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REACTIVITY OF METAL—METAL BONDS

XII*. THE PREPARATION OF SOME PHENYLCHLORO GROUP IVB DERIVATIVES OF PENTACARBONYLMANGANESE AND (π-CYCLOPENTADIENYL)DICARBONYLIRON AND THEIR REACTIVITIES TOWARDS PENTAFLUOROPHENYLLITHIUM

H.C. CLARK and A.T. RAKE

Department of Chemistry, University of Western Ontario, London, Ontario, N6A 3K7 (Canada)

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Summary

The reaction of the appropriate phenylgermanium halide with the transition metal anions $Mn(CO)_5^-$ or $Fe(CO)_2Cp^-$ (M′) in THF gave the compounds $Ph_{3-n}Cl_nGeM'$ ($n = 1$ or 2), while the analogous silicon compounds were prepared by the reaction of the appropriate phenylchloro- or phenylpentafluorophenyl-silane with the transition metal carbonyl dimers. The reactivities of the compounds $Ph_{3-n}Cl_nMM'$ [$n = 1$ to 3; M = Si, Ge or Sn and $M' = Mn(CO)_5$ or $Fe(CO)_2Cp$] towards pentafluorophenyllithium have been found to depend upon M, M′ and the number of phenyl groups bonded to the Group IV metal. With $M' = Mn(CO)_5$ the reactivity decreased in the order $Sn \approx Ge > Si$. For $M' = Fe(CO)_2Cp$, reaction occurred for all the tin containing species, but for M = Ge or Si only the trichloro derivatives underwent reaction. Some aspects of the infrared, NMR and ^{57}Fe Mössbauer spectra of these and related compounds are discussed.

Introduction

Even though the number of compounds containing a Group IVB—transition metal bond is very large [2—4], such compounds generally contain only one type of ligand bound to the Group IV atom. Exceptions include a number of silicon—metal systems prepared by the oxidative addition of an organohalosilane to some low valent rhodium, iridium, or platinum complexes [3]. While some analogous germanium- and tin-compounds have been prepared by the oxidative addition of organo Group IV halides to $CpCo(CO)_2$ [5], $M(CO)_4$—bipyridyl [6] (M = Mo or W) and $Fe(CO)_5$ [7], the majority of organohalotin—transition metal

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[*] For part XI see ref.1.

systems are made more available by the ready cleavage of the tin—carbon bond by the halogens and hydrogen halides [1]. Since a large number of compounds containing a Group IVB—manganese or —iron bond were required for other purposes [8,9] and since the reactivity of these halo compounds towards pentafluorophenyllithium has been only briefly explored [10], the purpose of this paper is to describe the preparation and spectral properties of a series of compounds of the type $Ph_{3-n}X_nMM'$ [$n = 0$ to 2; X = Cl or C_6F_5; M = Si, Ge, or Sn, and M' = $Mn(CO)_5$ or $Fe(CO)_2Cp$].

Results and discussion

The phenyldichlorogermanium and diphenylchlorogermanium derivatives of pentacarbonylmanganese and cyclopentadienyldicarbonyliron are readily prepared by the addition of the sodium salt of the transition metal carbonyl anion to an excess of the phenylgermanium halide in THF according to the general equation:

$$Ph_nGeCl_{4-n} + NaM' \xrightarrow{THF} Ph_nCl_{3-n}GeM' + NaCl$$

$n = 1$ or 2; M' = $Mn(CO)_5$ or $Fe(CO)_2Cp$

This type of preparation has previously been used to prepare some organohalotin and organohalogermanium derivatives of $Co(CO)_4$ [11,12] and also to prepare $Me_2ClSnMo(CO)_2Cp$ [13], $Ph_2ClSnMn(CO)_5$ [7], $Ph_2BrGeMn(CO)_5$ [14] and the series $Ph_{3-n}Cl_nSnFe(CO)_2Cp$ ($n = 1$ or 2) [15]. However, while the reaction of $NaMn(CO)_5$ with the phenylgermanium halides was simple and gave only one product, the reaction of phenylgermanium trichloride with $NaFe(CO)_2Cp$ gave in addition to the expected $PhCl_2GeFe(CO)_2Cp$, some $ClFe(CO)_2Cp$ as well as the previously unknown $PhClGe[Fe(CO)_2Cp]_2$. The formation of $ClFe(CO)_2Cp$ may reflect the greater nucleophilicity of the anion $Fe(CO)_2Cp^-$ over that of $Mn(CO)_5^-$, while the formation of $PhClGe[Fe(CO)_2Cp]_2$ is not unexpected since other transition metal anions such as $Co(CO)_4^-$ [11] and also $[Ni(CO)Cp]_2$ [16] react with a 1/1 molar ratio of phenyl trihalides and tetrahalides of the Group IV metals to give compounds containing more than one metal—metal bond.

