Hence, it was concluded that the iodine in the blue solution in 65% oleum was in the +1 oxidation state. However, in view of the fact that the +3 oxidation state has been shown to be stable in 100% acid,[9,15] it seems probable that the disproportionation of "I+" should be written as

$$3I_2 \longrightarrow 6I^+ + 6e^-$$
$$6I^+ \longrightarrow 2I_2 + 2I^{III}$$

in which case only 66% of the iodine would be recovered. On the other hand, the disproportionation of I_2^+ may be written as

$$6I_2 \longrightarrow 6I_2^+ + 6e^-$$
$$6I_2^+ \longrightarrow 5I_2 + 2I^{III}$$

and, therefore, a recovery of 83% of the iodine would be expected. Thus, the results of these experiments, in fact, provide evidence for I_2^+ rather than I^+.

(2) The results of conductivity measurements in 65% oleum were interpreted as showing that two HSO_7^- ions (or corresponding higher polyanions) are formed for each molecule of iodine,[2] *i.e.*

$$I_2 + 4H_2S_2O_7 \longrightarrow 2I^+ + 2HS_2O_7^- + SO_2 + 3H_2SO_4$$

However, we have been unable to repeat these results and our own conductivity measurements on solutions of iodine in disulfuric acid and in oleum indicate that only one $HS_2O_7^-$ ion is formed for each molecule of iodine, *i.e.*

$$2I_2 + 4H_2S_2O_7 \longrightarrow 2I_2^+ + 2HS_2O_7^- + SO_2 + 3H_2SO_4$$

These results will be fully discussed in a later paper on the formation of I_2^+ in oleum.[16]

Experimental Section

The methods used for the measurement of the conductivities and freezing points of solutions in fluorosulfuric acid and for the calculation of ν and γ values have been given previously.[6,7,17] $I_2/S_2O_6F_2$ mixtures, in exact stoichiometric ratios, were added to the cryoscopic or the conductivity cell in the form of a concentrated solution in fluorosulfuric acid, which was prepared in a drybox. Magnetic susceptibility measurements were made by the Gouy method. A permanent magnet with a field strength of 6000 gauss and a pole gap of 1.4 cm was used in conjunction with a Mettler Gramatic balance. The Gouy tube, which filled the pole gap, was standardized with a nickel chloride solution (β = 0.204). The susceptibilities were corrected for solvent and iodine fluorosulfate diamagnetism. The absorption spectra were taken on a Bausch and Lomb Spectronic 505 or a Cary Model B recording spectrophotometer. Quartz inserts to give path lengths down to 0.005 cm and reference beam filters were used to obtain spectra of iodine solutions at concentrations comparable to those used for the conductivity and magnetic susceptibility measurements. The spectra were found to be very sensitive to traces of moisture, and the solutions had to be prepared and the cells filled under very dry conditions in a drybox. The problem of adsorbed water was particularly serious when an insert was used to give a very short path length, because of the very large surface-to-volume ratio in the cell.

Commercial fluorosulfuric acid (Allied Chemical Co.) was purified as described previously.[7] Peroxydisulfuryl difluoride was prepared by the method of Cady and Shreeve.[18]

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The Reactivity of Metal–Metal Bonds. III. The Germanium–Manganese Bond

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The reaction of pentacarbonyl(trimethylgermyl)manganese with tetrafluoroethylene gives the insertion product $(CH_3)_3GeCF_2CF_2Mn(CO)_5$ in good yield. With trifluoroethylene, the reaction products are trimethylfluorogermane and *cis*- and *trans*-$CHF{=}CFMn(CO)_5$. The reactions of the germanium–manganese compound with trifluorochloroethylene, perfluoropropene, and ethylene are also described. A comparison of these reactions with those of the analogous tin–manganese compound shows a number of unexpected differences, and these are discussed in terms of the polarity of the metal–metal bond.

Introduction

The reactivities of the Sn–Sn and Sn–Mn bonds toward several fluoroolefins were examined in previous papers.[2,3] While the Sn–Sn bond of hexamethylditin is readily cleaved under free-radical conditions to give products whose formation can best be interpreted in terms of attack by the nucleophilic $(CH_3)_3Sn\cdot$ radical on the olefins, the behavior of the Sn–Mn bond under the same conditions is obviously different. Insertion products, such as $(CH_3)_3SnCF_2CF_2Mn(CO)_5$,

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are formed, but the more usual reaction products are fluorocarbon manganese carbonyl derivatives and organotin halides. Apparently, the polarity of the Sn–Mn bond in $(CH_3)_3SnMn(CO)_5$ is a determining factor in its mode of reaction, and clearly this polarity of a metal–metal bond can be changed by altering the metals involved and by changing the substituent groups on the metal atoms. As the first step in the systematic study of such effects, we are examining the reactions of the compounds $R_3MMn(CO)_5$ (where M = Ge, Sn, or Pb) with a number of olefins, and we now describe the behavior of $(CH_3)_3GeMn(CO)_5$.

