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THE REACTIVITY OF METAL–METAL BONDS
VIII*. A COMPARATIVE STUDY OF THE Si–Fe, Ge–Fe AND Sn–Fe BONDS, AND SOME FURTHER REACTIONS OF THE Sn–Mn BOND

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SUMMARY

The reactions of $(CH_3)_3SnMn(CO)_5$ with perfluoropropene, perfluoro-2-butyne and perfluorocyclobutene are described. Similar reactions of $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$ (M = Si, Ge, or Sn) with perfluorocyclobutene, perfluoro-2-butyne, and 3,3,3-trifluoropropyne are described, leading to the characterization of insertion products of the types $(CH_3)_3M(CF_3)C{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ and $(CH_3)_3MC_2H(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$. When M = Sn, other products formed by the elimination of trimethyltin fluoride from 1/1 insertion products, are also formed. The mechanisms of these reactions appear to involve four-centred type transition species.

INTRODUCTION

In previous papers[1-3] we have demonstrated the possibility of insertion into the metal–metal bonds of compounds such as $(CH_3)_3SnMn(CO)_5$, $Co_2(CO)_8$ and $R_3SnCo(CO)_4$. Insertion compounds such as $(CH_3)_3GeCF_2CF_2Mn(CO)_5$, or alternatively compounds derived from unstable insertion intermediates, have been obtained as reaction products. The mechanism of such reactions clearly differs from the free-radical insertion into homonuclear metal–metal bonds, such as Sn–Sn[4], and the orientation of the olefin with respect to the polar metal–metal bond must be important. Few significant conclusions about the mechanism of either the formation or decomposition of the insertion products can be drawn from available evidence. Moreover, it is also clear that the reactivity of the metal–metal bond will be dependent on the particular metals involved in any binuclear combination and on the nature of the ligands coordinated to them. Accordingly, we have studied the behavior of the compounds $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$ where M = Si, Ge, or Sn, thus providing a comparison of the three bonds in identical coordination environments. We have also conducted further studies of the behavior of $(CH_3)_3SnMn(CO)_5$ with olefins, the results of which provide some useful mechanistic comparisons.

RESULTS AND DISCUSSION

Reactions with fluoroalkenes

With perfluoropropene, under UV irradiation, $(CH_3)_3SnMn(CO)_5$ gave

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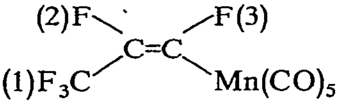
* For part VII see ref. 23.

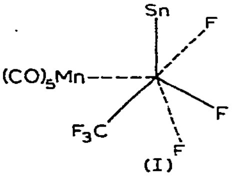
trimethyltin fluoride and a manganese carbonyl product. The IR spectrum of this product showed all the bands expected[5,6] for *trans*-$CF_3CF{=}CFMn(CO)_5$ together with those assigned previously[2] to the *cis* isomer. Characterization in terms of a mixture of *cis* and *trans* isomers was confirmed by the ^{19}F NMR spectrum which on integration showed that the *trans* isomer made up 15% of the product. For the *cis* isomer, the ^{19}F spectrum showed three peaks, of intensity ratio 3/1/1 at 64.1, 65.1 and 131 ppm relative to CCl_3F as solvent. The first which consisted of a doublet of doublets, because of its intensity, must be assigned to the CF_3 group and was coupled with the resonance at 65.1 ppm (J 7.6 Hz) and to the resonance at 131 ppm (J 13 Hz). The quartet at 131 ppm, formed by coupling with CF_3, was assigned to F(3) by



$\delta_1 = 64.1$ ppm $J_{12} = 7.6$ Hz
$\delta_2 = 65.1$ ppm $J_{23} = 2.2$ Hz
$\delta_3 = 131$ ppm $J_{13} = 13$ Hz

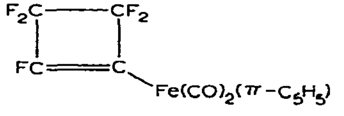
analogy with the *trans* isomer[5,6], leaving the quartet at 65.1 ppm to be assigned to F(2). A small coupling of 2.2 Hz was observed in these two quartets. There was also a second order effect, uncommon in ^{19}F NMR spectroscopy, in the peaks at 64.1 and 65.1 ppm, apparently caused by the similar magnitudes of coupling constants and chemical shift differences. For example in the 64.1 ppm doubleted doublet, the intensity ratio was approximately 1/2/1/2 instead of 1/1/1/1.

It is significant that in the reactions of perfluoropropene with both $(CH_3)_3SnMn(CO)_5$ and $(CH_3)_3GeMn(CO)_5$, *cis*-$CF_3CF{=}CFMn(CO)_5$ is the main product. The β-elimination of trimethyltin fluoride from the rotamer (I) of an unstable insertion compound, provides a ready route to this product, and is energetically favorable because of the considerable steric interaction between the CF_3 and $Mn(CO)_5$ groups.


(I)

The UV-assisted reaction of $(CH_3)_3SnMn(CO)_5$ and perfluorocyclobutene gave trimethyltin fluoride and pentacarbonyl-σ-perfluorocyclo-1-butenylmanganese. The latter compound has been prepared previously[7] by the nucleophilic attack of $Mn(CO)_5^-$ on perfluorocyclobutene. It is also knwon that $R_3SnCo(CO)_4$[3] and $(C_6H_5)_3SnMn(CO)_5$[8] produce $Co(CO)_4^-$ and $Mn(CO)_5^-$ ions in the highly solvating media acetone and dimethylformamide respectively. However, such behavior is unlikely in perfluorocyclobutene. In quite another connection we have found[9] no spectroscopic evidence for the formation of $Mn(CO)_5^-$ ions from $(CH_3)_3GeMn(CO)_5$ dissolved in $(CH_3)_3SnCF_3$ as solvent.

