ORGANOMETALLICS

Gas-phase ligand substitution reactions with the 17-electron transition-metal complexes (OC)4Fe-, (OC)5Cr-, and (OC)4MnH-

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Organometallics, **1988**, 7 (8), 1820-1827• DOI: 10.1021/om00098a020 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

$(C_2H_3Br)^{\bullet-}$, 114884-93-4; $(ON)Fe(C_2H_3Br)^{\bullet-}$, 114884-94-5; $(ON)_2Fe(C_3H_3N)^{\bullet-}$, 114884-95-6; $(ON_2)Fe(CH_2CHCO_2CH_3)^{\bullet-}$, 114884-96-7; $(ON)_2Fe(C_2F_4)^{\bullet-}$, 114884-97-8; $(ON)_2Fe(C_3H_3F_3O)^{\bullet-}$, 114907-16-3; $(ON)_2Fe(C_3F_6O)^{\bullet-}$, 114884-98-9; $(ON_2)Fe(CH_3COCOCH_3)^{\bullet-}$, 114884-99-0; $(ON)_2Fe(O_2)^{\bullet-}$, 114907-17-4; $(ON)Fe(O_2)^{\bullet-}$, 114907-18-5; $(ON)_2FeO^{\bullet-}$, 114885-00-6; $(ON)_2Fe(CO)_2^{\bullet-}$, 75345-61-8; $(OC)_2Co(NO)(PF_3)^{\bullet-}$, 114885-01-7; $(OC)Co(NO)(PF_3)^{\bullet-}$, 114885-02-8; $(OC)Co(NO)_2^{\bullet-}$, 114885-03-9; $(OC)Co(NO)(SO_2)^{\bullet-}$, 114907-19-6; $(OC)_2Co(NO)(C_3H_3N)^{\bullet-}$, 114885-04-0; $(OC)Co(NO)(C_3H_3N)^{\bullet-}$, 114885-05-1; $(OC)_2Co(NO)(C_2F_4)^{\bullet-}$, 114885-06-2; $(OC)Co(NO)(C_2F_4)^{\bullet-}$, 114885-07-3; $C_2(CN)_4^{\bullet-}$, 34512-48-6; $(OC)Co(NO)(C_6N_4)^{\bullet-}$, 114885-08-4; $(OC)Co(NO)(C_3F_6O)^{\bullet-}$, 114885-09-5; $(OC)_2Co(C_3F_6O)^-$, 114885-10-8; $(OC)_2Co(NO)(C_4H_6O_2)^{\bullet-}$, 114885-11-9; $(OC)Co(NO)(C_4H_6O_2)^{\bullet-}$, 114885-12-0; $(OC)Co(NO)(O_2)^{\bullet-}$, 114907-20-9; $(OC)_2Co(O_2)^-$, 114907-21-0; $(OC)Co(O_2)^-$, 114907-22-1; $(ON)CoO^{\bullet-}$, 114885-13-1; $(OC)_3Co(NO)^{\bullet-}$, 114885-14-2; $(OC)Co(NO)(CS_2)^{\bullet-}$, 114885-15-3; $(OC)_2Co(CS_2)^-$, 114885-16-4; $CpCo(CO)_2(PF_3)^{\bullet-}$, 114885-17-5; $CpCo(CO)(PF_3)^{\bullet-}$, 114885-18-6; $CpCo(CO)(NO)^-$, 114885-19-7; $CpCo(NO)^{\bullet-}$, 64236-02-8; $CpCo(CO)(SO_2)^{\bullet-}$, 114907-23-2; $[CpCo(CO)_2]$, 12078-25-0; $CpCo(CO)(O_2)^{\bullet-}$, 114907-24-3; $CpCo(CO)(O)^{\bullet-}$, 114885-20-0; $CpCo(O)^{\bullet-}$, 111189-21-0; $CpCo^{\bullet-}$, 61332-89-6; $CpCo(CO)_2(CS_2)^{\bullet-}$, 114885-22-2; $CpCo(CO)(CS_2)^{\bullet-}$, 114885-23-3; $CpCo(CS_2)^{\bullet-}$, 114885-24-4; $(C_3H_5)Co(CO)_2(PF_3)^{\bullet-}$, 114885-25-5; $(\eta^3\text{-}C_3H_5)Co(CO)(PF_3)^{\bullet-}$, 114885-26-6; $(\eta^3\text{-}C_3H_5)Co(CO)(NO)^-$, 114885-27-7; $(OC)_2Co(SO_2)^-$, 114907-25-4; $(\eta^3\text{-}C_3H_5)Co(CO)(SO_2)^{\bullet-}$, 114907-26-5; $(C_3H_5)Co(CO)_2(C_3H_3N)^{\bullet-}$, 114885-28-8; $(\eta^3\text{-}C_3H_5)Co(CO)(C_3H_3N)^{\bullet-}$, 114885-29-9; $(OC)_2Co(C_3H_3N)^-$, 114885-30-2; $(C_3H_5)Co(CO)_2(C_4H_6O_2)^{\bullet-}$, 114885-31-3; $(\eta^3\text{-}C_3H_5)Co(CO)(C_4H_6O_2)^{\bullet-}$, 114885-32-4; $(OC)_2Co(C_4H_6O_2)^-$, 114885-33-5; $(C_3H_5)Co(CO)_2(C_2F_4)^{\bullet-}$, 114885-34-6; $(\eta^3\text{-}C_3H_5)Co(CO)(C_2F_4)^{\bullet-}$, 114885-35-7; $(\eta^3\text{-}C_3H_5)Co(CO)_2$, 87511-72-6; $(\eta^3\text{-}C_3H_5)Co(CO)(C_3F_6O)^{\bullet-}$, 114885-36-8; $(OC)_3Co(PF_3)^{\bullet-}$, 114885-37-9; $(C_3H_5)Co(CO)_3(NO)^-$, 114885-38-0; $(C_3H_5)Co(CO)_2(NO)^-$, 114885-39-1; $[(\eta^3\text{-}C_3H_5)Co(CO)_3]$, 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 $(OC)_4Fe^{\bullet-}$, $(OC)_5Cr^{\bullet-}$, and $(OC)_4MnH^{\bullet-}$

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Received March 28, 1988

Three transition-metal complex negative ions, $(OC)_4Fe^{\bullet-}$, $(OC)_5Cr^{\bullet-}$, and $(OC)_4MnH^{\bullet-}$, were generated and studied in ligand substitution reactions with a variety of neutral ligand substrates. Only $(OC)_4Fe^{\bullet-}$ reacted with PF_3 and gave sequentially the product ions $(OC)_{4-x}Fe(PF_3)_x^{\bullet-}$ where $x = 1$–3. The three metal complex negative ions formed ligand substitution product anions with NO; the reaction with $(OC)_4MnH^{\bullet-}$ also produced some of the corresponding adduct anion. With SO_2, $(OC)_4Fe^{\bullet-}$ gave only ligand substitution, $(OC)_5Cr^{\bullet-}$ formed a mixture of the adduct and the product of ligand substitution, and $(OC)_4MnH^{\bullet-}$ 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 ($TCNE^{\bullet-}$) 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 $(OC)_5Cr^{\bullet-}$ with biacetyl were considered to involve initial electron transfer within the orbiting collision complex. The reaction of $(OC)_4MnH^{\bullet-}$ 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 $(OC)_4MnH^{\bullet-}$ with O_2.

