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DERIVATIVES OF DIVALENT GERMANIUM, TIN AND LEAD

XV *. SOME REACTIONS OF DICYCLOPENTADIENYLTIN AND BIS(METHYLCYCLOPENTADIENYL)TIN WITH METAL CARBONYL COMPOUNDS

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Summary

The addition of dicyclopentadienyltin or bis(methylcyclopentadienyl)tin to THF solutions of the complexes $M(CO)_5THF$ (M = Cr, Mo, W) yields the complexes $R_2Sn{:}M(CO)_5$ ($R = C_5H_5$, M = Cr, Mo, W; $R = MeC_5H_4$, M = Cr, W) as amorphous solids. Infrared spectral data confirm the retention of the *pentahapto* mode of bonding of the C_5 rings to tin, whilst the drastic lowering of the tin-119*m* Mössbauer isomer shift from 3.74—3.83 mm s^{-1} in the free stannylene ligands to 1.86—2.00 mm s^{-1} in the complexes, which is also accompanied by an increase from ca. 0.8 mm s^{-1} to 2.51—3.13 mm s^{-1} in the quadrupole splitting, serves to demonstrate the presence of synergic tin → metal σ- and metal → tin $(d \rightarrow p)\pi$-bonding along the tin—metal axis. With enneacarbonyl diiron, dimeric, tetranuclear $[R_2SnFe(CO)_4]_2$ complexes are formed, which now contain *monohapto* rings bound to tin. These complexes undergo ring fission in strong bases (B) affording the base stabilised $B \cdot R_2SnFe(CO)_4$ species, which contain trigonal bipyramidally coordinated iron. Reaction of bis(methylcyclopentadienyl)tin with octacarbonyl dicobalt produces $Sn[Co(CO)_4]_4$ as the only identifiable product. The product of the reaction between dicyclopentadienyltin and $(C_5H_5)W(CO)_3H$ has been reformulated as the divalent tin derivative $Sn[W(CO)_3(C_5H_5)]_2$.

Introduction

The σ-donor and π-acceptor properties of the divalent derivatives of the heavier Group IV metals (silylenes, germylenes, stannylenes, and plumbylenes)

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are topics of considerable interest currently. Several synthetic routes to complexes of these species and transition metal Lewis acids are available. Diiodosilylene may be "fixed" as the dimeric, iodine-bridged, complex, $[I_2SiW(CO)_5]_2$, by the irradiation of a pentane solution of $W(CO)_6$ and Si_2I_6. In THF solution, dissociation to a base-stabilised monomeric species, THF · $I_2SiW(CO)_5$, occurs [2]. Pentacarbonyl-chromium, -molybdenum, and -tungsten complexes of germanium(II) and tin(II) dihalides [3], however, as well as the corresponding trihalo-germanite and -stannite anions [3], tin(II) bis(β-ketoenolates) [4], and $[(Me_3Si)_2CH]_2Sn$ [5] complexes may be prepared directly by the irradiation of solutions of the metal hexacarbonyl and the appropriate germylene or stannylene. Because of their instability with respect to the corresponding tin—tin bonded diorganotin(IV) oligomers, analogous complexes of simple diorgano-germylenes and -stannylenes cannot be prepared in this way, but have been obtained stabilised by a molecule of base by the reaction of diorgano-germanium and -tin dihalides with $Na_2Cr_2(CO)_{10}$ [6]. The presence of a direct tin—chromium bond in the complexes, C_5H_5N-t-$Bu_2SnCr(CO)_5$ [7] and $[(Me_3Si)_2CH]_2SnCr(CO)_5$ [5] has since been confirmed by X-ray crystallography. The reduction of diorganometal dichlorides, R_2MCl_2 (M = Ge, Sn, Pb) by $Na_2Fe(CO)_4$ produced dimeric, tetranuclear $[R_2MFe(CO)_4]_2$ complexes which are characterised by a four-membered Fe_2Sn_2 ring. Again, monomeric, base-stabilised B · $R_2MFe(CO)_4$ complexes may be isolated upon treatment of the dimeric complexes with pyridine or DMSO [8]. Dimeric $[X_2SnFe(CO)_4]_2$ complexes are also obtained from the reaction of tin(II) halides or bis(β-ketoenolates) with enneacarbonyl diiron, although a monomer $\rightleftharpoons$ dimer equilibrium appears to be established with the more bulky β-ketoenolate residues. Addition of pyridine, however, forces the equilibrium totally towards the monomer in all cases [4]. With binuclear metal carbonyls a different mode of reaction, insertion into the metal—metal bond, is also possible. This type of reaction has been particularly well investigated in the case of tin(II) halides, which are known to insert into Fe—Fe [9-12], Co—Co [13], Mn—Mn [14], Cr—Cr [15], Mo—Mo [15], and W—W [15] bonds. In this paper, we report our investigations of the behaviour of dicyclopentadienyltin and bis(methylcyclopentadienyl)tin with some metal carbonyl derivatives.

Results and discussion

Dicyclopentadienyltin, $(C_5H_5)_2Sn$, and its methylcyclopentadienyl analogue, $(MeC_5H_4)_2Sn$, are extremely interesting compounds since they are the only stable divalent tin compounds containing only carbon, hydrogen and tin. An electron diffraction study [16] of dicyclopentadienyltin has shown that isolated molecules in the gas phase possess an angular sandwich structure in which the tin atom is associated equally with all five carbon atoms in each ring. The two C_5 axes subtend an angle of 125° at tin, indicating approximate sp^2 hybridisation for tin and placing the tin lone pair in a hybrid orbital of directional character. Further, the tin atom also has a vacant $5p_z$ orbital, and thus possesses the requirement to form synergic tin $\rightarrow$ metal σ-bonds and metal $\rightarrow$ tin $(d \rightarrow p)$ π-bonds with transition metal derivatives.

The addition of $(C_5H_5)_2Sn$ or $(MeC_5H_4)_2Sn$ to THF solutions containing $M(CO)_5THF$ (M = Cr, Mo, W) species results in the rapid formation of the pentacarbonyl-chromium, -molybdenum, and -tungsten—diorganotin complexes, I, as oxygen and moisture sensitive solids (eq. 1). Infrared data for the complexes

$$M(CO)_6 \xrightarrow{h\nu;\,THF} M(CO)_5THF \xrightarrow{R_2Sn} \underset{(I)}{R_2SnM(CO)_5} \qquad (1)$$

$R = C_5H_5$; M = Cr, Mo, W
$R = MeC_5H_4$; M = Cr, W

are listed in Tables 1 and 2. In the carbonyl stretching region, the complexes exhibit three bands of which two are sharp (at ca. 2055—2090 and 1980—2015 cm^{-1}) whilst the band at lowest energy (at ca. 1920—1940 cm^{-1}) is usually very broad and intense. These spectra are very similar to those obtained for the analogous complexes of tin(II) bis(β-ketoenolates), tin(II) and germanium(II) halides, and trihalo-stannites and -germanites. On the basis of "local" C_{4v} symmetry for the $M(CO)_5$ fragment, three infrared active carbonyl stretching frequencies ($2A_1 + E$) are predicted by group theoretical considerations. Although the highest and lowest energy bands may be reasonably assigned as A_1 and E modes, respectively, the band at 1980—2015 cm^{-1} is of too high energy to be the second A_1 mode which is most probably masked by the very broad intense E mode. This band is probably more correctly assigned as the B_1 mode, normally infrared inactive but Raman active in C_{4v} symmetry, indicating some relaxation from this "local" point group towards overall C_{2v} or C_s symmetry.

