toluene at -78 °C. This sample contained 0.33 equiv of toluene (^{1}H NMR). Anal. Calc for $C_{44}H_{43}BOZr{\cdot}0.33C_7H_8$: C, 77.22; H, 6.39; Zr, 12.66. Found: C, 76.80; H, 6.28; Zr, 12.79.

Preparation of [$Cp_2Zr(Ph)(THF)$][BPh_4] (6) from $Cp_2Zr(Ph)_2$. A slurry of $Cp_2Zr(Ph)_2$ (3.10 g, 8.26 mmol) and [$HN(Me)_2(Ph)$][BPh_4] (7.29 g, 16.52 mmol) in 60 mL of THF was prepared at -78 °C. The slurry was warmed to 23 °C and stirred for 1.5 h, after which 50 mL of THF was removed and 30 mL of toluene was added. The slurry was stirred for an additional 30 min and filtered, leaving a pale yellow precipitate. The precipitate was washed thoroughly with Et_2O and dried under vacuum overnight. Yield: 4.36 g (62.6%). This material contained excess THF (2 equiv by ^{1}H NMR).

$Cp_2Zr(Ph)(CH_2Ph)$ (10). A slurry of [$Cp_2Zr(CH_2Ph)(THF)$][BPh_4]$\cdot 0.43C_7H_8$ (2.02 g, 2.53 mmol) in THF (35 mL) was prepared at -78 °C. Under N_2 counterflow, 1.45 mL of PhLi solution (2.0 M in ether, 2.9 mmol) was added by syringe over a 2-min period. The mixture was stirred at -78 °C for 20 min, warmed to 0 °C, and stirred for an additional 40 min. The mixture was warmed to 23 °C and evaporated to dryness under vacuum. The resulting solid was extracted with hexane until the hexane extract was colorless. The hexane extracts were evaporated to dryness under vacuum yielding 0.83 g of crude **10**, which consisted of 83% **10** and a total of 17% of $Cp_2Zr(Ph)_2$ and $Cp_2Zr(CH_2Ph)_2$. Fractional recrystallization from toluene/hexane improved the ratio to 90:10. An additional recrystallization gave 0.34 g (32%) of >99% pure **10**. The reaction was reproducible at this scale; however, scale-up attempts resulted in increased amounts of $Cp_2Zr(Ph)_2$ and $Cp_2Zr(CH_2Ph)_2$. Anal. Calc for $C_{23}H_{22}Zr$: C, 70.99; H, 5.70; Zr, 23.41. Found: C, 70.63; H, 5.58; Zr, 23.15.

[$Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2NMe_3)$][$BPh_4$] (13). A slurry of $Cp_2Zr(CH_2Ph)_2$ (1.00 g, 2.48 mmol) and [$HNMe_3$][BPh_4] (0.47 g, 1.24 mmol) in THF (15 mL) was heated for 15 h at 50 °C. The THF was removed under vacuum, yielding a yellow foam. The foam was washed with hot toluene and filtered. The resulting white solid was washed with several small portions of toluene and dried under vacuum, yielding 0.61 g (64% based on [$HNMe_3$][BPh_4]) of **13**. Anal. Calc for $C_{48}H_{54}BNOZr$: C, 75.60; H, 7.15; N, 1.84. Found: C, 75.42; H, 6.95; N, 1.79.

[$Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2PMe_2Ph)$][$BPh_4$] (14). A solution of [$Cp_2Zr(CH_2Ph)(CH_3CN)$][$BPh_4$] (0.25 g, 0.36 mmol) and PMe_2Ph (55 μL, 0.39 mmol) in 10 mL of THF was stirred for 4 days at 55 °C. The THF was removed under vacuum, leaving a foam. The foam was recrystallized twice from THF/Et_2O at -78 °C, yielding 0.14 g (46%) of pale yellow **14**. Anal. Calc for $C_{53}H_{56}BOPZr$: C, 75.60; H, 6.70. Found: C, 75.73; H, 6.91. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 25.1.

[$Cp_2Zr(CH_3)(OCH_2CH_2CH_2CH_2NMe_3)$][$BPh_4$] (15). A slurry of $Cp_2Zr(CH_3)_2$ (0.18 g, 0.70 mmol) and [$HNMe_3$][BPh_4] (0.25 g, 0.66 mmol) in THF (20 mL) was stirred for 6 h at 23 °C. The THF was then removed under vacuum, leaving a white foam. The foam was washed with hot toluene and dried for 15 h under vacuum, yielding 0.34 g (76%) of **15**.