Experimental Section

The general experimental techniques have been described previously.[3] Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. Alfred Bernhardt, Mülheim, Germany. Ultraviolet irradiations of silica reaction tubes (80-ml capacity unless otherwise stated) were carried out with a 200-w Hanovia lamp, in a reflecting drum, at a distance of approximately 10 cm.

Preparation of Tetramethylgermane.—Tetramethylgermane was prepared by the reaction of methylmagnesium iodide with germanium tetrachloride in *n*-butyl ether at room temperature and was purified by fractional distillation, bp 43–44° (lit.[4] 43.4°).

Preparation of Trimethylbromogermane.—This was prepared by the reaction of tetramethylgermane with a 10 mole % excess of bromine in a Pyrex Carius tube at 40° over 24 hr. The red liquid mixture was then shaken with mercury and distilled to give pure trimethylbromogermane, yield *ca.* 80%, bp 113–115° (lit.[5] 113.7°). The proton nmr spectrum showed only one peak at −0.81 ppm, relative to internal tetramethylsilane. The infrared spectrum had characteristic peaks at 3010 (w), 2920 (w) (CH str); 1418 (w) (CH_3 asym def); 1251 (m) (CH_3 sym def); 836 (s) (Ge–CH_3 rock); 759 (w); 612 (s) (Ge–C asym str); 571 (w) (Ge–C sym str) cm^{-1}.

Preparation of Pentacarbonyl(trimethylgermyl)manganese.—The method described by Gorsich[6] was used. Dimanganese decacarbonyl (19.8 g, 50.8 mmoles) was added, with stirring, to a 1% sodium amalgam (400 g) under carefully dried tetrahydrofuran (300 ml) in a nitrogen atmosphere. The solution turned dark brown and was stirred for 30 min, before the excess amalgam was separated by decantation. Trimethylbromogermane (19.8 g, 100 mmoles) in 25 ml of tetrahydrofuran was added with stirring, and the mixture was stirred at room temperature for 2 hr. Sodium bromide was filtered off, and the orange solution was concentrated to about 50 ml by distilling off the solvent. Fractional distillation of this concentrate gave, at *ca.* 10 cm pressure, more tetrahydrofuran and some unreacted trimethylbromogermane (*ca.* 2 g) and at 40° (10^{-3} mm) a pale yellow liquid (16.1 g) which solidified at room temperature. Unreacted $Mn_2(CO)_{10}$ (2 g) remained in the still pot. The pale yellow material was further purified by sublimation to a water-cooled cold finger at 10^{-3} mm pressure to give large colorless crystals of pentacarbonyl(trimethylgermyl)manganese, obtained in 51% yield, mp 33.5–34.5° (uncor). *Anal.* Calcd for $C_8H_9O_5$-GeMn: C, 30.73; H, 2.90. Found: C, 30.79; H, 2.96. The proton nmr spectrum (10% solution in deuteriochloroform with tetramethylsilane as internal standard) showed a single sharp resonance at −0.62 ppm. The infrared spectrum (Nujol and halocarbon mulls) showed absorption bands at 3000 (m), 2920 (m) (CH str); 2810 (sh); 2345 (w); 2117 (m), 2030 (vs), 2000 (s) (CO str); 1413 (m) (CH_3 asym def); 1233 (m) (CH_3 sym def); 1085 (w); 1033 (w); 996 (w); 910 (w); 822 (s) (Ge–CH_3 rock); 750 (m) (Ge–CH_3 rock); 670 (sh), 667 (s), 660 (vs) (Mn–CO def); 586 (s) (Ge–C asym str); 556 (s) (Ge–C sym str); 481 (s); 412 (w) (Mn–CO str) cm^{-1}. The compound decomposed slowly in air to leave a brown, hygroscopic residue.