Reactions of perfluorocyclobutene with $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$, where M = Si, Ge, or Sn, did not give insertion products or fluorocarbon derivatives containing the $Fe(CO)_2(\pi\text{-}C_5H_5)$ group. The tin–iron compound, even under prolonged UV irradiation at 76° gave only small amounts of trimethyltin fluoride and $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$, the starting material being largely recovered. Similar results were obtained with the silicon and germanium analogues, although the extent of decomposition in both cases was somewhat greater. Since $(CH_3)_3MF$, M=Si, Ge, or Sn was formed in each appropriate case, and since the other expected elimination product from an unstable insertion compound, namely (II) is known[7] but was not

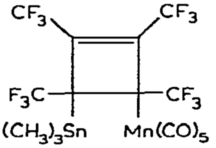


(II)

isolated in these present reactions, the results can best be interpreted in terms of instability of the metal–metal bonded compound under prolonged irradiation, rather than in terms of direct reaction with the olefin.

Reactions with fluoroalkynes

The reaction of perfluoro-2-butyne with $(CH_3)_3SnMn(CO)_5$ at 77° under UV irradiation gave a product containing two molecules of butyne per molecule of $(CH_3)_3SnMn(CO)_5$. The parent peak of the mass spectrum, at 685, was exactly consistent with this formulation, while peaks at masses 672, 657, 642, 616, 601, 585, and 571, corresponded to the successive loss of one or more methyl and/or trifluoromethyl groups. The IR spectrum (Table 1) indicated the presence of manganese carbonyl, C=C, fluorocarbon, and methyl–tin groups. Hence, structure (III) was postulated, the five observed carbonyl stretching absorptions being apparently due to the low symmetry about the $Mn(CO)_5$ group. The ^{19}F NMR spectrum consisted of four peaks of equal area at 51.0 ppm (quartet, J 19 Hz), 53.8 ppm (singlet, width 17 Hz), 56.9 ppm (broad quartet poorly resolved, J 20 Hz) and 57.0 ppm (singlet, width approx. 17 Hz) $[\delta(CFCl_3)=0]$. In view of the very similar chemical shifts, the CF_3 groups are probably in similar environments. In fact, for structure (III), greater differences between the chemical shifts might be anticipated. However, since the



(III)

intensity of the C=C stretching vibrations in the IR spectrum is very weak, structure (III) with a symmetrical configuration about the double bond is preferred to any other model.

A different product resulted when this reaction was performed at 25°, again under UV irradiation. While the products included (III), another component spectroscopically similar to (III) was also present. Complete separation of this new component, (IV), from (III) was not possible and its characterization, at present only tentative, is based on spectroscopic evidence, partly its IR similarity to $(CH_3)_3Sn$-$(CF_3)C$=$C(CF_3)Fe(\pi$-$C_5H_5)(CO)_2$, described below (see also Table 1). This similarity is also obvious in the ^{19}F NMR spectrum. Compound (IV) shows two peaks without fine structure at 49.7 ppm, and 50.9 ppm while the related spectrum of $(CH_3)_3SnC$-

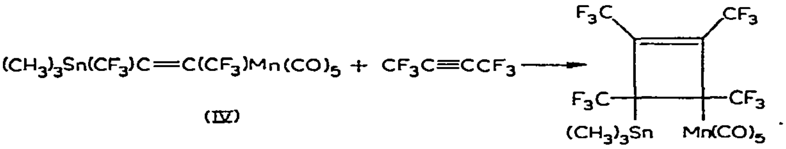
TABLE 1

SPECTRAL DATA OF PRODUCTS FORMED FROM PERFLUORO-2-BUTYNE WITH $(CH_3)_3SnMn(CO)_5$, OR $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$

Compound (III)	Compound (IV)[a]	$(CH_3)_3SnC_2(CF_3)_2Fe(CO)_2(\pi\text{-}C_5H_5)$	Assignment
		3140 vw	
2980 w[b]	2985 w	2980 w	C–H asymm. str.
2920 w	2920 w	2920 w	C–H symm. str.
2127 m	2115 s		Carbonyl str.
	2090 w	2020 vs	
2073 m		1975 vs	
2056 s			
	2045 vs	1940 m (sh)	
2027 s			
2011 s			
	1980 vs		
1615 vs	1530 m	1535 w	C=C str.
1295 w	1255 w		C–F str. region
1238 vs		1240 m	
	1209 vs	1210 vs	
1190 m		1160 m	
1167 m			
1145 vs			
1128 w		1120 vs	
1108 w		1110 vs	
	1038 w		
	1005 w	1010 vw	
866 w	900 w	850 m	
841 w	853 w	840 m	
780 w	785 w	770 m	
651 s	665 s		Mn–CO deform.
641 s	655 s	640 m	
563 m		575 m	
531 w		550 m	
511 w		530 w	
433 w		510 w	

[a] Absorptions assigned to compound (IV) were observed using the mixture of (III) and (IV) described in the Experimental Section, and deleting absorptions due to (III). [b] s = strong; m = medium; w = weak; v = very; br = broad; sh = shoulder.

