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# REACTIVITY OF METAL—METAL BONDS

## XI*. FURTHER CLEAVAGE REACTIONS OF SOME GROUP IVB—TRANSITION METAL BONDS WITH HALOGENS, PSEUDO-HALOGENS, HYDROGEN HALIDES OR TRIFLUOROIODOMETHANE

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## Summary

The reactions of HCl, HBr, $Cl_2$, $I_2$, ICl or $CF_3I$ with some trimethyl, triphenyl or phenyl(pentafluorophenyl) Group IV metal—transition metal derivatives containing M—Fe (M = Si, Ge or Sn) and Sn—M′ (M′ = Mn, Cr, Mo, or W) bonds are described. The reactions of HCl or HBr with systems containing Sn—Fe or Sn—M′ bonds, and $Cl_2$ with those containing Sn—Mn bonds resulted in partial or complete replacement of the organic groups bound to tin. In all other reactions, cleavage of the metal—metal bond occurred. Some of the factors affecting the relative reactivity of the Group IV metal—carbon and metal—metal bonds towards these reagents are discussed.

## Introduction

In a previous paper [2], the cleavage reactions of the metal—metal or metal—carbon bond in the trimethyltin and triethyllead derivatives of manganese pentacarbonyl by halogens, hydrogen halides, iodine monochloride and trifluoroiodomethane were described. Reactions involving halogens or the hydrogen halides have also been reported for systems containing tin—iron [3], tin—manganese [3], germanium—manganese [5], tin—rhenium [4, 6], tin—molybdenum [7] and tin—tungsten [7] bonds, but while it appears that the susceptibility of the metal—metal bond to cleavage by these reagents is partly dependent upon the nature of the metals and upon the substituents bound to tin, other factors are also involved. In an attempt to clarify these points we now report the results of similar studies on systems containing M—Fe (M = Si, Ge or Sn), Sn—M′ (M′ = Mn, Cr, Mo or W) bonds.

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*For part X see ref. 1.

## Experimental

Volatile reactants and products were in most cases manipulated by standard vacuum techniques and identified spectroscopically using the instrumentation described previously [1]. Mass spectra were obtained on an AEI MS-9 spectrometer operating at 70 eV.

The compounds $Me_3MFe(CO)_2Cp$ (M = Si [8], Ge [9] or Sn [10]), $Ph_3SnM'(CO)_3Cp$ (M' = Mo [11] or W [11]), $Me_3SnM'(CO)_3Cp$ (M' = Mo [11, 12] or W [11]) $Ph_{3-n}(C_6F_5)_nSnMn(CO)_5$ ($n$ = 0 to 3) [13] and $Ph_3SnFe(CO)_2Cp$ [3] were all obtained by the literature methods, while $Me_3SnCr(CO)_3Cp$ was obtained by a procedure exactly analogous to that used for the molybdenum and tungsten derivatives. The series of compounds $Ph_3SnFe(CO)_{2-x}(Cp)L_x$ [$x$ = 1, L = $PEt_3$ or $P(OPh)_3$ and $x$ = 2, L = $P(OPh)_3$] were prepared by a method similar to that previously reported for the preparation of $Ph_3SnFe(CO)(Cp)PPh_3$ [14]. The analytical, physical and spectroscopic properties for these compounds are given in Table 4.

Except for the triphenyltin or phenylpentafluorophenyltin derivatives, reactions involving a gaseous reactant were carried out in evacuated sealed Carius tubes, while those with non-gaseous reactants were carried out under nitrogen at the reflux temperature of the solvent. The reactions of the triphenyltin derivatives were performed by the addition, via a burette, of the exact stoichiometric amount of a freshly standardized solution of HCl dissolved in ether to a solution of the tin—iron compound in an appropriate solvent. Reactions with the phenylpentafluorophenyltin derivatives were accomplished by a similar method using a standardized solution of chlorine in carbon tetrachloride. The relevant experimental details for the reactions that resulted in the cleavage of the tin—carbon bond are given in Table 1, while those resulting in the cleavage of the metal—metal bond are given in Table 2. A typical example for each type of reaction is described below. The analytical and spectroscopic data for the new compounds formed by cleavage of the tin—carbon bond are given in Table 3.