Thermal Stability of $(CH_3)_3GeMn(CO)_5$.—A sample (0.43 g) was heated in a sealed 20-ml Pyrex tube at 130° for 18 hr. The white solid turned a very pale yellow, but only a small amount ($<3 \times 10^{-6}$ mmole) of carbon monoxide, identified spectroscopically, was obtained. The bulk of the compound, at least 98%, was recovered unchanged.

Stability of $(CH_3)_3GeMn(CO)_5$ to Ultraviolet Light.—A sample (0.24 g) was irradiated in a 20-ml silica tube at 50–60° for 5 hr. Traces of an unidentified violet solid formed on the walls of the tube, the solid turned yellowish, and a small amount of carbon monoxide (*ca.* 10^{-4} mmole) was formed. The bulk (>95%) of the compound was recovered.

Reaction with Tetrafluoroethylene.—Tetrafluoroethylene was prepared by the thermal decomposition of Teflon chips at 600°, *in vacuo*, and was purified by vacuum fractionation through traps cooled to −150 and −196°. The infrared spectrum indicated that less than 0.5% of the major impurity, hexafluoropropene, was present.

Pentacarbonyl(trimethylgermyl)manganese (1.66 g, 5.31 mmoles) in *n*-pentane (5 ml) and tetrafluoroethylene (1.54 g, 15.4 mmoles) were irradiated at 50° for 21 hr. The solution turned yellow, and carbon monoxide (1.45 mmoles), identified spectroscopically and by its molecular weight (calcd, 28.0; found, 30.7), was formed. Vacuum fractionation of the remaining material gave at −196° tetrafluoroethylene (7.89 mmoles), identified spectroscopically, and at −126 and −78°, mixtures of *n*-pentane with small amounts of fluorocarbons. A mixture (7.5×10^{-2} mmole) of trimethylfluorogermane (characterized as in the following reaction) and less volatile fluorocarbons was trapped at −46°, while the infrared spectrum of the small fraction which condensed at −10° suggested that it contained unreacted $(CH_3)_3GeMn(CO)_5$, a trace of the compound previously formulated[2] as $C_5F_9Mn(CO)_3$, and another compound. This fraction was combined with the dense orange oil (1.9 g) which remained in the reaction tube and was centrifuged to remove some white residue (0.1 g) whose infrared spectrum showed it to consist largely of low polymers of tetrafluoroethylene. Chromatography on Florisil with pentane separated the oil into unreacted $(CH_3)_3GeMn(CO)_5$, a trace of dimanganese decacarbonyl, and two new components, the first of which was the major reaction product. This was purified by slow crystallization from pentane solution and sublimation and was 1-trimethylgermyl(2-pentacarbonylmanganese)tetrafluoroethane, $(CH_3)_3GeCF_2CF_2Mn(CO)_5$, mp 32° (uncor). *Anal.* Calcd for $C_{10}H_9F_4O_5GeMn$: C, 29.1; H, 2.2; F, 18.4. Found: C, 28.0; H, 2.1; F, 18.4. A solution in deuteriochloroform with tetramethylsilane as external standard gave a single proton nmr peak at −0.43 ppm. The ^{19}F nmr spectrum showed two single resonances at +28.1 and −23.3 ppm from trifluoroacetic acid. Infrared bands were observed at 3000 (m), 2920 (m) (CH str); 2440 (w); 2147 (m), 2068 (vs), 2066 (vs), 2042 (s) (CO str); 1416 (m) (CH_3 asym def); 1300 (w); 1245 (m) (CH_3 sym def); 1084 (s), 1022 (s), 1005 (s), 985 (s) (C–F str), 836 (s), 769 (s) (Ge–CH_3 rock); 735 (w); 708 (s) (C–C str); 660 (w), 657 (vs), 649 (m), 640 (m) (Mn–CO def); 626 (w); 612 (m) (Ge–C asym str); 575 (m) (Ge–C sym str); 552 (w) (Ge–C–F str); 445 (s), 423 (m) (Mn–CO str) cm^{-1}. The other new chromatographic fraction was obtained in only trace amounts and showed both C–F and carbonyl infrared absorptions, suggesting by comparison with the spectra[2] of related tin compounds that it might be a mixture of adducts, $(CH_3)_3Ge(C_2F_4)_nMn(CO)_5$. The yield, however, was too low to allow further characterization.

