Coordination Chemistry Reviews, 130 (1994) 175–241

Bidentate oxygen donor chelates of silicon, germanium and tin

Chih Y. Wong and J.D. Woollins

The Evans Laboratory, Department of Chemistry, Imperial College, London SW7 2AY (UK)

(Received 30 October 1992; accepted 6 February 1993)

CONTENTS

ABSTRACT

The coordination chemistry of Si, Ge and Sn with bidentate O,O and O,O' ligands is reviewed for both five- and six-membered chelate rings.

ABBREVIATIONS

δ	chemical shift
18-c-6	18-crown-6
l-Np	naphthyl
AO	atomic orbital

Correspondence to: J.D. Woollins, The Evans Laboratory, Department of Chemistry, Imperial College, London SW7 2AY, UK.

0010-8545/94/$26.00

CD	circular dichroism
CPMAS	cross-polarization magic angle spinning
Cy	cyclohexyl
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulphoxide
fac	facial
HMPA	hexamethylphosphoramide
Hacac	acetylacetone
Hbzac	benzylacetone
Hdbzm	dibenzoylmethane
Hdiket	1,3-diketone
Hdmp	3-hydroxy- 1,2-dimethylpyridin-4-one
Hdpm	dipivalomethane
H(3-Etacac)	3-ethyl-2,4-pentanedione
Hhfac	1,1,1,5,5,5-hexafluoro-2,4-pentanedione
Hhfo	3-hydroxyflavone
Hhq	8-hydroxyquinoline
Hkoj	kojic acid
Hmal	maltol
Htfac	1,1,1-trifluoro-2,4-pentanedione
Htrop	tropolone
H_2(1,8-naph)	1,8-dihydroxynaphthalene
H_2(2,3-naph)	2,3-dihydroxynaphthalene
H_2cat	catechol
H_2dbcat	3,5-di-tert-butylcatechol
H_2gly	glycol
H_2ox	oxalic acid
H_2pin	pinacol
H_2tccat	tetrachlorocatechol
J	spin-spin coupling
mer	meridional
Oct	octyl
py	pyridine
skew	skew trapezoidal bipyramid
SP	square pyramidal
TBP	trigonal bipyramidal
THF	tetrahydrofuran
VT	variable temperature

A. INTRODUCTION

This review was stimulated by the diverse biochemical interactions of silicon with the biology of life. There is still very little evidence as to how silicon is biologically transported in nature and what species are involved. Bidentate, oxygen donor chelates tend to give the strongest silicon complexes and many naturally occurring chelates of this type are known. If discrete silicon complexes are involved, then the complexes are likely to utilize ligands similar to those described. Germanium and tin are the next members of the Group 14 elements and are often compared with one another to correlate the results obtained for silicon. In addition, there has been much interest recently in the anti-tumour activity of certain 1,3-diketonato tin(IV) complexes.

In this review, we have summarized the literature on a particular aspect of silicon, germanium and tin complexes. The survey has been restricted to bidentate ligands which possess O_2 donor sets and form five- or six-membered chelate rings with these elements. This allowed us to focus on some classical ligands such as the acetylacetones, the catechols and the tropolones, which still receive appreciable interest. More recent developments have established a new set of ligands derived from maltol, the 3-hydroxypyridin-4-ones. The stability, for silicon at least, indicate that they are stronger chelates than other monobasic ligands such as acetylacetones and tropolones. In all cases, stabilization is achieved by charge delocalization as the consequence of aromaticity or pseudo-aromaticity in the chelating agent. Complexes derived from saturated ligands, e.g. the diols, have been included only where they serve to increase our understanding of the unsaturated analogues. By restricting our survey to the above, we have been able to collate and present most (but not all) of the data reported in a logical way and establish the current knowledge of these complexes in coordination chemistry terms.

The complexation of these chelates with the transition metals has been the subject of many reviews [1] but is considerably less well studied for the main group elements. The Group 14 elements exhibit remarkable properties that are unique in the Periodic Table, for example: the change from non-metallic to metallic properties down the group, the increase in stability of higher coordination numbers and the +2 oxidation state down the group. It is also the only group in the Periodic Table in which all the elements possess at least one NMR active nucleus. Harrison [2] has reviewed *The Elements of Group 4* between 1979 and 1990 covering all aspects of what are now known as the Group 14 elements.

B. SILICON

Silicon is now considered as an essential biological trace element. There have been numerous studies reported on the biochemistry of silicon, in particular, its role in the biology of primitive organisms and biomineralization [3–10]. Certain groups of algae, e.g. diatoms, are known to incorporate large amounts of silicon and appear to be an essential element in the metabolism of the organisms. "Glass sponges" may absorb so much silica that the silica content of the water of inland seas is appreciably lowered. There are many examples of plants to which silica is an important or even essential element, for growth, as a nutrient, for protection and as a boron substitute. The precise chemical nature of the transported silicon species is unknown and remains an important and complex area of research.

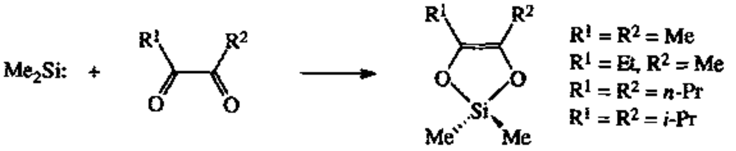
Organosilicon compounds are now of great importance in the development of new chemical reagents, polymers, glasses and ceramics. New synthetic routes to these materials are highly desirable especially if they can be prepared directly and cheaply from silica. The consequences to synthesis by nucleophilic displacement at the silicon centre have also been recognized [11].

Formation of four-coordinate bidentate silicon complexes is comparatively rare due to the ease with which these complexes hydrolyze. Recent structural studies have, however. stimulated much interest [12–18]. The corresponding five- and six-coordinate complexes have received far more attention. The molecular and electronic structure of five- and six-coordinate silicon compounds have been extensively reviewed by Tandura et al. [19] covering all aspects of chelation. The reactivity of silicon compounds with emphasis on the consequences to organic synthesis and the mechanistic implications have been reported by Corriu and co-workers [20,21]. The characterization of five-coordinate bis(bidentate ligand)silicon complexes over the last decade have been described by Holmes and co-workers [22–30]. Six-coordinate silicon complexes are dominated by tris-chelates and only a few examples are known of bis-chelates. The bis-chelate complexes become far more abundant for the heavier elements of this group. A number of papers [31–38] have reported the use of ^{29}Si NMR spectroscopy to probe five- and six-coordinate silicon complexes.

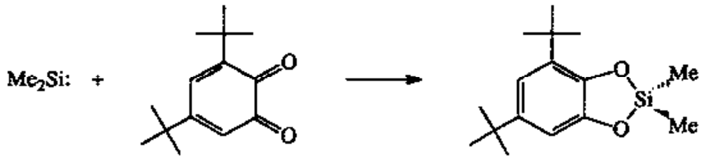
(i) Four-coordinate complexes

The chemistry of four-coordinate silicon(IV) with various saturated diols has been reported for numerous systems and has been reviewed by Frye [39]. He reported a convenient method to stable silicon(IV) diols by exploiting the cyclic stabilizing effect of the alkyl substituents and thus synthesized a series of spirosilicates derived from 1,2-, 1,3-, and 1,4-diols. The 1,2-diolato complexes form five-membered chelate rings, which are appreciably strained. As a consequence of this instability, a number of interesting transformations occur, which readily convert them to stable five-coordinate complexes [40].

The use of silylenes as synthetic intermediates has been reported by Ando and Ikeno [41]. In their studies of the reactions of dimethylsilylene, :SiMe$_2$, with 1,2-diketones, they reported the formation and reaction of various 1,2-diketonato derivatives (eqns. (1) and (2)).

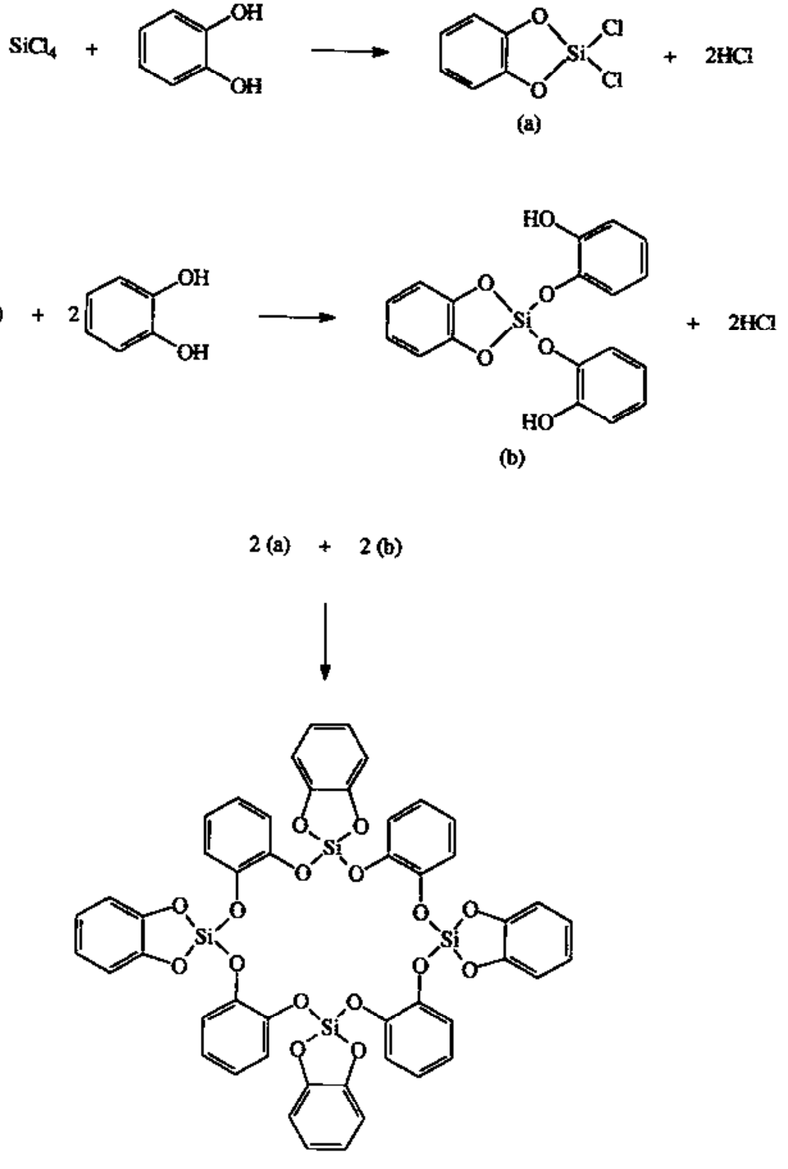


(1)



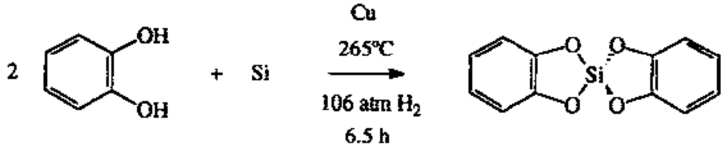
(2)

Four-coordinate catecholato silicon(IV) complexes were first reported by Schwarz and Kuchen in 1951[42]. The reaction of $SiCl_4$ with catechol (eqn. (3))



(3)

produced a chloroform soluble compound which was isolated by vacuum distillation followed by sublimation. The structure of the complex, $[Si(cat)_2]_4$, with four bridging catechols was proposed. The complex is highly moisture sensitive and readily hydrolyzes to give SiO_2 and catechol. Allcock et al. [43] subsequently isolated $Si(cat)Cl_2$ (**1**), $[Si(cat)Cl_2]_2$ (**2**) and $Si(cat)_2$ (**3**). Polymeric **3** was proposed on the basis of the broad melting point range observed (165–185°C), however, facile depolymerization occurred at elevated temperatures and only the monomer was observed in the mass spectrum. The synthesis of organo-substituted analogues of **1** and **2**, with organic groups in place of chlorine was also described. The synthesis of (2,2'-biphenylenedioxy)dimethoxysilane has been reported (Fig. 1), despite its high susceptibility to rearrange to bis(2,2'-biphenylenedioxy)silane as previously observed [44]. In 1962, Zuckerman [45] reported the synthesis of various bis(O_2-donor-aryl)silicon complexes, where O_2-donor-aromatic ligands were catechol, 2,2'-dihydroxybiphenyl, 2,3-dihydroxynaphthalene and related compounds. The reactions were carried out using silicon powder in the presence of a silicon-copper (9:1 w/w) catalyst under a high pressure of hydrogen (eqn. (4)).



(4)

The mechanism for the reaction was based on the formation of volatile silicon subhydrides which led to an abnormally high vapour pressure of silicon.

