such complexes there is a considerable crystal field stabilization incentive for octahedral over tetrahedral coordination. In the case of a d^5 Mn(II) compound there is no stabilization of this type for the high-spin octahedral configuration. This is consistent with the finding that reaction mixtures involving 7:1 PhLi:Mn ratios did not give any new compound suitable for an X-ray crystal structure. Magnetic measurements[21] at ambient temperature indicate that the magnetic moment of 1 is 2.9 μ_B. This low value is consistent with two high-spin tetrahedral Mn(II) centers with considerable antiferromagnetic metal–metal interaction. The Mn⋯Mn′ distance in both compounds is about 2.73 Å. This length is near to those seen in [{Mn(CMe_2Ph)_2}]_2,[3] [Mn{CH_2C_6H_4-2-NMe_2}]_2,[5] and the dialkylmanganese–phosphine dimers of Wilkinson and co-workers[11] and slightly shorter than the 2.851 Å seen in [{MnMes_2}_3] which also possess low magnetic moments. These distances are indeed probably too long for any significant metal–metal bonding. Similarly, the Li⋯Mn vector, 2.831 (7) Å, is merely a consequence of the association of the Li(Et_2O)_2^+ moieties with the negatively charged manganese dianion.

When mesityl groups are used instead of phenyls, the mononuclear anion [MnMes_3]^- is obtained. The lowered nuclearity is undoubtedly a result of the steric effects of the larger mesityl group. The magnetic moment of 5.9 μ_B indicates that the manganese has the high-spin, d^5, configuration. The three-coordinate environment at the manganese is also notable since this is a rare,[6,22] but by no means unknown, coordination number for the metal. The average Mn–C distance, 2.142 Å, is within the expected range for a three-coordinate high-spin Mn^{2+} complex. Thus, it is slightly longer than the 2.10 Å found in the two-coordinate Mn{C(SiMe_3)_3}_2 and Mn(CH_2-t-Bu)_2 and very close to the terminal Mn–C bond lengths in 2. The structural differences between 2 and 3 may be compared to the recently reported structures of the magnesiate ions [Mg_2Et_6]^{2-} and [Mg(CH_2-t-Bu)_3]^-.[23] Both pairs of compounds exhibit many similarities in the M–C bond distances and angles that underlines the close correspondence between many classes of magnesium and manganese compounds. Structural and reactivity studies on these and related species are continuing.

Acknowledgment. We thank the donors Petroleum Research Fund, administered by the American Chemical Society, for financial support.

(21) Evans, D. F. *J. Chem. Soc.* 1959, 2005.

(22) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* 1977, 24, 1–95. Murray, B. D.; Power, P. P. *Inorg. Chem.* 1984, 23, 4586.

(23) Squiller, E. P.; Whittle, R. H.; Rickey, H. G. *J. Am. Chem. Soc.* 1985, 107, 437.

Gas-Phase Ligand Substitution Reactions with (OC)Fe(NO)$_2$$^{\cdot-}$, (OC)$_2$Co(NO)$^{\cdot-}$, ($\eta^3$-C$_3H_5$)Co(CO)$_2$$^{\cdot-}$, (C$_3H_5$)Co(CO)$_3$$^{\cdot-}$, and CpCo(CO)$_2$$^{\cdot-}$ [†]

Richard N. McDonald* and Philip L. Schell

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

Received March 10, 1988

Three 17-electron transition-metal complex negative ions LM(CO)$_{x-1}$$^{\cdot-}$ ((OC)Fe(NO)$_2$$^{\cdot-}$, (OC)$_2$Co(NO)$^{\cdot-}$, and ($\eta^3$-C$_3H_5$)Co(CO)$_2$$^{\cdot-}$) and two parent molecular anion radicals LM(CO)$_x$$^{\cdot-}$ ((C$_3$H$_5$)Co(CO)$_3$$^{\cdot-}$ and CpCo(CO)$_2$$^{\cdot-}$) were generated by electron impact on the corresponding LM(CO)$_x$ complexes in the gas phase. The ion–molecule reactions of these five metal complex negative ions were studied with the neutral molecules PF$_3$, PMe$_3$, NO, SO$_2$, olefins with electron-donating and -withdrawing vinyl substituents, biacetyl, O$_2$, CO, and CS$_2$. In general, the LM(CO)$_{x-1}$$^{\cdot-}$ complexes and CpCo(CO)$_2$$^{\cdot-}$ reacted by ligand substitution involving the associative mechanism. In many cases, the product ions of adduct formation and ligand substitution were directly observed in the same reaction. These ligand substitution reactions appear to take advantage of the ability of the NO, η^3-C$_3$H$_5$, and Cp ligands to reduce their hapticities as the neutral ligand bonds to the metal. The reaction of (C$_3$H$_5$)Co(CO)$_3$$^{\cdot-}$ with PF$_3$ occurred by fragmentation of the allyl radical. This latter result was considered to occur by radical β-fragmentation of the excited acyl complex [C$_3$H$_5$C(=O)Co(CO)$_2$(PF$_3$)$^{\cdot-}$]* formed by CO insertion into the Co–allyl bond. Both parent molecular anion radicals were observed to undergo electron transfer with several of the neutral substrates yielding EA((η^3-C$_3$H$_5$)Co(CO)$_3$) = EA(CpCo(CO)$_2$) = 0.62 ± 0.1 eV; EA((η^3-C$_3$H$_5$)Co(CO)$_2$) = 0.9 ± 0.2 eV was also measured. The results of the reactions of the parent LM(CO)$_x$$^{\cdot-}$ species with the neutral ligands were consistent with their structures having a 17-electron configuration about the metal with η^3-Cp and η^1-C$_3$H$_5$ ligands.

Introduction

Ligand substitution reactions with transition-metal complexes represent a well-studied and reasonably well-understood chemical conversion.[1–3] In general, condensed-phase ligand substitution reactions are described

(1) For a recent review of ligand substitution reactions, see: Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* 1983, 83, 557.

as occurring by either a dissociative (eq 1) or an associative mechanism (eq 2). These mechanisms differ in the mo-

$$ML_m \xrightarrow{-L} ML_{m-1} \xrightarrow{+L'} ML_{m-1}L' \quad (1)$$

$$ML_m \xrightarrow{+L'} (ML_mL') \xrightarrow{-L} ML_{m-1}L' \quad (2)$$
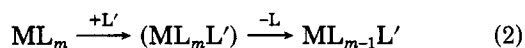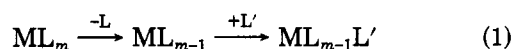
lecularity of the reaction and in the change in the coordination number of the metal in the rate-limiting first step. In the gas phase, the associative mechanism may operate as outlined in eq 2, but the dissociative mechanism (eq 1) involving predissociation of a ligand from the thermalized complex ML_m is not possible. However, if the bimolecular collision of ML_m with the ligand L' is sufficiently exothermic and exceeds the M–L bond strength, a ternary collision complex $[ML_{m-1}/L/L']$ could be formed and competition for capture of the coordinatively unsaturated metal complex ML_{m-1} by L and L' would occur within this collision complex.

In the present study of ligand substitution reactions of transition-metal carbonyl complex negative ions with neutral L' species, this latter mechanistic possibility must be considered. This is because formation of the loose orbiting collision complexes between ions and neutral molecules is exothermic by 10–20 kcal mol^{-1} due to attractive ion–dipole and ion-induced dipole forces. If this energy exceeds the binding energy of a carbonyl ligand in the original ionic metal complex $(OC)ML_n{}^-$, the ternary complex $[ML_n{}^-/CO/L']$ would result (eq 3). Competition

$$(OC)ML_n{}^- + L' \rightleftharpoons [ML_n{}^-/CO/L'] \rightarrow ML_nL'^- + CO \quad (3)$$
$$\mathbf{1}$$
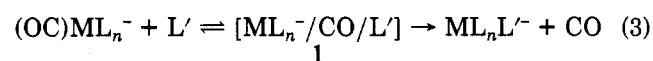
for the coordinatively unsaturated ionic complex $ML_n{}^-$ by CO and L' within the ternary complex 1 yields the starting materials or the products, respectively. We will refer to this latter mechanism as the ion–molecule collision-activated dissociative (IMCAD) mechanism.

Corderman and Beauchamp[4] reported that the molecular anion radical of nickelocene, $Cp_2Ni^{•-}$ ($Cp = c\text{-}C_5H_5$), did not react with CO, NO, HCl, HCN, or NH_3. However, these authors observed that $CpCo(CO)_2{}^{•-}$ and $CpCo(CO)^{•-}$ (both generated by electron impact on $CpCo(CO)_2$) underwent CO ligand substitution with NO and PF_3, but both ions failed to react with C_2F_4, HCN, CH_3CN, NH_3, $(CH_3)_3N$, and $(CH_3)_3P$.[5]

Ligand substitution reactions using several of the neutral ligands described in the present study have been used recently to establish the nature of the ligands present in transition-metal complex negative ions.[6-12] This application is important in the characterization of gas-phase negative ions in conjunction with their masses and isotope ratios.

The transition-metal complex negative ions selected for this investigation include the three 17-electron anionic complexes $(OC)Fe(NO)_2{}^{•-}$, $(OC)_2Co(NO)^{•-}$, and $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{•-}$ which contain a ligand (NO or $\pi\text{-}C_3H_5$) that can reduce its hapticity from $\eta^3 \rightarrow \eta^1$. The other two complexes are the parent negative ions $(C_3H_5)Co(CO)_3{}^{•-}$ and $CpCo(CO)_2{}^{•-}$ with unspecified organic ligand hapticities; we believe that the present results are most consistent with the $\eta^1\text{-}C_3H_5$ and $\eta^3\text{-}Cp$ ligand, 17-electron metal configuration structures for these two negative ions.

Experimental Section

The flowing afterglow (FA) apparatus used in these studies has been previously described.[13,14] Briefly, a fast flow of helium buffer gas ($P_{He} = 0.5$ Torr, but variable between 0.3 and 1.2 Torr; $\bar{v} = 80$ m s^{-1}, but variable down to 40 m s^{-1}) at 298 K was established and maintained during the experiment by adding helium in the upstream end of the flow tube and exhausting it at the downstream end with a large, fast pumping system. The electron gun was turned on, and a small concentration of the transition-metal complex was allowed to leak continuously into the FA via an inlet located 3 cm downstream of the electron gun. Attachment of thermal or near thermal energy electrons occurred associatively and/or dissociatively to generate the metal complex negative ions. While the main body of the flow was exhausted to the fast pumping system, it was sampled through 1-mm orifices in two molybdenum nose cones into a differentially pumped compartment ($P \approx 5 \times 10^{-7}$ Torr) containing a quadrupole mass filter and electron multiplier that continuously monitored the ion composition of the flow.

Neutral ligand substrates were then added to the dilute metal complex negative ion containing helium flow via a gas inlet located 75 cm downstream from the electron gun and 65 cm upstream from the first sampling nose cone. The kinetics of these bimolecular ion–molecule reactions were determined under pseudofirst-order conditions by procedures already discussed.[13,14] The rate constants for these reactions were determined by following the decay of the starting metal carbonyl complex anion radicals and, therefore, measure only the formation of the primary products. The rate constants were measured at two different sets of conditions: $P_{He} = 0.5$ Torr, $\bar{v} = 80$ m s^{-1}; $P_{He} = 1.0$ Torr, $\bar{v} = 40$ m s^{-1}. Generally, no P_{He} effects were observed on the bimolecular rate constants; P_{He} effects on branching fractions will be mentioned where they were observed. In the FA, we can measure rate constants for reactions that occur on every collision ($k_{total} \approx 10^{-9}$ cm^3 molecule^{-1} s^{-1}) to reactions that occur in one out of 10 000 collisions ($k_{total} = 10^{-13}$ cm^3 molecule^{-1} s^{-1}); the lower limit is most readily determined at $\bar{v} = 40$ m s^{-1}.

The helium used in this study was of 99.99% purity supplied by Welders Products (Topeka, KS) and was further purified by passage through two traps filled with Davison 4-Å molecular sieves cooled with liquid N_2 and then warmed to 298 K in a glass coil prior to introduction into the upstream end of the flow tube. Gas and liquid neutral reactants were obtained from standard commercial sources. The liquid reactants were distilled just prior to use, and a center-cut, constant boiling sample was transferred to a gas storage bulb after three freeze–pump–thaw degassing cycles. The gas reagents were used directly as received.

The complexes $(OC)_2Fe(NO)_2$[15] and $(\eta^3\text{-}C_3H_5)Co(CO)_3$[16] were prepared by Ms. Allison Fleming using literature procedures. $(OC)_3Co(NO)$ (Strem) and $CpCo(CO)_2$ (Alfa) were purchased and used as received.

Results

Introduction of the volatile transition-metal complexes $(OC)_2Fe(NO)_2$, $(OC)_oCo(NO)$, $(\eta^3\text{-}C_3H_5)Co(CO)_3$, and

(2) Stiegman and Tyler (Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215) recently reviewed ligand substitution reactions of metal complexes with 17- and 19-electron configurations.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.

(4) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1976**, *15*, 665.

(5) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 3135.

(6) McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *Organometallics* **1984**, *3*, 644.

(7) McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095.

(8) McDonald, R. N.; Schell, P. L.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 5578.

(9) McDonald, R. N.; Jones, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 8097.

(10) McDonald, R. N.; Chowdhury, A. K. *Organometallics* **1986**, *5*, 1187.

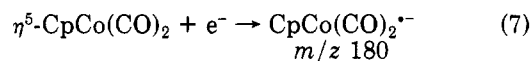(11) McDonald, R. N.; Jones, M. T. *Organometallics* **1987**, *6*, 1991.

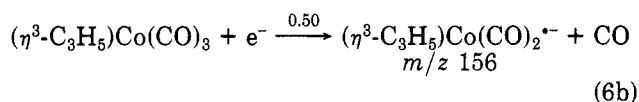(12) Wang, D. N.; Squires, R. R. *Organometallics* **1987**, *6*, 905.

(13) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123.

(14) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.

(15) King, R. B. *Organometallic Syntheses*; Academic: New York; 1965; p 167.

(16) Abel, E. W.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1973**, 1706.

Table I. Summary of Kinetic and Product Data for the Ligand Substitution Reactions of $(OC)Fe(NO)_2^{\cdot-}$

rxn	neutral reactant	product ion(s) + [assumed neutral]	fractn of product ion signal	$k_{total},^a$ cm³ molecule⁻¹ s⁻¹	$k_{ADO},^b$ cm³ molecule⁻¹ s⁻¹
1a	PF_3	$\xrightarrow{He}$ $(OC)Fe(NO)_2(PF_3)^{\cdot-}$	0.79^c	2.5×10^{-10}	8.1×10^{-10}
1b		$\rightarrow (ON)_2Fe(PF_3)^{\cdot-}$ + [CO]	0.21		
2	$P(CH_3)_3$	$\xrightarrow{He}$ $(OC)Fe(NO)_2(P(CH_3)_3)^{\cdot-}$	1.00	$2.6 \times 10^{-11 e}$	1.1×10^{-9}
3	$P(OCH_3)_3$	$\xrightarrow{He}$ $(OC)Fe(NO)_2(P(OCH_3)_3)^{\cdot-}$	1.00	g	
4	NO	$\rightarrow Fe(NO)_3^-$ + [CO]	1.00	1.1×10^{-10}	6.2×10^{-10}
5	SO_2	$\rightarrow (ON)_2Fe(SO_2)^{\cdot-}$ + [CO]	1.00	1.0×10^{-9}	1.1×10^{-9}
6a	$CH_2{=}CHBr$	$\rightarrow (ON)_2Fe(C_2H_3Br)^{\cdot-}$ + [CO]	0.81	1.5×10^{-12}	1.1×10^{-9}
6b		$\rightarrow (ON)Fe(C_2H_3Br)^-$ + [CO + NO]	0.19		
7	$CH_3CH{=}CH_2$	$\rightarrow$ no reaction		$<10^{-13}$	
8	$CH_2{=}CHOC_2H_5$	$\rightarrow$ no reaction		$<10^{-13}$	
9	$CH_2{=}CHCN$	$\rightarrow (ON)_2Fe(C_3H_3N)^{\cdot-}$ + [CO]	1.00	6.8×10^{-10}	2.4×10^{-9}
10	$CH_2{=}CHCO_2CH_3$	$\rightarrow (ON)_2Fe(C_4H_6O_2)^{\cdot-}$ [CO]	1.00	1.0×10^{-10}	1.3×10^{-9}
11	$CF_2{=}CF_2$	$\rightarrow (ON)_2Fe(C_2F_4)^{\cdot-}$ + [CO]	1.00	5.9×10^{-12}	6.2×10^{-10}
12	CH_3COCH_3	$\rightarrow$ no reaction		$<10^{-13}$	
13	CH_3COCF_3	$\rightarrow (ON)_2Fe(C_3H_3F_3O)^{\cdot-}$ + [CO]	1.00	4.4×10^{-11}	$9.4 \times 10^{-10 f}$
14	CF_3COCF_3	$\rightarrow (ON)_2Fe(C_3F_6O)^{\cdot-}$ + [CO]	1.00	3.9×10^{-10}	1.0×10^{-9}
15	$CH_3COCOCH_3$	$\rightarrow (ON)_2Fe(C_4H_6O_2)^{\cdot-}$ + [CO]	1.09	5.0×10^{-10}	9.1×10^{-10}
16a	O_2	$\rightarrow (ON)_2Fe(O_2)^{\cdot-}$ + [CO]	0.58^d	7.9×10^{-11}	5.7×10^{-10}
16b		$\rightarrow (ON)Fe(O_2)^-$ + [NO + CO]	0.39		
16c		$\rightarrow (ON)_2FeO^{\cdot-}$ + [CO_2]	0.03		
17	CO	$\xrightarrow{He}$ $(ON)_2Fe(CO)_2^{\cdot-}$	1.00	$6.1 \times 10^{-12 e}$	6.8×10^{-10}
18	CH_3CN	$\rightarrow$ no reaction		$<10^{-13}$	

^{a} These values are averages of at least three separate experiments; the maximum deviation in a particular rate constant determination was within ±10% of this average value. The errors due to systematic uncertainties in calibrations suggest that their accuracy is ±20%. ^{b} Reference 17. ^{c} P_{He} = 0.5 Torr; at P_{He} = 1.0 Torr, the a/b product ratio was 82/18. ^{d} P_{He} = 0.5 Torr; at P_{He} = 1.0 Torr, the a/b/c product ratio was 64/33/3. ^{e} Apparent bimolecular rate constant. ^{f} k_{LAN}; ref 17. ^{g} The rate constant was not measured.

