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REACTIVITY OF METAL–METAL BONDS

X*. FURTHER REACTIONS OF Si–Mn, Ge–Mn, AND Sn–Mn BONDS WITH UNSATURATED FLUOROCARBONS

H. C. CLARK and T. L. HAUW
Department of Chemistry, University of Western Ontario, London, Ontario (Canada)

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SUMMARY

The reactions of $(CH_3)_3SiMn(CO)_5$ with C_2F_4, C_2F_3H, and C_3F_6, and of $(CH_3)_3MMn(CO)_5$ ($M = Si$ or Ge) with perfluorocyclobutene, perfluoro-2-butyne and 3,3,3-trifluoropropyne are described. The new compounds which are formed are either the products of insertion into the M–Mn bond, or compounds formed by the decomposition of such insertion products.

INTRODUCTION

Compounds containing covalent metal–metal bonds have been extensively studied in recent years[1]. While the cleavage of many such bonds has been reported (see *e.g.* refs. 2 and 3), the addition of metal–metal bonded compounds across multiple bonds has been less extensively investigated. Previously we have described reactions of $(CH_3)_3MMn(CO)_5$ where $M = Ge$[4] or Sn[5,6] and $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$ where $M = Si$, Ge or Sn[6] with several fluorinated olefins and acetylenes, in which the products of a single addition of the metal–metal bond across C=C or C≡C were formed, or the decomposition compounds derived from such products. While the reactivity of metal–metal bonds is dependent on the particular metal atoms involved, and also on the substituents on the metals, nevertheless, the nature of this dependence is not clear. It therefore seemed worthwhile to examine the reactions of $(CH_3)GeMn(CO)_5$ towards some other fluoroalkynes, as well as to investigate the behavior of the analogous $(CH_3)_3SiMn(CO)_5$ towards both fluoroalkenes and alkynes.

EXPERIMENTAL

General techniques

Vacuum manipulations by standard methods were employed in handling volatile reactants and products. Molecular weights were determined in benzene solution using a Hitachi–Perkin–Elmer 115 molecular weight apparatus, calibrated

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[*] For Part IX, see ref. 1.

with benzil. Infrared spectra were obtained on a Beckman IR-10 spectrometer for routine purposes, while more accurate spectra, particularly for the carbonyl stretching region, were obtained on a Beckman IR-7 spectrometer. Proton NMR were run on a Varian T-60 spectrometer and ^{19}F NMR on a Varian HA-100 spectrometer at 94.1 MHz. Microanalyses were by A.B. Gygli of Toronto or Schwarzkopf Microanalytical Laboratories, New York.

(Trimethylgermyl)pentacarbonylmanganese was prepared by the procedure described previously[7]; (trimethylsilyl)pentacarbonylmanganese was obtained by the method of Berry and MacDiarmid[8], the yield usually being about 5%. 3,3,3-Trifluoropropyne was obtained as described by Finigan and Norris[9]. Tetrafluoroethylene, trifluoroethylene, perfluoropropene, perfluorocyclobutene, and perfluoro-2-butyne were all obtained commercially.

(*a*). *Reaction of tetrafluoroethylene with (trimethylsilyl)pentacarbonylmanganese*

(Trimethylsilyl)pentacarbonylmanganese (0.23 g, 0.89 mmol) in 2 ml of pentane was allowed to react with tetrafluoroethylene (8.6 mmol) under UV at 10° for 26 h.

After removing the volatile compounds which were mainly unreacted fluoroolefin and solvent, the reaction mixture, a yellow oil, was rinsed out of the tube with pentane, and the insoluble grease was centrifuged off. The remaining mixture contained four components, as shown by TLC, one of which had an R_f value identical to that of the starting material; the second component which had an R_f lower than that of $Me_3SiMn(CO)_5$, was the most abundant.

Chromatography on florisil with hexane as eluant gave three compounds, the last being strongly absorbed on the top of the column. These were: $Me_3SiMn(CO)_5$ (10 mg. 5% recovery) which was identified by its infrared spectrum; the second component, recovered as colourless crystals after resublimation at 25°/0.01 mmHg to a water cooled probe, was 1-(trimethylsilyl)-2-(pentacarbonylmanganese)tetrafluoroethane, $Me_3SiCF_2CF_2Mn(CO)_5$ (yield 60 mg, 15%, m.p. 35°). (Found: C, 32.72; H, 2.70; F, 22.65. $C_{10}F_2MnO_5Si$ calcd.: C, 32.70; H, 2.45; F, 20.70%.) The third component was a trace of a pale yellow oil, which showed only fluorocarbon and carbonyl infrared absorptions and may be a pentacarbonyl derivative of a fluorocarbon polymer. Fluorocarbon polymer was also observed on the wall of the reaction tube.