Since Zuckerman's proposed monomeric nature of **3**, there has been much debate over the solid state structure of this silicon compound. Meyer and Nargorsen [12] crystallized the carbon analogue of $Si(cat)_2$, $C(cat)_2$ (**4**) in which the distorted tetrahedral geometry was shown by X-ray crystallography (Fig. 2). Crystals of **3** suitable for X-ray diffraction were not obtained in most cases due to the glassy nature of the products. By X-ray rotation and Weissenberg photographs, the space group ($P2_1/c$, monoclinic) was satisfactorily determined and on this basis, along with EH calculations, a square-planar geometry was proposed for **3**. Pseudo-octahedral silicon coordination was achieved by intermolecular O–Si interactions in the crystal lattice. Würthwein and Schleyer [13] examined the problem using quantum mechanical (semi-empirical MNDO) calculations. They concluded that silicon is inherently better suited than carbon for planar four-coordinate structures. Compounds such as **3** may exhibit reduced energy difference between planar and tetrahedral forms, and the addition of possible six-coordinate silicon may increase the possibility of its experimental observation. However, Dunitz [14] challenged Meyer and

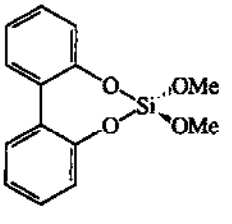


Fig. 1. (2,2'-Diphenylenedioxy)dimethoxysilane.

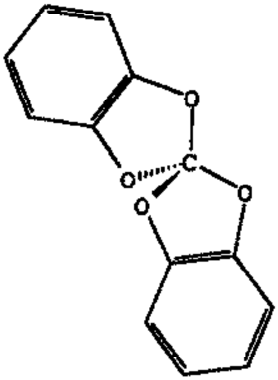


Fig. 2. The structure of **4**.

Nargorsen's planar Si(cat)$_2$ molecule and suggested a possible alternative space group of *P2/c* (due to the short *b* axis). Further, he suggested that the cell dimensions were actually similar to those of free catechol! Meyer and Nargorsen [15] replied that the space group determination was indeed based on the absence of a few reflections, as reported. The similar cell dimensions were plausible if the hydrogen bond system linking two catechol molecules in the plane were replaced by silicon. Supporting evidence for **3** was given based on the increased melting point and mass spectroscopy under crystal growth conditions.

In 1983, Schomburg [16] reported the X-ray structure of bis(tetramethylethylenedioxy)silane (**5**) (Fig. 3), and Zuckerman et al. [17] reported the X-ray structure of bis(1,8-naphthalenedioxy)silane (**6**) (Fig. 4). In both **5** and **6**, the geometry of the silicon was a distorted tetrahedron. In 1989, Hönle et al. [18] were finally able to obtain crystals of $[\mathrm{Si(cat)_2}]_n$ (**7**). An amorphous powder of **7** was synthesised as previously described [43] and single crystals were obtained by sublimation in sealed ampoules ($p < 10^{-4}$ Pa, 540–523 K, 4 weeks). The crystal structure consisted of one-dimensional infinite poly-

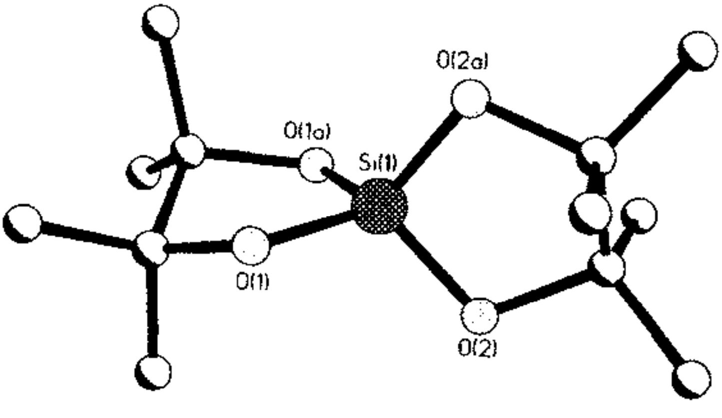


Fig. 3. The crystal structure of **5**.

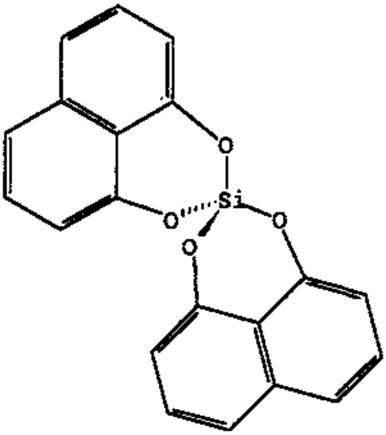


Fig. 4. The structure of **6**.

mers with tetrahedral SiO_4 coordination. Each catechol bridged two silicon atoms in all cases (Fig. 5).

(ii) Five-coordinate complexes

The silicon atom has five vacant 3d atomic orbitals (AOs) the participation of which leads to five- and six-coordinate states. For the five-coordinate case, there are two types of configuration, the trigonal bipyramid (TBP) with D_{3h} symmetry and the square pyramid (SP) with C_{4v} symmetry (although in most cases the geometry may be described more accurately as the rectangular pyramid). Both geometries require sp^3d hybridization; TBP and SP require $3d_z$ and $3d_{x^2-y^2}$ AO participation, respectively, and in both cases, two sets of non-equivalent bonds arise (axial and equatorial) [19,46]. The small energy barrier and small energy difference between the two geometries have stimulated much interest.

The reaction of aliphatic 1,2-diols with silicon to form five-coordinate complexes was first demonstrated by Müller and Heinrich [40]. The report included the synthesis of two alkali metal five-coordinate siliconate salts (Fig. 6). Frye [47] extended the work with

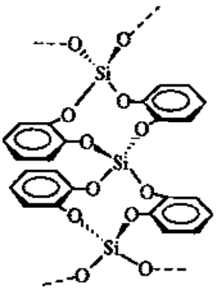


Fig. 5. Section of $[Si(cat)_2]_n$ polymer.

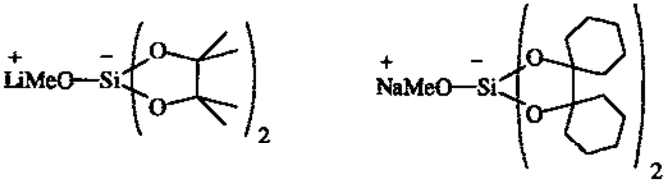
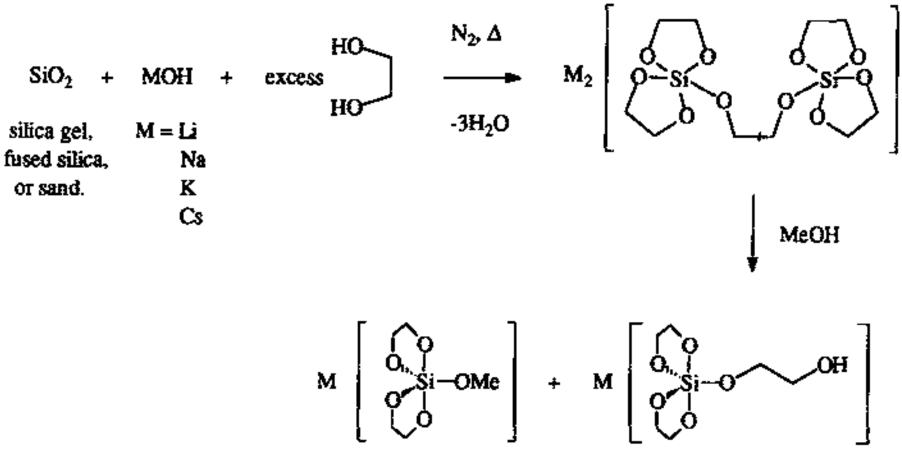


Fig. 6. Bis(tetramethylethylenedioxy)methoxysilane lithium salt and bis(dicyclohexylethylenedioxy)methoxysilane sodium salt.

examples containing Si–C bonds (Fig. 7). In both papers, the geometry around the silicon was not explicitly described. Later, Schomburg [48,49] reported the X-ray structures of bis(ethylenedioxy)methylsiliconate and bis(tetramethylethylenedioxy)fluorosiliconate anions (Figs. 8, 9). Both anions were found to exhibit TBP structures substantially distorted towards the SP configuration. Recently, Laine et al. [50] synthesized five-coordinate silicon complexes directly from SiO_2 (eqn. (5)).



(5)

The X-ray structure of $K[Si(OCH_2CH_2O)_2OCH_2CH_2OH]$ has typical TBP geometry (Fig. 10). This work represented a significant breakthrough in the synthesis of highly reactive

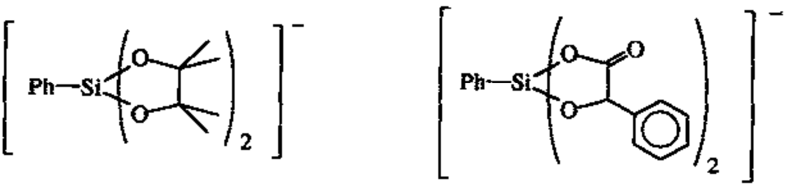


Fig. 7. Bis(tetramethylethylenedioxy)phenylsilane and bis(mandelato)phenylsilane anions.

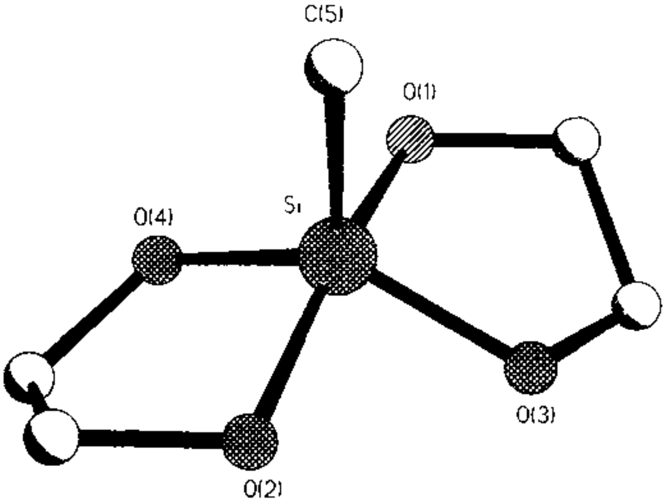


Fig. 8. The crystal structure of the bis(ethylenedioxy)methylsilane anion.

1,2-diolato silicon compounds directly from SiO_2 and it was suggested that this may provide a more economical route to highly desirable industrial materials.

Schott and Golz [51] reported the synthesis of various five-coordinate silicon complexes of the type $[RSi(diket)_2]X$, where R = Me, CH_2Cl and Ph, Hdiket = Hacac, Hbzac and Hdbzm, $X^- = Cl^-$, HCl_2^-, $FeCl_4^-$, $SnCl_5^-$ and picrate. The complexes were characterized by UV and IR spectroscopy and the same products $[RSi(diket)_2]Cl$, were identified

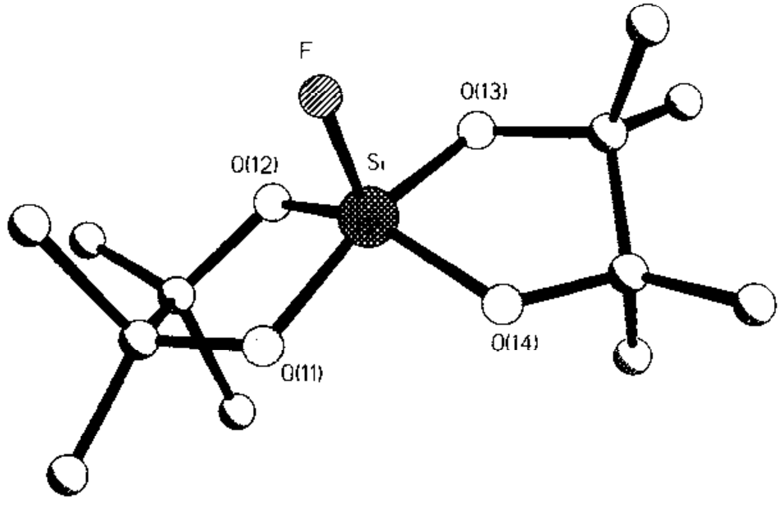


Fig. 9. The crystal structure of the bis(tetramethylethylenedioxy)fluorosilane anion.

