REACTIVITY OF METAL–METAL BONDS
VI*. CLEAVAGE REACTIONS OF (TRIMETHYLTIN)PENTACARBONYL-MANGANESE

M. R. BOOTH, D. J. CARDIN, N. A. D. CAREY, H. C. CLARK AND B. R. SREENATHAN

Department of Chemistry, University of Western Ontario, London (Canada)

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SUMMARY

The cleavage reactions of $(CH_3)_3SnMn(CO)_5$ with chlorine, iodine, hydrogen chloride, hydrogen bromide, hydrogen iodide, iodine monochloride, and trifluoro-iodomethane are described, as well as some similar reactions of $(C_2H_5)_3PbMn(CO)_5$. The results are compared with analogous reactions of other metal–metal bonded organometallic compounds. Boron trifluoride with $(CH_3)_3SnMn(CO)_5$ gave $[(CH_3)_2-SnMn(CO)_5]BF_4$, the same compound also being formed from silver tetrafluoro-borate and $Cl(CH_3)_2SnMn(CO)_5$. The analogous hexafluorophosphate and hexa-fluoroarsenate salts containing the $[(CH_3)_2SnMn(CO)_5]^+$ ion could not be obtained from similar reactions. The preparations of $CF_3(CH_3)_2SnMn(CO)_5$ and $[(CH_3)_2-SnMn(CO)_5]BF_3CF_3$ are described, but the reaction of sodium tetraphenylborate with $Cl(CH_3)_2SnMn(CO)_5$ gave $C_6H_5(CH_3)_2SnMn(CO)_5$ and not the expected tetra-phenylborate salt. The infrared spectra of $[(CH_3)_2SnMn(CO)_5]BF_4$ and the related $BF_3CF_3^-$ salt are very similar to those of their trimethyltin analogues, and their probable pentacoordinate structures are discussed.

INTRODUCTION

In previous papers, we have described some insertion reactions involving the $Sn–Sn^{2,3}$, $Sn–Mn^{3,4}$, $Ge–Mn^5$, and $Sn–Fe^6$ bonds. While cleavage of the metal–metal bond and insertion of multiple-bonded reagents such as olefins, acetylenes, and sulfur dioxide occurs readily, there are other sites of potential chemical reactivity in the organometallic compounds concerned. These are of the type $R_3M–M'(CO)_n$, *e.g.* $(CH_3)_3SnMn(CO)_5$, $(C_2H_5)_3GeFe(CO)_2(\pi-C_5H_5)$ etc. Clearly, the metal–carbon bonds are also sites of possible chemical reaction and there is considerable interest in determining the factors which distinguish between these various potential sites in a particular reaction. To date, insufficient study has been given to reactions in which there is competition between cleavage of metal–metal and metal–carbon bonds to allow meaningful conclusions to be drawn. Thus the metal–metal bonds of (triphenyl-lead)pentacarbonylrhenium[7], (π-cyclopentadienyldicarbonyliron)pentacarbonyl-rhenium[7], and hexamethylditin[8] are known to be cleaved by chlorine, bromine, and

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* For Part V see ref. 1.

hydrogen chloride. On the other hand, the metal–metal bonds of (triphenyltin)penta-carbonylmanganese[9], (triphenyltin)pentacarbonylrhenium[7], diphenyltinbis(penta-carbonylrhenium)[7] and (triphenyltin)-π-cyclopentadienyldicarbonyliron[7] are un-affected by chlorine or hydrogen chloride, and cleavage of the metal–alkyl (or –aryl) bond occurs preferentially. Clearly the Pb–Re bond is more susceptible to cleavage than Sn–Re or Sn–Mn, but a more systematic study is required to appreciate fully the factors involved. Our previous studies[1–6] have shown that $(CH_3)_3SnMn(CO)_5$ is an extremely useful model system to explore the reactivity of organometallic compounds containing metal–metal bonds, and in this paper we describe some reactions of it with halogens and halides. The preparations of some salts containing the $(CH_3)_2SnMn(CO)_5^+$ cation are also described.

EXPERIMENTAL

Standard high-vacuum techniques were employed in the handling of volatile compounds. The conditions and procedures employed to conduct reactions under thermal conditions or under ultraviolet irradiation have been described previously[1,4]. Infrared and NMR spectra (^1H and ^{19}F) were obtained with the instrumentation mentioned previously[3,6].

(Trimethyltin)pentacarbonylmanganese was prepared essentially by the pro-cedure of Clark and Tsai[4].