Introduction

We recently described a series of ligand substitution reactions[1-3] with the 17-electron transition-metal complexes $(OC)Fe(NO)_2^{\bullet-}$, $(OC)_2Co(NO)^{\bullet-}$, $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$ and the two parent molecular anions $CpCo(CO)_2^{\bullet-}$ and $(C_3H_5)Co(CO)_3^{\bullet-}$ carried out in the gas phase.[4] These reactions were generally characterized as occurring by the associative mechanism (eq 1). With several neutral ligand substrates and metal complex anion radicals, formation of the total adduct negative ions ($LL'M(CO)_n^{\bullet-}$) and of the product anion of ligand substitution ($LL'M(CO)_{n-1}^{\bullet-}$) were observed. Changes in the $(LL'M(CO)_n^{\bullet-})/(LL'M(CO)_{n-1}^{\bullet-})$ 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 $(LL'M(CO)_n^{\bullet-})^*$ (eq 2).

$$LM(CO)_n^{\bullet-} + L' \rightarrow LL'M(CO)_n^{\bullet-} \rightarrow LL'M(CO)_{n-1}^{\bullet-} + CO \quad (1)$$

$$LL'M(CO)_n^{\bullet-} \xleftarrow[He]{a} [LL'M(CO)_n^{\bullet-}]^* \xrightarrow{b} LL'M(CO)_{n-1}^{\bullet-} + CO \quad (2)$$

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 $LM(CO)_n^{\bullet-}$. If this occurred, the coordinatively unsaturated metal complex $LM(CO)_{n-1}^{\bullet-}$ in the resulting ternary complex 1 in eq 3

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(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.

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$$\mathrm{LM(CO)}_n^{\bullet-} + \mathrm{L'} \rightleftharpoons \underset{1}{[\mathrm{LM(CO)}_{n-1}^{\bullet-}/\mathrm{CO}/\mathrm{L'}]} \rightarrow \mathrm{LL'M(CO)}_{n-1}^{\bullet-} + \mathrm{CO} \quad (3)$$

(assuming CO dissociation) could competitively bind CO and L′. This is possible because of the 10–20 kcal mol^{-1} attractive energy in forming the ion–molecule orbiting collision complex due to ion–dipole and ion-induced dipole forces. The process outlined in eq 3 is called the ion–molecule activated dissociation (IMCAD) mechanism.

We know of no established examples of ligand substitution reactions occurring by the IMCAD mechanism.[5] While we have no simple way to predict when the IMCAD mechanism will occur with respect to the neutral ligand substrate, appearance potential (AP) data for the stepwise formation of $LM(CO)_n^{\bullet-}$ and $LM(CO)_{n-1}^{\bullet-}$ should be useful in identifying which $LM(CO)_n^{\bullet-}$ complexes might be susceptible to undergoing ligand substitution by the IMCAD mechanism. In the present study involving the 17-electron metal complex negative ions $(OC)_4Fe^{\bullet-}$, $(OC)_5Cr^{\bullet-}$, and $(OC)_4MnH^{\bullet-}$, the first two complexes could possibly undergo ligand substitution by the IMCAD mechanism. This is seen in the AP data for generating the $(OC)_{n-1}M^{\bullet-}$ and $(OC)_{n-2}M^{\bullet-}$ fragment ions by dissociative electron attachment with $Fe(CO)_5$[6] and $Cr(CO)_6$.[6a] Low-energy electrons (~0.1 eV) were required to produce the $(OC)_{n-1}M^{\bullet-}$ fragment ions while electrons only ≈ 0.5 eV higher in energy were needed to form the $(OC)_{n-2}M^{\bullet-}$ species. Although related AP values for generating the corresponding fragment negative ions from $(OC)_5MnH$ have not been reported, we estimate that $D°((OC)_3(H)Mn^{\bullet-}–(CO)) > D°((OC)_3Fe^{\bullet-}–(CO)) \approx D°((OC)_4Cr^{\bullet-}–(CO))$. This estimate comes from our inability to generate a significant ion signal for $(OC)_3MnH^{\bullet-}$ by energetic electron impact on $(OC)_5MnH$ using conditions where $Fe(CO)_5$ and $Cr(CO)_6$ readily from the fragment anions $(OC)_{4,3}Fe^{\bullet-}$ and $(OC)_{5,4}Cr^{\bullet-}$, respectively.[7] Therefore, $(OC)_4MnH^{\bullet-}$ would be the least likely of the three metal complex negative ions used in this study to undergo ligand substitution by the IMACD mechanism.

Experimental Section

The flowing afterglow (FA) apparatus used in this study has been described.[4,8] Briefly, a fast flow of helium buffer gas (standard conditions: P_{He} = 0.5 Torr (variable from 0.3 to 1.2 Torr) and $\bar{v}$ = 80 m s^{-1} (adjustable to 40 m s^{-1})) at 298 K was established and maintained during the experiments by adding helium through two inlet ports in the upstream end of the 1.5-m long flow tube and exhausting it at the downstream end with a large, fast pumping system. The electron gun was turned on, and the neutral metal carbonyl ($Fe(CO)_5$, $Cr(CO)_6$, or $(OC)_5MnH$) was continuously leaked into the flow via inlet 1 located 10-cm downstream of the electron gun. Thermal or near thermal energy electrons attach dissociatively to the metal carbonyl and cleanly produce the desired 17-electron metal complex negative ions ($(OC)_4Fe^{\bullet-}$, $(OC)_5Cr^{\bullet-}$, or $(OC)_4MnH^{\bullet-}$). The concentration of the added $M(CO)_n$ was controlled by a needle valve placed between the inlet and a reservoir of the metal carbonyl to capture all electrons within 25 cm of this inlet. The excited $(OC)_{n-1}M^{\bullet-}$ ions were cooled to their vibrational ground states by multiple collisions with the buffer gas in the 75-cm distance between inlet 1 and the neutral ligand substrate (NLS) inlet located about halfway downstream in the main flow tube. The gaseous neutral ligands were added via the NLS inlet, and the ion–molecule reaction occurred in the final 65 cm of the flow tube, the distance from the NLS inlet to the first sampling nose cone.

The fast, moderate-pressure flow was exhausted by the pumping system but was sampled via 1-mm orifices in each of two nose cones into a differentially pumped compartment ($P \approx 4 \times 10^{-7}$ Torr) containing a quadrupole mass filter (10–1200 amu mass range) and electron multiplier which continuously monitored the ion composition in the flow. The neutral reaction products were not directly observed but were assumed based on thermochemistry and mass balance.

Kinetics of the bimolecular ion–molecule reactions were determined under pseudo-first-order conditions where the concentration of the added neutral ligand substrate was in large excess compared to the ion concentration. The details of this procedure have been presented.[8] The integrated signals of the ion products from these reactions were also measured in these kinetic experiments.

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 two inlets in the upstream end of the flow tube. Gas and liquid ligand substrates were obtained from standard commercial sources. The gas substrates were used as received. The liquid substrates 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.

$Fe(CO)_5$ and $Cr(CO)_6$ were purchased from Aldrich Chemical Co. and used as received. $(OC)_5MnH$ was prepared by Ms. Allison Fleming using a literature procedure;[9] the sample yielded ion signals of >99% $(OC)_4MnH^{\bullet-}$ and a trace of $(OC)_5Mn^{-}$ (from trace $Mn_2(CO)_{10}$ contamination) on dissociative electron attachment.

Results

The three metal carbonyl reagents readily underwent dissociative electron attachment in the FA yielding the metal complex negative ions shown in eq 4–6. The M − 2, M + 1, and M + 2

$$\mathrm{Fe(CO)}_5 + e^- \rightarrow \underset{m/z\ 168}{\mathrm{(OC)}_4\mathrm{Fe}^{\bullet-}} + \mathrm{CO} \quad (4)$$

$$\mathrm{Cr(CO)}_6 + e^- \rightarrow \underset{m/z\ 192}{\mathrm{(OC)}_5\mathrm{Cr}^{-}} + \mathrm{CO} \quad (5)$$

$$\mathrm{(OC)}_5\mathrm{MnH} + e^- \rightarrow \underset{m/z\ 168}{\mathrm{(OC)}_4\mathrm{MnH}^{\bullet-}} + \mathrm{CO} \quad (6)$$

isotope signals for $(OC)_4Fe^{\bullet-}$ and $(OC)_5Cr^{\bullet-}$ due to the metal and ^{13}C and the M + 1 signal due to ^{13}C in $(OC)_4MnH^{\bullet-}$ were readily resolved in their negative ion mass spectra and served as fingerprints for product ions from their ion–molecule reactions.