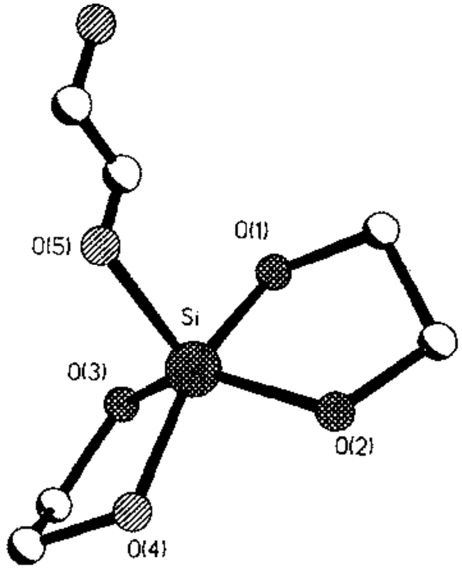
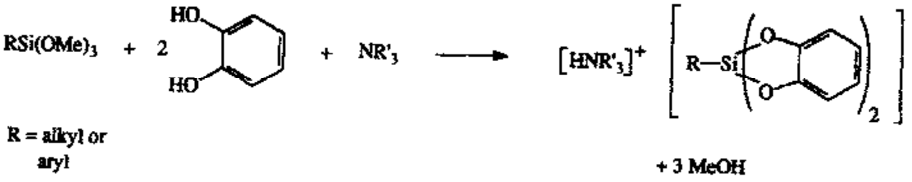


Fig. 10. The crystal structure of $K[Si(OCH_2CH_2O)_2OCH_2CH_2OH]$.

using either $RSiCl_3$ or $RSiFCl_2$. The stronger Si–F bond was split, thus suggesting that the Cl^- was a true counterion as opposed to a coordinated chlorine atom forming the six-coordinate $RSi(diket)_2Cl$ analogue.

The formation of five-coordinate bis(catecholato)arylsiliconates was first reported by Frye [52] (eqn. (6)).



(6)

The X-ray structure of the bis(catecholato)phenylsiliconate anion was later reported by Boer et al. [53], who confirmed the proposed distorted TBP configuration. In contrast, the corresponding bis(catecholato)fluorosiliconate anion was found to possess a distorted SP geometry [23]. Holmes and co-workers [22–30] have largely concentrated on a series of five-coordinate bis(bidentate ligand) anionic silicon complexes in the solid state with reference to the isoelectronic phosphoranes [54–57]. As a result, the influence of both the steric and the electronic effects on the geometry preference surrounding the silicon centre have been elucidated.

The degrees of distortion from the TBP to the SP geometry were calculated quantitatively by the dihedral angle method [54] (Table 1). The Berry pseudorotation mechanism for intramolecular rearrangement in five-coordinate complexes was first postulated

TABLE 1

Degree of trigonal bipyramidal-square pyramidal distortion of various solid five-coordinate silicon complexes determined by the dihedral angle method [54]

	Anion	Cation	% TBP-SP	Ref.
8	^{t}BuOSi(pin)$_2$	[K,18-c-6]	24.1	29
9	PhSi(dbcat)$_2$	NEt$_3$H	29.0	26
10	^{i}PrOSi(pin)$_2$	[K,18-c-6]	29.4	28
11	PhSi(cat)$_2$	NMe$_4$	29.5	53
12	1-NpSi(cat)$_2$	NEt$_4$	30.8	27
13	PhSi(1,8-naph)$_2$	[K,18-c-6]	32.5	30
14	2,5-C$_6$H$_3$Cl$_2$Si(cat)$_2$	C$_5$H$_5$NH	33.2	25
15	EtOSi(pin)$_2$	^{n}BuNH3	38.9	29
16	Neutral complex:	Ph$_3$POSi(cat)$_2$	46.6	58
17	MeSi(gly)$_2$	[NH$_3$(CH$_2$)$_6$NH$_3$]$_{0.5}$	53.3	48
18	1-NpSi(cat)$_2$	C$_5$H$_5$NH	58.7	25
19	PhSi(cat)$_2$	NEt$_3$H	59.4	26
20	^{n}BuSi(cat)$_2$	NEt$_4$	63.8	27
21	FSi(cat)$_2$	NEt$_4$	52.8, 68.7	23
22	FSi(pin)$_2$	NMe$_4$	52.3, 69.1	49
23	MeOSi(pin)$_2$	^{n}BuNH$_3$	71.2	29
24	PhSi(gly)$_2$	[NH$_3$(CH$_2$)$_6$NH$_3$]$_{0.5}$	72.1	24
25	^{n}BuSi(2,3-naph)$_2$	NEt$_4$	80.3	26
26	PhSi(tccat)$_2$	NEt$_4$	89.8	24
27	C$_6$H$_{11}$Si(cat)$_2$	Me$_2$NH$_2$	76.7, 90.1	28
28	^{t}BuSi(cat)$_2$	NEt$_4$	91.4	27
29	PhSi(2,3-naph)$_2$	C$_5$H$_5$NH	97.6	25

pin = pinacolate, dbcat = 3,5-di-tert-butylcatecholate, 1-Np = naphthyl, 1,8-naph = 1,8-naphthalenedioxylate, gly = glycolate, 2,3-naph = 2,3-naphthalenedioxylate, tccat = tetrachlorocatecholate and 18-c-6 = 18-crown-6.

in 1960 [59] (Fig. 11). The solid state studies (Table 1) show a series of complexes which span from the TBP to the SP configuration with distortions along the Berry pseudorotation pathway. The electronic effects of the substituents play a major role in the TBP–SP distortion. Electronegative substituents such as the fluoride in **21** [23] and **22** [49] and tetrachlorocatechol in **26** [24] showed larger distortions towards the SP. Compared to the TBP, the SP geometry has a higher degree of ligand–ligand interaction (d$_\pi$–d$_\pi$ interactions). Therefore, highly electronegative ligands reduce electron pair repulsions from atoms directly attached to silicon and thus increase the SP contribution. The increasing electronegativity of 1-Np to ^{n}Bu to ^{t}Bu in parallel with increasing TBP–SP distortion in **12**, **20** and **28**, respectively, also confirmed the influence of electronegativity by the unidentate donor [27]. Recently, Evans et al. [37] reported the 3,5-dinitrocatecholato complex (Fig. 12) which showed the more electronegative oxygen atom in the chelate (i.e. the oxygen adjacent to the 3-nitro substituent) crystallized in the axial position of a distorted

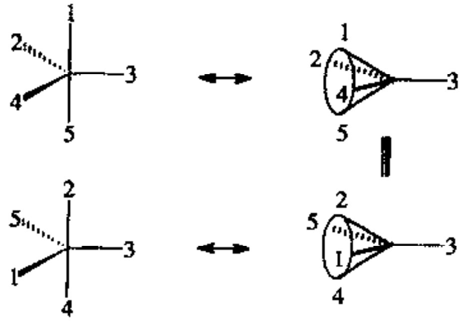


Fig. 11. The Berry pseudorotation mechanism.

TBP structure. This again suggests that the electronegativity of substituents reduce the electron-pair repulsions and thus the preferred isomer was observed.

The steric interactions of bulky substituents do not appear to directly influence the degree of TBP–SP distortion. However, the intermolecular interactions, especially hydrogen bonding, which do affect the degree of TBP–SP distortion, have been correlated with steric crowding [26]. Hydrogen bonding occurs between the oxygens around the central silicon and counterions such as $[NEt_3H]^+$. The increased N–H···O–Si interaction causes reduced electron density around the oxygen and in turn causes reduced electron pair repulsions and hence increased TBP–SP distortion. Direct comparisons have been made between **9** and **19** where the 3,5-di-t-butyl substituted derivative **9** showed less distortion than the unsubstituted derivative **19**, probably as the result of steric hindrance. Furthermore, a comparison of two complexes which differ only in the counterion, **11** [53] and **19** [26] showed that the non-hydrogen bonded $[NMe_4]^+$ cation in **11** has a much less distorted structure than the hydrogen bonded $[NEt_3H]^+$ cation in **19**.

Further evidence of hydrogen bonding effects were obtained from X-ray analysis of bis(pinacolate)alkoxysiliconate derivatives, **8**, **15** and **23** [29]. Unsaturated chelates, in contrast to the saturated analogues, aid TBP–SP distortion because they offer greater electron delocalization and thus reduce electron pair repulsion [25]. Saturated ligands such as pinacol do not normally show any significant SP distortion, e.g. **8**, a $[K, 18\text{-c-}6]^+$ salt. However, introduction of hydrogen bonding, e.g. **15** and **23** with butylammonium counterions showed considerable TBP–SP distortions. Complexes with the $[K, 18\text{-c-}6]^+$ cation were successfully prepared by two methods (eqns. (7) and (8)).

$$[K, 18\text{-c-}6][Si(OR)_5] + 2H_2pin \rightarrow [K, 18\text{-c-}6][ROSi(pin)_2] + 4ROH \tag{7}$$

$$Si(pin)_2 + KOR + 18\text{-c-}6 \rightarrow [K, 18\text{-c-}6][ROSi(pin)_2], \quad R = OEt, O\text{-}^iPr \tag{8}$$

Recently, Hey-Hawkins et al. [58] reported the synthesis of two neutral five-coordinate silicon complexes, $Si(cat)_2(OPPh_3)$ (**16**) and $Si(cat)_2\{OP(NC_5H_{10})_3.CH_2Cl_2$ (**30**). Compound **16** showed 46.6% TBP–SP distortion, whereas **30** showed near perfect SP ge-

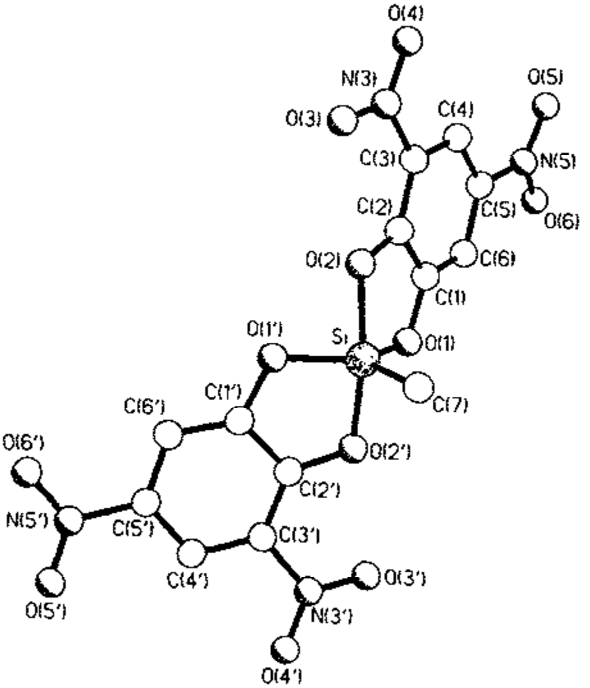
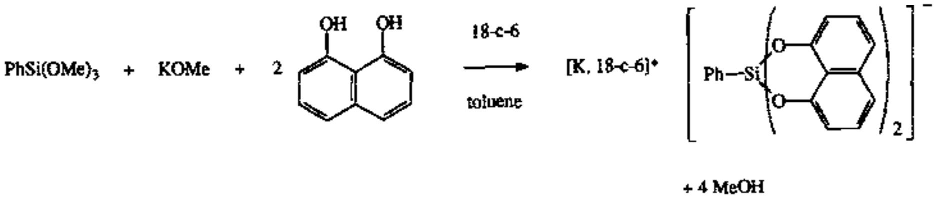


Fig. 12. The crystal structure of the $[MeSi(3,5\text{-dncat})_2]^-$ anion.

ometry. The SP geometry of **30** has again been attributed to weak hydrogen bonding, in this case, caused by interaction of hydrogen atoms in the solvent with the oxygen donor atoms.

The synthesis of the first five-coordinated silicon complex with O_2 donor sets forming a six-membered chelate ring was recently reported [30] (eqn. (9)).