### *(a) The reaction of chlorine with trimethyltin(cyclopentadienyl)dicarbonyliron*

Trimethyltin(cyclopentadienyl)dicarbonyliron (0.45 g, 0.75 mmoles) and chlorine (0.426 g, 6 mmoles) were sealed in a Pyrex Carius tube with carbon tetrachloride (45 ml) and stored at 0° for 15 minutes. The initially yellow solution turned red immediately. Upon opening the tube, the volatiles were removed and were found to contain carbon monoxide (0.3 mmoles) and trimethyltin chloride, which was identified by its NMR spectrum. The residue left in the Carius tube was extracted first with hexane and then with dichloromethane. The hexane extract was found to contain trimethyltin(cyclopentadienyl)dicarbonyliron (50 mg, 20% recovery), while the dichloromethane extract contained cyclopentadienyldicarbonyliron chloride, identified by a comparison of the infrared and NMR spectra with those of a genuine sample prepared by the literature method [15]. A considerable amount of an insoluble residue remained in the Carius tube.

*(b) The reaction of hydrogen chloride with triphenyltin(cyclopentadienyl)dicarbonyliron*

To a solution of triphenyltin(cyclopentadienyl)dicarbonyliron (2.11 g, 4 mmoles) in benzene (20 ml) was added via a burette a solution of hydrogen chloride in ether (7.14 ml, 8 mmoles of a 1.12 M solution) and as quickly as possible the flask was tightly stoppered. The initially yellow solution turned orange, and after three hours, the smell of HCl completely disappeared from the solution. The solvent was removed to leave an orange oil that rapidly crystallized upon tne addition of a few ml of benzene, followed by pentane until the precipitation of the product was complete. This gave yellow crystals of phenyldichlorotin(cyclopentadienyl)dicarbonyliron, $PhCl_2SnFe(CO)_2Cp$ (yield 1.2 g, 69%. m.p. 116 - 117°, lit. [16] 116 - 117°).

## Results and Discussion

Reactions with hydrogen chloride which lead to cleavage of the Group IVB metal—carbon bond are summarized in Table 1, while those which lead to Group IVB—transition metal bond cleavage are shown in Table 2. The tin derivatives tend to undergo Sn—C rather than Sn—M cleavage, in contrast to the silicon and germanium analogues for which metal—metal bond cleavage is more common. This may possibly be rationalized in terms of changes in the relative strength of the metal—carbon and metal—metal bonds as the Group IVB metal changes from silicon to tin. The lack of reaction between the trimethyl- and triphenylgermanium derivatives of manganese pentacarbonyl with excess HCl, even at high temperatures, contrasts with the Ge—Mo cleavage in reaction [17] of $Me_3GeMo(CO)_3Cp$. However, since the Ge—M bond strengths in $Me_3GeMn(CO)_5$ [18] and $Me_3GeMo(CO)_3Cp$ [19] are nearly equal at 61.5 and 60 kcal/mole respectively, factors other than relative bond strengths must be involved and may well be related to differences in the structure and reactivity of the reaction transition states.

For the triphenyltin—iron compounds, reaction with one molar equivalent of HCl gave $Ph_2ClSnFe(CO)_{2-x}CpL_x$ contaminated with some unreacted starting material and the $PhCl_2Sn$ analogue. The latter two contaminants were conveniently removed by recrystallization. With two molar equivalents, the $PhCl_2Sn$ compounds were formed cleanly while excess HCl readily gave the crystalline $Cl_3SnFe(CO)_{2-x}CpL_x$ compounds, as in the reactions [20] of HX (X = Cl, Br, or I) with $Ph_3SnFe(CO)_2Cp$. In contrast, $Ph_3SnFe(CO)_2Cp$ with one molar equivalent of HBr gave reasonably pure $Ph_2BrSnFe(CO)_2Cp$, but two molar equivalents of HBr gave $PhBr_2SnFe(CO)_2Cp$, severely contaminated with 30% of $Ph_2BrSnFe(CO)_2Cp$. This mixture was converted to pure $PhBr_2SnFe(CO)_2Cp$ by heating in vacuo at 150° with the calculated amount of $Br_3SnFe(CO)_2Cp$. These results suggest that in the reactions with HCl the overall equilibrium lies in favor of the formation of the phenyldichlorotin species, while with HBr the equilibrium favors the formation of the diphenylbromo compounds. It is worth noting that the diphenylhalotin derivatives of manganese pentacarbonyl cannot be made by this method, since regardless of the mole ratio of HX used, the equilibrium always lies in favor of the phenyldihalotin species, and under more forcing conditions cleavage of all three phenyltin bonds occurs [3].