(*b*). *Reaction of trifluoroethylene with (trimethylsilyl)pentacarbonylmanganese*

(Trimethylsilyl)pentacarbonylmanganese (0.5 g, 2.25 mmol) in 1 ml hexane was sealed with 7.6 mmol of trifluoroethylene in a silica Carius tube and irradiated under UV at 2° for 20 h. On opening the tube in vacuum, 0.6 mmol of carbon monoxide was removed. Trap-to-trap distillation followed by vacuum sublimation of the less volatile fractions, gave quantitative recovery of the $Me_3SiMn(CO)_5$.

When a similar reaction was carried out by irradiating the above amounts of reagents under UV at 35° for 5 days, 2.1 mmol of carbon monoxide was removed. The reaction mixture was rinsed out of the Carius tube with hexane and the dark grease was washed twice with methylene chloride before being discarded. The methylene chloride solution was found by TLC and infrared spectroscopy[4,5] to contain a mixture of (*cis*-1,2-difluorovinyl)pentacarbonylmanganese, $CFH{=}CFMn(CO)_5$, and $Mn_2(CO)_{10}$.

The hexane and methylene chloride solutions were combined and chromatographed on florisil, and eluted first with hexane, then with a 1/1 mixture of hexane and methylene chloride. Four compounds were collected: $Me_3SiMn(CO)_5$ (20 mg, 5% recovery), $Mn_2(CO)_{10}$ (53 mg, 14.5% yield), *cis*-CFH=CFMn$(CO)_5$, (70 mg, 27% yield), all of which were identified by their infrared spectra, and a small amount of a yellow oil, which could be sublimed at 25°/0.02 mmHg on to a water cooled probe. The first fraction which sublimed was a yellow oil, leaving a trace of $Mn_2(CO)_{10}$ in the flask. This yellow oil was resublimed at 25°/50 mmHg onto a water cooled probe 10 cm away from the oil. A trace amount of white crystals was obtained, for which the mass spectroscopic peaks could all be reconciled with the fragmentation of $(CH_3)_3SiCF{=}CFMn(CO)_5$.

(c). Reaction of perfluoropropene with (trimethylsilyl)pentacarbonylmanganese

Perfluoropropene (4.5 mmol) and $Me_3SiMn(CO)_5$ (1.8 g, 6.7 mmol) in 2 ml of hexane were sealed in a silica tube and put under UV irradiation for 4 days at 35°. The solution turned brown, with a brown precipitate being formed. On opening the tube in vacuum, carbon monoxide (0.8 mmol, 12%) was obtained. Fractional vacuum distillation of the volatiles at room temperature gave a mixture of perfluoropropene, hexane and trimethylfluorosilane in the −196° trap, and trimethylfluorosilane and hexane in the −78° trap. The total trimethylfluorosilane was estimated to be 3 mmol (30% yield), identified by its infrared spectrum. In the −23 and 0° traps, mixtures of $Me_3SiMn(CO)_5$, $Mn_2(CO)_{10}$ and the product, (perfluoropropenyl)pentacarbonylmanganese $CF_3CF{=}CFMn(CO)_5$, were trapped, these components being identified from their infrared spectra and their R_f values on TLC plates.

Sublimation of the remaining reaction mixture, a yellow wax, at 25°/0.02 mmHg onto a water-cooled probe afforded $Me_3SiMn(CO)_5$, contaminated by $Mn_2(CO)_{10}$. The impure sublimate and the residue were combined and chromatographed on florisil. Elution with hexane gave $Me_3SiMn(CO)_5$ (0.35 g, 23%), followed by $Mn_2(CO)_{10}$ (70 mg, 10%) and *cis*-$CF_3CF{=}CFMn(CO)_5$ (100 mg, 6%), and a trace of unidentified colourless crystals. Compounds were characterized by their infrared spectra.

(d) Reactions of perfluorocyclobutene with metal–manganese bonded compounds

(i). *With (trimethylgermyl)pentacarbonylmanganese.* (Trimethylgermyl)pentacarbonylmanganese (0.75 g, 2.42 mmol) and perfluorocyclobutene (8 mmol) in 10 ml of pentane were sealed in a silica tube and allowed to react under UV for 3 days at 2°. Carbon monoxide (0.3 mmol; 12%) was removed as uncondensed gas. Fractional vacuum distillation at room temperature gave perfluorocyclobutene and pentane in the −196° trap, while trimethylfluorogermane, trapped in the −78° trap, was identified by its infrared spectrum[5]. In the −23° trap, $Me_3GeMn(CO)_5$, (perfluoro-1-cyclobutenyl)pentacarbonylmanganese $\overline{CF_2-CF_2-CF{=}C}Mn(CO)_5$ and some unknown fluorocarbon polymer were collected. $Me_3GeMn(CO)_5$ was trapped at 0° as colourless crystals.