(9)

The X-ray crystal structure revealed a distorted TBP structure not atypical of five-membered chelate ring analogues. Similar five-coordinate complexes using 2,2'-dihydroxybiphenyl ligands which possess O_2 donors and complex to give seven-membered chelate rings were also described. Decomposition of these latter complexes has thus far prevented solid state analysis. $[(CH_2)_4SiF(cat)]^-$ (**31**) and $[(CH_2)_5SiF(cat)]^-$ (**32**) (Fig. 13) [60] have been successfully synthesized and the X-ray crystal structures determined. Despite the

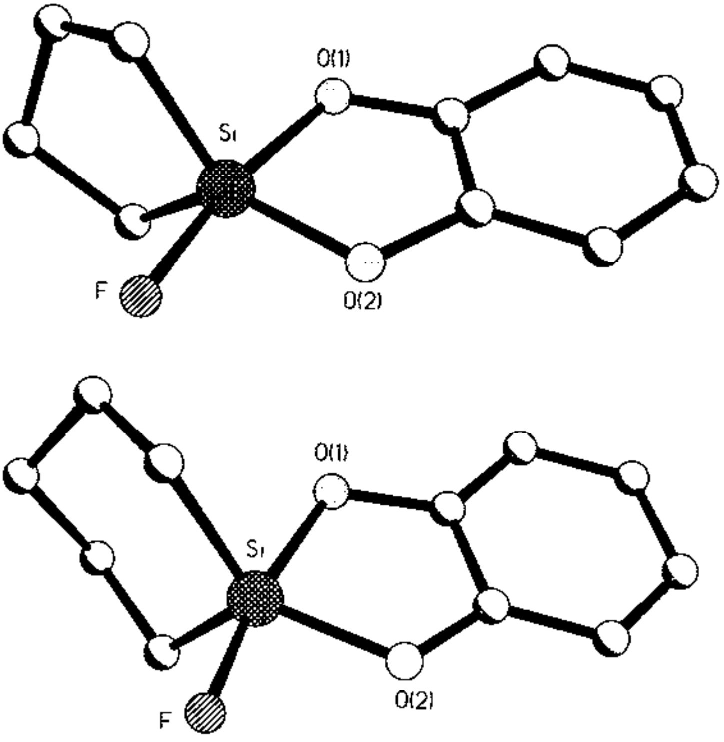


Fig. 13. The crystal structure of the $[(CH_2)_4SiF(cat)]^-$ and the $[(CH_2)_5SiF(cat)]^-$ anions.

similarity between **31** and **32**, distortions from the TBP geometry were found to be different; **32** was distorted along the Berry pseudorotation pathway but **31** was distorted along the "anti" Berry pseudorotation pathway.

Corriu and co-workers continue to examine the reactivity of five-coordinate anionic silicon complexes towards nucleophiles. The reactivity of $Na[RSi(cat)_2]$, where R = Me, Ph, 1-Np with various hydrides, Grignards and organolithiates, has been investigated [61]. It was concluded that these five-coordinate species were more reactive than the four-coordinate analogue, e.g. $Si(cat)_2$.

(iii) Six-coordinate complexes

Silicon acetylacetonates were first reported by Dilthey and Rosenheim et al. [62] who prepared a number of $[Si(acac)_3]^+$ (**33**) derivatives, formed by treating silicon tetrachloride with acetylacetone. Subsequent work on silicon 1,3-diketonates up to about 1967 has been reviewed by Pike [63]. The six-coordinate tris(bidentate ligand) nature of silicon was confirmed by IR [64] and NMR spectroscopy [65]. The hydrolysis and racemization process of the **33** cation was first described by Dhar et al. [66] using optical absorption and polarimetry) respectively. Larsen et al. [67] assigned the absolute configuration of the optically active isomer, (–)-[Si(acac)$_3$]$^+$ to Λ, on the basis of the CD spectrometric data. Subsequently, Inoue and Saito [68] reported a kinetic study of the racemization process in 33. They proposed that the racemization process proceeded via an intramolecular mechanism through a five-coordinate bis(bidentate ligand)(unidentate ligand)silicon intermediate. Recently, Shimizutani and Yoshikawa [69] reported the stereoselectivity and CD spectra of tris(diket)silicon complexes, where diket = (+)-(hydroxymethylene)-camphor and (+)-acetylcamphor. The absolute configuration of both complexes were Λ, in agreement with the assignment made by Larsen et al. The mechanism for the hydrolysis of silicon acetylacetonates to regenerate acetylacetone and silica has been investigated: Pearson et al. [70] proposed S_N2 type mechanisms based on kinetic studies, however, Muetterties and Wright [71] used ^{18}O isotopic labelling to establish that initial attack was at the ligand and not at the silicon centre.

The synthesis and characterization of $R_2Si(acac)_2$ type complexes, where R = alkyl, aryl, ester, chlorine or mixed, have been reported by a number of independent workers [64,72–76]. In most cases, the neutral, non-ionic, six-coordination of silicon was proposed based on IR spectroscopy. IR studies also indicates an equilibrium reaction which occurs in solution (eqn. (10)).

$$3Si(acac)_2Cl_2 \rightleftharpoons 2[Si(acac)_3]Cl + SiCl_4 \qquad (10)$$

NMR spectroscopy revealed the preferred configuration of various $R_2Si(acac)_2$ type complexes (Table 2).

In 1920, Rosenheim and Sorge [77] prepared the tris(catecholato)silicon dianion **34** from silicon tetrachloride and catechol in the presence of a base. The X-ray structure of the pyridinium derivative of **34** was determined in 1969 by Flynn and Boer [78]. The structure showed that the six oxygen atoms were placed at the vertices of a nearly regular octahedron centred on silicon (Fig. 14). In 1931, Rosenheim et al. [79] synthesized **34** by heating freshly prepared silicic acid, $Si(OH)_4$, with aqueous alkaline solutions of catechol. Since then, there have been a number of investigations to obtain the formation constants

TABLE 2

Configuration of various $R_2Si(acac)_2$ complexes

$R_2Si(acac)_2$ R_2	Configuration	Ref.
Cl_2	*trans*	74
Cl_2	*trans*	76
$(CH_3CO_2)_2$	*trans* (solid)	
	cis-trans (solution)	73
$(CH_3CO_2)_2$	*cis-trans* mixture	76
Ph, Cl	*cis*	75
Me, Cl	*cis*	75

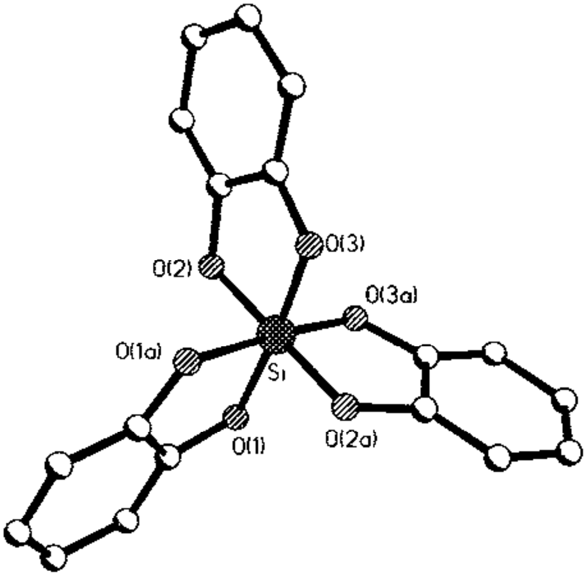


Fig. 14. The crystal structure of the $[Si(cat)_3]^{2-}$ dianion.

of tris(catecholato)silicon complexes [34,80–82]. From the equilibrium, eqn. (11), the formation constants were calculated based on known concentrations of reactants (Table 3).

$$Si(OH)_4 + 3H_2L \rightleftharpoons [SiL_3]^{2-} + 4H_2O + 2H^+, \quad K \tag{11}$$

Bartels [80] carried out base titrations taking the concentration of silicic acid as being the total amount added and equivalent to 6.67×10^{-3} mol dm^{-3}. Later studies [34,82] have shown that the saturation solubility of silicic acid is ca. 2×10^{-3} mol dm^{-3}, depending on various factors. Öhman et al. [82] based the equilibrium data on potentiometric and solubility measurements with equilibrium obtained after at least 3 weeks continuous stir-

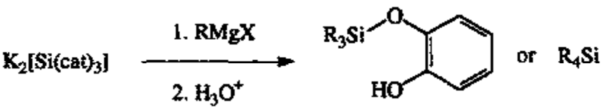
TABLE 3

Equilibrium data for various $[SiL_3]^{2-}$ type complexes (K values are defined by eqn. (11))

Ligand	K	Ref.
Catechol	$10^{-10.44}$	82
Catechol	1.3×10^{-11}	80
Catechol	4.8×10^{-12}	81
Catechol	3.8×10^{-13}	34
4,5-Dichlorocatechol	3.2×10^{-9}	34
4-Nitrocatechol	1.8×10^{-8}	34
3,4-Dinitrocatechol	5.4×10^{-5}	34

ring. Evans et al. [34] used ^1H and ^{29}Si NMR spectroscopy intensity measurements to calculate the K values with equilibrations obtained after at least 8 continuous shaking in sealed ampoules. Electronegative substituents on the catechol reduce the pK_1 of the ligand and consequently increase the value of K. VT NMR spectroscopic studies indicated that intermolecular exchange was slow and isomerism probably proceeded through a Si–O bond rupture to form a five-coordinate silicon intermediate.

Corriu and co-workers [83,84] have developed a general route for the preparation of organosilanes from silica via the **34** complex. The reaction of **34** with an excess of Grignard or organolithium reagent leads to the formation of R_4Si or $R_3Si(Hcat)$ (eqn. (12)).



(12)

Compound **34** also reacted with reducing reagents such as $LiAlH_4$ under very mild conditions to give SiH_4 quantitatively (eq. (13)).

$$Na_2[Si(cat)_3] + LiAlH_4 \xrightarrow[RT]{Et_2O \text{ or } n\text{-}Bu_2O} SiH_4 \qquad (13)$$

These general reactions have been used to synthesize a whole range of organosilanes and hydrides and provide an alternative route to these compounds normally made from elemental silicon under much more demanding conditions.

Muetterties and Wright [85] reported the synthesis of tris(tropolonato)silicon chloride by the reaction of silicon tetrachloride with tropolone in chloroform (eqn. (14)).

$$SiCl_4 + 3HL \rightleftharpoons [SiL_3]Cl + 3HCl \qquad (14)$$

Subsequently, Muetterties and Alegranti [86] examined the intermolecular exchange reaction between 2- and 3-methyltropolone and their tris(tropolonato)silicon complexes by ^1H NMR spectroscopy and did not find any exchange at 146°C. This reflects the stability and slow intermolecular reactions of these complexes. Ito et al. [87] determined the absolute configuration of the $[Si(trop)_3]^+$ cation and, on the basis of CD measurements, the cation was assigned as $(+)D\text{-}[Si(trop)_3]^+$. Kinetic studies on the racemization process were carried out by Inoue [88]. He proposed that the acid-catalyzed mechanism proceeded via bond rupture to give a five-coordinate silicon intermediate analogous to the species derived from the tris(acac)silicon complex.

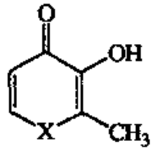
The formation constant of tris(tropolonato)silicon has been determined by Sjöberg et al. [38] and Evans et al. [36] and were found to be: $K = (1.2 \pm 0.1) \times 10^7$ and $K = 1.6 \times 10^7$, respectively, where K is the formation constant of the tris-complex according to eqn. (15).

$$\mathrm{Si(OH)_4} + 3\mathrm{HL} + \mathrm{H^+} \rightleftharpoons [\mathrm{SiL_3}]^+ + 4\mathrm{H_2O}, \quad K \tag{15}$$

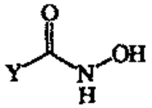
Sjöberg et al. determined the K values from potentiometric (glass electrode) and ^{29}Si NMR spectroscopy (using ^{29}Si enriched SiO_2). Evans et al. determined the K values using an analogous method to the catecholato complexes as described previously [34]. Evans et al. also indicated that the stability of complex was enhanced by electron pushing substituents on the tropolone (e.g. 4-methyltropolonato complex has $K = 9.2 \times 10^7$) which again reflects the pK dependence of these equilibrium values.

The tris(oxalato)silicon dianion was first characterized by Dean et al. [89] using IR and Raman spectroscopy. Assignments were made based on a D_3 symmetry for the dianion. Subsequently, Schott and Lange [90] characterized the complex using IR, conductivity and thermal decomposition measurements.

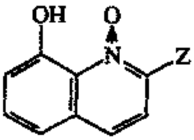
The synthesis of new six-coordinate tris(bidentate ligand) complexes have been reported by Evans and Wong [35]. The complexes were derived from various bidentate O_2 donor ligands which were monobasic and contained delocalized ring(s). Two routes of synthesis were described, the normal method using silicon tetrachloride (eqn. (14)) and a new and more preferable route using silicon tetraethoxide and ligand in the presence of a strong acid (eqn. (16)).



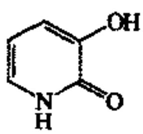
X = O, HL = maltol;
X = NH, HL = 3-hydroxypyridin-4-one;
X = NMe, HL = 3-hydroxy-1,2-dimethylpyridin-4-one;
X = NEt, HL = 1-ethyl-3-hydroxy-2-methylpyridin-4-one.



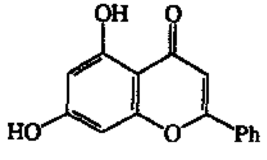
Y = Me, HL = acetohydroxamic acid;
Y = Ph, HL = benzohydroxamic acid.



Z = H, HL = 8-hydroxyquinoline-N-oxide;
Z = Me, HL = 8-hydroxyquinadine-N-oxide.