Reaction with Trifluoroethylene.—Trifluoroethylene (Columbia Organic Chemicals) was purified by fractionation through traps cooled to −126, −150, and −196°. The −150° fraction was shown by its infrared spectrum to contain only traces of the major impurities, 1,1-difluoroethylene and chlorotrifluoroethylene. Calcd for C_2F_3H: mol wt, 82.0. Found: mol wt, 83.0.

Pentacarbonyl(trimethylgermyl)manganese (2.13 g, 6.81 mmoles) in *n*-pentane (5 ml) and trifluoroethylene (1.71 g, 20.9

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mmoles) were irradiated at 50° for 21 hr. A small amount of brown solid formed on the walls of the tube, and the pentane solution turned yellow. Carbon monoxide (3.85 mmoles) was formed, and vacuum fractionation gave at −196° trifluoroethylene (14.75 mmoles, mol wt found 82.9) and at −126, −112, and −78° pentane containing small amounts of fluorocarbons. At −46°, a colorless liquid (0.26 g) was obtained, which was identified as trimethylfluorogermane. Characterization was achieved by means of its proton nmr and infrared spectra; a 10% solution in $CDCl_3$ with internal TMS as standard showed a doublet centered at −0.57 ppm with $J_{H-F} = 7$ cps. Schmidbauer and Ruidisch[7] reported for $(CH_3)_3GeF$ in carbon tetrachloride solution a value of −0.55 ppm with $J_{H-F} = 6.8$ cps. The infrared spectrum (vapor phase) of this −46° fraction was identical with that of $(CH_3)_3GeF$.[8] Spectroscopic examination (infrared and ^1H nmr) of the −10° fraction (0.2 g) and the material remaining in the reaction tube showed that both consisted largely of unreacted $(CH_3)_3GeMn(CO)_5$, and from the relative intensities and weights, it was estimated that approximately 60% was unreacted. The −10° fraction also contained *trans*-1,2-difluorovinylpentacarbonylmanganese and a much smaller amount of the related *cis* isomer. Both of these were identified by their very characteristic infrared and ^1H nmr spectra.[1] The reaction residue, consisting largely of unreacted $(CH_3)_3GeMn(CO)_5$, also contained small amounts of *cis*-1,2-difluorovinylpentacarbonylmanganese, mp[3] 77–78°, and a third component which was identified only by its ^1H nmr spectrum, which consisted of a resonance at −2.17 ppm.