Apart from the C—H stretching modes, the normal modes for the cyclopentadienyl rings will occur below 2000 cm^{-1}, and the observed bands for the $(C_5H_5)_2SnM(CO)_5$ (M = Cr, Mo, W) complexes are listed in Table 2. The vibrational spectra of *pentahapto*-cyclopentadienyltin compounds have been previously successfully assigned on the basis of C_{5v} "local" symmetry [17], and in this point group only seven normal modes are active in the infrared: two C—H stretching modes ($A_1 + E_1$), two C—C stretching modes ($A_1 + E_1$), two C—H out-of-plane wagging modes ($A_1 + E_1$), and one C—H in-plane wagging mode

TABLE 1

CARBONYL STRETCHING FREQUENCIES OF THE $M(CO)_5$ RESIDUE IN STANNYLENE-GROUP VI METAL CARBONYL COMPLEXES (cm^{-1}).

Complex	Phase	ν(C=O)		
$(C_5H_5)_2SnCr(CO)_5$	solid	2055m	1990vs	1940vs(vbr)
$(C_5H_5)_2SnGr(CO)_5$	CH_2Cl_2 solution	2070m	1980m	1940vs(vbr)
$(C_5H_5)_2SnMo(CO)_5$	solid	2060m	1985vs	1925vs(vbr)
$(C_5H_5)_2SnW(CO)_5$	solid	2065m	1980vs	1930s(vbr)
$(MeC_5H_4)_2SnCr(CO)_5$	solid	2080s		1930vs(vbr)
$(MeC_5H_4)_2SnW(CO)_5$	solid	2080ms	2015m(sh)	1920vs(vbr)
$Me_2SnCr(CO)_5 \cdot THF$ [a]	hexane solution	2038w	1941m	1920s
$t\text{-}Bu_2SnCr(CO)_5 \cdot THF$ [a]	hexane solution	2031s	1938m	1918s
$(acac)_2SnCr(CO)_5$ [b]	solid	2060ms	1980s	1935vs(br); 1910s
$(acac)_2SnCr(CO)_5$ [b]	CH_2Cl_2 solution	2070m	1970s	1940vs(br)
$(acac)_2SnMo(CO)_5$ [b]	solid	2070w	1985s	1930ms(br)
$(acac)_2SnMo(CO)_5$ [b]	CH_2Cl_2 solution	2075m	1980s(sh)	1940s(br)
$(acac)_2SnW(CO)_5$ [b]	solid	2080ms	1980s	1925vs(br)
$(acac)_2SnMo(CO)_5$ [b]	CH_2Cl_2 solution	2080m	1975m(sh)	1940vs(br)

[a] Ref. 6. [b] Ref. 4. acac = acetylacetonate.

TABLE 2

INFRARED SPECTRA (2000—250 cm^{-1}) OF THE $(C_5H_5)_2SnM(CO)_5$ (M = Cr, Mo, W) COMPLEXES (cm^{-1}) [a,b]

$(C_5H_5)_2SnCr(CO)_5$	$(C_5H_5)_2SnMo(CO)_5$	$(C_5H_5)_2SnW(CO)_5$	$(C_5H_5)_2Sn$ [c]	Assignment
1740vw	1740w		1745vvw	
1710w	1710w			
1620vw	1620vw		1640vw	
1580vw				
1510vw				
1410vw	1412w		1429m	ν_8, C—C stretch E_1
1365m	1366m	1368m	1369vw	
1260s	1260s	1263m		ν_4, CH bend A_2
1095s(br)	1090s(br)	1095m(br)	1116mw	ν_3, ring breathing A_1
			1064vw	ν_{11}, CH bend E_2
1020s(br)	1020s(br)	1015m(br)	1005s	ν_6, CH bend E_1
960vw	960w	940w		
915vw	915w			
891mw	891mw		893vvw	
870w	862w			
802s(br)	802s(br)	800m(br)	790vvs	ν_2, CH bend A_1
772ms(sh)		776ms	757vvs(br)	ν_7, CH bend E_1
759ms	768ms	761ms		
665s	665s	666mw		δ(MCO)
			664vw	

[a] Nujol mulls. [b] Assignments are made using the description convention of ref. 17. [c] Ref. 17.

(A_1). Any lowering of the symmetry will cause the infrared spectrum to become much richer in bands, for example, in C_{2v} symmetry, all the degeneracy is lost and 21 of the 24 ring modes become infrared active, whilst for C_s symmetry all 24 modes are infrared active. Thus, if *pentahapto*-cyclopentadienyl rings are retained on complex formation, the infrared spectra in the 2000—600 cm^{-1} range should resemble that of $(C_5H_5)_2Sn$ itself, whilst any change in the mode of attachment of the rings to the metal (e.g. to *monohapto*) should manifest itself as an enrichment of the number of bands in the infrared spectrum.

The infrared spectra for the $(C_5H_5)_2SnM(CO)_5$ complexes in the 2000—600 cm^{-1} range parallel closely that of $(C_5H_5)_2Sn$, having relatively few bands of significant intensity. Thus it is quite reasonable to assume that the mode of banding of the rings to the tin has not changed drastically on complexation. The band observed at ca. 665 cm^{-1} is assigned to a metal carbonyl deformation mode. The two C—H out-of-plane wagging modes are easily identified as strong bands occurring between 750 and 800 cm^{-1}. In $(C_5H_5)_2Sn$, the band at higher energy (790 cm^{-1}) was assigned as the E_1 mode (ν_7), and the band at 757 cm^{-1} as the A_1 mode ν_2) by comparison with the spectra of $(C_5H_5)Mn(CO)_3$ [18], $(C_5H_5)NiNO$ [19], and $(C_5H_5)_2Fe$ [20]. In the $M(CO)_5$ complexes, however, the lower energy band is split into two components, and it would appear that the higher energy band is better assigned as ν_2 and the two bands at lower energy to the E_1 mode, ν_7. The splitting of the E_1 mode in the complexes indicates some lowering of the symmetry from C_{5v}. The degree of lowering of symmetry is small, and may be rationalised by an interaction between the *pentahapto*-cyclopentadienyl rings and the four equatorial carbonyl groups of the $M(CO)_5$ residue due to their proximity (Fig. 1). Further support for this hypothesis is

