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Synthetic Approaches to Cationic Silylene-, Germylene-, and Stannylene-Transition Metal Complexes *via* Halide Ion Abstraction

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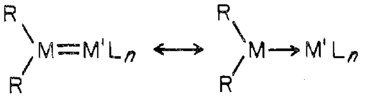
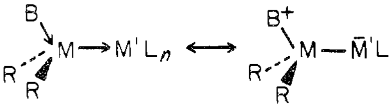
The reactions of chloro-silicon- and chloro-germanium-transition metal complexes with $AgBF_4$, $AgPF_6$, and $AgSbF_6$ produce, in high yield, the corresponding fluoro derivatives and BF_3, PF_3, and SbF_5, respectively. Secondary reactions involving the cleavage of silicon- and germanium-to-carbon bonds by PF_5 and SbF_5 are also observed. With chloro-tin-transition metal compounds, $AgBF_4$ yields covalent complexes in which BF_4^- is coordinated to tin. The reaction of $(C_5H_5)Fe(CO)_2Si(OCH_3)_3$ with HPF_6 also results in fluoro-silicon derivatives. In no case could a cationic silylene, germylene, or stannylene complex be isolated, and the reasons for the preferential fluorination are discussed in comparison with results for analogous carbenoid systems.

The intense interest among chemists in the nature of divalent group IV molecules[1] has included the extensive development of carbenoid-transition metal coordination chemistry.[2] The high stability of many transition metal-to-silicon, -germanium, and -tin bonds[3] suggested to us that analogous silylene, germylene, and stannylene complexes (**1**) might be obtainable and that the nature of the highly reactive divalent radicals might be better understood *via* the properties of the coordination compounds. In addition, synthetic approaches might represent new routes to the rational construction of metal-metal double bonds. With only one exception,[4] the compounds isolated to date[5] have contained a molecule of base strongly coordinated to the group IV metal (**2**). The bonding in these molecules finds analogy in carbenoid complex chemistry.[5e] Thus, an alternative preparative route was investigated,[6] in which cationic complexes could be generated *via* chemical transformations such as eq 1. In this paper we present a complete exposition of our studies involving halide abstraction reactions of halo-group IV metal-transition metal compounds and related attempts to generate cationic silylene, germylene, and stannylene complexes.



1a **1b**

M = Si, Ge, Sn; M' = transition metal



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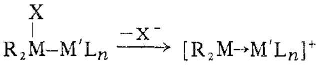

$$R_2\overset{\overset{X}{|}}{M}\text{–}M'L_n \xrightarrow{-X^-} [R_2M\rightarrow M'L_n]^+ \qquad (1)$$

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Experimental Section

The synthesis and handling of most organometallics were carried out in an atmosphere of prepurified nitrogen, employing Schlenk ware or a glove box. The solid group IV metal-transition metal compounds can be handled in air for brief periods of time without apparent decomposition; however, solutions are considerably more air sensitive. All common solvents were thoroughly dried in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Melting points were determined in sealed, nitrogen-filled capillaries and are uncorrected. Microanalyses were performed by either Dornis and Kolbe or Miss H. Beck of Northwestern University. The complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_3GeCl_3$,[7a] $(\eta^5\text{-}C_5H_5)Mo(CO)_3Ge(C_6H_5)_2Cl$,[7a] $(\eta^5\text{-}C_5H_5)Mo(CO)_3Sn(C_6H_5)_2Cl$,[7a] $(OC)_5MnGe(C_6H_5)_2Cl$,[7b] $(OC)_4CoGe(C_6H_5)_2Cl$,[7b] $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3$,[7c] $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnCl_3$,[7d] $(OC)_4CoGeCl_3$,[7e] and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(OCH_3)_3$[7f] were prepared by the literature procedures. The reagents AgF, $AgBF_4$, $AgPF_6$, $AgSbF_6$, and HPF_6 were purchased from Ozark-Mahoning Co., Tulsa, Okla., and were used (under nitrogen) without further purification. Phosphorus pentafluoride was purchased from Matheson Gas Co.