Reaction with Chlorotrifluoroethylene.—Chlorotrifluoroethylene (Matheson Co.) was purified by vacuum fractionation to give at −126° a spectroscopically pure sample. Pentacarbonyl(trimethylgermyl)manganese (2.56 g, 8.20 mmoles) in *n*-pentane (5 ml) and chlorotrifluoroethylene (1.84 g, 15.8 mmoles) were irradiated at 50–60° for 24 hr. A brown solid formed on the walls of the tube and the solution turned orange. Noncondensable gas (6.3 mmoles), identified spectroscopically and by its molecular weight (found, 31.1) as carbon monoxide, was formed. Vacuum fractionation gave, first, unreacted chlorotrifluoroethylene, (*ca.* 10.5 mmoles) although this could not be completely separated from pentane. A colorless liquid (0.662 g), which condensed in the −46° trap, was purified by gas chromatography (dinonyl phthalate column, 10 psi of helium, 100°, elution time 11 min) and found to be trimethylperfluorovinylgermane. *Anal.* Calcd for $C_5H_9F_3Ge$: C, 30.2; H, 4.6; F, 28.7. Found: C, 29.9; H, 4.4; F, 28.9. The proton spectrum showed a single resonance at −0.13 ppm (relative to external TMS in chloroform) with $J_{C^{13}-H} = 127.8$ cps. The ^{19}F spectrum of the pure liquid showed three quartets at +90.4, +121.5, and +195.4 ppm, relative to CCl_3F, with coupling constants $J_{gem} = 79.4$ cps, $J_{cis} = 30.9$ cps, and $J_{trans} = 117.4$ cps. These data agree well with those obtained by Coyle, *et al.*,[9] for $(CH_3)_2Ge(CF{=}CF_2)_2$. The infrared spectrum showed the following absorptions which were assigned according to the assignments for $(CH_3)_2Ge(CF{=}CF_2)_2$ by Stafford and Stone:[10] 3085 (w); 3020 (m) (C–H asym str); 2940 (w) (C–H sym str); 2840 (w, sh); 2765 (w, sh) (comb. 1028 + 1723?); 2550 (w) (comb. 2 × 1287?); 2495 (w); 2380 (s); 2285 (w) (comb. 2 × 1135); 2060 (w) (comb. 2 × 1028?); 1867 (w) (comb. 835 + 1028); 1818 (w); 1777 (m, w); 1723 (vs) (C=C str); 1424 (m) (CH_3 asym def); 1350 (m); 1287 (vs) (C–F str); 1256 (m) (CH_3 sym def); 1135 (s) (C–F str); 968 (vw); 835 (s) (CH_3–Ge rock); 765 (m) (CH_3–Ge rock); 700 (vw); 648 (w); 614 (s) (Ge–C asym str); 576 (m) (Ge–C sym str); 511 (w) cm^{-1}. The yellow oil (0.1 g) obtained in the −22° trap was combined with that from the centrifuged extract from the reaction tube, to give a total of 0.45 g. The infrared spectrum showed this to be a mixture of roughly equal amounts of $(CH_3)_3GeMn(CO)_5$ and $Mn_2(CO)_{10}$, with a small amount of $CF_2{=}CFCOMn(CO)_5$ identified by its characteristic absorptions[3] at 1712, 1240, 1042, and 960 cm^{-1}. The mixture was chromatographed in pentane on a Florisil column, to give $(CH_3)_3GeMn(CO)_5$ first, closely followed by $Mn_2(CO)_{10}$, and only a trace of the third component. The residue in the reaction tube was extracted with pentane, and on evaporation, a yellow oil (0.4 g) of $(CH_3)_3GeMn(CO)_{10}$ and $Mn_2(CO)_{10}$ remained. These two components were identified spectroscopically, and fractional sublimation gave a pure sample of $Mn_2(CO)_{10}$. *Anal.* Calcd for $C_{10}O_{10}Mn_2$: C, 30.80; H, 0.0. Found: C, 30.87; H, 0.0. Extraction of the pentane-insoluble residue with acetone gave, after evaporation, yellow-orange crystals (0.3 g) whose infrared spectrum in chloroform solution was identical[11] with that of $[Mn(CO)_4Cl]_2$. This fraction could not be analyzed because of its rapid decomposition both in solution and during an attempted sublimation. The above acetone extraction left a white, hygroscopic, unidentified solid (*ca.* 0.2 g) which was possibly a mixture of Mn(II) salts.

Reaction with Ethylene.—Pentacarbonyl(trimethylgermyl)manganese (2.75 g, 8.80 mmoles) in *n*-pentane (5 ml) and ethylene (0.38 g, 13.6 mmoles) were irradiated for 70 hr at 80°. A brown sediment formed in the tube, and the solution turned gold. Noncondensable gas (0.86 mmole), identified spectroscopically as carbon monoxide, was formed. Vacuum fractionation gave, at −196°, ethylene (11.3 mmoles), identified spectroscopically and by its molecular weight (calcd for C_2H_6, 28.1; found, 28.3). Pentane was separated at −126 and −78°, and some unreacted $(CH_3)_3GeMn(CO)_5$ (0.25 g) at −22°. A golden semisolid remained in the reaction tube, but this turned black on exposure to air for a few seconds. From its infrared spectrum the decomposed solid was mainly a mixture of $(CH_3)_3GeMn(CO)_5$ with small amounts of $Mn_2(CO)_{10}$. The black solid was dissolved in pentane and centrifuged, the pentane was evaporated, and the remaining material was subjected to vacuum sublimation at 10^{-3} mm (30°) to a cold finger at 20°. Yellow, crystalline $(CH_3)_3GeMn(CO)_5$ (1.75 g) was recovered, according to its infrared spectrum contaminated with about 5% $Mn_2(CO)_{10}$. Further sublimation at 10^{-3} mm (60°) gave a mixture (0.15 g) containing approximately equal amounts of $(CH_3)_3GeMn(CO)_5$ and $Mn_2(CO)_{10}$, but showing additional infrared absorptions at 1710 (m), 1460 (m), and 600 (m) cm^{-1}. A third fraction (0.1 g) which sublimed at 10^{-3} mm (80°) was almost pure $Mn_2(CO)_{10}$. Small amounts (0.06 g) of an insoluble, unidentified residue remained.