Addition of measured concentrations of the neutral ligand substrates, L, to the flows containing one of these metal complex negative ions gave excellent pseudo-first-order decay plots (log (ion signal) vs increasing [L]) with correlation coefficients >0.99.[4,8] The rate constants for these reactions listed in Tables I–III were determined at 0.5 and 1.0 Torr with generally no change outside of experimental error. While our ability to duplicate rate constants is <±10% of the average values cited, the errors due to systematic uncertainties in calibrations suggest that their accuracy for external comparisons is ±20%. The FA allows determination of rate constants for reactions that occur at the collision limit ($k_{total} \approx 10^{-9}$ cm^3 molecule^{-1} s^{-1} = k_{ADO}[10]) with the lower limit of $k_{total} = 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

The product ion branching fractions given were corrected for any secondary ion–molecule reactions with errors of ±4% absolute. Unless otherwise noted, the rate constants and branching fractions did not change outside of experimental error when the flow tube pressure (P_{He}) was changed from 0.5 to 1.0 Torr. Formation of total adduct product ions in these reactions was assumed to require collisional stabilization of the excited adduct negative ion with

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(5) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623.

(6) (a) Pignataro, S.; Foffani, A.; Grasso, F.; Contone, B. *Z. Phys. Chem. (Wiesbaden)* **1965**, *47*, 106. (b) Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 47.

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

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

(9) Gladyz, J. A.; Wilson, T.; Williams, G. M.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* **1979**, *18*, 1163.

(10) Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, Chapter 3.

Table I. Summary of the Kinetic and Product Data for the Ligand Substitution Reactions of $(OC)_4Fe^{\bullet-}$

rxn	neutral ligand substrate		primary product ion(s) + [assumed neutral]	fraction of product ion signal[a]	k_{total},[a] cm^3 molecule^{-1} s^{-1}	k_{ADO},[b] cm^3 molecule^{-1} s^{-1}
1	PF_3	→	$(OC)_3Fe(PF_3)^{\bullet-}$ + [CO]	1.00	2.9×10^{-11}	7.9×10^{-10}
2	$P(CH_3)_3$	→	no reaction		$<10^{-13}$	
3	NO	→	$(OC)_3Fe(NO)^-$ + [CO]	1.00	2.4×10^{-11}	6.1×10^{-10}
4	SO_2	→	$(OC)_3Fe(SO_2)^{\bullet-}$ + [CO]	1.00	2.0×10^{-10}	1.1×10^{-9}
5	$CH_2{=}CHCH_3$	→	no reaction		$<10^{-13}$	
6	$CH_2{=}CHOEt$	→	no reaction		$<10^{-13}$	
7	$CH_2{=}CHCO_2CH_3$	→	no reaction		$<10^{-13}$	
8	$CH_2{=}CHCN$	→	no reaction		$<10^{-13}$	
9	$F_2C{=}CF_2$	→	no reaction		$<10^{-13}$	
10	$CH_2{=}CHBr$	→	no reaction		$<10^{-13}$	
11a	$(NC)_2C{=}C(CN)_2$	→	$C_2(CN)_4^{\bullet-}$ + [$Fe(CO)_4$]	0.50	*c*	
11b		→	$(OC)_3Fe(C_2(CN)_4)^{\bullet-}$ + [CO]	0.50		
12	$(CH_3)_2C{=}O$	→	no reaction		$<10^{-13}$	
13	$CH_3C({=}O)CF_3$	→	no reaction		$<10^{-13}$	
14	$(CF_3)_2C{=}O$	→	$(OC)_3Fe(C_3F_6O)^{\bullet-}$ + [CO]	1.00	4.2×10^{-10}	9.8×10^{-10}
15	$(CH_3C({=}O)_2$	→	no reaction		$<10^{-13}$	
16	CO	→	no reaction		$<10^{-13}$	

[a] See Results for the errors associated with these measurements. [b] Calculated collision-limited rate constant using the *average dipole orientation* theory.[10] [c] Not measured.

the buffer gas for the adduct to be observed. Failure to observe P_{He} effects on adduct forming channels could mean that the process was already saturated at P_{He} = 0.5 Torr or that the small ΔP_{He} available was not sufficient to change the rate constant or branching fractions outside of the experimental errors.

Discussion

Reactions of the Three Metal Complex Negative Ions with PF_3 and $P(CH_3)_3$. Corderman and Beauchamp were the first investigators to employ PF_3 and $P(CH_3)_3$ as neutral ligand substrates.[11] Both $CpCo(CO)_2^{\bullet-}$ and $CpCo(CO)^{\bullet-}$ underwent CO ligand substitution with PF_3 (eq 7 and 8), but $P(CH_3)_3$ failed to react with either metal complex anion radical in their low-pressure ICR spectrometer.[11] In our reinvestigation of reaction 7,[4] we observed that the reaction is quite slow and that in the higher pressure of the FA the major product forming channel was formation of the total adduct $CpCo(CO)_2(PF_3)^{\bullet-}$ (98%) with only 2% of the product ion of ligand substitution at m/z 240.

$$\underset{m/z\ 180}{CpCo(CO)_2^{\bullet-}} + PF_3 \longrightarrow \underset{m/z\ 240}{CpCo(CO)(PF_3)^{\bullet-}} + CO \qquad (7)$$

$$\underset{m/z\ 152}{CpCo(CO)^{\bullet-}} + PF_3 \longrightarrow \underset{m/z\ 212}{CpCo(PF_3)^{\bullet-}} + CO \qquad (8a)$$

$$\Big\downarrow {\scriptstyle PF_3}$$

$$\underset{m/z\ 300}{CpCo(PF_3)_2^{\bullet-}} \qquad (8b)$$

In the present study, only $(OC)_4Fe^{\bullet-}$ reacted with PF_3 (modest rate constant) which formed the product of CO ligand substitution (eq 9). The product ion at m/z 228 then underwent secondary reactions sequentially replacing two more CO ligands by PF_3 (eq 9b and 9c). No evidence for formation of a total adduct was observed even at P_{He} = 1.0 Torr and at high sensitivity. The mechanism of reaction 9 is known. None of the three metal complex negative ions reacted with $P(CH_3)_3$ ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}).

$$\underset{m/z\ 168}{(OC)_4Fe^{\bullet-}} + PF_3 \longrightarrow \underset{m/z\ 228}{(OC)_3Fe(PF_3)^{\bullet-}} + CO \qquad (9a)$$

$$\Big\downarrow {\scriptstyle PF_3}$$

$$\underset{m/z\ 288}{(OC)_2Fe(PF_3)_2^{\bullet-}} + CO \qquad (9b)$$

$$\Big\downarrow {\scriptstyle PF_3}$$

$$\underset{m/z\ 348}{(OC)Fe(PF_3)_3^{\bullet-}} + CO \qquad (9c)$$

Reactions of the Three Metal Complex Negative Ions with NO. The free radical NO can add to 17-electron complexes to yield the 18-electron adducts with the NO ligand serving as a 1-electron donor. Since the NO ligand can also be a 3-electron donor ligand, substitution for a CO ligand would produce a new 18-electron complex with the overall process being exothermic.[4] This appears to be the case in the reactions of NO with the metal complex negative ions $CpCo(CO)_{2,1}^{\bullet-}$,[4,11] $(OC)Fe(NO)_2^{\bullet-}$,[4] $(OC)_2Co(NO)^{\bullet-}$,[4] and $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$,[4] where CO ligand substitution was exclusively observed; the reaction of $(C_3H_5)Co(CO)_3^{\bullet-}$ with NO formed mainly the adduct anion (70%) along with the product ion of CO substitution.[4]