$(\eta^5\text{-}C_5H_5)Mo(CO)_3GeF_3$. To 0.424 g (1.0 mmol) of $(C_5H_5)Mo(CO)_3GeCl_3$ in 20 ml of acetone at room temperature was added 0.584 g (3.0 mmol) of $AgBF_4$ in 20 ml of acetone. A white precipitate formed immediately. The reaction mixture was stirred for 15 min and was then filtered under nitrogen. The residue was washed with 10 ml of acetone, and the combined filtrate was evaporated *in vacuo* to *ca.* 3 ml. Next, 5 ml of hexane was added and the mixture was slowly cooled to −78° over a period of 5 hr. After this time, the supernatant was removed from the crystalline product *via* syringe, and the product was washed with 10 ml of hexane precooled to −78° and dried under high vacuum. Sublimation at 70° (0.01 mm) yielded 0.300 g (80%) of pale yellow, crystalline $(C_5H_5)Mo(CO)_3GeF_3$, mp 205° dec. *Anal.* Calcd for $C_8H_5GeMoF_3O_3$: C, 25.64; H, 1.34. Found: C, 25.53; H, 1.34. Pmr data ($CDCl_3$): τ 4.43 (s).

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(η^5-C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$F. Employing the procedure outlined above, 1.50 g (3.0 mmol) of (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$Cl was allowed to react with 0.564 g (3.0 mmol) of $AgBF_4$ in 30 ml of acetone. Recrystallization of the crude product from acetone-hexane yielded 1.20 g (80%) of (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$F as pale yellow-green crystals, mp 154°. *Anal.* Calcd for $C_{20}H_{15}GeMoFO_3$: C, 48.97; H, 3.08; mol wt 491. Found: C, 48.50; H, 2.98; mol wt 494 (osmometric in benzene). Pmr data ($CDCl_3$): τ 2.60 (10 H, m), 4.67 (5 H, s).

(OC)$_5$MnGe(C_6H_5)$_2$F. By the above procedure, 2.0 g (4.37 mmol) of (OC)$_5$MnGe(C_6H_5)$_2$Cl was allowed to react, in 30 ml of acetone, with 0.855 g (4.37 mmol) of $AgBF_4$. Recrystallization of the crude product from hexane (−78°) yielded 1.5 g (81%) of colorless crystals of (OC)$_5$MnGe(C_6H_5)$_2$F, mp 100–101°. *Anal.* Calcd for $C_{17}H_{10}GeMnFO_5$: C, 46.33; H, 2.29. Found: C, 46.51; H, 2.12. Pmr data ($CDCl_3$): τ 2.48 (m).

(η^5-C_5H_5)Fe(CO)$_2$SiF$_3$. In 20 ml of acetone, 0.370 g (1.19 mmol) of (C_5H_5)Fe(CO)$_2$SiCl$_3$ was allowed to react with 0.695 g (3.57 mmol) of $AgBF_4$. The crude product was recrystallized from 5 ml of hexane (−10°) to yield 0.323 g (75%) of yellow, needlelike crystals of (C_5H_5)Fe(CO)$_2$SiF$_3$, mp 122–123°. *Anal.* Calcd for $C_7H_5SiFeO_2F_3$: C, 32.08; H, 1.92; mol wt 262. Found: C, 31.93; H, 1.87; mol wt 286 (osmometric in benzene). Pmr data (C_6H_6): τ 5.61 (s).

(OC)$_4$CoGe(C_6H_5)$_2$F. The above procedure was employed with 1.30 g (3.0 mmol) of (OC)$_4$CoGe(C_6H_5)$_2$Cl and 0.585 g (3.0 mmol) of $AgBF_4$ in 30 ml of acetone. The crude product was recrystallized from 30 ml of hexane (−78°) to yield 1.06 g (85%) of pale yellow oil, freezing at *ca.* 0°. *Anal.* Calcd for $C_{16}H_{10}GeCoO_4F$: C, 46.01; H, 2.42. Found: C, 46.15; H, 2.59. Pmr data ($CDCl_3$): τ 2.50 (m).