3-Hydroxypyridin-2-one



Chrysin

Fig. 15. Examples of monobasic bidentate ligands of silicon.

$$\mathrm{Si(OEt)_4 + 3HL + HX \rightarrow [SiL_3]X + 4EtOH} \tag{16}$$

where X = $\mathrm{CF_3SO_3^-}$, $\mathrm{HSO_4^-}$, $\mathrm{CF_3CO_2^-}$, $\mathrm{Cl^-}$ or the 10-camphor-sulphonate anion. The ligands used were: maltol, 3-hydroxypyridin-4-ones, 3-hydroxypyridin-2-one, hydroxamic acids, 8-hydroxyquinoline-*N*-oxides and chrysin (Fig. 15). The principal technique used for analysis was ^{1}H and ^{29}Si NMR spectroscopy. The 3-hydroxypyridin-4-ones were shown to resist hydrolysis and represented only the third group of ligands to do so after the catecholates and the tropolonates. All other complexes described were completely hydrolyzed in aqueous solution. Consequently, Evans et al. [36] reported the equilibria between silica and the 3-hydroxypyridin-4-ones. Water stable, cationic complexes of silicic acid with 2hydroxypyridine-*N*-oxide (Fig. 16) have been reported in 1964 [91]. Attempts have been made to synthesize the tris-complex in aqueous solution but so far these have failed [92].

By collating the equilibrium data for the formation of tris(bidentate ligand)silicon complexes (Tables 3 and 4), the stability of both the monobasic and dibasic chelates may be compared. Thus,

$$\frac{[\mathrm{SiL_3}^+]}{([\mathrm{HL}]_{\mathrm{tot}})^3} = \frac{K' K_1^3 [\mathrm{H}^+]}{([\mathrm{H}^+] + K_1)^3} \tag{17}$$

and

$$\frac{[\mathrm{SiL_3}^{2-}]}{([\mathrm{H_2L}]_{\mathrm{tot}})^3} = \frac{K' [\mathrm{H}^+]}{([\mathrm{H}^+] + K_1)^3} \tag{18}$$

represent the equilibrium reactions derived from eqns. (15) and (11), respectively, where K_1 = ionization constant of ligand and $K' = [\mathrm{Si(OH)_4}]K$ = ca. $(2 \times 10^{-3})K$ [34,36]. The left-hand side of eqns. (17) and (18) are a measure of the extent of formation of the tris-complex and will have a maximum (determined by differentiation of eqns. (17) and (18)) when

$$\mathrm{pH_{opt}} = \mathrm{p}K_1 + 0.301 \tag{19}$$

By substituting (i) optimum pH for formation and (ii) pH = 7.4 (physiological pH), the values of the extent of formation for various chelates may be compared (Table 5). A number of conclusions may be drawn from the results. The extent of formation at the op-

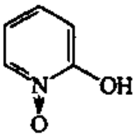


Fig. 16. 2-Hydroxypyridine-*N*-oxide.

TABLE 4

Equilibrium data for various $[SiL_3]^+$ type complexes (K values are defined by eqn. (15))

Ligand	K	Ref.
Tropolone	1.2×10^7	38
Tropolone	1.6×10^7	36
4-Methyltropolone	9.2×10^7	36
1-Ethyl-3-hydroxy-2-methylpyridin-4-one	3.1×10^8	36
3-Hydroxy-1,2-dimethylpyridin-4-one	1.2×10^9	36
3-Hydroxy-2-methylpyridin-4-one	1.3×10^9	36

timum pH for any particular ligand does not reflect the stability of complexation, K. As the pK_1 of ligand approaches 7.4, the difference in value for the extent of formation at optimum pH and pH = 7.4 narrows as expected (eqn. (19)). The most stable catecholato complex, the 3,4-dinitrocatecholato derivative, is not the most abundant system at pH = 7.4. Finally, the extent of formation may be used to reflect the comparable strength of complexation by catechols and 3-hydroxypyridin-4-ones, which cannot otherwise be easily concluded from K values alone. Thus, we can conclude that the "strength" of tris(bidentate ligand)silicon(IV) complexes at physiological pH for bidentate chelates decreases in the order

catechols > 3-hydroxypyridin-4-ones > tropolones

Glass is etched commercially by treatment with 1,2-diaminoethane and catechol in water, thus forming the tris(catecholato)silicon species [93]. However, in acidic media, hydrofluoric acid is the only species that etches glass at a significant rate. Previous investigations by Iler [10] have shown that catecholate compounds are unique in forming

TABLE 5

"Extent of formation", Σ for various $[SiL_3]^+$ and $[SiL_3]^{2-}$ type complexes (Σ is defined by the left-hand side of eqns. (17) and (18))

Ligand system[a]	Σ, (pH_{opt})	Σ(pH 7.4)
4,5-Dichlorocatechol	10^3	10^3
4-Nitrocatechol	10^2	10^2
Catechol	10^2	10^{-1}
3,4-Dinitrocatechol	10^1	10^{-1}
1-Ethyl-3-hydroxy-2-methylpyridin-4-one	10^2	10^{-1}
3-Hydroxy-1,2-dimethylpyridin-4-one	10^1	10^{-1}
3-Hydroxy-2-methylpyridin-4-one	10^2	10^{-1}
4-Methyltropolone	10^4	10^{-2}
Tropolone	10^4	10^{-3}

[a] Catechol derivatives, ref. 34; other derivatives, ref. 36.

complex ions with silicon that are not hydrolyzed in aqueous solution, but are destroyed by atmospheric oxygen forming dark insoluble residues, presumably due to formation of semiquinones and benzoquinones. Evans et al. [36] reported the rate of etching of glass by 1-ethyl-3-hydroxy-2-methylpyridin-4-one in dilute hydrochloric acid solution. Results indicated that these type of ligands may be as efficient an etcher as catechol under certain conditions and have the advantage of being stable in air.

^{29}Si NMR spectroscopy has been used to characterize five- and six-coordinate silicon complexes [31–38]. The reports of Williams and co-workers [31–33] indicated that five- and six-coordinate complexes may be characterized by the chemical shift (δ) range of the ^{29}Si nucleus. Further observations showed that in the six-coordinate complexes the δ between five- ($-130 > \delta > -150$ ppm) and six- ($-190 > \delta > -200$ ppm) membered chelate rings can also be identified. Evans and co-workers [34–37] confirmed Williams' reports and in some cases were able to further resolve the complexes into the various geometrical isomers. In six-coordinate complexes and for asymmetric bidentate chelates there is the possibility of facial *(fac)* and meridional *(mer)* isomers, each of which is enantiomeric [34,36]. With the tris(3-hydroxy-1,2-dimethylpyridin-4-onato)silicon cation, interconversion *of fac* and *mer* isomers was comparatively slow and partial separation by crystallization was achieved (Fig. 17). Kinetic studies by ^{1}H NMR spectroscopy in DMSO showed that the complex interconverted at a much faster rate ($fac \rightleftharpoons mer$, $k_1 = 2.1 \times 10^{-5}$ s^{-1}, $t_{1/2} = 9.2$ h and $k_2 = 7.0 \times 10^{-6}$ s^{-1}, $t_{1/2} = 27.5$ h) than 8-hydroxyquinaldine-*N*-oxide analogue ($k_1 = 1.1 \times 10^{-6}$ s^{-1}, $t_{1/2} = 184$ h and $k_2 = 9.5 \times 10^{-7}$ s^{-1}, $t_{1/2} = 202$ h), possibly reflecting the increase in steric bulk of the ligand. Two ^{29}Si

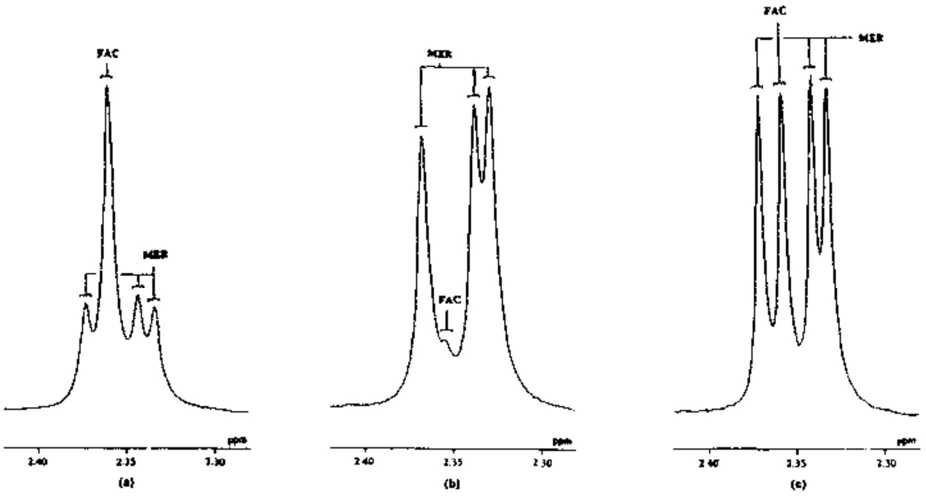


Fig. 17. ^{1}H NMR of 2-Me resonances in [Si(dmp)$_3$]Cl (270 MHz, DMSO-d_6): (a) recrystallized from chloroform 5 min after dissolution; (b) recrystallized from ethanol/ether 5 min after dissolution; (c) solution (a) after 2 days at room temperature.

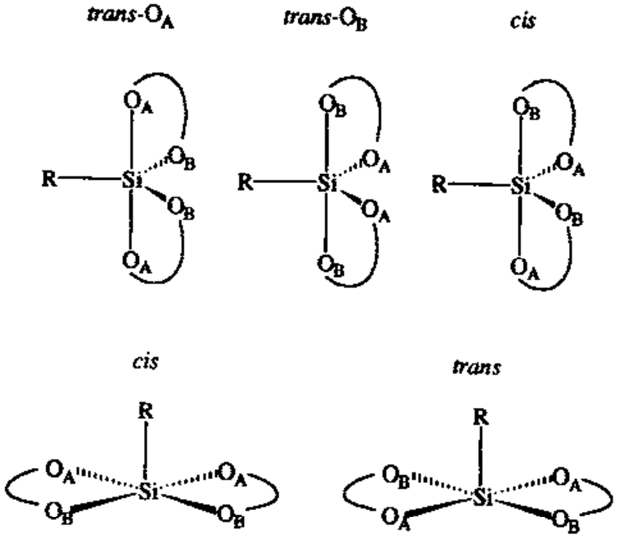


Fig. 18. Idealized geometrical isomers of five-coordinate bis(bidentate ligand)–silicon(IV) complexes.

resonances were observed for some complexes ($\Delta\delta < 0.5$ ppm) which was probably due to partial resolution of *fac* and *mer* isomers.

In the five-coordinate bis(asymmetric-catecholato)silicon complexes [37] it was shown that within either TBP or SP geometry, isomerism can occur (Fig. 18). Compared to the six-coordinate analogues, these five-coordinate species have a reduced symmetry (and a definite dipole moment), consequently the analogous isomers were better resolved. The ^{1}H, ^{13}C and ^{29}Si NMR spectra showed two sets of resonances in most cases and these have been attributed to isomerism within the distorted TBP or SP geometry. Resonances from two TBP isomers (*trans*-OA and *trans*-OB) were assumed coincident. The intensity ratio of the two resonances gave an indication of the degree of TBP–SP distortion.

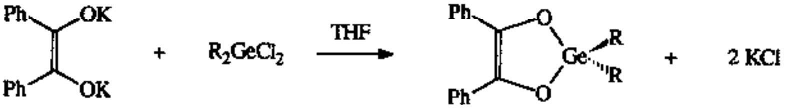
C. GERMANIUM

Germanium has no biological function, very little attention has been paid to its physiological, biochemical and toxicological interactions in living systems. Radioactive isotopes of germanium have been used, however, as a tracer or probe for investigating silicon metabolism [9]. The only commercial outlets for germanium are based on the semi-conductor properties of the metal, the use of GeO_2 in the production of optical glass of high refractive index and the addition of germanium or its compounds to lead-acid accumulators to reduce the cell resistance. The emergence of new chemical applications for germanium compounds will probably depend on the discovery of highly specific, possibly catalytic, processes; otherwise what can be done with germanium can almost certainly be achieved more cheaply with silicon or tin analogues [94]. Thus, much of the chemistry of germanium has been a comparison with the silicon or tin analogues.

(i) Low-coordinate complexes

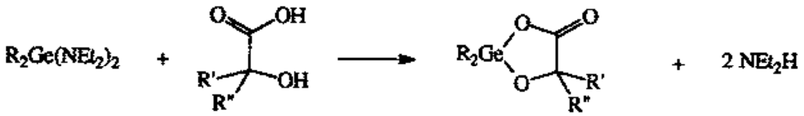
Despite the higher stability of the +2 oxidation state in germanium compared with silicon, there is no evidence for the existence of uncomplexed Ge^{2+} ions in solution. To our knowledge, the only three-coordinate germanium complex which utilizes a bidentate oxygen donor ligand is $Ge^{II}(acac)I$ reported in 1979 by Stobart et al. [95]. The complex is monomeric, three-coordinate about the germanium atom and approximates to a C_s symmetry molecule (Fig. 19).