$CpCo(CO)_2$ to the FA followed by electron impact produced the results shown in eq 4-7. In the generation of

$$(OC)_2Fe(NO)_2 + e^- \rightarrow (OC)Fe(NO)_2^{\cdot-} + CO \quad (4)$$
$$m/z \ 144$$

$$(OC)_3Co(NO) + e^- \rightarrow (OC)_2Co(NO)^{\cdot-} + CO \quad (5)$$
$$m/z \ 145$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_3 + e^- \xrightarrow{0.50} (C_3H_5)Co(CO)_3^{\cdot-} \quad (6a)$$
$$m/z \ 184$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_3 + e^- \xrightarrow{0.50} (\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-} + CO$$
$$m/z \ 156$$
$$(6b)$$

$$\eta^5\text{-}CpCo(CO)_2 + e^- \rightarrow CpCo(CO)_2^{\cdot-} \quad (7)$$
$$m/z \ 180$$
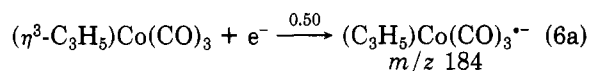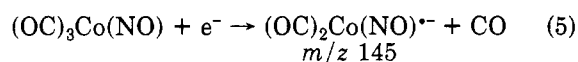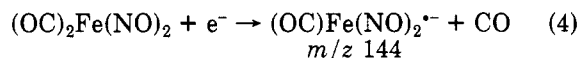
$(OC)Fe(NO)_2^{\cdot-}$, we observed formation of a small ion signal at m/z 168 attributed to $(OC)_4Fe^{\cdot-}$ from minor contamination by $Fe(CO)_5$ in the sample of $(OC)_2Fe(NO)_2$. Trace contamination by $Co_2(CO)_8$ in the sample of $(OC)_3Co(NO)$ was noted when a small (<1%) ion signal for $(OC)_4Co^-$ was also observed in the dissociative electron attachment mass spectrum of this sample. Neither of these two contaminating ions offered any problem in the present study.

Identification of the separate product forming channels from the two metal complex negative ions $(C_3H_5)Co(CO)_3^{\cdot-}$ and $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-}$ formed in the same flow (eq 6) was readily accomplished if their rate constants for reaction differed significantly or a P_{He} effect was observed on certain branching fractions in their product forming channels. Further comments relating to this problem and the individual product forming channel assignments will be made in the appropriate discussion sections of this paper.

All of the reactions for these five metal complex negative ions with the various neutral substrates listed in Tables I–V gave excellent pseudo-first-order decay plots with correlation coefficients >0.99. The rate constants and
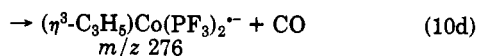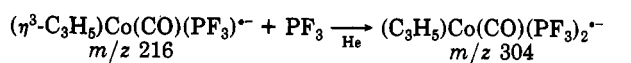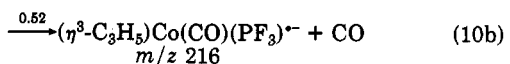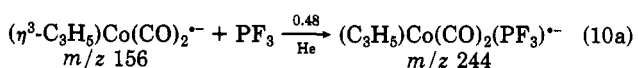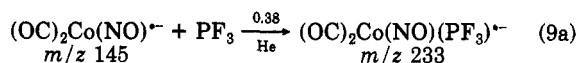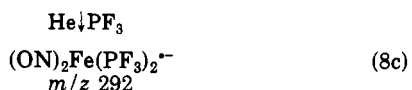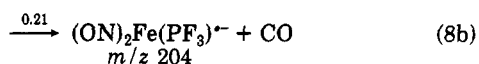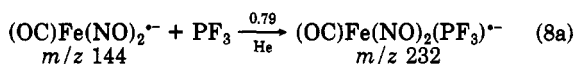
branching fractions listed in these tables are averages of at least three separate experiments at two P_{He}s (see Experimental Section). While our ability to duplicate rate constants is <±10% of the average value cited, the errors due to systematic uncertainties in calibrations suggest that their accuracy for external comparisons is ±20%. The errors in the branching fractions are ±4% absolute, and the branching fractions are corrected for any secondary reactions. Unless noted otherwise, the rate constants and product ion branching fractions did not change outside of experimental error with a change in the flow tube pressure (P_{He}) from 0.5 to 1.0 Torr.

Observation of total adduct product ions from these ion–molecule reactions was assumed to require collisional stabilization to remove excess energy from the excited adduct negative ion with the buffer gas. Absence of an observed change in the rate constant or product branching fraction with adduct formation as P_{He} was changed meant that either this step was already saturated at our lowest pressure or the small ΔP_{He} available was not sufficient to observe a pressure effect outside of the experimental error limits.

Discussion

Reactions of the Five Metal Complex Negative Ions with Some Phosphorus Ligands. The phosphines used in these studies were PF_3 and $P(CH_3)_3$. If the neutral substrate is to be effective in ligand substitution on a metal negative ion complex within our kinetic window, the ability of the incoming ligand molecule for π-back-bonding must equal or exceed that of the ligand being replaced to stabilize the anionic complex. This was the conclusion of Corderman and Beauchamp in their ligand substitution reactions of $CpCo(CO)_{2,1}^{\cdot-}$ [5] where PF_3 accomplished CO substitution while $(CH_3)_3P$ did not react.

The fast reactions of $(OC)Fe(NO)_2^{\cdot-}$ (eq 8), $(OC)_2Co(NO)^{\cdot-}$ (eq 9), and $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-}$ (eq 10) with PF_3 proceeded by primary formation of mixtures of the adduct and the (adduct–CO) negative ions. The large rate constants varied from 21 to 39% of the collision limit (k_{ADO}).[17]

$$(OC)Fe(NO)_2^{\cdot-} + PF_3 \xrightarrow[He]{0.79} (OC)Fe(NO)_2(PF_3)^{\cdot-} \quad (8a)$$
$$m/z\ 144 \qquad\qquad\qquad m/z\ 232$$

$$\xrightarrow{0.21} (ON)_2Fe(PF_3)^{\cdot-} + CO \quad (8b)$$
$$m/z\ 204$$

$$He\downarrow PF_3$$

$$(ON)_2Fe(PF_3)_2^{\cdot-} \quad (8c)$$
$$m/z\ 292$$

$$(OC)_2Co(NO)^{\cdot-} + PF_3 \xrightarrow[He]{0.38} (OC)_2Co(NO)(PF_3)^{\cdot-} \quad (9a)$$
$$m/z\ 145 \qquad\qquad\qquad m/z\ 233$$

$$\xrightarrow{0.62} (OC)Co(NO)(PF_3)^{\cdot-} + CO \quad (9b)$$
$$m/z\ 205$$

$$(OC)Co(NO)(PF_3)^{\cdot-} + PF_3 \xrightarrow{He} (OC)Co(NO)(PF_3)_2^{\cdot-} \quad (9c)$$
$$m/z\ 205 \qquad\qquad\qquad m/z\ 293$$

$$\rightarrow (ON)Co(PF_3)_2^{\cdot-} + CO \quad (9d)$$
$$m/z\ 265$$

$$He\downarrow PF_3$$

$$(ON)Co(PF_3)_3^{\cdot-} \quad (9e)$$
$$m/z\ 353$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-} + PF_3 \xrightarrow[He]{0.48} (C_3H_5)Co(CO)_2(PF_3)^{\cdot-} \quad (10a)$$
$$m/z\ 156 \qquad\qquad\qquad m/z\ 244$$

$$\xrightarrow{0.52} (\eta^3\text{-}C_3H_5)Co(CO)(PF_3)^{\cdot-} + CO \quad (10b)$$
$$m/z\ 216$$

$$(\eta^3\text{-}C_3H_5)Co(CO)(PF_3)^{\cdot-} + PF_3 \xrightarrow{He} (C_3H_5)Co(CO)(PF_3)_2^{\cdot-}$$
$$m/z\ 216 \qquad\qquad\qquad m/z\ 304$$
$$(10c)$$

$$\rightarrow (\eta^3\text{-}C_3H_5)Co(PF_3)_2^{\cdot-} + CO \quad (10d)$$
$$m/z\ 276$$

These fast reactions obviously have very small barriers separating the orbiting collision complexes and the excited total adduct negative ions. In all three cases, collisional stabilization of the excited adduct anion radicals by the helium buffer gas was competitive with fragmentation of a CO ligand as the primary product forming channels. This conclusion was supported by the observed increase in the (adduct)/(adduct–CO) ratios for the product ions when P_{He} was increased from 0.5 to 1.0 Torr (Tables I, II, and IV). These facts are consistent with the associative mechanism of ligand substitution in these three metal 17-electron complex negative ions where the η^3-NO and η^3-C_3H_5 ligands switch to η^1 to accommodate the incoming PF_3 molecule in forming the adducts.

The secondary ion–molecule reactions of the primary (adduct–CO) product ions with PF_3 followed a similar course (eq 9c,d and 10c,d) where the adduct and the (adduct–CO) product negative ions were observed. There was no evidence for substitution of an NO or the C_3H_5 ligand by PF_3 in these primary or secondary ion–molecule reactions.

We can now address the very different result obtained in the much slower reaction of PF_3 with the parent anion radical formed by electron attachment to $(\eta^3\text{-}C_3H_5)Co(CO)_3$ shown in eq 11. The loss of the allyl radical was apparent
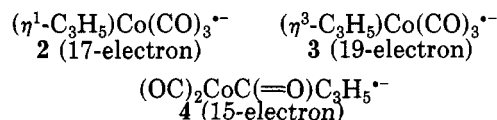
$$(C_3H_5)Co(CO)_3^{\cdot-} + PF_3 \rightarrow (OC)_3Co(PF_3)^- + {}^\bullet C_3H_5 \quad (11)$$
$$m/z\ 184 \qquad\qquad\qquad m/z\ 231$$

from the product ion mass and the halving of the (M + 1) ^{13}C isotope peak at m/z 232 compared to that in the

(17) Collison-limited rate constants were calculated by using the average dipole orientation theory (k_{ADO}) if the dipole moment of the neutral molecule was known or Langevin theory if the dipole moment was unknown. See: Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, Chapter 3.

starting ion at m/z 185. This expulsion of the allyl radical in reaction 11 rules out an IMCAD mechanism for this reaction since exclusive loss of a CO ligand occurred in the dissociative electron attachment to $(\eta^3\text{-}C_3H_5)Co(CO)_3$ (eq 6) and CO ejection would be similarily expected here.

Possible structures for the parent anion radical of $(\eta^3\text{-}C_3H_5)Co(CO)_3$ are **2–4**. The coordinatively and elec-

$$(\eta^1\text{-}C_3H_5)Co(CO)_3^{\cdot-} \qquad (\eta^3\text{-}C_3H_5)Co(CO)_3^{\cdot-}$$
$$\textbf{2 (17-electron)} \qquad\qquad \textbf{3 (19-electron)}$$
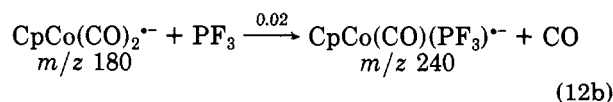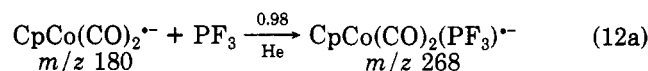
$$(OC)_2CoC(=O)C_3H_5^{\cdot-}$$
$$\textbf{4 (15-electron)}$$

tronically unsaturated structure **4** is unlikely as the ions at m/z 184 since the related 16/15-electron complex ions $(OC)_3Co^-$, $(OC)_3Fe^{\cdot-}$, $(OC)_4Mn^-$, and $(OC)_4Cr^{\cdot-}$ react with PF_3 yielding adducts and/or CO ligand substitution product ions with rate constants near the collision limit.[17] Of the structures **2** and **3**, **2** has considerable precedence in the structures of neutral complexes in the condensed phase.[3,18a] A related example was observed in the condensed and gas phases where the one-electron reduction of $(\eta^4\text{-}1,3\text{-butadiene})Fe(CO)_3$ yields the parent 17-electron complex anion radical $(\eta^2\text{-}1,3\text{-butadiene})Fe(CO)_3^{\cdot-}$ with an $\eta^4 \rightarrow \eta^2$ hapticity change in the diene ligand.[8,12,19]

Specific substitution for the allyl radical by the two-electron donor PF_3 would appear to require formation of an association adduct followed by radical fragmentation. We rationalize this process by either a concerted CO ligand insertion into the Co–allyl bond as the PF_3 molecule bonds to Co or stepwise via a 19-electron intermediate adduct yielding the acyl complex **5**. The CO insertion has the

$$(OC)_2(F_3P)CoC(=O)C_3H_5^{\cdot-}$$
$$\textbf{5}$$
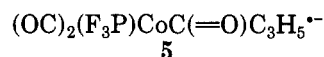
condensed-phase analogies of equilibria between alkylmetal carbonyl complexes with the corresponding acyl complexes.[18] If the radical is centered on Co in **5**, radical β-fragmentation would cleave the acyl ligand specifically with loss of the allyl radical generating the observed 18-electron product negative ions at m/z 231. On the basis of structure **2** representing the ions at m/z 184 and the above interpretation, the small rate constant for reaction 11 requires a significant kinetic barrier for the CO insertion step if addition–insertion is concerted, or in forming the 19-electron addition adduct if the process is stepwise.

In a related manner, the parent anion radical at m/z 180 formed by low-energy electron attachment to $CpCo(CO)_2$ could be the 17-electron complex $(\eta^3\text{-}Cp)Co(CO)_2^{\cdot-}$ (**6**) or the 19-electron complex $(\eta^5\text{-}Cp)Co(CO)_2^{\cdot-}$ (**7**). The reaction of the negative ions at m/z 180 with PF_3 was slow and produced mainly the total adduct at m/z 268 along with a trace of the CO ligand substitution product at m/z 240 (eq 12). These results are different from those reported

$$CpCo(CO)_2^{\cdot-} + PF_3 \xrightarrow[He]{0.98} CpCo(CO)_2(PF_3)^{\cdot-} \quad (12a)$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 268$$

$$CpCo(CO)_2^{\cdot-} + PF_3 \xrightarrow{0.02} CpCo(CO)(PF_3)^{\cdot-} + CO \quad (12b)$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 240$$

by Corderman and Beauchamp[5] for this reaction in their ICR spectrometer where only the ion product of ligand substitution at m/z 240 was observed. However, this is not unexpected since reactions in the FA are carried out

(18) (a) Cotton, F. A.; Wilkenson, G. W. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York; 1980. (b) Reference 3, Chapter 6.
(19) Krusic, P. J.; San Filippo, J. *J. Am. Chem. Soc.* **1982**, *104*, 2645.

Table II. Summary of Kinetic and Product Data for the Ligand Substitution Reactions of $(OC)_2Co(NO)^{\cdot-}$

rxn	neutral reactant	product ion(s) + [assumed neutral]	fractn of product ion signal	k_{total},[a] cm^3 molecule^{-1} s^{-1}	k_{ADO},[b] cm^3 molecule^{-1} s^{-1}
1a	PF_3	$\xrightarrow{He} (OC)_2Co(NO)(PF_3)^{\cdot-}$	0.38[c]	2.1×10^{-10}	8.1×10^{-10}
1b		$\rightarrow (OC)Co(NO)(PF_3)^{\cdot-} + [CO]$	0.62		
2	$P(CH_3)_3$	$\rightarrow$ no reaction			
3	NO	$\rightarrow (OC)Co(NO)_2^- + [CO]$	1.00	9.0×10^{-11}	6.2×10^{-10}
4	SO_2	$\rightarrow (OC)Co(NO)(SO_2)^{\cdot-} + [CO]$	1.00	8.9×10^{-10}	1.1×10^{-9}
5	$CH_3CH=CH_2$	$\rightarrow$ no reaction		$<10^{-13}$	
6	$CH_2=CHOC_2H_5$	$\rightarrow$ no reaction		$<10^{-13}$	
7	$CH_2=CHBr$	$\rightarrow$ no reaction		$<10^{-13}$	
8a	$CH_2=CHCN$	$\xrightarrow{He} (OC)_2Co(NO)(C_3H_3N)^{\cdot-}$	0.62	8.4×10^{-13}	2.4×10^{-9}
8b		$\rightarrow (OC)Co(NO)(C_3H_3N)^{\cdot-} + [CO]$	0.38		
9	$CH_2=CHCO_2CH_3$	$\rightarrow$ no reaction		$<10^{-13}$	
10a	$CF_2=CF_2$	$\xrightarrow{He} (OC)_2Co(NO)(C_2F_4)^{\cdot-}$	0.04	2.2×10^{-12}	6.2×10^{-10}
10b		$\rightarrow (OC)Co(NO)(C_2F_4)^{\cdot-} + [CO]$	0.96		
11a	$(NC)_2C=C(CN)_2$	$\rightarrow C_2(CN)_4^{\cdot-} + [(OC)_2Co(NO)]$	0.55	d	
11b		$\rightarrow (OC)Co(NO)(C_6N_4)^{\cdot-} + [CO]$	0.45		
12	CH_3COCH_3	$\rightarrow$ no reaction		$<10^{-13}$	
13	CH_3COCF_3	$\rightarrow$ no reaction		$<10^{-13}$	
14a	CF_3COCF_3	$\rightarrow (OC)Co(NO)(C_3F_6O)^{\cdot-} + [CO]$	0.71	3.9×10^{-10}	1.0×10^{-9}
14b		$\rightarrow (OC)_2Co(C_3F_6O)^- + [NO]$	0.29		
15a	$CH_3COCOCH_3$	$\xrightarrow{He} (OC)_2Co(NO)(C_4H_6O_2)^{\cdot-}$	0.12	2.4×10^{-10}	9.1×10^{-10}
15b		$\rightarrow (OC)Co(NO)(C_4H_6O_2)^{\cdot-} + [CO]$	0.88		
16a	O_2	$\rightarrow (OC)Co(NO)(O_2)^{\cdot-} + [CO]$	0.41	8.3×10^{-11}	5.7×10^{-10}
16b		$\rightarrow (OC)_2Co(O_2)^- + [NO]$	0.29		
16c		$\rightarrow (OC)Co(O_2)^- + [CO + NO]$	0.02		
16d		$\rightarrow (ON)CoO^{\cdot-} + [CO + CO_2]$	0.28		
17	CO	$\xrightarrow{He} (OC)_3Co(NO)^{\cdot-}$	1.00	$1.4 \times 10^{-12\,e}$	6.8×10^{-10}
18a	CS_2	$\rightarrow (OC)Co(NO)(CS_2)^{\cdot-} + [CO]$	0.50	d	
18b		$\rightarrow (OC)_2Co(CS_2)^- + [NO]$	0.50		
19	CO_2	$\rightarrow$ no reaction		$<10^{-13}$	
20	CH_3CN	$\rightarrow$ no reaction		$<10^{-13}$	

^{a,b} See Table I. $^c P_{He} = 0.5$ Torr; at $P_{He} = 1.0$ Torr, the a/b product ratio was 50/50. ^{d} The rate constant was not determined. ^{e} Apparent bimolecular rate constant.