TLC examination of the residue of distillation indicated that the major component in the mixture was $Me_3GeMn(CO)_5$, other components including $Mn_2(CO)_{10}$ and (perfluoro-1-cyclobutenyl)pentacarbonylmanganese. Chromatography on florisil and elution with hexane separated $Me_3GeMn(CO)_5$ (47% recovery) and the perfluorocyclobutenyl compound (3%), both identified by their infrared spectra and R_f values on TLC plates. Small amounts of white crystals were also obtained, these being identified as 1-(trimethylgermyl)-2-(pentacarbonylmanganese)perfluorocyclobutane, $\mathrm{Me_3Ge\overline{CFCF_2CF_2C}FMn(CO)_5}$ (yield 0.019 mmol, 0.8%; m.p. 106° dec.). (Found: C, 30.98; H, 1.79; F, 24.30. $\mathrm{C_{12}H_9F_6GeMnO_5}$ calcd.: C, 30.05; H, 1.90; F, 23.95%.)

(ii). *With (trimethylsilyl)pentacarbonylmanganese.* (Trimethylsilyl)pentacarbonylmanganese (0.88 g, 2.85 mmol) in 2 ml of pentane and 9.6 mmol of perfluorocyclobutene were sealed in a silica tube and allowed to react under UV at 25° for 24 h. The volatile compounds collected under vacuum were carbon monoxide (0.9 mmol, 30%) as uncondensed gas, perfluorocyclobutene and pentane (total 3.7 mmol) in the −196° trap, pentane in the −78° trap, fluorocarbon polymer and pentane in the −23° trap, all identified from their infrared spectra. No trimethylfluorosilane was observed. Both TLC and the infrared spectrum of the remaining yellow reaction mixture showed that it was mainly starting material, and chromatographic separation gave $\mathrm{Me_3SiMn(CO)_5}$ (0.56 g, 65% recovery), $\mathrm{Mn_2(CO)_{10}}$ (25 mg, 0.65 mmol, 5% conversion) and (perfluorocyclobutenyl)pentacarbonylmanganese (25 mg, 2.4% yield), all identified by their infrared spectra.

(e). *Reaction of perfluoro-2-butyne with metal–manganese bonded compounds*

(i). *With (trimethylgermyl)pentacarbonylmanganese.* (Trimethylgermyl)pentacarbonylmanganese (1.02 g, 3.34 mmol) in 5 ml of pentane, and hexafluorobutyne (11.2 mmol) were sealed in a silica tube and irradiated under UV at 35° for 48 h.

Carbon monoxide (0.5 mmol), pentane, and hexafluoro-2-butyne were removed on the vacuum line, leaving a black wax. in the tube. Hexane was added to the methylene chloride extract of the reaction mixture after the insoluble black grease had been removed by centrifugation. On cooling this extract, brown crystals formed, which were filtered off and purified by two sublimations at 50°/0.01 mmHg onto a water cooled probe, followed by recrystallization from methylene chloride/hexane mixture to afford white crystals of 1,2,3,4-tetrakis(trifluoromethyl)-3-(pentacarbonylmanganese)-4-(trimethylgermyl)cyclobutene, $\mathrm{Me_3Ge\overline{C(CF_3)\text{–}C(CF_3)\text{=}C(CF_3)\text{–}C}(CF_3)Mn(CO)_5}$ (m.p. 118–120°). (Found: C, 30.97; H, 1.30; F, 34.60; mol.wt., 650. $\mathrm{C_{16}H_9F_{12}GeMnO_5}$ calcd.: C, 30.75; H, 1.30; F, 34.95%; mol.wt., 626.)

The residue was separated on a florisil column, eluting with hexane, the first component being a red oil (20 mg) which was shown by its infrared spectrum to be a mixture of $\mathrm{Me_3GeMn(CO)_5}$ and a new compound, which had a single ^{19}F NMR peak at 55.9 ppm with respect to Freon-11. Its infrared spectrum showed an absorption due to C=C at 1550 cm^{-1}, as well as peaks due to $\mathrm{Mn(CO)_5}$ and $\mathrm{Me_3Ge}$ groups. Due to the similarity of its physical properties to those of $\mathrm{Me_3GeMn(CO)_5}$ further purification was not possible but the above spectroscopic features suggested that it was 2-(trimethylgermyl)-3-(pentacarbonylmanganese)hexafluoro-2-butene. $\mathrm{Me_3Ge(CF_3)C{=}C(CF_3)M(CO)_5}$. The other component separated chromatographically was the above cyclobutene derivative, identified by its infrared spectrum. Total yield 0.6 g, 28%.

(ii). *With (trimethylsilyl)pentacarbonylmanganese.* (Trimethylsilyl)pentacarbonylmanganese (0.16 g, 0.6 mmol) in 1 ml pentane. and 9.8 mmol of hexafluoro-2-butyne were sealed in a silica tube and allowed to react under UV at 35° for 35 h.