(Triethyllead)pentacarbonylmanganese was prepared by the method of Gor-sich[9], from dimanganese decacarbonyl (8 g, 0.02 mmole) and trimethyllead chloride (7 g, 0.021 mmole) with sodium amalgam. Vacuum distillation at 55–63° and 10^{-3} mm pressure gave (triethyllead)pentacarbonylmanganese (15 g, 85% yield), a yellow, light-sensitive liquid. (Found: C, 27.9; H, 3.23. $C_{11}H_{15}MnO_5Pb$ calcd.: C, 27.0; H, 3.07%.) A sample in an evacuated Pyrex tube, darkened and deposited a metallic film, on exposure to daylight for several days. No such decomposition occurred in the dark, even after many months. Ultaviolet irradiation at 77° for 12 h caused exten-sive decomposition.

Reactions of (trimethyltin)pentacarbonylmanganese, (I)

(*a*). Chlorine (6.5 mmole) and (I) (0.502 g, 1.44 mmole) and pentane (10 ml) were left at 25° for 2 days. Trimethyltin chloride (1.07 mmole, 76%), identified by its infrared and NMR spectra was removed, to leave a bright yellow solid in the reaction tube. This was identified from its infrared spectrum[10] as pentacarbonylmanganese chloride, $(CO)_5MnCl$, (0.81 mmole, 59%). Incomplete reaction was due to the con-sumption of chlorine in the photochemical chlorination of pentane.

(*b*). Iodine (1.7 mmole) and (I) (1.73 mmole) were sealed with pentane in a Pyrex tube. An orange solid formed slowly, and after 12 h at 25°, the iodine had disappeared. Trimethyltin iodide (1.28 mmole, 75%) and pentacarbonylmanganese iodide (1.7 mmole, 100%) were separated and identified spectroscopically[10].

Similar products were obtained from a reaction involving the ultraviolet irradiation of iodine and (I) in pentane, although some carbon monoxide was also evolved.

(*c*). (*i*). Hydrogen chloride (1.44 mmole) and (I) (1.4 mmole) were sealed with pentane (10 ml) in a Carius tube and heated at 110° for 6 days. A slightly soluble white

solid formed during the first 36 h and this did not visibly increase in amount during the remaining reaction time. The volatile products were carbon monoxide (0.1 mmole), unreacted (I) (15% recovered), pentane, and a trace of hydrogen chloride. Sublimation at 60° of the remaining solid gave (chlorodimethyltin)pentacarbonylmanganese (71% yield). (Found: C, 22.14; H, 1.66. $C_7H_6ClMnO_5Sn$ calcd.: C, 22.16; H, 1.58%.) Involatile manganese(II) chloride (6 mg) remained.

(c). (ii). Hydrogen chloride (2.82 mmole) and (I) (1.39 mmole) were heated in a sealed tube at 60° for one week. White crystals slowly formed which on sublimation gave (dichloromethyltin)pentacarbonylmanganese, $Cl_2CH_3SnMn(CO)_5$, m.p. 109–110°. (Found: C, 18.26; H, 1.41. $C_6H_3Cl_2MnO_5Sn$ calcd.: C, 18.10; H, 1.41%.) It is soluble in methylene chloride but only slightly soluble in nonpolar solvents.

(c). (iii). A large excess of hydrogen chloride was heated with (I) in pentane at 80° for 72 h. The only product was identified as (dichloromethyltin)pentacarbonylmanganese.

(d). Hydrogen bromide (2.88 mmole) and (I) (2.88 mmole) with pentane were sealed, and heated at 71° for 49 h. On cooling the solution, white crystals formed, from which the solvent containing unreacted (I) was decanted. Recrystallization of the residue from pentane gave (bromodimethyltin)pentacarbonylmanganese, $Br(CH_3)_2SnMn(CO)_5$, m.p. 81–82°, 21% yield. (Found: C, 18.7; H, 1.2; Br, 19.0. C_7H_6-$BrMnO_5Sn$ calcd.: C, 18.9; H, 1.4; Br, 19.0%.)

(e). Anhydrous hydrogen iodide (1.81 mmole), prepared from iodine and tetrahydronaphthalene[11], (I) (1.76 mmole) and pentane were heated at 71° for 48 h. Removal of the volatiles, followed by recrystallization, gave white (iododimethyltin)-pentacarbonylmanganese, $I(CH_3)_2SnMn(CO)_5$, m.p. 58–60°, 73% yield. (Found: C, 17.7; H, 1.52; I, 27.3. $C_7H_6IMnO_5Sn$ calcd.: C, 17.9; H, 1.28; I, 27.1%.) This compound is relatively stable in air, and shows no thermal decomposition up to 130°.