Table III. Summary of Kinetic and Product Data for the Ligand Substitution Reactions of $CpCo(CO)_2^{\cdot-}$

rxn	neutral reactant	product ion(s) + [assumed neutral]	fractn of product ion signal	k_{total},[a] cm^3 molecule^{-1} s^{-1}	k_{ADO},[b] cm^3 molecule^{-1} s^{-1}
1a	PF_3	$\xrightarrow{He} CpCo(CO)_2(PF_3)^{\cdot-}$	0.98	$5.0 \times 10^{-12\,d}$	7.8×10^{-10}
1b		$\rightarrow CpCo(CO)(PF_3)^{\cdot-} + [CO]$	0.02		
2	$P(CH_3)_3$	$\rightarrow$ no reaction		$<10^{-13}$	
3a	NO	$\rightarrow CpCo(CO)(NO)^- + [CO]$	0.80	3.2×10^{-11}	6.1×10^{-10}
3b		$\rightarrow CpCo(NO)^- + [2CO]$	0.20		
4a	SO_2	$\rightarrow SO_2^{\cdot-} + [CpCo(CO)_2]$	0.92	9.2×10^{-10}	1.1×10^{-9}
4b		$\rightarrow CpCo(CO)(SO_2)^{\cdot-} + [CO]$	0.08		
5	$CH_2=CHCH_3$	$\rightarrow$ no reaction		$<10^{-13}$	
6	$CH_2=CHCN$	$\rightarrow$ no reaction		$<10^{-13}$	
7	$CH_2=CHCO_2CH_3$	$\rightarrow$ no reaction		$<10^{-13}$	
8	$CH_2=CHOC_2H_5$	$\rightarrow$ no reaction		$<10^{-13}$	
9	$CH_2=CHBr$	$\rightarrow$ no reaction		$<10^{-13}$	
10	$CF_2=CF_2$	$\rightarrow$ no reaction		$<10^{-13}$	
11	$(NC)_2C=C(CN)_2$	$\rightarrow C_2(CN)_4^{\cdot-} + [CpCO(CO)_2]$	1.00	c	
12	CH_3COCH_3	$\rightarrow$ no reaction		$<10^{-13}$	
13	CH_3COCF_3	$\rightarrow$ no reaction		$<10^{-13}$	
14	CF_3COCF_3	$\rightarrow C_3F_6O^{\cdot-} + [CpCo(CO)_2]$	1.00	5.7×10^{-10}	9.6×10^{-10}
15	$CH_3COCOCH_3$	$\rightarrow C_4H_6O_2^{\cdot-} + [CpCo(CO)_2]$	1.00	1.2×10^{-10}	8.8×10^{-10}
16a	O_2	$\rightarrow CpCo(CO)(O_2)^{\cdot-} + [CO]$	0.08	6.7×10^{-11}	5.6×10^{-10}
16b		$\rightarrow CpCo(CO)(O)^{\cdot-} + [CO_2]$	0.09		
16c		$\rightarrow CpCo(O)^{\cdot-} + [CO + CO_2]$	0.71		
16d		$\rightarrow CpCo^{\cdot-} + [2CO_2]$	0.12		
17a	CS_2	$\xrightarrow{He} CpCo(CO)_2(CS_2)^{\cdot-}$	0.15	$5.0 \times 10^{-12\,e}$	
17b		$\rightarrow CpCo(CO)(CS_2)^{\cdot-} + [CO]$	0.77		
17c		$\rightarrow CpCo(CS_2)^{\cdot-} + [2CO]$	0.08		
18	CH_3CN	$\rightarrow$ no reaction		$<10^{-13}$	

^{a,b} See Table I. ^{c} The rate constant was not determined. ^{d} Apparent bimolecular rate constant. ^{e} Reference 38.

at relatively high buffer gas pressure while the reactions in the ICR are conducted at low pressure ($<10^{-5}$ Torr). Therefore, collisional stabilization and direct observation of intermediate adducts produced in ion–molecule reactions can occur in the FA.

Formation of the total adduct at m/z 268 in reaction 12 is consistent with the associative mechanism seen in re-

actions 8–10 and requires a reduction in the hapticity of the Cp ligand.[20,21] The small apparent bimolecular rate

(20) Casey et al. (Casey, C. P.; Jones, W. D.; Harsy, S. G. *J. Organomet. Chem.* 1981, *206*, C38) reported the $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ hapticity change in a Cp ligand in a tungsten complex by the sequential addition of two $(CH_3)_3P$ ligands.

Table IV. Summary of Kinetic and Product Data for the Ligand Substitution Reactions of $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\cdot-}$

rxn	neutral reactant	product ion(s) + [assumed neutral]	fractn of product ion signal	k_{total},[a] cm^3 molecule^{-1} s^{-1}	k_{ADO},[b] cm^3 molecule^{-1} s^{-1}
1a	PF$_3$	$\xrightarrow{He}$ $(C_3H_5)Co(CO)_2(PF_3)^{\cdot-}$	0.48[c]	3.1 × 10^{-10}	8.0 × 10^{-10}
1b		→ $(\eta^3\text{-}C_3H_5)Co(CO)(PF_3)^{\cdot-}$ + [CO]	0.52		
2	P(CH$_3$)$_3$	→ no reaction		<10^{-13}	
3	NO	→ $(\eta^3\text{-}C_3H_5)Co(CO)(NO)^-$ + [CO]	1.0	6.9 × 10^{-11}	6.2 × 10^{-10}
4a	SO$_2$	→ $(OC)_2Co(SO_2)^-$ + [$^{\cdot}C_3H_5$]	0.71	8.9 × 10^{-10}	1.1 × 10^{-9}
4b		→ $(\eta^3\text{-}C_3H_5)Co(CO)(SO_2)^{\cdot-}$ + [CO]	0.29		
5	CH$_3$CH=CH$_2$	→ no reaction		<10^{-13}	
6	CH$_2$=CHOC$_2$H$_5$	→ no reaction		<10^{-13}	
7	CH$_2$=CHBr	→ no reaction		<10^{-13}	
8a	CH$_2$=CHCN	$\xrightarrow{He}$ $(C_3H_5)Co(CO)_2(C_3H_3N)^{\cdot-}$	0.05	5.2 × 10^{-10}	2.4 × 10^{-9}
8b		→ $(\eta^3\text{-}C_3H_5)Co(CO)(C_3H_3N)^{\cdot-}$ + [CO]	0.08		
8c		→ $(OC)_2Co(C_3H_3N)^-$ + [$^{\cdot}C_3H_5$]	0.87		
9a	CH$_2$=CHCO$_2$CH$_3$	$\xrightarrow{He}$ $(C_3H_5)Co(CO)_2(C_4H_6O_2)^{\cdot-}$	0.47	2.6 × 10^{-11}	1.3 × 10^{-9}
9b		→ $(\eta^3\text{-}C_3H_5)Co(CO)(C_4H_6O_2)^{\cdot-}$ + [CO]	0.06		
9c		→ $(OC)_2Co(C_4H_6O_2)^-$ + [$^{\cdot}C_3H_5$]	0.47		
10a	CF$_2$=CF$_2$	$\xrightarrow{He}$ $(C_3H_5)Co(CO)_2(C_2F_4)^{\cdot-}$	0.01	8.6 × 10^{-13}	6.1 × 10^{-10}
10b		→ $(\eta^3\text{-}C_3H_5)Co(CO)(C_2F_4)^{\cdot-}$ + [CO]	0.99		
11	(NC)$_2$C=C(CN)$_2$	→ $C_2(CN)_4{}^{\cdot-}$ + [$(\eta^3\text{-}C_3H_5)Co(CO)_2$]	1.0	f	
12	CH$_3$COCH$_3$	→ no reaction		<10^{-13}	
13	CH$_3$COCF$_3$	→ g		1.1 × 10^{-11}	9.2 × 10^{-10} ^{d}
14a	CF$_3$COCF$_3$	→ $C_3F_6O^{\cdot-}$ + [$(\eta^3\text{-}C_3H_5)Co(CO)_2$]	0.61	3.7 × 10^{-10}	1.0 × 10^{-9}
14b		→ $(OC)_2Co(C_3F_6O)^-$ + [$^{\cdot}C_3H_5$]	0.25		
14c		→ $(\eta^3\text{-}C_3H_5)Co(CO)(C_3F_6O)^{\cdot-}$ + [CO]	0.14		
15a	CH$_3$COCOCH$_3$	$\xrightarrow{He}$ $(C_3H_5)Co(CO)_2(C_4H_6O_2)^{\cdot-}$	0.14	2.2 × 10^{-10}	9.0 × 10^{-10}
15b		→ $(\eta^3\text{-}C_3H_5)Co(CO)(C_4H_6O_2)^{\cdot-}$ + [CO]	0.02		
15c		→ $(OC)_2Co(C_4H_6O_2)^-$ + [$^{\cdot}C_3H_5$]	0.84		
16	CO	$\xrightarrow{He}$ $(C_3H_5)Co(CO)_3{}^{\cdot-}$	1.0	4.8 × 10^{-12} ^{e}	6.8 × 10^{-10}
17	CS$_2$	→ g		f	
18	CO$_2$	→ no reaction		<10^{-13}	
19	CH$_3$CN	→ no reaction		<10^{-13}	

^{a,b} See Table VI. $^c P_{He}$ = 0.5 Torr; at P_{He} = 1.0 Torr, the a/b product ratio was 62/38. $^d k_{LAN}$; ref 17. ^{e} Apparent bimolecular rate consant. ^{f} The rate constant was not determined. ^{g} See text.

Table V. Summary of Kinetic and Product Data for the Ligand Substitution Reactions of $(C_3H_5)Co(CO)_3{}^{\cdot-}$

rxn	neutral reactant	product ion(s) + [assumed neutral]	fractn of product ion signal	k_{total},[a] cm^3 molecule^{-1} s^{-1}	k_{ADO},[b] cm^3 molecule^{-1} s^{-1}
1	PF$_3$	$\xrightarrow{He}$ $(OC)_3Co(PF_3)^-$ + [$^{\cdot}C_3H_5$]	1.0	6.7 × 10^{-12}	7.7 × 10^{-10}
2	P(CH$_3$)$_3$	→ no reaction			
3a	NO	$\xrightarrow{He}$ $(C_3H_5)Co(CO)_3(NO)^-$	0.70[c,d]	1.9 × 10^{-11}	6.1 × 10^{-10}
3b		→ $(C_3H_5)Co(CO)_2(NO)^-$ + [CO]	0.30		
4a	SO$_2$	→ $SO_2{}^{\cdot-}$ + [$(\eta^3\text{-}C_3H_5)Co(CO)_3$]	0.82	9.0 × 10^{-10}	1.1 × 10^{-9}
4b		→ $(OC)_3Co(SO_2)^-$ + [$^{\cdot}C_3H_5$]	0.18		
5	CH$_2$=CHCH$_3$	→ no reaction		<10^{-13}	
6	CH$_2$=CHCN	→ no reaction		<10^{-13}	
7	CH$_2$=CHCO$_2$CH$_3$	→ no reaction		<10^{-13}	
8	CH$_2$=CHOC$_2$H$_5$	→ no reaction		<10^{-13}	
9	CH$_2$=CHBr	→ no reaction		<10^{-13}	
10	CF$_2$=CF$_2$	→ no reaction		<10^{-13}	
11	(NC)$_2$C=C(CN)$_2$	→ $C_2(CN)_4{}^{\cdot-}$ + [$(\eta^3\text{-}C_3H_5)Co(CO)_3$]	1.0	f	
12	CH$_3$COCH$_3$	→ no reaction		<10^{-13}	
13	CH$_3$COCF$_3$	→ g		5.8 × 10^{-11}	8.9 × 10^{-10} ^{e}
14	CF$_3$COCF$_3$	→ $C_3F_6O^{\cdot-}$ + [$(\eta^3\text{-}C_3H_5)Co(CO)_3$]	1.00	3.8 × 10^{-10}	9.6 × 10^{-10}
15	CH$_3$COCOCH$_3$	→ $C_4H_6O_2{}^{\cdot-}$ + [$(\eta^3\text{-}C_3H_5)Co(CO)_3$]	1.00	1.0 × 10^{-11}	8.8 × 10^{-10}
16	CS$_2$	→ g		f	
17	CH$_3$CN	→ no reaction		<10^{-13}	

^{a,b} See Table I. $^c P_{He}$ = 0.5 Torr; at P_{He} = 1.0 Torr, the a/b product ratio was 79/21. ^{d} The formulas shown assume NO is a three-electron donor and the allyl ligand is σ-bound. $^e k_{LAN}$; ref 17. ^{f} The rate constant was not measured. ^{g} See text.

constant in reaction 12 may be due to a sizeable kinetic barrier separating the orbiting collision complex and the excited adduct because of the $\eta^x \rightarrow \eta^{x-2}$ hapticity change in the Cp ligand. The efficiency in collisional stabilization of this adduct should be as high as those observed in reactions 8–10 that yield larger apparent bimolecular rate constants and suggests that the kinetic bottleneck occurred in forming the adduct.
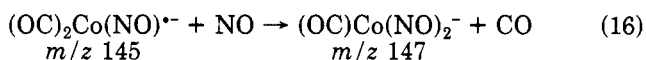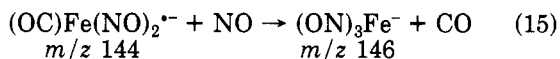
(21) Wang and Squires (Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 7557) describe hapticity changes in a Cp ligand in the gas phase similar to those in ref 20 for the condensed phase.

With $(CH_3)_3P$ as the potential ligand, only $(OC)Fe(NO)_2{}^{\cdot-}$ was observed to react and produced the total adduct at m/z 220 (eq 13) within the time (kinetic) con-

$$(OC)Fe(NO)_2{}^{\cdot-} + (CH_3)_3P \xrightarrow{He}$$
$$m/z\ 144$$

$$(OC)Fe(NO)_2(P(CH_3)_3)^{\cdot-} \quad (13)$$
$$m/z\ 220$$
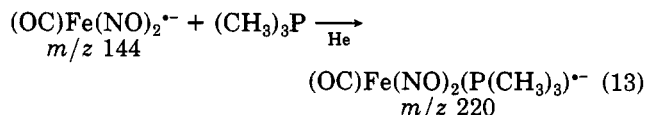
straints of our experiments. The rate constant for reaction 13 was an order of magnitude smaller than that for the reaction of this same negative ion with PF$_3$. With this success, the reaction of $(OC)_2Fe(NO)_2{}^{\cdot-}$ with $(CH_3O)_3P$ was

carried out. Although determination of the kinetics of this reaction was not possible due to the low vapor pressure of the neutral, exclusive formation of the total adduct was observed (eq 14). The reactions of the other four metal negative ion complexes with $(CH_3O)_3P$ were not examined.

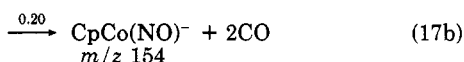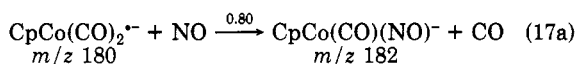$$(OC)Fe(NO)_2^{\bullet-} + (CH_3O)_3P \xrightarrow{He}$$
$$m/z\ 144$$

$$(OC)Fe(NO)_2(P(OCH_3)_3)^{\bullet-} \quad (14)$$
$$m/z\ 268$$
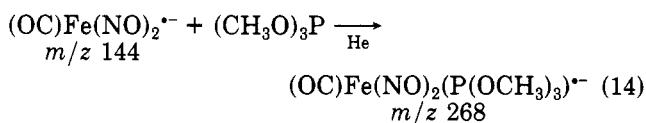
The results of the reactions of four of the five metal complex negative ions with PF_3 demonstrated that these ligand substitution reactions occur by the associative mechanism (eq 2) *by observation of the total adduct ions and the product ions of CO ligand substitution.* In reactions 8–10 where both types of product ions were observed, P_{He} effects on the (adduct)/(adduct–CO) ratio were observed which established that both ion products were derived from the same excited adduct anion radical intermediate. The only question of mechanism could be in the reaction of $(C_3H_5)Co(CO)_3^{\bullet-}$ with PF_3 where only the (adduct–$^{\bullet}C_3H_5$) product negative ion was observed.