On opening the tube in vacuum, carbon monoxide (0.35 mmol), pentane, and hexafluoro-2-butyne were removed as volatile compounds. A small amount of brown crystals was trapped in a 0° trap, and was combined with the residue in the tube. Most of the grease was centrifuged off from the methylene chloride extract of the reaction mixture, and then hexane was added to it. On cooling and reducing the amount of solvent, brown crystals separated which were recrystallized from hexane/methylene chloride mixture to give white crystalline 1,2,3,4-tetrakis(trifluoromethyl)-3-(pentacarbonylmanganese)-4-(trimethylsilyl)cyclobutene, $Me_3Si(CF_3)\overline{C{-}C(CF_3){=}C(CF_3)C}(CF_3)Mn(CO)_5$, in 14% yield. (Found: C, 32.30; H, 1.40; F, 38.38; mol. wt., 589. $C_{16}H_9F_{12}MnO_5Si$ calcd.: C, 32.35; H, 1.52; F, 38.50%; mol.wt., 592.)

On chromatographing a solution of the residue on florisil with hexane as eluant, a red oil was first obtained which from its infrared spectrum was a mixture of $Me_3SiMn(CO)_5$ and a new compound which has similar infrared C–F stretching absorptions as the red oil obtained in the analogous reaction with $Me_3GeMn(CO)_5$. It had a single ^{19}F NMR peak at +56 ppm relative to $CFCl_3$ and a methyl proton NMR peak at +5.12 ppm relative to methylene chloride. Complete characterization of this red oil was not possible since it could not be purified free from $Me_3SiMn(CO)_5$, which had similar physical properties. The spectroscopic data suggested that it was 2-(trimethylsilyl)-3-(pentacarbonylmanganese)hexafluoro-2-butene, $Me_3Si(CF_3)C{=}C(CF_3)Mn(CO)_5$.

(*f*). *Reaction of* 3,3,3-*trifluoropropyne and metal–manganese bonded compounds*

(i). *With (trimethylsilyl)pentacarbonylmanganese.* (Trimethylsilyl)pentacarbonylmanganese (0.6 g, 2.34 mmol) in 2 ml of hexane and 3,3,3-trifluoropropyne (7.7 mmol) were allowed to react under UV at 2° for 26 h. Carbon monoxide (0.5 mmol), 3,3,3-trifluoropropyne and solvent were removed in vacuum. The residue, a brown oil, was chromatographed on florisil and eluted, first with hexane and then with methylene chloride. The starting material was eluted as the first fraction (55% recovery), followed by a new compound which was recovered in small amounts as white crystals after sublimation at 25°/0.01 mmHg onto a water-cooled probe. Its ^{19}F NMR spectrum was composed of a doublet at 58.9 ppm (J 2 Hz), and the proton NMR spectrum showed a methyl proton peak at 0.45 ppm. Infrared absorptions due to the C=C double bond and C–F groups were observed, as well as absorptions for $Mn(CO)_5$ and Me_3Si. These data suggest that the product may be $Me_3SiC_2H(CF_3)Mn(CO)_5$.

The third chromatographic fraction was a brown oil, from which colourless crystals were recovered after sublimation at 25°/0.01 mmHg on to a −78° probe. The ^{19}F and proton NMR spectroscopic studies suggested that the compound was formed by insertion of trimerised propyne into the Si–Mn bond (see Discussion). Its mass spectrum showed peaks due to $(CF_3C_2H)_3^+$, $Mn(CO)_5^+$ and Me_3Si^+. Analytical data confirmed that it was $Me_3Si[CHC(CF_3)]_3Mn(CO)_5$. (Found: C, 37.66; H, 2.35; F, 29.63; mol.wt., 598. $C_{17}H_{12}F_9MnO_5Si$ calcd.: C, 37.20; H, 2.19; F, 31.05%; mol.wt., 550.)

(ii). *With (trimethylgermyl)pentacarbonylmanganese.* (Trimethylgermyl)pentacarbonylmanganese (0.46 g, 1.62 mmol) in 8 ml of pentane and 3,3,3-trifluoropropyne (8 mol) were sealed in a silica tube and allowed to react under UV irradiation at 2° for 42 h. Carbon monoxide, unreacted propyne, and solvent were removed in vacuum as volatile compounds, leaving a black grease which on chromatographic separation on florisil, eluting first with hexane then with methylene chloride, afforded four compounds. The first fraction was $Me_3GeMn(CO)_5$ (30% recovered) followed by a small amount of a yellow oil, whose C–F stretching region in the infrared spectrum was similar to that of the compound $Me_3SiC_2H(CF_3)Mn(CO)_5$ prepared above. This compound was therefore tentatively identified as $Me_3GeC_2H(CF_3)Mn(CO)_5$. The third fraction was a small amount of a yellow wax, whose infrared spectrum showed absorption due to the presence of the C=C double bond, Me–Ge and C–F groups. However, its C–F stretching absorptions were different from those observed in either $Me_3SiC_2H(CF_3)Mn(CO)_5$ or $Me_3Si(CHCCF_3)_3Mn(CO)_5$, so that the assignment of structure by infrared spectroscopic methods was not possible, and since only a small amount was obtained, analytical data are not available. The fourth chromatographic fraction, which eluted with methylene chloride, was a yellow solid which afforded white crystals after sublimation at 23°/0.01 mmHg onto a water-cooled probe. Its infrared spectrum showed a C=C double bond absorption at 1620 cm^{-1}, and C–F stretching absorptions which were similar to those of $Me_3Si(CHCCF_3)_3Mn(CO)_5$. Microanalytical data confirmed that it was $Me_3Ge(CHCCF_3)_3Mn(CO)_5$. M.p. 95–96°. (Found: C, 35.05; H, 2.16; F, 28.72. $C_{17}H_{12}F_9GeMnO_5$, calcd.: C, 34.40; H, 2.04; F, 28.60%.)

