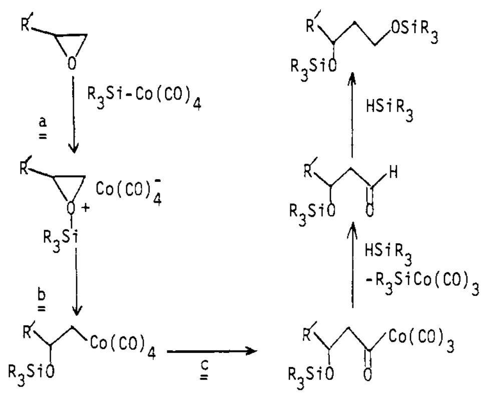
Scheme I



regioisomeric product was detected.

It is apparent from eq 1 that one molecule of carbon monoxide and two molecules of the hydrosilane have been incorporated into the product molecule. The catalytic transformation may be explained by the processess outlined in Scheme I,[8] in which silylcobalt carbonyl ($R_3SiCo(CO)_4$)[6] is suggested as the key catalyst species.[9] Synthetically, the $Co(CO)_4^-$ group participating in step b of Scheme I could be regarded as a masked form of a nucleophilic oxymethylating agent since it is transformed into the siloxymethyl group in the final product.

The results obtained for various oxiranes are summarized in Table I. Highly regioselective siloxymethylation has been observed for many oxiranes having a primary carbon center (runs 1-8).[10] In runs 3, 5, 6, 8, and 10, $HSiMe_3$ was used instead of $HSiEt_2Me$, since the latter reacted only sluggishly in these cases. Probably steric congestion[11] at the silicon atom in $HSiEt_2Me$ would have retarded step a in Scheme I. Importantly the functional groups such as ester and halogen contained in the oxiranes have not been affected under the present reaction conditions. The known oxymethylating agents[5] are generally of organolithium or organomagnesium type and may not tolerate these functional groups.

The result obtained for cyclopentene oxide (run 9) indicates the stereochemical course of the ring opening to be trans. This is also the case with cyclohexene oxide (65% yield of the corresponding disilyl ether).[12] The trans opening has been further demonstrated in the acyclic system, namely, the stereospecific synthesis of *threo-* and *erythro*-2-methylbutane-1,3-diol derivatives (runs 11 and 12). These results imply that the carbon–oxygen bond cleavage with concomitant formation of the carbon–cobalt bond (step b in Scheme I) would proceed with inversion of configuration at the carbon atom.[13]

Further study on the scope of this unique carbon chain extention reaction using carbon monoxide of normal pressure is now in progress.

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Supplementary Material Available: Spectral and analytical data for all compounds prepared (11 pages). Ordering information is given on any current masthead page.

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(7) All new compounds were adequately characterized. See supplementary material.

(8) An alternative mechanism involving an cobalt carbenoid intermediate instead of the aldehyde intermediate may exist.[1b,c,e]

(9) For related processes observed by Gladysz in the stoichiometric reaction of $(CH_3)_3SiMn(CO)_5$: (a) Brinkman, K. C.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1260. (b) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

(10) Unsubstituted oxirane, i.e., ethylene oxide, gave disilylated propane-1,3-diol quantitatively. Ethyl oxirane gave a mixture of branched and straight chain isomers (ca. 1:2) in quantitative combined yield.

(11) Cartledge, F. K. *Organometallics* **1983**, *2*, 425.

(12) Examples of the trans opening of oxiranes with metal carbonyl species: (a) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 1460. (b) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23. See also ref 1e and 9.

(13) The subsequent alkyl migration (step c in Scheme I) is known to proceed with retention. Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

Generation and Reactions of $(OC)_3Fe^{-\cdot}$ in a Flowing Afterglow Apparatus

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The involvement of coordinatively unsaturated transition-metal complexes in condensed-phase reactions is generally implied from the nature of reaction products rather than by direct observation of the metal-containing reactive intermediate. Gas-phase studies of such unsaturated complexes can yield valuable information on these processes if the intermediate can be generated in an appropriate oxidation state for monitoring by the technique employed. While formation of $(OC)_{x-n}M^{-\cdot}$ species ($n = 1-x$) by electron impact (EI) on $M(CO)_x$ has been reported using low-pressure mass spectrometers[1] and $n = 1-3$ in ion cyclotron resonance spectrometers,[2] only the $(OC)_{x-1}M^{-\cdot}$ anion radicals have been reported produced by EI in flowing afterglow (FA) systems operating at higher pressures.[3] We recently observed that a mixture of $(OC)_{x-2}M^{-\cdot}$ and $(OC)_{x-1}M^{-\cdot}$ species are obtained in the FA from mononuclear transition-metal carbonyls (M = Fe, Cr, Mo, W) by significantly increasing the emission current of the electron gun located in the ion-preparation region of the flow tube. In this communication, we describe this procedure using $Fe(CO)_5$ and preliminary results of ion–molecule reactions of $(OC)_3Fe^{-\cdot}$ with small neutral molecules.[4] Although the structures (other than composition) of the ion products of these adduct-forming reactions are not established at this time, we wish to draw attention to the reactivity of this type of species.