[$Cp_2Zr(Ph)(PMe_3)_2$][BPh_4] (16). A solution of [$Cp_2Zr(Ph)(THF)$][BPh_4] (0.57 g, 0.81 mmol) and PMe_3 (0.16 mL, 1.6 mmol) in THF (25 mL) was prepared at -78 °C and warmed to 23 °C. After 10 min, a white solid precipitated. The slurry was stirred for an additional 30 min and filtered, leaving a white precipitate. The precipitate was recrystallized from THF and dried under vacuum overnight. Yield: 0.55 g (55%). This material contained excess THF (6 equiv by ^{1}H NMR) and <5% other unidentified Cp-containing impurities. $^{31}P\{^1H\}$ NMR (THF-d_8, -43 °C): δ -12.4.

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Ligand Addition vs Substitution in the Reaction of ^{13}CO with $(OC)_3Fe^-$ in a Flowing Afterglow Apparatus

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The gas-phase reactions of $(OC)_3Fe^-$ with CO and ^{13}CO were investigated. Only addition was observed with CO yielding $(OC)_4Fe^-$ ($k_{app} = (1.6 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), but ^{13}CO revealed both addition and ligand substitution with an appropriate increase in the rate constant. The average branching fractions for the addition and substitution channels were 0.71 and 0.29, respectively. From these results and the collision frequency for the excited intermediate $[(OC)_3(O^{13}C)Fe^-]^*$ (1) with the helium buffer gas, k_s[He], lower limits on the lifetime of **1** and the rate constants for its unimolecular decomposition are calculated. The large k_{app} for the reaction of $(OC)_3Fe^-$ with CO yielding the adduct $(OC)_4Fe^-$ with a doublet electronic ground state suggests that $(OC)_3Fe^-$ also has a doublet electronic ground state.

Introduction

Many condensed-phase ligand substitution reactions are stepwise, involving thermal dissociation of a ligand from the initial metal complex followed by association of the new ligand to the intermediate coordinatively unsaturated complex. For example, the 18-electron metal carbonyls $Ni(CO)_4$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ undergo ligand substitution with ^{13}CO,[1] amines,[2] and phosphines[3] by this dissociative mechanism. This mechanism is expected since the associative mechanism would require formation of a 20-electron intermediate. However, a number of other 18-electron complexes, i.e. $V(CO)_6^-$,[4] $Mn(CO)_5^-$,[5] $Re(CO)_5^-$,[5]

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[1] (a) Keeley, D. F.; Johnson, R. E. *Inorg. Nucl. Chem.* **1959**, *4*, 33. (b) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082.

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and $Fe(CO)_5$,[6] fail to react with either labeled CO or phosphines.

The dissociative mechanism is not possible in the gas phase at 298 K with thermalized neutral or ionic complexes in the absence of an external perturbation due to the endothermicity of the ligand dissociation step. Thus, the 18-electron complex $Mn(CO)_6^+$ failed to undergo ligand exchange while the coordinatively unsaturated ions $Mn(CO)_x^+$ (x = 1–5) readily substituted CO for ^{13}CO at the low pressures of the ICR spectrometer.[7]

Another mechanism for ligand substitution in 17-electron metal carbonyl negative ions in the gas phase involves initial electron transfer from the anion to the neutral ligand. The ligand anion radical binds covalently to the neural 16-electron metal carbonyl fragment with subsequent loss of one or two CO ligands in the ICR experiments.[8] This mechanism is analogous to that described for the gas-phase halogen-atom transfer reactions between haloalkanes and a series of 17-electron metal complex negative ions.[9] In the latter case, electron transfer is followed by halide ion transfer from $RX^{\bullet-}$ to the neutral 16-electron metal complex forming the 18-electron complexes L_nMX^- in the high pressure of the flowing afterglow.

In our reports of ligand substitution reactions of eight 17-electron transition metal complex negative ions with various neutral reactants,[10] no evidence was found for the formation of 19-electron intermediates. Two additional examples are the failure of $(OC)_4Mn(CF_3)^-$ to react with ^{13}CO or PF_3,[11] and the present case of no reaction of $(OC)_4Fe^-$ with ^{13}CO. The 19-electron count on the metal center can be avoided if the odd electron is in an oribtal associated with the ligands.