Reaction with Hexafluoropropene.—Hexafluoropropene (2.24 g, 14.9 mmoles), pentacarbonyl(trimethylgermyl)manganese (2.27 g, 7.28 mmoles), and *n*-pentane (5 ml) were irradiated at 50° for 24 hr. Orange crystals formed initially on the tube walls, and later a brown solid was deposited, while the solution became yellow. Carbon monoxide (4.8 mmoles) was formed, and vacuum fractionation gave mixtures of pentane and hexafluoropropene in the low-temperature traps. At −46°, a clear liquid (0.32 g) was obtained, which could not be purified further by chromatography because of decomposition on the column. The infrared spectrum suggested that this liquid contained a trimethylgermanium fluorocarbon derivative, with observed absorption bands at 3010 (w), 2940 (w) (C–H str); 2060 (w); 2020 (w); 1605 (w) (C=C str?); 1425 (w, br) (CH_3 def); 1355 (s); 1305 (w); 1255 (m); 1217 (s) (C–F str); 1163 (s) (C–F str); 1135 (m); 1095 (m); 923 (w); 836 (s) (CH_3–Ge rock); 765 (m); 733 (w); 670 (sh); 668 (w); 666 (m); 620 (m) (Ge–C asym str); 581 (w) (Ge–C sym str). The proton nmr spectrum (deuteriochloroform solution with TMS as external standard) showed a doublet, with a separation of 1 cps, centered at −0.35 ppm, as well as weaker peaks due to $(CH_3)_3GeMn(CO)_5$ (about 13%) and pentane. The yellow oil from the room temperature trap together with that from the reaction tube (total 1.9 g) showed infrared absorptions of $(CH_3)_3GeMn(CO)_5$, $Mn_2(CO)_{10}$, and at least one other component. Chromatography on a Florisil column separated the first components,

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in an approximately 4:1 ratio, and gave a faint trace of a third component which showed the same pattern of carbonyl infrared absorptions as the fourth component obtained in somewhat larger amounts (20 mg). This last fraction was perfluoropropenylpentacarbonylmanganese, $CF_3CF{=}CFMn(CO)_5$. *Anal.* Calcd for $C_8F_5O_5Mn$: C, 29.5; F, 29.1. Found: C, 29.7; F, 29.1. In a Nujol mull, the compound gave infrared absorptions at 2065, 2020, 1985 (vs, br); 1634 (m); 1368 (sh); 1348 (m); 1325 (m); 1185 (s); 1120 (m); 1085 (m); 1035 (w); 983 (m); 878 (m); 808 (w); 725 (m); 657 (s); 637 (s); 611 (sh); 470 (w); 434 (m) cm^{-1}. The principal peaks are in good agreement with those reported by McClellan,[12] and by Pitcher and Stone,[13] although there are some differences. These may be related to the different conditions under which spectra were recorded, but may alternatively be due to the fact that our product was essentially the *cis* isomer, whereas Pitcher and Stone[13] and McClellan[12] reported the isolation of the *trans* isomer.

Discussion

The reactant, pentacarbonyl(trimethylgermyl)manganese, $(CH_3)_3GeMn(CO)_5$, readily prepared by methods described by Gorsich,[6] and Seyferth *et al.*,[14] shows in its infrared spectrum the features expected for the $(CH_3)_3Ge$ group and for the $Mn(CO)_5$ group of C_{4v} symmetry. It is interesting that the carbonyl frequencies are approximately 25–30 cm^{-1} higher than for the analogous frequencies[3] of $(CH_3)_3SnMn(CO)_5$. The manganese atom is therefore more positively charged in $(CH_3)_3GeMn(CO)_5$, and, in view of the relative electronegativities of germanium and tin, the Ge–Mn bond may be less polar than the Sn–Mn bond. Also worth noting is the fact that the frequencies for the Ge–C stretching vibrations of $(CH_3)_3GeMn(CO)_5$ are quite similar[15] to those of $(CH_3)_6Ge_2$. The compound shows a considerable degree of stability to heat and to ultraviolet light, and it is probably even more stable under these conditions than trimethyltinpentacarbonylmanganese.[3]

