−150 ± 1 °C using graphite-monochromated Mo Kα radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). The $\omega/2\theta$ scan mode was employed with an ω scan rate of 32° min^{-1}. Weak reflections ($F < 10\sigma(F)$) were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time vs background time was 2:1. Of the 4677 independent reflections measured, 3343 had $I > 3\sigma(I)$ and were regarded as being observed. That the crystal was not subject to decay during the measurement of intensities was checked by monitoring three reflections at regular intervals (150 reflections). Intensity data were corrected for Lorentz and polarization effects but not for absorption. Unit cell parameters were obtained from diffractometer setting angles for 25 reflections in the range 47° < 2θ < 49°. The structure was solved by direct methods (MITHRIL)[30] and subsequent electron density calculations. Full-matrix least-squares refinement of positional anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms, located from a difference map, gave a final $R = 0.035$ and $R_w = 0.041$ for 426 parameters and 3343 reflections. Atomic scattering factors and anomalous dispersion corrections were taken from ref 31, and the F_o values were weighted according to $w = [\sigma^2(F_o)]^{-1}$. A final difference map showed a maximum and minimum residual electron densities of 1.25 and −0.82 e·Å^{-3}, respectively. All calculations were carried out with the TEXSAN program system.[32] Crystal data and experimental details of the structure determination are compiled in Table V.

Acknowledgment. Financial support from Shell Research B.V. is gratefully acknowledged.

Registry No. 1, 98720-36-6; 2, 106333-13-5; 4, 137232-35-0; 5, 137232-36-1; 6, 137232-37-2; 7, 137232-38-3; 8, 137232-39-4; [Cp*$_2$LaH]$_2$, 98720-39-9; (Me$_3$Si)$_2$CH$_2$, 2117-28-4; di-*tert*-butyl ketone, 815-24-7; acetone, 67-64-1; 4-hydroxy-4-methyl-2-pentanone, 123-42-2; 3-pentanone, 96-22-0; 4-methyl-5-hydroxy-5-ethyl-3-heptanone, 3677-86-9.

Supplementary Material Available: For 5, tables of bond distances and angles, torsion angles, and thermal parameters (17 pages); a full listing of F_o, F_c, and $\sigma(F)$ values (31 pages). Ordering information is given on any current masthead page.

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[30] Gilmore, C. J. *J. Appl. Crystallogr.* 1984, *17*, 42.

[31] *International Tables for X-ray Crystallography*; Vol. IV; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[32] *TEXSAN Structure Solution Package*; Molecular Structure Corp.: The Woodlands, TX 77381, 1989.

Reactions of (OC)$_{3,2}$Fe$^{\bullet-}$ and (OC)$_{4,3}$Mn$^-$ with Trimethylsilane, Silane, and Germane

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(OC)$_3$Fe$^{\bullet-}$ and (OC)$_4$Mn$^-$ reacted with Me$_3$SiH, SiH$_4$, and GeH$_4$ to yield the corresponding adducts. The smaller rate constants for the (OC)$_4$Mn$^-$ reactions are attributed to different spin multiplicities of the starting and product ions. (OC)$_2$Fe$^{\bullet-}$ and (OC)$_3$Mn$^-$ reacted rapidly with Me$_3$SiH to give the products of dehydrogenation, (OC)$_x$M(η^2-CH$_2$=Si(CH$_3$)$_2$)$^-$, which added additional Me$_3$SiH to form the corresponding adducts; the latter reaction also formed the adduct negative ions as primary products. (OC)$_2$Fe$^{\bullet-}$ (mainly) and (OC)$_3$Mn$^-$ (exclusively) reacted rapidly with silane to yield the product ions of α-dehydrogenation, (OC)$_x$M(H)(≡SiH)$^-$. The reaction of (OC)$_3$Mn(D)$_2^-$ with silane formed mainly the (adduct − H$_2$ − D$_2$)$^-$, (adduct − HD)$^-$, and (adduct − D$_2$)$^-$ products. With germane as the neutral reactant, (OC)$_2$Fe$^{\bullet-}$ and (OC)$_3$Mn$^-$ reacted rapidly to give the germylide complexes (OC)$_x$M(=Ge)$^-$ as the major or exclusive product, respectively. The germylide complex negative ions reacted with excess germane to produce the corresponding adducts. Lower limits for the binding energies of the CH$_2$–Si(CH$_3$)$_2$ and Ge atom ligands to the metal centers of these negative ions are given.

The success in the oxidative insertion of the 13-electron transition-metal complex negative ion (OC)$_2$Fe$^{\bullet-}$ into the C–H bonds of methane and 2,2-dimethylpropane yielding the corresponding hydrido–alkyl complexes[1] stimulated our interest in the corresponding reactions with the other available group 14 hydrides silane and germane. Additions of Si–H[2] and Ge–H bonds[3] to multiple bonds in unsaturated hydrocarbons, aldehydes, and ketones are catalyzed by transition-metal complexes. Although hydrosilation and hydrogermylation reactions are often complex and the mechanisms are not well understood, oxidative insertion of the coordinatively unsaturated metal center into the Si–H or Ge–H bond is assumed to be required in the process.[4]

Kang, et al.[5] reported the gas-phase reactions of Ni$^+$, Co$^+$, Fe$^+$, Cr$^+$, V$^+$, and Ti$^+$ atomic cations with silane and various methylated silanes. With SiH$_4$, Ni$^+$, Co$^+$, and Ti$^+$ reacted to produce the corresponding (adduct − H$_2$)$^+$ ions assumed to have the M=SiH$_2^+$ structures.[6] The reactions with the methylsilanes, (CH$_3$)$_x$SiH$_{4-x}$ where x = 1–4, gen-

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[1] McDonald, R. N.; Jones, M. T.; Chowdhury, A. K. *J. Am. Chem. Soc.* 1991, *113*, 113.