(f). Freshly sublimed iodine monochloride (0.5 g, 3.0 mmole) and (I) (3.0 mmole) were dissolved in pentane and left for 12 h at room temperature. Vacuum fractionation gave a mixture of trimethyltin chloride and trimethyltin iodide, characterized by typical infrared absorption peaks at 780, 540 and 510 cm^{-1}. This mixture could not be separated by vapor phase chromatography; and it was also found impossible to separate a mixture of the authentic compounds by this means. In the proton NMR spectrum, this mixture showed a single peak at τ 9.25 in chloroform. Trimethyltin chloride shows a peak at τ 9.38, and trimethyltin iodide one at τ 9.12 ppm also in chloroform, an authentic mixture showed just one peak, intermediate in position between the peaks of the separate compounds.

The remaining solid was fractionally sublimed to give pentacarbonylmanganese iodide, (chlorodimethyltin)pentacarbonylmanganese, and tetracarbonylmanganese iodide dimer identified by its infrared spectrum[12]. A small amount of manganese(II) iodide remained in the sublimation apparatus.

(g). Trifluoroiodomethane (15.9 g), used as both solvent and reactant, and (I) (0.944 g) were exposed to ultaviolet irradiation for 48 h at 25°. Carbon monoxide (1.97 mmole, 12%), hexafluoroethane (0.3 g) and trifluoroiodomethane (15.02 g) were recovered as volatiles, together with trimethyltin iodide (0.3 g, 40%) identified by its infrared and proton NMR spectra. Pentacarbonylmanganese iodide (0.108 g, 13%) was separated from the residue by fractional sublimation, as well as (iododimethyltin)-pentacarbonylmanganese (0.4 g, 30%).

Reactions of (triethyllead)pentacarbonylmanganese, (II)

(a). Chlorine (1.44 mmole), (II) (1.44 mmole) and pentane were kept in the dark for 12 h at 25°. Unreacted (II) (39%) was removed with pentane to leave yellow, crystalline (chlorodiethyllead)pentacarbonylmanganese, $Cl(C_2H_5)_2PbMn(CO)_5$, 57% yield. (Found: C, 21.1; H, 2.13. $C_9H_{10}ClMnO_5Pb$ calcd.: C, 21.8; H, 2.02%.) The compound decomposed at 135° without melting, and slowly decomposed in light and air. It is slightly soluble in carbon tetrachloride, but insoluble in hydrocarbons.

(b). Iodine (2.88 mmole), (II) (0.96 mmole) and pentane were allowed to react at 25° in the dark. The iodine color disappeared rapidly and reaction appeared to be complete after 2 h. Sublimation of the yellow residue, following removal of the volatiles, gave pentacarbonylmanganese iodide, identified spectroscopically[10], and lead(II) iodide.

(c). Hydrogen chloride (1.44 mmole) and (II) (1.44 mmole) in pentane, were allowed to react in the dark for 12 h at 25°. Pentane extraction of the resulting yellow solid gave unreacted (II) (5%) and (chlorodiethyllead)pentacarbonylmanganese (90%).

A reaction in which the molar ratio of HCl/(II) was 2/1 gave $(CO)_5MnCl$, $Cl(C_2H_5)_2PbMn(CO)_5$ and lead(II) chloride.

Reaction of (trimethyltin)pentacarbonylmanganese with boron trifluoride

Boron trifluoride (0.414 g, 6.10 mmole) and (I) (0.701 g, 1.90 mmole) were sealed in a Pyrex tube and left for 14 days at 25°. Vacuum fractionation gave a gaseous mixture containing unreacted BF_3, CH_3BF_2, and traces of $(CH_3)_2BF$, the latter two compounds being identified by their infrared absorptions[13]. The remaining solid was extracted with dry petroleum ether (60–80°) to give unreacted (I) (0.019 g), leaving a pale yellow solid which was purified by vacuum sublimation at 90–110°, and identified as $(F_4B)(CH_3)_2SnMn(CO)_5$ (0.71 g, 86% yield). (Found: C, 20.11; H, 1.47; F, 16.03. $C_7H_6BF_4MnO_5Sn$ calcd.: C, 19.55; H, 1.42; F, 17.87%.) The compound is very hygroscopic, and on heating in vacuum at 150°, undergoes some decomposition, forming BF_3 and possibly $F(CH_3)_2SnMn(CO)_5$.