The reactions of $(OC)_4Fe^{\bullet-}$ and $(OC)_5Cr^{\bullet-}$ with NO gave the corresponding product anions of CO ligand substitution (eq 10 and 11). However, the reaction of $(OC)_4MnH^{\bullet-}$ with NO produced the adduct anion at m/z 198 along with the product anion of CO ligand substitution at m/z 170 (eq 12); no P_{He} effect was observed on the branching fractions or the rate constant. None of the product ions in eq 10–12 reacted further with NO ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}) suggesting that each was an 18-electron species.

$$\underset{m/z\ 168}{(OC)_4Fe^{\bullet-}} + NO \rightarrow \underset{m/z\ 170}{(OC)_3Fe(NO)^-} + CO \qquad (10)$$

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + NO \rightarrow \underset{m/z\ 194}{(OC)_4Cr(NO)^-} + CO \qquad (11)$$

$$\underset{m/z\ 168}{(OC)_4MnH^{\bullet-}} + NO \xrightarrow[He]{0.14} \underset{m/z\ 198}{(OC)_4Mn(H)(NO)^-} \qquad (12a)$$

$$\underset{m/z\ 168}{(OC)_4MnH^{\bullet-}} + NO \xrightarrow{0.86} \underset{m/z\ 170}{(OC)_3Mn(H)(NO)^-} + CO \qquad (12b)$$

Observation of the adduct anion at m/z 198 in eq 12a suggests that this reaction, and probably reactions 10 and 11, occurred by the associative mechanism with initial formation of the excited adduct negative ion. The structure of the adduct at m/z 198 could be either $(OC)_4Mn(H)(\eta^1\text{-}NO)^-$ or $(OC)_3Mn(CHO)(\eta^3\text{-}NO)^-$.

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

Table II. Summary of the Kinetic and Product Data for the Ligand Substitution Reactions of $(OC)_5Cr^{\bullet-}$

rxn	neutral ligand substrate		primary product ion(s) + [assumed neutral]	fraction 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	→	no reaction		$<10^{-13}$	
2	$P(CH_3)_3$	→	no reaction		$<10^{-13}$	
3	NO	→	$(OC)_4Cr(NO)^-$ + [CO]	1.00	1.2×10^{-11}	6.1×10^{-10}
4a	SO_2	$\xrightarrow{He}$	$(OC)_5Cr(SO_2)^{\bullet-}$	0.25[c]	7.1×10^{-10}	1.1×10^{-9}
4b		→	$(OC)_4Cr(SO_2)^{\bullet-}$ + [CO]	0.75[c]		
5	$CH_2{=}CHCH_3$	→	no reaction		$<10^{-13}$	
6	$CH_2{=}CHOEt$	→	no reaction		$<10^{-13}$	
7	$CH_2{=}CHCO_2CH_3$	→	no reaction		$<10^{-13}$	
8	$CH_2{=}CHCN$	→	no reaction		$<10^{-13}$	
9	$F_2C{=}CF_2$	→	no reaction		$<10^{-13}$	
10	$CH_2{=}CHBr$	→	no reaction		$<10^{-13}$	
11a	$(NC)_2C{=}C(CN)_2$	→	$C_2(CN)_4^{\bullet-}$ + [$Cr(CO)_5$]	0.65	*e*	
11b		→	$(OC)_4Cr(C_2(CN)_4)^{\bullet-}$ + [CO]	0.25		
11c		→	$(OC)_3Cr(C_2(CN)_4)^{\bullet-}$ + [2CO]	0.10		
12	$(CH_3)_2C{=}O$	→	no reaction		$<10^{-13}$	
13	$CH_3C({=}O)CF_3$	→	no reaction		$<10^{-13}$	
14a	$(CF_3)_2C{=}O$	$\xrightarrow{He}$	$(OC)_5Cr(C_3F_6O)^{\bullet-}$	0.54[d]	1.9×10^{-10}	9.5×10^{-10}
14b		→	$(OC)_4Cr(C_3F_6O)^{\bullet-}$ + [CO]	0.27[d]		
14c		→	$(OC)_3Cr(C_3F_6O)^{\bullet-}$ + [2CO]	0.19[d]		
15a	$(CH_3C({=}O))_2$	$\xrightarrow{He}$	$(OC)_5Cr(C_4H_6O_2)^{\bullet-}$	0.94	2.6×10^{-12}	8.8×10^{-10}
15b		→	$(OC)_4Cr(C_4H_6O_2)^{\bullet-}$ + [CO]	0.06		
16	CO	→	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 42:58. [d] P_{He} = 0.5 Torr; at P_{He} = 1.0 Torr the a:b:c ratio was 69:13:18. [e] Not measured.

Table III. Summary of the Kinetic and Product Data for the Ligand Substitution Reactions of $(OC)_4MnH^{\bullet-}$

rxn	neutral ligand substrate		primary product ion(s) + [assumed neutral]	fraction 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	→	no reaction		$<10^{-13}$	
2	$P(CH_3)_3$	→	no reaction		$<10^{-13}$	
3a	NO	$\xrightarrow{He}$	$(OC)_4(H)Mn(NO)^-$	0.14	2.7×10^{-11}	6.1×10^{-10}
3b		→	$(OC)_3(H)Mn(NO)^-$ + [CO]	0.86		
4	SO_2	→	$(OC)_4(H)Mn(SO_2)^{\bullet-}$	1.00	2.1×10^{-10}[c]	1.1×10^{-9}
5	$CH_2{=}CHCH_3$	→	no reaction		$<10^{-13}$	
6	$CH_2{=}CHOEt$	→	no reaction		$<10^{-13}$	
7	$CH_2{=}CHCO_2CH_3$	→	no reaction		$<10^{-13}$	
8	$CH_2{=}CHCN$	→	no reaction		$<10^{-13}$	
9	$F_2C{=}CF_2$	→	no reaction		$<10^{-13}$	
10	$CH_2{=}CHBr$	→	no reaction		$<10^{-13}$	
11a	$(NC)_2C{=}C(CN)_2$	→	$C_2(CN)_4^{\bullet-}$ + [$(CO)_4MnH$]	0.58	*d*	
11b		→	$(OC)_3(H)Mn(C_2(CN)_4)^{\bullet-}$ + [CO]	0.42		
12	$(CH_3)_2C{=}O$	→	no reaction		$<10^{-13}$	
13	$CH_3C({=}O)CF_3$	→	no reaction		$<10^{-13}$	
14	$(CF_3)_2C{=}O$	→	$(OC)_3(H)Mn(C_3F_6O)^{\bullet-}$ + [CO]	1.00	3.0×10^{-10}	9.8×10^{-10}
15	$(CH_3C({=}O))_2$	→	no reaction		$<10^{-13}$	
16	CO	→	no reaction		$<10^{-13}$	
17a	O_2	→	HCO_2^- + [$(OC)_3MnO$]	0.29	2.9×10^{-11}	5.6×10^{-10}
17b		→	$(OC)_3MnO^-$ + [$H^\bullet$ + CO_2]	0.14		
17c		→	$(OC)_2(H)MnO^{\bullet-}$ + [CO + CO_2]	0.09		
17d		→	$(OC)(H)MnO^{\bullet-}$ + [2CO + CO_2]	0.27		
17e		→	$(OC)(H)Mn(O)_2^{\bullet-}$ + [3CO]	0.12		
17f		→	$(OC)_2MnO^-$ + [HCO + CO]	0.09		

[a,b] See Table I. [c] Apparent bimolecular rate constant. [d] Not measured.