Reactions of the Five Metal Complex Negative Ions with NO. Nitric oxide is interesting as a potential neutral ligand in its reactions with the five metal complex anion radicals since it is a free radical. Association of NO with a 17-electron metal complex negative ion would generate the corresponding excited 18-electron nitrosyl adduct anions. The rapid reactions of $(OC)Fe(NO)_2^{\bullet-}$ and $(OC)_2Co(NO)^{\bullet-}$ with NO occurred with exclusive formation of the corresponding CO ligand substitution product anions (eq 15 and 16).

$$(OC)Fe(NO)_2^{\bullet-} + NO \rightarrow (ON)_3Fe^- + CO \quad (15)$$
$$m/z\ 144 \qquad\qquad\qquad m/z\ 146$$

$$(OC)_2Co(NO)^{\bullet-} + NO \rightarrow (OC)Co(NO)_2^- + CO \quad (16)$$
$$m/z\ 145 \qquad\qquad\qquad m/z\ 147$$

The reaction of $CpCo(CO)_2^{\bullet-}$ with NO was somewhat slower and produced the primary product ions of substitution for *one and two* CO ligands (eq 17). This was

$$CpCo(CO)_2^{\bullet-} + NO \xrightarrow{0.80} CpCo(CO)(NO)^- + CO \quad (17a)$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 182$$

$$\xrightarrow{0.20} CpCo(NO)^- + 2CO \quad (17b)$$
$$m/z\ 154$$

$$He \downarrow NO$$

$$CpCo(NO)_2^{\bullet-} \quad (17c)$$
$$m/z\ 184$$

followed by ligand addition of NO to the m/z 154 ion giving $CpCo(NO)_2^{\bullet-}$ (m/z 184). The hapticity of binding the Cp and NO ligands in these product ions is not known due to their variable nature. However, the electronic configurations at the metal in the m/z 154 and 182 anion products (eq 15 and 16) are likely to be 18, while that of the anion radical at m/z 184 in eq 17c is probably 17. It was interesting that the rate constants of these three ion–molecule reactions only differed by a factor of 3. This similarity in rate constants suggests that formation of the excited nitrosyl adducts was rate-limiting.
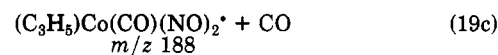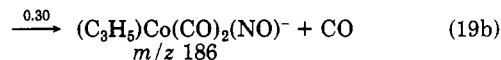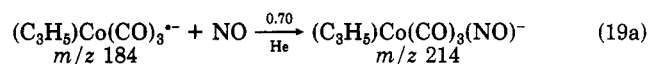
In the reactions of $(C_3H_5)Co(CO)_3^{\bullet-}$ and $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$ with NO, both starting ions reacted with similar rate constants differing by only a factor of 3.6. Three primary product ions at m/z 158, 186, and 214 that incorporate the NO molecule were generated. These product ions differ in the number of CO ligands present, $(C_3H_5)Co(CO)_{3,2,1}(NO)^-$. It was obvious that the ion at m/z 214,

$(C_3H_5)Co(CO)_3(NO)^-$, containing three CO ligands *must* be the total adduct formed by addition of NO to $(C_3H_5)Co(CO)_3^{\bullet-}$. However, the source of the remaining two product ions could be either one or both of the starting metal complex anion radicals. This question was answered when we observed a P_{He} effect on the two channels leading to $(C_3H_5)Co(CO)_{3,2}(NO)^-$; at P_{He} = 0.5 Torr, the $(m/z\ 214)/(m/z\ 186)$ ratio was 70:30, while at P_{He} = 1.0 Torr this ratio changed to 79:21. No P_{He} effect was observed on the amount of $(C_3H_5)Co(CO)(NO)^-$ produced that was equal to the amount of decay of the starting ion ($\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$.

These observations led us to conclude that $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$ reacted with NO exclusively by CO ligand substitution forming the 18-electron product ion at m/z 158 (eq 18), similar to the reactions of NO with $(OC)Fe$-

$$(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-} + NO \rightarrow$$
$$m/z\ 156$$

$$(\eta^3\text{-}C_3H_5)Co(CO)(NO)^- + CO \quad (18)$$
$$m/z\ 158$$
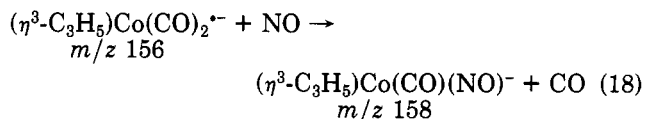
$(NO)_2^{\bullet-}$ and $(OC)_2Co(NO)^{\bullet-}$. The reaction of $(C_3H_5)Co(CO)_3^{\bullet-}$ with NO was more extensive in terms of the reaction channels observed. The total adduct and the (adduct–CO) were the primary product ions with the latter ion undergoing sequential secondary CO substitution reactions to finally produce a trace of the m/z 190 ions where all three of the original CO ligands in the starting complex have been replaced by NO ligands (eq 19).

$$(C_3H_5)Co(CO)_3^{\bullet-} + NO \xrightarrow[He]{0.70} (C_3H_5)Co(CO)_3(NO)^- \quad (19a)$$
$$m/z\ 184 \qquad\qquad\qquad\qquad m/z\ 214$$

$$\xrightarrow{0.30} (C_3H_5)Co(CO)_2(NO)^- + CO \quad (19b)$$
$$m/z\ 186$$

$$\downarrow NO$$

$$(C_3H_5)Co(CO)(NO)_2^{\bullet} + CO \quad (19c)$$
$$m/z\ 188$$

$$\downarrow NO$$

$$(C_3H_5)Co(NO)_3^- + CO \quad (19d)$$
$$m/z\ 190$$
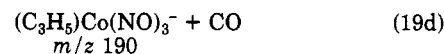
Observation of the total adduct at m/z 214 in eq 19a is consistent with the associative mechanism of NO adding to $(C_3H_5)Co(CO)_3^{\bullet-}$ forming the 18-electron adduct negative ion; no further reaction of this adduct with NO occurred. The observed P_{He} effect on the $(m/z\ 214)/(m/z\ 186)$ ratio requires that both primary product ions are derived from the common excited adduct. While the ion structure for this adduct shown in eq 19a accommodates the basic information known for this product with the allyl and NO ligands as one-electron donors, another structure is possible, namely, the acyl complex 8. In 8, the NO could

$$(OC)_2(ON)CoC(=O)C_3H_5^-$$
$$\mathbf{8}$$
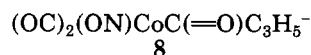
serve as a three-electron donor ligand. A related CO insertion was suggested for an unobserved intermediate in the reaction of $(C_3H_5)Co(CO)_3^{\bullet-}$ with PF_3 (eq 11) to account for exclusive fragmentation of the allyl radical. However, structure 8 has a closed shell 18-electron configuration at Co and fragmentation would be expected to occur by exclusive CO expulsion rather than radical cleavage of the acyl ligand. This is observed in product channel 19b.
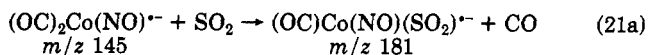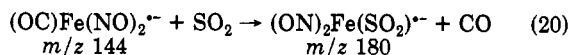
The primary product ions of ligand substitution at m/z 186 could achieve the 18-electron configuration around Co with either the C_3H_5 or the NO ligand as a three-electron

donor. The ions at m/z 186 undergo a slow secondary substitution reaction with NO giving a small amount of the ions at m/z 188 and even a trace of the ions at m/z 190.
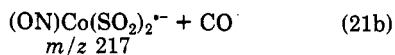
Although adduct formation was only observed in the reaction of NO with $(C_3H_5)Co(CO)_3{}^{\cdot-}$, we favor the associative mechanism in the CO ligand substitution reactions of these five transition-metal complex negative ions with NO. The similarity of the rate constants and reaction efficiencies (k_{total}/k_{ADO}) of these five reactions with NO suggest that the five metal complex anion radicals each have 17-electron configurations about the metal center.

Reactions of the Five Metal Complex Negative Ions with SO$_2$. Sulfur dioxide can coordinate to metal centers in several different modes generally serving as a two-electron donor ligand.[3] However, SO$_2$ can also act as a pure π-acid or a zero-electron donor.[22] The modest electron affinity of SO$_2$ (1.097 ± 0.036 eV)[23,24] allows for electron transfer from metal complex negative ions with EAs of <1.1 eV.

The ion–molecule reactions of the five metal complex anion radicals with SO$_2$ proceeded with rate constants that were essentially those of the collision limit.[17] This suggests that these reactions are quite exothermic. The reactions with $(OC)Fe(NO)_2{}^{\cdot-}$ (eq 20) and $(OC)_2Co(NO)^{\cdot-}$ (eq 21)

$$(OC)Fe(NO)_2{}^{\cdot-} + SO_2 \rightarrow (ON)_2Fe(SO_2)^{\cdot-} + CO \quad (20)$$
$$m/z\ 144 \qquad\qquad\qquad m/z\ 180$$

$$(OC)_2Co(NO)^{\cdot-} + SO_2 \rightarrow (OC)Co(NO)(SO_2)^{\cdot-} + CO \quad (21a)$$
$$m/z\ 145 \qquad\qquad\qquad m/z\ 181$$

$$\downarrow SO_2$$

$$(ON)Co(SO_2)_2{}^{\cdot-} + CO \quad (21b)$$
$$m/z\ 217$$

occurred by exclusive CO ligand substitution; with the Co complex, both CO ligands were replaced sequentially by SO$_2$. The reaction of the parent anion radical CpCo(CO)$_2{}^{\cdot-}$ with SO$_2$ proceeded mainly by electron transfer giving SO$_2{}^{\cdot-}$ and a minor amount of ligand substitution (eq 22).

$$CpCo(CO)_2{}^{\cdot-} + SO_2 \xrightarrow{0.92} SO_2{}^{\cdot-} + CpCo(CO)_2 \quad (22a)$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 64$$

$$CpCo(CO)_2{}^{\cdot-} + SO_2 \xrightarrow{0.08} CpCo(CO)(SO_2)^{\cdot-} + CO$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 216$$
$$(22b)$$
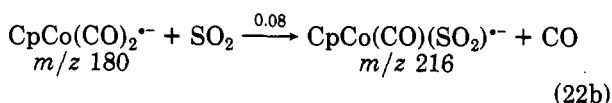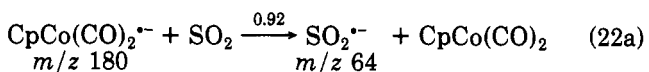
Formation of SO$_2{}^{\cdot-}$ in eq 22a requires that EA(CpCo(CO)$_2$) < 1.1 eV.

The fast reactions of the mixture of $(C_3H_5)Co(CO)_3{}^{\cdot-}$ and $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\cdot-}$ with SO$_2$ produced four primary product ions at m/z 64, 179, 192, and 207. These correspond to the negative ions SO$_2{}^{\cdot-}$, $(OC)_2Co(SO_2)^-$, $(\eta^3\text{-}C_3H_5)Co(CO)(SO_2)^{\cdot-}$, and $(OC)_3Co(SO_2)^-$, respectively. The product ion $(OC)_3Co(SO_2)^-$ containing three CO ligands must arise from the reaction of $(C_3H_5)Co(CO)_3{}^{\cdot-}$ with SO$_2$ by loss of the allyl radical. We had previously observed exclusive loss of the allyl radical from the reaction of this parent anion radical with PF$_3$ (eq 11). The sum of the product ion signals for SO$_2{}^{\cdot-}$ and $(OC)_3Co(SO_2)^-$ was equal to the decay of $(C_3H_5)Co(CO)_3{}^{\cdot-}$ at various concentrations of added SO$_2$ leading us to conclude that these were the

two primary product forming channels from this starting ion (eq 23). Formation of the electron transfer product

$$(C_3H_5)Co(CO)_3{}^{\cdot-} + SO_2 \xrightarrow{0.82} SO_2{}^{\cdot-} + (\eta^3\text{-}C_3H_5)Co(CO)_3$$
$$m/z\ 184 \qquad\qquad\qquad m/z\ 64$$
$$(23a)$$

$$(C_3H_5)Co(CO)_3{}^{\cdot-} + SO_2 \xrightarrow{0.18} (OC)_3Co(SO_2)^- + {}^\cdot C_3H_5$$
$$m/z\ 184 \qquad\qquad\qquad m/z\ 207$$
$$(23b)$$
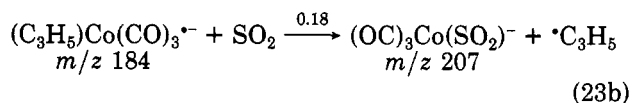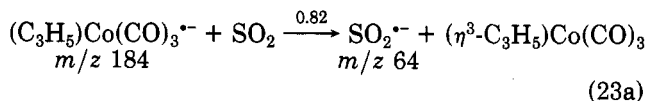
SO$_2{}^{\cdot-}$ in reaction 23 appeared reasonable since we expect the electron affinity of a 16-electron metal complex to be greater than that of the corresponding 18-electron complex differing by one CO ligand and a likely difference in the hapticity of the allyl ligand.

On the basis of the above conclusion, the reaction of $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\cdot-}$ with SO$_2$ produced the two primary product ions, m/z 179 and 192 (eq 24). Both of these ion

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\cdot-} + SO_2 \xrightarrow{0.71} (OC)_2Co(SO_2)^- + {}^\cdot C_3H_5$$
$$m/z\ 156 \qquad\qquad\qquad m/z\ 179$$
$$(24a)$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\cdot-} + SO_2 \xrightarrow{0.29}$$
$$m/z\ 156$$

$$(\eta^3\text{-}C_3H_5)Co(CO)(SO_2)^- + CO \quad (24b)$$
$$m/z\ 192$$

$$m/z\ 179 + SO_2 \rightarrow (OC)Co(SO_2)_2{}^- + CO \quad (24c)$$
$$m/z\ 243$$

$$m/z\ 192 + SO_2 \rightarrow (OC)Co(SO_2)_2{}^- + {}^\cdot C_3H_5 \quad (24d)$$
$$m/z\ 243$$
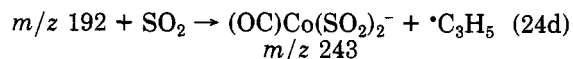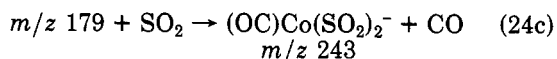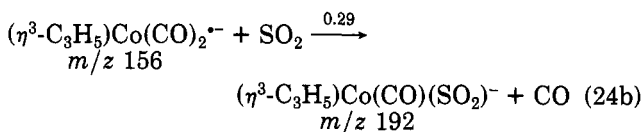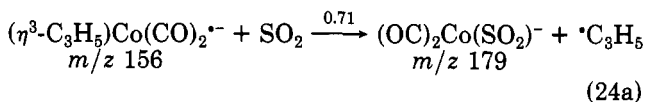
products were observed to undergo slower secondary reactions with SO$_2$ to yield the negative ions $(OC)Co(SO_2)_2{}^-$. The branching fractions (0.71 and 0.29) for the primary encounter between $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\cdot-}$ and SO$_2$ in eq 24 may be the ratio of the excited isomeric $[(C_3H_5C(=O))\text{-}Co(CO)(SO_2)^{\cdot-}]^*$ and $[(\eta^1\text{-}C_3H_5)Co(CO)_2(SO_2)^{\cdot-}]^*$ complexes produced with the former isomer expelling the allyl radical and the latter structure extruding a CO ligand. As expected, no P_{He} effect was observed for the bimolecular channels in reactions 23 and 24.

The fast reaction rates and ligand substitution reactions afforded in the ion–molecule reactions of the five transition-metal complex negative ions with SO$_2$ make this neutral ligand most interesting for structure elucidation of the original metal complex anion radical.[8-12,25] The observation of electron transfer of $(C_3H_5)Co(CO)_3{}^{\cdot-}$ and CpCo(CO)$_2{}^{\cdot-}$ with SO$_2$ means that the EAs of the two corresponding neutral complexes are <1.1 eV.

Reactions of the Five Metal Complex Negative Ions with Olefins. The olefins used in this study included a simple hydrocarbon (CH$_3$CH=CH$_2$), one with an electron-donating group (CH$_2$=CHOC$_2$H$_5$), and several with various electron-attracting groups (CH$_2$=CHBr, CH$_2$=CHCO$_2$CH$_3$, CH$_2$=CHCN, C$_2$F$_4$, and C$_2$(CN)$_4$). No reaction ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}) was observed for the five metal complex negative ions with CH$_3$CH=CH$_2$ and CH$_2$=CHOC$_2$H$_5$.
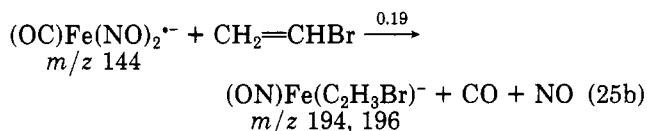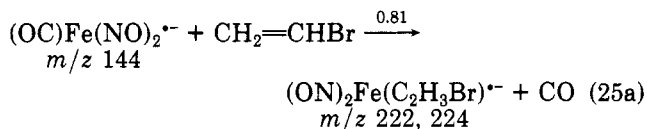
Only $(OC)Fe(NO)_2{}^{\cdot-}$ reacted with CH$_2$=CHBr in a slow reaction to yield mainly the CO ligand substitution product at m/z 222 and 224 (^{79,81}Br) along with a most unusual product of CO *plus* NO substitution at m/z 194 and 196 (eq 25). Since the reaction was so slow, we were unable

(22) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.
(23) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740.
(24) See: Drzaic, P. S.; Marks, J.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1984; Vol. 3, Chapter 21 for a review of gas-phase molecular EAs.

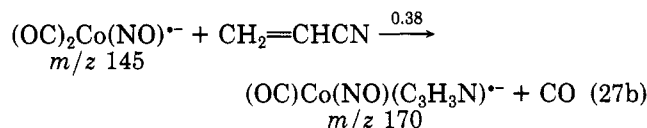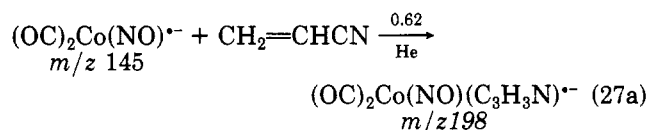(25) Jones, M. T. Ph.D. Thesis, Kansas State University, 1987.

$$(OC)Fe(NO)_2^{\cdot-} + CH_2=CHBr \xrightarrow{0.81}$$
$$m/z \; 144$$

$$(ON)_2Fe(C_2H_3Br)^{\cdot-} + CO \quad (25a)$$
$$m/z \; 222, \; 224$$

$$(OC)Fe(NO)_2^{\cdot-} + CH_2=CHBr \xrightarrow{0.19}$$
$$m/z \; 144$$

$$(ON)Fe(C_2H_3Br)^{-} + CO + NO \quad (25b)$$
$$m/z \; 194, \; 196$$

to carry out further ion–molecule reactions with these product ions to give additional structural information. The major ion product appears to be the simple CO ligand substitution product generated by π-coordination to the bromoethylene molecule. The nature of the bonding in the minor product ions is unknown but likely has generated an Fe–Br bond.