(OC)$_4$CoGeF$_3$. To 0.580 g (1.65 mmol) of (OC)$_4$CoGeCl$_3$ in 30 ml of benzene was added 0.968 g (4.96 mmol) of $AgBF_4$. The mixture was stirred at room temperature until gas (BF_3) evolution ceased (15 hr). The solvent was then evaporated under vacuum, and the residue was extracted with 50 ml of ether. The filtered extract was next reduced in volume to 20 ml, and 10 ml of pentane was added. Slow cooling to −78° produced yellow crystalline material. Final sublimation at 50° (0.01 mm) yielded 0.33 g (60%) of (OC)$_4$CoGeF$_3$ as yellow crystals, mp 63°. *Anal.* Calcd for $C_4GeCoO_4F_3$: C, 16.01; H, 0.00; mol wt 300. Found: C, 17.3; H, 0.00; mol wt 300 (mass spectrometric).

(η^5-C_5H_5)Mo(CO)$_3$Sn(C_6H_5)$_2$BF$_4$. In 30 ml of benzene, 0.190 g (3.34 mmol) of (C_5H_5)Mo(CO)$_3$Sn(C_6H_5)$_2$Cl was treated with 0.067 g (3.34 mmol) of $AgBF_4$. After 12 hr, the reaction mixture was filtered under nitrogen and the filtration residue washed with 10 ml of benzene. The combined filtrates were evaporated *in vacuo* to yield a yellow solid. This was washed twice with 10 ml of hexane and was dried under high vacuum, to yield 0.172 g (85%) of pale yellow microcrystalline solid, mp 150° dec. *Anal.* Calcd for $C_{20}H_{15}SnMoO_3BF_4$: C, 39.72; H, 2.50. Found: C, 36.99; H, 2.87. Ir data (cm^{-1}, Nujol mull): 2036 (vs), 1987 (vs), 1938 (vs), 1070 (vs, br) 1000 (vs, br), 920 (vs, br), 870 (w), 838 (s, br), 732 (vs), 697 (s), 677 (w), 660 (w), 635 (w). Pmr data (acetone-d_6): τ 2.64 (10 H, m), 4.35 (5 H, s).

(η^5-C_5H_5)Fe(CO)$_2$SnF$_3$. To 1.14 g (2.83 mmol) of (C_5H_5)Fe(CO)$_2$SnCl$_3$ in 50 ml of distilled water was added 1.08 g (2.83 mmol) of AgF. A white precipitate formed immediately. The reaction mixture was stirred for 15 hr, and then the water was evaporated under high vacuum. The residue was next treated with 50 ml of methanol and 0.50 g of charcoal; the mixture was stirred for 5 min and then suction filtered under nitrogen. The filtration residue was washed with 10 ml of methanol, and the combined filtrates were evaporated until crystals began to form. Addition of 2 ml of hexane and slow cooling to −78° produced yellow crystalline material. The supernatant was removed with a syringe, and the product was washed with 10 ml of hexane. Vacuum drying yielded 0.90 g (90%) of (C_5H_5)Fe(CO)$_2$SnF$_3$ as yellow crystals, mp 196° dec. *Anal.* Calcd for $C_7H_5SnFeO_2F_3$: C, 22.78; H, 1.36. Found: C, 23.17; H, 1.74. Pmr data (D_2O): τ 4.89 (s), $J_{^{117,119}Sn-H} = 9.0$ Hz.