Although four-coordinate germanium compounds are comparatively common, complexes with bidentate oxygen donors are less common. Complexes of the type R_2GeL and :GeL, where R = organic substituent or halogen and L = bidentate oxygen donor ligand, have been reported [96–99]. Lavayssiere and co-workers [96,97] described the synthesis of R_2GeL using germanium(IV) synthons (eqns. (20) and (21)).



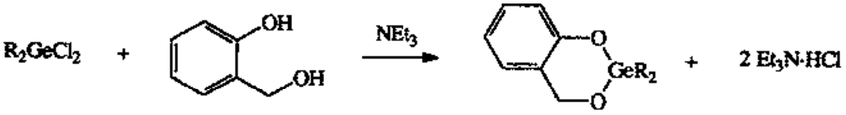
(20)

R = Ph: 45% ; R = Et: 25%



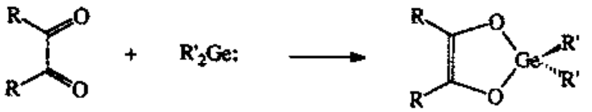
(21)

By a similar method, Cragg and Nazery [100] reacted various dichlorogermanes with *o*-hydroxybenzyl alcohol to form complexes as shown (eqn. (22)).



(22)

These complexes were subsequently analyzed in detail by mass spectrometry and compared with the silicon and boron analogues. The syntheses are in contrast to the normal method by oxidative cycloaddition of germylenes to 1,2-diketones (eqn. (23)).



(23)

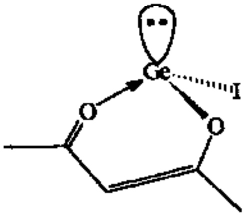


Fig. 19. Acetylacetonatogermanium(II) iodide.

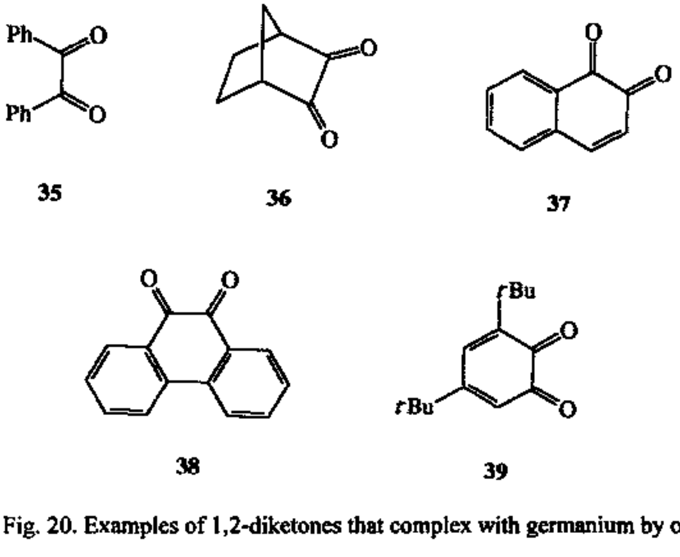
Michels and Neumann [98] synthesized Me_2GeL complexes using excess 1,2-diketones ranging from open-chained to alicyclic to orthoquinones (Fig. 20) in high or even quantitative yields. The reactivity increases in the sequence **35** < **37** ~ **38** < **39**.

Rivière et al. [99] reported the synthesis of various complexes using **39**. Reaction of **39** with $:GeF_2$ in THF produced the THF adduct, $F_2Ge(dbcat)$–THF, however the same reaction in benzene produced $Ge(dbcat)_2$, where H_2dbcat = 3,5-di-t-butylcatechol or reduced form of **39**. The reaction using $:GeCl_2$ in THF produced $Ge(dbcat)_2$-THF only, and :GePh(Cl) in benzene produced Ph(Cl)Ge(dbcat). The synthesis of $R_2Ge(dbcat)$ was also achieved using R_2GeCl_2 or $R_2Ge(OMe)_2$ with H_2dbcat (eqns. (24) and (25)).

$$R_2GeCl_2 + H_2dbcat + 2NMe_3 \rightarrow R_2Ge(dbcat) \qquad (24)$$

$$R_2Ge(OMe)_2 + H_2dbcat \rightarrow R_2Ge(dbcat) + 2MeOH \qquad (25)$$

Müller and Heinrich [101] reported the synthesis of various germanium alkoxides including, bis(2,2'-biphenylenedioxy)germane **40**. The syntheses were compared with the silicon analogues described above.

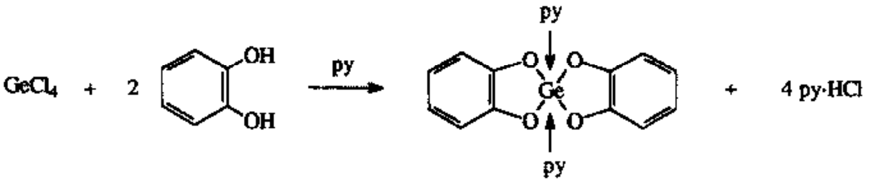


35 **36** **37**

38 **39**

Fig. 20. Examples of 1,2-diketones that complex with germanium by oxidative addition.

Yoder and Zuckerman [102] synthesized Ge(cat)$_2$·2py by direct reaction of GeCl$_4$ with catechol in pyridine (eqn. (26)).



(26)

In view of the problems encountered in elucidating the structure of Si(cat)$_2$ (see Section B(i)), it is not surprising that in all the reports described above there is no analysis of the geometry around germanium, in particular, in the bis(catecholato)germanium complex. The possibility of the polymeric species, [Ge(cat)$_2$]$_n$, also remains unsolved.

(ii) Five-coordinate complexes

Müller and Heinrich had suggested that titration of **40** with sodium methoxide gives rise to a five-coordinate germanium species (Fig. 21). The characterization of five-coordinate bis(catecholato)germanium complexes have been described by Holmes and coworkers [103–106] as part of the group's investigation into Group 14 complexes with reference to the isoelectronic phosphoranes [54–57]. The crystal structures of [XGe(cat)$_2$]$^-$, where X = F, Cl and Br; and [(HO)Ge(dbcat)$_2$]$^-$ have been determined (Table 6).

Compounds **41**, **42** and **43** were synthesized by reaction of bis(catecholato)-germanium dihydrate (see below) with the appropriate tetraethylammonium salt (eqn. (27)) [103].

$$Ge(cat)_2(H_2O)_2 \quad + \quad Et_4N^+X^- \quad \xrightarrow[25°C]{CH_3CN} \quad [NEt_4][XGe(cat)_2] \quad + \quad 2\,H_2O \qquad (27)$$

Alternatively, the direct reaction of GeCl$_4$ and 2 equiv. of H$_2$dbcat in the presence of a base also yielded a five-coordinate germanium product (eqn. (28)) [104].

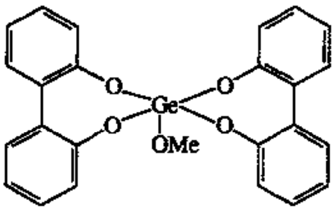


Fig. 21. Bis(2,2'-diphenylenedioxy)methoxygermane.

TABLE 6

Degree of trigonal bipyramidal-square pyramidal distortion of various solid five-coordinate germanium complexes determined by the dihedral angle method [54]

	Anion	Cation	% TBP–SP	Ref.
41	$\mathrm{BrGe(cat)_2}$	$\mathrm{NEt_4}$	70.4	106
42	$\mathrm{FGe(cat)_2}$	$\mathrm{NEt_4}$	80.6	105
43	$\mathrm{ClGe(cat)_2}$	$\mathrm{NEt_4}$	90.7	103
44	$\mathrm{(HO)Ge(cat)_2}$	$\mathrm{NEt_3H}$	95.7	106

$$\mathrm{GeCl_4} + 2\,\mathrm{H_2dbcat} + 4\,\mathrm{NEt_3} \xrightarrow[\mathrm{H_2}]{\mathrm{Cu}} [\mathrm{NEt_3H}][\mathrm{ClGe(dbcat)_2}] + 3\,\mathrm{Et_3NH^+Cl^-} \qquad (28)$$

However, recrystallization of the product in a 1:1 mixture of water and acetonitrile yielded **44**. The hydrolytic stability of $[\mathrm{XGe(cat)_2}]^-$ anions decreases in the order $\mathrm{F} > \mathrm{Cl} > \mathrm{Br}$ [106]. The pronounced TBP–SP distortion in the germanium complexes compared with the silicon analogues is in accord with the reduced electronegativity going down the Group 14 series. Increased SP stabilization may also be implicated by increasing stereochemical non-rigidity on increasing ionic radii from silicon to germanium.

(iii) Six-coordinate complexes

The structures of the complexes of the type $\mathrm{Ge(cat)_2S_2}$, where S = solvent molecule, is debatable. Formation of bis(catecholato)germanium(IV) and related orthodiphenolic chelates were reported by Bévillard [107] and the empirical formulation, $\mathrm{GeL_2 \cdot 2H_2O}$, was based on microanalytical data. For S = pyridine, Yoder and Zuckerman [102] have indicated direct coordination of pyridine molecules to form a six-coordinate germanium(IV) complex. Kumevich and Vishnevskii [108] also concluded, based on IR data, that $\mathrm{Ge(cat)_2(H_2O)_2}$ was six-coordinate with a *trans* configuration. From hydrogen bonding observations of **44**, Sau and Holmes [104] proposed a polymeric structure based on six-coordinate germanium but with only one solvent molecule directly coordinated to germanium (Fig. 22). Other six-coordinated complexes based on two solvent molecule donors include: S = DMF, DMSO [109] and HMPA [104]. The $\mathrm{Ge(cat)_2(NEt_3)_2}$ adduct proposed by Yoder and Zuckerman [102] has been challenged by Sau and Holmes [104] and they reformulated the compound isolated as $[\mathrm{NEt_3H}]_2[\mathrm{Ge(cat)_3}]$.

Six-coordinate bis(1,3-diketonato)dihalogenogermanium complexes was first reported in 1924 by Morgan and Drew [110] by reaction of germanium tetrachloride or bromide with excess acetylacetone in dry chloroform. The reaction with germanium tetrabromide was found to proceed much more slowly and often with a low yield on account of the higher stability of $\mathrm{H_2GeBr_6}$. The monomeric nature of these complexes was adopted by molecular weight determinations using ebullioscopic and cryoscopic methods

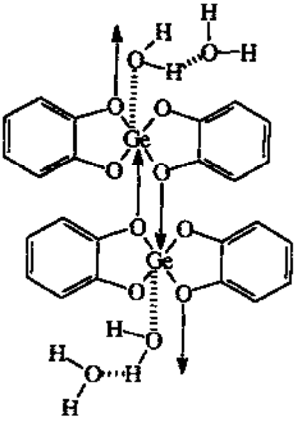
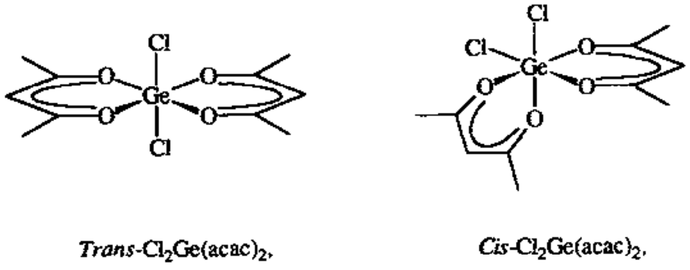


Fig. 22. Proposed polymeric structure of $Ge(cat)_2(H_2O)_2$.

on the more soluble derivative, bis(propionylacetonato)germanium dichloride. Cox et al. [111] used conductivity experiments to confirm the non-electrolytic and hence the formula $Ge(acac)_2Cl_2$ (**45**) for the 2:1 acetylacetone–germanium complex.