[2] General references for hydrosilylation reactions: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, Ca. 1987. (b) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1986. (c) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (d) Khan, M. M. T.; Martell, A. E. *Homogeneous Catalysis by Metal Complexes*; Academic Press: New York, 1974; Vol. 2, p 66.

[3] (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 56. (b) Green, M.; Howard, J. A. N.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipsi, C. A. *J. Chem. Soc., Chem. Commun.* 1976, 671.

[4] Direct spectroscopic evidence for oxidative insertion of coordinatively unsaturated metal centers into Si–H bonds are reported: (a) Fernandez, M.-J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* 1984, *106*, 5458. (b) Fernandez, M.-J.; Maitlis, P. M. *Organometallics* 1983, *2*, 164.

[5] Kang, H.; Jacobson, D. B.; Shin, S. K.; Beauchamp, J. L.; Bowers, M. T. *J. Am. Chem. Soc.* 1986, *108*, 5668.

[6] We use the formalism M=SiH$_2$ and M=Ge (Si and Ge as 2-electron donors), and M≡SiH and M≡GeH (Si and Ge as 3-electron donors) to be consistent with the valence of the Si and Ge atoms rather than designating the number of σ-bonds in the structure. In each case, π-back-bonding from the metal to Si or Ge is involved as one of the multiple bonds.

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erated the corresponding products of α- and β-dehydrogenation, hydride abstraction, and methane loss depending on the structure of the silane.

The chemistry of the fragment metal carbonyl negative-ion complexes appears to be very similar to that of the isoelectronic neutral metal complexes. Thus, the results obtained with the negative-ion complexes likely apply to those expected of the neutral fragment metal carbonyls. Two factors that are important in the present studies are the significant differences in the bond energies in the group 14 series methane, silane,[7] and germane and the increased potential for M–Si and M–Ge back-bonding from the metal in the product negative ions.[5] The results of the reactions of the negative-ion complexes $(OC)_{4,3}Mn^-$ and $(OC)_{3,2}Fe^{\bullet -}$ with trimethylsilane, silane, and germane are the subject of this paper.

Experimental Section

Our gas-phase studies are carried out in a previously described flowing afterglow apparatus at 298 K.[8] The conditions have been described to separately generate $(OC)_4Fe^{\bullet -}$ and $(OC)_5Mn^-$, and mixtures of $(OC)_{4,3}Fe^{\bullet -}$ or $(OC)_{4,3,2}Fe^{\bullet -}$, and $(OC)_{5,4}Mn^-$ or $(OC)_{5,4,3}Mn^-$ by dissociative attachment of electrons of different energies with $Fe(CO)_5$ and $Mn_2(CO)_{10}$, respectively, in a fast flow of helium buffer gas ($P_{He} \approx 0.9$ Torr, $\bar{v} \approx 57$ m s^{-1}, 298 K).[1] Variations in P_{He} in these experiments are very limited in order to retain the ion signals of $(OC)_2Fe^{\bullet -}$ and $(OC)_3Mn^-$. These fragment ions are cooled to their electronic and vibrational ground states by multiple collisions with the helium buffer gas in their flight down the first 75 cm of the flow tube. The gaseous neutrals are added via a radial inlet and the ion/molecule reactions occur in the final 65 cm of the flow tube. The flow is maintained by a large, fast-pumping system. The flow is sampled via 1-mm orifices in two nose cones into a differentially pumped chamber ($P \approx 10^{-7}$ Torr) containing a quadrupole mass filter and electron multiplier, which continuously monitor the ion composition of the flow. The neutral products of these reactions are not directly observed but are assumed on the basis of thermochemistry and mass balance. Endothermic reactions are not observed in these gas-phase reactions, and the magnitudes of the rate constants are generally related to the reaction exothermicities.

The kinetics of these bimolecular reactions are determined under pseudo-first-order conditions where the concentration of the neutral reactant, [N], is always in large excess compared to the ion concentration. The slopes of the plots of log [starting ion signal] vs increasing [N] added to the flow yield the bimolecular rate constants by equations already given.[8b]

Results and Discussion

The 18-electron $(OC)_5Mn^-$ and 17-electron $(OC)_4Fe^{\bullet -}$ complexes failed to react with the neutrals used in this study ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}). However, the remaining fragment metal carbonyl negative ions did react with these neutrals. This is illustrated in Figure 1 for the reaction of $(OC)_3Mn^-$ with germane. From the slope of the linear decay of the $(OC)_3Mn^-$ ion signal, the rate constant for the primary step is obtained. The reproducibility of rate constants in the FA is ±10% of the average values given, and the errors in branching fractions are ±3% absolute. The data in Figure 1 can be computer modeled to derive the rate constant for the secondary reactions of the primary product ions with the neutral reactant.

Several of these reactions produce adduct ions. In these reactions, stabilization of the adduct ions by collisions with the helium buffer gas is needed to remove excess energy or the adduct will dissociate. The apparent bimolecular rate constants, k_{app}, are reported for these formally ter-

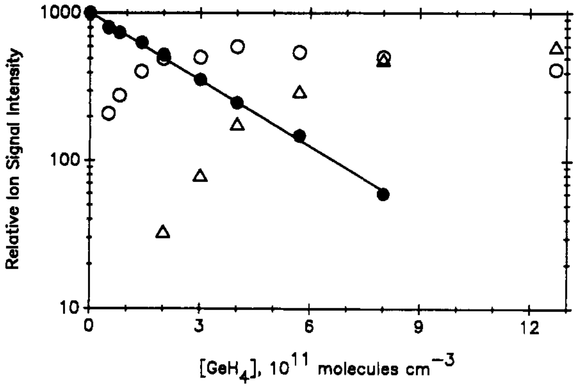

Figure 1. Semi-logarithm plot of the starting and product ion signal intensities vs the concentration of added neutral in the reaction of $(OC)_3Mn^-$ with GeH_4; $(OC)_3Mn^-$ (●), the primary product $(OC)_3Mn({=}Ge)^-$ (○), and the secondary product $(OC)_3Mn(Ge_2H_4)^-$ (△).

molecular reactions due to the inability to significantly vary P_{He}. All of the product ions exhibited their expected isotopic "fingerprints" for the number of silicon and germanium atoms present.