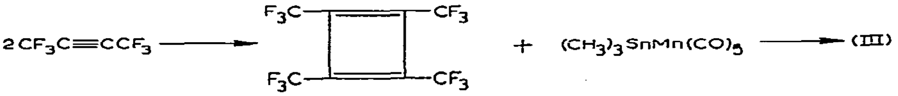
$(CF_3)=C(CF_3)Fe(\pi\text{-}C_5H_5)(CO)_2$ shows peaks at 49.4 and 50.4 ppm. Heating of compound (IV) with or without UV irradiation caused rapid decomposition, but compound (III) was not identified as a decomposition product. Apparently, compound (III) is not produced from compound (IV), but may be formed when (IV) reacts with a further molecule of perfluoro-2-butyne:



(IV)

(III)

Alternatively, the formation of (III) may arise from the addition of $(CH_3)_3SnMn(CO)_5$ across one of the carbon–carbon double bonds of tetrakis(trifluoromethyl)cyclobutadiene:

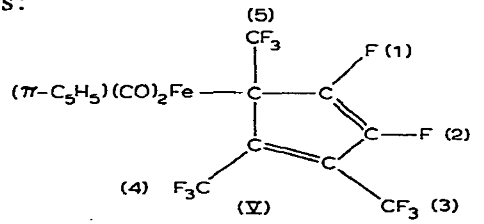


It is known[6,10] that perfluoro-2-butyne will trimerize under UV irradiation to hexakis(trifluoromethyl)benzene, and it is not unreasonable to expect that dimerization is an intermediate step, and that this reactive dimer will react with $(CH_3)_3SnMn(CO)_5$. It is interesting that (III) does not decompose with the elimination of trimethyltin fluoride.

Attempts to react $(CH_3)_3SnMn(CO)_5$ with 3,3,3-trifluoropropyne were unsuccessful; even under conditions sufficiently vigorous to cause some decomposition, the recovery of $(CH_3)_3SnMn(CO)_5$ exceeded 65% and no metal–fluorocarbon product could be detected.

Under UV irradiation at 25°, $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ reacted with perfluoro-2-butyne to give a product of empirical formula corresponding to $(CH_3)_3SnC_2(CF_3)_2Fe(CO)_2(\pi\text{-}C_5H_5)$. The IR spectrum was consistent with the presence of $(CH_3)_3Sn$ and $Fe(CO)_2(\pi\text{-}C_5H_5)$ groups, and integration of the proton NMR spectrum gave the expected 9/5 ratio for methyl/cyclopentadienyl resonances. The methyl resonance also showed a small coupling of approximately 1 Hz suggesting that fluorine atoms were in close proximity to trimethyltin. The two resonances in the ^{19}F spectrum at 49.4 and 50.4 ppm with respect to $CFCl_3$ indicated only two different magnetic environments for the fluorine atoms. These data, coupled with the observed IR absorption at 1530 cm^{-1}, assignable to a C=C stretching mode, lead to the conclusion that the product is indeed $(CH_3)_3SnC(CF_3){=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$. The evidence does not differentiate between the *cis* and *trans* isomeric possibilities.

Since $(CH_3)_3SnMn(CO)_5$ with the butyne gave the cyclobutene derivatives as well as the 1/1 insertion product, the above reaction was also studied under more vigorous conditions. Following UV irradiation at 76°, two new products were isolated, neither of which was a cyclobutene derivative. The major product, of empirical formula corresponding to $(\pi\text{-}C_5H_5)(CO)_2FeC_8F_{11}$, was apparently the result of elimination of trimethyltin fluoride from the expected cyclobutene derivative. Its IR spectrum showed two intense bands at 1650 and 1780 cm^{-1}, indicative[11,12] of conjugated C=C bonds. The carbon–fluorine stretching region is very complex, consistent with the presence of both =C–F and CF_3 groups. The proton NMR spectrum showed a single resonance at τ 5.2, assignable to the cyclopentadienyl protons. The ^{19}F spectrum showed five well-separated multiplets centred at 60.5, 62.9, 63.9, 84.3 and 87.5 ppm. These have been assigned in terms of structure (V) as follows:

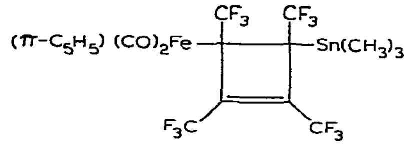


(V)

$J_{1,2} = 33.5$ Hz
$J_{2,3} = 9.4$ Hz
$J_{3,4} = 5.7$ Hz
$J_{4,5} = 3.2$ Hz
$J_{1,5} = 7.0$ Hz

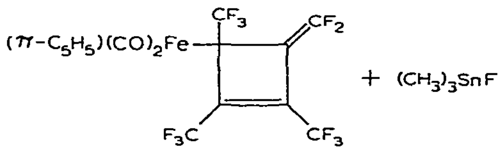
The resonances at 60.5, 62.9, and 63.9 ppm (intensity ratio 1/1/1) are attributed to the three CF_3 groups in the above structure. The multiplet at 87.5 ppm, assigned to F(1), consists of a doublet due to coupling with F(2) (*J* 33.5 Hz) further split into a pair of quartets by coupling with F(5) (*J* 7 Hz). In addition, there appears to be a small coupling with F(3) (*J* 1.5 Hz) to further split each line in the observed pair of quartets. The multiplet at 84.3 ppm is assigned to F(2), which is coupled to F(1) (*J* 33.5 Hz) and to F(3) (*J* 9.4 Hz) resulting in a pair of quartets. The lines in the multiplet are further split, presumably by coupling with F(4) (*J* ~2 Hz). The multiplet at 63.9 ppm, assigned to F(3), is split into a doublet by coupling with F(2) (*J* 9.4 Hz), and split further into overlapping quartets by coupling with F(4) (*J* 5.7 Hz). The multiplet at 62.9 ppm is assigned to F(5) which is coupled to F(1) (*J* 7 Hz) and to F(4) (*J* 3.2 Hz) resulting in an overlapping pair of quartets. The remaining complex multiplet at 60.5 ppm is then assigned to F(4) by elimination.

Since a good yield of trimethyltin fluoride was also obtained, the course of the reaction can be rationalized in terms of the formation of an unstable cyclobutene derivative (VI).



(VI)

The β-elimination of trimethyltin fluoride would give the exocyclic compound (VII), which might readily rearrange to (V). The spectroscopic data distinguish between



(VII)

(V) and (VII) only with respect to the magnitude of the coupling between F(1) and F(2). For structure (VII), the coupling for $=C\genfrac{}{}{0pt}{}{\nearrow F(1)}{\searrow F(2)}$ should be[10] $J_{1,2}$ ~70 Hz. The observed value of 33.5 Hz is more consistent with (V) than with (VII).