Reaction of (chlorodimethyltin)pentacarbonylmanganese with silver tetrafluoroborate

Silver tetrafluoroborate (0.463 g, 2.37 mmole) and $Cl(CH_3)_2SnMn(CO)_5$ (0.905 g, 2.37 mmole) were heated overnight in refluxing dry chloroform. The resulting purplish mixture was filtered, and the filtrate upon evaporation under vacuum afforded unreacted $Cl(CH_3)_2SnMn(CO)_5$ (25.1%). Sublimation of the residue under vacuum yielded yellow, crystalline $(F_4B)(CH_3)_2SnMn(CO)_5$, m.p. 138°. (Found: C, 19.93; H, 1.82. $C_7H_6BF_4MnO_5Sn$ calcd.: C, 19.55; H, 1.42%.)

Reaction of (chlorodimethyltin)pentacarbonylmanganese with silver hexafluoroantimonate

An equimolar mixture of silver hexafluoroantimonate and the tin–manganese compound was heated overnight in refluxing dry chloroform. Attempts to separate the reaction products by extraction with methanol (distilled directly after magnesium drying) or with other dry solvents led to either decomposition or further reaction. The resulting product after removal of all solvent, was very hygroscopic, and attempts to obtain a pure product by sublimation gave only the original tin–manganese reactant. However, the infrared spectrum of the product showed absorptions substantially different from those of the reactants.

Reaction of (trimethyltin)pentacarbonylmanganese with phosphorus pentafluoride

(*a*). In chloroform, phosphorus pentafluoride (700 mm pressure) was admitted to a solution of (I) in chloroform, contained in an NMR tube sealed onto a vacuum system. The solution turned a very pale yellow and a slight turbidity was observed; after 2 h the excess phosphorus pentafluoride was removed, and the tube cooled (−196°) and sealed. The ^{19}F NMR spectrum showed two quartets, (coupling ~7 Hz) with centres separated by 970 Hz, as well as other peaks.

(*b*). Without solvent, compound (I), (1.15 g, 3.2 mmole) was placed in a stainless steel autoclave, and phosphorus pentafluoride (0.5 g, 3.9 mmole) was condensed in a vacuum system. The vessel was maintained at 30° (24 h). Volatiles were removed in vacuum, affording phosphorus pentafluoride, (0.5 g, 100%); the vessel was then heated to 100°, and (I), (1.1 g, 95.5%) was recovered as a colorless sublimate.

Preparation of [(trifluoromethyl)dimethyltin]pentacarbonylmanganese

Dimanganese decacarbonyl (4.7 g) and sodium amalgam (1.3 g sodium in 150 g mercury) were allowed to react in 150 ml of dry tetrahydrofuran. The solution was added to a solution of (trifluoromethyl)dimethyltin chloride[14] in tetrahydrofuran (100 ml) and stirred vigorously for an hour at room temperature. The solvent was then removed on a flash evaporator, to leave a green solid which was further extracted with petroleum ether (30–60°). Evaporation of this solution followed by sublimation at $24°/10^{-3}$ mm to a cold finger at −78° gave white crystalline [(trifluoromethyl)dimethyltin]pentacarbonylmanganese (7.5 g, 76% yield), m.p. 49°. (Found: C, 23.1; H, 1.65; F, 14.7; mol.wt., 450±20. $C_9H_6F_3MnO_5Sn$ calcd.: C, 23.3; H, 1.46; F, 13.8%; mol.wt., 412.) No decomposition occurred after 5 h at 90° under vacuum. The ^1H NMR spectrum gave a single line at τ 9.44 with $J(^{119}Sn–CH_3)$ 48.5 and $J(^{117}Sn–CH_3)$ 46.3 Hz, in benzene solution. The ^{19}F spectrum showed a single line at 46.56 ppm to high field of Freon 11 as external reference with $J(^{119}Sn–CF_3)$ 255 and $J(^{117}Sn–CF_3)$ 242 Hz.