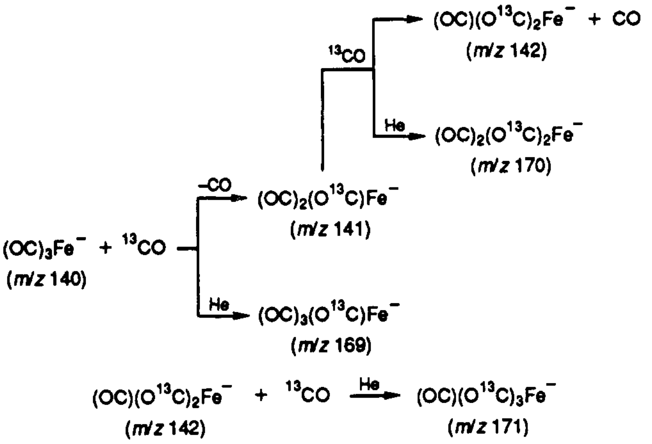
The sole example where a 19-electron intermediate might be involved is the reaction of $(OC)_4Fe^-$ with PF_3. The product ions $(OC)_xFe(PF_3)_y^-$ (where x = 3–1 and y = 1–3) were formed sequentially by substitution of CO with PF_3.[10b] However, the five-coordinate negative ion could also be the transition state in a direct, one-step displacement process. Alternatively, a ternary collision complex $[(OC)_3Fe^-/CO/PF_3]$ might be generated if the exothermicity in forming the original collision complex $[(OC)_4Fe^-/PF_3]$ equals or exceeds the Fe–CO bond energy in $(OC)_4Fe^-$. The mechanism of this reaction is unknown.

To gain insight into the fate of an intermediate complex formed by addition of a ligand to a coordinatively unsaturated precursor in a relatively high pressure of an inert bath gas, we have examined the reaction of ^{13}CO with the mixture of $(OC)_{4,3}Fe^-$ ions in a flowing afterglow (FA) apparatus. The results of this study are the subject of this paper.

Experimental Section

The FA used in this study[12] and the method to generate the $(OC)_{4,3}Fe^-$ ion mixture[13] have been described. The $(OC)_{4,3}Fe^-$ mixture (~3/2) was produced by dissociative electron attachment of energetic electrons to $Fe(CO)_5$ in the upstream end of a 1.5 m long flow tube. The flow conditions were P_{He} = 0.7 to 1.1 Torr and $\bar{v} \approx 55$ m s^{-1} at 298 K. With these conditions, the ion signal for $(OC)_3Fe^-$ was maximized and no signal for $(OC)_2Fe^-$ was present in the negative ion mass spectrum. The $(OC)_{4,3}Fe^-$ ions were thermalized by numerous collisions with the helium buffer gas in the first 75 cm of the flow tube prior to reaching the ^{13}CO gas radial inlet. The gas flow was sampled into a differentially pumped compartment ($P \approx 10^{-7}$ Torr) containing a quadrupole mass filter and electron multiplier, which continuously monitored the ion composition in the flow.

Scheme I



The kinetics of the bimolecular ion/molecule reactions were determined under pseudo-first-order conditions with the concentration of CO or ^{13}CO (MSD isotopes, 99.8% isotopic purity) in large excess compared to the ion concentration. The plots of log $[(OC)_3Fe^-]$ vs CO or ^{13}CO concentration gave linear decays through >95% loss of $(OC)_3Fe^-$. The rate constants were calculated by standard first-order rate laws already given.[12b]