The reaction of pentacarbonyl(trimethylgermyl)manganese with tetrafluoroethylene gave as the principal product 1-trimethylgermyl(2-pentacarbonylmanganese)tetrafluoroethane, $(CH_3)_3GeCF_2CF_2Mn(CO)_5$, the only other products being traces of carbon monoxide, trimethylfluorogermane, $C_5F_9Mn(CO)_5$, and $Mn_2(CO)_{10}$. These latter products clearly result from secondary decomposition reactions, the only reaction of importance being that described by the equation

$$(CH_3)_3GeMn(CO)_5 + C_2F_4 \longrightarrow (CH_3)_3GeCF_2CF_2Mn(CO)_5$$

While the similar compound, $(CH_3)_3SnCF_2CF_2Mn(CO)_5$, is also formed in the analogous reaction[3] of the tin–manganese derivative with tetrafluoroethylene, the yield is much less, and equal or slightly larger yields of $C_5F_9Mn(CO)_5$, $CF_2{=}CFCOMn(CO)_5$, and $[CF_2{=}CFMn(CO)_4]_2$ are obtained. Apparently, the adduct $(CH_3)_3GeCF_2CF_2Mn(CO)_5$ is more stable under these reaction conditions than is the related tin adduct and does not so readily decompose with the elimination of trimethylfluorogermane. Whether this is due to an inherently greater thermodynamic stability for $(CH_3)_3GeCF_2CF_2Mn(CO)_5$ or to the fact that the formation of *crystalline* trimethyltin fluoride is energetically more favorable than is the formation of *gaseous* trimethylfluorogermane is not at all clear.

Also, in this reaction, a trace of a product was separated which might be $(CH_3)_3Ge(C_2F_4)_nMn(CO)_5$. However, the yield was extremely small and this formulation as a polyadduct is based entirely on the similarity of its complex infrared spectrum to those of related tin compounds.[2] Even if the formulation is correct, the formation of such polyadducts obviously does not occur readily.

In spite of this difference in their reactions with tetrafluoroethylene, the germanium–manganese and tin–manganese compounds behave very similarly toward trifluoroethylene, with which the former gives trimethylfluorogermane and the *cis* and *trans* isomers of 1,2-difluorovinylpentacarbonylmanganese. The analogous products also were produced[3] in the reaction with $(CH_3)_3SnMn(CO)_5$, although here the reaction proceeded much further toward completion than with the germanium–manganese reactant. This may again be related to the lower tendency to form $(CH_3)_3GeF$, as compared with the more ready formation of $(CH_3)_3SnF$. However, there seems no reason why the adduct $(CH_3)_3GeC_2F_3HMn(CO)_5$ should not be the principal product, particularly in view of the ready formation of $(CH_3)_3GeCF_2CF_2Mn(CO)_5$.

In contrast, the reaction of $(CH_3)_3GeMn(CO)_5$ with chlorotrifluoroethylene follows a completely different route from the analogous reaction of the tin–manganese compound, giving trimethylperfluorovinylgermane (48% yield), $[Mn(CO)_4Cl]_2$, $Mn_2(CO)_{10}$, and a small amount of $CF_2{=}CFCOMn(CO)_5$. There is no evidence that either trimethylchlorogermane or trimethylfluorogermane is formed, although both $(CH_3)_3SnCl$ and $(CH_3)_3SnF$ are formed in the reaction of $(CH_3)_3SnMn(CO)_5$ with chlorotrifluoroethylene. The latter reaction also gave a considerable yield of $CF_2{=}CFCOMn(CO)_5$. In both instances, however, there seems no explanation for the apparent decomposition of GeC_2F_3ClMn and SnC_2F_3ClMn units, which are probably present in the reaction intermediates.

The lack of any significant reaction between ethylene and $(CH_3)_3GeMn(CO)_5$ is in marked contrast to the extensive displacement[3] of carbon monoxide by ethylene from $(CH_3)_3SnMn(CO)_5$ to form $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$.

Finally, the reaction of $(CH_3)_3GeMn(CO)_5$ with perfluoropropene did not give the adduct $(CH_3)_3GeC_3F_6Mn(CO)_5$, but rather perfluoropropenylpentacarbonylmanganese, $CF_3CF\text{–}CFMn(CO)_5$, and an unidentified trimethylgermanium–fluorocarbon compound, as well as $Mn_2(CO)_{10}$.