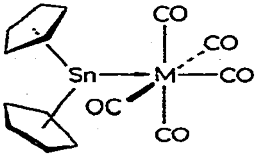


Fig. 1. Proposed structures of the $(C_5H_5)_2SnM(CO)_5$ (M = Cr, Mo, W) complexes.

available from the A_1 ring breathing mode (ν_3) and the E_1 C—H in-plane deformation (ν_6). Although both these fundamentals occur in the expected positions and have intensities similar to the equivalent bands in $(C_5H_5)_2Sn$, both vibrations are relatively very broad. The E_2 C—H out-of-plane wagging mode (ν_1), which occurs as a very weak band at 1064 cm^{-1} in $(C_5H_5)_2Sn$, is presumably masked by the broad ν_3 and ν_8 modes. In addition, all the complexes exhibit a medium-strong band at ca. 1260 cm^{-1}, which is absent in the solid spectrum of $(C_5H_5)_2Sn$. The position of this band suggests that it is the A_2 C—H in-plane deformation mode (ν_4), which is inactive in both the infrared and Raman under C_{5v} symmetry, but is observed as a very weak band at 1263 cm^{-1} for $(C_5H_5)_2Sn$ in CCl_4 solution. Similar positions have been deduced for other model cyclopentadienylmetal derivatives, and it would again seem likely that the increase in intensity is due to lowering of the "local" symmetry via interaction with the $M(CO)_5$ fragment. The infrared spectra of the bis(methylcyclopentadienyl)tin complexes are also qualitatively similar to that of $(MeC_5H_4)_2Sn$, and again it is inferred that no drastic change in bonding has taken place upon complexation.

The tin-119*m* Mössbauer data for the $R_2SnM(CO)_5$ (R = C_5H_5, MeC_5H_4; M = Cr, Mo, W) complexes are presented in Table 3 together with data for related complexes. The spectra for all the complexes consist of quadrupole

TABLE 3

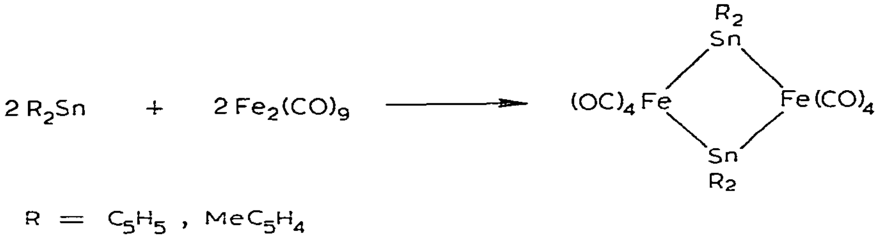
MÖSSBAUER DATA FOR $R_2SnM(CO)_5$ (R = C_5H_5, MeC_5H_4; M = Cr, Mo, W) COMPLEXES AND RELATED COMPOUNDS (mm s^{-1})

Complex	*I.S.*	*Q.S.*	Γ_1	Γ_2
$(C_5H_5)_2Sn$ [a]	3.74	0.86		
$(MeC_5H_4)_2Sn$ [b]	3.83	0.78		
$(C_5H_5)_2SnCr(CO)_5$	1.86	2.60_5	0.87	0.92
$(C_5H_5)_2SnMo(CO)_5$	1.96	2.71	0.93	1.10
$(C_5H_5)_2SnW(CO)_5$	2.00	3.13	1.02	0.98
$(MeC_5H_4)_2SnCr(CO)_5$	1.92	2.51	1.03	1.34
$(MeC_5H_4)_2SnW(CO)_5$	1.90	2.51	1.06	1.43
$t\text{-}Bu_2SnCr(CO)_5 \cdot THF$ [c]	2.11	4.14	1.32	1.14
$t\text{-}Bu_2SnCr(CO)_5 \cdot DMSO$ [c]	1.98	3.60	1.31	1.62
$t\text{-}Bu_2SnCr(CO)_5 \cdot NC_5H_5$ [c]	2.01	3.44	1.31	1.17
$(acac)_2SnM(CO)_5$ [d]	1.80—1.82	2.28—2.35		
$(bac)_2SnM(CO)_5$ [d]	1.90—2.02	2.07—2.51		
$(tfac)_2SnM(CO)_5$ [d]	1.93—2.00	2.29—2.31		
$(hfac)_2SnM(CO)_5$ [d]	1.99—2.13	2.45—2.60		
$(C_5H_5)_2SnMX_3$ [e]	3.71—3.83	0		

[a] Ref. 21. [b] Ref. 17. [c] Ref. 22. [d] Ref. 4 (M = Cr, Mo, W; acac = acetylacetonate, bac = benzoylacetonate, tfac = trifluoromethylacetonate, hfac = bis(trifluoromethyl)acetylacetonate). [e] Ref. 1 (MX_3 = BF_3, BBr_3, $AlCl_3$, $AlBr_3$).

split doublet resonances with isomer shifts in the range 1.86—2.00 mm s^{-1} and quadrupole splittings in the range 2.51—3.13 mm s^{-1}. Both parameters increase in the order $Cr < Mo < W$. The values of the isomer shift for the free ligands [3.74 mm s^{-1} for $(C_5H_5)_2Sn$ [21]; 3.83 mm s^{-1} for $(MeC_5H_4)_2Sn$ [17]) reflect the very high 5*s* electron density at the tin nucleus in the compounds, but on complexation with the $M(CO)_5$ residue, a drastic reduction by ca. 1.8—2.0 mm s^{-1}, accompanied by an equally drastic increase in the electric field gradient at the tin nucleus, is observed. This behaviour is in sharp contrast to that observed of the formation of adducts with boron and aluminium trihalides [1], where the Mössbauer parameters are the same as the free ligands within experimental error. The observed lowering of the isomer shift in the case of the $R_2SnM(CO)_5$ complexes cannot therefore be due to the formation of a coordinate $Sn \rightarrow M$ bond, although this involves a net transfer of electron density away from tin towards M, and would be expected to reduce $[\psi_{5s}(0)]^2$ and hence the isomer shift. However, any multiple bonding along the Sn—M bond would transfer electron density from filled *d* orbitals on M to the vacant $5p_z$ (or 5*d*) orbital on tin, would be expected to lower the effective $[\psi_{5s}(0)]^2$ by shielding and at the same time create a substantial electric field gradient at the tin nucleus. This is precisely the behaviour observed, and lends strong support to the hypothesis of significant synergic transition metal $d \rightarrow$ tin $5p_z$ (or 5*d*) π-bonding (viz. Fig. 2) in these compounds. We have previously postulated the occurrence of such interactions to rationalise the Mössbauer data for bis(β-ketoenolato)tin—chromium, —molybdenum, and —tungsten pentacarbonyl complexes [4]. The complexes t-$Bu_2SnCr(CO)_5 \cdot B$ (B = THF, DMSO, C_5H_5N), prepared from tin(IV) materials but containing formally divalent tin, also exhibit isomer shifts in the similar range 1.98—2.11 mm s^{-1}, but have much larger quadrupole splittings (3.44—4.14 mm s^{-1}). Explanations based upon ylide structures involving the base B were proposed to account for the large splittings observed [22].

