bonds supported by bridging carbonyl groups. On the other hand, in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and $Mn_2(CO)_{10}$, bridging carbonyl groups are absent, and tin(II) chloride does not insert.[5]

It appeared that the importance of carbonyl bridges might be clarified by examining the behavior of the substituted cobalt carbonyl, $[(C_6H_5)_3PCo(CO)_3]_2$; this compound does *not* have bridging carbonyl groups[8] but presumably has an unsupported cobalt–cobalt covalent bond. Contrary to our expectation, the insertion product was formed, but only at higher temperatures and longer reaction times than sufficed for dicobalt octacarbonyl itself. However, this result cannot be taken as proof that tin(II) chloride can insert into a cobalt–cobalt bond unsupported by carbonyl bridges. A nonbridged form of $Co_2(CO)_8$ has been shown to exist in equilibrium with the bridged form in solution;[9] it is possible that a bridged form of the triphenylphosphine substitution product may also exist in solution, and the reaction could proceed *via* this form.

While one cannot conclude that carbonyl bridges are required for tin(II) halide and germanium(II) iodide insertion, the evidence suggests that reaction proceeds more readily when this is the case. The point of attack may well be the electron pair in the bent metal–metal bond generally assumed in the carbonyl-bridged derivatives. In this connection, it is interesting to note that the insertion of GeH_2 into $Mn_2(CO)_{10}$ has been suggested as a possible step in the reaction of germane with manganese pentacarbonyl hydride.[10]

Among the compounds described here are several with metal–metal bonds which do not appear to have been reported previously. Discussion of the infrared spectra will be deferred until completion of a detailed analysis and comparison with other related compounds.

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The Reactivity of Metal–Metal Bonds. II. The Tin–Manganese Bond[1]

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The reactions of trimethyltinpentacarbonylmanganese with tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, and ethylene are described. Only with tetrafluoroethylene is an adduct, namely, $(CH_3)_3SnCF_2CF_2Mn(CO)_5$, obtained, although trimethyltin fluoride and fluorocarbon–carbonylmanganese products are also formed. With trifluoroethylene and chlorotrifluoroethylene, trimethyltin halides and fluorovinylpentacarbonylmanganese compounds are produced, although in the latter case perfluoroacryloylpentacarbonylmanganese, $CF_2{=}CFCOMn(CO)_5$, is a major product. Ethylene does not cleave the Sn–Mn bond, but rather displaces carbon monoxide to form $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$. The spectroscopic properties of the new compounds are discussed.

Introduction

In the previous paper,[3] we discussed the behavior of hexamethylditin and polymeric diorganotin species with a series of fluoroolefins, whereby the considerable reactivity of the Sn–Sn bond toward homolytic fission under suitable free-radical conditions was revealed. We now consider the analogous behavior of the Sn–Mn bond as the first step in some studies of the reactivities of the bonds formed between group IV-A elements (Si, Ge, Sn, and Pb) and transition metals. Many factors will influence these reactivities, including the electron configuration of the transition metal, the bond polarity, and the nature of the other substituents on the two metal atoms. The importance of each of these factors has yet to be determined, since most studies of these metal–metal bonded compounds have been synthetic in nature, as illustrated by the work of Gorsich,[4,5] Graham *et al.*,[6] and Dighe and Orchin.[7] The reactions of trimethyltinpentacarbonylmanganese, $(CH_3)_3SnMn(CO)_5$, with some olefins are described here, and similar reactions of other metal–metal bonded compounds will be described later.

Triphenyltinpentacarbonylmanganese has been investigated to some extent by Gorsich,[4,5] who established the general synthetic route

$$R_{4-n}SnCl_n + nNaMn(CO)_5 \longrightarrow R_{4-n}Sn[Mn(CO)_5]_n + nNaCl$$

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Several reactions of the triphenyltin compound show the stability of the Sn–Mn bond. When heated with triphenylphosphine or triphenylarsine, replacement of 1 mole of carbon monoxide occurs[4,5]

$$(C_6H_5)_3SnMn(CO)_5 + L(C_6H_5)_3 \longrightarrow (C_6H_5)_3SnMn(CO)_4L(C_6H_5)_3 + CO$$

Of particular interest is the reaction[4] of $(C_6H_5)_3SnMn(CO)_5$ with chlorine, in which the tin–carbon bond rather than the tin–manganese bond is cleaved

$$(C_6H_5)_3SnMn(CO)_5 + 3Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + 3C_6H_5Cl$$

Similarly, the diphenyltin derivative, $(C_6H_5)_2Sn[Mn(CO)_5]_2$, undergoes a two-step reaction[4,5] with chlorine involving first the rupture of the tin–phenyl bonds, followed by attack of the tin–manganese bond by chlorine, to give $Cl_3SnMn(CO)_5$ and $ClMn(CO)_5$. Hydrogen chloride is even more selective; it cleaves only the tin–carbon bonds of $(C_6H_5)_2Sn[Mn(CO)_5]_2$ to give $Cl_2Sn[Mn(CO)_5]_2$ and benzene. Interestingly, a reexamination[5] of the reaction of tetraphenylcyclopentadienone with $(C_6H_5)_3SnMn(CO)_5$ at 190° shows that the Sn–Mn bond is, in fact, broken. With simple olefins, under suitable conditions, insertion into the Sn–Mn bond might occur to give products based on the Sn–C–C–Mn unit, or replacement of carbon monoxide to form π complexes might take place.

Experimental Section

Vacuum manipulation by standard techniques was employed in the handling of reactants and products. Molecular weights of volatile compounds were determined by Regnault's method, and other molecular weights were measured in benzene solutions with a Mechrolab Model 301A vapor pressure osmometer. Microanalyses were performed by Alfred Bernhardt, Germany (for fluorine determinations), and by the Microanalytical Laboratory, University of British Columbia. A Beckman Model GC-2A gas chromatograph was employed for analytical and preparative separations, with dinonyl phthalate on Chromosorb W or firebrick columns. Infrared spectra were recorded on Perkin-Elmer Model 21 and Model 137 potassium bromide spectrophotometers; solid samples were prepared as Nujol mulls, liquids were taken as neat liquid samples, and a 10-cm gas cell (KBr windows) was used for gases. Proton magnetic resonance spectra were measured on a Varian Associates A-60 spectrometer and F^{11} spectra on a Varian V-4300 spectrometer.

Preparation of Trimethyltinpentacarbonylmanganese.—To 500 g of mercury in a 500-ml flask, sliced metallic sodium (5 g, 217 mg-atoms) was slowly added, followed by decacarbonyldimanganese (19.5 g, 50 mmoles) in 250 ml of tetrahydrofuran. The reaction mixture, which was maintained under a nitrogen atmosphere in a drybox, was stirred at room temperature for 1 hr, and the resulting brownish green solution was then separated from mercury by decantation. Trimethyltin bromide (24 g, 100 mmoles) was added, and after stirring at room temperature for 1 hr, the reaction mixture was allowed to stand overnight, and the supernatant solution was decanted. The remaining solid was washed with 10-ml portions of tetrahydrofuran several times and then separated by centrifuging.