Reactions of the Three Metal Complex Negative Ions with SO_2. SO_2 has become a useful neutral ligand substrate in a number of studies with its large rate constants and general effect of ligand substitution.[4,12] The fast bimolecular reaction of $(OC)_4Fe^{\bullet-}$ with SO_2 produced the product ion of CO ligand substitution at *m/z* 204 (eq 13). We were surprised to find that the faster reaction

$$\underset{m/z\ 168}{(OC)_4Fe^{\bullet-}} + SO_2 \rightarrow \underset{m/z\ 204}{(OC)_3Fe(SO_2)^{\bullet-}} + CO \qquad (13)$$

of $(OC_5)Cr^{\bullet-}$ with SO_2 at P_{He} = 0.5 Torr yielded both the adduct at *m/z* 256 and the ion product of ligand substitution at *m/z* 228 (eq 14) with the branching fractions

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + SO_2 \xrightarrow[He]{0.25} \underset{m/z\ 256}{(OC)_5Cr(SO_2)^{\bullet-}} \qquad (14a)$$

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + SO_2 \xrightarrow{0.75} \underset{m/z\ 228}{(OC)_4Cr(SO_2)^{\bullet-}} + CO \qquad (14b)$$

shown. The formation of both product ions in reaction 14 was shown to occur via the excited adduct $[(OC)_5Cr(SO_2)^{\bullet-}]^*$ by competitive collisional stabilization with the buffer gas and fragmentation; at P_{He} = 1.0 Torr, the 14a/14b ratio increased to 42/58 with no change in the rate constant. A further shock occurred when we observed only formation of the total adduct in the reaction $(OC)_4MnH^{\bullet-}$ with SO_2 (eq 15). Thus, we have in these three examples coverage of the extremes from only ligand substitution to

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(12) (a) McDonald, R. N.; Schell, P. L.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 5578. (b) McDonald, R. N.; Chowdhury, A. K.; Jones, M. T. *Ibid.* **1986**, *108*, 3105. (c) McDonald, R. N.; Jones, M. T. *Ibid.* **1986**, *108*, 8097. (d) Wang, D. N.; Squires, R. R. *Organometallics* **1987**, *6*, 905.

exclusive adduct formation.

$$\underset{m/z\ 168}{(OC)_4MnH^-} + SO_2 \xrightarrow{He} \underset{m/z\ 232}{(OC)_4Mn(H)(SO_2)^-} \quad (15)$$

The results shown in eq 14 and the P_{He} dependency of the branching fraction clearly requires the associative mechanism in this reaction. We suggest that the adduct structure is that of the Lewis acid–base association complex with SO_2 serving as a 0-electron donor, thus maintaining the 17-electron configuration on Cr.[13] Since the ion product of CO ligand substitution at *m/z* 228 failed to react further with SO_2, its structure is most likely that of the 17-electron complex with SO_2 behaving as a stabilizing 2-electron donor ligand. The total adduct in reaction 15 may have the corresponding Lewis acid–base structure or the isomeric formyl structure $(OC)_3(SO_2)Mn(CHO)^{\bullet-}$ with SO_2 as a 2-electron donor ligand. We are unable to distinguish between these two isomeric structures for the adduct at *m/z* 232.

It seems reasonable to conclude that all three metal complex negative ions react with SO_2 by the associative mechanism.

Reactions of the Three Metal Complex Negative Ions with Olefins. In our previous report of ligand substitution reactions with 17-electron metal complex negative ions containing NO, η^3-C_3H_5, and η^3-Cp ligands,[4] while no reaction was observed with electron-rich olefins ($CH_3CH{=}CH_2$, $C_2H_5OCH{=}CH_2$), ligand substitution was frequently observed with olefins containing electron-attracting groups ($CH_2{=}CHCO_2CH_3$, $CH_2{=}CHCN$, and C_2F_4). With $(NC)_2C{=}C(CN)_2$ (TCNE), the general reaction was electron transfer with a single example of CO ligand substitution as an additional product forming channel.

No reaction was observed between the present three metal complex negative ions and the above olefins and $CH_2{=}CHBr$ ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}) with the exception of TCNE. In each reaction with TCNE, electron transfer yielding $C_2(CN)_4^{\bullet-}$ was competitive with ligand substitution (eq 16–18). Due to the low vapor pressure of TCNE, a reservoir containing solid TCNE was attached to a "high boiling" neutral inlet located just downstream of NLS inlet and TCNE vapors were directly inletted to the flow tube. With use of this method, the branching fractions could be measured, but kinetics were impossible.

$$\underset{m/z\ 168}{(OC)_4Fe^{\bullet-}} + TCNE \xrightarrow{0.50} \underset{m/z\ 128}{C_2(CN)_4^{\bullet-}} + Fe(CO)_4 \quad (16a)$$

$$\underset{m/z\ 168}{(OC)_4Fe^{\bullet-}} + TCNE \xrightarrow{0.50} \underset{m/z\ 268}{(OC)_3Fe(C_2(CN)_4)^{\bullet-}} + CO \quad (16b)$$

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + TCNE \xrightarrow{0.65} \underset{m/z\ 128}{C_2(CN)_4^{\bullet-}} + Cr(CO)_5 \quad (17a)$$

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + TCNE \xrightarrow{0.25} \underset{m/z\ 292}{(OC)_4Cr(C_2(CN)_4)^{\bullet-}} + CO \quad (17b)$$

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + TCNE \xrightarrow{0.10} \underset{m/z\ 264}{(OC)_3Cr(C_2(CN)_4)^{\bullet-}} + 2CO \quad (17c)$$

$$\underset{m/z\ 168}{(OC)_4MnH^{\bullet-}} + TCNE \xrightarrow{0.58} \underset{m/z\ 128}{C_2(CN)_4^{\bullet-}} + (OC)_4MnH \quad (18a)$$

$$\underset{m/z\ 168}{(OC)_4MnH^{\bullet-}} + TCNE \xrightarrow{0.42} \underset{m/z\ 268}{(OC)_3(H)Mn(C_2(CN)_4)^{\bullet-}} + CO \quad (18b)$$

The electron-transfer channels 16a, 17a, and 18a were expected because of the large electron affinity of TCNE (EA = 3.17 ± 0.2 eV).[14] Only in the case of $(OC)_4Fe^{\bullet-}$ has the EA of the corresponding neutral complex been measured, EA($Fe(CO)_4$) = 2.4 ± 0.3 eV.[15] From an unrelated study of the kinetics and mechanism of the halogen atom transfer reactions between alkyl halides and these three (and other) metal complex negative ions,[16,17] we estimate the order of EAs of the corresponding 16-electron complexes to be EA($Fe(CO)_4$) > EA($Cr(CO)_5$) ≈ EA($HMn(CO)_4$). Therefore, electron transfer between these three metal complex negative ions and TCNE will be exothermic by >0.8 eV.

How then are the products of ligand substitution formed in product channels 16b, 17b, 17c, and 18b? The simplest explanation would be to consider electron transfer to occur within the excited, attractive orbiting collision complex $[(OC)_{n-1}M^{\bullet-}/TCNE]^*$ yielding the complex $[(OC)_{n-1}M/TCNE^{\bullet-}]^*$. Separation of the latter complex would yield the observed $C_2(CN)_4^{\bullet-}$. However, the neutral coordinatively and electronically unsaturated $(OC)_{n-1}M$ species in this complex may add the $C_2(CN)_4^{\bullet-}$ as a ligand giving the excited adducts $[(OC)_{n-1}M(C_2(CN)_4)^{\bullet-}]^*$ which then fragment to yield the products of ligand substitution.