From these and the earlier studies, it is clear that these reactions are complex. There is no uniform relationship between the behavior of $(CH_3)_3GeMn(CO)_5$ and $(CH_3)_3SnMn(CO)_5$ toward the same set of olefins,

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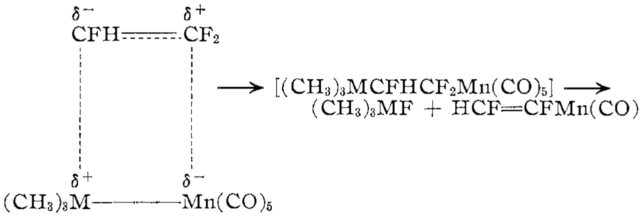
and, in addition, different substituents on the olefin lead to very different products. The fact that there is, as yet, no good evidence for the formation of polyadducts containing, for example, the $M(C_2F_4)_nMn$ unit (M = Ge or Sn) reinforces further our previous suggestion[3] that a free-radical process is unlikely. Moreover, we have very recently found[16] that the course of these reactions of olefins with metal–metal bonded compounds is dependent on the polarity of the solvent medium. An ionic or four-center type of mechanism therefore seems more probable, and for these the direction and degree of polarity of the M–Mn bonds (M = Ge or Sn) are among the most important controlling factors. The polarity $(CH_3)_3M^{\delta+}\text{–}Mn^{\delta-}(CO)_5$ (M = Ge or Sn), together with a fluorine atom migration, is consistent with the reactions of both the germanium and tin derivatives with trifluoroethylene



$$\begin{array}{ll} \overset{\delta-}{\mathrm{CFH}}\cdots\overset{\delta+}{\mathrm{CF_2}} & \\ \vdots \qquad\quad \vdots & \longrightarrow [(CH_3)_3MCFHCF_2Mn(CO)_5] \longrightarrow \\ \overset{\delta+}{(CH_3)_3M}\text{——}\overset{\delta-}{Mn(CO)_5} & \quad (CH_3)_3MF + HCF{=}CFMn(CO)_5 \end{array}$$

However, if this polarity is the determining factor, then these reactions involve essentially the attack of the $Mn(CO)_5^-$ anion on the olefin. Such reactions have been studied recently,[17] and one would then anticipate that the Ge–Mn and Sn–Mn compounds would behave similarly. Clearly, however, these two compounds behave very differently with, for example, chlorotrifluoroethylene, so that the above type of argument is not sufficient in itself. It is conceivable that bonds such as Ge–Mn and Sn–Mn have a very low degree of intrinsic polarity or that some degree of polarity is induced by the specific reagent or reaction conditions. The direction of polarity may even be reversed under appropriate circumstances, and this may be elucidated by further studies. Certainly the infrared spectra of $(CH_3)_3GeMn(CO)_5$ and $(CH_3)_3SnMn(CO)_5$ indicate a different polarity for the Ge–Mn and Sn–Mn bonds. On the other hand, the over-all energy changes of these reactions must be important, and consideration must also be given to the relative bond energies of Ge–C, Sn–C, Ge–X, and Sn–X (X = halogen) bonds.

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Organometallic Compounds with Metal–Metal Bonds. III. Tetracarbonylcobalt Derivatives of Gallium, Indium, and Thallium[1]

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Twelve compounds having Ga–Co, In–Co, or Tl–Co bonds have been prepared by halide displacement with $Co(CO)_4^-$ or by unusual "insertion" reactions. In the latter, $Co_2(CO)_8$ reacts in tetrahydrofuran (THF) with InBr or GaX_2 (X = Cl, Br) affording $BrIn[Co(CO)_4]_2\cdot THF$ or $X_2GaCo(CO)_4\cdot THF$. Also described are the types $XGa[Co(CO)_4]_2\cdot THF$ and $In[Co(CO)_4]_3$, and acetylacetonate (acac) derivatives such as $(acac)Ga[Co(CO)_4]_2$. The number of strong infrared carbonyl stretching frequencies compares well with expectations based on symmetry.

Introduction

Many compounds are now known in which a transition metal is covalently bonded to silicon, germanium, tin, or lead.[2] Cases in which a transition metal is bonded to an element of main group III are, by contrast, few in number.[3] In an early paper on mixed-metal carbonyls, Hieber and Teller[6] obtained the compounds $In[Co(CO)_4]_3$, $Tl[Co(CO)_4]_3$, and $TlCo(CO)_4$ by direct reaction of the finely divided metals under vigorous conditions (200°, 200 atm). There was some evidence for the occasional formation in trace amounts of a

[1] Presented in part at the Symposium on the Metal–Metal Bond in Inorganic Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. Abstracts, paper H70.

[2] For leading references, see previous papers of this series: (a) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966) (part I); (b) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1405 (1966) (part II).

[3] With the exception of boron, metal–metal bonding of any kind involving main group III elements is rare. A gallium–gallium bond exists in GaS,[4] while an aluminum–aluminum covalent bond is believed to occur in $Al_4B[N(CH_3)_2]_3(CH_3)_6$.[5]

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