Results and Data Analysis

The reaction of the 15-electron negative ion, $(OC)_3Fe^-$, with CO forming the adduct $(OC)_4Fe^-$ (eq 1) has been reported.[14] Although adduct formation in the gas phase

$$\underset{(m/z\ 140)}{(OC)_3Fe^-} + CO \rightleftarrows [(OC)_4Fe^-]^* \xrightarrow{He} \underset{(m/z\ 168)}{(OC)_4Fe^-} \quad (1)$$

requires removal of the excess energy by collisions with the helium, the apparent bimolecular rate constant, k_{app}, for this formally termolecular reaction was $(1.6 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (P_{He} = 0.5 torr, $\bar{v}$ = 80 m s^{-1}).[11] The apparent bimolecular reaction efficiency, k_{app}/k_{LAN}, is 0.24; k_{LAN} is the collision limited rate constant.[15] No change in k_{app} outside of the errors was observed by increasing P_{He} to 1.1 Torr.[16] Either this change in P_{He} is too small to cause a change in k_{app} or the collisional stabilization step is already saturated at P_{He} = 0.5 Torr. A further increase in P_{He} was not possible because the generation of $(OC)_3Fe^-$ was adversely affected. No reaction was observed between the 17-electron complex $(OC)_4Fe^-$ and CO ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}), and the increase in the ion signal at m/z

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[14] McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095. Under these flow conditions, a trace amount of $(OC)_2Fe^-$ at m/z 112 was present in the flow. This trace ion was assumed to react rapidly with CO to yield $(OC)_3Fe^-$. The previously reported rate constant (1.4×10^{-10} cm^3 molecule^{-1} s^{-1}) has been corrected for an error in the computer program used to calculate rate constants.

[15] The collision limited rate constant, k_{LAN}, is calculated using Langevin theory; see: Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 3. k_{LAN} (reaction 1) = 6.8×10^{-10} cm^3 molecule^{-1} s^{-1}.

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Table I. Summary of Kinetic and Product Data for the Reactions of $(OC)_3Fe^-$ with ^{13}CO

run no.	P_{He}, Torr	product ions	branching fraction[a]	k_{total},[b] cm^3 molecule^{-1} s^{-1}	rate constants for substitution and addition,[c] cm^3 molecule^{-1} s^{-1}
1	0.7	*m/z* 141, 142, and 170	0.32 ± 0.07	$(2.6 \pm 0.1) \times 10^{-10}$	$k_{sub} = (8.3 \pm 1.7) \times 10^{-11}$
		m/z 169	0.68 ± 0.06		$k_{add} = (1.8 \pm 0.1) \times 10^{-10}$
2	1.1	*m/z* 141, 142, and 170	0.25 ± 0.08	$(2.1 \pm 0.1) \times 10^{-10}$	$k_{sub} = (5.3 \pm 1.6) \times 10^{-11}$
		m/z 169	0.75 ± 0.08		$k_{add} = (1.6 \pm 0.1) \times 10^{-10}$

[a] These are the average branching fractions from all of the data points in the run; 10 points in run 1 and 11 points in run 2. The errors are the largest difference from the average; these occurred in early, low conversion points. [b] The total rate constant measured from the decay of $(OC)_3Fe^-$. [c] Obtained by multiplying k_{total} by the average branching fraction for that process.

168 accounted for >90% of the $(OC)_3Fe^-$ ion signal decayed. Repeating this reaction in this study at $P_{He} = 1.0$ torr and $\bar{v} = 55$ m s^{-1} gave the same k_{app} for the decay of $(OC)_3Fe^-$.

In the present work, $(OC)_4Fe^-$, generated separately or in the mixture, failed to react with ^{13}CO. However the reaction of $(OC)_3Fe^-$ with ^{13}CO proceeded rapidly and produced a mixture of ions by both primary and secondary ligand addition (*m/z* 169–171) and substitution (*m/z* 141 and 142) as shown in Scheme I. Signals for the completely labeled ions, $(O^{13}C)_3Fe^-$ (*m/z* 143) and $(O^{13}C)_4Fe^-$ (*m/z* 172), were not observed. The mass filter was operated at greater than unit mass resolution and mass discrimination was ignored over the 33 amu range in assigning relative product concentrations.

To accurately determine the branching fractions for the competitive addition and substitution product forming channels, the signals of the product ions should be large to reduce the effect of the background counts. To achieve this requires that a relatively large concentration of ^{13}CO be added to the flow, which causes the secondary reactions of $(OC)_2(O^{13}C)Fe^-$ shown in Scheme I to occur. Corrections for the contributions of the naturally occurring isotopes of Fe, C, and O from ions at other nominal masses to each ion signal are required to determine the true ion signal intensity at that mass. The largest errors occur (a) in early, low conversion data points and (b) in the small ion signals of the (M + 2) for the ions in the two groups of ions. These latter errors, however, are small due to the minor contribution of these ion signals to the total branching fraction for the two primary processes. The signal for the ions at *m/z* 171, which was barely observed above background in the final data point, was not included in this analysis.