Both $(C_5H_5)_2Sn$ and $(MeC_5H_4)_2Sn$ react slowly with enneacarbonyl diiron in benzene at room temperature to afford the dimeric tetranuclear complexes $R_2SnFe(CO)_4$ ($R = C_5H_5$, MeC_5H_4) as red-brown solids (eq. 2). The dimeric nature of the cyclopentadienyl derivative, deduced in solution by osmometry, has been confirmed in the solid by an X-ray diffraction study [23]. The molecular geometry of the compound is shown in Fig. 3, and consists of slightly distorted tetrahedral and octahedral coordination for tin and iron, respectively. The structure of the methyltin derivative is very similar [24]. The most striking feature of the structure is the change in mode of attachment of the cyclopentadienyl rings from *pentahapto* in $(C_5H_5)_2Sn$ to *monohapto* in the tetracarbonyliron complex. In addition, the two cyclopentadienyl rings, which are not equivalent,



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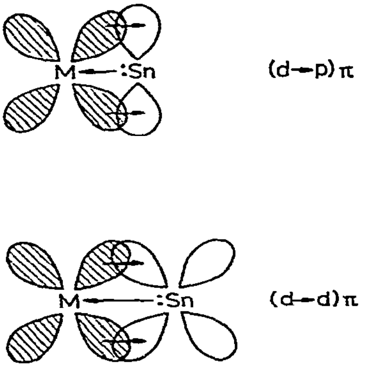


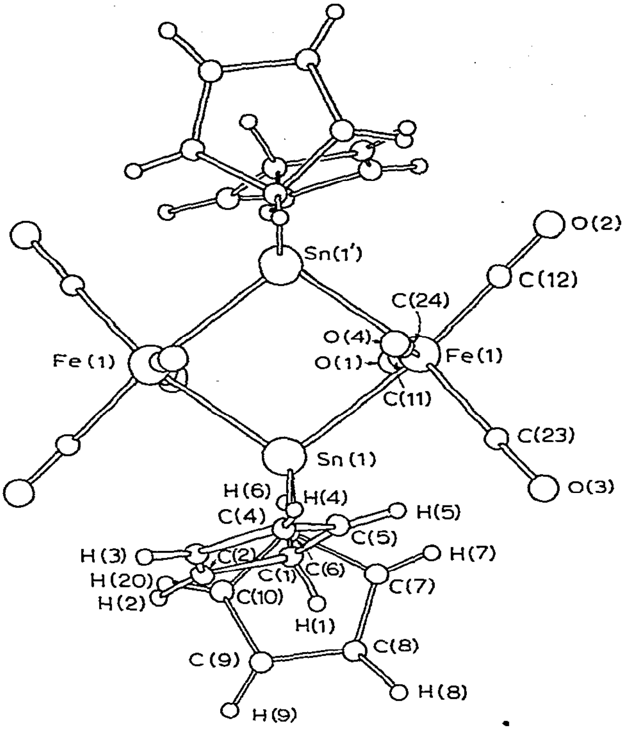
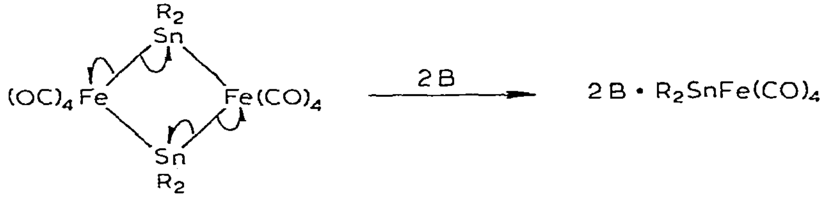


Fig. 2. Bonding phenomena along the tin—transition metal axis.

Fig. 3. Molecular structure of $[(C_5H_5)_2SnFe(CO)_4]_2$.

are planar, rather than puckered as in $(\eta^5\text{-}C_5H_5)(CO)_2FeSn(\eta^1\text{-}C_5H_5)_2$ [25]. This change in ring—metal bonding is reflected in the infrared spectrum of the complex [26].

The bands observed in the metal—carbonyl stretching region for the complexes $[R_2SnFe(CO)_4]_2$ ($R = C_5H_5$, MeC_5H_4) in the solid as well as in various solvents are listed in Table 4. The spectra for the two derivatives in the solid and in dichloromethane solution are essentially the same. However dissolution of the dimeric species in pyridine results in a dramatic change in the carbonyl stretching region of the spectrum, and the previously observed bands are replaced by two new bands, an intense broad band at ca. 1930 cm^{-1} and a weaker sharp band at ca. 2030 cm^{-1}. Marks [8] has observed similar changes in the spectra of other bis(μ-dialkyltin)—bis(μ-tetracarbonyliron) complexes, and has attributed these to a base-induced homolytic fission of the iron—tin bonds (eq. 3) and the heterolytic process (eq. 4) was rejected on the basis of the very low electrical



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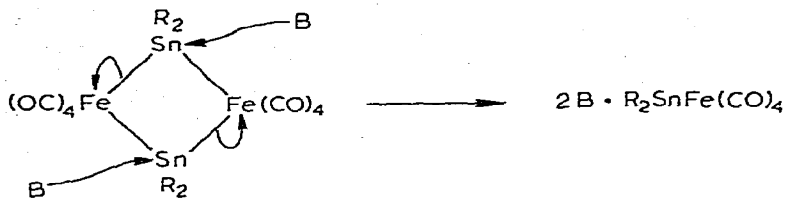


(4)

conductivities observed. Since, however, no ionic species are formed in the heterolytic cleavage, no increase in conductivity would be expected, and therefore there is no reason for the homolytic process to be preferred on these grounds. The synthesis of the cyclopentadienyl complexes from divalent tin sources strongly suggests that the dimeric species are formed by the initial formation of $[R_2SnFe(CO)_4]$ species, which subsequently dimerise because of the electron-rich, nucleophilic iron and electron-deficient, coordinatively unsaturated tin atoms. The introduction of a strong base such as pyridine enables the complete displacement of the weaker iron donors, and the monomeric species are stabilised as Lewis acid—Lewis base adducts. With weaker donors such as THF, a dynamic competition is set up between the THF and iron donors, and the infrared spectra indicate the presence of both monomeric and dimeric species. The $\eta^5 \rightarrow \eta^1$ rearrangement of the mode of attachment of the cyclopentadienyl groups to tin probably does not occur with the initial formation of $R_2SnFe(CO)_4$ monomers, since no rearrangement takes place on complexation with $M(CO)_5$