Reaction of (η^5-C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$Cl with AgSbF$_6$. Method 1. To 0.232 g (0.46 mmol) of (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$Cl in 10 ml of CH_2Cl_2 at room temperature was added 0.157 g (0.46 mmol) of $AgSbF_6$. Precipitation of AgCl was immediate. After 2 hr of stirring, the reaction mixture was suction filtered under nitrogen, and the filtration residue was washed with 10 ml of CH_2Cl_2. The combined filtrates were next evaporated to *ca.* 2 ml, 2 ml of hexane was added, and the solution was cooled to −78° over a period of 5 hr. Next, the supernatant was removed from the crystalline product *via* syringe, and the product was washed with 5 ml of precooled (−78°) hexane. Drying under high vacuum yielded 0.136 g (80%) of (C_5H_5)Mo(CO)$_3$GeF$_3$, mp 205° dec, also identified by elemental analysis and ir data.

Method 2. To 0.286 g (0.56 mmol) of (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$Cl in 10 ml of benzene was added 0.193 g (0.56 mmol) of $AgSbF_6$. A white precipitate and a grayish oil began to separate from the reaction mixture. After being stirred for 48 hr, the mixture was filtered under nitrogen, and the filtrate evaporated under high vacuum, to yield a yellow solid. This was recrystallized from CH_2Cl_2-hexane to yield 0.178 g (85%) of (C_5H_5)Mo(CO)$_3$GeF$_3$, identified by its melting point and ir and nmr data.

Reaction of (η^5-C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$Cl with AgPF$_6$. To 3.00 g (5.9 mmol) of (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$Cl in 200 ml of benzene was added 1.50 g (5.9 mmol) of $AgPF_6$. The reaction mixture was stirred at room temperature until gas (PF_5) evolution ceased (11 hr) and was then suction filtered under nitrogen. Evaporation of the filtrate and recrystallization of the residue from $CHCl_3$-hexane yielded a mixture of (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$F and (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)F$_2$ in a ratio of 4:1, respectively. These account for *ca.* 90% of the original Mo compound. The above mixture was separated by fractional recrystallization, the difluoro species being more soluble in $CHCl_3$-hexane. This procedure yielded 0.43 g (17%) of pale yellow, crystalline (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)F$_2$, mp 126–127°. *Anal.* Calcd for $C_{14}H_{10}GeMoO_3F_2$: C, 39.30; H, 2.36. Found: C, 38.95; H, 2.22. Pmr data ($CDCl_3$): τ 2.60 (5 H, m), 4.53 (5 H, s).

Reactions of (η^5-C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$F with PF$_5$. Phosphorus pentafluoride was slowly bubbled through a solution of 2.00 g (4.08 mmol) of (C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$F in 150 ml of benzene over a period of 4.5 days. The solvent was next evaporated and the residue was recrystallized from CH_2Cl_2-hexane to yield 1.22 g (80%) of (C_5H_5)Mo(CO)$_3$GeF$_3$, identified by melting point, elemental analysis, and ir spectrum.

Reaction of (η^5-C_5H_5)Fe(CO)$_2$Si(OCH$_3$)$_3$ with HPF$_6$. To 0.100 g (0.336 mmol) of (C_5H_5)Fe(CO)$_2$Si(OCH$_3$)$_3$ in 1.0 ml of benzene-d_6 in a serum-capped nmr tube was added incrementally *via* syringe 0.25 ml (1.01 mmol) of 65% HPF_6 in sulfolane. The final product resonance occurred at τ 5.61 (s); this was shown to be (C_5H_5)Fe(CO)$_2$SiF$_3$ by comparison with an identical sample and by addition of (C_5H_5)Fe(CO)$_2$SiF$_3$ to this mixture. Intermediate species were identified as partially fluorinated products by the resonance positions and integration.

Spectroscopic Measurements. Infrared spectra were recorded on Beckman IR-5 or IR-9 spectrophotometers and were calibrated with polystyrene film. Solution spectra were obtained from dilute cyclohexane or benzene solutions. Nuclear magnetic resonance spectra were recorded on Varian T-60 or Perkin-Elmer R-20B (60-MHz) instruments. Abbreviations employed for data are s = singlet and m = multiplet. Samples were studied in serum-capped nmr tubes, using degassed solvents. Mass spectra were recorded on a CEC21-104 instrument at low ionizing voltage (15 eV). Solids were introduced *via* the direct-inlet technique. We thank Mr. D. A. Netzel for assistance.