TABLE 1

REACTIONS RESULTING IN THE CLEAVAGE OF THE METAL—CARBON BOND

| Compound | Mole ratio of reactants | Reaction solvent $^{h}$/ Temp. (°C)/ Time (h) | Product(s) | Yield (%) | Colour | m.p. (°C) | Recrystallization solvents$^{h}$ |
|---|---|---|---|---|---|---|---|
| *(a) Reactions with HCl* | | | | | | | |
| $Ph_3SnFe(CO)_2Cp$ | 1/1 | A,B/RT/3 | $Ph_2ClSnFe(CO)_2Cp$ | 63 | yellow | 93-95$^{a}$ | E |
| | 1/2 | A,B/RT/3 | $PhCl_2SnFe(CO)_2Cp$ | 68 | yellow-orange | 116-117$^{b}$ | A,E |
| $Ph_3SnFe(CO)(Cp)PPh_3$ | 1/1 | A,B/RT/3 | $Ph_2ClSnFe(CO)(Cp)PPh_3$ | 47 | orange | 172-175(dec.) | E |
| | 1/2 | A,B/RT/3 | $PhCl_2SnFe(CO)(Cp)PPh_3$ | 77 | red | 164-168 | A,E |
| | excess HCl | A,B/RT/3 | $Cl_3SnFe(CO)(Cp)PPh_3$ | 95 | maroon | 183-185$^{c}$ | A,D |
| $Ph_3SnFe(CO)(Cp)PEt_3$ | 1/1 | A,B/RT/3 | $Ph_2ClSnFe(CO)(Cp)PEt_3$ | 30 | orange | 141-143(dec.) | E |
| | 1/2 | A,B/RT/3 | $PhCl_2SnFe(CO)(Cp)PEt_3$ | 50 | red | 110-112 | A,E |
| | excess HCl | A,B/RT/3 | $Cl_3SnFe(CO)(Cp)PEt_3$ | 90 | maroon | 116-123(dec.) | A,D |
| $Ph_3SnFe(CO)(Cp)P(OPh)_3$ | 1/1 | A,B/RT/3 | $Ph_2ClSnFe(CO)(Cp)P(OPh)_3$ | 56 | yellow | 155-157 | E |
| | 1/2 | A,B/RT/3 | $PhCl_2SnFe(CO)(Cp)P(OPh)_3$ | 58 | yellow | 168-171 | A,E |
| | excess HCl | A,B/RT/3 | $Cl_3SnFe(CO)(Cp)P(OPh)_3$ | 88 | yellow-orange | 205-207(dec.) | A,D |
| $Ph_3SnFe(Cp)[P(OPh)_3]_2$ | 1/1 | A,B/RT/3 | $Ph_2ClSnFe(Cp)[P(OPh)_3]_2$ | 68 | yellow | 105-108(dec.) | E |
| | 1/2 | A,B/RT/3 | $PhCl_2SnFe(Cp)[P(OPh)_3]_2$ | 75 | yellow | 160-163 | A,E |
| | excess HCl | A,B/RT/3 | $Cl_3SnFe(Cp)[P(OPh)_3]_2$ | 92 | orange | 172-177(dec.) | A,D |
| $Ph_3SnFe(CO)(Cp)P(OEt)_3$$^{f}$ | excess HCl | A,B/RT/3 | $Cl_3SnFe(CO)(Cp)P(OEt)_3$ | ~85 | yellow | 106-108 | A,D |
| $Me_3SnFe(CO)_2Cp$ | excess HCl | C/RT/1/6 | $Me_2ClSnFe(CO)_2Cp$ + some $Me_3SnCl$ | $^{d}$ | yellow | $^{d}$ | |
| $Me_3SnMo(CO)_3Cp$ | 1/3 | D/RT/12 | $Me_2ClSnMo(CO)_3Cp$ | 90 | pale yellow | $^{d,g}$ | |
| | 1/3 | D/120/8 | $MeCl_2SnMo(CO)_3Cp$ | $^{d}$ | pale yellow | $^{d}$ | |
| $Ph_3SnMo(CO)_3Cp$ | 1/1, 1/2 or 1/3 | C/RT/48 | $Cl_3SnMo(CO)_3Cp$ | $^{d}$ | yellow | $^{d,g}$ | |
| $Me_3SnW(CO)_3Cp$ | 1/6 | B/RT/12 | $MeCl_2SnW(CO)_3Cp$ | 33$^{e}$ | | | |
| | | | $Me_2ClSnW(CO)_3Cp$ | 66 | | | |
| | 1/6 | 13/110/4 | $MeCl_2SnW(CO)_3Cp$ | 66$^{e}$ | | | |
| | | | $Me_2ClSnW(CO)_3Cp$ | 33 | | | |
| *(b) Reactions with HBr* | | | | | | | |
| $Ph_3SnFe(CO)_2Cp$ | 1/1 | A,B/RT/3 | $Ph_2BrSnFe(CO)_2Cp$ | 60 | orange | 107-110 | E |
| | 1/2 | A,B/RT/3 | $PhBr_2SnFe(CO)_2Cp$ + (30%) $Ph_2BrSnFe(CO)_2Cp$ | ~60 | orange | 96-98 | A,E |
| *(c) Reactions with $Cl_2$* | | | | | | | |
| $Ph_2(C_6F_5)SnMn(CO)_5$ | 1/1 | F/RT/72 | $Cl_2(C_6F_5)SnMn(CO)_5$ + $[ClMn(CO)_4]_2$ | 15 | white | 75-77 | F,D |
| $Ph(C_6F_5)_2SnMn(CO)_5$ | 1/2 | F/RT/72 | $Cl(C_6F_5)_2SnMn(CO)_5$ | 25 | white | 87-90 | F |