Reactions with Trimethylsilane. The reactions of the fragment metal carbonyl negative ions with trimethylsilane were investigated with the hope that they would be fast addition reactions to coordinatively unsaturated metal complex anions without effecting ligand substitution. This result would be useful in our structural characterization of metal complex negative ions that is based on the ion/molecule chemistry of these ions. Further, trimethylsilane could be useful in establishing the presence of a M–H bond in a coordinatively unsaturated complex negative ion according to eq 1.

$$L_xMH^- + (CH_3)_3SiH \rightarrow [L_xM(H)_2(Si(CH_3)_3)^-]^* \xrightarrow{-H_2} [L_xM(Si(CH_3)_3)^-]^* \rightarrow L_xM(H)(\eta^2\text{-}CH_2{=}Si(CH_3)_2)^- \quad (1)$$

Both $(OC)_3Fe^{\bullet -}$ and $(OC)_4Mn^-$ reacted with trimethylsilane to yield the corresponding adducts (eqs 2 and 3). The rate constant for reaction 2 is 38 times larger than that for reaction 3.

$$\underset{m/z\ 140}{(OC)_3Fe^{\bullet -}} + (CH_3)_3SiH \xrightarrow{He} \underset{m/z\ 214}{(OC)_3Fe(H)(Si(CH_3)_3)^{\bullet -}} \quad (2)$$

$$\underset{m/z\ 167}{(OC)_4Mn^-} + (CH_3)_3SiH \xrightarrow{He} \underset{m/z\ 241}{(OC)_4Mn(H)(Si(CH_3)_3)^-} \quad (3)$$

The fast bimolecular reaction of $(OC)_2Fe^{\bullet -}$ with trimethylsilane produced exclusively the primary product ions of dehydrogenation (eq 4). In the corresponding reaction of $(OC)_3Mn^-$, the major primary product was the adduct at m/z 213 along with a smaller amount of the (adduct − H_2)$^-$ ions at m/z 211 (eq 5). The observation

$$\underset{m/z\ 112}{(OC)_2Fe^{\bullet -}} + (CH_3)_3SiH \rightarrow \underset{m/z\ 184}{(OC)_2Fe(\eta^2\text{-}CH_2{=}Si(CH_3)_2)^{\bullet -}} + H_2 \quad (4)$$

$$\underset{m/z\ 139}{(OC)_3Mn^-} + (CH_3)_3SiH \xrightarrow[0.70]{He} \underset{m/z\ 213}{(OC)_3Mn(H)_2(\eta^2\text{-}CH_2{=}Si(CH_3)_2)^-} \quad (5a)$$

$$\xrightarrow[0.30]{} \underset{m/z\ 211}{(OC)_3Mn(\eta^2\text{-}CH_2{=}Si(CH_3)_2)^-} + H_2 \quad (5b)$$

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[7] Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

[8] (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.

that the adduct ions at *m/z* 213 in reaction 5 did not react further with trimethylsilane ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}) suggests that the structure of the adduct is the 18-electron dihydrido(η^2-2-methyl-2-silapropene) complex **1** rather than the 16-electron insertion product **2**. Anion **1** is the direct precursor of the 1,2-dehydrogenation product ions at *m/z* 211 in eq 5b.

$$\underset{\mathbf{1}}{(OC)_3Mn(H)_2(\eta^2\text{-}CH_2{=}Si(CH_3)_2)^-}$$

$$\underset{\mathbf{2}}{(OC)_3Mn(H)(Si(CH_3)_3)^-}$$

Both of the (adduct − H_2)$^-$ ion products in eqs 4 and 5b reacted rapidly ($k_{app} \approx 10^{-10}$ cm^3 molecule^{-1} s^{-1}) with excess trimethylsilane to yield the corresponding adducts (eq 6). Observation of these secondary reactions of the primary ion products *m/z* 184 and 211 establishes these ions as unsaturated 15- and 16-electron species, respectively.

$$m/z\ 184 \text{ or } 211 + (CH_3)_3SiH \xrightarrow{He} \underset{m/z\ 258 \text{ or } 285}{(CO)_xM(H)(\eta^2\text{-}CH_2{=}Si(CH_3)_2)(Si(CH_3)_3)^-} \quad (6)$$

Reactions 4 and 5 are related to the reactions of $(OC)_2Fe^{\bullet-}$ and $(OC)_3Mn^-$ with 2-methylpropane (eq 7). The overall dehydrogenation reactions were shown to involve initial oxidative insertion into the primary and tertiary (major) C–H bonds of the alkane leading ultimately to the 17- (M = Fe, x = 2) and 18-electron (M = Mn, x = 3) product ions **3**.[1] The major differences in the reactions with the alkane and the silane are (i) the faster rates with the silane, (ii) the observation of the adduct in reaction 5, and (iii) the failure of the metal center to intramolecularly insert into the allylic C–H bonds of the 2-methyl-2-silapropene ligand. Assuming a collision frequency for reactions 4 and 5 of 2×10^{-9} cm^3 molecule^{-1} s^{-1}, the reaction efficiencies ($k_{tot.}/k_{col}$) are 0.2 for these two reactions compared to 0.03 for the reactions with 2-methylpropane.[1] The larger reaction efficiencies (factor of 9) for the reactions of these two metal carbonyl anions with trimethylsilane are consistent with dominant or exclusive oxidative insertion of the metal center into the Si–H bond. On the basis of the reaction efficiencies per bond type of $(OC)_3Mn^-$ with hydrocarbons, we estimate the reactivity of the Si–H bond in trimethylsilane toward oxidative insertion to be ≈*200* times that of a primary C–H bond and ≈*20* times more reactive than a tertiary C–H bond. The reactivities of the C–H bonds are derived from the reactions of $(OC)_3Mn^-$ with ethane and 2-methylpropane.[1]