Reaction of [CF₃(CH₃)₂Sn]Mn(CO)₅ with boron trifluoride
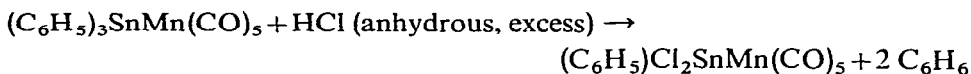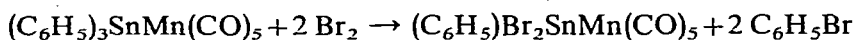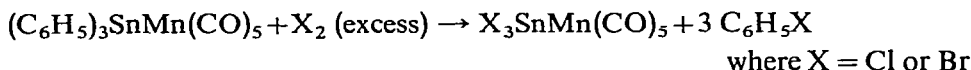
Boron trifluoride (2.34 mmole) and $CF_3(CH_3)_2SnMn(CO)_5$ (2.33 mmole) were allowed to react in carbon tetrachloride at 25° under reduced pressure in a 250-ml round-bottomed flask. After 15 h, all the BF_3 had been consumed, and the solution had become brown, with a green-brown precipitate. On filtering, under a dry nitrogen atmosphere an extremely air-sensitive green-colored residue was obtained. This was dissolved in the minimum volume of methylene dichloride and the solution then added dropwise to a large excess of pentane; a pale yellow solid slowly settled out of the solution. After 3 h, the pentane was decanted, and the final traces were removed from the solid by pumping. The product was $[(CH_3)_2SnMn(CO)_5]^+(BF_3CF_3)^-$ (0.47 g, 42.5% yield). (Found: C, 19.8; H, 1.52; B, 2.43; F, 24.2. $C_8H_6BF_6MnO_5Sn$ calcd: C, 20.0; H, 1.25; B, 2.25; F, 23.8%.) A solution in acetonitrile gave a molar conductance of 115 ohms$^{-1}\cdot$cm^2, this being of the right order of magnitude for a 1/1 electrolyte in acetonitrile[15]. The ^1H NMR spectrum, for a dichloromethane solution, showed a single line with no broadening at τ 8.93 ppm with $J(^{119}Sn–CH_3)$ 44.5 and $J(^{117}Sn–CH_3)$ 42.5 Hz.

Reaction of (chlorodimethyltin)pentacarbonylmanganese with sodium tetraphenyl-borate

(Chlorodimethyltin)pentacarbonylmanganese (2.1 g, 5.5 mmole) and sodium tetraphenylborate (2.0 g, 5.8 mmole) were heated (12 h) in refluxing tetrahydrofuran. After cooling to room temperature the solvent was removed in vacuum and the residue extracted with dichloromethane (35 ml). The white solid (2.7 g 85%) was filtered off, and identified as sodium chloride. The filtrate was evaporated to dryness in vacuum, and extracted with acetone (30 ml). The excess sodium tetraphenylborate was filtered off, and the acetone removed in vacuum. The residue was transferred to a sublimation apparatus and sublimation in vacuum afforded an upper layer of yellow needles, and a lower region of white prisms separated by a large region of mixed product. The two extreme portions were separated and resublimed (in the same apparatus) affording triphenylboron (0.16 g, 12.3%), m.p. 142°, and (dimethylphenyltin)pentacarbonylmanganese (0.80 g, 33.5%), m.p. 99–100°. The products were characterized further by their infrared and NMR spectra.

DISCUSSION

Gorsich[9] described the following reactions of (triphenyltin)pentacarbonylmanganese.

$$(C_6H_5)_3SnMn(CO)_5 + X_2 \text{ (excess)} \rightarrow X_3SnMn(CO)_5 + 3 C_6H_5X$$

$$\text{where } X = Cl \text{ or } Br$$

$$(C_6H_5)_3SnMn(CO)_5 + 2 Br_2 \rightarrow (C_6H_5)Br_2SnMn(CO)_5 + 2 C_6H_5Br$$