Extensive ^1H NMR spectroscopy carried out by Smith and Wilkins [112] gave strong evidence that these bis-chelates possess a *cis* configuration. This was deduced by analysis of ^1H NMR of **45** and $Ge(bzac)_2Cl_2$ (**46**). The former complex has symmetric bidentate chelates, while the latter complex has asymmetric bidentate chelates. For **45**, the *trans* isomer should have D_{2h} symmetry and only one ring methyl resonance, but the *cis* isomer should have C_2 symmetry and two different ring methyl resonances corresponding to methyl groups *trans* to either a chloride or another acac (Fig. 23). For **46**, the *trans*-halogen isomers will have the possibility of *cis* or *trans* $bzac^-$, hence two resonances are expected. The *cis*-halogen isomers will have three possibilities corresponding to *trans*-methyl, *trans*-phenyl or the *cis-cis-cis* configuration (Fig. 24). The spectra observed

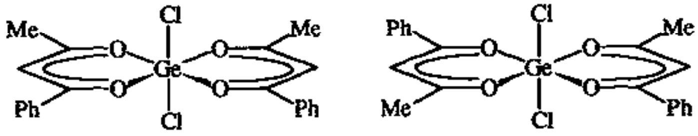


Trans-$Cl_2Ge(acac)_2$, single CH_3 resonance in ^1H NMR spectrum.

Cis-$Cl_2Ge(acac)_2$, CH_3 resonances *cis* and *trans* to Cl are different.

Fig. 23. *Cis* and *trans* isomers of $Cl_2Ge(acac)_2$ and their respective number of methyl resonances expected in the ^1H NMR spectra.

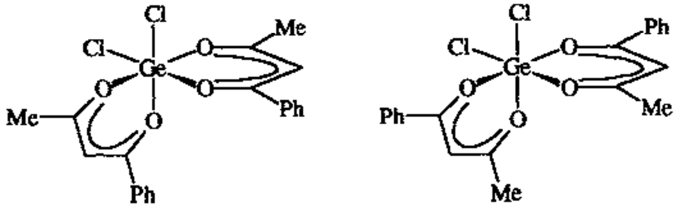
TRANS-HALOGEN



Cis-Me, one Me resonance

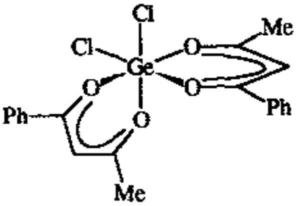
Trans-Me, one Me resonance

CIS-HALOGEN



Trans-Me, one Me resonance

Trans-Ph, one Me resonance



Cis-cis-cis, two Me resonances

Fig. 24. *Cis* and *trans* isomers of $Cl_2Ge(bzac)_2$ and their respective number of methyl resonances expected in the ^1H NMR spectra.

showed two methyl resonances in **45** and four in **46**, consistent with *cis* configuration for these complexes.

Subsequently, Pinnavalia et al. [113] and Haworth et al. [76] used ^1H and ^{13}C NMR spectroscopy, respectively, to show a mixture of the *cis* and *trans* isomers for $Ge(diket)_2X_2$ type complexes. Serpone and Hersh [75] reported a mainly *cis* configuration for $PhClGe(acac)_2$ with ≤5% of the *trans* isomer based on ^1H NMR studies. The preferred configuration of $Ph_2Ge(acac)_2$ was not unequivocally assigned. A number of $Ge(acac)_2R_2$ complexes have been synthesized by direct reaction of Hacac with R_2GeO in benzene and the water is removed azeotropically (eqn. (29)) [114].

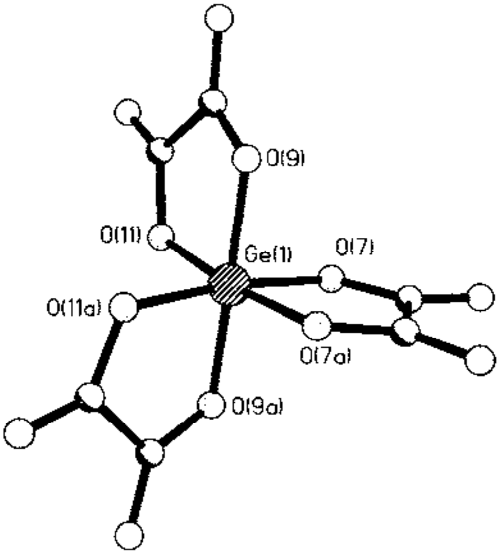


Fig. 25. The crystal structure of the tris(oxalato)germanium(IV) dianion.

$$R_2GeO + 2Hacac \rightarrow R_2Ge(acac)_2 + H_2O, \quad R = Bu \text{ or } Ph \tag{29}$$

$[NBu_4][Ph_2Ge(ox)_2]$ and $[NBu_4][Cl_2Ge(ox)_2]$, where H_2ox = oxalic acid, have been characterized by IR, conductivity and thermal decomposition studies and compared with results with the analogous silicon complexes [90]. In the same paper, the synthesis of the tris-oxalate anions were reported, $[Ge(ox)_3]^{2-}$, and the IR spectral assignments compared with the previous studies [89]. Later, Jorgensen and Weakley [115] reported the crystal structure of $K_2[Ge(ox)_3] \cdot H_2O$ (Fig. 25). The structure has a distorted octahedral geometry with three chelating oxalate ligands around a germanium atom and two independent anions are present in the lattice. The potassium ions are in irregular eight-coordination to oxygen atoms of the oxalate ligands and of the water molecule. As well as **45**, Morgan and Drew [110] were also the first to report the synthesis of the tris(acetylacetonato)germanium(IV) cation **47**. The tetrachloroferrate salt of **47** was prepared by the reaction of **45** and anhydrous iron(III) chloride. The compound can also be prepared directly from germanium tetrachloride and acetylacetone in the presence of iron(III) chloride, where **45** was shown to be the possible intermediate in the reaction [116].

Other work on **47** involves its optical resolution and racemization and has been described by Saito and co-workers [117–120]. The cation **47** has been resolved by the crystallization of its hydrogen-*R*,*R*-dibenzoyltartrate in a mixture acetonitrile, ethanol and water [117]. The absence of ligand isotopic exchange and of decomposition clearly indicates that the racemization proceeds via an intramolecular mechanism. A bond-breaking racemization mechanism involving an intermediate with a unidentate ligand was proposed based on kinetic studies of acid and base catalysis observations and the influence of ionic strength and solvent effects. Additional evidence has been reported [118] by a study of the pressure effects on the intramolecular racemization of the perchlorate salt of **47** in organic solvents. Further ligand isotopic exchange studies [119] suggest that the rate-determining step for the exchange is governed by the ease of the proton transfer between the leaving and the incoming acac$^-$ anion in an intermediate. The crystal structure of the perchlorate salt of **47** has been determined, which revealed the $(-)_{589}$-$[Ge(acac)_3]^+$ to be Δ consistent with results obtained from the exciton CD approach [120].

Tropolonato germanium(IV) derivatives were first reported by Muetterties and Wright [85]. In non-aqueous media, germanium tetrachloride tends to give a material of the composition $Ge(trop)_2Cl_2$ which undergoes reaction with water to give $[Ge(trop)_3]^+$. Under forcing conditions, the simple chloride salt, $[Ge(trop)_3]Cl$ (**48**), is formed. Reaction of **48** and silver tropolonate in aqueous acetonitrile gives $[Ge(trop)_3][trop] \cdot 2H_2O$ as indicated by IR and NMR data.

The reaction of GeO_2 and 3 equiv. of various orthodiphenolates were reported by Bévillard [121]. Solution studies indicated formation of dianionic $[GeL_3]^{2-}$ species. The tris(catecholato)germanium(IV) dianion was isolated by Yoder and Zuckerman [102] but was incorrectly formulated at the time (see above). Subsequently, equilibrium studies analogous to the silicon analogues (eqn. (11)) have been established for $[Ge(cat)_3]_2$ [122,123] and other substituted catechol derivatives [124–126]. Generally, it was found that catecholato germanium(IV) showed a much higher degree of stability than the corresponding silicon(IV) analogues. The relationship between pK_a of ligand and the equilibrium constant, K, of catecholato silicon(IV) complexes described earlier also appear to hold for the germanium complexes. As observed for the silicon analogues [34], *fac* and

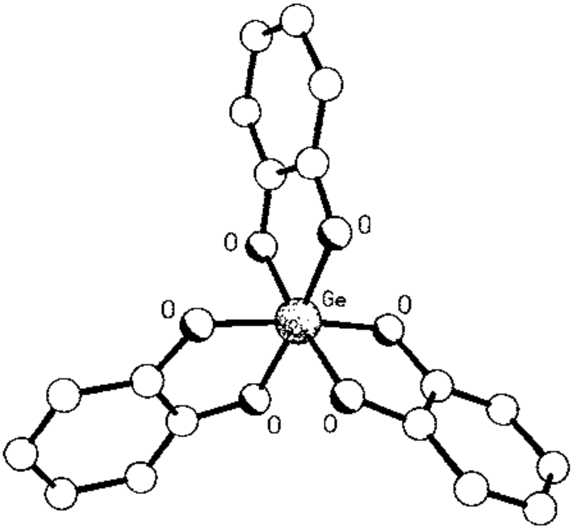


Fig. 26. The crystal structure of the tris(catecholato)germanium(IV) dianion.

mer isomers are separated on the ^{1}H NMR spectra of tris(asymmetric catecholato)-germanium complexes [126]. The crystal structure of $K_2[Ge(cat)_3]$ has recently been obtained (Fig. 26) [127]. The germanium is six-coordinate, as expected, and the dianion adopts a near perfect octahedron around germanium.

The complexes of the type $[GeL_3]Cl$, where HL is the group of monodentate ligands as discussed earlier with respect to silicon (Fig. 15) has been synthesized [127]. Interconversion of *fac* and *mer* isomers in $[Ge(dmp)_3]Cl$ may be separated by crystallization by a similar method to the silicon analogue (Fig. 17). The corresponding rates of *fac–mer* interconversion are considerably slower ($k_1 = 1.0 \times 10^{-6}$ s^{-1}, $t_{1/2} = 11.6$ days and $k_2 = 3.3 \times 10^{-7}$ s^{-1}, $t_{1/2} = 34.7$ days). This may support a bond breaking five-coordinate intermediate mechanism for these silicon and germanium complexes where it is well known that five-coordinate silicon species are more stable than the larger germanium analogues.

D. TIN

Tin has no known biological function but its bioavailability and toxicity will depend upon its speciation. Although the oral toxicity of inorganic tin is considered to be low due to low absorption and rapid excretion, complexation with chelates may increase absorption [128,129]. The chemistry of tin is well documented in a recent publication edited by Harrison and should be considered a leading reference [128].

Tin has a wide range of industrial applications. For example, SnO_2 is used in the ceramics industry as an opacifier for glazes and enamels, films of various thickness of SnO_2 give different degrees of protection to the surface structure of the glass and various tin–vanadium and tin–antimony oxides have been used as heterogeneous catalysts. Organotin compounds are widely used in the plastics and polymer industries and as agricultural biocides [130]. Note that subtle changes in substituents of the tin complex may dramatically alter its chemistry. For example, mono- and diorganotin complexes are not biologically active whereas triorganotin complexes usually act as powerful biocides [128]. The anti-tumour activity of certain chelated tin complexes has also stimulated much interest in the understanding of its chemistry [128,131].

The steady trend towards increasing stability of the +2 oxidation state down the Group 14 elements, reflecting the "inert-pair effect", has induced an appreciable amount of work on tin(II) complexes. Comprehensive reviews have been reported which describe the bonding, structure and reactivity of various tin(II) complexes [128,132]. The larger Sn^{4+} cation as compared with Si^{4+} and Ge^{4+} has increased the stability of higher coordination complexes. Structural aspects of tin complexes have been reviewed by Zubieta and Zuckerman in 1978 [133]. The subject of six-coordinate tin(IV) complexes is a diverse field and many groups have reported mono-, bis- and tris-chelates of tin(IV). Bis(1,3-diketonato)tin(IV) complexes remain an important area of research and in particular, with reference to both the stereochemical and anti-tumour activity aspects. Other significant examples include, a patent which describes the bis(acetylacetonato)dibutyltin(IV) as a catalyst for formation of polyurethane in foams [134].

The advent of Mössbauer's discovery in the late 1950s has produced a great number of tin papers using Mössbauer spectroscopy. The applications of ^{119m}Sn Mössbauer spectroscopy to the study of organotin complexes have been reviewed by Zuckerman in 1970 [135]. The easily accessible NMR active isotopes, ^{117}Sn and, in particular, ^{119}Sn have been used to probe the coordination geometry of the tin complexes. The heteronuclear spin-spin couplings with tin have also been utilized to reveal information on the chemical environment surrounding the tin centre.