The minor product in this reaction of empirical formula corresponding to $(\pi\text{-}C_5H_5)(CO)_2FeC_4F_6H$, showed IR absorptions at 1610 cm^{-1} (C=C stretching mode), and 1290, 1220 and 1120 cm^{-1} (C–F stretching modes) in addition to the expected carbonyl and cyclopentadienyl peaks. The proton NMR spectrum consisted of a singlet (cyclopentadienyl resonance) and a quartet of quartets with $J_1 = 8.5$ Hz, and $J_2 = 1.5$ Hz. The ^{19}F spectrum consisted of a pair of quartets and another overlapping pair of quartets. This is consistent with the *trans* isomer of $(\pi\text{-}C_5H_5)(CO)_2FeC(CF_3){=}C(CF_3)H$ with geminal CF_3–H coupling of 8.5 Hz, *cis*-CF_3–H coupling of 1.5 Hz, and *trans* CF_3–CF_3 coupling of 2 Hz. For the *cis*-butene structure, the *trans* CF_3–H coupling should be close to zero[13]. This product might result from hydrogen abstraction by the radical $CF_3\dot{C}{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$, possibly formed by addition of $\cdot Fe(CO)_2(\pi\text{-}C_5H_5)$ to $CF_3C{\equiv}CCF_3$.

Both $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$, where M = Si or Ge, gave only 1/1 insertion products when irradiated with perfluoro-2-butyne at 76°. These were characterized analytically and spectroscopically. They showed IR absorptions due to the C=C stretch at 1530 (for M = Ge) and 1515 (for M = Si) cm^{-1}, and very characteristic patterns at 1240, 1210, 1160, 1120 and 1100 cm^{-1} due to C–F stretching modes. The ^{19}F NMR spectra were completely consistent with those of the analogous insertion products from the Sn–Fe and Sn–Mn compounds, and showed just two rather broad absorptions of equal intensity at 50.0 and 50.5 ppm for M = Ge, and 50.0 and 51.7 ppm for M = Si. Unfortunately the width of these resonances made it impossible to determine if any coupling to the methyl protons of the $(CH_3)_3M$ groups occurred. Reaction of the silicon and germanium compounds with excess butyne under irradiation did not result in the formation of cyclobutene products or any derivatives thereof.

Attempts were next made to obtain insertion products with 3,3,3-trifluoropropyne, since the presence of the hydrogen atom in the derivatives of this alkyne should prove useful in the spectroscopic determination of the isomeric composition. The tin compound, $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$, gave only a low yield of *cis*-H-$(CF_3)C{=}C(H_3)Fe(CO)_2(\pi\text{-}C_5H_5)$, and a corresponding amount of trimethyltin fluoride. Interestingly, the former is also obtained[14] in the reaction of $Fe(CO)_2(\pi\text{-}C_5H_5)^-$ and 3,3,3-trifluoropropyne. Both $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$ where M = Si or Ge reacted with 3,3,3-trifluoropropyne to give products of empirical formula corresponding to $(CH_3)_3MC_2H(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$. Their IR spectra showed in addition to the absorptions characteristic of $(CH_3)_3M$ (M = Si or Ge) and $Fe(CO)_2(\pi\text{-}C_5H_5)$ groups, bands of medium intensity at 1555 (M = Ge) and 1550 (M = Si) cm^{-1} (C=C stretch) and very strong absorptions at 1210, 1125 and 1090 cm^{-1} (C–F stretch). The proton NMR spectra consisted in each case, of two sharp singlets and a quartet while each showed a doublet in the ^{19}F spectra. The data are given in Table 2, and are clearly consistent with a *cis* arrangement of H and CF_3 with respect to the C=C bond. However, the positions of H and CF_3 relative to the silicon (or germanium) and iron atoms cannot be assigned unambiguously. Cullen *et al.*[15] have shown that a coupling of 1 Hz is observed in the methyl resonance of a trimethyltin or dimethylarsenic group when there is a CF_3 group in the geminal position with respect to tin or arsenic. In the proton NMR spectra of the perfluoro-2-butyne insertion products discussed earlier, this 1 Hz coupling was observed in the methyl resonance of the $(CH_3)_3M$ where M = Si, Ge, or Sn group. The absence of such coupling in the 3,3,3-

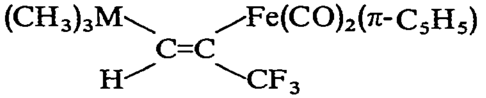
TABLE 2

NMR DATA FOR $(CH_3)_3MCHC(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ (M = Ge OR Si)

M	Proton data[a]				^{19}F data[b]	
	$\tau(CH_3)$	$\tau(C_5H_5)$	$\tau(H)$	$J(H\text{-}F)$	δ	$J(H\text{-}F)$
Si	9.8	5.1	3.0 (q)	2	60.1 (d)	2
Ge	9.7	5.2	2.8 (q)	2	59.4 (d)	2

[a] In chloroform solution; q = quartet, d = doublet. [b] In cyclohexane solution; $\delta = 0$ for external $CFCl_3$.

trifluoropropyne products suggests that hydrogen rather than CF_3 is geminal to silicon or germanium and that structure (VIII) may be more likely.



(VIII) M = Si or Ge.

It was unfortunate that the corresponding compound where M = Sn could not be obtained, since a large ^{119}Sn–C–H coupling should then be observed for (VIII).