TABLE 4

THE INFRARED CARBONYL STRETCHING FREQUENCIES (cm^{-1}) OF $[R_2SnFe(CO)_4]_2$ ($R = C_5H_5$, MeC_5H_4 AND Me [8])

Solid	CH_2Cl_2 solution	Hydrocarbon solution	THF solution	Pyridine solution
$[(C_5H_5)_2SnFe(CO)_4]_2$				
	2069w(sh)			
	2053vvs		2051m	
2025vvs			2034vs	2028ms
			2022s(sh)	
	2007vs(sh)		2009s	
1985vvs	1988vvs		1990mw	
1952m(sh)				
1937m(sh)			1933vvs(br)	1929vvs(br)
$[(MeC_5H_4)_2SnFe(CO)_4]_2$				
	2063mw(sh)			
2041vs	2049vvs		2048m	
			2013ms	2031vs
2005vs	1999vvs(sh)		2005ms	
1983vs(br)	1988vvs		1984m	
1941ms(sh)	1945mw(sh)			
			1924vs(br)	1934vvs(br)
$[Me_2SnFe(CO)_4]_2$:				
		2050s		
		2000s		2010s
		1990vs		
			1936w	1928m(sh)
			1906m	1903vs
				1895vs

TABLE 5

MÖSSBAUER DATA FOR TETRACARBONYLIRON-TIN COMPLEXES (mm s^{-1})

Compound	Nuclide	*I.S.*	*Q.S.*	Γ_1	Γ_2
$[(C_5H_5)_2SnFe(CO)_4]_2$ Solid	^{119}Sn	1.86	—	1.24	—
	^{57}Fe	0.01	—	0.47	—
$[(MeC_5H_4)_2SnFe(CO)_4]_2$, Solid	^{119}Sn	1.81	—	1.03	—
	^{57}Fe	0.01	—	0.68	—
$[(MeC_5H_4)_2SnFe(CO)_4]_2$, THF solution	^{119}Sn	1.78	—		
	^{57}Fe	0.20	—		
$[(MeC_5H_4)_2SnFe(CO)_4]_2$, Pyridine solution	^{119}Sn	1.45	1.89		
	^{57}Fe	−0.08	2.36	0.28	0.35
$[Me_2SnFe(CO)_4]_2$[a]	^{119}Sn	1.22	1.47		
	^{57}Fe	−0.11	0.15		
$[n\text{-}Bu_2SnFe(CO)_4]_2$[b]	^{119}Sn	1.70	1.26		
$[t\text{-}Bu_2SnFe(CO)_4]_2$[c]	^{119}Sn	1.83	1.16	0.85	1.36
$[Me_2Sn[Fe(CO)_4]_2]_2Sn$[a]	^{119}Sn	1.24	1.45		
	^{57}Fe	−0.10	0.30		
$t\text{-}Bu_2SnFe(CO)_4 \cdot DMSO$[c]	^{119}Sn	1.87	3.45	1.14	1.09
$t\text{-}Bu_2SnFe(CO)_4 \cdot C_5H_5N$[c]	^{119}Sn	1.82	3.06	1.34	1.12
$Fe(CO)_5$[d]	^{57}Fe	−0.09	2.57		
$Ph_3PFe(CO)_4$[d]	^{57}Fe	−0.09	2.54		
$(EtO)_3RFe(CO)_4$[d]	^{57}Fe	−0.12	2.31		

[a] Ref. 27. [b] Ref. 32. [c] Ref. 22. [d] Ref. 28.

(M = Cr, Mo, W) residues, but rather simultaneously with their dimerisation to reduce the steric requirements of the C_5 rings close to the tin atoms.

The iron-57 and tin-119*m* Mössbauer data for the complexes as solids and frozen solutions are collected in Table 5, together with available data for related compounds. The nearly octahedral and tetrahedral geometries at iron and tin in the solids are reflected by single resonances in both the iron and tin spectra, the electronegativities of the groups bonded to each metal being apparently very similar. Replacement of the electron-withdrawing cyclopentadienyl groups on tin by relatively electron-donating methyl or butyl groups causes an electron imbalance in the σ-framework resulting in an electric field gradient and a small quadrupole splitting [27]. The dimeric species are formally tin(IV) and the tin-119*m* isomer shifts of ca. 1.8 mm s^{-1} are similar to those for related compounds. The data for a frozen THF solution of $[(MeC_5H_4)_2SnFe(CO)_4]_2$ are the same within experimental error with those the neat solid, indicating that the monomer ⇌ dimer equilibrium is forced completely towards the dimer on cooling to 77 K. Dissolution in pyridine, in contrast, has a dramatic effect on both the iron and tin spectra, and the single resonances observed for the solids are replaced by quadrupole split doublets. The induction of a quadrupole splitting in the iron spectrum reflects the change in stereochemistry at iron from octahedral to trigonal bipyramidal accompanying the dimer → monomer dissociation, and the value (ca. 2.4 mm s^{-1}) is similar to that in $Fe(CO)_5$ (2.57 mm s^{-1}) $Ph_3PFe(CO)_4$ (2.54 mm s^{-1}), and $(EtO)_3PFe(CO)_4$ (2.31 mm s^{-1}) [28], which have similar geometries. The quadrupole splittings observed in the tin spectra result from the coordination of pyridine to tin, which is coordinated by two cyclopentadienyl groups and a tetracarbonyliron residue, which have very similar electronegativities, and a much more electronegative pyridyl nitrogen atom.

Thus, imbalances in the σ-framework and any deviation from tetrahedral geometry will create an electric field gradient at tin, and a quadrupole splitting of ca. 1.9 mm s^{-1} is observed.

The monomeric B · $R_2SnFe(CO)_4$ species contain base-diorganostannylene ligands coordinated to tetracarbonyliron residues, and so are formally analogous to the $R_2SnM(CO)_5$ (M = Cr, Mo, W) complexes discussed previously. The tin-119*m* isomer shifts of ca. 1.5 mm s^{-1} observed for the $[C_5H_5N \cdot R_2SnFe(CO)_4]$ (R = C_5H_5, MeC_5H_4) species indicate that the $[C_5H_5N(\eta^1\text{-}C_5H_4X)_2Sn]$ (X = H, Me) moiety is a better π-acceptor than the $[(\eta^5\text{-}C_5H_4X)_2Sn]$ species. A qualitative measure of the σ-donor ability of the $[C_5H_4N(\eta^1\text{-}C_5H_4X)_2Sn]$ group is available from the iron-57 isomer shift of the pyridine-solvated monomers. The observed values of ca. —0.1 mm s^{-1} compare with those for $LFe(CO)_4$ (L = CO, PPh_3, $(EtO)_3P$), and hence it may be inferred that the stannylene ligands have similar σ-donor capacities.