Although this type of reaction is of great importance in the preparation of tin— and germanium—transition metal bonds it is in most cases unsuitable for the preparation of silicon—transition metal bonds except under special or forcing conditions. The latter are best prepared by the reaction in solution of a silane with a transition metal carbonyl under UV radiation to give a silicon—transition metal hydride species [17—19], followed by the elimination of CO or hydrogen [20] to give a silicon—transition metal bonded compound. As for the preparation of the trichlorosilicon [20], triphenylsilicon [21,22] and tris(pentafluorophenyl)silicon [22] derivatives of pentacarbonylmanganese and cyclopentadienyldicarbonyliron, we have prepared analogous phenylchloro- and phenyl(pentafluorophenyl)silicon derivatives according to the general equation:

$$2Ph_{3-n}X_nSiH + (M')_2 \longrightarrow 2Ph_{3-n}X_nSiM' + H_2$$

$n = 1$ or 2; X = Cl or C_6F_5 and M' = $Mn(CO)_5$ or $Fe(CO)_2Cp$

This method is similar to that used for the preparation of $PhCl_2SiCo(CO)_4$ [23] and $MeCl_2SiFe(CO)_2Cp$ [20]. In the reactions of the phenylchlorosilanes a large excess of silane must be used since otherwise the principal product is a white infusible material containing no $Mn(CO)_5$ groups. The reaction of the phenyl(pentafluorophenyl)silanes with dimanganese decacarbonyl was also investigated and was shown by infrared studies to give the desired product but the high solubility of these phenyl(pentafluorophenyl)silicon pentacarbonylmanganese compounds in the involatile excess silane made their isolation very difficult.

The trichlorogermanium derivatives of pentacarbonylmanganese and cyclopentadienyldicarbonyliron have been prepared via the reaction of trichlorogermane with the appropriate transition metal carbonyl chloride [24,25], or by the reaction of $GeCl_4$ with the transition metal carbonyl anions [14,26]. $Cl_3GeMn(CO)_5$ has also been prepared by the cleavage of the phenylcarbon bond in $Ph_3GeMn(CO)_5$ [20] by chlorine at elevated temperatures, while $Cl_3GeFe(CO)_2Cp$ has been obtained from the reaction of $GeCl_4$ with $[Fe(CO)_2Cp]_2$ [16]. However, a more convenient preparation which gives quantitative yields of these derivatives involves the reaction of trichlorogermane with the appropriate transition metal carbonyl dimer. As in the preparation of $Cl_3SiMn(CO)_5$ [20], the reaction of Cl_3GeH with $Mn_2(CO)_{10}$ proceeds only above 100°, in contrast to the analogous reaction with $[Fe(CO)_2Cp]_2$ which proceeds spontaneously at ambient temperature. On the other hand, this reaction with trichlorosilane gives a variety of products other than $Cl_3SiFe(CO)_2Cp$, depending on the mole ratio of reactants and the conditions used [18].

The phenyl(pentafluorophenyl) compounds were prepared by the general reaction:

$$Ph_{3-n}X_nMM' + n\ C_6F_5Li \xrightarrow{\text{ether}} Ph_{3-n}(C_6F_5)_nMM' + n\ LiCl$$

X = Cl or Br; $n = 1$ to 3; M = Si or Ge where $M' = Mn(CO)_5^-$, and M = Sn for $Fe(CO)_2Cp$; and $n = 3$ for M = Si or Ge where $M' = Fe(CO)_2Cp$

This is exactly analogous to the preparation of the series $Ph_{3-n}(C_6F_5)_nSnMn(CO)_5$ ($n = 1$ to 3) [10]. Despite the fact that the formation of pentafluorophenyllithium is considerably faster in THF than in diethyl ether [27], the latter solvent is generally preferable. The preparation of $(C_6F_5)_3SnM'$ [$M' = Mn(CO)_5$ or $[Fe(CO)_2Cp]$] can be equally well accomplished in either solvent but the reaction of pentafluorophenyllithium with $Cl_3SiMn(CO)_5$ in THF gave on work up a very large quantity of a white high melting material which showed no carbonyl absorptions in its infrared spectrum. This material is probably similar to the polymer formed in the reaction of triphenylsilicon chloride with C_6F_5Li in THF, possibly by the attack upon the solvent [28]. The reaction of $Ph_2BrSnMn(CO)_5$ with C_6F_5Li in ether did not give any compound other than $Ph_2(C_6F_5)SnMn(CO)_5$, in contrast to the reaction of $Ph_2ClSnMn(CO)_5$ which has been reported to give an equimolar mixture of the pentafluorophenyl derivative and the four-centre compound $[-SnPh_2Mn(CO)_5]_2$ [10]. This observation could be due to the better leaving capacity of bromine over chlorine since the products formed from the reaction of the anions $Mn(CO)_5^-$ and $Fe(CO)_2Cp^-$ and Ph_2GeX_2 (X = Cl or Br) have been shown to vary quite markedly [29], but the reaction of