$$(C_6H_5)_3SnMn(CO)_5 + HCl \text{ (anhydrous, excess)} \rightarrow$$

$$(C_6H_5)Cl_2SnMn(CO)_5 + 2 C_6H_6$$

$$Cl_3SnMn(CO)_5 + 2 (C_6H_5)_3SnMn(CO)_5 \rightarrow 3 (C_6H_5)_2ClSnMn(CO)_5$$
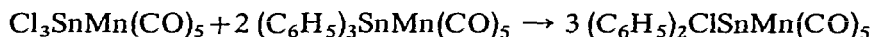
He also pointed out that "the point of attack in a tin–manganese compound by a specific electrophilic reagent is dependent on the type of organic radical attached to tin". Our present results confirm this in that the methyl analogue, $(CH_3)_3SnMn(CO)_5$ is readily cleaved by chlorine or iodine to give trimethyltin halide and pentacarbonylmanganese halide. There is no evidence in these reactions for the formation of compounds $X_n(CH_3)_{3-n}SnMn(CO)_5$ where $n = 1–3$. The cleavage of the Sn–Mn bond by chlorine and iodine in preference to the Sn–CH_3 bond contrasts with the behavior of $(C_6H_5)_3SnMn(CO)_5$ and is not readily explained. Even if possible kinetic and mechanistic effects are ignored, these results are still the reverse of those expected on the basis of relative bond energies. Thus, in compounds SnR_4, the mean bond dissociation energy[16] for R = CH_3 is 52.1 kcal/mole, whereas for R = C_6H_5, the value is 61.4 kcal/mole. There may, however, be some variation in the R_3SnMn bond energy as R is varied and this is supported by spectroscopic data[17]. Moreover, other workers[18,19] have suggested that the chromophoric properties of the C_6H_5–M–M group (M = Si, Ge, or Sn) can be explained, at least in part, in terms of a π-interaction, between the phenyl rings and the metal d-orbitals. The explanation may therefore lie in a strengthening of the Sn–Mn bond by phenyl, rather than in the relative Sn–CH_3 and Sn–C_6H_5 bond energies.

The reactions of the hydrogen halides with $(CH_3)_3SnMn(CO)_5$ resemble more closely those with its triphenyltin analogue. When a 1/1 molar ratio is used, the hydrogen halides, HX (X = Cl, Br or I), cleave a methyl group forming $X(CH_3)_2SnMn(CO)_5$. There is no cleavage of the Sn–Mn bond under either thermal or ultraviolet irradiation conditions. With hydrogen chloride in a 2/1 molar ratio, a second methyl group is readily removed giving $Cl_2(CH_3)SnMn(CO)_5$. However, suprisingly, excess HCl did not remove the last CH_3 group. This again contrasts with the behavior of $(C_6H_5)_3$-$SnMn(CO)_5$ from which all phenyl groups can be easily cleaved with chlorine. Hydrogen chloride cleavage of methyl from $(CH_3)_3SnMn(CO)_5$ becomes progressively more difficult and does not proceed beyond $Cl_2(CH_3)SnMn(CO)_5$.

In view of the above results, the observed cleavage of the Pb–Mn bond of $(C_2H_5)_3PbMn(CO)_5$ by chlorine or iodine is not unexpected. Hydrogen chloride, however, removed an ethyl group to give the monochloro derivative, $Cl(C_2H_5)_2$-$PbMn(CO)_5$. While electronic effects, such as π-interactions involving the metal atoms, may well be important in these simple cleavage reactions with halogens and hydrogen halides, the mechanistic aspects cannot be ignored. The most closely related systems for which kinetic parameters have been determined are those involving cleavage by halogen of the tin–tin bond in R_6Sn_2 compounds. Significantly, here also, the slower rate of reaction[20] with iodine, when R = phenyl, has been interpreted in terms of increased stabilization of the Sn–Sn bond due to π-interaction. It is also concluded that, for compounds $(C_6H_5)_3SnSnR_3$ (R = alkyl), electrophilic attack by iodine will preferentially occur at the tin atom bearing the alkyl groups. Both points may be relevant to the present observations.

(Trimethyltin)pentacarbonylmanganese also reacted with iodine monochloride but the products form a complex mixture. Both trimethyltin chloride and iodide were formed, and additionally, in this connection, the proton NMR spectra suggested that some rapid exchange process occurs in solution between these two halides. The other products were manganese carbonyl iodides and some (chlorodimethyltin)pentacarbonylmanganese. The latter is probably formed in a secondary reaction due to traces of hydrogen chloride, and the most interesting point is that no manganese carbonyl chloride was observed, all chloride appearing as trimethyltin chloride. In the similar reaction with trifluoroiodomethane, no (trifluoromethyl)-metallic derivative was produced, the principal products being trimethyltin iodide, (iododimethyltin)pentacarbonylmanganese, and pentacarbonylmanganese iodide.