The proton NMR data for the $[R_2SnFe(CO)_4]_2$ (R = C_5H_5, MeC_5H_4) complexes, listed in Table 6, show that the localised *monohapto*-cyclopentadienyl rings present in the solid become fluxional in solution. $[(C_5H_5)_2SnFe(CO)_4]_2$ exhibits just a single sharp resonance at τ3.87, compared with $Me_3Sn\text{-}\eta^1\text{-}C_5H_5$ (τ4.06) and $(\eta^5\text{-}C_5H_5)_2Sn$ (τ4.19) [21,29]. In $(\eta^5\text{-}MeC_5H_4)_2Sn$ [17], the four ring protons have approximately the same chemical shift, but in $Me_3Sn\text{-}\eta^1\text{-}C_5H_4Me$ [29] and $[(\eta^1\text{-}MeC_5H_4)_2SnFe(CO)_4]_2$ the 2,5- and 3,4-ring protons occur in different positions resulting in spectra indicative of fluxional systems. In contrast to the small separation of the two resonances (Δ) in $Me_3Sn\text{-}\eta^1\text{-}C_5H_4Me$ (13 Hz) [29], the separation in $[(MeC_5H_4)_2SnFe(CO)_4]_2$ in $CDCl_s$ or CS_2 is between 90 and 100 Hz. Attempts to collapse the spectrum by cooling the sample resulted only in line broadening and very small temperature effects on the chemical shifts of the two resonances before crystallisation occurred at —80°C. Qualitatively similar spectra were obtained when the sample was dissolved in pyridine, indica-

TABLE 6

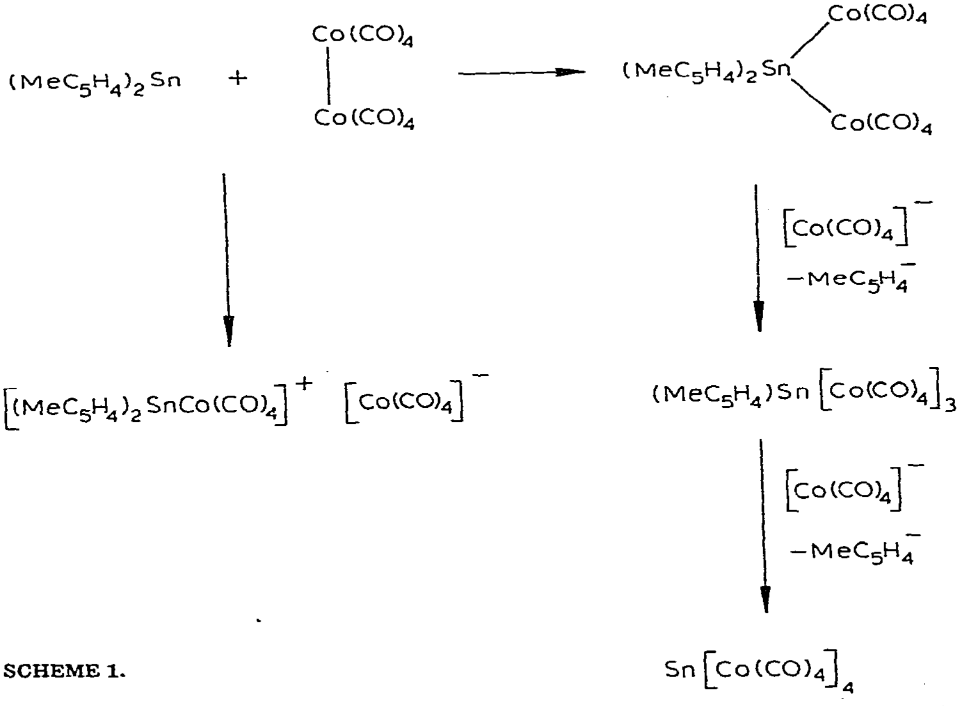
^{1}H NMR DATA FOR $[R_2SnFe(CO)_4]_2$ (R = C_5H_5 AND MeC_5H_4) AND OTHER CYCLOPENTADIENYL-TIN COMPOUNDS (τ)

Compound	Solvent	Temperature (°C)	Ring protons τ(ppm)	Δ (Hz)	$\tau(C_5H_4Me)$ (ppm)
$[(C_5H_5)_2SnFe(CO)_4]_2$	$CDCl_3$	31.5	3.87		
$[(MeC_5H_4)_2SnFe(CO)_4]_2$	$CDCl_3$	31.5	3.70, 4.61	91	7.92
		—40	3.68, 4.65	97	7.92
		—60	3.65, 4.64	99	7.91
	CS_2	31.5	3.82, 4.77	95	7.97
$[(MeC_5H_4)_2SnFe(CO)_4]_2$	C_5H_5N	31.5	3.85, 4.44	59	7.92
		—50	3.81, 4.38	57	7.91
		—70	3.79, 4.33	54	7.91
		—90	3.73, 4.21	48	7.91
		—107	3.68, 4.00	32	7.91
$(C_5H_5)_2Sn$ [a]			4.19		
$(MeC_5H_4)_2Sn$ [b]			ca. 4.30 [c]		7.97
$Me_3SnC_5H_5$ [d]			4.06		
$Me_3SnC_5H_4Me$ [d]			4.34, 4.47	13	7.96

[a] Ref. 21. [b] Ref. 17. [c] Unresolved multiplet. [d] Ref. 28.

ting that fluxional *monohapto*-methylcyclopentadienyl rings are also present in the pyridine-stabilised monomer species in solution. The separation of the two ring proton resonances in the monomeric species is much less (59 Hz at 31.5°C) than that of the dimer, and moreover decreases dramatically upon reduction in temperature being only 32 Hz at −107°C. Again no collapse of the spectrum was observed before crystallisation occurred. The large decrease in Δ on cooling most probably reflects changes in the degree of solvation at tin by pyridine. Brice and Cotton [7] have shown that only one pyridine molecule is bound to tin in the similar chromium complex C_5H_5N-t-$Bu_2SnCr(CO)_5$, but in the present case the actual degree of solvation of the tin is uncertain, and increased solvation may occur as molecular vibrational modes are frozen out. The change in Δ going from the dimer to monomer illustrates the effect of replacing iron by the more electronegative pyridyl nitrogen in the first coordination sphere of the tin.