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TABLE 1

SPECTROSCOPIC DATA

Compound	ν(CO) (cm^{-1})^{a}			
	A_1''	B_1	E	A_1'
(a) Pentacarbonylmanganese derivatives				
$Ph_3SiMn(CO)_5$	2097 2098	2029 2030	2002 2003	2002 2003^{b}
$Ph_2ClSiMn(CO)_5$	2108	2043	2016	2016
$PhCl_2SiMn(CO)_5$	2116	2055	2022	2024
$Cl_3SiMn(CO)_5$	2123	*e*	2035	2035^{d}
$Ph_3GeMn(CO)_5$	2097 2098	2032 2032	2003 2006	2003 2002^{b}
$Ph_2ClGeMn(CO)_5$	2109 2105	2048 2045	2020 2023	2010 2011^{h}
$PhCl_2GeMn(CO)_5$	2123	2063	2033	2023
$Cl_3GeMn(CO)_5$	2130 2130	*e*	2047 2048	2037 2038^{d}
$Ph_3SnMn(CO)_5$	2093 2093	2029 2027	2003 2002	2003 2002^{b}
$Ph_2ClSnMn(CO)_5$	2103	2044	2018	2018^{c}
$PhCl_2SnMn(CO)_5$	2113	2058	2023	2031^{c}
$Cl_3SnMn(CO)_5$	2126	2070^{f}	2046	2039^{b}
$Ph_3SiMn(CO)_5$	2097	2029	2002	2002
$Ph_2(C_6F_5)SiMn(CO)_5$	2107	2041	2009	2014
$Ph(C_6F_5)_2SiMn(CO)_5$	2113	2048	2018	2022
$(C_6F_5)_3SiMn(CO)_5$	2118 2118	2059 2057	2024 2023	2030 2028^{g}
$Ph_3GeMn(CO)_5$	2097	2032	2003	2003
$Ph_2(C_6F_5)GeMn(CO)_5$	2107	2043	2019	2008
$Ph(C_6F_5)_2GeMn(CO)_5$	2115	2050	2026	2020
$(C_6F_5)_3GeMn(CO)_5$	2120	2060	2028 2032	2023
$Ph_3SnMn(CO)_5$	2093	2029	2003	2003
$Ph_2(C_6F_5)SnMn(CO)_5$	2100 2101	2038 2038	2012 2012	2016 2015^{c}
$Ph(C_6F_5)_2SnMn(CO)_5$	2108 2107	2047 2045	2020 2020	2020 2020^{c}
$(C_6F_5)_3SnMn(CO)_5$	2116 2116	2059 2059	2029 2025	2034 2029^{c}

(b) Cyclopentadienyldicarbonyliron derivatives

$Ph_3SiFe(CO)_2Cp$	2004	1954	5.13
$Ph_2ClSiFe(CO)_2Cp$	2014	1972(sh)	5.04
		1964	
	2012	1963[j]	
$PhCl_2SiFe(CO)_2Cp$	2027	2023(sh)	4.90
	1980	1976(sh)	
	2027	1980[j]	
$Cl_3SiFe(CO)_2Cp$	2039	1995	4.73
	2039	1995[d]	
$Ph_3GeFe(CO)_2Cp$	2003	1955	5.08
$Ph_2ClGeFe(CO)_2Cp$	2020(sh)	2016	4.97
	1980(sh)	1970	
$PhCl_2GeFe(CO)_2Cp$	2032	2027(sh)	4.70
	1992	1986(sh)	
$Cl_3GeFe(CO)_2Cp$	2049	2005	4.53
	2050	2008[k,l]	
$Ph_3SnFe(CO)_2Cp$	1997	1950	4.97
	1995	1944[k,l]	
$Ph_2ClSnFe(CO)_2Cp$	2014	1966	4.77
	2010	1961[m]	
$PhCl_2SnFe(CO)_2Cp$	2030	1986	4.57
	2029	1984[m]	
$Cl_3SnFe(CO)_2Cp$	2050	2010	4.45
	2048	2008[k,l]	

$Ph_3SiFe(CO)_2Cp$	2004		1954	5.13
$Ph_2(C_6F_5)SiFe(CO)_2Cp$	2015		1967	5.00
$Ph(C_6F_5)_2SiFe(CO)_2Cp$	2026		1980(sh)	4.94
			1977	
$(C_6F_5)_3SiFe(CO)_2Cp$	2034		1987	4.94
	2029		1982[g]	
$(C_6F_5)_3GeFe(CO)_2Cp$	2038		1994	4.85
$Ph_3SnFe(CO)_2Cp$	1999		1951	4.97
$Ph_2(C_6F_5)SnFe(CO)_2Cp$	2011		2000(sh)	4.92
	1965		1953(sh)	
$Ph(C_6F_5)_2SnFe(CO)_2Cp$	2023		1982	4.82
$(C_6F_5)_3SnFe(CO)_2Cp$	2029		1988	4.77
$PhClGe[Fe(CO)_2Cp]_2$	2055w	2025m	2016m	4.93
	2013s	2996m	1967m	
	1948m			

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[a] In cyclohexane solution unless otherwise stated; sh shoulder, w weak, m medium, s strong. [b] Ref.21. [c] Ref.10. [d] Ref.20. [e] Band not observed. [f] Calculated value. [g] Ref.22. [h] Ref.36. [i] In acetone-d_6. [j] Ref. 35. [k] In chloroform. [l] Ref.26. [m] Ref.15. [n] In methylene chloride.