The product ion $(OC)_3(O^{13}C)Fe^-$ at *m/z* 169 is unique in that it is the primary product from addition of ^{13}CO to $(OC)_3Fe^-$ and it does not react further (see Scheme I). The other three product ions at *m/z* 141, 142, and 170 are produced via the primary substitution channel and their signal intensities are summed for the determination of the branching fraction of this product forming channel. The corrected ion signal intensities for $(OC)_3Fe^-$ and the product ions of primary addition and substitution channels for run 1 are presented as a semilog plot in Figure 1. The slope of the decay of the $(OC)_3Fe^-$ ions is used to calculate the overall rate constant, k_{total},[12b] and the signal intensities of the product ions yield the branching fractions of the two product forming channels.

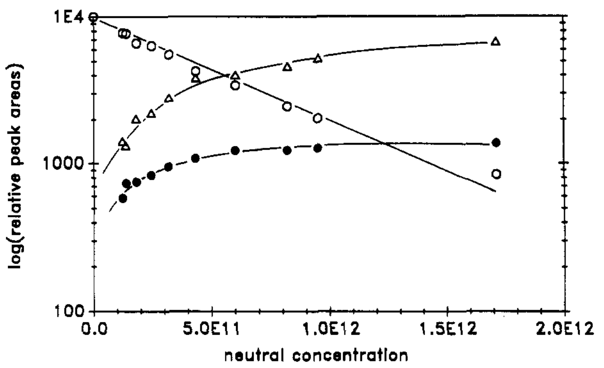
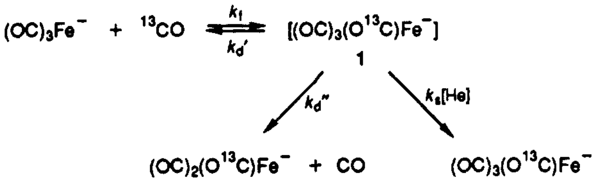


Figure 1. Semilog plot of the corrected ion signal intensities vs mass for the reaction of $(OC)_3Fe^-$ with ^{13}CO (run 1, Table I); $(OC)_3Fe^-$ (○), substitution products (●), and the primary addition product $(OC)_3(O^{13}C)Fe^-$ (△). The [^{13}CO] is in units of molecules cm^3 added to the flow.

Scheme II



The data for the two runs are summarized in Table I. The errors in the rate constants and branching fractions in the two runs are about those of our normal limits; ±10% of the value for rate constants and ±5% absolute in branching fractions. The average value of $k_{add} = (1.7 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} agrees with the previously measured $k_{app} = (1.6 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reaction of $(OC)_3Fe^-$ with CO. From this and the previous data given, we conclude that within the error limits there is no P_{He} effect for this reaction over this small range studied on the rate constant for CO addition (P_{He} = 0.5 and 1.1 Torr) or on the addition/substitution branching fractions (P_{He} = 0.7 and 1.1 Torr) measured with ^{13}CO.

Discussion

We assume that the associative mechanism is operating in the reaction of ^{13}CO to $(OC)_3Fe^-$ to yield the vibrationally excited adduct $[(OC)_3(O^{13}C)Fe^-]^*$ (1). If we further assume that the structure of $(OC)_3Fe^-$ is trigonal planar,[17] coordination of the ^{13}CO ligand from either face will lead to the trigonal pyramide structure of 1[18] with the ^{13}CO ligand initially in the axial site. Scrambling of the three COs and the ^{13}CO would be expected to occur rapidly (a few molecular vibrations) compared to the lifetime of 1 (see below). Therefore, we will treat 1 as fully equilibrated with respect to the isotopic level and internal energy.[19] In

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(18) Breeze, P. A.; Burdett, J. K.; Turner, J. J. *Inorg. Chem.* **1981**, *20*, 3669.