$$(OC)_xM^- + (CH_3)_3CH \xrightarrow{-H_2} [(OC)_xM(\eta^2\text{-}CH_2{=}C(CH_3)_2^-)] \rightarrow \underset{\mathbf{3}}{(OC)_xM(H)(\eta^3\text{-2-methylallyl})^-} \quad (7)$$

The absence of intramolecular insertion of the Fe and Mn centers into an allylic bond of the 2-methyl-2-silapropene ligand suggests that the rearrangement to the hydrido(η^3-2-methyl-2-silallyl) complex is not energetically favorable. For the dehydrogenation of $(CH_3)_3SiH \rightarrow CH_2{=}Si(CH_3)_2 + H_2$, $\Delta H° = 46$ kcal mol^{-1},[5] which requires a metal—(η^2-$CH_2{=}Si(CH_3)_2$) binding energy >46 kcal mol^{-1} in the product ions of the exothermic reactions 4 and 5. This heat of reaction is ≈10 kcal mol^{-1} larger than the corresponding dehydrogenation of 2-methylpropane, $(CH_3)_3CH \rightarrow CH_2{=}C(CH_3)_2 + H_2$, where $\Delta H° = 36.6$ kcal mol^{-1}.[9] The greater exothermicity of reaction 4 and 5 compared to the corresponding reactions with 2-methylpropane is evidenced by the larger reaction efficiencies for the reactions with trimethylsilane. This is consistent with stronger metal—ligand bonds with 2-methyl-2-silapropene than with 2-methylpropene by >10 kcal mol^{-1}. The increased bond lengths involved in the coordinated η^2-2-methyl-2-silapropene and/or η^3-2-methyl-2-silallyl ligands may inhibit the allylic hydrogen shift, but such structural features are not known for these complex negative ions. Neither η^2-silaolefin or η^3-2-silallyl ligand containing complexes have been isolated in the condensed phase despite several attempts.[10,11] However, such complexes appear to be intermediates in a number of reactions.[10]

Reactions with Silane. The reactions of $(OC)_3Fe^{\bullet-}$ and $(OC)_4Mn^-$ with silane are similar to those described for the reactions with trimethylsilane with the generation of 17- and 18-electron adduct ions at *m/z* 172 and 199, respectively (eqs 8 and 9). As in the reactions of these two metal carbonyl negative ions with trimethylsilane, the rate constant for reaction 8 is larger than that for reaction 9 by a factor of 35.

$$\underset{m/z\ 140}{(OC)_3Fe^{\bullet-}} + SiH_4 \xrightarrow{He} \underset{m/z\ 172}{(OC)_3Fe(H)(SiH_3)^{\bullet-}} \quad (8)$$

$$\underset{m/z\ 167}{(OC)_4Mn^-} + SiH_4 \xrightarrow{He} \underset{m/z\ 199}{(OC)_4Mn(H)(SiH_3)^-} \quad (9)$$

The results of the reactions of the 13- and 14-electron complexes $(OC)_2Fe^{\bullet-}$ and $(OC)_3Mn^-$, respectively, with silane are given in eqs 10 and 11. The Langevin collision limited rate constant for reactions 10 and 11 is 1.1×10^{-9} cm^3 molecule^{-1} s^{-1}, which yields reaction efficiencies ($k_{tot.}/k_{LAN}$) of 0.42 and 0.47, respectively. The product ions at *m/z* 144 (eq 10a), 142 (eq 10b), and 169 (eq 11) failed to undergo further reactions with SiH_4. The adduct ions at *m/z* 169 (eq 11) also did not react with D_2, H_2S, and $(CH_3)_3SiH$ but did react with SO_2 to produce the ligand substitution product $(OC)_3Mn(SO_2)^-$ with ejection of SiH_2.[12] These results suggest that the structures of these ion products are saturated toward further addition.

$$\underset{m/z\ 112}{(OC)_2Fe^{\bullet-}} + SiH_4 \xrightarrow[He]{0.13} \underset{m/z\ 144}{(OC)_2Fe(H)_2({=}SiH_2)^{\bullet-}} \quad (10a)$$

$$\xrightarrow{0.87} \underset{m/z\ 142}{(OC)_2Fe(H)({\equiv}SiH)^{\bullet-}} + H_2 \quad (10b)$$

$$\underset{m/z\ 139}{(OC)_3Mn^-} + SiH_4 \rightarrow \underset{m/z\ 169}{(OC)_3Mn(H)({\equiv}SiH)^-} + H_2 \quad (11)$$

In reaction 10, collisional stabilization of the adduct by the helium buffer gas is competitive with unimolecular reductive elimination of H_2 leading to the ion product at *m/z* 142. The structure of the adduct product ions at *m/z* 144 in eq 10a is assigned as the 17-electron metal complex $(OC)_2Fe(H)_2({=}SiH_2)^{\bullet-}$, a precursor to the *m/z* 142 product ions. The structures of the (adduct-H_2)$^-$ ions at *m/z* 142 (eq 10b) and 169 (eq 11) are believed to be those of the

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(9) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York; 1970. $\Delta H_f°_{298}((CH_3)_3CH) = 32.4$ kcal mol^{-1} and $\Delta H_f°_{298}(CH_2{=}C(CH_3)_2) = -4.2$ kcal mol^{-1}.