C_6F_5Li with $Ph_2ClGeMn(CO)_5$ gave only $Ph_2(C_6F_5)GeMn(CO)_5$ in high yield. In view of the very similar nature of the tin and germanium compounds, the anomalous behaviour of $Ph_2ClSnMn(CO)_5$ is not easy to explain. The very low reactivity of $Cl_3SiFe(CO)_2Cp$ towards C_6F_5Li cannot be attributed entirely to the highly nucleophilic nature of $Fe(CO)_2Cp$, since $Cl_3MFe(CO)_2Cp$ (M = Ge or Sn) shows normal reactivity. In contrast to the reactivity of the derivatives of pentacarbonylmanganese the inertness of the compounds $Ph_2ClMFe(CO)_2Cp$ and $PhCl_2MFe(CO)_2Cp$ (M = Si or Ge) is not easy to explain on either electronic or steric grounds. Construction of molecular models show that the presence of one or more phenyl groups bonded to the Group IV atom does not effectively crowd the chlorine atom which is probably more sterically crowded by $Mn(CO)_5$ than by $Fe(CO)_2Cp$.

All of the new compounds described in this work are indefinitely stable in dry air at room temperature with the exception of $(C_6F_5)_3SnFe(CO)_2Cp$, which although it is stable under nitrogen is only stable in air at 0°. The reactivity of the series $Ph_{3-n}(C_6F_5)_nSnFe(CO)_2Cp$ towards HCl and Cl_2 was also investigated. Chlorine readily cleaves the tin—iron bond, while excess HCl gives a mixture of products for which analyses and NMR studies showed that partial cleavage of both the phenyl—tin and pentafluorophenyl—tin bonds had occurred. The 1/1 or 2/1 molar addition of HCl to $Ph_2(C_6F_5)SnFe(CO)_2Cp$ or $Ph(C_6F_5)_2SnFe(CO)_2Cp$ respectively in ether after four days gave no identifiable product other than starting material which was recovered in over 80% yield; and although NMR studies showed that some reaction had occurred, none of these products were isolated or identified.

The carbonyl stretching infrared absorption bands for the derivatives of pentacarbonylmanganese in this work along with their previously known congeners are given in Table 1. All spectra exhibited the three characteristic absorptions associated with the local C_{4v} symmetry of the manganese atom; a high frequency band of a_1 symmetry and two bands at lower frequency, one of a_1 symmetry and one of e symmetry, such that the latter is approximately twice as intense as the former. This is the case for the highly symmetric trichloro Group IV derivatives [21] but when one or more of the chlorine atoms is replaced by a phenyl or pentafluorophenyl group a new band of b_1 symmetry appears between 2030 and 2070 cm^{-1} due to the lowering of symmetry around the manganese atom. This latter band is infrared inactive for molecules of strict C_{4v} symmetry, and concurrent with its appearance, there should also be a splitting of the e mode, which may be further enhanced by the introduction of a fluorocarbon group since several fluorocarbon derivatives of pentacarbonylmanganese also show a splitting of the e mode [30]. In this work only $(C_6F_5)_3GeMn(CO)_5$ showed a resolvable splitting although in most other cases the low frequency a and e modes were of similar intensity but of differing line widths thus suggesting that some splitting was occurring. The present assignments are based on the assumption that the wider line is due to the e mode, an argument which has been advanced to account for the band shape in $(C_6F_5)_3SnMn(CO)_5$ [10].

For compounds containing the cyclopentadienyldicarbonyliron group with a symmetric R_3M ligand, the infrared spectra in the carbonyl stretching region (Table 1) showed two bands of equal intensity. However, when two different

TABLE 2

^{57}Fe MÖSSBAUER DATA AT 298 K

Compound	*C.S.* (mm/sec)^{a,b}	*Q.S.* (mm/sec)^{b}
$Ph_3SiFe(CO)_2Cp$	0.22	1.80
$Ph_3GeFe(CO)_2Cp$	0.27	1.78
$Ph_3SnFe(CO)_2Cp$	0.29	1.78
$Ph_3PbFe(CO)_2Cp$	0.33	1.69
$Cl_3SiFe(CO)_2Cp$	0.20	1.91
$Cl_3GeFe(CO)_2Cp$	0.22	1.76
$Cl_3SnFe(CO)_2Cp$	0.33	1.81
$(C_6F_5)_3SiFe(CO)_2Cp$	0.23	1.82
$(C_6F_5)_3GeFe(CO)_2Cp$	0.30	1.80
$(C_6F_5)_3SnFe(CO)_2Cp$	0.31	1.81
$Ph(C_6F_5)_2SnFe(CO)_2Cp$	0.29	1.77
$Ph_2(C_6F_5)SnFe(CO)_2Cp$	0.31	1.70