Results

Reactions with AgBF$_4$. In all cases examined, chlorosilicon- and chloro-germanium-transition metal complexes reacted with $AgBF_4$ to yield the corresponding fluoro derivatives, as given in eq 2. This reaction proceeds rapidly in

$$L_nM'\text{-}MCl_mR_{3-m} + mAgBF_4 \rightarrow L_nM'\text{-}MF_mR_{3-m} + mAgCl + mBF_3 \qquad (2)$$

M′ = transition metal, M = Si, Ge

either coordinating or aromatic solvents ($AgBF_4$ is soluble in both) and the fluoro derivatives are produced in high yield. Indeed, this reaction appears to be a more efficient and straightforward method than others[8,9] employed in the synthesis of fluoro-group IV metal-transition metal compounds, provided the corresponding chloro derivative is available (which is usually the case[3]). Our procedure avoids high tem-

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Table I. Infrared Spectra in the C–O Stretching Region for Corresponding Pairs of Fluoro- and Chloro-Group IV Metal-Transition Metal Compounds[a]

Compd	X = F	X = Cl
$(C_5H_5)Mo(CO)_3GeX_3$	2052 s, 1987 vs, 1976 vs	2047 s, 1985 vs, 1975 vs
$(C_5H_5)Mo(CO)_3Ge(C_6H_5)_2X$	2019 s, 1958 s, 1929 s	2016 s, 1960 s, 1933 s
$(OC)_5MnGe(C_6H_5)_2X$	2112 s, 2052 m, 2027 vs, 2020 vs	2105 s, 2045 m, 2023 vs, 2011 vs
$(C_5H_5)Fe(CO)_2SiX_3$	2033 s, 1990 vs	2034 s, 1995 vs
$(OC)_4CoGe(C_6H_5)_2X$	2102 s, 2044 s, 2024 vs, 2012 vs	2109 s, 2051 s, 2031 vs, 2019 vs
$(OC)_4CoGeX_3$	2119 s, 2059 m, sh, 2051 vs	2116 s, 2062 s, 2044 vs
$(C_5H_5)Mo(CO)_3Ge(C_6H_5)X_2$	2026 s, 1987 s, 1931 vs	
$(C_5H_5)Fe(CO)_2SnX_3$	2045 vs, 1997 vs	2056 vs, 2000 vs

[a] In cm^{-1}. Key: m, medium; v, very; s, strong; sh, shoulder. Corresponding pairs of compounds were recorded in the same solvent, and frequencies are considered accurate to ±2 cm^{-1}.

peratures and high pressures, and good yields (70-90%) are obtained with unexceptional work-up techniques. An examination of the reaction of $(C_5H_5)Fe(CO)_2SiCl_3$ with 1 equiv of $AgBF_4$ showed (*via* pmr) the fluorination to be rather unselective. Resonances due to the trifluoro and difluoro species were observed even when the reaction was carried out between dilute reactants at $-30°$ in acetone, with rapid stirring. No pmr spectral evidence was found for equilibration of the various products subsequent to fluorination.

The exceptional thermal and electronic properties imparted to metal complexes by fluorinated ligands[10] suggested that the fluoro-silicon- and fluoro-germanium-transition metal compounds might possess similar properties. The observed shortening of the Co-Si bond length in $F_3SiCo(CO)_4$[11] *vs.* $Cl_3SiCo(CO)_4$[12] also suggested this. However, infrared data in the C-O stretching region (Table I) are relatively insensitive to substitution of chlorine by fluorine, and it appears that the π-accepting ability of the group IV ligand has increased only slightly.[13] Also, similar conclusions can be drawn from data in the $X_3PMo(CO)_5$ series, where for X = F, ν_{CO} = 2104, 2012, 1990 cm^{-1} [14] and for X = Cl, ν_{CO} = 2095, 1999, 1985 cm^{-1}.[15] Qualitative observations[8] have indicated that the fluorinated silicon compounds have high thermal stability. Our experiments also confirm this for the germanium analogs, but no quantitative data (*e.g.*, thermolysis rates in solution) are yet available. It will also be seen (*vide infra*) that a number of potent reactants readily cleave functionalities attached to the group IV metal but leave the metal-metal bond untouched. Similar observations have been made before[3] and are by no means restricted to fluoro derivatives.