The combined supernatant solutions and tetrahydrofuran washings were reduced to 50 ml by distillation [64° (76 cm)] and with an efficient column, the last traces of solvent and unreacted trimethyltin bromide were removed at 25° (3 cm) and at 30° (1 cm), respectively. The fraction which was then collected at 47° (10^{-3} cm) was a pale yellow liquid which solidified on standing and was recrystallized from cold *n*-pentane solution to give white, crystalline $(CH_3)_3SnMn(CO)_5$, mp 29.5° (uncor), $\rho^{30°}$, 1.62 g ml^{-1}. *Anal.* Calcd for $C_8H_9SnMnO_5$: C, 26.8; H, 2.5; mol wt, 358.8. Found: C, 27.0; H, 3.3; mol wt, 361.5.

Decomposition of $(CH_3)_3SnMn(CO)_5$. (a) **Pyrolysis.**—The compound (0.83 g) in a sealed tube was heated to 130° in the dark for 48 hr. No appreciable change in appearance was noted. Vacuum fractionation gave 0.01 mmole of carbon monoxide (mol wt found, 27), a trace of tetramethyltin identified spectroscopically, and unchanged $(CH_3)_3SnMn(CO)_5$ (0.81 g) identified by its infrared spectrum and by gas chromatography.

(b) **Photolysis.**—The tin–manganese compound (1.12 g) in a sealed silica tube was irradiated with ultraviolet light (Hanovia 200-w lamp) at 50° for 1 hr. A purple color appeared very rapidly, and the tube content was blackish purple at the end of the irradiation. Vacuum fractionation gave carbon monoxide (0.057 mmole) and tetramethyltin (0.02 g, 0.11 mmole) as volatile products. Sublimation of the residue gave unchanged $(CH_3)_3SnMn(CO)_5$ (1.05 g, 94% recovery) and left a black gum (0.05 g).

Reactions with Tetrafluoroethylene.—In a typical reaction, trimethyltinpentacarbonylmanganese (3.3 g, 9.2 mmoles) in 6 ml of *n*-pentane was allowed to react with tetrafluoroethylene (3.3 g, 33 mmoles) in a sealed silica tube under ultraviolet irradiation at 50°. When the irradiation was stopped after 4 hr, the tube contained a pale yellow liquid and a considerable amount of white solid. Vacuum fractionation gave only carbon monoxide (0.5 mmole; mol wt found, 29; calcd, 28), unchanged tetrafluoroethylene (1.93 g, 19.3 mmoles), *n*-pentane, and a small amount of clear liquid (0.1 g) which condensed at −10°. The latter was shown spectroscopically to be a mixture of $(CH_3)_3SnMn(CO)_5$, $C_5F_9Mn(CO)_5$, and $CF_2{=\!=}CFCOMn(CO)_5$, the latter two being completely characterized as components which largely remained in the reaction tube.

The reaction tube, containing the involatile residue, was rinsed several times with 1-ml portions of *n*-pentane, to leave a white solid (1.6 g) which was completely separated from the pentane washings by centrifuging. Evaporation of the pentane with a stream of dry nitrogen gave a brown oil (3.15 g) which was chromatographically separated by eluting with *n*-pentane on a Florisil column (2 × 50 cm). Five-milliliter fractions were collected and, by infrared spectroscopic examination in the carbonyl-stretching region (1800–2200 cm^{-1}), the separation into four chromatographic bands was observed. All fractions containing the same component were combined and the pentane was removed at −10° (10 cm). The first eluted band contained unreacted trimethyltinpentacarbonylmanganese (0.1 g), identified spectroscopically. A white solid, recovered from the second set of fractions, was recrystallized from cyclohexane and identified as 1-trimethyltin-2-pentacarbonylmanganesetetrafluoroethane, $(CH_3)_3SnCF_2CF_2Mn(CO)_5$ (0.6 g, 1.3 mmoles), mp 57.5° (uncor). *Anal.* Calcd for $C_{10}H_9F_4O_5SnMn$: C, 26.2; H, 1.96; F, 16.7; mol wt, 458.2. Found: C, 26.5, 26.3; H, 1.89, 1.65; F, 16.6; mol wt, 482. The third eluted component, a pale liquid, was $C_5F_9Mn(CO)_5$, (0.8 g, 1.8 mmoles), formulated on the basis of analytical data and the observed molecular weight. *Anal.* Calcd for $C_{10}F_9O_5Mn$: C, 28.2; F, 40.2; mol wt, 426. Found: C, 28.4; F, 40.0; mol wt, 435. The white, volatile solid obtained as the last eluted component was purified by sublimation [25° (10^{-3} cm)] and identified as perfluoroacryloylpentacarbonylmanganese, $CF_2{=\!=}CFCOMn(CO)_5$ (0.4 g, 1.7 mmoles), mp 41° (uncor). (This compund was first characterized from the reaction of $(CH_3)_3SnMn(CO)_5$ with $CF_2{=\!=}CFCl$, and analytical data are therefore given below.)

A brown ring remaining on the top of the column was finally eluted with a 10% methanol–pentane mixture, and evaporation of the resulting solution gave about 0.1 g of a dark gum. Its infrared spectrum showed a broad band of medium intensity centered at 1700 cm^{-1} (acyl, bridging carbonyl, and/or C=C stretching vibrations) and two very broad and strong bands centered at 1150 and 1000 cm^{-1} (C–F stretching modes) in addition to absorptions associated with the carbonylmanganese group.

The white residue, which was not soluble in pentane, was extracted several times with acetone (1-ml portions) leaving a white crystalline residue identified by its infrared spectrum as trimethyltin fluoride (0.9 g, 4.95 mmoles). No polymerized tetrafluoroethylene could be detected by infrared spectroscopic examination. The acetone extracts were combined, and the acetone was evaporated under a flow of dry nitrogen; the resulting residue was extracted four or five times with 2-ml portions of hot carbon tetrachloride and finally washed twice with chloroform. The residue was identified as one of the isomers (called dimer 2) of dimeric perfluorovinyltetracarbonylmanganese, [CF_2=$CFMn(CO)_4$]$_2$ (0.2 g, 0.4 mmole). (See Figure 1.) The volume of the combined carbon tetrachloride extracts was reduced until a white cloudiness formed. The solution was then chilled in ice for about 1 hr and filtered to give the other isomer (dimer 1) of [CF_2=$CFMn(CO)_4$]$_2$ (0.4 g, 0.8 mmole). *Anal.* Calcd for $C_{12}F_6O_8Mn_2$: C, 29.0; F, 23.0; mol wt, 496. Found for dimer 1: C, 30.7; F, 23.5; mol wt, 489. Found for dimer 2: C, 29.8; F, 24.9; mol wt, 466. Neither isomer had a definite melting point but decomposed at 150° to a brown solid.

Reaction with Trifluoroethylene.—Trifluroethylene (1.9 g, 23.2 mmoles) was allowed to react with trimethyltinpentacarbonylmanganese (1.7 g, 4.7 mmoles) in 4 ml of *n*-pentane in a sealed silica tube under ultraviolet light at 63° for 4 hr. Vacuum fractionation gave carbon monoxide (mol wt found, 25.5) (0.8 mmole), unreacted trifluoroethylene (1.7 g, 20.2 mmoles), *n*-pentane, and a pale yellow liquid (0.2 g) which condensed at −46°. From a comparison of its infrared spectrum with those of the pure compounds, the latter was identified as a mixture of *trans*-(CFH=CF)$Mn(CO)_5$ (identified fully below), $(CH_3)_3SnCF$=CF_2, and $(CH_3)_3SnMn(CO)_5$ in the approximate ratio of 4:1:4.