[a] *C.S.* values relative to sodium nitroprusside. [b] Errors are to ± 0.02 mm/sec and all line widths are about 0.26 mm/sec.

groups are bonded to the Group IV atom most of the spectra exhibited a shoulder on one or both of these two main absorptions. These are presumably due to the presence of rotational conformers in solution similar to those proposed for $MeCl_2SiFe(CO)_2Cp$ [20] for which the small energy barrier to rotation has been attributed to steric hindrance of the $Fe(CO)_2Cp$ group and not to the presence of a strong π bond between silicon and iron [31].

The ^{57}Fe Mössbauer data for the compounds $Ph_3PbFe(CO)_2Cp$ and $X_3MFe(CO)_2Cp$ (X = Ph, Cl or C_6F_5 and M = Si, Ge or Sn) are given in Table 2. Unlike the ^{119}Sn data for compounds containing a tin—metal bond [8,32] the quadrupole splitting values for these compounds are quite insensitive to both the nature of the Group IV metal and to the ligands bound to that metal. This insensitivity suggests that the iron atom is acting as a charge sink and is adopting the same *p*-orbital imbalance and charge density from compound to compound, while the obviously differing bonding natures of the ligands are reflected in the carbonyl stretching frequencies and in the value of the chemical shift of the cyclopentadienyl ring.

It can be shown [39] for carbonyl(π-cyclopentadienyl)iron(II) compounds, that the centre shift (*C.S.*), the chemical shift of the cyclopentadienyl ring protons, and the carbonyl stretching frequencies are dependent upon the σ and π bonding abilities of the other ligands. The centre shift is proportional to $-(\sigma + \pi)$ while the chemical shift of the cyclopentadienyl ring is proportional to $(\sigma - \pi)$ and the carbonyl stretching frequencies are proportional to $(\sigma - \pi)$. Thus, a good σ donor such as Ph_3Si will lead to a relatively high value for the *C.S.* and the chemical shift of the cyclopentadienyl ring, but a low value for the carbonyl stretching frequency. However, a group such as Cl_3Sn which acts as a σ donor and π acceptor will lead to a lower value for the *C.S.* but a higher value for the carbonyl stretching frequency and a lower value for the chemical shift of the cyclopentadienyl ring. However, the variation in the *C.S.* is so very small that there is, within experimental error, no variation between the triphenyl and tris(pentafluorophenyl) derivatives.

Experimental

All reactions were performed under a dry nitrogen atmosphere, but with the exception of the hydrolytically sensitive compounds, the work up of the solutions and final recrystallizations were performed in air. Compounds that were sensitive to hydrolysis were manipulated under a dry nitrogen atmosphere with minimum exposure to atmospheric moisture. Sealed tube reactions were carried out in evacuated thick walled Carius tubes of sufficient size that the inside pressure was unlikely to exceed five atmospheres. High resolution infrared spectra in the carbonyl stretching region were run on a Beckman IR-7 spectrometer as solutions between a matched pair of KBr plates. The spectra were calibrated using the 1601.8 cm^{-1} band of polystyrene film, and the positions of maximum band intensity are believed to be reliable to ± 2 cm^{-1}, except where the solvent is chloroform where the accuracy is ± 4 cm^{-1}.

Proton NMR measurements were made on a Varian T-60 NMR spectrometer using TMS as the internal standard. The chemical shift of the cyclopentadienyl ring protons is reliable to ± 0.03 ppm, the values being in excellent agreement with the shifts obtained when the compound was run as a composite mixture with its congeners. Mössbauer spectra were taken at room temperature with a 50 mc $^{57}Co/Pd$ source on an Austin Associates spectrometer, coupled to a Nuclear Data multichannel analyzer. The point of maximum absorption was visually estimated directly from the analyser output, and the velocity sweep calibration was made with iron foil.

Microanalyses were performed by Chemalytics Inc., Arizona, or by Schwarzkopf Microanalytical Laboratory, New York.

Dimanganese decacarbonyl was prepared by the method of King [33], while cyclopentadienyldicarbonyliron dimer and pentafluorobenzene were obtained from the Pressure and Pierce Chemical Companies respectively. All other starting materials were obtained from Alfa Inorganics. Commercial Grade tetrahydrofuran (THF) was dried over sodium or potassium benzophenone ketyl immediately before use.