When reaction 2 was attempted with transition metal-tin compounds, the products isolated contained the BF_4^- anion, *e.g.*, $(C_5H_5)Mo(CO)_3Sn(C_6H_5)_2BF_4$, despite solubility in aromatic solvents such as benzene. The vibrational spectrum in the B-F stretching region (ν 920 (vs), 1000 (vs), 1070 (vs) cm^{-1}) indicates considerable perturbation from the tetrahedral symmetry of an ionic BF_4^-, and these compounds are no doubt analogous to $(CH_3)_3SnBF_4$, which is believed to have a covalent polymeric structure consisting of five-coordinate tin and bridging BF_4 linkages.[16,17] A similar structural proposal has also been made for $BF_4(CH_3)_2SnMn(CO)_5$.[18] Our attempts to convert transition metal-tin tetrafluoroborates to the corresponding fluorides by heating resulted in extensive decomposition. That there is nothing intrinsically unstable about fluoro-tin-transition metal compounds was demonstrated by the high-yield synthesis of $(C_5H_5)Fe(CO)_2$-SnF_3 *via* eq 3 (see Experimental Section for details).

$$(C_5H_5)Fe(CO)_2SnCl_3 \xrightarrow[\text{in water}]{AgF} (C_5H_5)Fe(CO)_2SnF_3 + 3AgCl \qquad (3)$$

Reactions with $AgPF_6$ and $AgSbF_6$. The considerably greater affinity of PF_5 and especially SbF_5 for fluoride ion over that of BF_3[19] prompted attempts to generate cationic silylene and germylene complexes with these counterions. In all cases, fluorination occurred with release of PF_5 or SbF_5 (eq 4). Over longer reaction periods, secondary

$$L_nM'\text{-}MCl_mR_{3-m} + mAgEF_6 \rightarrow L_nM'\text{-}MF_mR_{3-m} + mAgCl + mEF_5 \qquad (4)$$

$$E = P, Sb$$

products were observed in the nmr spectrum. These were shown (see Experimental Section) to result from cleavage of silicon- and germanium-alkyl linkages by PF_5 and SbF_5, eq 5. Such reactions have been previously reported for tetra-

$$M\text{-}R + EF_5 \rightarrow M\text{-}F + REF_4 \qquad (5)$$

alkyl-[20] and tetraaryltin[21] compounds. In the present systems, this reaction occurs in preference to cleavage of the metal-metal bond.

Other Reactions. The reaction of $(C_5H_5)Mo(CO)_3Ge$-$(C_6H_5)_2F$ with PF_5 in benzene resulted in progressive cleavage of the germanium-phenyl bonds (without precipitation of an ionic product), eq 6. No other $(C_5H_5)Mo$ species were ob-

$$MoGe(C_6H_5)_2F \rightarrow MoGe(C_6H_5)F_2 \rightarrow MoGeF_3 \qquad (6)$$

served in the pmr spectrum during the reaction, and the

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cleavage products could be isolated in the pure state by fractional crystallization.