(19) The reaction of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ shows a marked tendency to expel ^{13}CO from the intermediate cations (Kerley, E. L.; Russell, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 5959). This result may be related to the observed CID of $Cr_2(CO)_5^-$, formed in the reaction of Cr^- with $Cr(CO)_6$, yielding $Cr(CO)_5^-$ and Cr suggesting an unsymmetrical structure for $Cr_2(CO)_5^-$ (Squires, R. R. *Chem. Rev.* **1987**, *87*, 623). These ICR results indicate ligand nonfluxtionality in these dinuclear complex ions in the gas phase. However, this differs from the intramolecular ligand equilibration in a mononuclear complex where a vibrational mechanism is involved.

Scheme II, the mechanism and the rate constants governing formation of the product ions in the primary steps of addition and substitution are shown.

Decomposition of excited 1 could occur by the microscopic reverse of the addition process with loss of ^{13}CO (k_d') or CO (k_d''). These unimolecular rate constants are statistically related by the equation $3k_d' = k_d''$, since there will be no appreciable isotope effect. The decomposition path k_d' leads to no net reaction since the starting ion $(OC)_3Fe^-$ is regenerated. Thus, the total rate constant for the unimolecular decomposition of 1, k_d, is the sum $k_d = k_d' + k_d''$.

In gas-phase reactions, formation of adduct products, e.g. $(OC)_3(O^{13}C)Fe^-$, requires removal of the excess energy from the excited adduct by collisions with a third body or decomposition of the adduct will occur. In these FA experiments, the third body is the helium buffer gas. This is shown in Scheme II with the collision frequency for 1 with the buffer gas given by the product of the rate constant k_s and the helium concentration.

The process of ligand substitution is solely concerned with the conversion of $(OC)_3Fe^-$ with ^{13}CO to $(OC)_2(O^{13}C)Fe^-$ (eq 2). Therefore, the intermediate 1 ions that

$$(OC)_3Fe^- + {}^{13}CO \rightarrow (OC)_2(O^{13}C)Fe^- + CO \quad (2)$$

decompose by k_d' with loss of ^{13}CO are ignored in the analysis. Once the product ion and CO molecule have separated, the labeled metal complex negative ion will not find another CO molecule due to the high dilution ($[\text{ion products}]_{max} = [CO]_{max} < 10^8$ molecules cm^{-3}; $[He] \approx 10^{16}$ atoms cm^{-3}) and the short time frame (~10 ms) in these FA experiments. Therefore, reversibility of reaction 2 is not possible.

The relationship between the product forming rate processes in Scheme II and the average branching fractions (Table I) assuming that a single collision is adequate for stabilization of the adduct is shown in eq 3. Langevin theory[15] was used to calculate the collision cross section of the 1 ions with the helium atoms (He polarizability = 0.203×10^{24} cm^3);[20] $k_s = 5.3 \times 10^{-10}$ cm^3 atom^{-1} s^{-1}. From the ideal gas law, $[He] = 3.1 \times 10^{16}$ atoms cm^{-3} at the average $P_{He} = 0.9$ Torr. Thus, $k_s[He] = 1.6 \times 10^7$ s^{-1}. The reciprocal of this value, 6.3×10^{-8} s, is the lower limit of the average lifetime of the intermediate 1. From eq 3, we derive the following lower limits for the unimolecular rate constants in Scheme II, $k_d'' = 6.5 \times 10^6$ s^{-1} and $k_d' = 2.2 \times 10^6$ s^{-1}, as well as the total rate constant for the decomposition of 1, $k_d = 8.7 \times 10^6$ s^{-1}.

$$\frac{\text{substitution branching fraction}}{\text{addition branching fraction}} = \frac{\dfrac{k_d''}{k_d'' + k_s[He]}}{\dfrac{k_s[He]}{k_d'' + k_s[He]}} \quad (3a)$$

$$\frac{0.29}{0.71} = \frac{k_d''}{k_s[He]} \quad (3b)$$

The rate constant k_f in Scheme II can also be estimated from the present data assuming that all 1 ions formed decompose via Scheme II. The average k_{total} for the destruction of $(OC)_3Fe^-$ in the two runs in Table I is $(2.4 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This rate constant is composed of contributions from addition (1.7×10^{-10} cm^3 molecule^{-1} s^{-1}) and substitution (0.7×10^{-10} cm^3 molecule^{-1} s^{-1}). However, 1 also decomposes by k_d' to return to $(OC)_3Fe^-$ and ^{13}CO. Correcting for the 25% contribution of $k_{d'}$ gives $k_f = (2.6 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Since k_f is 38% of k_{LAN},[15] a small barrier separates the long-lived ion/neutral collision complex $[(OC)_3Fe^-/^{13}CO]$ and 1. The height of this barrier appears to be similar to those in the reactions of $(OC)_3Fe^-$ with the unsaturated molecules propene, allene, and acetylene.[14] The data also point out that the collisional stabilization efficiency of 1 by helium is 65% at $P_{He} \approx 1$ Torr.