The phenylchlorosilanes and phenylpentafluorophenylsilanes were prepared by the methods of Emeléus [34] and Gilman [28] respectively while the compounds Ph_3MM' [M = Si [21], Ge [21,35] or Sn [21,36] for M' = $Mn(CO)_5$ or $Fe(CO)_2Cp$], Cl_3MM' [M = Si [20] or Sn [36] for M' = $Mn(CO)_5$ or $Fe(CO)_2Cp$], $Ph_{3-n}Br_nSnMn(CO)_5$ (n = 1 or 2 [36,38]), $Ph_{3-n}(C_6F_5)_{3-n}SnMn(CO)_5$ (n = 1 to 3 [10]), and $Ph_{3-n}Cl_nSnFe(CO)_2Cp$ [1] (n = 1 or 2) were all prepared by the literature methods. The colours, melting points, yields and analytical data for the compounds prepared in this work are given in Table 3.

(a) Reactions with transition metal carbonyl anions

(i) Diphenylchloro- and phenyldichloro-germaniumpentacarbonylmanganese. A solution of sodium pentacarbonylmanganese (1.53 g, 7 mmoles) prepared from the reduction of dimanganese decacarbonyl (1.37 g, 3.5 mmoles) with sodium amalgam (150 g) containing about 0.7% sodium in dry THF (60 ml) was added dropwise to a stirred solution of diphenylgermanium dichloride (2.1 g, 7 mmoles) in THF (50 ml) at 0°.

The almost colourless solution was then stirred for 14 h at room temperature and filtered to remove the precipitated sodium chloride. The solvent was removed in vacuo and the oily residue was exhaustively extracted with pentane and refiltered. Concentration and cooling of the filtrate afforded white crystals of diphenylchlorogermaniumpentacarbonylmanganese (1.50 g). Phenyldichlorogermaniumpentacarbonylmanganese was prepared in essentially the same way, using phenylgermanium trichloride.

(ii) Diphenylchlorogermaniumcyclopentadienyldicarbonyliron. Cyclopentadienyldicarbonyliron dimer (3.54 g, 10 mmoles) in THF (60 ml) was reduced for 2 h at room temperature with sodium amalgam (150 g) containing approximately 0.7% of sodium. The excess amalgam was then removed and the solution of sodiocyclopentadienyldicarbonyliron was added dropwise to a stirred solution of diphenylgermanium dichloride (5.95 g, 20 mmoles) in THF (60 ml) at 0°. The resultant brown solution was stirred overnight and then filtered to remove the precipitated sodium chloride. After the removal of the solvent, the brown oil was exhaustively extracted with hot cyclohexane, refiltered and concentrated to a small volume whereupon yellow crystals of diphenylchlorogermaniumcyclopentadienyldicarbonyliron (3.01 g) separated from the solution.

(iii) Phenyldichlorogermaniumcyclopentadienyldicarbonyliron. A solution of sodiocyclopentadienyldicarbonyliron (3.0 g, 15 mmoles) in THF (60 ml) was added dropwise to a well-stirred solution of phenylgermanium trichloride (3.84 g, 15 mmoles) in THF (50 ml) at 0°. An instantaneous red colour developed and after the addition was complete the solution was stirred for 12 h at room temperature. The resulting deep red solution was filtered and the solvent removed in vacuo to leave a red viscous oil which was then redissolved in a minimum amount of a 1/1 benzene/cyclohexane mixture, refiltered and stored at 0° overnight. The orange crystals that formed were shown to be phenylchlorogermanium bis(cyclopentadienyldicarbonyliron) (600 mg), and were recrystallized from benzene to give 570 mg of the pure compound. The remaining red solution was then concentrated further and cooled to —10°, whereupon dark red crystals of chlorocyclopentadienyldicarbonyliron (256 mg) as determined by analysis (found: C, 39.43; H, 2.47; Cl, 17.10. $C_7H_5O_2ClFe$ calcd.: C, 39.54; H, 2.35; Cl, 16.70%) separated from the solution. The remaining orange solution was then concentrated further to yield orange crystals of phenyldichlorogermaniumcyclopentadienyldicarbonyliron (846 mg).

(b) Reactions with phenylchloro- or phenylpentafluorophenyl-silanes

(i) Diphenylchlorosiliconpentacarbonylmanganese. Dimanganese decacarbonyl (2.34 g, 6 mmoles) was heated with a large excess of diphenylchlorosilane (8.5 g, 19.5 mmoles) in a Carius tube at 150° for 24 h, whereupon the initial green colour of the solution changed to a pale yellow. After cooling to room temperature the tube was opened and the contents extracted with pentane and filtered to remove a small quantity of a white insoluble substance. The pentane was then removed in vacuo and the resulting oil cooled to —78° whereupon a mass of white crystals appeared. These were removed by filtration under nitrogen and then the filtrate cooled again to yield further portions of the product. The oily crude product was then separated from the adhering silane by sublimation at 60° under 10^{-2} mm of mercury to yield fine white crystals of diphenylchlorosiliconpentacarbonylmanganese (1.43 g).