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[a] Literature values are 100-101°. [b] 116-117° see Ref. 15. [c] 175-185° see Ref. 14. [d] Not determined. [e] Invariably an inseparable mixture of the two compounds resulted. The relative amount of each was determined by the integration of the NMR spectra. [f] Not isolated in a solid state, $Cl_3SnFe(CO)(Cp)P(OEt)_3$ was prepared by the reaction of excess HCl upon the reaction mixture formed by the irradiation of $Ph_3SnFe(CO)_2Cp$ with $P(OEt)_3$. [g] For analytical or spectroscopic details see Ref. 11 and 39. [h] A, benzene; B, diethyl ether; C, methylene chloride; D, pentane; E, cyclohexane and F, carbon tetrachloride.

As in the reactions of $Me_3SnMn(CO)_5$ [2], the reactions of $Me_3MFe(CO)_2Cp$ (M = Si, Ge or Sn) and $Me_3SnMo(CO)_3Cp$ with chlorine even at low temperatures, result in instantaneous cleavage of the metal—metal bond (Table 2). This is again in contrast to the reactions of $Ph_3SnMn(CO)_5$ with chlorine, where at 0°C cleavage of all three phenyl—tin bonds occurs, but leaves the tin—manganese bond intact [3]. This is not due to a difference in the tin—manganese bond strength between $Me_3SnMn(CO)_5$ and $Ph_3SnMn(CO)_5$ since these are nearly equal at 55 ± 7 [18] and 61 ± 8 kcal/mole [21] respectively, and can probably be attributed to a difference in the reaction transition states.

In the reactions of $Ph_2(C_6F_5)SnMn(CO)_5$ and $Ph(C_6F_5)_2SnMn(CO)_5$ with chlorine, preferential cleavage of the phenyl—tin bond occurs suggesting that this bond may be significantly weaker than the $C_6F_5$—Sn bond. This is also consistent with the observations that excess chlorine does not react with $(C_6F_5)_3$-$SnMn(CO)_5$ and that neither of the compounds $Ph_{3-n}(C_6F_5)_nSnMn(CO)_5$, $n$ = 1 or 2, reacts with hydrogen chloride.

The reactions of $Me_3SnFe(CO)_2Cp$, $Me_3SnM'(CO)_3Cp$ (M′ = Cr, Mo or W), and $Ph_3SnM'(CO)_3Cp$ (M′ = Mo or W) with iodine resulted in the simple cleavage of the metal—metal bond (Table 2). However, the reaction of $Me_3SnFe(CO)_2Cp$ with iodine in refluxing carbon tetrachloride did not give $Me_3SnI$ as expected, but $Me_3SnCl$ along with a considerable amount of decomposition products. Roberts [22] reported that the same reaction in $CDCl_3$ at room temperature gave only the trimethyltin iodide.

The reactions of ICl with $Me_3MFe(CO)_2Cp$ (M = Si, Ge, or Sn) resulted in the cleavage of the metal—metal bond (Table 2), the only iron-containing species being $IFe(CO)_2Cp$. The results thus indicate some specific orientation of ICl with respect to the metal—metal bond in these reactions. A similar orientation of $CF_3I$ also appears to occur; with $Me_3SiFe(CO)_2Cp$ the products are $Me_3SiF$ and $IFe(CO)_2Cp$ although with the germanium and tin analogues the reactions with $CF_3I$ give mixtures of $Me_3MF$, $Me_3MI$ (M = Ge or Sn), $CF_3Fe(CO)_2Cp$ and $IFe(CO)_2Cp$. The $Me_3MF$ species may well arise by elimination of $CF_2$ from $Me_3MCF_3$, which is known to occur for such trifluoromethyl derivatives [24—26].