The involatile material remaining in the reaction tube was extracted with acetone (3 ml) several times to leave a white solid, identified by its infrared spectrum as trimethyltin fluoride (0.55 g, 3 mmoles). The residue obtained on evaporation of the combined acetone extracts was sublimed at 25° (10^{-3} cm). A fraction, which passed the cooled probe (10°) and condensed in a −46° trap, was chromatographed on a Florisil column with *n*-pentane as eluant to give *trans*-1,2-difluorovinylpentacarbonylmanganese (0.05 g, 0.2 mmole). This was identified by its infrared and proton magnetic resonance spectra, which are discussed later. The solid which condensed on the 10° cold probe was washed with three 0.5-ml portions of cold *n*-pentane and recrystallized from cyclohexane to yield white, crystalline *cis*-1,2-difluorovinylpentacarbonylmanganese, *cis*-(CFH=CF)$Mn(CO)_5$ (0.35 g, 1.4 mmoles), mp 78° (uncor). *Anal.* Calcd for $C_7F_2HO_5Mn$: C, 32.55; H, 0.38; F, 14.74; mol wt, 258. Found: C, 32.64; H, 0.64; F, 14.85; mol wt, 295. Evaporation [−10° (10 cm)] of the pentane washings gave unreacted trimethyltinpentacarbonylmanganese (0.4 g, 1.1 mmoles). The sublimation residue (0.2 g), a dark gum, showed two infrared bands of medium intensity at 1700 and 1610 cm^{-1} and a strong broad band at 1100 cm^{-1} as well as absorptions of a carbonylmanganese group, but no further investigation was made.

Reaction with Trifluorochloroethylene.—The reaction of trimethyltinpentacarbonylmanganese (2.3 g, 6.3 mmoles) with trifluorochloroethylene (4.7 g, 40.2 mmoles) in 5 ml of *n*-pentane, under ultraviolet irradiation at 70° for 3 hr, gave carbon monoxide (0.82 mmole), solvent and unreacted olefin which could not be separated, and an involatile blackish brown oil (~2.8 g) containing a solid. The solid was separated by centrifuging off the oil and then was washed with three 2-ml portions of *n*-pentane and five 2-ml portions of acetone. The remaining white solid was spectroscopically identical with trimethyltin fluoride (0.1 g, 0.55 mmole).

The combined acetone washings were evaporated to leave a black gum (0.3 g). This corresponded to the fraction in the C_2F_4 reaction from which the dimers [CF_2=$CFMn(CO)_4$]$_2$ were isolated, but this gum did not show any of the infrared absorptions expected for these or the related dimers. This material was not treated further.

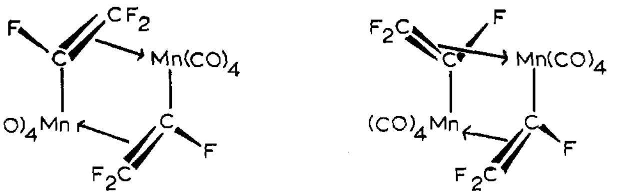

Figure 1.—Isomeric forms of [CF_2=$CFMn(CO)_4$]$_2$.

The *n*-pentane washings were combined with the original brown oil, and the pentane was removed. Chromatographic separation of the resulting oil on a Florisil column with *n*-pentane as eluant afforded three fractions. The first eluted fraction was unchanged $(CH_3)_3SnMn(CO)_5$ (0.5 g, 1.4 mmoles) identified spectroscopically. The second fraction, a clear liquid (0.1 g), gave an infrared spectrum which suggested that it could contain at least three components, Thus three bands observed at 1790, 1690, and 1640 cm^{-1} could all arise from C=C stretching vibrations, although these could also be due to acyl or bridging carbonyl groups. Trap-to-trap fractionation did not clearly separate the components, but from the changes in their relative intensities among the various fractions, it was clear that the above three absorptions were due to three different compounds. The infrared spectrum of the mixture showed no C–H stretching or CH_3–Sn rocking (750–800 cm^{-1}) absorptions, so that bands at 550 and 508 cm^{-1} could not be attributed to Sn–C stretching modes. Moreover, no proton resonance was observed in the nmr spectrum. The F^{19} nmr spectrum, however, consisted of three distinct sets of absorptions apparently arising from three fluorovinyl groups. The three quartets (each with intensity ratio 1:1:1:1) centered at +7.4, +51.0, and +64.9 ppm (TFA) were undoubtedly due to perfluoroacryloylpentacarbonylmanganese, CF_2=$CFCOMn(CO)_5$, whose F^{19} spectrum is discussed more fully later. The two doublets centered at +23.6 and +43.6 ppm (TFA) with J_{FF} = 126 cps may be assigned to *trans*-1,2-difluoro-2-chlorovinylpentacarbonylmanganese, *trans*-CFCl=CFMn(CO)$_5$, on the basis of the large F–F coupling constant.[8,9] The two doublets centered at −10.1 and +10.95 ppm with J_{FF} = 58.5 cps may be attributed to either the *cis*-CFCl=F or the CF_2CCl group. However, in view of the high unshielding of one of the F atoms (−10.1 ppm) which shows a chemical shift characteristic for a fluorine nucleus of a CF–M group, where M is a transition metal atom,[10] these resonances were tentatively assigned to *cis*-1,2-difluoro-2-chlorovinylpentacarbonylmanganese, *cis*-CFCl=CFMn(CO)$_5$. Judging from the peak intensities in the F^{19} spectrum, the mixture contained approximately 55% CF_2=$CFCOMn(CO)_5$, 9% *trans*-CFCl=CFMn(CO)$_5$, and 36% *cis*-CFCl=CFMn(CO)$_5$.

The last and major chromatographic fraction was further sublimed [25° (10^{-3} cm)] onto a cooled probe at −78° to give white, crystalline perfluoroacryloylpentacarbonylmanganese, $CF_2CFCOMn(CO)_5$ (1.1 g, 3.6 mmoles), mp 41° (uncor). *Anal.* Calcd for $C_8F_3O_6Mn$: C, 31.6; F, 18.8; mol wt, 304. Found: C, 31.40; F, 18.85; mol wt, 299. The column was finally eluted with a 10% methanol–pentane mixture to give on evaporation a brown residue (0.7 g). Sublimation [25° (10^{-3} cm)] gave white crystals on the −78° probe which were identified by the infrared spectrum, the H^1 nmr spectrum (δ_{CH_3} = −37 cps, TMS), and the melting point of 37° as trimethyltin chloride (0.55 g, 2.8 mmoles).

Pyrolysis of Perfluoroacryloylpentacarbonylmanganese.—When CF_2=$CFCOMn(CO)_5$ (0.01 g) was heated at 100° in the dark for 3 hr, carbon monoxide was the only volatile product. Sublimation of the residue gave unchanged starting material and some black oil. However, the infrared spectrum of the latter showed that decarbonylation to the dimers [CF_2=$CFMn(CO)_4$]$_2$ had not occurred.