Reactions of the Three Metal Complex Negative Ions with Carbonyl Containing Reagents. The neutral carbonyl containing reagents selected for this study were $(CH_3)_2C{=}O$, $CH_3C({=}O)CF_3$, $(CF_3)_2C{=}O$, the α-diketone $(CH_3C({=}O){-})_2$, and CO. No reaction was observed for the three metal complex negative ions and the first two ketones or CO. However, all three metal complex negative ions reacted rapidly with $(CF_3)_2C{=}O$ to give the products of CO ligand substitution (eq 19–21). The adduct was also

$$\underset{m/z\ 168}{(OC)_4Fe^{\bullet-}} + (CF_3)_2C{=}O \longrightarrow \underset{m/z\ 306}{(OC)_3Fe(C_3F_6O)^{\bullet-}} + CO \quad (19)$$

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + (CF_3)_2C{=}O \underset{He}{\xrightarrow{0.54}} \underset{m/z\ 358}{(OC)_5Cr(C_3F_6O)^{\bullet-}} \quad (20a)$$

$$\xrightarrow{0.27} \underset{m/z\ 330}{(OC)_4Cr(C_3F_6O)^{\bullet-}} + CO \quad (20b)$$

$$\xrightarrow{0.19} \underset{m/z\ 302}{(OC)_3Cr(C_3F_6O)^{\bullet-}} + 2CO \quad (20c)$$

$$m/z\ 302 + (CF_3)_2C{=}O \longrightarrow \underset{m/z\ 440}{(OC)_2Cr(C_3F_6O)_2^{\bullet-}} + CO \quad (20d)$$

$$\underset{m/z\ 168}{(OC)_4MnH^{\bullet-}} + (CF_3)_2C{=}O \longrightarrow \underset{m/z\ 306}{(OC)_3(H)Mn(C_3F_6O)^{\bullet-}} + CO \quad (21a)$$

$$\Big\downarrow (CF_3)_2C{=}O$$

$$\underset{m/z\ 416}{(OC)(H)Mn(C_3F_6O)_2^{\bullet-}} + 2CO$$

$$+$$

$$\underset{m/z\ 388}{(H)Mn(C_3F_6O)_2^{\bullet-}} + 3CO \quad (21b)$$

$$m/z\ 388 + (CF_3)_2C{=}O \longrightarrow \underset{m/z\ 554}{(H)Mn(C_3F_6O)_3^{\bullet-}} \quad (21c)$$

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[13] Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

[14] Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 5453.

[15] Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569.

[16] Schell, P. L. Ph.D. Thesis, Kansas State University, 1986.

[17] Jones, M. T. Ph.D. Thesis, Kansas State University, 1987.

observed as a product in the reaction of $(OC)_5Cr^{\bullet-}$ with this ketone. The branching fractions for the primary reaction products given in eq 20a–c measured at P_{He} = 0.5 Torr changed to 69:13:18 when P_{He} was increased to 1.0 Torr. This result means that all three primary product ions arise from a common excited adduct, $[(OC)_5Cr(C_3F_6O)^{\bullet-}]^*$, by competitive collisional stabilization (eq 20a) and fragmentation (eq 20b and 20c). The branching fractions in eq 20a–c were measured at low concentrations of added ketone where the signal for the secondary product ion at *m*/*z* 440 was not detected.

Only $(OC)_5Cr^{\bullet-}$ reacted with $(CH_3C({=}O)-)_2$ in a slow reaction to produce mainly the total adduct at *m*/*z* 278 and a small amount of the product ion of ligand substitution at *m*/*z* 250 (eq 22).

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + (CH_3C({=}O)-)_2 \xrightarrow[\text{He}]{0.94} \underset{m/z\ 278}{(OC)_5Cr(C_4H_6O_2)^{\bullet-}} \tag{22a}$$

$$\underset{m/z\ 192}{(OC)_5Cr^{\bullet-}} + (CH_3C({=}O)-)_2 \xrightarrow{0.06} \underset{m/z\ 250}{(OC)_4Cr(C_4H_6O_2)^{\bullet-}} + CO \tag{22b}$$

The most intriguing feature of the above reactions is the observation of the adduct ion structures in the reactions of $(OC)_5Cr^{\bullet-}$ with the two ketones $(CF_3)_2C{=}O$ (eq 20a) and biacetyl (eq 22). When we examine the properties of the four ketones used in this study, we note that $(CF_3)_2C{=}O$ (EA $\geq$ 1.46 eV)[18] and biacetyl (EA = 0.69 eV)[21] have sizeable positive EAs while the EAs of $(CH_3)_2C{=}O$[22] and $CH_3C({=}O)CF_3$[23] are negative or, perhaps, a small positive value for the latter ketone. This leads us to suggest that reactions 20 and 22 occur by electron transfer (possibly endothermic) within the orbiting collision complex, e.g., $[(OC)_5Cr^{\bullet-}/(CF_3)_2C{=}O \rightleftharpoons (OC)_5Cr/(CF_3)_2CO^{\bullet-}]$. If endothermic, the electron transfer can take advantage of the 10–20 kcal mol^{-1} of attractive energy in forming the ion–neutral collision complex. The collision complex resulting from electron transfer contains the 16-electron $(OC)_5Cr$ neutral and the ketyl anion radical derived from the ketone. If we assume that the ketyl anion radical is reasonably represented by the valence bond structure $R_2\dot{C}{-}O^-$, bonding of the ketyl anion radical to $(OC)_5Cr$ via the oxyanion would give the structure $(OC)_5Cr^-{-}O\dot{C}R_2$ as the initially formed adduct which has an 18-electron configuration on Cr.[25] Depending on the exothermicity of this overall process, we may then observe fragmentation of a CO ligand to give the product ion of substitution, e.g., $(OC)_4Cr(\eta^2\text{-ketone})^{\bullet-}$, with the ketone bonded as a η^2 ligand in the 17-electron complex anion radical.

This electron transfer mechanism is also consistent with the data for the reactions of $(OC)_4Fe^-$ with $(CF_3)_2C{=}O$ (eq 19) and biacetyl (no reaction). Electron transfer within the collision complex $[(OC)_4Fe^{\bullet-}/(CF_3)_2CO]$ giving $[(OC)_4Fe/(CF_3)_2CO^{\bullet-}]$ would be <21.6 ± 7.5 kcal mol^{-1} endothermic and possible, while electron transfer in $[(OC)_4Fe^{\bullet-}$/biacetyl]forming $[(OC)_4Fe$/biacetyl$^{\bullet-}]$ would be endothermic by 38.7 ± 7 kcal mol^{-1} and would not occur. The fact that $(OC)_5Cr^{\bullet-}$ reacted considerably slower with biacetyl (lower EA) than with $(CF_3)_2C{=}O$ while $(OC)_4Fe^{\bullet-}$ did not react with biacetyl agrees with the estimated order of the EAs of $(OC)_5Cr$ and $(OC)_4Fe$ given in the previous section. That $(OC)_4MnH^{\bullet-}$ failed to react with biacetyl implies that $EA((OC)_4MnH) > EA((OC)_5Cr)$ based on this mechanism.

It is interesting that the product ions of ligand substitution, $(OC)_3Fe(C_3F_6O)^{\bullet-}$, $(OC)_4Cr(C_3F_6O)^{\bullet-}$, and $(OC)_3(H)Mn(C_3F_6O^{\bullet-})$, behave so differently. While the Fe and Cr ions were unreactive toward additional ketone, the latter Mn ion readily reacted with $(CF_3)_2C{=}O$ to eventually produce $(H)Mn(C_3F_6O)_3^{\bullet-}$ (*m*/*z* 554). Outside of the obvious difference in the central metal and their coordination number in these three product ions, we consider the presence of the hydride ligand in the Mn anion to be the reason for the reactivity difference in these ions. Although the presence of the formyl isomer can always be invoked to open a coordination site with a hydrido–carbonyl complex, the above initial electron-transfer mechanism offers a potentially more desirable rationalization.