(10) Gusel'Nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(11) Radnia, P.; Mckennis, J. S. *J. Am. Chem. Soc.* **1980**, *102*, 6349.

(12) The Lewis acid SO_2 is an excellent reagent for effecting ligand substitution even in certain 18-electron metal complex negative ions; see: McDonald, R. N.; Schell, P. L. *Organometallics* **1988**, *7*, 1806, 1820. Reference 1 gives the details of the C–H bond activation studies involving $(OC)_2Fe^{\bullet-}$ and $(OC)_3Mn^-$ with alkanes, and the use of SO_2 in certain ligand substitution reactions to define structure.

corresponding hydridosilylyne complexes $(OC)_xM(H)(\equiv SiH)^-$ (**4**) rather than the dihydridosilides $(OC)_xM(H)_2(=Si)$ (**5**).[6] This assignment is based on the comparison of the reaction enthalpies for processes and 12 and 13;

$$SiH_2(^1A_1) \rightarrow SiH(^2\Pi) + H^\bullet \qquad (12)$$

$$SiH_2(^1A_1) \rightarrow Si + 2H^\bullet \qquad (13)$$

$\Delta H°(12) = D°(HSi—H) = 73$ kcal mol^{-1} [13,14] and $\Delta H°(13) = 144.1$ kcal mol^{-1}.[13,15] The H atoms in eqs 12 and 13 will become M—H bonds in products **4** and **5** with $D°(M^- - H) = 30–50$ kcal mol^{-1}.[16] If we reasonably assume the same bond dissociation energy value for the M—H bonds in structures **4** and **5** with the same metal center, formation of the silide complexes **5** requires twice the bond strength for the M═Si bond than for the M≡SiH bond.[6] This is contrary to our expectations.

Obviously, the generation of the product ions in reactions 10 and 11 require α-hydrogen migrations from Si to the metal center in the intermediates. This type of migration is unusual in the gas-phase chemistry of the fragment metal carbonyl negative ions to date. The unique report of α-migration of hydrogen was the reaction of $(OC)_2Fe^{\bullet-}$ with $(CH_3)_2O$, yielding the carbene complex $(OC)_2Fe(=CHOCH_3)^{\bullet-}$ where a β-hydrogen shift was impossible.[17] With neutral reactants such as CH_4 and $(CH_3)_4C$, the reactions with $(OC)_2Fe^{\bullet-}$ produce the hydridoalkyl complexes.[1] This is understandable when we compare the reaction enthalpies for the conversions of $SiH_4 \rightarrow SiH_2(^1A_1) + H_2$, $\Delta H° = 61$ kcal mol^{-1}, and of $CH_4 \rightarrow CH_2(^3B_1) + H_2$, $\Delta H° = 112$ kcal mol^{-1}.[5]

The reaction of $(OC)_3Mn(D)_2^-$ with silane was examined to see if additional information could be gained about the structure of intermediates formed in these Si–H activation processes. The $(OC)_3Mn(D)_2^-$ ions are generated in the reaction of the ion mixture $(OC)_{5-3}Mn^-$ with D_2, along with the 18-electron ions $(OC)_3Mn(D)_4^-$ and $(OC)_4Mn(D)_2^-$ which do not react with silane. The results of the reaction of the m/z 143 ions with silane are given in eq 14. The

$$\underset{m/z\ 143}{(OC)_3Mn(D)_2^-} + SiH_4 \xrightarrow[0.42]{} \underset{m/z\ 172}{(OC)_3Mn(SiH_3D)^-} + HD \qquad (14a)$$

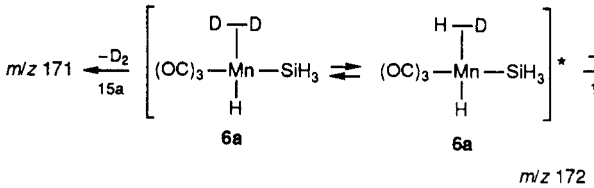
$$\xrightarrow[0.33]{} \underset{m/z\ 169}{(OC)_3Mn(H)(\equiv SiH)^-} + D_2 + H_2 \text{ (or 2HD)} \qquad (14b)$$

$$\xrightarrow[0.21]{} \underset{m/z\ 171}{(OC)_3Mn(SiH_4)^-} + D_2 \qquad (14c)$$

$$\xrightarrow[0.04]{} \underset{m/z\ 173}{(OC)_3Mn(SiH_2D_2)^-} + H_2 \qquad (14d)$$

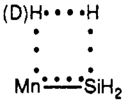
branching fractions were determined following correction of the product ion signal intensities for the isotopes of silicon and carbon.

The product ions at m/z 169 in eq 14b are believed to arise by expulsion of D_2 in the initially formed excited collision complex $[(OC)_3Mn(D)_2^-/SiH_4]^*$, leading to the same product ion formed from $(OC)_3Mn^-$ with SiH_4 in reaction 11. The 2/1 ratio of the product forming channels 14a and 14c is consistent with the statistical loss of HD vs D_2 from six-coordinate intermediates **6a** and **6b** with molecular D_2 or HD bound to the metal (eq 15);[18] the probability of forming **6b** is twice that of **6a**. The fluxional behavior of transition-metal polyhydrides has been observed.[18,19] Structures **6a** and **6b** are preferred to that of a seven-coordinate hydride–dideuteride complex; however, the results will be the same.