Reaction with Ethylene. (a) At 10 Atm of Ethylene Pressu—Trimethyltinpentacarbonylmanganese (1.4 g, 3.96 mmo

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in 3 ml of *n*-pentane was allowed to react with ethylene (0.6 g, 21.7 mmoles) in a sealed silica tube under ultraviolet irradiation at 50° for 4 hr and then at 80° for a further 20 hr. Removal under vacuum of carbon monoxide (1.3 mmoles), unreacted ethylene (19 mmoles), and solvent left a brown oil–solid mixture (1.2 g). This was extracted with pentane (6 ml), and the solution was separated from a black solid (0.1 g) by centrifuging. Evaporation of the pentane left 1.1 g of brown oil which was then sublimed at 25° (10^{-3} cm). The first sublimate (0.5 g) on the cooled probe (−78°) was removed, and continuation of the sublimation [30° (10^{-3} cm)] gave a yellow oil identified as trimethyltintetracarbonyl(π-ethylene)manganese, $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$ (0.4 g, 1.1 mmoles). *Anal.* Calcd for $C_9H_{13}O_4SnMn$: C, 30.1; H, 3.6; mol wt, 358.8. Found: C, 30.0; H, 4.27; mol wt, 349. Resublimation of the first sublimate yielded another 0.2 g of $(CH_3)_3SnMn(CO)_4,(\pi\text{-}C_2H_4)$, making a total yield of 43% based on $(CH_3)_3SnMn(CO)_5$, and unchanged $(CH_3)_3SnMn(CO)_5$ (0.3 g).

(b) **Reaction with Ethylene at 1 Atm in the Presence of Hydrogen.**—A similar reaction was carried out in which $(CH_3)_3SnMn(CO)_5$, ethylene, and hydrogen in a silica tube were irradiated at 60° for 4 hr. The products included a mixture of unreacted ethylene and ethane in a 9:1 ratio, carbon monoxide, unchanged $(CH_3)_3SnMn(CO)_5$ (~53% recovery), and $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$ (20% yield).

Table I

Infrared Bands of Reaction Products Containing the $(CH_3)_3Sn$ Group[a]

$(CH_3)_3SnMn(CO)_5$	$(CH_3)_3SnCF_2CF_2Mn(CO)_5$	$(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$	Assignment
		3100 vw	
3008 m	3000 m	3015 m	CH asym str
2924 m	2959 m	2925 m	CH sym str
		2880 vw	
2460 w			
		2380 w	
2092 s	2125 m	2055 m	
		1983 sh	
1992 vs	2025 vs	1976 vs [b]	CO str
1960 s	2003 vs	1959 sh	
		1440 m	C═C str
1425 w, br	1420 w, br	1420 w, br	CH_3 asym def
1214 sh	1235 s		
1195 m	1195 w	1192 s	
1185 m	1183 w	1182 m	
1080 w, br	1065 s		
1030 w	1020		
	1000 s		CF str
	975		
900 w		965 w, br	
768 s, br	788 s, br	765 s, br	CH_3Sn rock
700 m		700 m, br	
	698 vs		
665 s	662 vs, br	650 s	Mn–CO def
655 s		643 s	
		556 m	
517 s	539 s	514 s	Sn–C asym str
500 s	518 m	500 s	Sn–C sym str
480 s	448 s	483 s	Mn–C str
412 w, br	422 w, br	410 w, br	

[a] vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder. [b] CO stretching frequencies were measured in cyclohexane solution.

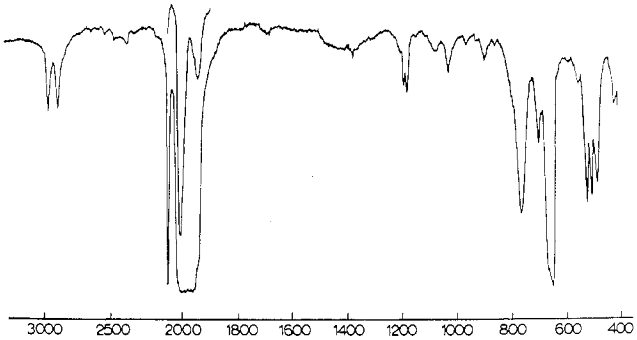

Figure 2.—The infrared spectrum of $(CH_3)_3SnMn(CO)_5$.

Discussion

The reaction of trimethyltin bromide with sodium pentacarbonylmanganate(I), according to the method of Gorsich,[4,5] gives trimethyltinpentacarbonylmanganese in excellent yield. This compound has appreciable stability, showing only negligible decomposition on heating at 130° for prolonged periods, or under ultraviolet irradiation for briefer periods. Although readily soluble in most organic solvents, it decomposes in some; *e.g.*, on prolonged standing in carbon tetrachloride solution, a brown solid is deposited. The infrared spectrum of $(CH_3)_3SnMn(CO)_5$ (Table I and Figure 2) in the carbonyl-stretching region shows three principal bands at 2092 (s), 1992 (vs), and 1960 (s) cm^{-1}, these being of the $2A_1 + E$ pattern due to the C_{4v} symmetry of the $Mn(CO)_5$ group.[11,12] This pattern and the frequencies of the bands are characteristic of $Mn(CO)_5$ derivatives containing the Mn–M bond, where M = Mn, Re,[13] or Au.[14] In the far-infrared region, two absorptions at 517 (s) and 500 (s) cm^{-1} are assigned to the Sn–C asymmetric and symmetric stretching vibrations, respectively, and are characteristic of the $(CH_3)_3Sn$–M group, where M = Sn.[15] Moreover, the value of the Sn^{119}–CH_3 coupling constant, 48.8 ± 0.2 cps, in conjunction with these Sn–C stretching frequencies, indicates that the s character of the tin orbitals in the Sn–Mn bond is very similar in magnitude to that in the Sn–Sn,[15] Sn–Mo, or Sn–Fe[6] bond in the corresponding trimethyltin derivatives. Furthermore, since the most intense band is approximately at the average carbonyl absorption frequency (*i.e.*, 2000 cm^{-1}) and since a positive or negative charge is known[16] to raise or lower, respectively, the carbonyl-stretching frequencies by roughly 100 cm^{-1}, to about 2100 or 1900 cm^{-1}, it seems that the charge separation in the Sn–Mn bond of $(CH_3)_3SnMn(CO)_5$ is very small.

Reaction with Tetrafluoroethylene.—The reaction of trimethyltinpentacarbonylmanganese with tetrafluoroethylene occurred most readily under ultraviolet irradiation at 50°, with about 70% consumption of the tin–manganese compound after 6 hr. The principal product was trimethyltin fluoride, obtained in approximately 55% yield, together with five carbonylmanganese derivatives. One of these was the 1:1 adduct, 1-trimethyltin-2-pentacarbonylmanganesetetrafluoroethane, $(CH_3)_3SnCF_2CF_2Mn(CO)_5$, obtained

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[11] L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

[12] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[13] N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964), and references cited therein.

[14] A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 3407 (1965).