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TABLE 3

ANALYTICAL AND PHYSICAL PROPERTIES

Compound	Colour	M.p. (°C)	Analysis found (calcd.) (%)			Yield (%)	Recrystallisation solvents
			C	H	Cl		
(a) Phenylchloro compounds							
$Ph_2ClGeMn(CO)_5$	White	100–102	45.71 (44.51)	2.25 (2.19)	7.46 (7.75)	47	Pentane
$PhCl_2GeMn(CO)_5$	White	92–93	32.37 (31.76)	1.34 (1.20)	16.96 (17.07)	39	Pentane
$Ph_2ClGeFe(CO)_2Cp$	Yellow	91–94	52.12 (51.89)	3.45 (3.43)	8.76 (8.07)	42	Cyclohexane
$PhCl_2GeFe(CO)_2Cp$	Orange	101–103	39.32 (39.28)	2.38 (2.52)	17.68 (17.86)	7	Cyclohexane/ benzene
$Ph(Cl)Ge[Fe(CO)_2Cp]_2$	Orange-red	150 (dec.)	44.51 (44.55)	2.87 (2.80)	6.46 (6.58)	3	Benzene
$Ph_2ClSiMn(CO)_5$	White	69–71	49.20 (49.49)	2.45 (2.42)	8.49 (8.58)	30	Sublimed
$PhCl_2SiMn(CO)_5$	White	60–62	35.30 (35.57)	1.43 (1.35)	19.20 (19.12)	30	Sublimed
$Ph_2ClSiFe(CO)_2Cp$	Pale yellow	89–94 (95–96)[a]	57.61 (57.78)	3.92 (3.80)	8.72 (9.00)	32	Cyclohexane followed by sublimation
$PhCl_2SiFe(CO)_2Cp$	Yellow	82–83 (81–83)[a]	43.98 (44.18)	2.57 (2.83)	18.54 (20.11)	40	Cyclohexane followed by sublimation
			C	H	F		
(b) Pentafluorophenyl compounds							
$Ph_2(C_6F_5)SiFe(CO)_2Cp$	Pale yellow	139–142	57.28 (57.03)	2.95 (2.85)	18.30 (18.06)	50	Cyclohexane
$Ph(C_6F_5)_2SiFe(CO)_2Cp$	Pale yellow	148–150	48.81 (48.69)	1.67 (1.64)	30.89 (30.83)	32	Cyclohexane
$(C_6F_5)_3SiFe(CO)_2Cp$	Pale yellow	185–187				5	Cyclohexane/

		(195)[b]					pentane
$Ph_2(C_6F_5)SiMn(CO)_5$	White	84—85	50.59 (50.55)	1.72 (1.84)	17.84 (17.46)	30	Pentane
$Ph(C_6F_5)_2SiMn(CO)_5$	White	105—106	42.87 (43.51)	0.56 (0.79)	30.55 (29.96)	35	Pentane
$(C_6F_5)_3SiMn(CO)_5$	White	180—182 (180—182)[b]				33	Cyclohexane/ pentane
$Ph_2(C_6F_5)GeMn(CO)_5$	White	81—83	46.71 (46.89)	1.65 (1.70)	15.86 (16.14)	60	Pentane
$Ph(C_6F_5)_2GeMn(CO)_5$	White	104—106	40.80 (40.66)	0.86 (0.74)	28.41 (27.99)	61	Pentane
$(C_6F_5)_3GeMn(CO)_5$	White	168—171	35.94 (35.95)	0.00 (0.00)	36.75 (37.05)	51	Cyclohexane/ pentane
$(C_6F_5)_3GeFe(CO)_2Cp$	Yellow	192—194	40.16 (39.95)	0.76 (0.67)	37.61 (37.93)	53	Cyclohexane/ pentane
$Ph_2(C_6F_5)SnFe(CO)_2Cp$	Yellow	111—113	49.41 (49.47)	2.41 (2.47)	15.43 (15.68)	73	Cyclohexane/ pentane
$Ph(C_6F_5)_2SnFe(CO)_2Cp$	Yellow	119—121	42.49 (42.45)	1.40 (1.42)	26.74 (26.88)	60	Cyclohexane/ pentane
$(C_6F_5)_3SnFe(CO)_2Cp$	Yellow	192—196	37.80 (37.63)	0.65 (0.63)	36.09 (35.74)	69	Cyclohexane
$(C_6F_5)_3SnMn(CO)_5$	White	150—153 (151—154)[c]				58	Cyclohexane
$Ph(C_6F_5)_2SnMn(CO)_5$	White	100—101 (100—102)[c]				49	Pentane
$Ph_2(C_6F_5)SnMn(CO)_5$	White	91—93 (94—95)[c]				49	Pentane

[a] Lit. m.p., see ref.38. [b] Lit. m.p., see ref.22. [c] Lit. m.p., see ref.10.

Phenyldichlorosiliconpentacarbonylmanganese was prepared similarly from dimanganese decacarbonyl and an excess of phenyldichlorosilane.

Diphenylchlorosiliconcyclopentadienyldicarbonyliron was obtained from cyclopentadienyldicarbonyliron dimer and excess diphenylchlorosilane using essentially the same procedure, but cyclohexane was used for extraction.