The reaction of $(CH_3)_3SnMn(CO)_5$ with boron trifluoride surprisingly did not lead to cleavage of the tin–manganese bond. A tin–methyl bond was cleaved leading to the formation of CH_3BF_2 and $(CH_3)_2BF$, and interestingly (dimethyltin)-pentacarbonylmanganese tetrafluoroborate, $[(CH_3)_2SnMn(CO)_5]BF_4$. Presumably the fluoride $F(CH_3)_2SnMn(CO)_5$ is formed first but is rapidly converted to the tetrafluoroborate by the excess boron trifluoride. The same product can also be obtained by the reaction:

$$Cl(CH_3)_2SnMn(CO)_5 + AgBF_4 \rightarrow AgCl + [(CH_3)_2SnMn(CO)_5]BF_4$$
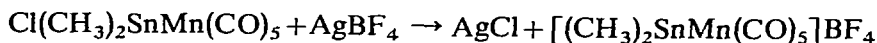
The compound is very hygroscopic and decomposes thermally above $150°$. The most interesting feature of this compound is its infrared spectrum, shown in Fig. 1. The similarity of this spectrum to that of trimethyltin tetrafluoroborate[21] is remarkable, although formally, the two compounds are, of course, closely related through the
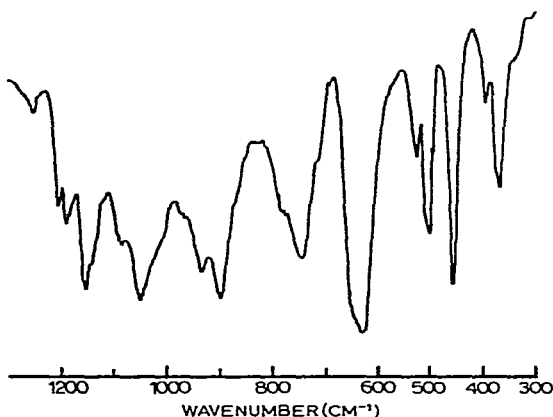
Fig. 1.

substitution of $Mn(CO)_5$ for a CH_3 group on tin. Many studies of trialkyltin compounds, particularly trimethyltin[21–24], provide strong evidence for co-ordinated structures in which anions such as ClO_4 and BF_4 interact strongly with planar $(CH_3)_3$-Sn. In this case also, the complete removal of the triple degeneracy of v_3 for BF_4, leading to the three strong absorptions at 900, 1055, and 1155 cm^{-1}, together with the appearance of the usually "forbidden" v_1, at 750 cm^{-1}, is consistent with C_{2v} symmetry for the BF_4 group. Again, also, weaker bands at 935, 1090, and 1190 cm^{-1} can be assigned to the ^{10}B–F stretching modes. All evidence is thus consistent with a structure involving bridging BF_4 groups. These strong splittings of usually degenerate infrared bands have been attributed by some authors[25] to solid state effects, particularly low site symmetry. Arguments against this have been presented elsewhere[26], and are further supported by the present results. It seems most unlikely that the same environment about BF_4 will be produced by such differently sized cations as $(CH_3)_3$-Sn^+ and $[(CH_3)_2SnMn(CO)_5]^+$ and a co-ordinated structure involving some degree of covalent bonding is clearly more acceptable.

    This is further supported by the infrared spectroscopic features of the product obtained from $Cl(CH_3)_2SnMn(CO)_5$ and silver hexafluoroantimonate, although since a pure compound was not isolated, the interpretation of these features is open to question. However, the spectrum was noticeably different from that of $Cl(CH_3)_2$-$SnMn(CO)_5$ itself, and similar to that described for trimethyltin hexafluoroanti-monate[21], so that it is reasonable to suppose that the product was chiefly a mixture of silver chloride and $[(CH_3)_2SnMn(CO)_5]SbF_6$. In the 400–1000 cm^{-1} region, absorption bands were observed at 935(m) and 911(m); 760(s) and 730(s, b); 697(s), 667(vs), and 647(vs); 540(w) and 512(m); and 470(s) with two shoulders at 490 and 457 cm^{-1}. By comparison with the spectrum[21] of trimethyltin hexafluoroantimonate, the 760 and 730 cm^{-1} bands can be assigned to methyl–tin rocking modes, the peaks at 697, 667, and 647 cm^{-1} to the triply split v_3 mode of SbF_6^- together with the carbonyl deformation modes, and the peaks at 540 and 512 cm^{-1} to the Sn–C stretching vibrations. The spectrum is thus consistent with interaction with the SbF_6 group so as to remove the three-fold degeneracy of the v_3 mode. Attempts to obtain the analogous $[(CH_3)_2SnMn(CO)_5]PF_6$ were even less successful.