In an effort to stabilize a complexed silylene center with proximate π-donating atoms, such as is observed for numerous transition metal-carbenoid complexes,[2] the cleavage of $(C_5H_5)Fe(CO)_2Si(OCH_3)_3$ by HPF_6 was attempted. Monitoring of the reaction in benzene-d_6 *via* pmr revealed a progressive cleavage of the methoxy groups upon incremental HPF_6 addition, to produce, successively, the corresponding fluoro compounds, eq 7. The final product of the reaction was $(C_5H_5)Fe(CO)_2SiF_3$.

$$\text{Fe-Si(OCH}_3)_3 \rightarrow \text{Fe-Si(OCH}_3)_2\text{F} \rightarrow \text{Fe-Si(OCH}_3)\text{F}_2 \rightarrow \text{etc.} \qquad (7)$$

Discussion

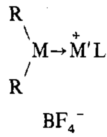
All attempts to generate cationic species of type **3** where M = Si or Ge have resulted in fluoride abstraction from the counterion BF_4^-, PF_6^-, or SbF_6^-. This is in contrast to the cationic carbenoid systems where neither isolable[22] (*e.g.*, $[(C_5H_5)Fe(CO)(L)C(OCH_3)CH_3][BF_4]$[22a]) nor proposed transient species (*e.g.*, $[(C_5H_5)Fe(CO)_2CH_2][BF_4]$[23]) have yet been shown to undergo such facile fluoride transfer. However, some precedent for transfer to carbon can be found in the Schiemann reaction,[24] eq 8, where the conditions

$$ArN_2^+BF_4^- \xrightarrow[\Delta]{} ArF + N_2 + BF_3 \qquad (8)$$

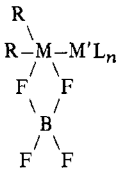
Ar = aromatic hydrocarbon

employed are far more drastic. The principal driving force for fluorination in the present case appears to be the greater strength of Si-F and probably Ge-F bonds in comparison to C-F bonds. Average thermochemical bond energies are 139 kcal/mol for Si-F and 116 kcal/mol for C-F.[25] In addition, the carbenoid carbon may be better stabilized by π bonding to adjacent lone-pair atoms,[2c] as well as to the transition metal.[2,3] The ability of silicon, germanium, and tin more readily to take on higher coordination numbers[26] is no doubt an important kinetic factor in the fluorination.

Mechanistically, whether the observed reaction involves at any stage actual cationic silylene, germylene, and stannylene complexes, *e.g.*, **4**, or whether covalent compounds *e.g.*, **5**



4



5

analogous to those isolated for tin are important intermediates remains undetermined and may even be a function of solvent.[27] In any case, our results further support the growing evidence[5] that complexed silylene, germylene, and stannylene species are strong,[28] hard Lewis acids. Our results are also in agreement with unsuccessful attempts to prepare "siliconium ions" (R_3Si^+).[29] Finally, this work underscores the important point that widely used counterions such as BF_4^-, PF_6^-, and SbF_6^- are not truly "innocent."[30]

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Registry No. $AgBF_4$, 14104-20-2; $(\eta^5\text{-}C_5H_5)Mo(CO)_3GeCl_3$, 12300-50-4; $(\eta^5\text{-}C_5H_5)Mo(CO)_3GeF_3$, 33680-01-2; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Ge(C_6H_5)_2Cl$, 33680-04-5; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Ge(C_6H_5)_2F$, 33680-03-4; $(OC)_5MnGe(C_6H_5)_2Cl$, 32093-52-0; $(OC)_5MnGe(C_6H_5)_2F$, 33678-87-4; $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3$, 34742-07-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiF_3$, 33039-23-5; $(OC)_4CoGe(C_6H_5)_2Cl$, 16560-98-8; $(OC)_4CoGe(C_6H_5)_2F$, 33678-89-6; $(OC)_4CoGeCl_3$, 16560-96-6; $(OC)_4CoGeF_3$, 16702-78-6; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Sn(C_6H_5)_2Cl$, 51329-50-1; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Sn(C_6H_5)_2BF_4$, 51329-51-2; AgF, 7775-41-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnCl_3$, 12192-93-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnF_3$, 51329-53-4; $AgSbF_6$, 26042-64-8; $AgPF_6$, 26042-63-7; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Ge(C_6H_5)F_2$, 51329-52-3; PF_5, 7647-19-0; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(OCH_3)_3$, 43175-62-8; HPF_6, 16940-81-1.

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