In the usual operation of the FA,[3,5] the ion of interest is formed in the upstream end of the flow tube in a fast flow of helium buffer gas ($P_{He} = 0.5$ torr, $\bar{v} = 80$ m s^{-1}, 298 K) with the electron gun operated at ≤ 50-μA emission current. Under these conditions, the thermal or near-thermalized electrons effect dissociative electron attachment with $Fe(CO)_5$ giving $(OC)_4Fe^{-\cdot}$ (*m/z* 168) exclusively. Increasing the current applied to the filament of the electron gun[5a] until the emission current was ~5 mA produced large signals for $(OC)_3Fe^{-\cdot}$ (*m/z* 140) and $(OC)_4Fe^{-\cdot}$. Only limited quantities of $Fe(CO)_5$ could be added since $(OC)_3Fe^{-\cdot}$ reacted rapidly with excess $Fe(CO)_5$ giving $Fe_2(CO)_6^{-\cdot}$.[4] This means that some free electrons are present downstream in the flow.

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(1) For reports of transition metal carbonyl negative fragment ions produced in mass spectrometers, see: (a) Winters, R. E.; Kiser, R. W. *J. Chem. Phys.* **1966**, *44*, 1964-1966. (b) Pignatoro, S.; Foffani, A.; Grasso, F.; Cantone, B. *Z. Phys. Chem. (Wiesbaden)* **1965**, *47*, 106-113. (c) Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass. Spectrom. Ion Phys.* **1976**, *22*, 47-55.

(2) (a) Dunbar, R. C.; Ennever, J. F.; Fackler, J. P. *Inorg. Chem.* **1973**, *12*, 2734-2736. (b) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808-4814. (c) Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *Ibid.* **1974**, *96*, 3671-3673. (d) Rynard, C. M.; Brauman, J. I. *Inorg. Chem.* **1980**, *19*, 3544-3545. (e) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67-71.

(3) (a) McDonald, R. N.; Schell, P. L.; McGhee, W. D. *Organometallics* **1984**, *3*, 182-184. (b) McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *Ibid.* **1984**, *3*, 644-645. (c) Lane, K.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719-2721.

(4) $(OC)_3Fe^{-\cdot}$ has been previously reported to react with $Fe(CO)_5$.[2a-c,e]

(5) (a) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491-6498. (b) McDonald, R. N.; Chowdhury, A. K. *Ibid.* **1983**, *105*, 2194-2203.

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Table I. Kinetic Data for the Ion–Molecule Reactions of $(OC)_3Fe^{-\cdot}$ with Neutral Molecules

neutral	k_{total},[a] cm^3 $molecule^- s^{-1}$	k_{ADO},[c] cm^3 $molecule^{-1} s^{-1}$
H_2	5.9×10^{-12} [b]	1.5×10^{-9}
CO	1.4×10^{-10} [b]	6.8×10^{-10}
N_2	7.0×10^{-12} [b]	6.4×10^{-10}
$H_2C{=}CHCH_3$	3.2×10^{-10} [b]	1.0×10^{-9}
$H_2C{=}C{=}CH_2$	4.1×10^{-10}	9.9×10^{-10}
$HC{\equiv}CH$	2.0×10^{-10}	9.1×10^{-10}
CH_3Br	6.3×10^{-10}	1.2×10^{-9}

[a] k_{total}'s determined at $P_{He} = 0.5$ torr and 298 K are estimated to be accurate at ±25%. [b] The apparent bimolecular rate constant is given for this termolecular adduct forming reaction. [c] Calculated collision-limited bimolecular rate constants using the average orientation theory (ADO): Su, T.; Bowers, M. T. *J. Chem. Phys.* **1973**, *58*, 3027–3037; *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347–356.