In reactions such as these the nature of the products can be only partly dependent on the relative strength of the metal—metal and metal—carbon bonds. Thus, there is practically no difference in the metal—metal bond dissociation energies between the compounds $Me_3SnMn(CO)_5$ (55 ± 9 kcal/mole) and $Ph_3SnMn(CO)_5$ (61 ± 8 kcal/mole), yet the tin—manganese bond only in the latter is resistant to attack by chlorine or iodine. Quite clearly, even allowing for possible changes in the methyltin or phenyltin bond energies upon the bonding of the tin to a transition metal, our results cannot be explained simply on the basis of relative strength of the metal—metal and metal—carbon bonds. Therefore, the differences in reactivity must be a result of kinetic and mechanistic aspects of the reactions.

From kinetic data for tetraorgano derivatives of Group IV the rate of cleavage of an alkyl or aryl group increases in the order $Si < Ge \ll Sn < Pb$ [27] and in general aryl groups are more easily cleaved than are alkyl groups.
In non-polar media it has been proposed that in the absence of ultraviolet light the reduction does not involve free radicals and proceeds via an activated

*(continued on p. 375)*

TABLE 2

REACTIONS RESULTING IN THE CLEAVAGE OF THE METAL—METAL BOND

| Compound | Mole ratio of reactants | Reaction solvent/temp. (°C)/ Time (h) | Products (identified by) |
|---|---|---|---|
| *(a) Reactions with chlorine* | | | |
| $Me_3SiFe(CO)_2Cp$ | 1/1 | $CHCl_3$/0/12 | $Me_3SiCl$ (NMR)[p] + $ClFe(CO)_2Cp$ (IR and NMR)[b] |
| $Me_3GeFe(CO)_2Cp$ | 1/1 | $CHCl_3$/0/12 | $Me_3GeCl$(NMR)[a] + $ClFe(CO)_2Cp$ (IR and NMR)[b] |
| $Me_3SnFe(CO)_2Cp$ | 1/8 | $CCl_4$/0/1/4 | $Me_3SnCl$(NMR)[a] + $ClFe(CO)_2Cp$ (IR and NMR)[b] |
| $Me_3SnFe(CO)_2Cp$ | 1/1 | $C_5H_{12}$/−78/3 | $Me_3SnCl$(NMR)[a] + $ClFe(CO)_2Cp$ (analysis)[c] |
| $Me_3SnMo(CO)_3Cp$ | 1/10 | $C_5H_{12}$/RT/24 | $Me_3SnCl$ + $Cl_3Mo(CO)_2Cp$ (IR and analysis)[d] |
| *(b) Reactions with HCl* | | | |
| $Me_3SiFe(CO)_2Cp$ | 1/1 or 2/3 | $CH_2Cl_2$/60/1 | $Me_3SiCl$ (IR)[p] + $HFe(CO)_2Cp$ (IR and NMR)[e] + $[Fe(CO)_2Cp]_2$ (IR and analysis)[f] |
| $Me_3GeFe(CO)_2Cp$ | 1/1 | $CH_2Cl_2$/60/1 | $Me_3GeCl$ (NMR)[a] + $HFe(CO)_2Cp$ (IR and NMR)[e] + $[Fe(CO)_2Cp]_2$(IR)[f] |
| $Me_3SnFe(CO)_2Cp$ | 1/2 | $CH_2Cl_2$/50/0.5 | $Me_3SnCl$ (NMR)[a] + unidentified material |
| *(c) Reactions with Iodine* | | | |
| $Me_3SnFe(CO)_2Cp$ | 1/1 | $C_5H_{12}$/60/2 | $Me_3SnI$ + $IFe(CO)_2Cp$ (analysis)[g] |
| $Me_3SnMo(CO)_3Cp$ | 1/1 | $[MeOCH_2]_2$/RT/1 | $Me_3SnI$ (IR and NMR)[a] + $IMo(CO)_3Cp$ (IR and analysis)[i,j] |
| $Ph_3SnMo(CO)_3Cp$ | 1/1 | $CHCl_3$/RT/12 | $Ph_3SnI$ (IR)[h] + $IMo(CO)_3Cp$ (IR)[j] |
| $Me_3SnW(CO)_3Cp$ | 1/1 | $CHCl_3$/RT/12 | $Me_3SnI$ (IR)[n] + $IW(CO)_3Cp$ (IR and analysis)[j,k] |
| $Ph_3SnW(CO)_3Cp$ | 1/1 | $CHCl_3$/RT/12 | $Ph_3SnI$ (IR) + $IW(CO)_3Cp$ (IR)[k] |
| $Me_3SnCr(CO)_3Cp$ | 1/1 | $CHCl_3$/RT/0.5 | $Me_3SnI$ (IR and NMR)[a,n] + $ICr(CO)_3Cp$ (mass spectrometry)[l] |
| *(d) Reactions with ICl* | | | |
| $Me_3SiFe(CO)_2Cp$ | 1/1 | $C_6H_{12}$/80/0.5 | $Me_3SiCl$ (IR)[p] + $IFe(CO)_2Cp$ (IR and NMR)[b] |
| $Me_3GeFe(CO)_2Cp$ | 1/1 | $C_6H_{12}$/80/0.5 | $Me_3GeCl$ (NMR)[a,r] + $Me_3GeI$ (NMR)[a,r] + $IFe(CO)_2Cp$ (IR and NMR)[m] |
| $Me_3SnFe(CO)_2Cp$ | 1/1 | $C_6H_{12}$/80/0.5 | $Me_3SnCl$ (NMR)[a,s] + $Me_3SnI$ (NMR)[a,s] + $IFe(CO)_2Cp$ (IR and NMR)[m] |
| *(e) Reactions with $CF_3I$* | | | |
| $Me_3SiFe(CO)_2Cp$ | excess $CF_3I$ | $CF_3I$/80/90 | $Me_3SiF$ (NMR)[q] + $IFe(CO)_2Cp$ (NMR)[b] |
| $Me_3GeFe(CO)_2Cp$ | excess $CF_3I$ | $CF_3I$/80/40 | $Me_3GeF$ (NMR)[a,t] + $Me_3GeI$ (NMR)[a,t] + $CF_3Fe(CO)_2Cp$ (IR)[h] + $IFe(CO)_2Cp$ (IR)[b] |
| $Me_3SnFe(CO)_2Cp$ | 1/1 | $CCl_4$/60/7 | $IFe(CO)_2Cp$ (IR and NMR)[b] + unidentified material |
| | excess $CF_3I$ | $CF_3I$/60/7 | $Me_3SnF$ (IR)[n] + $Me_3SnI$ (NMR)[a] + $CF_3Fe(CO)_2Cp$ (analysis)[o] + $IFe(CO)_2Cp$ (IR)[b] |
| | excess $CF_3I$ | $CF_3I$/VV irradiation at RT/2 | |