(15)

Although product channel 14d is minor, it is interesting to consider how H_2 is eliminated and the original two deuterons are retained in the product ions at m/z 173. One possibility is that this minor amount of elimination occurs via a four-centered transition state, e.g. shown in the partial structure **7**, which is competitive with the reductive elimination of D_2 from **6a** (path 15a). Four-centered mechanisms have been suggested for various dehydrogenations, especially in the reactions of the early-transition-metal atomic cations with methane and the higher alkanes[20] and the methane-exchange reaction of $(\eta^5\text{-}C_5(CH_3)_5)_2LuCH_3$ with $^{13}CH_4$.[21] Since intermediate **6b** contains an Mn–D bond, statistically there will be twice as much loss of HD than H_2 by this competitive pathway assuming **6a** ⇄ **6b** equilibration. Subtracting this component from the branching fraction of product channel 14a maintains the ratio of ≈2 for that portion of channel 14a (0.36 ± 0.03) involved with the loss of HD from intermediate **6b** by path 15b in eq 15.



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The fact that the product ions $(adduct - HD)^-$ in eq 14a, $(adduct - D_2)^-$ in eq 14c, and $(adduct - H_2)^-$ in eq 14d did not react further with silane or the excess D_2 present in the flow suggests that each is structurally the complex $(OC)_3Mn(H)_2(=SiH_2)^{-\,6}$ containing varying D for H substitutions. That such complexes were not observed in the direct reaction of $(OC)_3Mn^-$ with silane means that the ejected HD, D_2, and H_2 molecules in reaction 14 remove sufficient energy from the residual ion/neutral structure to allow for observation of these products.

Reactions with Germane. With germane as the neutral reactant, both $(OC)_3Fe^{\bullet-}$ and $(OC)_4Mn^-$ reacted to yield adduct ion products (eqs 16 and 17) similar to the results

$$\underset{m/z\ 140}{(OC)_3Fe^{\bullet-}} + GeH_4 \xrightarrow{He} \underset{m/z\ 214–220}{(CO)_3Fe(H)(GeH_3)^{\bullet-}} \qquad (16)$$

$$\underset{m/z\ 167}{(OC)_4Mn^-} + GeH_4 \xrightarrow{He} \underset{m/z\ 241–247}{(OC)_4Mn(H)(GeH_3)^-} \qquad (17)$$

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[13] Reference 5, footnote 31, $\Delta H_f°_{298}(SiH_2(^1A_1)) = 69 \pm 3$ kcal mol^{-1}.

[14] JANAF Thermochemical Tables. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, NSRDS-NBS 37. $\Delta H_f°_{298}(SiH(^2\Pi)) = 90 \pm 2$ kcal mol^{-1}.

[15] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2. $\Delta H_f°_{298}(SiH_4) = 10.5$ kcal mol^{-1}, $\Delta H_f°_{298}(Si) = 108.9$ kcal mol^{-1}, $\Delta H_f°_{298}(GeH_4) = 21.7$ kcal mol^{-1}, and $\Delta H_f°_{298}(Ge) = 90.0$ kcal mol^{-1}.

[16] Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4379. This reference gives $D°(M^- - H)$ for FeH^- and CoH^- as 47.3 ± 3 and 42.4 ± 3 kcal mol^{-1}, respectively.

[17] McDonald, R. N.; Reed, D. J.; Chowdhury, A. K. *Organometallics* **1989**, *8*, 1122.

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[21] Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

obtained in the reactions with trimethylsilane and silane. Here, also, the rate constant for adduct formation with $(OC)_3Fe^{\bullet-}$ is greater than that for the reaction with $(OC)_4Mn^-$.

The corresponding reactions of $(OC)_2Fe^{\bullet-}$ and $(OC)_3Mn^-$ with germane are more spectacular with the observed formation of the product ions of bis dehydrogenation. These results are shown in eqs 18 and 19.

$$\underset{m/z\ 112}{(OC)_2Fe^{\bullet-}} + GeH_4 \xrightarrow[0.31]{} \underset{m/z\ 184\text{–}190}{(OC)_2Fe(H)({\equiv}GeH)^{\bullet-}} + H_2 \qquad (18a)$$

$$\xrightarrow[0.69]{} \underset{m/z\ 182\text{–}188}{(OC)_2Fe({=}Ge)^{\bullet-}} + 2H_2 \qquad (18b)$$

$$\underset{m/z\ 139}{(OC)_3Mn^-} + GeH_4 \rightarrow \underset{m/z\ 209\text{–}215}{(OC)_3Mn({=}Ge)^-} + 2H_2 \qquad (19)$$

The Fe-containing (adduct − H_2)$^-$ product ions in eq 18a did not react further with germane, suggesting that their structures are the hydrido–germylyne complex shown, by analogy to our assignment of the (adduct − H_2)$^-$ product formed with silane. The details of the conversion of $(OC)_xM(H)({\equiv}GeH)^-$ to $(OC)_xM({=}Ge)^-$ plus H_2 are not known.[6] However, direct four-centered elimination of H_2 from the hydrido–germylyne complex is probable. We do not know if direct elimination of H_2 from an excited germylene complex ($(L_xM{=}GeH_2^-)^* \rightarrow L_xM{=}Ge^- + H_2$) is possible.

The reaction enthalpy for producing Ge atoms from germane, $GeH_4 \rightarrow Ge + 2H_2$, is 68.3 kcal mol^{-1},[15] which requires that the M═Ge binding energy exceeds this value in the fast exothermic reactions 18b and 19. This value is only 7 kcal mol^{-1} greater than forming silylene (SiH_2($^1A_1$)) from silane. The reaction enthalpy for the corresponding production of Si atoms from silane, $SiH_4 \rightarrow Si + 2H_2$, is 98.4 kcal mol^{-1},[15] which explains why the $(OC)_xM({=}Si)^-$ complexes are not observed in reactions 10 and 11.