RESULTS AND DISCUSSION

The reaction of tetrafluoroethylene with $Me_3SiMn(CO)_5$ under ultraviolet irradiation gave the insertion compound $Me_3SiC_2F_4Mn(CO)_5$ as expected[4,5]. No trimethylfluorosilane or (perfluoroalkyl)pentacarbonylmanganese was formed. In the analogous reaction of $Me_3SnMn(CO)_5$[5], in addition to the insertion compound, large quantities of $C_5F_9Mn(CO)_5$, $CF_2{=}CFMn(CO)_5$, $[CF_2{=}CFMn(CO)_4]_2$ and trimethyltin fluoride were also obtained. In the case of $Me_3GeMn(CO)_5$[4], only the insertion product and $C_5F_9Mn(CO)_5$ were formed. A spectroscopic examination indicates few differences between the C_2F_4 derivatives. Thus, for $Me_3MC_2F_4Mn(CO)_5$, M=Si, Ge or Sn, $\nu(C{\equiv}O)$ in the infrared spectra are observed at 2125 m, 2025 vs, 2003 s cm^{-1} for M=Si, at 2147 m, 2068 vs, 2006 vs cm^{-1} for M=Ge; and at 2140 m, 2036 vs, 2007 s cm^{-1} for M=Sn. The C–F stretching absorptions are at 1065 s, 1020 s, 1000 s and 975 s cm^{-1} for M=Si; at 1084 s, 1022 s, 1005 s, and 985 s cm^{-1} for M=Ge; and 1113 m, 1022 s, 1012 s and 993 s cm^{-1} for M=Sn. The proton spectra (Table 1) all show the expected methyl proton peaks with the chemical shifts decreasing in the order Ge > Si > Sn, as expected from the electronegativities of these Group IV elements[10]. The ^{19}F NMR spectra (Table 1) each consist of two singlets

TABLE 1

NMR DATA[a] FOR TETRAFLUOROETHYLENE DERIVATIVES, $Me_3MCF_2^{\beta}CF_2^{\alpha}Mn(CO)_5$

Compound	*δ(CH₃)*	*J(M–H)(Hz)*	*F^α*	*F^β*	*Ref.*
M=Si	−0.36		+55.3	+110	This work
Ge	−0.43		+53.3	+104.7	4
Sn	−0.32	58	+52.5	+100.9	5

[a] Chemical shifts relative to TMS for proton NMR, and to CFCl for ^{19}F data.

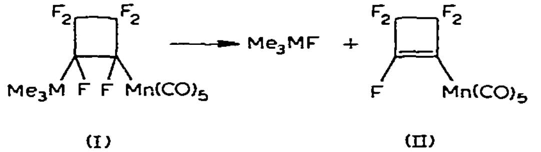
with the chemical shifts decreasing in the order Si > Ge > Sn. The broader singlet at lower field is assigned to the CF$_2$ group α to the Mn(CO)$_5$ group[11].

The reaction of Me$_3$SiMn(CO)$_5$ with trifluoroethylene proceeded much further toward completion than did the analogous reaction with tetrafluoroethylene, with the compound *cis*-CFH=CFMn(CO)$_5$ being the major product[4,5]. Apparently the polar nature of trifluoroethylene not only assists the liberation of Me$_3$MF (M = Si, Ge, Sn) from the suggested[4,5] reaction intermediates Me$_3$MCFHCF$_2$Mn(CO)$_5$ but also facilitates the attack by trifluoroethylene on the slightly polar metal–metal bond[12]. In the present reaction, *trans*-CFH=CFMn(CO)$_5$ was not observed as a reaction product in contrast to its formation in the analogous reaction of Me$_3$SnMn(CO)$_5$ with trifluoroethylene[5].