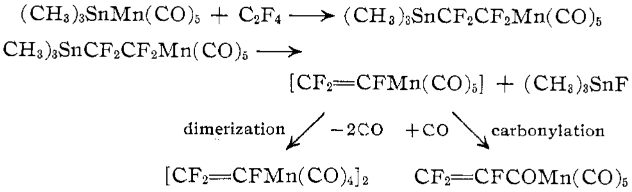
[15] T. L. Brown and G. L. Morgan, *Inorg. Chem.*, **2**, 736 (1963).

as a white crystalline solid in 14% yield. In slightly greater yield (21%), a component was obtained with the composition $C_{10}F_9MnO_5$. The three principal carbonyl-stretching frequencies at 2133, 2043, and 2014 cm^{-1} suggest the presence of an $Mn(CO)_5$ group of C_{4v} symmetry, and other bands indicate a fluorocarbon group with a C=C bond. The proton nmr spectrum confirmed the absence of hydrogen, while the F^{19} nmr spectrum (five groups of absorptions centered at +110.0, +33.4, +30.8, +17.5, and −14.2 ppm relative to trifluoroacetic acid) indicated the presence of at least five kinds of fluorine atoms in chemically nonequivalent environments. Unfortunately, the fine structure of these absorptions could not be resolved, so that the compound can be formulated only as $C_5F_9Mn(CO)_5$.

The other three products were identified as perfluoroacryloylpentacarbonylmanganese, $CF_2{=}CFCOMn(CO)_5$, for which a more detailed discussion of its spectroscopic behavior is given later, and the two stereoisomers of dimeric perfluorovinyltetracarbonylmanganese, $[CF_2{=}CFMn(CO)_4]_2$. These two isomers, separated by their different solubilities in hot carbon tetrachloride, were identified by the analytical data and particularly by the observed dimeric molecular weights, and they can be regarded as "boat" and "chair" forms of the dimeric ring structure (Figure 1). Unfortunately, their solubilities were too low to allow a study of their F^{19} nmr spectra, but, significantly, their infrared spectra showed medium intensity absorptions at 1620 (dimer 1) and 1617 (dimer 2) cm^{-1}, approximately 100 cm^{-1} lower than normally observed for the C=C stretching frequency of a perfluorovinyl group, but consistent with the π-bonded $CF_2{=}CF^-$ group required in the dimeric structure.

From reactions of $(CH_3)_3SnMn(CO)_5$ with tetrafluoroethylene performed under different conditions, the following conclusions were evident: (1) under the same irradiation conditions, an increase in reaction temperature had no effect; (2) no reaction, other than polymerization of the olefin, occurred when the reactants were heated in the dark; (3) in the absence of solvent, more rapid decomposition of the reactants occurred and the yield of the 1:1 adduct was reduced. This suggests that a facile one-phase reaction may take place in solution owing to the ready solubility of tetrafluoroethylene in *n*-pentane.

The 1:1 adduct, $(CH_3)_3SnCF_2CF_2Mn(CO)_5$, is the first example of a two-carbon-atom insertion into a mixed metal–metal bond.[16] An insertion of the tetrafluoroethylene molecule into the Co–Co bond of dicobalt octacarbonyl to give $(CO)_4CoCF_2CF_2Co(CO)_4$ has been reported,[16] and a similar type of compound, $(CO)_5MnCF_2CF_2CF_2Mn(CO)_5$, has been prepared[17] by the decarbonylation of the perfluoroglutaryl derivative, $(CO)_5MnCO(CF_2)_3COMn(CO)_5$. The overall reaction of trimethyltinpentacarbonylmanganese with tetrafluoroethylene therefore appears to proceed as follows



$$(CH_3)_3SnMn(CO)_5 + C_2F_4 \longrightarrow (CH_3)_3SnCF_2CF_2Mn(CO)_5$$

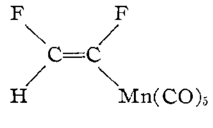
$$(CH_3)_3SnCF_2CF_2Mn(CO)_5 \longrightarrow [CF_2{=}CFMn(CO)_5] + (CH_3)_3SnF$$

$$\begin{tikzcd} & {[CF_2{=}CFMn(CO)_5]} \arrow[dl, "\text{dimerization}"', "-2CO"] \arrow[dr, "+CO"', "\text{carbonylation}"] & \\ {[CF_2{=}CFMn(CO)_4]_2} & & CF_2{=}CFCOMn(CO)_5 \end{tikzcd}$$

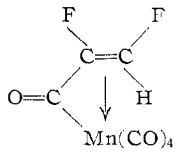
Since the structure of $C_5F_9Mn(CO)_5$ is still uncertain, the route by which it is formed also cannot be decided, although some combination of C_3F_6 and C_2F_4 units is probably involved. The C_3F_6 units must arise from hexafluoropropene present as an impurity in the tetrafluoroethylene. It is interesting that a similar product of unknown structure, formulated as $CH_3(C_4F_8)Re(CO)_5$, was obtained[18] from the reaction of $CH_3Re(CO)_5$ with C_2F_4 in a 3:8 ratio at 130°.

Reaction with Trifluoroethylene.—The reaction of trimethyltinpentacarbonylmanganese with trifluoroethylene also proceeds readily under the same conditions in which the $-CF_2CF_2-$ is smoothly inserted into the Sn–Mn bond. However, few secondary products are formed and the reaction can be more easily followed. The main product was again trimethyltin fluoride, formed in almost quantitative yield based on the recovery of the tin–manganese reactant. In addition, the *cis* and *trans* isomers of (1,2-difluorovinyl)pentacarbonylmanganese, $CFH{=}CFMn(CO)_5$, were also isolated. These isomers exist as air-stable monomers, unlike the analogous, possibly intermediate, species $CF_2{=}CFMn(CO)_5$, which apparently eliminates CO groups to form the dimers. Surprisingly, no evidence could be found for the adduct $(CH_3)_3SnC_2F_3HMn(CO)_5$.

The formulation of *cis*-$CFH{=}CFMn(CO)_5$ is supported by analytical data and by spectroscopic studies (Tables II and III), although the latter require some comment. In the carbonyl-stretching region of the infrared spectrum (Figure 3a) five bands are observed with the following relative intensities: 2132 (4%), 2071 (3%), 2037 (58%), 2014 (32%), 1975 (2%). Such complexity could be due to (i) a lack of axial symmetry along the C–C–M axis, causing infrared activity for all four fundamental vibrations ($2A_1 + B_1 + E$) as predicted theoretically,[11] or (ii) the formation of structural isomer II rather than I.



I



II

The first explanation is more probably correct, since the appearance of the B_1 vibration has been observed and discussed in other instances.[19,20] For such a lack

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(16) K. F. Watterson and G. Wilkinson, *Chem. Ind.* (London), 1358 (1960).

(17) R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963).

(18) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965).

(19) J. B. Wilford and F. G. A. Stone, *ibid.*, **4**, 389 (1965).

(20) J. B. Wilford and F. G. A. Stone, *J. Organometal. Chem.*, **2**, 371 (1964).