With the exception of secondary reactions associated with the formation of trimethyltin fluoride, these reactions with alkenes and alkynes (summarized in Table 3) do not indicate any great trend in the reactivities of the Si–F, Ge–Fe and Sn–Fe bonds. This is consistent with the spectroscopic properties of these compounds. Table 4, containing IR and proton NMR spectroscopic data for them, as well as for $Cl(CH_3)_2Sn(CO)_2(\pi\text{-}C_5H_5)$, shows only a very small trend in ν(CO) to higher frequencies as M changes from Sn to Ge to Si, this being the expected[16] order if the change is due to the inductive effect of the Group IV atom, or largely of the chlorine atom in the chlorodimethyltin compound. In the NMR spectra, only for this chloro-compound are any noticeable changes observed. It seems reasonable, therefore, to conclude that identical mechanisms may be involved in the reactions of the silicon–, germanium–, and tin–iron with the propyne and butyne, leading to insertion products. Although these reactions are UV assisted, no products suggestive of a radical mechanism[4] were found, and a four-centred type of mechanism seems more likely. The *cis*-

TABLE 3

REACTIONS AND REACTION PRODUCTS

Reactants	Conditions[a]	Products (% yield)
$Me_3SnMn(CO)_5 + CF_3CF{=}CF_2$	UV	*cis*- and *trans*-$CF_3CF{=}CFMn(CO)_5$ (60%), Me_3SnF (>15%)
$Me_3SnMn(CO)_5$ + cyclo-C_4F_6	UV	cyclo-$C_4F_5Mn(CO)_5$(~20%), Me_3SnF (20%)
$Me_3SiFe(CO)_2Cp$ + cyclo-C_4F_6	UV	$[Fe(CO)_2Cp]_2$ (14%)
$Me_3GeFe(CO)_2Cp$ + cyclo-C_4F_6	UV	$[Fe(CO)_2Cp]_2$ (18%), Me_3GeF, Me_4Ge
$Me_3SnFe(CO)_2Cp$ + cyclo-C_4F_6	UV	No reaction
$Me_3SnMn(CO)_5 + CF_3C{\equiv}CCF_3$	UV	(III) (~25%), $Me_3Sn(CF_3)C{=}C(CF_3)Mn(CO)_5$ (~30%)
$Me_3SnMn(CO)_5 + CF_3C{=}CH$	UV	No reaction
$Me_3SnFe(CO)_2Cp + CF_3C{\equiv}CCF_3$	UV	$Me_3Sn(CF_3)C{=}C(CF_3)Fe(CO)_2Cp$ (15%)
	UV, 76°	(V) and $Cp(CO)_2FeC(CF_3){=}C(CF_3)H$ (15% total), Me_3SnF (20%)
$Me_3GeFe(CO)_2Cp + CF_3C{\equiv}CCF_3$	UV	$Me_3Ge(CF_3)C{=}C(CF_3)Fe(CO)_2Cp$ (15%), Me_3GeF, Me_4Ge
$Me_3SiFe(CO)_2Cp + CF_3C{\equiv}CCF_3$	UV, 76°	$Me_3Si(CF_3)C{=}C(CF_3)Fe(CO)_2Cp$ (8%), Me_3SiF
$Me_3SnFe(CO)_2Cp + CF_3C{\equiv}CH$	UV	*cis*-$H(CF_3)C{=}CHFe(CO)_2Cp$ (5%), Me_3SnF
$Me_3GeFe(CO)_2Cp + CF_3C{\equiv}CH$	UV	$Me_3GeC_2H(CF_3)Fe(CO)_2Cp$ (7%)
$Me_3SiFe(CO)_2Cp + CF_3C{\equiv}CH$	UV	$Me_3SiC_2H(CF_3)Fe(CO)_2Cp$ (6%)

[a] All reactions at 25° unless otherwise stated.

TABLE 4

SPECTROSCOPIC DATA FOR $R(CH_3)_2M^{IV}Fe(CO)_2(\pi\text{-}C_5H_5)$

Compound M^{IV}	R	ν(CO) (cm^{-1})	$\tau(M^{IV}\text{-}CH_3)^a$ (ppm)	$J(^{119}Sn\text{-}C\text{-}H)$ (Hz)	$\tau(C_5H_5)^a$ (ppm)
Si	CH_3	1998,1944	9.6		5.3
Ge	CH_3	1997,1945	9.6		5.3
Sn	CH_3	1991,1942	9.7	47	5.3
Sn	Cl	1999,1959	9.2	40	5.1

[a] In $CHCl_3$.

configuration of the insertion products of 3,3,3-trifluoropropyne is also indicative of a four-centred reaction mechanism.

It is also clear, particularly in the reactions of the tin–manganese compound and in the formation of a cyclopentadiene product from perfluoro-2-butyne, that the β-elimination of trimethyltin fluoride (from insertion products) is an important process. This is consistent with the behavior of the compounds $(CH_3)_3MCFHCF_2Sn(CH_3)_3$ and $(CH_3)_3MCF[Sn(CH_3)_3]CF_2H$, where M = Si, Ge, or Sn, which have been shown[17] to decompose by the β-elimination of trimethyltin fluoride, and with the construction of scale models of the addition products which establishes the considerable steric interaction between the $(CH_3)_3Sn$ group and a β-fluorine.

EXPERIMENTAL

Vacuum manipulation by standard techniques was employed in the handling of reactants and products. Microanalyses were performed by Dr. Alfred Bernhardt, Germany, or the Schwarzkopf Microanalytical Laboratory, New York. UV irradiations were performed with a 400 watt G.E. lamp at 77°, or a 200 watt Hanovia lamp at room temperature. IR spectra of solids were recorded as nujol mulls and as cyclohexane solutions (when sufficiently soluble), while liquids were used neat as films between potassium bromide discs. The spectra were recorded with a Beckman IR 10 Spectrometer, while high resolution spectra were obtained in the carbonyl stretching region (1930–2200 cm^{-1} region) on a Beckman IR 7 Spectrometer. Scale expansion to 10 cm^{-1} per inch (below 2050 cm^{-1}) and to 40 cm^{-1} per inch (above 2050 cm^{-1}) was employed, and calibration was achieved against the 1942.6 cm^{-1} line of atmospheric water vapor.