With $CH_2=CHCN$ as the neutral reactant, the parent negative ion complexes $(C_3H_5)Co(CO)_3^{\cdot-}$ and $CpCo(CO)_2^{\cdot-}$ failed to react ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}). (OC)Fe-$(NO)_2^{\cdot-}$ reacted rapidly with $CH_2=CHCN$ and gave the product of CO ligand substitution (eq 26). The reaction

$$(OC)Fe(NO)_2^{\cdot-} + CH_2=CHCN \rightarrow$$
$$m/z \; 144$$

$$(ON)_2Fe(C_3H_3N)^{\cdot-} + CO \quad (26)$$
$$m/z \; 169$$
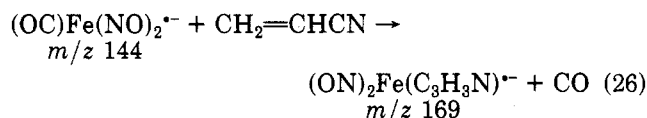
of $(OC)_2Co(NO)^{\cdot-}$ with $CH_2=CHCN$ was very slow, but produced the total adduct along with the product ion of CO ligand substitution (eq 27). The fast reaction of

$$(OC)_2Co(NO)^{\cdot-} + CH_2=CHCN \xrightarrow[He]{0.62}$$
$$m/z \; 145$$

$$(OC)_2Co(NO)(C_3H_3N)^{\cdot-} \quad (27a)$$
$$m/z \; 198$$

$$(OC)_2Co(NO)^{\cdot-} + CH_2=CHCN \xrightarrow{0.38}$$
$$m/z \; 145$$

$$(OC)Co(NO)(C_3H_3N)^{\cdot-} + CO \quad (27b)$$
$$m/z \; 170$$

$(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-}$ with $CH_2=CHCN$ generated the total adduct along with the products of ligand substitution for both the allyl and CO ligands (eq 28). The major disso-

$$(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-} + CH_2=CHCN \xrightarrow[He]{0.05} \quad (28a)$$
$$m/z \; 156$$

$$(C_3H_5)Co(CO)_2(C_3H_3N)^{\cdot-}$$
$$m/z \; 209$$

$$\xrightarrow{0.08} (\eta^3\text{-}C_3H_5)Co(CO)(C_3H_3N)^{\cdot-} + CO \quad (28b)$$
$$m/z \; 181$$

$$\xrightarrow{0.87} (OC)_2Co(C_3H_3N)^{-} + {}^{\cdot}C_3H_5 \quad (28c)$$
$$m/z \; 168$$

$$He \downarrow CH_2=CHCN$$
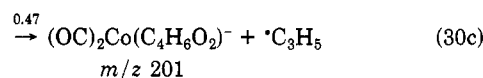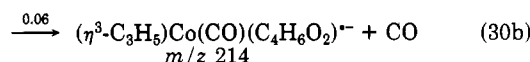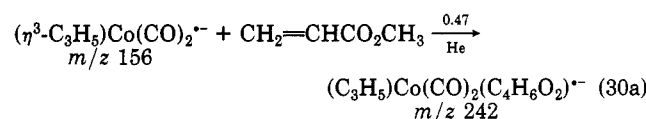
$$(OC)_2Co(C_3H_3N)_2^{-} \quad (28d)$$
$$m/z \; 221$$
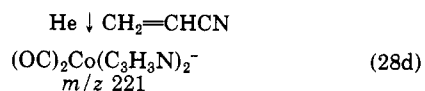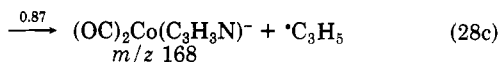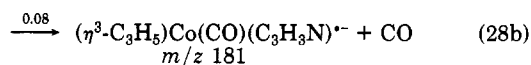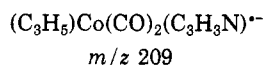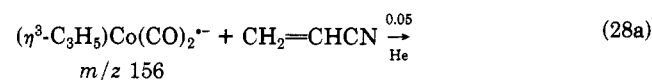
ciation of the allyl radical (eq 28c) vs a CO ligand (eq 28b) from the total adduct (m/z 209) is similar to that observed in the reaction of $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-}$ with SO$_2$. Observation of the secondary ion–molecule reaction in eq 28d suggests that the $CH_2=CHCN$ is η^2-π-bound to Co via the C=C in the m/z 168 product ions. Bonding to the nitrile group appears to be unlikely since none of the five metal complex negative ions were observed to react with CH_3CN.

The reactions of the five metal complex negative ions with the α,β-unsaturated ester $CH_2=CHCO_2CH_3$ followed
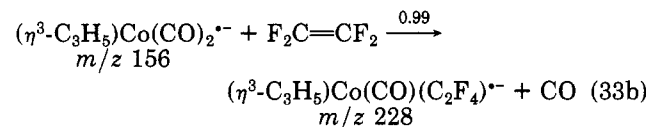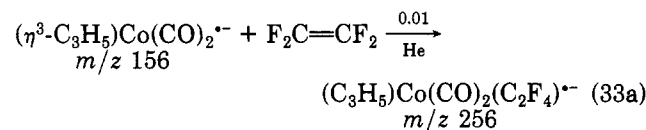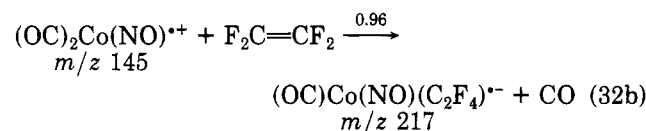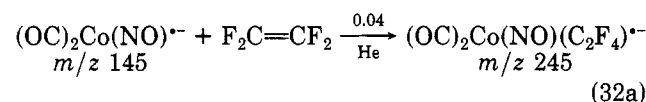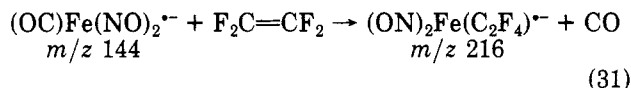
a similar course to those observed above with $CH_2=CHCN$ except that the rate constants were smaller; $(OC)_2Co$-$(NO)^{\cdot-}$, $(C_3H_5)Co(CO)_3^{\cdot-}$, and $CpCo(CO)_2^{\cdot-}$ did not react with this ester. The fast reaction of $(OC)Fe(NO)_2^{\cdot-}$ with $CH_2=CHCO_2CH_3$ occurred exclusively by CO ligand substitution (eq 29). The reaction of this neutral ester

$$(OC)Fe(NO)_2^{\cdot-} + CH_2=CHCO_2CH_3 \rightarrow$$
$$m/z \; 144$$

$$(ON)_2Fe(C_4H_6O_2)^{\cdot-} + CO \quad (29)$$
$$m/z \; 202$$
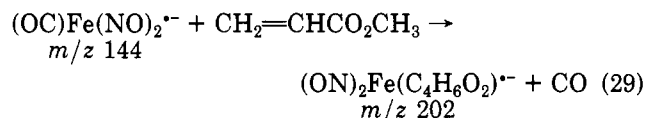
with $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-}$ proceeded with a modest rate constant and generated the total adduct along with the ion products of allyl radical (major) and CO (minor) ligand substitution (eq 30). The m/z 201 product ions were observed to undergo a slow secondary reaction with the ester to give a trace of the ions at m/z 287.

$$(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-} + CH_2=CHCO_2CH_3 \xrightarrow[He]{0.47}$$
$$m/z \; 156$$

$$(C_3H_5)Co(CO)_2(C_4H_6O_2)^{\cdot-} \quad (30a)$$
$$m/z \; 242$$

$$\xrightarrow{0.06} (\eta^3\text{-}C_3H_5)Co(CO)(C_4H_6O_2)^{\cdot-} + CO \quad (30b)$$
$$m/z \; 214$$

$$\xrightarrow{0.47} (OC)_2Co(C_4H_6O_2)^{-} + {}^{\cdot}C_3H_5 \quad (30c)$$
$$m/z \; 201$$

$$He \downarrow CH_2=CHCO_2CH_3$$

$$(OC)_2Co(C_4H_6O_2)_2^{-} \quad (30d)$$
$$m/z \; 287$$
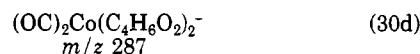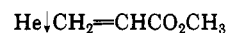
The reactions of $(OC)Fe(NO)_2^{\cdot-}$, $(OC)_2Co(NO)^{\cdot-}$, and $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-}$ with $F_2C=CF_2$ were very slow and formed exclusively or mainly the CO ligand substitution product ion (eq 31–33). The much smaller rate constants

$$(OC)Fe(NO)_2^{\cdot-} + F_2C=CF_2 \rightarrow (ON)_2Fe(C_2F_4)^{\cdot-} + CO$$
$$m/z \; 144 \qquad\qquad\qquad\qquad m/z \; 216$$
$$(31)$$

$$(OC)_2Co(NO)^{\cdot-} + F_2C=CF_2 \xrightarrow[He]{0.04} (OC)_2Co(NO)(C_2F_4)^{\cdot-}$$
$$m/z \; 145 \qquad\qquad\qquad\qquad\qquad m/z \; 245$$
$$(32a)$$

$$(OC)_2Co(NO)^{\cdot+} + F_2C=CF_2 \xrightarrow{0.96}$$
$$m/z \; 145$$

$$(OC)Co(NO)(C_2F_4)^{\cdot-} + CO \quad (32b)$$
$$m/z \; 217$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-} + F_2C=CF_2 \xrightarrow[He]{0.01}$$
$$m/z \; 156$$

$$(C_3H_5)Co(CO)_2(C_2F_4)^{\cdot-} \quad (33a)$$
$$m/z \; 256$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-} + F_2C=CF_2 \xrightarrow{0.99}$$
$$m/z \; 156$$

$$(\eta^3\text{-}C_3H_5)Co(CO)(C_2F_4)^{\cdot-} + CO \quad (33b)$$
$$m/z \; 228$$

for these three reactions with $F_2C=CF_2$ and the absence of allyl radical cleavage in reaction 33 suggest that addition of $F_2C=CF_2$ to these metal complex anion radicals is less exothermic than the corresponding reactions with $CH_2=CHCN$ and $CH_2=CHCO_2CH_3$. $(C_3H_5)Co(CO)_3^{\cdot-}$ and $CpCo(CO)_2^{\cdot-}$ did not react with $F_2C=CF_2$ ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}).
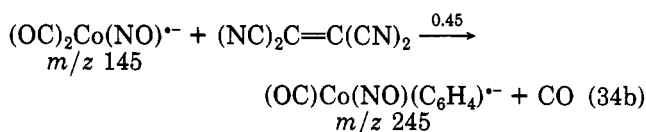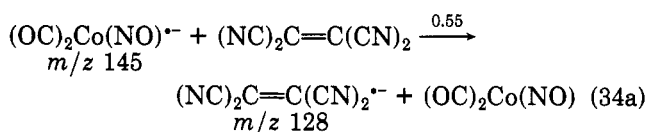
In the reactions of $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\cdot-}$ with the above three olefins, the magnitudes of the rate constants (considered to be proportional to the binding energy of the

Table VI. Rate Constants and Ligand Substitution Product Ratios for the Reactions of $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$ with Certain Olefins

olefin	k_{total}, cm^3 molecule^{-1} s^{-1}	product ratio (adduct-$^{\bullet}C_3H_5$)/ (adduct-CO)
CH_2=CHCN	5.2×10^{-10}	87:8
CH_2=CHCO$_2$CH$_3$	2.6×10^{-11}	47:6
F_2C=CF$_2$	8.6×10^{-13}	0:99

olefin) correlated with the ratios of the ligand substitution products (adduct-$^{\bullet}C_3H_5$)/(adduct-CO) (Table VI). Bonding of the olefin via the C=C is consistent with the data of these three reactions. We suggest that mixtures of two excited adducts $[(\eta^1\text{-}C_3H_5)Co(CO)_2(\text{olefin})^{\bullet-}]^*$ ($\rightarrow$ (adduct-CO)) and $[C_3H_5C(=O)Co(CO)(\text{olefin})^{\bullet-}]^*$ ($\rightarrow$ (adduct-$^{\bullet}C_3H_5$)) are formed. The ratio of the two adducts generated, which controls the branching fractions of the product forming channels, would depend on the reaction exothermicity and steric factors in the excited-adduct structure. This is the same argument we applied to the two related fragmentation channels observed in the reaction of this metal complex negative ion with SO$_2$.

Due to the relatively low vapor pressure of $(NC)_2C$=C(CN)$_2$ (TCNE) under the operating conditions of the FA, we were unable to carry out kinetic studies of the metal complex negative ions with this neutral. However, we could observe the products of these reactions by inletting the vapors of the solid TCNE from a reservoir attached directly to the flow tube. Although the reaction of $(OC)Fe(NO)_2^{\bullet-}$ with TCNE was not examined, the exclusive product of electron transfer, TCNE$^{\bullet-}$, was observed with $CpCo(CO)_2^{\bullet-}$, $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$, and $(C_3H_5)Co(CO)_3^{\bullet-}$. The reaction of $(OC)_2Co(NO)^{\bullet-}$ with TCNE produced almost equal amounts of the product ions of electron transfer and CO ligand substitution (eq 34).

$$(OC)_2Co(NO)^{\bullet-} + (NC)_2C=C(CN)_2 \xrightarrow{0.55}$$
$$m/z\ 145$$

$$(NC)_2C=C(CN)_2^{\bullet-} + (OC)_2Co(NO)\ (34a)$$
$$m/z\ 128$$

$$(OC)_2Co(NO)^{\bullet-} + (NC)_2C=C(CN)_2 \xrightarrow{0.45}$$
$$m/z\ 145$$

$$(OC)Co(NO)(C_6H_4)^{\bullet-} + CO\ (34b)$$
$$m/z\ 245$$

Formation of both types of products in reaction 34 can be explained by formation of the loose orbiting collision complex with electron transfer producing the complex $[(OC)_2Co(NO)/TCNE^{\bullet-}]$. This complex can separate yielding TCNE$^{\bullet-}$ and effect addition of TCNE$^{\bullet-}$ to the 16-electron metal complex $(OC)_2Co(NO)$ followed by decarbonylation as competitive processes. The electron-transfer channels were expected because of the large EA for TCNE (3.17 ± 0.2 eV).[26]

In summary, the reactions of the five transition-metal complex negative ions with olefins proceed with (i) no reaction observed with the more electron-rich olefins CH_3CH=CH$_2$ and CH_2=CHOC$_2$H$_5$, (ii) adduct and ligand substitution products observed in the reactions of H_2C=CHCN, H_2C=CHCO$_2$CH$_3$, and F_2C=CF$_2$ with the three complex anion radicals containing a NO or a η^3-C$_3$H$_5$ ligand

that can switch hapticity, and (iii) mainly electron transfer observed in the reactions with TCNE.

Reactions of the Five Metal Complex Negative Ions with Ketones. All five of the metal complex anion radicals failed to react with acetone. Although $CH_3C(=O)CF_3$ did not react with $(OC)_2Co(NO)^{\bullet-}$ or $CpCo(CO)_2^{\bullet-}$ for unknown reasons, this ketone did react with the remaining three metal complex negative ions by ligand substitution. $(OC)Fe(NO)_2^{\bullet-}$ reacted with $CH_3C(=O)CF_3$ to yield the product ion of CO ligand substitution (eq 35).

$$(OC)Fe(NO)_2^{\bullet-} + CH_3C(=O)CF_3 \rightarrow$$
$$m/z\ 144$$

$$(ON)_2Fe(C_3H_3F_3O)^{\bullet-} + CO\ (35)$$
$$m/z\ 228$$
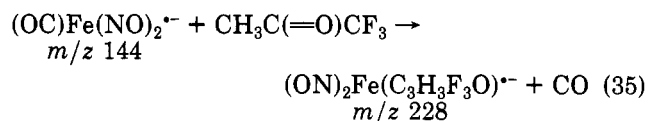
Since $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$ and $(C_3H_5)Co(CO)_3^{\bullet-}$ are generated together in the same flow (eq 6), we require some distinguishing factor, e.g. different rates of reaction or a P_{He} effect on product channels, to be able to sort out their separate product forming channels. In the present reactions with $CH_3C(=O)CF_3$, $(C_3H_5)Co(CO)_3^{\bullet-}$ exhibited *the larger rate constant* of these two metal complex negative ions. Two product ions at m/z 227 ($(OC)_2Co(C_3H_3F_3O)^{\bullet-}$) and 268 ($(C_3H_5)Co(CO)_2(C_3H_3F_3O)^{\bullet-}$) were formed. Since we are unable to identify conclusively which starting ion(s) formed which product(s), no further comment is justified on these results.

With $(CF_3)_2C$=O as the ketone substrate, the possibility for electron transfer becomes real since EA($(CF_3)_2C$=O) $\geq$ EA(phenylnitrene) = 1.46 ± 0.02 eV.[27,28] The fast reaction of $(OC)Fe(NO)_2^{\bullet-}$ with $(CF_3)_2C$=O occurred by exclusive CO ligand substitution (eq 36). The equally fast

$$(OC)Fe(NO)_2^{\bullet-} + (CF_3)_2C=O \rightarrow$$
$$m/z\ 144$$

$$(ON)_2Fe(C_3F_6O)^{\bullet-} + CO\ (36)$$
$$m/z\ 282$$
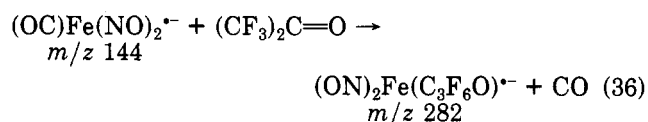
reaction between $(OC)_2Co(NO)^{\bullet-}$ and $(CF_3)_2C$=O formed the product ions of both CO and NO ligand substitution (eq 37). This is the first time we observed competitive

$$(OC)_2Co(NO)^{\bullet-} + (CF_3)_2C=O \xrightarrow{0.29} (OC)_2Co(C_3F_6O)^- + NO$$
$$m/z\ 145 \qquad\qquad\qquad\qquad\qquad m/z\ 281$$
$$(37a)$$

$$\xrightarrow{0.71} (OC)Co(NO)(C_3F_6O)^{\bullet-} + CO \qquad (37b)$$
$$m/z\ 283$$

$$\downarrow (CF_3)_2C=O$$
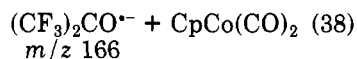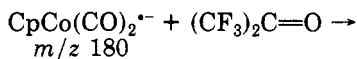$$(ON)Co(C_3F_6O)_2^{\bullet-} + CO \qquad (37c)$$
$$m/z\ 421$$
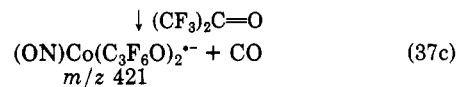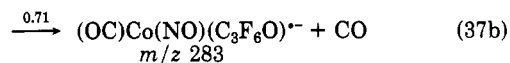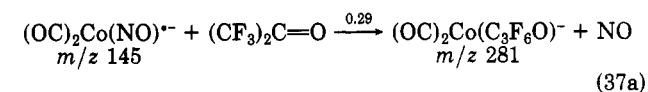
CO and NO ligand substitution. Even though the total adduct product ion was not observed in this reaction, we believe that these results of ligand substitutions are most reasonably considered to occur by the associative mechanism where NO is η^1 in the unobserved intermediate adduct. Since the product of electron transfer, $(CF_3)_2CO^{\bullet-}$, was not observed in reactions 36 and 37, the EAs of the 16-electron complexes $(OC)Fe(NO)_2$ and $(OC)_2Co(NO)$ are greater than EA($(CF_3)_2C$=O).