TABLE II

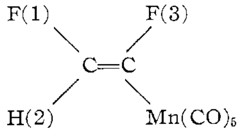
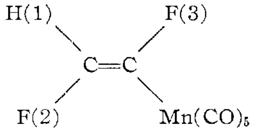
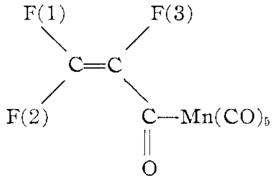
INFRARED BANDS OF REACTION PRODUCTS CONTAINING CARBONYLMANGANESE GROUPS[a]

	I	II	III	IV	V
ν_{CH}	3100 w	3000 w			
	2132 m	2123 m	2133 m	2133 m	2138 m
	2071 m		2063 sh	2063 s	
ν_{CO}	2037 vs	2039 vs	2043 vs	2033 s	2023 vs, br
	2014 s	2012 s	2012 vs	1989 s	
	1975 w	1964 w	1976 w		
$\nu_{C=C}$	1630 s	1670 w	1712 s	1620 m	1617 m
$\nu_{C=O}$			1685 sh		
	1310 vw	1310 vw			
	1297 m	1272 m		1292 w	1287 w
		1240 w	1265 sh	1245 w	1243 w
			1240 vs		
				1183 w	1183 m
				1150 w	1194 w
	1045 vs	1088 vs	1042 vs	1111 s	1104 s
		1035 w		1076 m	1065 m
ν_{C-F}				1020	1022
				992 s	990 s
	968 vs, br	1010 vs, br	960 vs	965	980
				893 m	897 m
					885 m
				824 w	
	775 s	758 s		743 s	735 s
	750 s				
	720 w		720 w	721 w	713 m
			658 vs	657 sh	655 vs
δ_{MCO}	645 vs, br	650 vs, br	646 vs	642 vs	643 vs
		563 w			
		540 w	512 m	450 sh	453 sh
ν_{M-CO}	446 m	437 m	447 s, br	445 m	444 m
			427 sh		
	424 w	420 vw	420 m	426 m	427 m

[a] I, *cis*-CFH=CFMn(CO)$_5$; II, *trans*-CFH=CFMn(CO)$_5$; III, CF$_2$=CFCOMn(CO)$_5$; IV, [CF$_2$=CFMn(CO)$_4$]$_2$, dimer 1; V, [CF$_2$=CFMn(CO)$_4$]$_2$, dimer 2; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder.

TABLE III

NMR DATA FOR SOME FLUOROVINYLPENTACARBONYLMANGANESE COMPLEXES

			
δ_H[a]	−5.7 ± 0.5	−8.1 ± 0.5	
$\delta_{F(1)}$[b]	+50.1 ± 0.2		+7.4 ± 0.1
$\delta_{F(2)}$[b]		. . .[c]	+51.0 ± 0.1
$\delta_{F(3)}$[b]	+14.2 ± 0.2	. . .[c]	+64.9 ± 0.1
$J_{H(1)F(2)}$[d]		86.5 ± 0.1	
$J_{H(1)F(3)}$		10.2 ± 0.1	
$J_{H(2)F(1)}$ [~F(1)H(2)]	80.0 ± 0.1		
$J_{H(2)F(3)}$ [~F(3)H(2)]	25.0 ± 0.1		
$J_{F(1)F(2)}$ [~F(2)F(1)]			92.5 ± 1
$J_{F(1)F(3)}$ [~F(3)F(1)]	~2.4		40.6 ± 1
$J_{F(2)F(3)}$		. . .[c]	111.5 ± 1

[a] TMS as internal standard (ppm). Each resonance was observed as a doubleted doublet. [b] TFA as external standard (ppm) Each resonance was observed as a doubleted doublet. [c] Not measured. [d] Coupling constants in cps.

of axial symmetry, a splitting of the E mode should also be observed, although other examples are known[20] where the splitting is too small to be resolved. An isomer similar to II has been proposed[21] for a related cobalt derivative, but in this present case, the observed ν_{CO} frequencies do not show the relative intensities and band separations to be expected[11] for a mole-

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[21] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

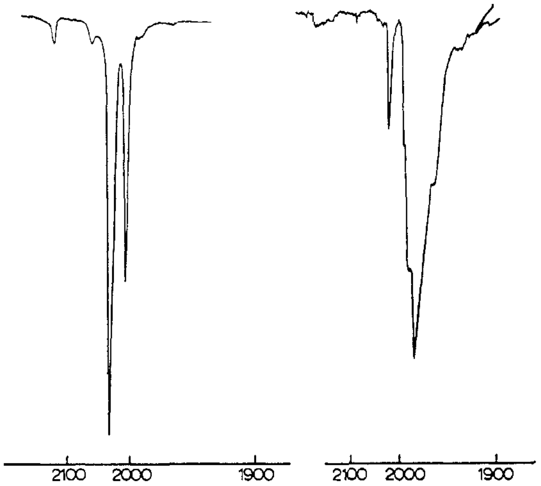

Figure 3.—Infrared absorptions in the carbonyl-stretching region for (a) *cis*-$CFH{=}CFMn(CO)_5$ and (b) $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$.

cule of C_s symmetry, *i.e.*, *cis*-$LL'M(CO)_4$. Moreover, two peaks in the 1400–1650 cm^{-1} region would then be expected, associated with the coordinated $C{=}C$ and the ketonic $C{=}O$ stretching vibrations, but only one sharp peak at 1630 cm^{-1} is observed. The carbonyl-stretching frequencies of the *trans* isomer are those expected for an $Mn(CO)_5$ group, and moreover only one peak at 1670 cm^{-1} is observed in the 1400–1700 cm^{-1} region, attributable to the $C{=}C$ stretching vibration. Only the simple vinylpentacarbonylmanganese structure therefore occurs.

The H^1 and F^{19} nmr spectra also support the *cis* and *trans* configurations for these two isomers. An examination of H–F coupling constants in several fluoroolefins and their organometallic derivatives[8,22] shows that $J_{HF(gem)} > J_{HF(trans)} > J_{HF(cis)}$ and that their values are in the ranges $J_{HF(gem)} = 72\text{–}81$ cps, $J_{HF(trans)} = 12\text{–}34$ cps, and $J_{HF(cis)} = 1\text{–}8$ cps. The coupling constants (Table III) observed in the proton magnetic resonance spectra of the two compounds thus confirm the *cis* and *trans* configurations, particularly since the other possible configuration $CF_2{=}CHMn(CO)_5$ should give J_{HF} values not higher than 40 cps. The F^{19} nmr spectrum of the *cis* isomer consists of two sets of doublets at +14.2 and +50.1 ppm. The H–F coupling constants are in excellent agreement with those observed in the proton spectrum, so that these two resonances are readily assigned to the F atoms *trans* and geminal to the vicinal proton, respectively. Each component of these doublets is further split into a doublet due to the F–F interaction. The J_{FF} value of 2.4 cps clearly shows again that the two F atoms are not *trans* to each other for which a coupling constant of 110–130 cps would be expected.[22] However, the value is also abnormally small for the *cis* configuration. However, for both the *cis* and *trans* compounds, the observed chemical shifts and coupling constants are completely consistent with those found for fluorovinyltin compounds.[23] It should be noted that these two isomers of 1,2-difluorovinylpentacarbonylmanganese and the dimers of perfluorovinyltetracarbonylmanganese are among the few transition metal complexes[24] containing σ-bonded fluorovinyl groups. The compounds $CF_2{=}CFRe(CO)_5$ and $CF_2{=}CFFe(CO)_2(\pi\text{-}C_5H_5)$ were reported[25] while this work was in progress.