Proton NMR spectra were measured on a Varian Associates A-60 Spectrometer, with chemical shifts being determined relative to tetramethylsilane as internal standard. The ^{19}F NMR spectra were recorded on a Varian Associates DP-60 or HA-100 Spectrometer, and fluorine chemical shifts were measured relative to CCl_3F. Mass spectra were obtained on a Varian M-66 Spectrometer.

Fluoroolefins were obtained from Peninsular Chem Research, Gainsville, unless otherwise stated. (Trimethylstannyl)pentacarbonylmanganese was prepared by the procedure described previously[1]. (Trimethylstannyl)cyclopentadienyliron dicarbonyl was prepared by the method of Gorsich[18]. (Found: C, 35.96; H, 4.42. $C_{10}H_{14}FeO_2Sn$ calcd.: C, 35.24; H, 4.11%.) The same procedure, using trimethylbromogermane, was used to obtain (trimethylgermyl)cyclopentadienyliron dicarbonyl. (Found: C, 40.64; H, 4.91. $C_{10}H_{14}GeFeO_2$ calcd.: C, 40.76; H, 4.76%.) (Trimethylsilyl)cyclopentadienyliron dicarbonyl was prepared by the method of Piper and Wilkinson[19].

Reactions with fluoroalkenes

(*a*). *Perfluoropropene with* $(CH_3)_3SnMn(CO)_5$

(Trimethylstannyl)pentacarbonylmanganese (0.7 g, 1.96 mmoles), perfluoropropene (2.08 g, 14 mmoles, Columbia Organic Chemicals) and pentane (0.76 g) were irradiated in a sealed silica tube for 16 h at 25°. After this period, the tube contained a precipitate and an orange solution. Carbon monoxide (0.04 mmoles) and unreacted perfluoropropene (ca. 13 mmoles) were removed, as well as a volatile fraction (500 mg) which condensed at −23°, to leave an involatile solid in the reaction tube. From this solid, after acetone extraction, trimethyltin fluoride (30 mg) was isolated and identified spectroscopically. The acetone-soluble portion (70 mg) contained starting material and was not investigated further.

The −23° fraction was a mixture of colorless crystals in a yellow liquid, whose IR and ^{19}F NMR spectra established the presence of *cis*- and *trans*-$CF_3CF{=}CFMn(CO)_5$, the *trans* isomer constituting 15% of the mixture. The IR spectrum showed all the bands reported[6] for the *trans* isomer and also agreed well with that reported for a similar mixture from the reaction[2] of (trimethylgermyl)pentacarbonylmanganese with perfluoropropene.

(*b*). *Perfluorocyclobutene with* $(CH_3)_3SnMn(CO)_5$

(Trimethylstannyl)pentacarbonylmanganese (2.0 g, 5.6 mmoles) and perfluorocyclobutene (22 mmoles) in pentane (5 g) were irradiated at 25° for 48 h. A small amount of carbon monoxide (0.03 mmole) was formed, and after removal of the solvent and unreacted olefin, the pentane-soluble residue was distilled under vacuum to give (perfluorocyclobutenyl)pentacarbonylmanganese. (Found: C, 31.89; H, 0.0; F, 28.4. $C_9F_5MnO_5$ calcd.: C, 31.90; H, 0.0; F, 28.1%.) The IR spectrum (cyclohexane solution and Nujol mull) agreed with that reported previously[7]. The pentane-insoluble portion was trimethyltin fluoride, identified spectroscopically.

(*c*). *Perfluorocyclobutene with* $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$, *M = Si, Ge, or Sn*

(*i*). A five-fold excess of perfluorocyclobutene with $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$ were sealed with hexane in a silica Carius tube and irradiated for 48 h at 25°. For M = Si, only cyclopentadienyliron dicarbonyl dimer (14%) was separated in addition to the starting material. For M = Ge, the yield of dimer was 18%, and recovery of starting material was 40%, with some trimethylfluorogermane and tetramethylgermane also present in the volatile fractions. For M = Sn, recovery of starting material was quantitative.

(*ii*). For M = Si and Sn, the above reactions were repeated with UV irradiation at 76° for 48 h. With M = Si, the starting material (20%), an unidentified fluorocarbon polymer, and decomposition products were obtained. For M = Sn, starting material, cyclopentadienyliron dicarbonyl dimer, and trimethyltin fluoride (7%) resulted.

Reactions with fluoroalkynes

(*a*). *Perfluoro-2-butyne with* $(CH_3)_3SnMn(CO)_5$

(*i*). (Trimethylstannyl)pentacarbonylmanganese (1.038 g, 2.82 mmoles) and perfluoro-2-butyne (2.27 g, 14 mmoles) in pentane (12.2 g) were irradiated at 77° for

126 h. Carbon monoxide, solvent, and excess fluorocarbon were removed under vacuum to leave an involatile solid. Organometallic compounds were separated from an inorganic residue by sublimation. Fractional sublimations (60°/10^{-3} mm) and crystallizations from pentane and methanol of this original sublimate gave unreacted (trimethylstannyl)pentacarbonylmanganese and a white solid identified as 1,2,3,4-tetrakis(trifluoromethyl)-3-(pentacarbonylmanganyl)-4-(trimethylstannyl)cyclobutene. (Found: C, 27.8; H, 1.34. $C_{16}H_9F_{12}MnO_5Sn$ calcd.: C, 27.9; H, 1.32%.) Inconsistent values were obtained from tin, manganese and fluorine determinations. The mass spectroscopic molecular weight was 685 (calcd. 685). IR and NMR data are discussed elsewhere.