However, $CpCo(CO)_2^{\bullet-}$ reacted with $(CF_3)_2C$=O exclusively by electron transfer forming $(CF_3)_2CO^{\bullet-}$ at m/z 166 (eq 38).
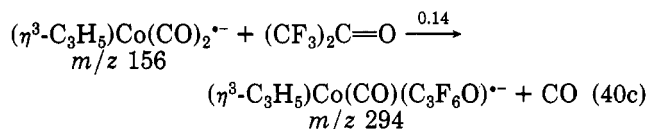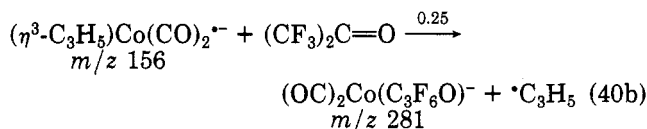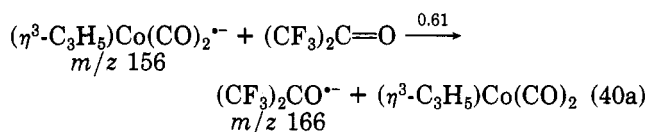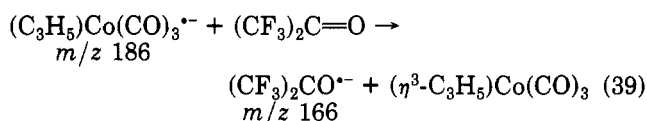
(26) Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 5453. This value for EA(TCNE) is considerably larger than that reported by Lyons and Palmer (Lyons, L. E.; Palmer, L. D. *Aust. J. Chem.* **1976**, *29*, 1919) (2.3 ± 0.3 eV) but is in reasonable agreement with the value of 2.9 ± 0.1 eV reported by Farragher and Page (Farragher, A. L.; Page, F. M. *Trans. Faraday Soc.* **1967**, *63*, 2369).

(27) Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443.
(28) McDonald and Chowdhury (McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 198) observed electron transfer in the ion–molecule reaction between PhN$^{\bullet-}$ and $(CF_3)_2C$=O forming $(CF_3)_2CO^{\bullet-}$.

$$CpCo(CO)_2{}^{\bullet-} + (CF_3)_2C{=}O \rightarrow$$
$$m/z \; 180$$

$$(CF_3)_2CO^{\bullet-} + CpCo(CO)_2 \quad (38)$$
$$m/z \; 166$$

The results of the reactions of $(C_3H_5)Co(CO)_3{}^{\bullet-}$ and $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-}$ with $(CF_3)_2C{=}O$ were interesting because the product ions of electron transfer, $(CF_3)_2CO^{\bullet-}$, and of ligand substitution, $(OC)_2Co(C_3F_6O)^-$ (m/z 281) and $(\eta^3\text{-}C_3H_5)Co(CO)(C_3F_6O)^{\bullet-}$ (m/z 294), were observed. The amount of $(CF_3)_2CO^{\bullet-}$ generated was equal to 80% of the *sum* of the signal intensities decayed for *both* $(C_3H_5)Co(CO)_3{}^{\bullet-}$ and $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-}$. This means that both starting negative ions undergo at least partial electron transfer to $(CF_3)_2C{=}O$. Formation of the two ligand substitution products at m/z 281 (major) and 294 (minor) was most consistent with competitive fragmentation of the excited complexes $[(\eta^1\text{-}C_3H_5)Co(CO)_2(C_3F_6O)^{\bullet-}]^*$ and $[C_3H_5C({=}O)Co(CO)(C_3F_6O)^{\bullet-}]^*$ derived from the addition of the ketone to $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-}$. On this basis and the result shown in reaction 38, we suggest that the products of these two reactions occur according to eq 39 and 40.

$$(C_3H_5)Co(CO)_3{}^{\bullet-} + (CF_3)_2C{=}O \rightarrow$$
$$m/z \; 186$$

$$(CF_3)_2CO^{\bullet-} + (\eta^3\text{-}C_3H_5)Co(CO)_3 \quad (39)$$
$$m/z \; 166$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-} + (CF_3)_2C{=}O \xrightarrow{0.61}$$
$$m/z \; 156$$

$$(CF_3)_2CO^{\bullet-} + (\eta^3\text{-}C_3H_5)Co(CO)_2 \quad (40a)$$
$$m/z \; 166$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-} + (CF_3)_2C{=}O \xrightarrow{0.25}$$
$$m/z \; 156$$

$$(OC)_2Co(C_3F_6O)^- + {}^{\bullet}C_3H_5 \quad (40b)$$
$$m/z \; 281$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-} + (CF_3)_2C{=}O \xrightarrow{0.14}$$
$$m/z \; 156$$

$$(\eta^3\text{-}C_3H_5)Co(CO)(C_3F_6O)^{\bullet-} + CO \quad (40c)$$
$$m/z \; 294$$

Electron transfer as the exclusive channel in the reactions of the two parent anion radicals $CpCo(CO)_2{}^{\bullet-}$ and $(C_3H_5)Co(CO)_3{}^{\bullet-}$ was reasonable since both metal complex negative ions were observed to undergo electron transfer with SO_2 (EA = 1.1 eV).

Formation of $(CF_3)_2CO^{\bullet-}$ in reaction 40 means that $EA((CF_3)_2C{=}O) > EA((\eta^3\text{-}C_3H_5)Co(CO)_2)$. Each of the three product negative ions could be produced from the collision complex involving electron transfer $[(\eta^3\text{-}C_3H_5)\text{-}Co(CO)_2/(CF_3)_2CO^{\bullet-}]$. Separation and addition of the two components of this collision complex then are competitive processes leading to the products.

The reactions using biacetyl, $(CH_3C({=}O))_2$, as the carbonyl reactant proved interesting, especially with $(C_3H_5)Co(CO)_3{}^{\bullet-}$ and $CpCo(CO)_2{}^{\bullet-}$. In both of these reactions, only the product ions of electron transfer were observed (eq 41 and 42). It was possible to separately
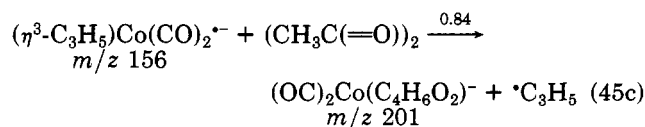
$$(C_3H_5)Co(CO)_3{}^{\bullet-} + (CH_3C({=}O))_2 \rightarrow$$
$$m/z \; 184$$

$$(CH_3C(O))_2{}^{\bullet-} + (\eta^3\text{-}C_3H_5)Co(CO)_3 \quad (41)$$
$$m/z \; 86$$

$$CpCo(CO)_2{}^{\bullet-} + (CH_3C({=}O))_2 \rightarrow$$
$$m/z \; 180$$

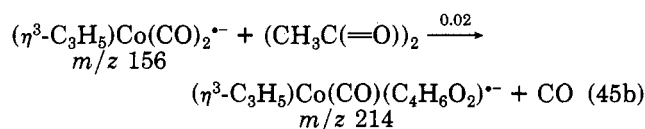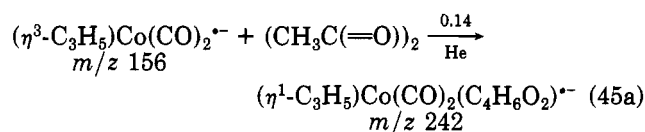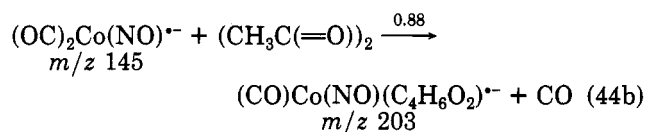$$(CH_3C(O))_2{}^{\bullet-} + CpCo(CO)_2 \quad (42)$$
$$m/z \; 86$$
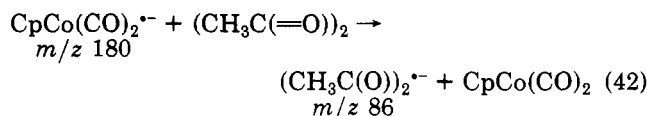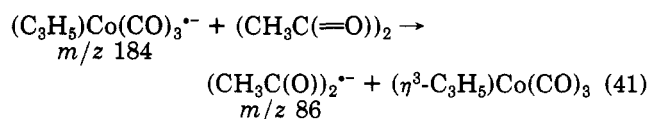
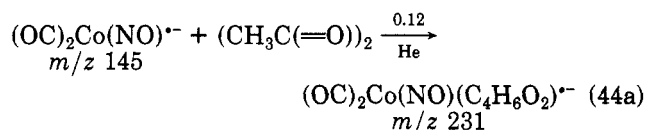observe reaction 41 since it was 20 times slower than the corresponding reaction of $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-}$ with biacetyl. Kebarle et al.[29] recently reported the $EA((CH_3C({=}O))_2)$ = 0.69 eV which becomes the upper limit to this point for the EAs of the neutral, 18-electron metal complexes $CpCo(CO)_2$ and $(\eta^3\text{-}C_3H_5)Co(CO)_3$.

We note that while the rate constant for reaction 42 is large, it is only 14% of the collision-limited rate constant k_{ADO}.[17] This fact is unusual for an exothermic electron transfer;[29] the rate constants k_{total} for the electron transfers from $CpCo(CO)_2{}^{\bullet-}$ to SO_2 and $(CF_3)_2C{=}O$ were 80% and 60%, respectively, of k_{ADO}. However, the rate constant for reaction 41 is an *order of magnitude smaller* than that for reaction 42. The previous electron-transfer reactions of $(C_3H_5)Co(CO)_3{}^{\bullet-}$ with SO_2 and $(CF_3)_2C{=}O$ occurred with rate constants that were 82% and 40%, respectively, of k_{ADO}.[17] These lower efficiencies for electron transfer to biacetyl, however, are consistent with a significant change in the geometry of the neutral metal complex $LM(CO)_x$ and its lowest energy anion radical $LM(CO)_x{}^{\bullet-}$, as the EAs of the neutral metal complex and biacetyl approach one another.[29] These changes in the rate constants for electron transfer from the two parent negative ions are consistent with the structures of these ions being $(\eta^3\text{-}Cp)Co(CO)_2{}^{\bullet-}$ (6) and $(\eta^1\text{-}C_3H_5)Co(CO)_3{}^{\bullet-}$ (2).

The reactions of biacetyl with the remaining three metal complex negative ions involved ligand addition and/or substitution. With $(OC)Fe(NO)_2{}^{\bullet-}$, the CO ligand substitution product was exclusively formed (eq 43) in a fast

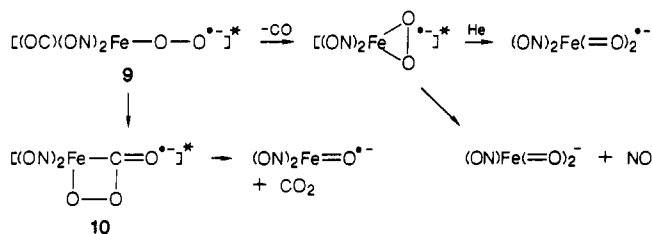$$(OC)Fe(NO)_2{}^{\bullet-} + (CH_3C({=}O))_2 \rightarrow$$
$$m/z \; 144$$

$$(ON)_2Fe(C_4H_6O_2)^{\bullet-} + CO \quad (43)$$
$$m/z \; 202$$
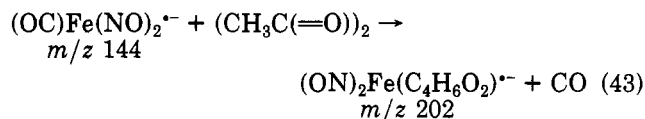
reaction. The related reactions of $(OC)_2Co(NO)_2{}^{\bullet-}$ and $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-}$ with $(CH_3C({=}O))_2$ were almost as fast and produced the product ions of overall addition and ligand substitution (eq 44 and 45). That electron transfer

$$(OC)_2Co(NO)^{\bullet-} + (CH_3C({=}O))_2 \xrightarrow[He]{0.12}$$
$$m/z \; 145$$

$$(OC)_2Co(NO)(C_4H_6O_2)^{\bullet-} \quad (44a)$$
$$m/z \; 231$$

$$(OC)_2Co(NO)^{\bullet-} + (CH_3C({=}O))_2 \xrightarrow{0.88}$$
$$m/z \; 145$$

$$(CO)Co(NO)(C_4H_6O_2)^{\bullet-} + CO \quad (44b)$$
$$m/z \; 203$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-} + (CH_3C({=}O))_2 \xrightarrow[He]{0.14}$$
$$m/z \; 156$$

$$(\eta^1\text{-}C_3H_5)Co(CO)_2(C_4H_6O_2)^{\bullet-} \quad (45a)$$
$$m/z \; 242$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-} + (CH_3C({=}O))_2 \xrightarrow{0.02}$$
$$m/z \; 156$$

$$(\eta^3\text{-}C_3H_5)Co(CO)(C_4H_6O_2)^{\bullet-} + CO \quad (45b)$$
$$m/z \; 214$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-} + (CH_3C({=}O))_2 \xrightarrow{0.84}$$
$$m/z \; 156$$

$$(OC)_2Co(C_4H_6O_2)^- + {}^{\bullet}C_3H_5 \quad (45c)$$
$$m/z \; 201$$

(29) (a) Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* 1985, *107*, 4627. (b) Kebarle, P.; Chowdhury, S. *Chem. Rev.* 1987, *87*, 513.
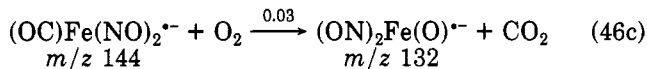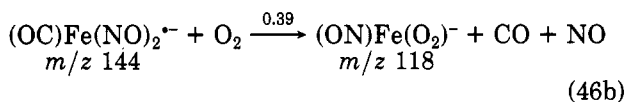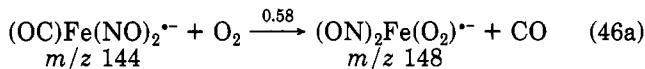
Scheme I

$$[(OC)(ON)_2Fe{-}O{-}O^{\bullet-}]^* \xrightarrow{-CO} [(ON)_2Fe\underset{O}{\overset{O}{<}}^{\bullet-}]^* \xrightarrow{He} (ON)_2Fe(=O)_2^{\bullet-}$$

9

$$[(ON)_2Fe{-}C{=}O^{\bullet-}]^* \longrightarrow (ON)_2Fe{=}O^{\bullet-} \qquad (ON)Fe(=O)_2^- + NO$$
$$\underset{O{-}O}{|\quad|} \qquad\qquad + CO_2$$
10

Scheme II

$$(OC)_2Co(=O)_2^-$$

$$\uparrow He$$

$$[(OC)_2Co(=O)_2^-]^* \xrightarrow{-CO} (OC)Co(=O)_2^-$$

$$\uparrow -NO \qquad\qquad \uparrow -NO$$

$$[(OC)_2(ON)Co{-}O{-}O^{\bullet-}]^* \xrightarrow{-CO} [(OC)(ON)Co\underset{O}{\overset{O}{<}}^{\bullet-}]^* \xrightarrow{He}$$
11

$$\qquad\qquad\qquad\qquad\qquad\qquad (OC)(ON)Co(=O)_2^{\bullet-}$$

$$\downarrow$$

$$[(OC)(ON)Co{-}C{=}O^{\bullet-}]^* \xrightarrow{-CO_2} [(OC)(NO)Co{=}O^{\bullet-}]^* \xrightarrow{-CO}$$
$$\underset{O{-}O}{|\quad|}$$

$$\qquad\qquad\qquad\qquad\qquad (ON)Co{=}O^{\bullet-}$$

was observed in the reaction of biacetyl with $(C_3H_5)Co(CO)_3{}^{\bullet-}$, but not with $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-}$, means that EA-$((\eta^3\text{-}C_3H_5)Co(CO)_2) = 0.9 \pm 0.2$ eV [bracketed between 1.1 (EA(SO_2)) and 0.69 eV (EA(biacetyl))] while EA$((\eta^3\text{-}C_3H_5)Co(CO)_3) < 0.69$ eV.

Observation of the product adduct ions in reactions 44 and 45 leads us to the following generalization. For those reactions of the metal complex negative ions with neutral ketones where a product of ligand substitution is observed, the reaction mechanism is that of addition followed by dissociation of the ligand from the intermediate adduct. Although we are unable to establish the nature of the bonding of the ketone ligands in these negative ion complexes, they appear most likely to be η^2 by analogy with the condensed-phase results.[30]

Reactions of Three of the Metal Complex Negative Ions with O_2. The reactions of transition-metal complex anions $((OC)_5Cr^{\bullet-}, (OC)_4Fe^{\bullet-},$ and $(OC)_5Mo^{\bullet-})$ with O_2 were described by Squires et al.[31] These authors established that addition of O_2 to the metal was accompanied by displacement of CO ligands and loss of CO_2 that produced several novel metal oxide negative ions. We have examined the reactions of the complexes $(OC)Fe(NO)_2{}^{\bullet-}, (OC)_2Co(NO)^{\bullet-},$ and $CpCo(CO)_2{}^{\bullet-}$ with O_2 to expand our understanding of this interesting reaction.