In separate experiments, the electrons produced at the high emission current (a) produced $SF_5^{-\cdot}$ from SF_6 $[D°(F_5S^{-\cdot} - F) = 1.1\ eV]$[6] but gave only $SF_6^{-\cdot}$ when 10^{13} molecules cm^{-3} of CH_4 was mixed with the helium buffer gas ($P_{He} = 0.5$ torr, 10^{16} atoms cm^{-3}), and (b) $(OC)_3Fe^{-\cdot}$ was *not* formed using the mixed He/CH_4 buffer gas (above) when $Fe(CO)_5$ was added via an inlet port 10-cm downstream from the electron gun.[7] These results suggest that formation of $(OC)_3Fe^{-\cdot}$ occurs by dissociative attachment of higher energy electrons with $Fe(CO)_5$ under the conditions of larger emission currents.[1,2] In the present experiments, CH_4 was added to the helium flow via a port 20-cm downstream from the $Fe(CO)_5$ inlet and 30-cm upstream of the neutral reactant inlet port.[7] We believe that this effects thermalization of residual electrons and provides for ample collisions of excited $(OC)_3Fe^{-\cdot}$ with the bath gas to cool the anion radical to its vibrational ground state prior to reaching the neutral inlet port and the desired ion–molecule reaction commences.

Using the above conditions, several reactions of $(OC)_3Fe^{-\cdot}$ with neutral molecules have been examined (eq 1–7) with the kinetic

$$\underset{m/z\ 140}{(OC)_3Fe^{-\cdot}} + H_2 \xrightarrow{He} \underset{m/z\ 142}{(OC)_3FeH_2^{-\cdot}} \qquad (1)$$

$$(OC)_3Fe^{-\cdot} + CO \xrightarrow{He} \underset{m/z\ 168}{(OC)_4Fe^{-\cdot}} \qquad (2)$$

$$(OC)_3Fe^{-\cdot} + N_2 \xrightarrow{He} \underset{m/z\ 168}{(OC)_3Fe(N_2)^{-\cdot}} \qquad (3)$$

$$(OC)_3Fe^{-\cdot} + H_2C{=}CHCH_3 \xrightarrow{He} \underset{m/z\ 182}{(OC)_3Fe(C_3H_6)^{-\cdot}} \qquad (4)$$

$$\begin{aligned} &(OC)_3Fe^{-\cdot} + H_2C{=}C{=}CH_2 \rightarrow \underset{m/z\ 180}{(OC)_3Fe(C_3H_4)^{-\cdot}} + \\ &\underset{m/z\ 152}{(OC)_2Fe(C_3H_4)^{-\cdot}} + CO \xrightarrow[C_3H_4]{He} \underset{m/z\ 192}{(OC)_2Fe(C_3H_4)_2^{-\cdot}} \end{aligned} \qquad (5)$$

$$(OC)_3Fe^{-\cdot} + HC{\equiv}CH \rightarrow \underset{m/z\ 138}{(OC)_2Fe(C_2H_2)^{-\cdot}} + CO \qquad (6)$$

$$\begin{aligned} &(OC)_3Fe^{-\cdot} + CH_3Br \rightarrow \\ &\quad \underset{m/z\ 219,\ 221}{(OC)_3FeBr^-} + \cdot CH_3 + \underset{m/z\ 178,\ 180}{(OC)Fe(Br)CH_3^{-\cdot}} + 2CO \end{aligned} \qquad (7)$$

data listed in Table I. *$(OC)_4Fe^{-\cdot}$ does not react with these neutrals*, i.e., $k \leq 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The slow reaction of H_2 with $(OC)_3Fe^{-\cdot}$ producing the adduct $(OC)_3FeH_2^{-\cdot}$ (*m/z* 142) (eq 1) appears to be that of oxidative addition.[3b] When CO (eq 2) or N_2 (eq 3) was allowed to react with $(OC)_3Fe^{-\cdot}$, the signal for *m/z* 140 decreased concomitant with an increase in the *m/z* 168 signal (due to $(OC)_4Fe^{-\cdot}$ formed originally) of the adducts $(OC)_4Fe^{-\cdot}$ and $(OC)_3Fe(N_2)^{-\cdot}$, respectively. Each of these reactions forming total adduct products require termolecular collisional stabilization with the He/CH_4 buffer gas.