(*ii*). (Trimethylstannyl)pentacarbonylmanganese (1.032 g, 2.81 mmoles) and perfluoro-2-butyne (1.78 g) in pentane (5.6 g) were irradiated at 25° for 72 h. From the weight of fluorocarbon recovered, it was calculated that 0.515 g had reacted. From the residue in the reaction tube, extraction with pentane left an insoluble brown solid (0.144 g) which showed only broad, weak IR absorptions. The pentane extract contained no (trimethylstannyl)pentacarbonylmanganese, but contained both the cyclobutene derivative described in the above experiment and also $(CH_3)_3Sn(CF_3)$-$C{=}C(CF_3)Mn(CO)_5$. Both were identified spectroscopically but complete separation could not be achieved because of their very similar solubilities. Approximately 0.95 g of mixture was isolated containing approximately equal yields of the two compounds. When a sample of this mixture was heated (at 77° for 10 h) and irradiated, decomposition of $(CH_3)_3Sn(CF_3)C{=}C(CF_3)Mn(CO)_5$ occurred.

(*b*). 3,3,3-*Trifluoropropyne with* $(CH_3)_3SnMn(CO)_5$

A large excess of the propyne, prepared by the method of Finnegan and Norris[20], (trimethylstannyl)pentacarbonylmanganese (1.03 g, 2.9 mmoles) and pentane (6 g) were irradiated for 72 h at 77°. During this time a large quantity of a black precipitate was deposited. Pentane and unreacted propyne were removed, and hence 0.6 g of the propyne was found to have been consumed. (Trimethylstannyl)pentacarbonylmanganese (0.70 g, 67%) was recovered as a fraction of low volatility. The dark brown residue was extracted with pentane leaving a residue (0.4 g) which showed essentially no IR absorptions and which gave positive tests for manganese and fluoride. Evaporation of the pentane extract left a yellow-brown material (0.06 g) which showed typical carbonyl IR absorptions as well as very broad fluorocarbon absorptions, typical of polymerized fluorocarbon.

(*c*). *Perfluoro-2-butyne with (trimethylstannyl)cyclopentadienyliron dicarbonyl*

(*i*). Perfluoro-2-butyne (13 mmoles) and the tin–iron compound (1.4 g, 4 mmoles) were sealed in a silica Carius tube with hexane (10 ml) and irradiated for 84 h. The solution in the tube turned black. The reaction volatiles were removed and the residues extracted with hexane. The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the tin–iron compound (0.55 g, 40% recovery). The second fraction gave a yellow solid (0.12 g, 15% yield, m.p. 86–88° after recrystallization from pentane), formulated as $(CH_3)_3$-$SnC(CF_3){=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$. (Found: C, 33.42; H, 2.77. $C_{14}H_{14}F_6FeO_2Sn$ calcd.: C, 33.43; H, 2.78%.) The IR spectra indicated that the later fractions contained increasing amounts of fluorocarbon polymer.

(*ii*). Perfluoro-2-butyne (12 mmole) and the tin–iron compound (1.5 g, 4.5 mmoles) were sealed in a silica Carius tube with hexane (10 ml) and irradiated for

40 h at 76°. Carbon monoxide (1.7 mmoles) was formed. The reaction volatiles were removed and the residues extracted with hexane. The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the tin–iron compound (0.5 g, 30% recovery) as well as some of the 1/1 insertion product, which was identified spectroscopically. The second fraction gave a mixture of two fluorocarbon compounds of iron (250 mg, 15%). This mixture was again chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction gave a yellow powder, *trans*-$H(CF_3)C{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ m.p. 37.5–39°), (Found: C, 38.52; H, 1.92; F, 33.89. $C_9H_6F_6FeO_2$ calcd.: C, 38.85; H, 1.76; F, 33.55%.) IR spectrum (mull): 3150 vw, 2950 w, 2860 w, 2040 vs, 1990 vs, 1960 m (sh), 1610 m, 1435 vw, 1290 s, 1220 s, 1120 s, 850 m, 840 m, 650 s, 640 m, 575 m, 545 m.

The second fraction gave a yellow, waxy solid (m.p. 40–42°): formulated as compound (V). (Found: C, 37.00; H, 1.08; F, 42.77. $C_{15}H_5F_{11}FeO_2$ calcd.: C, 37.36; H, 1.04; F, 43.38%.) IR spectrum (mull): 3140 vw, 2980 w, 2920 w, 2020 vs, 1975 vs, 1940 m (sh), 1535 m, 1435 vw, 1240 m, 1210 vs, 1160 m, 1120 vs, 1100 vs, 1010 vw, 850 m, 840 m, 770 m, 640 m, 575 m, 550 m, 530 m, 510 w.

The dichloromethane-insoluble residue contained trimethyltin fluoride (165 mg, 20%), identified by its IR spectrum.

The volatile fraction of the reaction products contained tetramethyltin, identified by its NMR spectrum[21].

(*d*). *Perfluoro-2-butyne with (trimethylgermyl)cyclopentadienyliron dicarbonyl*

(*i*). Perfluoro-2-butyne (12 mmoles) and the germanium–iron compound (1.0 g, 3.5 mmoles) were sealed in a silica Carius tube with hexane (10 ml) and irradiated at 76° for 42 h. Carbon monoxide (0.7 mmole) was formed. Treatment of the involatile mixture as in (*c*)-(*i*) above gave a first fraction of the original germanium–iron compound (0.60 g, 60% recovery). The second fraction gave $(CH_3)_3GeC(CF_3){=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$, 15%. (Found: C, 36.63; H, 3.14; F, 25.83. $C_{14}H_{14}F_6FeGeO_2$ calcd.: C, 36.81; H, 3.06; F, 24.98%.) IR spectrum (mull): 3150 vw, 2970 w, 2900 w, 2030 vs, 1990 vs, 1960 m (sh), 1530 w, 1240 w, 1210 vs, 1165 w, 1130 vs, 1100 vs, 1000 vw, 845 m, 830 m (sh), 645 m, 600 w, 575 m, 565 w (sh), 550 m.