Small quantities of Mn$_2$(CO)$_{10}$ and Me$_3$SiCF=CFMn(CO)$_5$ were also obtained, the latter apparently being formed by the elimination of hydrogen fluoride from the insertion compound Me$_3$SiCFHCF$_2$Mn(CO)$_5$. The similarity of its infrared spectrum, particularly the C–F stretching frequencies, to those[5,15] of *trans*-CFH=CFMn(CO)$_5$ and *trans*-Me$_3$SiCF=CFH, suggest that this compound probably has the *trans* configuration.

Perfluoropropene with Me$_3$SiMn(CO)$_5$ gave (*cis*-perfluoropropenyl)pentacarbonylmanganese, *cis*-CF$_3$CF=CFMn(CO)$_5$. Trimethylfluorosilane was detected spectroscopically[14] as a volatile product. No *trans*-CF$_3$CF=CFMn(CO)$_5$ was observed, though it has been prepared previously[15,16] and probably has a higher stability, since the *trans* isomer of the similar compound CF$_3$CCl=CFMn(CO)$_5$[9] has a higher thermodynamic stability than the *cis* isomer. However, both *cis* and *trans* isomers of CF$_3$CF=CFMn(CO)$_5$ were formed in the analogous reactions[4,5] of Me$_3$SnMn(CO)$_5$ and Me$_3$GeMn(CO)$_5$.

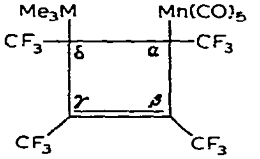
In reactions of perfluorocyclobutene, pure insertion products are observed in many cases, but elimination reactions may also occur[17] so as to form a stable olefinic compound. As in the case[6] of Me$_3$SnMn(CO)$_5$, the ultraviolet-assisted reaction of perfluorocyclobutene with the silicon and germanium analogues gave (perfluorocyclobutenyl)pentacarbonylmanganese as the major product. It has been suggested[6] that this is formed by the β-elimination of Me$_3$MF from *trans* insertion products, Me$_3$MCFCF$_2$CF$_2$CFMn(CO)$_5$:



(I) (II)

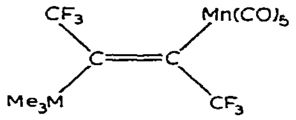
In the reaction with Me$_2$GeMn(CO)$_5$, a very small amount of the insertion compound (I) (M = Ge) was isolated. Its infrared spectrum showed absorptions due to Me$_3$Ge and Mn(CO)$_5$, as well as strong C–F stretching absorptions at 1198 and 1015 cm^{-1} in addition to those observed for (II). No peak attributable to ν(C=C) was observed, while the *E* mode of the carbonyl absorptions, observed at 2040 cm^{-1} for (II), showed a splitting of 16 cm^{-1} to two intense peaks at 2041 and 2025 cm^{-1}. A splitting of this magnitude may indicate that the Me$_3$Ge and Mn(CO)$_5$ groups are close to one another[18] and hence, in light of the above data, that the compound has structure (I).

Perfluoro-2-butyne, C_4F_6, has been reported[6] to give products containing one or two C_4F_6 units with $Me_3SnMn(CO)_5$ and $Me_3MFe(CO)_2$ (π-C_5H_5) (M=Si, Ge, Sn). The present reaction of C_4F_6 with $Me_3MMn(CO)_5$ (M=Si, Ge) gave similar results, with the compounds (III) containing two units of butyne as the main products. Other oily products which could not be obtained pure had ^{19}F NMR spectra and C–F infrared stretching patterns which suggested that they were the 1/1 insertion compounds (IV). The compound where M=Sn was also obtained in the analogous reaction[6] of $Me_3SnMn(CO)_5$ and C_4F_6.



(III)

M=Si, Ge or Sn



(IV)

Although both C–F and carbonyl stretching frequencies (Table 2) of the compounds (III) are independent of the nature of M, and indeed are remarkably similar, the double bond stretching frequencies decrease slightly in the order Si > Ge > Sn. The compounds (III) may exist as *cis* and *trans* isomers but the available data provide no distinction between them. The ^{19}F NMR spectra of compounds (III) consist of four peaks of equal intensity, two of which were singlets and the other two quartets (Table 3). Since the peaks to highest field are affected most by changing M, and