Weitz et al.[21] examined the addition reactions of CO to $Fe(CO)_4$ and to $Fe(CO)_3$ at the high-pressure limit and observed a large difference in the two bimolecular rate constants (eqs 4 and 5). Their explanation for this difference was that reaction 4 is spin forbidden (triplet $Fe(CO)_4 \rightarrow$ singlet $Fe(CO)_5$), while reaction 5 is spin allowed ($Fe(CO)_3$ was predicted[22] to have a triplet ground state). The triplet electronic ground state of $Fe(CO)_4$ is based on the results of magnetic circular dichroism studies.[23] This kinetic characterization of ground electronic states has been applied to a number of fragment metal carbonyls.[24-32] With the exception of $V(CO)_2$,[24] all of the rate constants for addition of CO to the fragment species were within an order of magnitude of the collision limit. From these results, the like spin states of the starting fragment metal carbonyl and the adduct product are assigned. However, the generality of this kinetic method has been questioned recently in the reactions of the $Mn(CO)_{1-5}^+$ ions with ^{13}CO which occur by ligand exchange.[7] Each of the rates are fast even though ground states other than singlets appear reasonable for the lower mass CO homologues, especially, for $Mn(CO)^+$.

$$Fe(CO)_4 + CO \xrightarrow{M} Fe(CO)_5 \quad (4)$$

$$k = (5.8 \pm 1.5) \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$Fe(CO)_3 + CO \xrightarrow{M} Fe(CO)_4 \quad (5)$$

$$k = (2.2 \pm 0.3) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The large value of k_{app} (24% of k_{LAN}[15]) for reaction of $(OC)_3Fe^-$ with CO giving $(OC)_4Fe^-$ (eq 1) suggests that this ligand addition reaction takes place on a potential energy surface of the same spin multiplicity. The isoelectronic neutral fragments are $Co(CO)_{3,4}$ with their doublet ground states.[27,33]

To determine the spin state of $(OC)_3Fe^-$, we need to establish the spin state of the 17-electron product ions

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(OC)$_4$Fe$^-$. This was done in the following way. Dissociative attachment of thermal energy electrons to Fe(CO)$_5$ occurs readily to yield (OC)$_4$Fe$^-$; $\Delta H° = -14.3 \pm 10.5$ kcal mol^{-1}.[34] We assume that the vibrationally excited doublet ground state is initially produced. The reactions of the collisionally thermalized (OC)$_4$Fe$^-$ ions in the FA include halogen–atom transfer with certain haloalkanes, which occur by initial electron transfer followed by X$^-$ transfer from RX$^{\bullet -}$ to Fe(CO)$_4$.[9] For example, the bimolecular reaction of (OC)$_4$Fe$^-$ with CCl$_3$Br produces the 18-electron complex (OC)$_4$FeBr$^-$ ($k_{total} = 2.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). When CCl$_3$Br was added to the flow of (OC)$_4$Fe$^-$ produced by reaction 1 (~40%) and those (OC)$_4$Fe$^-$ ions initially formed by dissociative electron attachment (~60%),[12,35] the sole ionic product was (OC)$_4$FeBr$^-$. More significant was the observed linear decay in the plot of log [(OC)$_4$Fe$^-$] vs Cl$_3$CBr concentration through >95% loss of the (OC$_4$)Fe$^-$ ion signal yielding the same rate constant given above. Thus, all of the (OC)$_4$Fe$^{\bullet -}$ ions are in their doublet electronic ground state. *These kinetic and product results are consistent with formation of the doublet electronic ground state of (OC)$_4$Fe$^-$ from the addition of CO to the doublet electronic ground state of (OC)$_3$Fe$^-$.*