[a] H. Schmidbaur and I. Ruidisch, Inorg. Chem., 3(1964) 599.
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[c] Calc. for $C_7H_5O_2ClFe$: C, 39.58; H, 2.47; Found: C, 39.52; H, 2.67%.
[d] R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc. A, (1966) 1606. Calc. for $C_7H_5O_2Cl_3Mo$: C, 25.99; H, 1.55; Cl, 32.88; Found: C, 24.40, H, 2.07; Cl, 31.87%.
[e] A. Davison, J.A. McCleverty and G. Wilkinson, J. Chem. Soc., (1963) 1133.
[f] F.A. Cotton, A.D. Liehr and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1955) 175. Calc. for $C_{14}H_{10}O_4Fe_2$: C, 47.51; H, 2.83; Found: C, 47.67; H, 2.84%.
[g] Calc. For $C_7H_5O_2IFe$: C, 27.66; H, 1.65; Found: C, 27.48; H, 1.47%.
[h] By comparison with the spectra of an authentic sample.
[i] Calc. for $C_8H_5O_3IMo$: C, 26.11; H, 1.8; Found: C, 26.28; H, 1.4%.
[j] T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
[k] Calc. for $C_8H_5O_3IW$: C, 20.9; H, 1.09; I, 27.6; Found: C, 21.4; H, 1.33; I, 27.1%. $\nu$(CO) at 2024, 1946 and 1938 $cm^{-1}$.
[l] Mol. wt. Calc.: 318; Found: 318.
[m] T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 2 (1955) 38.
[n] R. Okawara, D.E. Webster, and E.G. Rochow, J. Amer. Chem. Soc., 82 (1960) 3287.
[o] Calc. for $C_8H_5O_2F_3Fe$: C, 39.06; H, 2.04; Found: C, 37.56; H, 2.03%.
[p] A.L. Smith, J. Chem. Phys., 21 (1955) 1999.
[q] H. Schmidbaur, J. Amer. Chem. Soc., 85 (1963) 2336.
[r] Ratio of $Me_3GeCl$ to $Me_3GeI$ is 3/1.
[s] Ratio of $Me_3SnCl$ to $Me_3SnI$ is 3/1.
[t] Ratio of $Me_3GeF$ to $Me_3GeI$ is 1/1