As frequently observed in the condensed phase with coordinatively unsaturated metal complexes, the reactions of $(OC)_3Fe^{-\cdot}$ with the π-systems of $H_2C{=}CHCH_3$, $H_2C{=}C{=}CH_2$, and $HC{\equiv}CH$ exhibit different results.[8] With propene (eq 4), only the total adduct *m/z* 182 was formed. With allene (eq 5), two primary product ions *m/z* 180 (adduct; 42%) and 152 (adduct – CO; 58%) were formed followed by addition of a second allene molecule to *m/z* 152 yielding *m/z* 192. The reaction of $(OC)_3Fe^{-\cdot}$ with acetylene (eq 6) gave only the (adduct – CO), *m/z* 138. The structures of these adducts formed in these three fast reactions could be π-complexes or the products of CH insertion. It is our present opinion that π-complex formation better explains the results with allene (eq 5) where collisional stabilization (→ *m/z* 180) competes with decarbonylation (→ *m/z* 152) from the primary excited adduct ($(OC)_3Fe(C_3H_4)^{-\cdot *}$). π-Complexation with an additional allene molecule would then occur at a vacant coordination site of of $(OC)_2Fe(C_3H_4)^{-\cdot}$ (*m/z* 152) giving *m/z* 192. Exclusive formation of the adduct – CO, *m/z* 138, in the reaction of $(OC)_3Fe^{-\cdot}$ with acetylene by stronger π-bonding with the acetylene ligand allowed for more ready decarbonylation of that excited adduct. The fact that a second acetylene is not added to this complex (as with allene) suggests that the acetylene ligand in *m/z* 138 functions as a four-electron donor occupying two coordination sites on the metal. The development of suitable radical and ligand exchange reactions which should characterize these adducts as π-complexes or CH-insertion products is under way.

The fast reaction of $(OC)_3Fe^{-\cdot}$ with CH_3Br (eq 7) was interesting since $(OC)_4Fe^{-\cdot}$ failed to react with CH_3Br and CH_3I.[3a] Product ions from both Br atom transfer (50%) and total oxidative addition with loss of two CO ligands (50%) were observed. Formation of these products is analogous to observation of $(OC)_4FeX^-$ and $(OC)_2Fe(X)CF_3^{-\cdot}$ as the products from the reactions of $(OC)_4Fe^{-\cdot}$ with F_3CX molecules (X = Br, I).[3a] This suggests that a similar mechanism may be involved where the initially formed ion/radical collision complex **1** produced by Br atom transfer can separate (→*m/z* 219, 221) competitive with addition of the methyl radical followed by loss of two CO ligands (→*m/z* 178, 180) (eq 8). Since iron in $(OC)_3Fe^{-\cdot}$ formally has

$$\begin{aligned} &\underset{m/z\ 219,\ 221}{(OC)_3FeBr^-} + \cdot CH_3 + \leftarrow \underset{\mathbf{1}}{[(OC)_3FeBr^-/\cdot CH_3]} \rightarrow \\ &\qquad\qquad\qquad\qquad \underset{m/z\ 178,\ 180}{(OC)Fe(Br)CH_3^-} + 2CO \end{aligned} \qquad (8)$$

available two coordination sites, a concerted oxidative addition with CH_3Br cannot be ruled out as competitive with Br atom transfer. Irrespective of the mechanism of its formation, the fact that the vibrationally excited, oxidative-addition intermediate fragments two CO ligands strongly suggests that CH_3 and Br are separate metal ligands in the complex.

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Registry No. $(OC)_3Fe^-$, 53221-56-0; $(OC)_4Fe^-$, 51222-96-9; H_2, 1333-74-0; N_2, 7727-37-9; $H_2C{=}C{=}CH_2$, 463-49-0; $HC{\equiv}CH$, 74-86-2; $H_2C{=}CHCH_3$, 115-07-1; CO, 630-08-0; CH_3Br, 74-83-9; $Fe(CO)_5$, 13463-40-6.

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(6) (a) Streit, G. E. *J. Chem. Phys.* **1982**, *77*, 826–833. (b) Lifshits, C.; Tiernam, T. O.; Hughes, B. M. *Ibid.* **1973**, *59*, 3182–3192. (c) Compton, R. N.; Cooper, C. D. *Ibid.* **1973**, *59*, 4140–4144. (d) Leffert, C. B.; Tang, S. Y.; Rothe, E. W.; Cheng, T. C. *Ibid.* **1974**, *61*, 4929–4930. (e) Hubers, M. M.; Los, J. *Chem. Phys.* **1975**, *10*, 235–259. (f) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 2023–2036.

(7) Methane does not react with $(OC)_3Fe^{-\cdot}$. However, methane does appear to serve as an efficient electron and ion thermalizing agent and as a quenching reagent for metastable He (2^3S) atoms which are also produced at the electron gun.

(8) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.