TABLE 2

SOME INFRARED SPECTROSCOPIC DATA FOR PERFLUORO-2-BUTYNE DERIVATIVES

Assignment	*Compound (III)*[a]			*Compounds (IV)*[a]		
	Si	*Ge*	*Sn*	*Si*	*Ge*	*Sn*[b]
ν(CO)	2127 m	2125 m	2140 m	2035 w	2025 w	2080 w
	2073 m	2069 m	2085 m	2020 m	2020 m	
	2056 s	2054 vs	2065 s	1978 m	2005 m	2000 s
	2027 s	2027 vs	2038 vs	1958 w	1972 m	1980 s
	2011 s	2013 s	2022 vs			
ν(C=C)	1615 w	1610 w	1602 w	1550 w	1560 m	1530 m
ν(C–F)	1295 s	1295 m	1297 w	1270 (sh)	1270 (sh)	1255 (sh)
	1238 vs	1240 vs	1240 vs	1242 s	1245 s	1238 s
	1190 m	1195 s	1197 s	1212 w	1210 w	1207 s
		1181 (sh)	1185 (sh)	1162 m	1163 w	1190 m
	1167 m	1160 vs	1160 vs	1142 m	1143 m	1150 vs
	1145 vs	1133 m	1133 m	1120 m	1120 m	1130 vs
	1128 m	1110 m	1110 m	1060 s	1058 s	1117 vs
	1108 m	1090 (sh)		1030 (sh)	1030 (sh)	1035 w
						1010 w

[a] See texts. [b] Obtained for a mixture with compound (III), M=Sn.

since the resonances at 53–54 ppm show a splitting due to coupling with ^{31}P when one carbon monoxide is replaced by triphenyl phosphite[19], these two resonances can be assigned to the δ-CF_3 and α-CF_3 groups respectively. The two quartets are therefore due to the β- and γ-CF group with J(F–F) 19 Hz. It is interesting that the chemical shifts for F (δ) decrease in the order Sn > Ge > Si, although the F–F coupling constants, not surprisingly, are unaffected by changing M.

TABLE 3

NMR DATA[a] FOR $Me_3MC(CF_3)C(CF_3)=C(CF_3)C(CF_3)Mn(CO)_5$

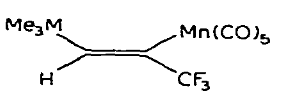
M	$\delta(CH_3)$	$F(\alpha)^c$	$F(\beta)^b$	$F(\gamma)^b$	$F(\delta)^c$	$J(F_\beta - F_\delta)(Hz)$
Si	−0.33	52.8	54.9	50.8	54.9	19
Ge	−0.6	53.9	55.0	51.1	56.0	19
Sn		53.8	56.9	51.0	60.7	19

[a] ^{19}F chemical shifts measured relative to CFCl (ppm); ^1H chemical shifts measured relative to TMS (ppm). [b] 1/3/3/1 quartet. [c] Singlet.

The second type of product, compounds (IV), show very similar C–F stretching patterns in their infrared spectra to that of the tin compound[6], which is believed to have the *trans* configuration since no F–F coupling is observed in the ^{19}F NMR spectrum[20]. The C=C stretching frequencies decrease in the order Ge > Si > Sn (Table 2). For M = Ge or Si, the ^{19}F NMR spectra surprisingly showed only a singlet. in contrast to that for M = Sn which has two singlets.

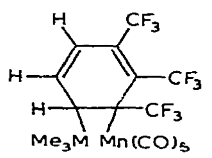
3,3,3-Trifluoropropyne, C_3F_3H, did not give an isolable compound from the reaction with $Me_3SnMn(CO)_5$[21], but with $Me_3SnFe(CO)_2(\pi\text{-}C_5H_5)$, it gave *cis*-$H(CF_3)C{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$, and with $Me_3MFe(CO)_2(\pi\text{-}C_5H_5)$, where M = Si, Ge, the insertion compounds *cis*-$Me_3MC_2H(CF_3)Fe(CO)_2Cp$ were obtained[6]. Apart from these 1/1 insertion products, this acetylene is also capable of forming derivatives containing more than one unit of acetylene. For example, $Co_2(CO)_4(CF_3C_2H)_3$ was obtained[22] when C_3F_3H was allowed to react with $Co_2(CO)_8$.

The reactions of $Me_3Mn(CO)_5$ (M = Si or Ge) with C_3F_3H, gave two compounds in each case, (V) and (VI). The first derivatives, (V), from their infrared spectra, each contain a fluorocarbon group, a manganese carbonyl moiety of C_{4v} symmetry, and an Me_3M group (M = Ge, Si). The carbonyl stretching frequencies of (V) (2130 w, 2060 w, 2030 s cm^{-1} for M = Si; 2125 m, 2070 w, 2030 vs cm^{-1} for M = Ge) are all higher than those[23] of the compound $CH_3(CF_3C{=}CH)Mn(CO)_5$, and are similar to those of $Me_3MC(CF_3){=}C(CF_3)Mn(CO)_5$. This suggests that the CF_3 group is more likely to be at the α position relative to the manganese carbonyl moiety. Moreover,



(V)

M=Si or Ge



(VI)

TABLE 4

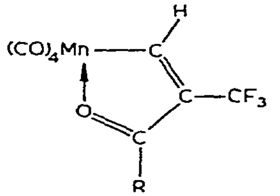
INFRARED SPECTRA^a OF 3,3,3-TRIFLUOROPROPYNE DERIVATIVES

A = $Me_3Ge(CHCCF_3)_3Mn(CO)_5$; B = $Me_3Si(CHCCF_3)_3Mn(CO)_5$; C = $Me_3Ge(CHCCF_3)Mn(CO)_5$; D = $Me_3Si(CHCCF_3)Mn(CO)_5$
s = strong; m = medium; w = weak; sh = shoulder; v = very.