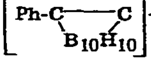
Bis(methylcyclopentadienyl)tin reacts with dicobalt octacarbonyl slowly at room temperature (48 h) in cyclohexane to afford tetrakis(tetracarbonylcobalt)tin(IV) as a black solid. More of this product was slowly deposited from the remaining red oil, but the tin-119*m* Mössbauer spectrum showed that unreacted $(MeC_5H_4)_2Sn$ and $Sn[Co(CO)_4]_4$ were the only tin-containing products present. Tin(II) halides are known to undergo facile insertion into the Co—Co bond of $Co_2(CO)_8$ [13] (formal oxidative-addition of the Co—Co bond to the tin lone pair) and a similar reaction is not unlikely in the present case. Displacement of methylcyclopentadienyl groups from tin most likely involves the participation of the highly nucleophilic $[Co(CO)_4]^-$ anions, which in a solvent of low polarity as cyclohexane must arise from the base-induced dissociation of $Co_2(CO)_8$, where $(MeC_5H_4)_2Sn$ functions as the base (cf. THF solutions of $Co_2(CO)_8$). Thus, the formation of $Sn[Co(CO)_4]_4$ may be summarised as in Scheme 1.



SCHEME 1.

TABLE 7

MÖSSBAUER DATA FOR SOME TIN—METAL COMPOUNDS (mm s^{-1})

Compound	*I.S.*	*Q.S.*
$Sn[W(CO)_3(C_5H_5)]_2$ [a]	2.08	2.05
$Sn[Co(CO)_4]_4$ [b]	1.96	0
$Sn[SnPh_3]_4$ [c]	1.33	0
$[Me_2Sn[Fe(CO)_4]_2]_2Sn$ [d]	2.20	0
$Sn[CH(SiMe_3)_2]_2$ [e]	2.16	2.31
 —Sn [f]	2.95	1.90

[a] Ref. 30. [b] Ref. 31. [c] Ref. 33. [d] Ref. 27. [e] Ref. 5. [f] Ref. 34.

It is appropriate here to comment further on the structure of the product from the reaction between $(C_5H_5)_2Sn$ and $(C_5H_5)(CO)_3WH$. We initially formulated this compound as the tin—tin bonded oligomer $\{Sn[W(CO)_3(C_5H_5)]_2\}_n$ containing tetravalent tin on the basis of the tin-119*m* Mössbauer isomer shift, which is very low for a divalent tin compound [30]. The features of highest mass in the mass spectrum of the product correspond to the polyisotopic fragments $(P - n\mathrm{CO})^+$ (n = 4—6) and $(P - C_5H_5 - m\mathrm{CO})^+$ (m = 5,6), whilst an osmometric determination of the molecular weight in chloroform solution gives a value of 1007 compared with a calculated value of 785 for the monomer. The value of the Mössbauer isomer shift (2.08 mm s^{-1}) falls within the range of other metal carbonyl derivatives of divalent tin, and therefore cannot now be considered unusual. Our previous formulation as a tin—tin bonded oligomer implies approximately tetrahedral coordination of each tin atom by two tin atoms and two tungsten atoms. Such an arrangement would be expected to give rise to only a very small quadrupole splitting, since the electronegativities of tin and tungsten will not be too different. The observed value of 2.05 mm s^{-1} is, however, of a magnitude expected for a divalent tin derivative with a bent W—Sn—W backbone, whether or not the lone pair is stereochemically active (Table 7).

Experimental

All manipulations were performed under an atmosphere of dry argon or nitrogen. Infrared spectra were recorded using a Perkin—Elmer 457 or 521 spectrophotometer calibrated with polystyrene film. NMR spectra were obtained using a Varian HA-100 spectrometer using TMS as an internal lock signal. Samples for examination were dissolved in the appropriate dry, oxygen-free solvent. Tin-119*m* Mössbauer spectra were obtained at 77°K using a Harwell spectrometer equipped with a 256 multichannel analyser against a $Ba^{119m}SnO_3$ (^{119}Sn) or a $^{57}Co/Pd$ (^{57}Fe) source. Data reduction to Lorentzian line shapes was effected by usual least squares methods. Ultraviolet irradiations were performed using a medium-pressure arc (ca. 180—256 nm) (Hanovia Ltd.) Dicyclopentadienyltin and bis(methylcyclopentadienyl)tin were prepared from tin(II) chloride and the lithium salt in THF.

Preparation of the complexes

1. Dicyclopentadienyltin—(pentacarbonyl)chromium. To the orange solution of $Cr(CO)_5THF$ (from the irradiation of $Cr(CO)_6$ (1.00 g, 4.5 mmol) in THF until evolution of CO had ceased) was added $(C_5H_5)_2Sn$ (1.13 g, 4.5 mmol) also in THF (20 ml). The colour of the reaction mixture became pale brown over a period of ca. 0.5 h, after which time the volume of the solvent was slowly reduced and any $Cr(CO)_6$ filtered off. Addition of pentane followed by slow evaporation of the solvent yielded the complex as a pale brown powder. Found: C, 41.02; H, 2.17. $C_{15}H_{10}CrO_5Sn$ calcd.: C, 40.81; H, 2.28%. Dec. >150°C.

2. Dicyclopentadienyltin—(pentacarbonyl)molybdenum. Procedure as in (1) from $Mo(CO)_6$ (0.59 g, 2.25 mmol) and $(C_5H_5)_2Sn$ (0.56 g, 2.25 mmol) in THF. Found: C, 36.91; H, 2.51. $C_{15}H_{10}MoO_5Sn$ calcd.: C, 37.30; H, 2.06%. Green-brown powder, dec. >150°C.

3. Dicyclopentadienyltin—(pentacarbonyl)tungsten. Procedure as in (1) from $W(CO)_6$ (1.20 g, 3.42 mmol) and $(C_5H_5)_2Sn$ (0.85 g, 3.42 mmol) in THF. Found: C, 31.12; H, 2.20. $C_{15}H_{10}O_5SnW$ calcd.: C, 31.45; H, 1.76%. Brown powder, dec. >150°C.

4. Bis(methylcyclopentadienyl)tin—(pentacarbonyl)chromium. Procedure as in (1) from $Cr(CO)_6$ (0.51 g, 2.3 mmol) and $(MeC_5H_4)_2Sn$ (0.64 g, 2.3 mmol) in THF. Found: C, 43.15; H, 3.56. $C_{17}H_{14}CrO_5Sn$ calcd.: C, 43.53; H, 3.01%. Green waxy solid, dec. >150°C.