The germylide structures of the (adduct − $2H_2$)$^-$ product ions formed in reactions 18b and 19 are consistent with their further reactions with excess GeH_4 in the flow to yield the adducts shown in eq 20. The expected isotopic cluster

$$(OC)_xM({=}Ge{:})^- + GeH_4 \xrightarrow{He} (OC)_xM(Ge_2H_4)^- \qquad (20)$$

$$M = Fe,\ x = 2;\ M = Mn,\ x = 3$$

for the two Ge atoms present in these two adducts was observed. The nature of the bonding between the metal centers and the elements of Ge_2H_4 in these adducts is unknown. The plot of log[ion signal] vs concentration of GeH_4 added is shown in Figure 1. Computer modeling of this data and that of reaction 18 yield $k_{app} = 2.2 \times 10^{-10}$ and 1.8×10^{-10} cm^3 molecule^{-1} s^{-1} for the secondary adduct forming reactions given in eq 20 for M = Mn, $x = 3$, and M = Fe, $x = 2$, respectively. Separately, it was shown that $(OC)_3Mn({=}Ge)^-$ reacted with D_2 to form the corresponding adduct, the structure of which is analogous to the (adduct − H_2)$^-$ product generated in eq 18a.

Formation of the germylide negative-ion complexes, $(OC)_xM({=}Ge)^-$, in reactions 18 and 19 is *unique* with these mononuclear metal complexes. Although a number of complexes containing a substituent-free germanium atom are known, the atom serves as a bridging ligand between two or more metal centers.[3a] In our experiments, the *anion–anion repulsion* and low concentration of starting and product ions would prevent reactive collisions between the anionic metal–germylene and metal–germylide complexes with the coordinatively unsaturated metal complex negative ions present in the flow. The present results indicate that the Ge–H bond energies in the germylene complexes are lower than the Si–H bond energies in the corresponding silylene complexes.

The above results raise the intriguing question of whether mononuclear germylene and/or germylide complexes are intermediates in the formation of μ_x-Ge polynuclear complexes in the condensed phase.

The Question of the Slower Rates of Adduct Formation from $(OC)_4Mn^-$ vs $(OC)_3Fe^{\bullet-}$. The adduct forming reactions of $(OC)_4Mn^-$ with trimethylsilane, silane, and germane consistently occurred with smaller rate constants (factors of 38, 35, and 23, respectively) than the corresponding reaction of $(OC)_3Fe^{\bullet-}$. This observation is *not* due to different efficiencies of the collisional stabilization of the Mn- and Fe-containing product ions with the helium buffer gas in each reaction set because it is opposite to expectations. In each pair of reactions with the same neutral, the helium concentration and the collisional frequencies of the adduct anions with the helium buffer gas are the same. The additional CO ligand in the Mn-derived adducts will increase the density of vibrational states in these adducts compared to those of the Fe-derived adducts. This will increase the lifetime of the Mn-containing adducts, which *increases* the collisional efficiency of the Mn-derived adducts.

We believe that these and certain other kinetic results of adduct-forming reactions of these two negative ions can be best explained in terms of spin conservation discussed by Weitz for the adduct-forming reactions of the neutral fragment metal carbonyls.[22] For example, the reaction of $Fe(CO)_4$ with CO yielding $Fe(CO)_5$ is much slower than the corresponding reaction of $Fe(CO)_3$ forming $Fe(CO)_4$. Since $Fe(CO)_4$ is known to have a triplet electronic ground state[23] and $Fe(CO)_5$ is a singlet, the former reaction is spin-forbidden, while the latter reaction is a spin-allowed triplet → triplet process.

Since $(OC)_4Mn^-$ is isoelectronic with $Fe(CO)_4$, it is reasonable that $(OC)_4Mn^-$ will have a triplet ground electronic state. Since the 18-electron product adduct ions in reactions 3, 9, and 17 will have singlet ground states, these reactions are spin-forbidden. (We note that the rate decreases observed in these adduct-forming ion/molecule reactions of $(OC)_4Mn^-$ compared to $(OC)_3Fe^{\bullet-}$ are smaller than that measured for $(OC)_{4,3}Fe$ adding CO by factors of 6.6–10.) Conversely, $(OC)_3Fe^{\bullet-}$ is isoelectronic with $Co(CO)_3$, a doublet ground state species which reacts rapidly in adduct-forming reactions of the same spin multiplicity.[24] Consistent with this is the observation of the fast addition of CO to $(OC)_3Fe^{\bullet-}$ forming $(OC)_4Fe^{\bullet-}$, where both ions have doublet ground states.[25] These conclusions and the linear decay of the starting ions in the plots of log[ion signal] vs concentration of added neutrals (trimethylsilane, silane, germane) support our contention that we are dealing exclusively with the ground electron states of the metal carbonyl negative ions in these FA experiments.

Conclusions

The reactions of $(OC)_3Fe^{\bullet-}$ and $(OC)_4Mn^-$ with trimethylsilane, silane, and germane yield the corresponding adduct product ions by oxidative insertion into the Si–H or Ge–H bonds. The smaller rate constants for the $(OC)_4Mn^-$ reactions compared to those of $(OC)_3Fe^{\bullet-}$ are ra-

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Table I. Kinetics of the Reactions of $(OC)_{3,2}Fe^{\bullet-}$ and $(OC)_{4,3}Mn^-$ with Trimethylsilane, Silane, and Germane