The over-all reaction with trifluoroethylene can therefore be described as

$$(CH_3)_3SnMn(CO)_5 + CF_2{=}CFH \longrightarrow [(CH_3)_3SnCFHCF_2Mn(CO)_5] \longrightarrow (CH_3)_3SnF + CFH{=}CFMn(CO)_5 \ (\textit{cis} \text{ and } \textit{trans})$$

Reaction with Trifluorochloroethylene.—In this reaction of trimethyltinpentacarbonylmanganese, trimethyltin fluoride (9% yield) and carbon monoxide were again formed. However, a considerable quantity (45% yield) of trimethyltin chloride was formed, and, as with trifluoroethylene, no adduct containing the Sn–C–C–Mn skeleton could be isolated. Instead, the principal product containing a carbonylmanganese group was perfluoroacryloylpentacarbonylmanganese, $CF_2{=}CFCOMn(CO)_5$. Other products, formed in much smaller amounts, and identified spectroscopically, were the *cis* and *trans* isomers of (1,2-difluoro-2-chlorovinyl)pentacarbonylmanganese, $CFCl{=}CFMn(CO)_5$. The formation of these products can be accounted for in terms of either chlorine elimination (as $(CH_3)_3SnCl$) or fluorine elimination (as $(CH_3)_3SnF$) from an unstable 1:1 adduct

$$(CH_3)_3SnMn(CO)_5 + C_2F_3Cl \longrightarrow [(CH_3)_3SnC_2F_3ClMn(CO)_5] \longrightarrow \text{(a) } (CH_3)_3SnF + C_2F_2ClMn(CO)_5$$

or

$$\text{(b) } (CH_3)_3SnCl + [C_2F_3Mn(CO)_5]$$

$$[C_2F_3Mn(CO)_5] + CO \longrightarrow CF_2{=}CFCOMn(CO)_5$$

However, since either a fluorine or a chlorine migration from the β position in the group Sn–C(α)–C(β)–Mn could occur, this reaction provides no information regarding the direction of addition. On the other hand, it is surprising, firstly that no chlorine abstraction by manganese was observed, *e.g.*

$$[(CH_3)_3SnC_2F_3ClMn(CO)_5] \longrightarrow (CH_3)_3SnCF{=}CF_2 + [ClMn(CO)_4]_2 + 2CO$$

and secondly that dimerization was not observed, *i.e.*

$$2[CF_2{=}CFMn(CO)_5] \longrightarrow [CF_2{=}CFMn(CO)_4]_2 + 2CO$$

It is interesting to consider briefly the factors responsible for the high yield of $CF_2{=}CFCOMn(CO)_5$ in this reaction. The carbonylation of pentacarbonylmanganese derivatives has been studied kinetically,[26] and it is known that the rate of carbonylation decreases as the electronegativity of the substituent group on manganese increases. Thus, methylpenta-

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[22] H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

[23] A. D. Beveridge, H. C. Clark, and J. T. Kwon, *Can. J. Chem.*, **44**, 179 (1966).

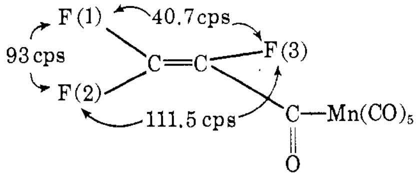
[24] H. C. Clark, J. H. Tsai, and W. S. Tsang, *Chem. Commun.*, 171 (1965).

[25] P. W. Jolly and F. G. A. Stone, *ibid.*, 86 (1965).

[26] F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

carbonylmanganese carbonylates readily[27] at 25°, while trifluoromethylpentacarbonylmanganese cannot be carbonylated. Our results therefore suggest that, in this respect, the $CF_2{=}CF^-$ group must be less electronegative than other perfluoroalkyl groups allowing a facile carbonylation to occur. Certainly an attempt to decarbonylate $CF_2{=}CFCOMn(CO)_5$ at 100° was quite unsuccessful.

The spectroscopic properties of $CF_2{=}CFCOMn(CO)_5$ are also worth comment. In the infrared spectrum, the principal ν_{CO} frequencies are essentially of the $2A_1 + E$ pattern expected for the $Mn(CO)_5$ group; there is also a weak shoulder at 2063 cm^{-1}, and the E band at 2043 cm^{-1} is broad. This suggests a splitting of the E band and the simultaneous appearance of the B_1 mode with low intensity due to a lack of axial symmetry.[11] Stone, *et al.*,[19] reported that all acyl metal carbonyls exhibit this splitting of the E mode, as high as 12 cm^{-1} accompanied by the appearance of the weak B_1 band. This compound also shows a strong absorption at 1712 cm^{-1} and a shoulder at 1685 cm^{-1}, which are assigned to the C=C and acyl C=O stretching vibrations, in agreement with previous assignments.[28,29] The F^{19} nmr spectrum of $CF_2{=}CFCOMn(CO)_5$ (Table III) consists of three sets of quartets (each with intensity ratio 1:1:1:1) centered at +7.4, +41.0, and +64.9 ppm, a typical spectrum of an ABC system. From a consideration of the F^{19} spectra of perfluorovinyl derivatives,[30] the +51 and +64.9 ppm quartets are assigned to the two fluorine atoms *trans* to each other, the former to the geminal fluorine atom (F(2)) and the latter to F(3), with the coupling constants as shown in III.



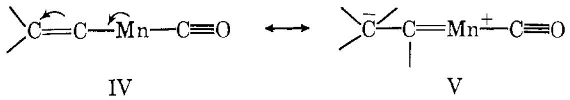
III

The lowest field quartet at +7.4 ppm is assigned to the F(1) atom, and the coupling constants of 92.5 and 40.6 cps are in good agreement with those obtained from the quartets due to F(2) and F(3).

Reaction with Ethylene.—Prolonged periods of heating were required to attain a reasonable degree of reaction of ethylene with trimethyltinpentacarbonylmanganese, although unexpectedly the reaction products were carbon monoxide and a π-bonded ethylene complex, $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$. The latter is a pale yellow oil which decomposed slowly on standing in air. Its infrared spectrum (Table I and Figure 3b) shows only poorly resolved ν_{CO} bands consisting of a medium-intensity band at 2055 cm^{-1} and a very strong, broad band centered at 1976 cm^{-1} accompanied by two shoulders at 1983 and 1959 cm^{-1}. Assuming that the complex has an octahedral geometry about the manganese atom, *cis* and *trans* isomers are possible. The former would have C_s symmetry with four infrared-active ν_{CO} modes, whereas the more symmetrical *trans* isomer with C_{4v} symmetry should show only two ν_{CO} modes, assuming that the two substituents can rotate freely along the *trans* axis. Such free rotation is unlikely in view of the strong π-bonding character of ethylene, so that the *trans* isomer could well have only C_{2v} symmetry with an increased number of ν_{CO} bands. The ν_{CO} vibrations therefore do not provide any distinction between the two isomers. The spectrum also shows a weak, sharp band at 1440 cm^{-1} which is assigned to the C=C stretching vibration. The corresponding C=C olefinic-stretching vibrations for $\pi\text{-}C_5H_5Mn(CO)_2(\pi\text{-}C_2H_4)$ and $(C_2H_4PtCl_2)_2$ are observed at 1499[31a] and 1406[31b] cm^{-1}.