The reaction of $(OC)Fe(NO)_2{}^{\bullet-}$ with O_2 proceeded to form the three primary product ions shown in eq 46.

$$(OC)Fe(NO)_2{}^{\bullet-} + O_2 \xrightarrow{0.58} (ON)_2Fe(O_2)^{\bullet-} + CO \quad (46a)$$
$$\text{m/z } 144 \qquad\qquad\qquad \text{m/z } 148$$

$$(OC)Fe(NO)_2{}^{\bullet-} + O_2 \xrightarrow{0.39} (ON)Fe(O_2)^- + CO + NO$$
$$\text{m/z } 144 \qquad\qquad\qquad \text{m/z } 118$$
$$(46b)$$

$$(OC)Fe(NO)_2{}^{\bullet-} + O_2 \xrightarrow{0.03} (ON)_2Fe(O)^{\bullet-} + CO_2 \quad (46c)$$
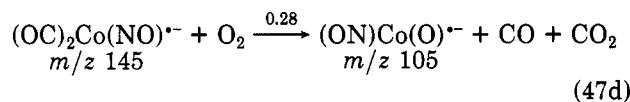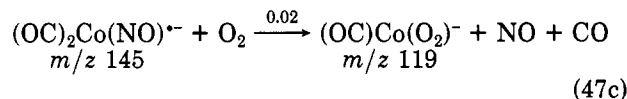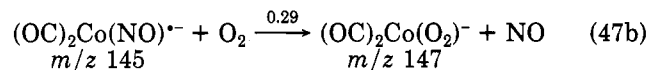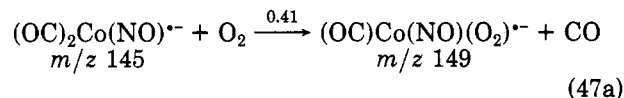$$\text{m/z } 144 \qquad\qquad\qquad \text{m/z } 132$$

Generation of these three product ions can be rationalized by initial formation of the excited η^1-superoxide structure **9** (Scheme I) formed by radical–radical coupling of the starting anion radical and triplet O_2. In the structures shown for product ions, the coordination and electron configuration were maximized in the two anion radicals (17-electron) and in the anion $(ON)Fe(O)_2{}^-$. Expulsion of CO_2 was considered to occur via the perlactone **10**. Doubling of the flow tube pressure (P_{He}) from 0.5 to 1.0 Torr produced a minor change in the branching fractions given in eq 46 for channels 46a–c to 64:33:3, respectively; although these changes are within our general errors, they are duplicable. Such a variation in the branching fractions
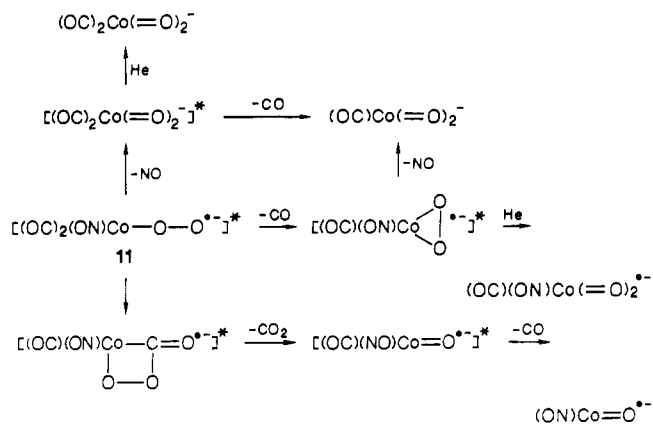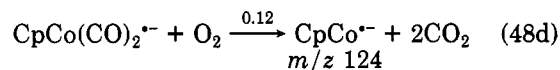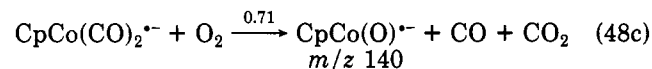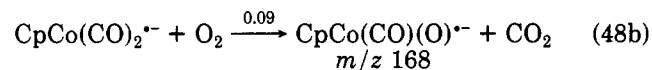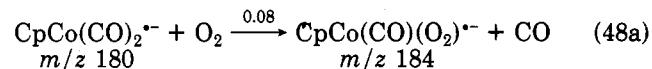
is at least consistent with the mechanism in Scheme I.

The reaction between $(OC)_2Co(NO)^{\bullet-}$ and O_2 gave the product ions of both CO and NO substitution as well as those formed by the loss of two ligands (eq 47). Doubling

$$(OC)_2Co(NO)^{\bullet-} + O_2 \xrightarrow{0.41} (OC)Co(NO)(O_2)^{\bullet-} + CO$$
$$\text{m/z } 145 \qquad\qquad\qquad \text{m/z } 149$$
$$(47a)$$

$$(OC)_2Co(NO)^{\bullet-} + O_2 \xrightarrow{0.29} (OC)_2Co(O_2)^- + NO \quad (47b)$$
$$\text{m/z } 145 \qquad\qquad\qquad \text{m/z } 147$$

$$(OC)_2Co(NO)^{\bullet-} + O_2 \xrightarrow{0.02} (OC)Co(O_2)^- + NO + CO$$
$$\text{m/z } 145 \qquad\qquad\qquad \text{m/z } 119$$
$$(47c)$$

$$(OC)_2Co(NO)^{\bullet-} + O_2 \xrightarrow{0.28} (ON)Co(O)^{\bullet-} + CO + CO_2$$
$$\text{m/z } 145 \qquad\qquad\qquad \text{m/z } 105$$
$$(47d)$$

of P_{He} from 0.5 to 1.0 Torr did not change the branching fractions shown in eq 47 ($\pm1\%$), suggesting that the three major product ions were formed competitively rather than consecutively. A mechanism consistent with competitive generation of these major product ions is shown in Scheme II. As in Scheme I, the starting point is generation of the superoxide structure **11**.
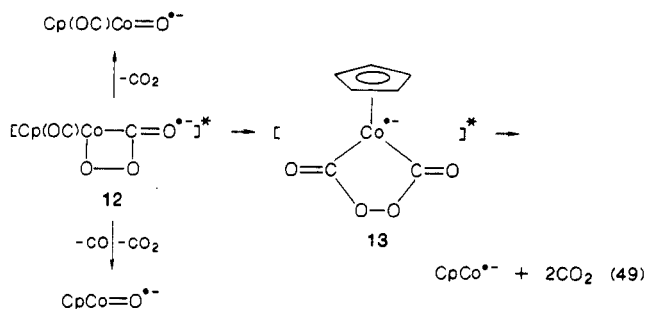
$CpCo(CO)_2{}^{\bullet-}$ was the third metal complex negative ion investigated in these reactions with O_2 (eq 48). The first

$$CpCo(CO)_2{}^{\bullet-} + O_2 \xrightarrow{0.08} CpCo(CO)(O_2)^{\bullet-} + CO \quad (48a)$$
$$\text{m/z } 180 \qquad\qquad\qquad \text{m/z } 184$$

$$CpCo(CO)_2{}^{\bullet-} + O_2 \xrightarrow{0.09} CpCo(CO)(O)^{\bullet-} + CO_2 \quad (48b)$$
$$\qquad\qquad\qquad\qquad \text{m/z } 168$$

$$CpCo(CO)_2{}^{\bullet-} + O_2 \xrightarrow{0.71} CpCo(O)^{\bullet-} + CO + CO_2 \quad (48c)$$
$$\qquad\qquad\qquad\qquad \text{m/z } 140$$

$$CpCo(CO)_2{}^{\bullet-} + O_2 \xrightarrow{0.12} CpCo^{\bullet-} + 2CO_2 \quad (48d)$$
$$\qquad\qquad\qquad\qquad \text{m/z } 124$$

three product ions in eq 48a–c are similar to those observed previously in the reaction of O_2 with $(OC)Fe(NO)_2{}^{\bullet-}$ and $(OC)_2Co(NO)^{\bullet-}$. However, formation of $CpCo^{\bullet-}$ in eq 48d is unique. To extrude two CO_2 molecules from an excited intermediate to yield $CpCo^{\bullet-}$, we suggest that the excited perlactone **12** competitively fragments to $Cp(OC)Co{=}O^{\bullet-}$ and $CpCo{=}O^{\bullet-}$, and CO inserts to give the peranhydride **13** which bis-decarboxylates to $CpCo^{\bullet-}$ (eq 49). The driving force for this rearrangement could be the η^3-Cp in **12** to η^5-Cp in **13** change in the bonding of the Cp ligand.

(30) For Pt complexes, see: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, Chapter 39, and references therein. For Ni complexes, see: Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311 and references therein.
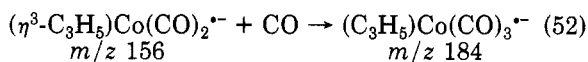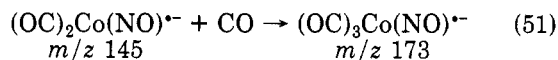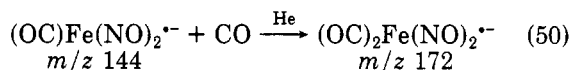
(31) Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719.

$$Cp(OC)Co=O^{\bullet-}$$

$$\downarrow -CO_2$$

$$[Cp(OC)Co-C=O^{\bullet-}]^* \longrightarrow [\quad]^* \longrightarrow$$
$$\qquad\qquad |$$
$$\qquad O-O$$
$$\qquad \mathbf{12}$$

$$\mathbf{13}$$

$$-CO \bigg| -CO_2$$
$$\downarrow$$
$$CpCo=O^{\bullet-}$$

$$CpCo^{\bullet-} + 2CO_2 \quad (49)$$

Wang and Squires[21] recently reported their results of reaction 48 yielding $CpCo(CO)(O_2)^{\bullet-}$ (8%), $CpCo(CO)(O)^{\bullet-}$ (12%), $CpCo(O)^{\bullet-}$ (48%), and $CpCo^{\bullet-}$ (30%) at $P_{He} = 0.4$ Torr with $k_{total} = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The large difference in the $[CpCo(O)^{\bullet-}/CpCo^{\bullet-}]$ ratio from the present results may be due to a significant P_{He} effect on the fragmentation vs rearrangement of **12** suggested in eq 49.

In the three examples studied of the reactions of 17-electron metal complex anion radicals with O_2, we suggest that the first formed intermediate is that of the excited 18-electron superoxide anion radical by radical–radical coupling. We note that the rate constants for these reactions with O_2 are quite similar.[21,31] The ability to effect NO ligand dissociation eq 46b, 47b, and 47c is associated with formation of two strong metal oxide bonds.

Reactions of the Metal Complex Negative Ions with CO, CO$_2$, and CS$_2$.[32] The reactions of CO with the three $LM(CO)_{x-1}{}^{\bullet-}$ complex negative ions were studied. In all three cases, ligand addition forming the parent molecular anion radicals was the exclusive process observed and small apparent bimolecular rate constants for these termolecular reactions were measured (eq 50–52). That the molecular
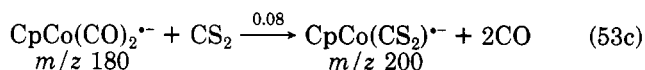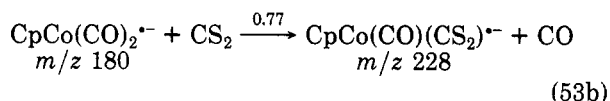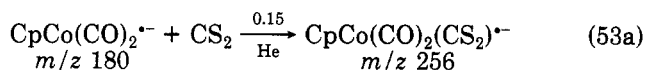
$$(OC)Fe(NO)_2{}^{\bullet-} + CO \xrightarrow{He} (OC)_2Fe(NO)_2{}^{\bullet-} \quad (50)$$
$$m/z\ 144 \qquad\qquad\qquad m/z\ 172$$

$$(OC)_2Co(NO)^{\bullet-} + CO \rightarrow (OC)_3Co(NO)^{\bullet-} \quad (51)$$
$$m/z\ 145 \qquad\qquad\qquad m/z\ 173$$

$$(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-} + CO \rightarrow (C_3H_5)Co(CO)_3{}^{\bullet-} \quad (52)$$
$$m/z\ 156 \qquad\qquad\qquad m/z\ 184$$

anion radicals were not observed in the electron attachment to $(OC)_2Fe(NO)_2$ and $(OC)_3Co(NO)$ requires that the EAs of these two complexes exceeds the CO ligand binding energies in the molecular anion radicals[33,37] and that collisional stabilization with the buffer gas helium is not competitive with CO dissociation with these two species. In $(OC)_2Fe(NO)_2{}^{\bullet-}$ and $(OC)_3Co(NO)^{\bullet-}$, we consider that the NO ligand is η^1. We plan to reinvestigate these and

several other CO addition reactions with ^{13}CO to determine the rate constants for CO exchange.

In our single attempt to use CO_2 as a potential ligand,[32] $(OC)_2Co(NO)^{\bullet-}$ failed to react with this neutral reactant. Wang and Squires reported that CO_2 reacted with the complex $(TMM)Fe(CO)_3{}^{\bullet-}$ by CO ligand substitution but failed to react with $(\eta^2\text{-butadiene})Fe(CO)_3{}^{\bullet-}$.[12]

Kebarle et al.[29] recently reported $EA(CS_2) = 0.51$ eV. We examined the reactions of several of the metal complex negative ions with CS_2 by inletting the vapors of this reactant neutral directly into the flow tube via the high boiling neutral inlet port. Although the reaction kinetics were not determined by using this method, we could observe the product ions and their branching fractions. The reaction of $CpCo(CO)_2{}^{\bullet-}$ with CS_2 produced the total adduct and the ion products of one and two CO ligand dissociation (eq 53). A reinvestigation of this reaction de-
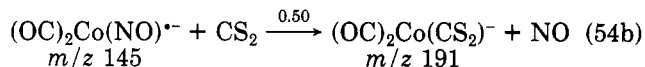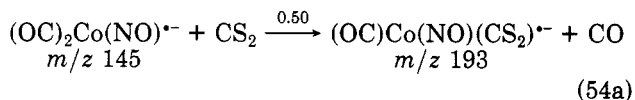
$$CpCo(CO)_2{}^{\bullet-} + CS_2 \xrightarrow[He]{0.15} CpCo(CO)_2(CS_2)^{\bullet-} \quad (53a)$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 256$$

$$CpCo(CO)_2{}^{\bullet-} + CS_2 \xrightarrow{0.77} CpCo(CO)(CS_2)^{\bullet-} + CO$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 228$$
$$(53b)$$

$$CpCo(CO)_2{}^{\bullet-} + CS_2 \xrightarrow{0.08} CpCo(CS_2)^{\bullet-} + 2CO \quad (53c)$$
$$m/z\ 180 \qquad\qquad\qquad m/z\ 200$$

termined the rate constant to be $k_{total} = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[38] Observation of the minor substitution complex at m/z 200 indicates the strong bonding of the CS_2 ligand[32] once barriers on the potential surface are overcome as well as the desire of the Cp ligand to be η^5.

The reactions of CS_2 with the mixture of $(C_3H_5)Co(CO)_3{}^{\bullet-}$ and $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-}$ formed three product ions, $(C_3H_5)Co(CO)_2(CS_2)^{\bullet-}$ (m/z 232; major), $(\eta^3\text{-}C_3H_5)Co(CO)nCS_2)^{\bullet-}$ (m/z 204; trace), and $(OC)_2Co(CS_2)^-$ (m/z 202; major). At this time, we are unable to be certain which starting ion(s) yields which product(s).

In the reactions of CS_2 with $(C_3H_5)Co(CO)_3{}^{\bullet-}$ or $CpCo(CO)_2{}^{\bullet-}$, we did *not* observe formation of $CS_2{}^{\bullet-}$, the product of electron transfer. Therefore, $EA((C_3H_5)Co(CO)_3) = EA(CpCo(CO)_2) = 0.60 \pm 0.1$ eV from the bracketing between $EA(biacetyl) = 0.69$ eV[29] and $EA(CS_2) = 0.51$ eV.[29]

The reaction of $(OC)_2Co(NO)^{\bullet-}$ with CS_2 produced equal amounts of the ion products of CO and NO substitution (eq 54). This is the second example of competitive CO

$$(OC)_2Co(NO)^{\bullet-} + CS_2 \xrightarrow{0.50} (OC)Co(NO)(CS_2)^{\bullet-} + CO$$
$$m/z\ 145 \qquad\qquad\qquad m/z\ 193$$
$$(54a)$$

$$(OC)_2Co(NO)^{\bullet-} + CS_2 \xrightarrow{0.50} (OC)_2Co(CS_2)^- + NO \quad (54b)$$
$$m/z\ 145 \qquad\qquad\qquad m/z\ 191$$

and NO ligand substitution with this metal complex negative ion. Since we believe that ligand substitutions with this complex proceed via the associative mechanism, the Co–CO and Co–(η^1-NO) bond energies in these excited adducts must be similar.

Summary of Results

Three of the transition-metal complex negative ions $((OC)Fe(NO)_2{}^{\bullet-}, (OC)_2Co(NO)^{\bullet-}$, and $(\eta^3\text{-}C_3H_5)Co(CO)_2{}^{\bullet-})$ used in this study were considered to be the 17-electron $LM(CO)_{x-1}{}^{\bullet-}$ complexes generated by dissociative electron

(32) For a review of the reactivities of CS_2, CO_2, and COS with some transition-metal complexes, see: Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57.

(33) From $\Delta H_f{}^\circ(Fe(CO)_5) = -173.0 \pm 1.5$ kcal mol^{-1},[34] $D^\circ((OC)_4Fe-(CO)) = 41 \pm 2$ kcal mol^{-1},[35] $\Delta H_f{}^\circ(CO) = -26.42 \pm 0.04$ kcal mol^{-1},[34] and $EA(Fe(CO)_4) = 55.3 \pm 7$ kcal mol^{-1},[36] the dissociative electron attachment reaction $Fe(CO)_5 + e^- \rightarrow (OC)_4Fe^{\bullet-} + CO$ is calculated to be *exothermic* by 14.3 ± 10.5 kcal mol^{-1}.

(34) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970.

(35) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

(36) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569.