Summary and Conclusions

The fast reaction of (OC)$_3$Fe$^-$ with ^{13}CO ($k_{total} = (2.4 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) occurs by competitive collisional stabilization (65%) and unimolecular dissociation (35%) of the excited adduct [(OC)$_3$(O^{13}C)Fe$^-$]* (1). The absence of an observable P_{He} effect on k_{total} or the branching fractions suggests that the slopes of the plots of these parameters vs helium concentration are small in the P_{He} regime (0.5–1.1 Torr) investigated. Only 75% of the dissociation of 1 appears as product ions of ligand substitution with the rate constant $k_d'' \geq 7.8 \times 10^{-6}$ s^{-1}, while the remaining 25% of 1 returns to the unlabelled starting ions and ^{13}CO with $k_d' \geq 2.6 \times 10^{-6}$ s^{-1}. These lower limits of the unimolecular rate constants k_d'' and k_d' are arrived at by calculation of the collision frequency, k_s[He] = 1.9 × 10^{-7} s^{-1}, for stabilizing the adduct [(OC)$_3$(O^{13}C)Fe$^-$]*.

The high efficiency of the reaction of (OC)$_3$Fe$^-$ with CO to give (OC)$_4$Fe$^-$ ($k_{app}/k_{LAN} = 0.24$) suggests that both the starting and product ions are doublet electronic ground state species.

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(35) To the helium flow containing the (OC)$_{4,3}$Fe$^-$ mixture, sufficient CO was added via a gas inlet to convert >95% of the (OC)$_3$Fe$^-$ ions into (OC)$_4$Fe$^-$ within a 10-cm distance of the flow tube. CCl$_3$Br was then added via another inlet located 20 cm downstream of the CO inlet.

Clusters Containing Ynamine Ligands. 3. Syntheses and Structural Characterizations of Re$_2$(CO)$_8$(μ-MeC$_2$NMe$_2$) and Re$_2$(CO)$_7$[μ-C(Me)C(NMe$_2$)C(NMe$_2$)C(Me)]

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The reaction of Re$_2$(CO)$_8$[μ-C(H)=C(H)Bu](μ-H) with MeC$_2$NMe$_2$ at 25 °C yielded the product Re$_2$(CO)$_8$(μ-MeC$_2$NMe$_2$) (1; 25%). Compound 1 was characterized by single-crystal X-ray diffraction analysis and was found to contain an unsymmetric bridging ynamine ligand in which the amine-substituted carbon atom is coordinated to only one metal atom. Compound 1 reacts with additional MeC$_2$NMe$_2$ at 68 °C to yield the three isomeric products Re$_2$(CO)$_7$[μ-C(Me)C(NMe$_2$)C(NMe$_2$)C(Me)] (2; 54%), Re$_2$(CO)$_7$[μ-C(Me)C(NMe$_2$)C(Me)C(NMe$_2$)] (3; 9.5%), and Re$_2$(CO)$_7$[μ-C(NMe$_2$)C(Me)C(Me)C(NMe$_2$)] (4; 17%). Compound 2 was analyzed crystallographically and was found to contain a metallacyclic ring formed by the head-to-head coupling of two ynamine ligands. This ring is π-bonded to a Re(CO)$_3$ grouping. On the basis of IR, ^{1}H NMR, and mass spectrometry compounds 3 and 4 were proposed to have similar structures formed by the head-to-tail and tail-to-tail coupling of two ynamine ligands, respectively. Crystal data: for 1, space group $P2_1/c$, $a = 9.776$ (2) Å, $b = 11.315$ (4) Å, $c = 15.695$ (4) Å, $\beta = 97.56$ (1)°, $Z = 4$, $R = 0.034$, and $R_w = 0.040$ for 1800 reflections; for 2, space group $Pca2_1$, $a = 17.668$ (4) Å, $b = 8.510$ (2) Å, $c = 14.058$ (4) Å, $Z = 4$, $R = 0.018$, and $R_w = 0.021$ for 1429 reflections.

Introduction

Recent investigations of the coordination of unsymmetric ynamines, RC≡CNR$_2$, in polynuclear metal complexes have revealed a structural pattern that strongly suggests the existence of a carbene-like character at the amine-substituted carbon atom.[1-5] In both di- and trinuclear metal complexes the amine-substituted carbon atom is bonded to only one metal atom as in A and B. The spectroscopic and reactivity properties of these ligands also support the existence of carbene-like character.[5-7]

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