Phenyldichlorosiliconcyclopentadienyldicarbonyliron was likewise prepared from an excess of phenyldichlorosilane and cyclopentadienyldicarbonyliron dimer.

(ii) Diphenyl(pentafluorophenyl)- and phenylbis(pentafluorophenyl)siliconcyclopentadienyldicarbonyliron. Cyclopentadienyldicarbonyliron dimer (1.1 g, 3 mmoles) was heated with an excess of diphenyl(pentafluorophenyl)silane (2.7 g, 9 mmoles) at 200° for 2 days. The tube was cooled and opened, and the contents were extracted with cyclohexane and filtered to remove the black decomposition products. The resulting orange filtrate was then concentrated and cooled to 0° to give yellow crystals of diphenyl(pentafluorophenyl)siliconcyclopentadienyldicarbonyliron (1.84 g). Similarly, phenylbis(pentafluorophenyl)siliconcyclopentadienyldicarbonyliron was prepared from phenylbis(pentafluorophenyl)silane, and cyclopentadienyldicarbonyliron dimer.

(c) Reactions with trichlorogermane

(i) Trichlorogermaniumpentacarbonylmanganese. Dimanganese decacarbonyl (0.78 g, 2 mmoles) was sealed with an excess of trichlorogermane (1.08 g, 6 mmoles) at 100° for 24 h to give a completely homogeneous colourless solution. Upon cooling long colourless crystals of trichlorogermaniumpentacarbonylmanganese (1.50 g) formed in essentially quantitative yield. Final purification was achieved by vacuum sublimation at $60°/10^{-2}$ mm.

(ii) Trichlorogermaniumcyclopentadienyldicarbonyliron. An excess of trichlorogermane (0.8 g, 4.4 mmoles) was added dropwise to a stirred solution of cyclopentadienyldicarbonyliron dimer (0.71 g, 2 mmoles) in cyclohexane (20 ml) at room temperature. An immediate and exothermic reaction occurred to leave an orange solution which was then concentrated to a small volume. An essentially quantitative yield of trichlorogermaniumcyclopentadienyldicarbonyliron (1.43 g) was achieved by the addition of pentane until precipitation of the product was complete.

(d) Reactions with pentafluorophenyllithium

With the exception of the preparation of $Ph_2(C_6F_5)SiFe(CO)_2Cp$ and $Ph(C_6F_5)_2SiFe(CO)_2Cp$ which have already been described, these reactions are essentially identical except for the final recrystallizations (see Table 3).

(i) Tris(pentafluorophenyl)germaniumcyclopentadienyldicarbonyliron. To a three necked flask fitted with a mechanical stirrer and pressure equalising dropping funnel was added a solution of pentafluorobenzene (2.18 g, 13 mmoles) in anhydrous diethyl ether (60 ml). The flask and contents were then cooled to —78° with a dry ice acetone bath and the whole system flushed with dry nitrogen for 10 min. After this time a solution of n-butyllithium (13 mmoles, 5.4 ml of 23.1 wt % solution in hexane) was added and the solution stirred for at least two hours. Then a slurry of finely ground trichlorogermaniumcyclopentadienyldicarbonyliron (1.43 g, 4 mmoles) in ether (80 ml) was added after which time

the flask and contents were allowed to reach room temperature. At a temperature of about —20° all the trichlorogermaniumcyclopentadienyldicarbonyliron had dissolved and a fine white precipitate began forming. After the flask had reached room temperature complete reaction was ensured by refluxing the contents of the flask in a warm water bath for a further 15 min. The contents of the flask were then filtered to remove the lithium chloride and the ether removed in vacuo to leave a yellow viscous oil which was then redissolved in cyclohexane and refiltered. Concentration and cooling of this solution yielded yellow platelets of tris(pentafluorophenyl)germaniumcyclopentadienyldicarbonyliron (1.58 g).

The reactions of $Ph_2ClMFe(CO)_2Cp$ (M = Si or Ge) and $PhCl_2SiFe(CO)_2Cp$ with pentafluorophenyllithium were unsuccessful. Even with a very large excess of pentafluorophenyllithium (ca. 4 fold) and letting the flask and contents reach room temperature very gradually over a period of several hours, there was no precipitation of lithium chloride and only starting material was recovered in low yield (ca. 40—30%). The reaction of $PhCl_2GeFe(CO)_2Cp$ with C_6F_5Li gave a small quantity of a yellow crystalline substance that was shown by analysis to contain a low percentage of fluorine. The mass spectrum of a carefully recrystallised sample showed a molecular ion and peaks due to the loss of two carbonyls, each having the correct mass to charge value and isotope pattern for the compound having the formula $PhCl(C_6F_5)GeFe(CO)_2Cp$. However, the analysis does not agree with this formulation and from the infrared and NMR results it was concluded that the compound is a mixture containing mainly $PhCl_2GeFe(CO)_2Cp$, along with some other pentafluorophenylgermanium species, perhaps $PhCl(C_6F_5)GeFe(CO)_2Cp$, as a minor and more volatile impurity.

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