(*ii*). Perfluoro-2-butyne (3 mmoles) and the 1/1 butyne insertion obtained from the last reaction (1.7 mmoles) were irradiated in a silica tube at 76° for 20 h. Carbon monoxide (0.2 mmole) was removed, and the hexane extract of the residue gave, after chromatography on silica gel with hexane/benzene mixture as eluent, the 1/1 butyne insertion product (37%) recovery), identified spectroscopically. Subsequent fractions were found spectroscopically to contain increasing amounts of fluorocarbon polymer.

(*e*). *Perfluoro-2-butyne with (trimethylsilyl)cyclopentadienyliron dicarbonyl*

Hexafluoro-2-butyne (12 mmoles) and the silicon–iron compound (0.75 g, 3 mmoles) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 43 h at 76°.

Carbon monoxide (0.8 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the silicon–iron compound (0.40 g, 50% recovery). The second fraction gave a yellow solid, $(CH_3)_3SiC(CF_3){=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ (100 mg, 8% yield). (Found: C, 41.59; H, 3.48; F, 27.00. $C_{14}H_{14}F_6FeO_2Si$ calcd.: C, 40.79; H, 3.4; F, 27.68%.) IR spectrum (mull):

3150 vw, 2960 m, 2900 m, 2030 vs, 1990 vs, 1960 m (sh), 1515 w, 1250 m, 1210 vs, 1160 m, 1130 vs, 1105 vs, 1000 vw, 840 s, 670 w, 645 m, 620 w, 575 m, 550 m. The IR spectra showed that subsequent fractions contained increasing amounts of fluorocarbon polymer.

Trimethylfluorosilane and tetramethylsilane, identified by their NMR spectra[21,22] were found in the volatile fraction of the reaction products.

(*f*). 3,3,3-*Trifluoropropyne with* (*trimethylstannyl*)*cyclopentadientyliron dicarbonyl*

The propyne (11 mmoles) and the tin–iron compound were irradiated in hexane in a silica tube at 25° for 30 h. After removing carbon monoxide (1.6 mmoles) and solvent, the residue was treated chromatographically on silica gel to give unreacted tin–iron compound (15% recovery), and a yellow oil, *cis*-$H(CF_3)C{=}CHFe(CO)_2(\pi\text{-}C_5H_5)$. (Found: C, 43.88; H, 2.54; F, 23.21, 19.67. $C_{10}H_7F_3FeO_2$ calcd.: C, 44.15; H, 2.57; F, 20.97%.) IR spectrum (liquid film): 3140 w, 2960 w, 2930 w, 2860 w, 2030 vs, 1970 vs, 1930 (sh), 1570 m, 1435 m, 1425 m, 1340 m, 1310 w, 1270 vs, 1240 w (sh), 1195 vs, 1100 vs (br), 1060 w (sh), 1015 w, 1005 w, 970 w, 840 s, 670 w, 625 m, 605 m, 590 m, 570 m, 530 w, 500 w. Subsequent fractions contained fluorocarbon polymer.

(*g*). 3,3,3-*Trifluoropropyne with* (*trimethylgermyl*)*cyclopentadienyliron dicarbonyl*

3,3,3-Trifluoropropyne (15 mmoles) and the germanium–iron compound (0.75 g, 2.5 mmoles) were irradiated in a silica Carius tube with hexane (10 ml) for 24 h at 25°.

Carbon monoxide (0.1 mmole) and other volatiles were removed. The hexane extract of the residues, after chromatography on silica gel with a hexane/benzene mixture as eluent, gave the germanium–iron compound (100 mg, 15% recovery). The second fraction gave a yellow oil (60 mg, 7% yield), formulated as $(CH_3)_3GeC_2H(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$. (Found: C, 40.74; H, 3.70; F, 14.35. $C_{13}H_{15}F_3FeGeO_2$ calcd.: C, 40.16; H, 3.86; F, 14.68%.) IR spectrum (liquid film): 3130 vw, 2970 w, 2910 w, 2020 vs, 1980 vs, 1555 m, 1425 w, 1280 w, 1235 m, 1205 vs, 1125 vs, 1090 vs, 860 s (sh), 825 vs, 625 m, 600 m, 595 s, 575 s, 565 s (sh), 550 m. The IR spectra showed that subsequent fractions contained increasing amounts of fluorocarbon polymer.

A similar reaction conducted with irradiation at 76° for 48 h, gave approximately 20% yield of the above insertion product; however impurities were present due to the extensive polymerization of the propyne.

(*h*). 3,3,3-*Trifluoropropyne with* (*trimethylsilyl*)*cyclopentadienyliron dicarbonyl*

3,3,3-Trifluoropropyne (13 mmoles) and the silicon–iron compound (0.75 g, 3 mmoles) were irradiated in a silica Carius tube with hexane (5 ml) for 48 h at 25°.

Carbon monoxide (0.9 mmole) and other reaction volatiles were removed. The hexane extract of the residues in the tube was chromatographed on silica gel. The first fraction contained the silicon–iron compound (0.22 g, 30% recovery). The second fraction gave a yellow oil, $(CH_3)_3SiC_2H(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ (70 mg, 6%). (Found: C, 46.12; H, 4.45. $C_{13}H_{15}F_3FeO_2Si$ calcd.: C, 45.36; H, 4.36%.) IR spectrum (liquid film): 3130 vw, 2980 m, 2900 w, 2020 vs, 1980 vs, 1550 m, 1425 w, 1290 w, 1250 s, 1210 vs, 1125 vs, 1090 vs, 870 m (sh), 840 vs, 665 m, 610 s, 575 s, 560 s.

A similar reaction at 76° for 48 h with irradiation gave a slightly higher yield (11%) of this product.

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