The H^1 nmr spectrum of $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$ shows, in addition to the peak due to the methyl protons at −0.46 ppm relative to tetramethylsilane, a single peak at −2.65 ppm. This can be regarded as consistent with the *trans* configuration but can also be attributed to an extremely rapid exchange taking place in solution between coordinated and free ethylene molecules. The latter is in agreement with the single peak observed for the $Sn\text{-}Pt(\pi\text{-}C_2H_4)$ complex.[32] The fact that an ethylene π complex was formed with no rupture of the Sn–Mn bond prompted a preliminary study of the catalytic behavior of $(CH_3)_3SnMn(CO)_5$. However, a reaction of this compound with ethylene and hydrogen (both in excess) at 1 atm led to only a very small conversion to ethane. More detailed study of this type of reaction is necessary.

Spectroscopic Properties.—For compounds containing the $Mn(CO)_5$ group, the ν_{CO} frequencies are shifted significantly toward higher energies in the order $(CH_3)_3SnMn(CO)_5 < (CH_3)_3SnCF_2CF_2Mn(CO)_5 <$ *trans*-$CFH{=}CFMn(CO)_5 \sim CF_2{=}CFCOMn(CO)_5 \sim C_5F_9Mn(CO)_5$. These shifts suggest that inductive effects and π-acceptor capacity, which are believed[19] to be responsible for raising the ν_{CO} frequencies of metal carbonyl complexes, are much smaller in the $(CH_3)_3Sn$ group than in fluorocarbon groups. In fact it is interesting that the three ν_{CO} bands of methylpentacarbonylmanganese are very similar[19] to those of $(CH_3)_3SnMn(CO)_5$. The difference in the ν_{CO} frequencies of $(CH_3)_3SnCF_2CF_2Mn(CO)_5$ and (*trans*-$CFH{=}CF)Mn(CO)_5$ may be rationalized in terms of resonance which can occur much more readily in the latter compound



IV V

Because of the contribution of structure V in which electrons on the Mn atom are less available for π bond-

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[27] R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

[28] E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

[29] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

[30] T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, **17**, 968 (1961).

[31] (a) H. P. Kogler and E. O. Fischer, *Z. Naturforsch.*, **15b**, 676 (1960); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[32] R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

ing with the carbonyl groups, there is an increase in the C–O bond order as previously suggested[19,28] for R_f-$COMn(CO)_5$. Such resonance should also be apparent in a lowering of the C═C stretching frequencies, and this is in fact observed, since these frequencies decrease from 1789 cm^{-1} for $C_5F_9Mn(CO)_5$ (an unconjugated C═C bond?) to 1712 cm^{-1} for $CF_2{=}CFCOMn(CO)_5$, to 1670 cm^{-1} for *trans*-$CFH{=}CFMn(CO)_5$, and to 1630 cm^{-1} for the corresponding *cis* isomer.

Secondly, for $CF_2{=}CFCOMn(CO)_5$, it is possible to assign the three strong bands in the 800–1400-cm^{-1} region to C–F stretching vibrations, by comparison with assignments for other $CF_2{=}CFM$ compounds.[33,34] On this basis, the band at 1240 cm^{-1} is assigned to the $CF_2{=}$ asymmetric stretching vibration, that at 1042 cm^{-1} to the ═CF— stretch, and that at 960 cm^{-1} to the $CF_2{=}$ symmetric stretching vibration. In this region, the spectra of the isomers of $[CF_2{=}CFMn(CO)_4]_2$ are much more complex than for $CF_2{=}CFCOMn(CO)_5$ and other $CF_2{=}CFM$ compounds. This can be related to the changes of symmetry of the $CF_2{=}CF$— groups that must accompany the formation of the dimers. The carbonylmanganese deformation mode was observed for all compounds as a strong, broad band in the very constant region at 642–665 cm^{-1}. Interestingly, this band was resolved into a doublet with a separation of about 10 cm^{-1} for all of the compounds except $(CN_3)_3SnCF_2CF_2Mn(CO)_5$ and the two isomers of $CHF{=}CFMn(CO)_5$. Similar splittings of the δ_{MCO} bands have been reported[35] for $(CO)_5$-M–L_2R_4–$M(CO)_5$ where L_2R_4 is $P_2(C_2N_5)_4$ or $As_2(CH_3)_4$ and M is Mo or W.

The Sn–C stretching frequencies changed significantly depending on whether the $(CH_3)_3Sn$ was attached to an Mn atom or to a fluorocarbon group. In $(CH_3)_3SnMn(CO)_5$ and $(CH_3)_3SnMn(CO)_4(\pi$-$C_2H_4)$, in both of which the Sn–Mn bond is present, the Sn–C symmetric and asymmetric stretching vibrations were observed at 500 and 514–517 cm^{-1}, respectively. On the other hand, for $(CH_3)_3SnCF_2CF_2Mn(CO)_5$, these modes appear at 518 and 539 cm^{-1}, respectively. Similar shifts of these frequencies were also observed[8] from hexamethylditin to its fluorocarbon derivatives and, according to the suggestion of Brown and Morgan,[15] indicate an increase in the s character of the tin orbitals in the fluorocarbon derivatives.

These reactions confirm the reactivity of the metal–metal bond in compounds such as $(CH_3)_3SnMn(CO)_5$, but it is clear that the mode of reaction is different from that of the Sn–Sn bond in hexamethylditin. The latter reacts with fluoroolefins through a free-radical mechanism,[8] but this seems unlikely for trimethyltinpentacarbonylmanganese. Although the latter compound reacts most readily with tetrafluoroethylene under free-radical conditions (*i.e.*, ultraviolet irradiation), the formation of $(CH_3)_3Sn\cdot$ radicals should lead to the formation of the same products as are formed in the reaction of hexamethylditin with tetrafluoroethylene. There is, however, no evidence that products of the type $(CH_3)_3Sn(C_2F_4)_nH$ are produced, and it is also particularly remarkable that not more than 1 mole of olefin is inserted into each Sn–Mn bond; *i.e.*, compounds $(CH_3)_3Sn(C_2F_4)_nMn(CO)_5$ where $n > 2$ are not formed. A four-center type of mechanism therefore seems more likely than a free-radical process, but in view of the considerable dependence of the products on the nature of the reagents employed, the need to examine a wider range of both metal–metal bonded compounds and of olefins is obvious. The very considerable difference between the behavior of tetrafluoroethylene and ethylene toward the Sn–Mn bond is not readily understood, and there seems no reason why adducts such as $(CH_3)_3SnC_2F_3ClMn(CO)_5$ should apparently break down to trimethyltin halides and carbonylmanganese derivatives. Even with a cyclic fluoroolefin, this same type of process seems to occur. For example, perfluorocyclobutene reacts with $(CH_3)_3SnMn(CO)_5$ to give[36] trimethyltin fluoride and perfluorocyclobutenylpentacarbonylmanganese. We are currently investigating a wide variety of related reactions to establish in more detail the factors which influence the behavior of the metal–metal bond.

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