rx no.	neutral reactant	product ion [+assumed neutral(s)]	branching fraction	$k_{tot.}$,[a] cm^3 molecule^{-1} s^{-1}
		$(OC)_3Fe^{\bullet-}$		
1	$(CH_3)_3SiH$	$(OC)_3Fe(H)(Si(CH_3)_3)^{\bullet-}$	1.00	$(3.4 \pm 0.3) \times 10^{-10}$[b]
2	SiH_4	$(OC)_3Fe(H)(SiH_3)^{\bullet-}$	1.00	$(5.2 \pm 0.2) \times 10^{-10}$[b]
3	GeH_4	$(OC)_3Fe(H)(GeH_3)^{\bullet-}$	1.00	$(5.4 \pm 0.4) \times 10^{-10}$[b]
		$(OC)_4Mn^-$		
4	$(CH_3)_3SiH$	$(OC)_4Mn(H)(Si(CH_3)_3)^-$	1.00	$(8.9 \pm 0.6) \times 10^{-12}$[b]
5	SiH_4	$(OC)_4Mn(H)(SiH_3)^-$	1.00	$(1.5 \pm 0.1) \times 10^{-11}$[b]
6	GeH_4	$(OC)_4Mn(H)(GeH_3)^-$	1.00	$(2.4 \pm 0.3) \times 10^{-11}$[b]
		$(OC)_2Fe^{\bullet-}$		
7	$(CH_3)_3SiH$	$(OC)_2Fe(CH_2{=}Si(CH_3)_2)^{\bullet-}$ [$+H_2$]	1.00	$(4.4 \pm 0.2) \times 10^{-10}$
8a	SiH_4	$(OC)_2Fe(H)_2({=}SiH_2)^{\bullet-}$	0.13	$(4.6 \pm 0.4) \times 10^{-10}$
8b		$(OC)_2Fe(H)({\equiv}SiH)^{\bullet-}$ [$+H_2$]	0.87	
9a	GeH_4	$(OC)_2Fe(H)({\equiv}GeH)^{\bullet-}$ [$+H_2$]	0.31	$(4.8 \pm 0.4) \times 10^{-10}$
9b		$(OC)_2Fe({=}Ge)^{\bullet-}$ [$+2H_2$]	0.69	
		$(OC)_3Mn^-$		
10a	$(CH_3)_3SiH$	$(OC)_3Mn(H)_2(CH_2{=}Si(CH_3)_2)^-$	0.70	$(4.4 \pm 0.4) \times 10^{-10}$
10b		$(OC)_3Mn(CH_2{=}Si(CH_3)_2)^-$ [$+H_2$]	0.30	
11	SiH_4	$(OC)_3Mn(H)({\equiv}SiH)^-$ [$+H_2$]	1.00	$(5.2 \pm 0.4) \times 10^{-10}$
12	GeH_4	$(OC)_3Mn({=}Ge)^-$ [$+2H_2$]	1.00	$(6.0 \pm 0.4) \times 10^{-10}$

[a] These values are averages of at least two separate measurements. The listed errors are the maximum deviations in the measured rate constants from this average value, which is generally <±10%. The errors due to systematic uncertainties in calibrations suggest that their accuracy is ±20% for external comparisons. [b] Apparent bimolecular rate constant for the assumed termolecular adduct-forming reaction.

tionalized on the basis of the isoelectronic relationship between $(OC)_4Mn^-$ and $Fe(CO)_4$, the latter having been established as having a triplet ground electronic state.[23] Thus, the reactions of triplet $(OC)_4Mn^-$ with singlet neutrals giving the singlet ground state 18-electron adducts are spin forbidden. However, $(OC)_{3,4}Fe^{\bullet-}$ are isoelectronic with $Co(CO)_{3,4}$ which are known to be ground-state doublets. Therefore, the adduct-forming reactions of $(OC)_3Fe^{\bullet-}$ proceed rapidly on a potential energy surface of the same spin multiplicity.

The product of the fast reactions of $(OC)_2Fe^{\bullet-}$ and $(OC)_3Mn^-$ with trimethylsilane were the corresponding dehydrogenation complexes $(OC)_xM(\eta^2\text{-}CH_2{=}Si(CH_3)_2)^-$ along with the adduct $(OC)_3Mn(H)_2(\eta^2\text{-}CH_2{=}Si(CH_3)_2)^-$ in the $(OC)_3Mn^-$ reaction. The (adduct − H_2)$^-$ product ions reacted further with trimethylsilane to yield the corresponding adduct negative ions. The difference of >10 kcal mol^{-1} in the relative ligand-binding energies $D°(M^- - (\eta^2\text{-}CH_2Si(CH_3)_2) > D°(M^- - (\eta^2\text{-}CH_2{=}C(CH_3)_2)$ was consistent with these results.

The reactions with silane produced exclusively (with $(OC)_3Mn^-$) or mainly (with $(OC)_2Fe^{\bullet-}$) the products of dehydrogenation, $(OC)_xM(H)({\equiv}SiH)^-$. The structural assignment is based on the failure of these (adduct − H_2)$^-$ product ions to react with excess silane and thermodynamic considerations.

The reaction of $(OC)_3Mn(D)_2^-$ with silane demonstrated that two processes were competitive for dehydrogenation of the intermediate formed by oxidative insertion into an Si-H bond. While the losses of HD and D_2 in a 2/1 ratio from the intermediates **6a** and **6b** were anticipated, the observed minor loss of H_2 suggested that a second mechanism involving a four-centered transition state was competing in this reaction.

The reactions with germane as the neutral reactant were more dramatic in that the product ions of bis dehydrogenation, $(OC)_xM({=}Ge)^-$, were formed exclusively in the reaction with $(OC)_4Mn^-$ and were the major product-forming channel with $(OC)_2Fe^{\bullet-}$. The germylide complex negative ions reacted rapidly with excess germane to yield the corresponding adducts in secondary ion/molecule reactions. These germylide complexes are the first transition-metal complexes to be reported involving a substituent-free germanium atom as a multibonded ligand to a single metal center.

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Registry No. $(OC)_3Fe^{\bullet-}$, 53221-56-0; $(OC)_4Mn^{\bullet-}$, 53290-40-7; $(OC)_2Fe^{\bullet-}$, 71701-39-8; $(OC)_3Mn^{\bullet-}$, 101953-17-7; $HSi(CH_3)_3$, 993-07-7; SiH_4, 7803-62-5; GeH_4, 7782-65-2.