If we assume that electron transfer occurs in the collision complex of $[(OC)_4MnH^{\bullet-}/(CF_3)_2CO]$ giving $[(OC)_4MnH/(CF_3)_2CO^{\bullet-}]$, the adduct formed by bonding the oxyanion of the ketyl anion radical to Mn would initially be $(OC)_4(H)Mn^-{-}O\dot{C}(CF_3)_2$. We believe that 1,3-migration of the H atom from Mn to the carbon free radical center would be exothermic yielding the Mn–alkoxide complex $(OC)_4Mn(OCH(CF_3)_2)^{\bullet-}$ with a 17-electron configuration on Mn.[27] This complex is formally the adduct of the alkoxide $(CF_3)_2CHO^-$ with the 15-electron species $(OC)_4Mn^{\bullet}$. As such the overall reaction to this point would be expected to be reasonably exothermic. Loss of a CO ligand would generate the observed ion product of ligand substitution at *m*/*z* 306 (eq 21a) which would be represented by structure **1**. Contribution of structure **1b** will be reduced by the presence of the CF_3 groups compared to the multiple Mn=OR bonds suggested in

$$\underset{\substack{\text{15-electron}\\ \mathbf{1a}}}{(OC)_3Mn\text{-}OCH(CF_3)_2^{\bullet-}} \leftrightarrow \underset{\substack{\text{17-electron}\\ \mathbf{1b}}}{(OC)_3Mn{=}OCH(CF_3)_2^{\bullet-}}$$

$(OC)_2(H)Mn(OH)^-$[12] and $(OC_2(H)Mn(OCH_3)^-$.[28] Structure 1 might then be expected to undergo association of an additional molecule of $(CF_3)_2C{=}O$ to give the product ions of eq 21b. It is possible in these latter product ions that the H atom migrates back to Mn forming the metal hydride species. We believe that the $(CF_3)_2C{=}O$ molecule is most reasonably bound to the metal in the Fe (eq 19) and Cr substitution products (eq 20b and 20c) as an η^2 ligand.[4,29]

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(18) $EA((CF_3)_2C{=}O) \geq EA(PhN)$ = 1.46 ± 0.02 eV.[19,20]

(19) McDonald and Chowdhury (McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 198) observed electron transfer in the ion–molecule reaction of $PhN^{\bullet-}$ with $(CF_3)_2C{=}O$ forming $(CF_3)_2CO^{\bullet-}$.

(20) Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443.

(21) $EA((CH_3C({=}O-)_2)$ = 0.69 eV; Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627.

(22) $EA((CH_3)_2C{=}O)$ = −1.51 eV; Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

(23) While $(CF_3)_2C{=}O$ and biacetyl readily attach thermal energy electrons in the FA to yield the corresponding parent anion radicals, $CH_3C({=}O)CF_3$ does not. Electron transfer was not observed in the reaction of $CH_3C({=}O)CF_3$ with allyl anion ($EA(C_3H_5)$ = 0.362 ± 0.020 eV);[24] Chowdhury, A. K., unpublished results. Thus, $EA(CH_3C({=}O)CF_3)$ < 0.36 eV.

(24) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734.

(25) The suggested structures for the adducts generated in the reactions of $(OC)_5Cr^-$ with $(CF_3)_2C{=}O$ and biacetyl are analogous to those of several stable 19-electron complexes which have been isolated.[26] In those cases, the unpaired electron has been shown to be in a predominately ligand-based orbital.

(26) (a) Fenske, D. *Chem. Ber.* **1979**, *112*, 363. (b) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 2101. (c) Kaim, W. *Inorg. Chem.* **1984**, *23*, 504.

(27) We consider this 1,3-H-atom transfer to be an intramolecular analogue of the intermolecular H-atom transfer between $HCo(CN)_5^{3-}$ and olefins in the $Co(CN)_5^{3-}$ catalyzed hydrogenation of olefins; see: Masters, C. *Homogeneous Transition-metal Catalysis*; Chapman and Hall: New York; 1981; Section 2.1.1(b).

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

Reactions of the Three Metal Complex Negative Ions with O_2. Lane, Sallans, and Squires[31] reported that the reactions of $(OC)_4Fe^{\bullet-}$ and $(OC)_5Cr^{\bullet-}$ with O_2 yield various oxidation products formed by displacement of one or more CO ligands and/or loss of CO_2. We have described several examples of organo-transition-metal complex negative ions where an NO ligand can be displaced by O_2.[4]

The reaction of $(OC)_4MnH^{\bullet-}$ with O_2 (eq 23) was interesting from two respects. First, six primary product ions were observed to be formed in this reaction, three of which underwent further reactions with O_2 to yield secondary ion products. Second, one of the major primary product forming channels was the formation of HCO_2^- (eq 23d).[32] The primary ion products in eq 23a–c reacted further with O_2 forming MnO_{2-4}^- as the dominate terminal ions.

$$\underset{m/z\ 168}{\mathrm{(OC)_4MnH^{\bullet-}}} + \mathrm{O_2} \xrightarrow{0.27} \underset{m/z\ 100}{\mathrm{(OC)Mn(H)(O)^{\bullet-}}} + \mathrm{2CO} + \mathrm{CO_2} \qquad (23a)$$

$$\underset{m/z\ 168}{\mathrm{(OC)_4MnH^{\bullet-}}} + \mathrm{O_2} \xrightarrow{0.12} \underset{m/z\ 116}{\mathrm{(OC)Mn(H)(O_2)^{\bullet-}}} + \mathrm{3CO} \qquad (23b)$$

$$\underset{m/z\ 168}{\mathrm{(OC)_4MnH^{\bullet-}}} + \mathrm{O_2} \xrightarrow{0.09} \underset{m/z\ 128}{\mathrm{(OC)_2Mn(H)(O)^{-}}} + \mathrm{CO} + \mathrm{CO_2} \qquad (23c)$$

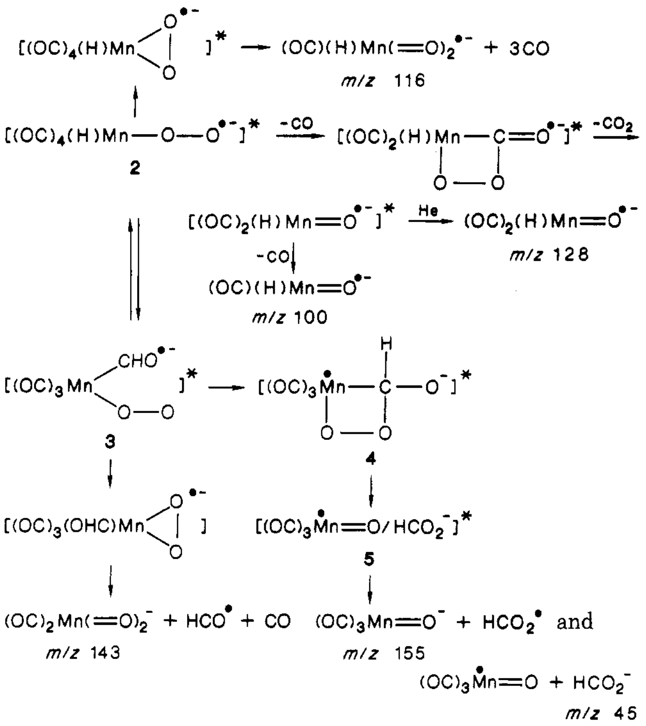
$$\underset{m/z\ 168}{\mathrm{(OC)_4MnH^{\bullet-}}} + \mathrm{O_2} \xrightarrow{0.29} \underset{m/z\ 45}{\mathrm{HCO_2^-}} + \mathrm{(OC)_3MnO} \qquad (23d)$$

$$\underset{m/z\ 168}{\mathrm{(OC)_4MnH^{\bullet-}}} + \mathrm{O_2} \xrightarrow{0.14} \underset{m/z\ 155}{\mathrm{(OC)_3MnO^-}} + \mathrm{H^\bullet} + \mathrm{CO_2} \qquad (23e)$$

$$\underset{m/z\ 168}{\mathrm{(OC)_4MnH^{\bullet-}}} + \mathrm{O_2} \xrightarrow{0.09} \underset{m/z\ 143}{\mathrm{(OC)_2Mn(O_2)^-}} + \mathrm{H^\bullet} + \mathrm{2CO} \qquad (23f)$$