Assignment	*A*	*B*	*C*	*D*	*Assignment*	*A*	*B*	*C*	*D*
CH asym. stretch	5060 w^b	2980 w	2960 w	2960 m	CF stretch	1010 w	1025 w		
			2920 w			955 w	1010 w		
CH sym. stretch	2840 w	2840	2840 w	2880			960 w		
			2780 w				920 vw		920 w
C≡O stretch^a	2175 m	2122 m	2125 m	2130 w			890 w	975 w	875 w
	2063 w	2066 w					870 m	850 w	
	2031 vs	2033 vs	2070 w	2060 w	MeM rock	830 m	841 m	830 m	840 s
		2011 s	2030 vs	2030 s		725 w	760 w	755 w	766 m
	2009 s							730 w	
	1963 w		1995 m	1960 m			790 w		
			1960 vw				750 vs		
C=C stretch	1625 w	1625 m	1740 vw	1740 w			735 vw		
	1560 vw		1635 vw	1640 w			725 w		
	1540 vw			1615 w		690 w	690 w		690 (sh)
CH stretch	1400 m	1400 m	1410 w	1405 w	M–CO	660 s	660 s	660 s	675 (sh)
		1252 (sh)				650 s	650 s		660 s
	1350 vw			1250 s	M–C stretch^b			640 m	
CF stretch	1310 w	1320 m	1310 w	1310 w		610 w	610 w	605 w	630 m
	1280 m	1285 m	1260 w	1250 s		550 w	580 w	570 w	545 w
	1245 m	1245 m	1230 m	1220 s			560 w	560 w	
	1235 m	1232 m	1215 s	1185 (sh)			550 w		
		1195 (sh)	1185 (sh)	1175 m	M–CF stretch^b	485 w	510 w	510 w	
	1170 vs	1170 s	1172 m	1150 m			485 w		
	1140 s	1140 m	1145 s	1145 s			475 w		
	1125 s	1130 m	1140 s	1130 (sh)			460 w		
	1110 m	1115 m	1125 m	1105 m	Mn–CO stretch^b	475 w	450 m	450 w	460 m
	1100 m	1100 m	1105 m	1040 w		450 m	445 (sh)	430 w	440 w
	1030 w	1060 w	1040 w						

^{a} Measured in cyclohexane. ^{b} Measured as nujol mull.

the ^{19}F chemical shift of (V) for $M=Si$ (58.9 ppm) is smaller than that for the compound (VII) (64.3 ppm[23]) again indicating that the CF_3 group must be at the α position with respect to the $Mn(CO)_5$ group[11]. Furthermore, the splitting of the ^{19}F



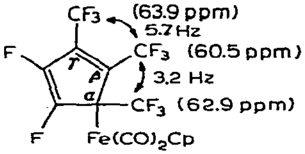
(VII)

R=H or CH$_3$

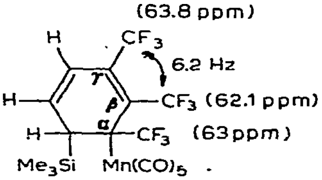
NMR signal by the proton (J 3 Hz) suggests that the CF_3 group is *cis* to hydrogen. All these facts support the formulation of the compounds as (V). The proton NMR spectra of (V) show only the resonances due to the methyl protons, the vinyl proton peaks being too weak to be observed.

The ^{19}F NMR spectrum of compound (VI) ($M=Si$) shows the presence of three different CF_3 groups. It consists of a quartet (δ 63.8 ppm; J 6.2 Hz) and two singlets at 63.0 and 62.1 ppm, of which the latter is broad, and appears to originate from a poorly resolved quartet. Since the infrared evidence shows that one of the CF_3 groups is α to $Mn(CO)_5$, and since the mass spectrum shows a strong peak due to $(CF_3CCH)_3^+$ suggesting the presence of a six-membered ring, the coupling of the two CF_3 groups implies that they are *cis* to each other with respect to a double bond. Furthermore, if the broadening of the quartet into a broad singlet is due to the close proximity of that CF_3 group to the manganese atom, then the only possible structure for the compound is (VI).

Compound (VIII) contains the same $-C(CF_3)=C(CF_3)-C(CF_3)M$ structural system[6], and it is interesting to find that in both compounds the ^{19}F chemical shifts



(VIII)



(VI) (M=Si)

decrease in the order of F(γ), F(α), F(β). The F(γ)–F(β) coupling of (VIII) is lower than that of (VI) ($M=Si$) while the F(α)–F(β) coupling of (VIII) is the larger. The infrared spectra of the other derivatives (VI) are also consistent with this structure.

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