TABLE 3

ANALYTICAL AND SPECTROSCOPIC DATA

| Compound | Found (%) | | | Calcd. (%) | | | $\nu$(CO)(cm$^{-1}$)[a] | Γ(Cp)[c] |
|---|---|---|---|---|---|---|---|---|
| | C | H | Cl | C | H | Cl | | |
| $Ph_2ClSnFe(CO)_2Cp$ | 47.77 | 3.06 | 7.43 | 47.01 | 3.09 | 7.32 | 1966, 2014[j] | 5.12s |
| $PhCl_2SnFe(CO)_2Cp$ | 35.37 | 2.05 | 15.71 | 35.15 | 2.25 | 16.00 | 1986, 2030[j] | 4.96s |
| $Ph_2BrSnFe(CO)_2Cp$[e] | 42.71 | 2.41 | — | 43.07 | 2.83 | — | 1963, 2010 | 4.77s [d] |
| $PhBr_2SnFe(CO)_2Cp$[e] | 29.86 | 1.65 | — | 29.31 | 1.85 | — | 1983, 2028 | 4.60s [d] |
| $Me_2ClSnFe(CO)_2Cp$ | 29.76 | 2.75 | — | 29.92 | 3.09 | — | 1959, 1999[b] | 5.1s[a,g] |
| $MeCl_2SnMo(CO)_3Cp$ | 24.26 | 2.19 | — | 24.04 | 1.78 | — | 1941, 1970, 2038[b] | 4.6s[a,h] |
| $Cl_2(C_6F_5)SnMn(CO)_5$[f] | 24.03 | 0.00 | 14.00 | 23.92 | 0.00 | 12.87 | 2035, 2045, 2067, 2124[b] | — |
| $Cl(C_6F_5)_2SnMn(CO)_5$[f] | 29.58 | 0.00 | 4.80 | 29.79 | 0.00 | 5.03 | 2038, 2062, 2119[b] | — |
| $Ph_2ClSnFe(CO)(Cp)PPh_3$ | 59.59 | 3.99 | 5.76 | 60.18 | 4.18 | 4.95 | 1932 | 5.48d[i] |
| $PhCl_2SnFe(CO)(Cp)PPh_3$ | 53.73 | 3.94 | 10.27 | 53.22 | 3.70 | 10.48 | 1949 | 5.32d |
| $Ph_2ClSnFe(CO)(Cp)PEt_3$ | 50.78 | 5.14 | 6.96 | 50.09 | 5.22 | 6.17 | 1924 | 5.36d |
| $PhCl_2SnFe(CO)(Cp)PEt_3$ | 40.67 | 4.51 | 12.98 | 40.49 | 4.68 | 13.28 | 1945 | 5.30d |
| $Cl_3SnFe(CO)(Cp)PEt_3$ | 29.49 | 3.92 | 21.83 | 29.26 | 4.06 | 21.63 | 1968 | 5.22d |
| $Ph_2ClSnFe(CO)(Cp)P(OPh)_3$ | 56.68 | 3.68 | 5.07 | 56.40 | 3.92 | 4.64 | 1957 | 5.62d |
| $PhCl_2SnFe(CO)(Cp)P(OPh)_3$ | 50.51 | 3.38 | 10.02 | 49.70 | 3.45 | 9.79 | 1972 | 5.59d |
| $Cl_3SnFe(CO)(Cp)P(OPh)_3$ | 41.53 | 2.64 | 15.66 | 42.10 | 2.92 | 15.57 | 1996 | 5.54d |
| $Ph_2ClSnFe(Cp)[P(OPh)_3]_2$ | 62.43 | 4.22 | 3.84 | 60.63 | 4.29 | 3.38 | — | 5.66t |
| $PhCl_2SnFe(Cp)[P(OPh)_3]_2$ | 56.14 | 3.88 | 7.62 | 55.99 | 4.01 | 7.04 | — | 5.61t |
| $Cl_3SnFe(Cp)[P(OPh)_3]_2$ | 52.02 | 3.67 | 11.21 | 50.93 | 3.11 | 11.02 | — | 5.61t |
| $Cl_3SnFe(CO)(Cp)P(OEt)_3$ | 26.87 | 3.53 | 19.86 | 26.67 | 3.70 | 19.70 | 1985 | 5.55d |