(37) Guerra et al. (Guerra, M.; Jones, D.; Distefano, G.; Foffani, A.; Modelli, A. *J. Am. Chem. Soc.* **1988**, *110*, 375) report their results of electron transmission spectroscopy and MS-Xα calculations from which they conclude that "no anion state (of Fe(CO)$_5{}^{\bullet-}$) is stable and Σ anion states are not present in the 0–5 eV energy range".

(38) We thank Dr. Michael T. Jones for determination of this rate constant.

attachment with the corresponding neutral 18-electron LM(CO)$_x$ complexes. The other two metal complex negative ions employed were the parent molecular anions LM(CO)$_x$·⁻, formed by electron attachment to (η^3-C$_3$H$_5$)-Co(CO)$_3$ and CpCo(CO)$_2$. We believe that the kinetic and product data for the latter two molecular anion radicals are most consistent with the parent ions also being 17-electron species where the organic ligand underwent a reduction in its hapticity (η^3-C$_3$H$_5$ → η^1-C$_3$H$_5$ and η^5-Cp → η^3-Cp, respectively) on attachment of the electron.

In general, the ligand substitution reactions of the 17-electron LM(CO)$_{x-1}$·⁻ complex negative ions and CpCo-(CO)$_2$·⁻ occurred by the associative mechanism. *Direct observation of the addition adducts and the products of ligand substitution and P$_{He}$ effects on the branching fractions of these product forming channels established this mechanism in numerous examples.* In these cases, the metal complex negative ion contains a ligand that can reduce its hapticity (η^3-NO, η^3-C$_3$H$_5$, or η^3-Cp) when the ligand binds to the metal. The associative mechanism was also considered to be operating in the reactions with the free radicals NO and O$_2$ although the adducts were not observed. Similar conclusions have been reached for related studies in the condensed phase.

The reactions of the five metal complex anion radicals with PF$_3$ were particularly informative. The three LM-(CO)$_{x-1}$·⁻ complexes reacted rapidly with PF$_3$, forming adducts, LM(CO)$_{x-1}$(PF$_3$)·⁻, and the products of CO ligand substitution, LM(CO)$_{x-2}$(PF$_3$)·⁻. Competitive collisional stabilization of the adduct with the helium buffer gas and CO ligand fragmentation clearly established operation of the associative mechanism in these reactions. The similar product results observed in the much slower reaction of CpCo(CO)$_2$·⁻ with PF$_3$ indicate the larger energy required for the η^3-Cp → η^1-Cp change than for the η^3 → η^1 change for the allyl ligand. The slow reaction of (C$_3$H$_5$)Co(CO)$_3$·⁻ and PF$_3$ gave (OC)$_3$Co(PF$_3$)·⁻. It was suggested that this latter reaction occurred via radical β-fragmentation of the unobserved acyl intermediate (OC)$_2$(F$_3$P)CoC(=O)C$_3$H$_5$·⁻ (5) formed by CO insertion into the Co–allyl bond.

All five metal complex negative ions reacted with NO with similar rate constants to yield the product ion of CO substitution; only (C$_3$H$_5$)Co(CO)$_3$·⁻ was observed to form the total adduct. We believe that each of these reactions proceeded by association of the radical NO initially yielding the corresponding excited 18-electron adduct with the NO serving as a one-electron donor ligand.

With SO$_2$ as the potential ligand, the five metal complex negative ions reacted at nearly the collision limit to yield the product ions of electron transfer (SO$_2$·⁻) and/or ligand substitution. With (OC)Fe(NO)$_2$·⁻ and (OC)$_2$Co(NO)·⁻, only the product ions of CO ligand substitution were observed. Both CpCo(CO)$_2$·⁻ and (C$_3$H$_5$)Co(CO)$_3$·⁻ formed the product ions of electron transfer and of ligand substitution (CO and allyl radical, respectively). The reaction of (η^3-C$_3$H$_5$)Co(CO)$_2$·⁻ with SO$_2$ was the first time that *both* CO and allyl radical ligand substitution channels were observed. The dual substitution with this latter metal complex anion radical was considered to depend on the ion–ligand addition exothermicity and possibly steric congestion in the addition complex yielding mixtures of excited adducts [(η^1-C$_3$H$_5$)Co(CO)$_2$L·⁻]* (→ (adduct–CO)) and [C$_3$H$_5$C(=O)Co(CO)L·⁻]* (→ (adduct-·C$_3$H$_5$)).

With use of the olefins CH$_2$=CHCN, CH$_2$=CHCO$_2$CH$_3$, and F$_2$C=CF$_2$, only the more reactive LM(CO)$_{x-1}$·⁻ complexes reacted and were found to produce adducts and/or ligand substitution product ions. With (NC)$_2$C=C(CN)$_2$, the four metal complex negative ions investigated under-

went mainly electron transfer forming (NC)$_2$C=C(CN)$_2$·⁻.

Although acetone failed to react with any of the five metal complex negative ions, CH$_3$C(=O)CF$_3$, (CF$_3$)$_2$C=O, and biacetyl did react, forming product ions of electron transfer and/or ligand substitution. (OC)Fe(NO)$_2$·⁻ reacted with the three ketones by CO ligand substitution exclusively. CpCo(CO)$_2$·⁻ did not react with CH$_3$C(=O)-CF$_3$ but underwent only electron transfer with (CF$_3$)$_2$C=O and biacetyl. (C$_3$H$_5$)Co(CO)$_3$·⁻ also reacted with (CF$_3$)$_2$-C=O and biacetyl by exclusive electron transfer but did react with CH$_3$C(=O)CF$_3$ by CO ligand substitution. While (OC)$_2$Co(NO)·⁻ did not react with CH$_3$C(=O)CF$_3$, extensive ligand substitution was observed with (CF$_3$)$_2$-C=O and biacetyl. The complex (η^3-C$_3$H$_5$)Co(CO)$_2$·⁻ formed only the (adduct-·C$_3$H$_5$) with CH$_3$C(=O)CF$_3$, suffered electron transfer and ligand substitution with (CF$_3$)$_2$C=O, and was observed to yield the adduct and the product ions of ligand substitution with biacetyl. Therefore, the two fluorinated acetones and the α-diketone biacetyl serve as useful reagents for ligand substitution with metal complex negative ions in the gas phase. The relatively slow rates of electron transfer from CpCo(CO)$_2$·⁻ and (C$_3$H$_5$)Co(CO)$_3$·⁻ to biacetyl were consistent with significant structural changes in the LM(CO)$_x$ neutrals and the lowest energy LM(CO)$_x$·⁻ complexes. These structural changes were suggested to be caused by the organic ligands in the negative ions (η^3-Cp and η^1-C$_3$H$_5$) changing their hapticities in the neutrals (η^5-Cp and η^3-C$_3$H$_5$).

The reaction of (OC)Fe(NO)$_2$·⁻ and (OC)$_2$Co(NO)·⁻ with O$_2$ were similar in that product ions formed by addition of O$_2$ with loss of CO, CO$_2$, and (NO + CO) were observed. The ejection of NO ligands was associated with the formation of metal oxides. Loss of CO$_2$ was considered to occur via a metallaperlactone structure. The unusual product negative ion CpCo·⁻ was observed in the reaction of CpCo(CO)$_2$·⁻ with O$_2$. It was suggested that this anion radical was produced via a metallaperanhydride 13 which then suffered bisdecarboxylation.

Each of the three LM(CO)$_{x-1}$·⁻ complexes added CO to form the parent molecular anion radicals LM(CO)$_x$·⁻. While CO$_2$ was not observed to be a useful neutral ligand substitution reagent, the results with CS$_2$ were interesting. CS$_2$ was observed to effect CO ligand substitution with all five metal complex negative ions and even displaced NO in its reaction with (OC)$_2$Co(NO)·⁻.

The observed electron transfer in the reactions of CpCo(CO)$_2$·⁻ and (C$_3$H$_5$)Co(CO)$_3$·⁻ with biacetyl, but not with CS$_2$, yielded EA((η^3-C$_3$H$_5$)Co(CO)$_3$) = 0.60 ± 0.1 eV = EA(CpCo(CO)$_2$). From other results, EA((η^3-C$_3$H$_5$)Co-(CO)$_2$) = 0.9 ± 0.2 eV, and 1.46 eV < [EA((OC)$_2$Co(NO)) and EA((OC)Fe(NO)$_2$)] < 3.17 eV were bracketed.

$(C_2H_3Br)^{·-}$, 114884-93-4; $(ON)Fe(C_2H_3Br)^{·-}$, 114884-94-5; $(ON)_2Fe(C_3H_3N)^{·-}$, 114884-95-6; $(ON_2)Fe(CH_2CHCO_2CH_3)^{·-}$, 114884-96-7; $(ON)_2Fe(C_2F_4)^{·-}$, 114884-97-8; $(ON)_2Fe(C_3H_3F_3O)^{·-}$, 114907-16-3; $(ON)_2Fe(C_3F_6O)^{·-}$, 114884-98-9; $(ON_2)Fe(CH_3COCOCH_3)^{·-}$, 114884-99-0; $(ON)_2Fe(O_2)^{·-}$, 114907-17-4; $(ON)Fe(O_2)^{·-}$, 114907-18-5; $(ON)_2FeO^{·-}$, 114885-00-6; $(ON)_2Fe(CO)_2^{·-}$, 75345-61-8; $(OC)_2Co(NO)(PF_3)^{·-}$, 114885-01-7; $(OC)Co(NO)(PF_3)^{·-}$, 114885-02-8; $(OC)Co(NO)_2^{·-}$, 114885-03-9; $(OC)Co(NO)(SO_2)^{·-}$, 114907-19-6; $(OC)_2Co(NO)(C_3H_3N)^{·-}$, 114885-04-0; $(OC)Co(NO)(C_3H_3N)^{·-}$, 114885-05-1; $(OC)_2Co(NO)(C_2F_4)^{·-}$, 114885-06-2; $(OC)Co(NO)(C_2F_4)^{·-}$, 114885-07-3; $C_2(CN)_4^{·-}$, 34512-48-6; $(OC)Co(NO)(C_6N_4)^{·-}$, 114885-08-4; $(OC)Co(NO)(C_3F_6O)^{·-}$, 114885-09-5; $(OC)_2Co(C_3F_6O)^-$, 114885-10-8; $(OC)_2Co(NO)(C_4H_6O_2)^{·-}$, 114885-11-9; $(OC)Co(NO)(C_4H_6O_2)^{·-}$, 114885-12-0; $(OC)Co(NO)(O_2)^{·-}$, 114907-20-9; $(OC)_2Co(O_2)^-$, 114907-21-0; $(OC)Co(O_2)^-$, 114907-22-1; $(ON)CoO^{·-}$, 114885-13-1; $(OC)_3Co(NO)^{·-}$, 114885-14-2; $(OC)Co(NO)(CS_2)^{·-}$, 114885-15-3; $(OC)_2Co(CS_2)^-$, 114885-16-4; $CpCo(CO)_2(PF_3)^{·-}$, 114885-17-5; $CpCo(CO)(PF_3)^{·-}$, 114885-18-6; $CpCo(CO)(NO)^-$, 114885-19-7; $CpCo(NO)^{·-}$, 64236-02-8; $CpCo(CO)(SO_2)^{·-}$, 114907-23-2; $[CpCo(CO)_2]$, 12078-25-0; $CpCo(CO)(O_2)^{·-}$, 114907-24-3; $CpCo(CO)(O)^{·-}$, 114885-20-0; $CpCo(O)^{·-}$, 111189-21-0; $CpCo^{·-}$, 61332-89-6; $CpCo(CO)_2(CS_2)^{·-}$, 114885-22-2; $CpCo(CO)(CS_2)^{·-}$, 114885-23-3; $CpCo(CS_2)^{·-}$, 114885-24-4; $(C_3H_5)Co(CO)_2(PF_3)^{·-}$, 114885-25-5; $(\eta^3-C_3H_5)Co(CO)(PF_3)^{·-}$, 114885-26-6; $(\eta^3-C_3H_5)Co(CO)(NO)^-$, 114885-27-7; $(OC)_2Co(SO_2)^-$, 114907-25-4; $(\eta^3-C_3H_5)Co(CO)(SO_2)^{·-}$, 114907-26-5; $(C_3H_5)Co(CO)_2(C_3H_3N)^{·-}$, 114885-28-8; $(\eta^3-C_3H_5)Co(CO)(C_3H_3N)^{·-}$, 114885-29-9; $(OC)_2Co(C_3H_3N)^-$, 114885-30-2; $(C_3H_5)Co(CO)_2(C_4H_6O_2)^{·-}$, 114885-31-3; $(\eta^3-C_3H_5)Co(CO)(C_4H_6O_2)^{·-}$, 114885-32-4; $(OC)_2Co(C_4H_6O_2)^-$, 114885-33-5; $(C_3H_5)Co(CO)_2(C_2F_4)^{·-}$, 114885-34-6; $(\eta^3-C_3H_5)Co(CO)(C_2F_4)^{·-}$, 114885-35-7; $(\eta^3-C_3H_5)Co(CO)_2$, 87511-72-6; $(\eta^3-C_3H_5)Co(CO)(C_3F_6O)^{·-}$, 114885-36-8; $(OC)_3Co(PF_3)^{·-}$, 114885-37-9; $(C_3H_5)Co(CO)_3(NO)^-$, 114885-38-0; $(C_3H_5)Co(CO)_2(NO)^-$, 114885-39-1; $[(\eta^3-C_3H_5)Co(CO)_3]$, 12144-85-3; $(OC)_3Co(SO_2)^-$, 114907-27-6; $(OC)_2Co(NO)$, 61332-94-3.

Gas-Phase Ligand Substitution Reactions with the 17-Electron Transition-Metal Complexes $(OC)_4Fe^{·-}$, $(OC)_5Cr^{·-}$, and $(OC)_4MnH^{·-}$

Richard N. McDonald* and Philip L. Schell

*Department of Chemistry, Kansas State University, Manhattan, Kansas 66506*

Three transition-metal complex negative ions, $(OC)_4Fe^{·-}$, $(OC)_5Cr^{·-}$, and $(OC)_4MnH^{·-}$, were generated and studied in ligand substitution reactions with a variety of neutral ligand substrates. Only $(OC)_4Fe^{·-}$ reacted with PF_3 and gave sequentially the product ions $(OC)_{4-x}Fe(PF_3)_x^{·-}$ where $x = 1-3$. The three metal complex negative ions formed ligand substitution product anions with NO; the reaction with $(OC)_4MnH^{·-}$ also produced some of the corresponding adduct anion. With SO_2, $(OC)_4Fe^{·-}$ gave only ligand substitution, $(OC)_5Cr^{·-}$ formed a mixture of the adduct and the product of ligand substitution, and $(OC)_4MnH^{·-}$ produced only the adduct. Both the NO and SO_2 reactions were believed to occur by the associative mechanism with the SO_2 reactions proceeding via Lewis acid–base complexes. Only $(NC)_2C=C(CN)_2$ (TCNE) of the seven olefins examined reacted with the metal complex negative ions forming the product of electron transfer (TCNE·⁻) as well as the product ions of ligand substitution. The reactions of all three metal complex negative ions with $(CF_3)_2C=O$ and of $(OC)_5Cr^{·-}$ with biacetyl were considered to involve initial electron transfer within the orbiting collision complex. The reaction of $(OC)_4MnH^{·-}$ with O_2 produced various oxidation products, the most noteworthy being HCO_2^- as a major product anion. This latter result is considered to be evidence for the migratory insertion reaction, $OC-Mn-H \rightleftharpoons Mn-CHO$, in the adduct formed from $(OC)_4MnH^{·-}$ with O_2.

Introduction

We recently described a series of ligand substitution reactions[1-3] with the 17-electron transition-metal complexes $(OC)Fe(NO)_2^{·-}$, $(OC)_2Co(NO)^{·-}$, $(\eta^3-C_3H_5)Co(CO)_2^{·-}$ and the two parent molecular anions $CpCo(CO)_2^{·-}$ and $(C_3H_5)Co(CO)_3^{·-}$ carried out in the gas phase.[4] These reactions were generally characterized as occurring by the associative mechanism (eq 1). With several neutral ligand

$$LM(CO)_n^{·-} + L' \rightarrow LL'M(CO)_n^{·-} \rightarrow$$
$$LL'M(CO)_{n-1}^{·-} + CO \quad (1)$$
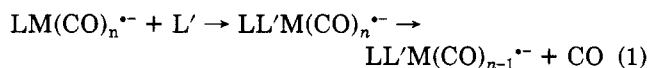
substrates and metal complex anion radicals, formation of the total adduct negative ions $(LL'M(CO)_n^{·-})$ and of the product anion of ligand substitution $(LL'M(CO)_{n-1}^{·-})$ were observed. Changes in the $(LL'M(CO)_n^{·-})/(LL'M(CO)_{n-1}^{·-})$ ratios effected by changes in the P_{He} established that both of these product ions were formed by competitive collisional stabilization (a) and fragmentation (b) of the initially produced excited adducts $(LL'M(CO)_n^{·-})^*$ (eq 2).

$$LL'M(CO)_n^{·-} \xleftarrow[He]{a} [LL'M(CO)_n^{·-}]^* \xrightarrow{b}$$
$$LL'M(CO)_{n-1}^{·-} + CO \quad (2)$$
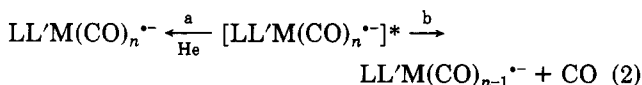
In the gas phase, a thermalized metal complex ion cannot dissociate a ligand in the absence of a perturbing influence since such a process would be endothermic. However, dissociation of a ligand from the metal complex ion could occur in the ion–ligand orbiting collision complex *if* the exothermicity in forming the collision complex equals or exceeds a M–ligand bond energy in $LM(CO)_n^{·-}$. If this occurred, the coordinatively unsaturated metal complex $LM(CO)_{n-1}^{·-}$ in the resulting ternary complex 1 in eq 3

(1) For a recent review of ligand substitution reactions, see: Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* 1983, 83, 557.

(2) Stiegman and Tyler (Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* 1986, 5, 215) recently reviewed ligand substitution reactions of metal complexes with 17- and 19-electron configurations.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapter 4.

(4) McDonald, R. N.; Schell, P. L. *Organometallics*, preceding paper in this issue.