We rationalize the formation of the product ions from eq 23a–f via Scheme I starting with generation of the excited η^1-superoxide structure **2**.[4] Peroxide structures are considered to be the precursors to the dioxides m/z 116 and 143 while perlactone intermediates offer a convenient way to effect the loss of CO_2.[4,32] Formation of **4** by addition of the terminal oxygen of the formyl superoxide structure **3** to the formyl carbonyl group appears necessary to produce HCO_2^- as a major product ion in this reaction. *The formation of HCO_2^- in the reaction is the first substantial evidence available for the migratory insertion of a carbonyl ligand into the Mn–H bond in gas-phase experiments.*[33] The involvement of the common excited complex **5** to yield both HCO_2^- and $(OC)_3Mn{=}O^{\bullet-}$ (m/z 155) is an assumption based on the similarity of the products except for the location of the electron. On the basis of this premise, $EA((OC)_3Mn{=}O) \approx EA(HCO_2) = 3.53$ eV.[34]

Scheme I



Summary of the Results

Of the three 17-electron metal complex negative ions used in this study, $(OC)_4Fe^{\bullet-}$, $(OC)_5Cr^{\bullet-}$, and $(OC)_4MnH^{\bullet-}$, only $(OC)_4Fe^{\bullet-}$ was observed to react with PF_3 (modest rate constant) yielding sequentially the product ions of ligand substitution, $(OC)_{4-x}Fe(PF_3)_x^{\bullet-}$ where $x = 1$–3. The mechanism of this reaction was not defined. None of the three metal complex negative ions were observed to react with $P(CH_3)_3$ ($k_{\mathrm{total}} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}).

All three metal complex negative ions reacted with NO with similar modest rate constants to yield the products of ligand substitution; the reaction of $(OC)_4MnH^{\bullet-}$ with NO also produced a minor amount of the addition adduct anion. We believe that each of these reactions occur by the associative mechanism forming the corresponding excited 18-electron nitrosyl adducts.

The three fast reactions of the metal complex negative ions with SO_2 were characterized as proceeding via the Lewis acid–base association adducts maintaining a 17-electron configuration on the metal. While the reaction with $(OC)_4Fe^{\bullet-}$ gave only the CO ligand substitution product ion, adduct formation was minor or exclusive in the reactions of SO_2 with $(OC)_5Cr^{\bullet-}$ and $(OC)_4MnH^{\bullet-}$, respectively.

Of the seven olefin substrates examined with these three metal complex negative ions, only $(NC)_2C{=}C(CN)_2$ (TCNE) was found to react. In each case, the product ions of electron transfer and of ligand substitution were observed. We considered it most likely that both types of product ions were formed from the same collision complex $[(OC)_xM/TCNE^{\bullet-}]^*$. Separation of the collision complex would give $TCNE^{\bullet-}$ while association of $TCNE^{\bullet-}$ with the 16-electron neutral metal complex $(OC)_xM$ within this

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[29] The η^2 binding of ketones in transition-metal complexes is common.[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.

[30] Reference 3, Chapter 3.

[31] Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719.

[32] See ref 5 for some additional examples of reactions of $(OC)_xM^-$ with O_2. It was reported that $CH_3CO_2^-$ was a minor product ion from the reaction of $(OC)_4MnCH_3^{\bullet-}$ with O_2; Wang, D.; Lane, K. R.; Squires, R. R., unpublished results.

[33] Migratory insertion of a CO ligand into the Mn–CH_3 bond by a mechanism analog to that given in Scheme I is probably how $CH_3CO_2^-$ is generated in the reaction of $(OC)_4MnCH_3^{\bullet-}$ with O_2.[32]

[34] Yamdagni an Kebarle (Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 4050) estimated this value for $EA(HCO_2)$ along with $EA(CH_3CO_2) = 3.39$ eV. The difference in these carboxyl radicals EAs would explain why the $(HCO_2^-)/((OC)_3MnO^-)$ ratio is >1 in the present case while the analogous ratio $(CH_3CO_2^-/((OC)_3MnO^-)$ was <1 in the reaction of $(OC)_4MnCH_3^{\bullet-}$ with O_2.[32]

collision complex would produce the excited adduct which could decarbonylate.

None of the three metal complex negative ions reacted with $(CH_3)_2C{=}O$ or $CH_3C({=}O)CF_3$ ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}). All three metal complex negative ions reacted rapidly with $(CF_3)_2C{=}O$ and gave the corresponding ligand substitution products; a major amount of the adduct was formed in the reaction of $(OC)_5Cr^{\bullet -}$. Only $(OC)_5Cr^{\bullet -}$ reacted with biacetyl forming mainly the adduct anion. The successful reactions were considered to occur by electron transfer within the ion–neutral orbiting collision complex. The initially formed adducts produced with $(CF_3)_2C{=}O$ were believed to have the structures $[(OC)_xM^{-}{-}O\dot{C}(CF_3)_2]^*$ with an 18-electron metal configuration. This adduct structure for the Mn-containing species $[(OC)_4(H)Mn(O\dot{C}(CF_3)_2)^{-}]^*$ offers a pathway to open a metal coordination site by 1,3-migration of the H atom from Mn to the carbon free radical forming $[(OC)_4Mn(OCH(CF_3)_2)^{\bullet -}]^*$. Decarbonylation of this latter ion to $(OC)_3Mn(OCH(CF_3)_2)^{\bullet -}$ was used to explain why this ligand substitution product ion underwent secondary ion–molecule reactions with $(CF_3)_2C{=}O$ while the primary product ions derived from $(OC)_4Fe^{\bullet -}$ and $(OC)_5Cr^{\bullet -}$ were unreactive.

The reaction of $(OC)_4MnH^{\bullet -}$ with O_2 formed three product ions containing Mn and the hydride ($(OC)(H)Mn({=}O)_2^{\bullet -}$ (27%), $(OC)_2(H)Mn{=}O^{\bullet -}$ (9%), and $(OC)(H)Mn{=}O^{\bullet -}$ (27%)), two ions containing Mn *without* the hydride ($(OC)_2Mn({=}O)_2^{-}$ (9%) and $(OC)_3Mn{=}O^{-}$ (14%)), and one anion containing the hydride but *not* the metal HCO_2^{-} (29%). We believe that formation of these latter three product negative ions requires formation of an intermediate Mn-formyl complex early in the reaction mechanism. *This is the first evidence for the migratory insertion reaction, $OC{-}Mn{-}H \rightleftharpoons Mn{-}CHO$, occurring in gas-phase chemistry of transition-metal complex negative ions.* The absence of reaction between $(OC)_4MnH^{\bullet -}$ and PF_3 strongly suggests that this starting ion exists exclusively as the hydride structure. The above data for the reaction of this ion with O_2 support our belief that the formyl isomeric structure should only be considered when excited adducts have been generated, e.g. in ion–molecule reactions. The presence of the nonbonded electron pair on O_α of the superoxide ligand may facilitate this migratory insertion reaction by allowing the thermodynamics to be more favorable.[35]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and Professors E. A. Maatta and R. R. Squires for helpful discussions.

Registry No. $(OC)_4Fe^{\bullet -}$, 51222-96-9; $(OC)_5Cr^{\bullet -}$, 39586-86-2; $(OC)_4MnH^{\bullet -}$, 115162-34-0; PF_3, 7783-55-3; $P(CH_3)_3$, 594-09-2; NO, 10102-43-9; SO_2, 7446-09-5; $CH_2{=}CH_3$, 115-07-1; $CH_2{=}CHOEt$, 109-92-2; $CH_2{=}CHCO_2CH_3$, 96-33-3; $CH_2{=}CHCN$, 107-13-1; $F_2C{=}CF_2$, 116-14-3; $CH_2{=}CHBr$, 593-60-2; $(NC)_2C{=}C(CN)_2$, 670-54-2; $(CH_3)_2C{=}O$, 67-64-1; $CH_3C({=}O)CF_3$, 421-50-1; $CH_3)_2C{=}O$, 684-16-2; $(CH_3C({=}O))_2$, 431-03-8; CO, 630-08-0; O_2, 7782-44-7.

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[35] Reference 3, Chapter 6.