[a] $CHCl_3$ solution. [b] Cyclohexane solution. [c] $CDCl_3$ solution. s = singlet; d = doublet and t = triplet. [d] $(CD_3)_2CO$ solution. [e] Calcd. for $Ph_2BrSnFe(CO)_2Cp$: Br, 16.09, Found: Br, 15.89%; Calcd. for $PhBr_2SnFe(CO)_2Cp$: Br, 30.02, Found: Br, 29.70%. [f] Calcd. for $Cl(C_6F_5)_2SnMn(CO)_5$: F, 17.18, Found: F, 17.44%; Calcd. for $(C_6F_5)_2ClSnMn(CO)_5$: F, 27.75, Found: F, 27.84% [g] Γ(Me) 9.2, $J(H-C-^{119}Sn)$ 40 Hz. [h] Γ(Me) 8.8, $J(H-C-^{119}Sn)$ 46.5 Hz. [i] All $J(Cp-P)$ 1.5 Hz. [j] Literature values from Ref. 15 are 1961 and 2010 cm$^{-1}$ for $Ph_2ClSnFe(CO)_2Cp$ and 1984 and 2029 cm$^{-1}$ for $PhCl_2SnFe(CO)Cp$ both in $CH_2Cl_2$ solution.

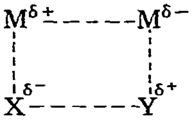
TABLE 4

ANALYTICAL, SPECTROSCOPIC AND PHYSICAL PROPERTIES FOR THE COMPOUNDS $Ph_3SnFe(CO)_{2-x}Cp_2L_x$

| | | Colour | m.p. (°C) | yield (%) | found (calcd.) (%) | | $\nu$(CO) (cm$^{-1}$) | $\tau$(Cp) | Recrystallization solvents |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | | | |
| $x$ = 1, | L = $PEt_3$ | orange | 154-156 | 68 | 58.62<br>(58.39) | 5.43<br>(5.68) | 1905 | 5.52 | cyclohexane/benzene |
| $x$ = 1, | L = $P(OPh)_3$ | v. pale yellow | 126-128 | 65 | 62.95<br>(62.30) | 4.27<br>(4.33) | 1940 | 5.74 | cyclohexane |
| $x$ = 2, | L = $P(OPh)_3$[a] | yellow | 185-187 | 41 | 65.11<br>(64.91) | 4.58<br>(4.58) | — | 5.69 | cyclohexane/benzene |

[a] Separated from the monosubstituted derivative by fractional crystallization.

transition state resulting from either nucleophilic displacement at tin or electrophilic cleavage of the tin—carbon bond. Among the various transition states that have been proposed is a four centre cyclic transition state similar to that proposed for the iodination of hexaphenylditin [28]. By contrast the reactions of iodine or triphenylphosphine with the decacarbonyls $Mn_2(CO)_{10}$ [29] or $Re_2(CO)_{10}$ [30] proceed via an aryl intermediate, while the reaction of $[Fe(CO)_2Cp]_2$ with iodine proceeds via the formation of bridging carbonyl and iodo cationic species [31]. Since there is no reason to suppose that cationic species were formed in any of the reactions in this work, and since in non-polar solvents, solvent-assisted halogenations are not considered likely [27], a four-centre transition state such as that shown in I could very well be involved.



(I)

(M′ = Fe, Mn, Mo or W;
M = Si, Ge or Sn)

[(a) X = Cl, Y = H, (b) X = Y = Cl, (c) X = Y = I, (d) X = Cl, Y = I, (e) X = I, Y = $CF_3$ for M = Si and X = Y = $CF_3$ or I for M = Ge or Sn]

By contrast, the reaction of HCl with $Ph_3PAuGePh_3$ proceeds in the opposite direction to that predicted by I giving $Ph_3PAuCl$ and $Ph_3GeH$, thus suggesting that in this compound the gold—germanium bond is polarized as $Au^{\delta+}$—$Ge^{\delta-}$ [32]. Similar results have also been found for the reaction of HCl with silicon—zirconium [33], silicon—platinum, germanium—platinum [34] and lead—platinum bonds [35].

The differences in the reactivities of the phenyltin compounds compared with their methyl analogues may be due to a difference in the availability of the transition state caused by involvement of the $\pi$-electrons of the phenyl rings.

Finally, it appears that the reactivity of these metal—metal bonded compounds is in part dependent on the nucleophilicity of the transition metal carbonyl moiety since if these reactions are indeed electrophilic, the greater the nucleophilicity of the transition metal carbonyl anion the greater the charge in the tin—carbon bond thus making it more susceptible to cleavage. Thus in tin—metal systems containing weak nucleophilic anions such as $Co(CO)_4^-$ [36], the reaction with HCl occurs at the metal—metal bond [37], and is no doubt influenced by the dissociation of the tin—cobalt bond in polar media [38], while the very nucleophilic $Fe(CO)_2Cp^-$ anion results in the ready cleavage of all three phenyl—tin bonds, while the less nucleophilic $Mn(CO)_5^-$ anion results in the cleavage of only two.

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