Another reaction predicted to yield a salt containing the $[(CH_3)_2SnMn(CO)_5]^+$ cation, namely that between $Cl(CH_3)_2SnMn(CO)_5$ and sodium tetraphenyl borate instead gave decomposition products from the expected salt. Sodium chloride was separated in good yield, but instead of $[(CH_3)_2SnMn(CO)_5]B(C_6H_5)_4$, the other products were triphenylboron and (dimethylphenyltin)pentacarbonylmanganese:

$$Cl(CH_3)_2SnMn(CO)_5 + NaB(C_6H_5)_4 \rightarrow$$
$$NaCl + B(C_6H_5)_3 + (CH_3)_2C_6H_5SnMn(CO)_5$$
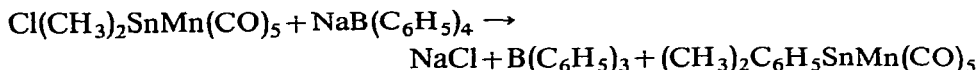
The extraction of $C_6H_5^-$ from the tetraphenylborate anion, presumably by $[(CH_3)_2SnMn(CO)_5]^+$ is also in agreement with our discussion above of the analogous tetrafluoroborate derivative.

A compound closely related to the above tetrafluoroborate was obtained by a similar reaction:

$$CF_3(CH_3)_2SnMn(CO)_5 + BF_3 \rightarrow [(CH_3)_2SnMn(CO)_5]CF_3BF_3$$
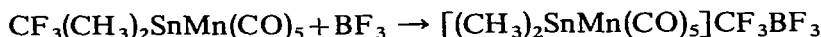
The compound $CF_3(CH_3)_2SnMn(CO)_5$ was readily obtained from sodium pentacarbonylmanganese(I) and (trifluoromethyl)dimethyltin chloride[14]. The above reaction is completely analogous to that[27] of $(CH_3)_3SnCF_3$:

$$(CH_3)_3SnCF_3 + BF_3 \rightarrow [(CH_3)_3Sn]CF_3BF_3$$
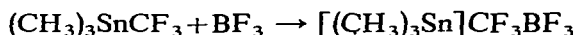
Apart from the formation of the $CF_3BF_3^-$ anion, a point of some interest concerns the infrared spectrum of $[(CH_3)_2SnMn(CO)_5]^+$ as compared with that of $(CH_3)_3SnMn(CO)_5$. Because of solubility problems, the solution infrared spectrum could only be examined in acetonitrile solution, which is not ideal for observing carbonyl stretching absorptions. Stretching modes due to B–F were observed at 1070(vs, br) and 1020(s), and those due to C–F stretching at 980(s) and 950(s) these being in agreement with these reported[27] for $BF_3CF_3^-$. Absorptions at lower frequencies, observed at 770(m), 720(w), 660(vs), 640(vs), 530(m), 512(m), 465(ms) and 385(m) cm^{-1} are fully consistent with $(CH_3)_2SnMn(CO)_5$. The lack of complexity in the carbonyl stretching region (2000–2150 cm^{-1}) is noticeable and the appearance of only two bands is consistent with, say C_{2v} symmetry, in which the Sn–Mn bond lies in the C–Sn–C plane, and in which the equatorial carbonyls are in the two vertical planes. It is also noticeable that removal of the CF_3 group to form the cation has not significantly changed the carbonyl frequencies, although such frequencies are known to be solvent dependent.

In view of the course of the reaction of boron trifluoride with $(CH_3)_3SnMn(CO)_5$, phosphorus pentafluoride might also be expected to react similarly to give $(CH_3)_2SnMn(CO)_5^+ PF_6^-$. Suprisingly, this product was not formed. When the reaction was carried out in chloroform, NMR spectroscopic evidence was obtained for the formation of methyltetrafluorophosphorane, CH_3PF_4. However, no reaction occurred between phosphorus pentafluoride and $(CH_3)_3SnMn(CO)_5$ at 30° in a stainless steel autoclave, in the absence of solvent. Apparently, the reaction observed in chloroform was due to traces of moisture, while under strictly anhydrous conditions at 30° these two compounds do not react.

The reaction of sulfur tetrafluoride with $(CH_3)_3SnMn(CO)_5$ was also examined but although some spectroscopic evidence for the formation of some methyl derivative

of a sulfur fluoride was obtained, other products in the complex reaction mixture could not be characterized.

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