5. Bis(methylcyclopentadienyl)tin—(pentacarbonyl)tungsten. Procedure as (1) from $W(CO)_6$ (0.95 g, 2.7 mmol) and $(MeC_5H_4)_2Sn$ (0.75 g, 2.7 mmol) in THF. Found: C, 31.89; H, 2.20. $C_{17}H_{14}O_5SnW$ calcd.: C, 32.47; H, 2.24%. Pale brown powder, dec. >150°C.

6. Bis(dicyclopentadienyltin)—bis(tetracarbonyl)iron. $Fe_2(CO)_9$ (0.660 g, 1.81 mmol) and $(C_5H_5)_2Sn$ (1.14 g, 4.58 mmol) were stirred in benzene (25 ml) overnight during which time the majority of the insoluble carbonyl dissolved to form a red solution. The small amount of solid was filtered off, and the red filtrate reduced in volume to yield red crystals of the complex. Found: C, 39.89; H, 2.47%; mol. wt. 846.8. $C_{28}H_{20}O_8Fe_2Sn_2$ calcd.: C, 40.35; H, 2.42%; mol. wt. 833.5.

7. Bis[bis(methylcyclopentadienyl)tin]—bis(tetracarbonyl)iron. $Fe_2(CO)_9$ (3.09 g, 8.49 mmol) and $(MeC_5H_4)_2Sn$ (2.35 g, 8.48 mmol) were allowed to react together as in (6), and after 24 h a brick-red solid was filtered off, washed with benzene and dried in vacuo to yield the complex. Found: C. 42.75; H, 3.08%; mol. wt. 876.5 (by osmometry in benzene). $C_{32}H_{28}Fe_2O_8Sn_2$ calcd.: C, 43.20; H, 3.17%; mol. wt. 889.6.

8. The reaction of bis(methylcyclopentadienyl)tin with octacarbonyl dicobalt. $(MeC_5H_4)_2Sn$ (1.38 g, 4.98 mmol) in cyclohexane (10 ml) was added dropwise with stirring to $Co_2(CO)_8$ (1.71 g, 4.98 mmol) also in cyclohexane (30 ml). After stirring for 43 h a dark solid was filtered off leaving a dark red filtrate. The dark solid was identified as $Sn[Co(CO)_4]_4$ by microanalysis (Found: C, 24.13; H, 0.05%. $C_{16}O_{16}Co_4Sn$ calcd.: C, 23.96; H, 0.00%) and its Mössbauer spectrum (*I.S.* 1.94 mm s^{-1}, *Q.S.* 0.00; lit [31] *I.S.* 1.96 mm s^{-1}, *Q.S.* 0.00). Removal of the solvent from the filtrate left a red oil which slowly deposited more $Sn[Co(CO)_4]_4$. A Mössbauer spectrum of the red oil showed the presence of only dissolved $Sn[Co(CO)_4]_4$ and unreacted $(MeC_5H_4)_2Sn$.

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References

1 P.G. Harrison and J.A. Richards, J. Organometal. Chem., 108 (1976) 35.
2 G. Schmid and R. Boese, Chem. Ber., 105 (1972) 3306.
3 D. Uhlig, H. Behrens and E. Lindner, Z. Anorg. Allg. Chem., 401 (1973) 233.
4 A.B. Cornwell and P.G. Harrison, J. Chem. Soc. Dalton, (1975) 1486.
5 P.J. Davidson and M.F. Lappert, J. Chem. Soc. Chem. Commun., (1973) 317; J.D. Cotton, P.J. Davidson, D.F. Goldberg, M.F. Lappert and K.M. Thomas, J. Chem. Soc. Chem. Commun., (1974) 893.
6 T.J. Marks, J. Amer. Chem. Soc., 93 (1971) 7090.
7 M.D. Brice and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 4529.
8 T.J. Marks and A.R. Newman, J. Amer. Chem. Soc., 95 (1973) 769.
9 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 179.
10 S.R.A. Bird, J.D. Donaldson, A.F. Le C. Holding, B.J. Senior and M.J. Tricker, J. Chem. Soc. (A), (1971) 1616.
11 P.F. Barret and W.J. Jacobs, Canad. J. Chem., 50 (1972) 972.
12 P. Hackett and A.R. Manning, J. Chem. Soc. Dalton, (1972) 1487.
13 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 5 (1966) 1405.
14 J. Hoyano, D.J. Patmore and W.A.G. Graham, Inorg. Nucl. Chem. Letters, 4 (1968) 201.
15 P. Hackett and A.R. Manning, J. Chem. Soc. Dalton, (1972) 2434.
16 A. Almenningen, A. Haaland and T. Motsfeldt, J. Organometal. Chem., 7 (1967) 97.
17 M.A. Healy and P.G. Harrison, J. Organometal. Chem., 51 (1973) 153.
18 I.J. Hyams, R.T. Bailey and E.R. Lippincott, Spectrochim. Acta, Part A, 23 (1967) 273.
19 R.D. Feltham and W.G. Fateley, Spectrochim. Acta, 20 (1964) 1081.
20 E.R. Lippincott and R.D. Nelson, Spectrochim. Acta, 10 (1958) 307.
21 P.G. Harrison and J.J. Zuckerman, J. Amer. Chem. Soc., 91 (1969) 6885.
22 G.W. Grynkewich, B.Y.K. Ho, T.J. Marks, D.L. Tomaja and J.J. Zuckerman, Inorg. Chem., 12 (1973) 2522.
23 P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc. Dalton, (1975) in press.
24 C.J. Gilmore and P. Woodward, J. Chem. Soc. Dalton, (1972) 1387.
25 B.P. Biryukov, Y.T. Struchkov, K.N. Anisimov, N.E. Kolobova and V.V. Skripkin, Chem. Commun., (1968) 1193.
26 P.G. Harrison and J.A. Richards, J. Organometal. Chem., 108 (1976) 61.
27 M.T. Jones, Inorg. Chem., 6 (1967) 1249.
28 N.N. Greenwood and T.C. Gibb, Mössbauer Spectroscopy, Chapman and Hall Ltd., London, 1971, p. 227.
29 A. Davison and P.E. Rakita, Inorg. Chem., 9 (1970) 289.
30 P.G. Harrison and S.R. Stobart, J. Chem. Soc. Dalton, (1973) 940.
31 D.E. Fenton and J.J. Zuckerman, J. Amer. Chem. Soc., 90 (1968) 6227; Inorg. Chem., 8 (1969) 1771.
32 R.H. Herber, Application of the Mössbauer Effect in Chemistry and Solid State Physics, International Atomic Energy Agency, Vienna, 1966, p. 121.
33 T.C. Gibb and N.N. Greenwood, J. Chem. Soc. A, (1966) 43.
34 A.Yu. Aleksandrov, V.I. Bregadze, V.I. Goldanski, L.I. Zakcharkin, O.Yu. Okhlobystin and V.V. Khrapov, Dokl. Phys. Chem., 165 (1965) 804.