(i) Tin(II) complexes

In 1963, Zuckerman [136] reported the synthesis of catecholatotin(II) and 2,2'-biphenylenedioxytin(II) by reaction of the ligand at 150°C under a high pressure of hydrogen on a tin-copper contact mass (eqn. (30)).

$$H_2L + Sn \xrightarrow[H_2]{Cu} :SnL + H_2 \tag{30}$$

H_2L = catechol or 2,2'-dihydroxybiphenyl

The presence of the copper metal served as a catalyst. The products were isolated by sublimation and aroused interest due to their high thermal stability (e.g. in air to ~500°C) compared with other tin(II) and tin(IV) alkoxides which are of low hydrolytic and thermal stability [137,138]. A more conventional route utilizes tin(II) chloride and sodamide (eqn. (31)) [139].

$$H_2L + SnCl_2 + 2NaNH_2 \rightarrow :SnL + 2NaCl + 2NH_3 \tag{31}$$

H_2L = catechol or 2,2'-dihydroxybiphenyl

Similar products were later reported using stannous oxide as the starting material (eqn. (32)) [140].

$$H_2L + :SnO \xrightarrow{Cu} :SnL + H_2O \tag{32}$$

where H_2L = catechol, 3-methylcatechol, 2,3-dihydroxynaphthalene or 2,2'-dihydroxybiphenyl. The reaction using :SnS also gave the analogous complexes with H_2S as the by-product [141]. For H_2L = salicylic acid in eqn. (32), the reaction proceeded with the copper metal showing no catalytic activity. By continuous washing in a Soxhlet apparatus with triethylamine the salicylatotin(II)–triethylamine adduct was obtained, (Fig. 27). Evidence for the three-coordinate tin(II) complex was provided by ^{1}H NMR, IR and Mössbauer spectroscopy [141].

A more convenient method for synthesis of :SnL complexes was later reported using :Sn(OMe)$_2$ with various diols and salicylic acids, to give MeOH as the by-product.

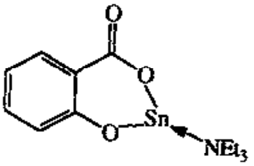
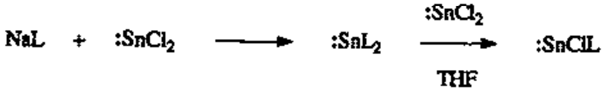


Fig. 27. Proposed structure of salicylatotin(II)–triethylamine.

The Mössbauer studies indicated possible intermolecular interactions, thus resulting in a polymeric lattice [142]. The crystal structures of oxalatotin(II) and dipotassium-bis(oxalato)tin(II) monohydrate have been reported [143]. Both structures feature infinite chains due to intermolecular Sn···O interactions (Fig. 28). Bos et al. [144] reported the synthesis of 1,3-diketonatotin(II) and bis(1,3-diketonato)tin(II) complexes by the reaction of tin(II) chloride and the sodium salt of the 1,3-diketone in THF solution (eqn. (33)).



$$\mathrm{NaL} + \mathrm{{:}SnCl_2} \longrightarrow \mathrm{{:}SnL_2} \xrightarrow[\mathrm{THF}]{\mathrm{{:}SnCl_2}} \mathrm{{:}SnClL} \qquad (33)$$

Ebulliometry in benzene solution indicated monomeric species and Mössbauer spectroscopy indicated divalent tin species.

Harrison and co-workers [145–148] have characterized various bis(bidentate ligand)tin(II) (**49**) complexes. Bis(cyclopentadienyl)tin(II) (**50**) was demonstrated as a novel source for the synthesis of tin(II) derivatives [145]. Mössbauer spectroscopy was used to confirm formation of bis(*N*-phenylbenzohydroxamato)tin(II) and bis(benzohydroxamato)-tin(II) by protolysis of **50**. The synthesis of 1,3-diketonato **49** derivatives were obtained by the reaction of tin(II) methoxide, bis(methylcyclopentadienyl)tin(II), tin(II) chloride or

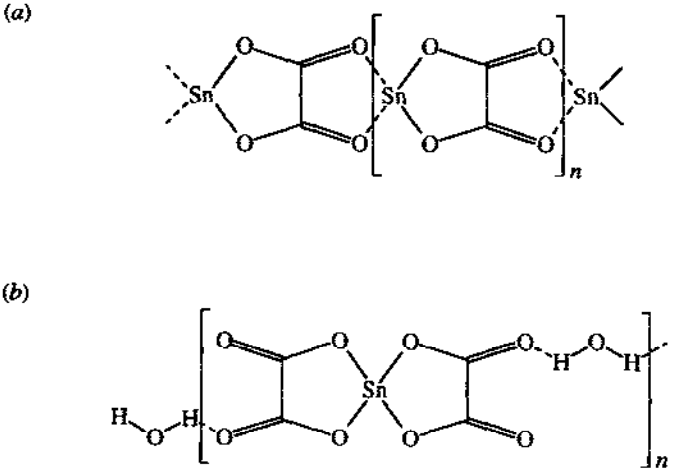


Fig. 28. (a) Polymeric structure of [Sn^{II}(ox)]. (b) Polymeric structure of [Sn^{II}(ox)$_2$–H$_2$O]$^{2-}$.

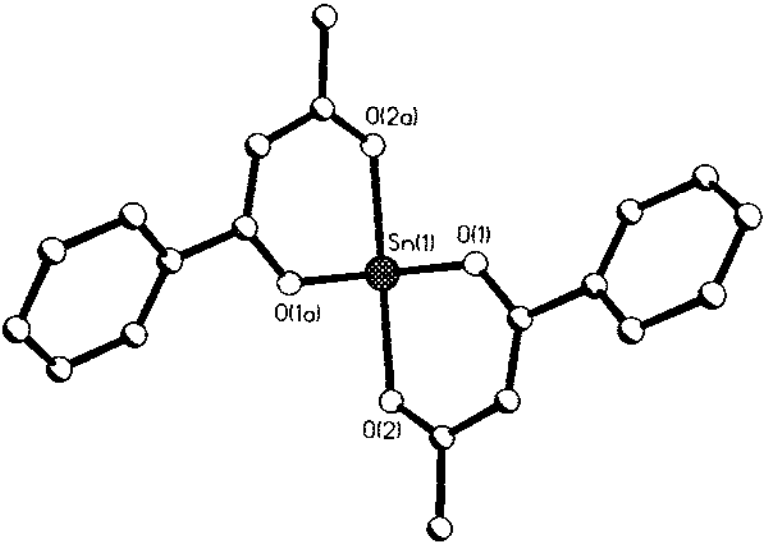
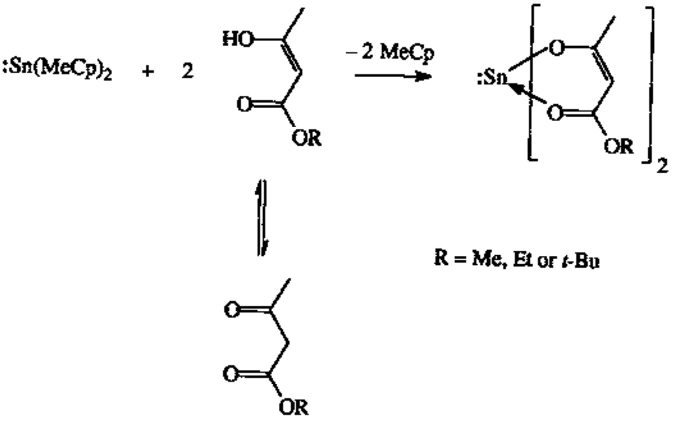


Fig. 29. The crystal structure of bis(benzylacetonato)tin(II).

tin(II) bromide with 2 equiv. of the 1,3-diketone (or its corresponding sodium salt for reactions with the dihalides, see eqn. (33)). 1,3-Diketonato **49** derivatives from acac$^-$, tfac$^-$ and hfac$^-$ were shown to be monomeric in the vapour phase (by mass spectrometry), benzene solution (by osmometry) and indicated in the solid state by the ease of solubility and volatility of the complexes [146]. In addition, ligand redistribution readily occurred between :Sn(hfac)$_2$ and :SnCl$_2$ in solution to give :Sn(hfac)Cl. The crystal structure of :Sn(bzac)$_2$ confirmed the distorted TBP structure of these four-coordinate complexes, where the lone pair occupies an equatorial site (Fig. 29) [147]. Subsequently, the Hdbzm and Htrop derivatives were similarly prepared [148]. The occurrence of an exchange process of :Sn(trop)$_2$ in solution was evident from low temperature ^{1}H NMR spectroscopy. 1-Alkoxy-1,3-diketonato **49** derivatives form monomeric complexes analogous to the 1,3-diketonato complexes but were thermally unstable and rapidly oxidized/hydrolyzed in air (eqn. (34)) [148].



R = Me, Et or *t*-Bu

(34)

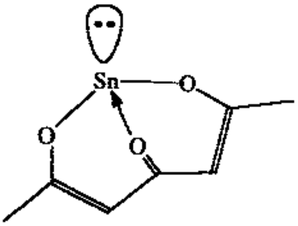


Fig. 30. Proposed tridenticity in 1,3,5-triketonatotin(II) complexes.

The reaction of mono- and disodium 1,3,5-triketones with tin(II) chloride has been reported (eqns. (35) and (36)) [149].

$$:SnCl_2 + Na_2L \rightarrow :SnL + 2NaCl \quad (35)$$

$$:SnCl_2 + 2NaHL \rightarrow :Sn(HL)_2 + 2NaCl \quad (36)$$

On the basis of IR and Mössbauer spectroscopy data and other tin(II) systems, the :SnL complexes, where H_2L = 1,3,5-triketone, are three-coordinate (Fig. 30). The IR data for $:Sn(HL)_2$ show the presence of one free carbonyl and two different coordinated carbonyl groups corresponding to σ-bonded and dative bonded Sn–O stretches. A four-coordinated SP geometry was suggested for these complexes (Fig. 31). Recently, Annan et al. [150] reported the electrochemical oxidation of metallic tin in a non-aqueous solution to form $:SnL_2$ where HL = maltol (see Fig. 15). Further oxidation leads to tin(IV) species (see later).

(iv) Four-coordinate tin(IV) complexes

The stable stannylene, $:SnR_2$, where R = bis(trimethylsilyl)methyl) reacts with 1,2-diketones in benzene at room temperature to form the oxidative cycloaddition product, $R_2Sn^{IV}L$, analogous to the silicon (eqn. (1)) and germanium (eqn. (23)) systems [151]. By analogy, various derivatives of $:Sn(OR)_2$, where R = Et, Ph, $-CH_2CH_2NMe_2$, o-$PhCO_2Et$,

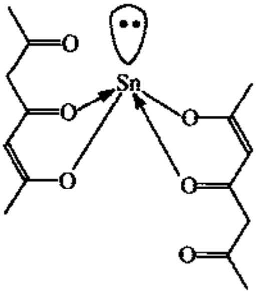


Fig. 31. Proposed SP structure of bis(1,3,5-triketonato)tin(II) complexes.

$CH_3C{=}CHCOCH_3$ and $CH_3C{=}CHCO_2Et$, with benzil **35** (Fig. 20), have been synthesized [152]. A comparison of the electronegativity of substituent, R, and the reactivity of the alkoxotin(II) starting material revealed that R bearing an electron releasing group will behave most effectively towards **35**.

Alternative sources of stannylenes have been reported [153,154] which generate $:SnR_2$ by thermal or photochemical decomposition of the distannane, $Me_2(PhS)Sn$–$Sn(SPh)Me_2$, and polycyclostannane, $(R_2Sn)_n$, respectively. Subsequent reactivity towards 1,2-diketones to give four-coordinate R_2SnL complexes confirm the intermediate $:SnR_2$ species formed.

Four-coordinate tin(IV) complexes can also be synthesized directly from tin(IV) (eqn. (37)) [139].

$$H_2L + R_2SnCl_2 + 2NaNH_2 \rightarrow R_2SnL + 2NaCl + 2NH_3 \qquad (37)$$

where H_2L = catechol or 2,2'-dihydroxybiphenyl; R = Me or Bu, analogous to eqn. (31). No reaction occurred when H_2L = 2,2'-dihydroxybiphenyl and R = Bu. When R = Ph, Sn–Ph, cleavage occurred resulting in $:SnL$ complexes. Reaction of diorganotin(IV) oxide and a diol have been investigated (eqn. (38)) [142].

$$R_2SnO + H_2L \rightarrow R_2SnL + H_2O \qquad (38)$$

where H_2L = catechol, 2,2'-dihydroxybiphenyl, 2,3-dihydroxypyridine, salicylic acid and R = Me, Bu or Ph, analogous to eqn. (32). Characterization of complexes were based on IR and Mössbauer spectroscopy. Similar reactions of 1,3,5-triketones as described in eqns. (35) and (36) but using tin(IV) chloride produced the corresponding tin(IV) complexes (eqns. (39) and (40)) [149].

$$SnCl_4 + H_2L \rightarrow Cl_2SnL + 2HCl \qquad (39)$$

$$SnCl_4 + 2Na_2L \rightarrow SnL_2 + 4NaCl \qquad (40)$$

On the basis of IR and Mössbauer spectroscopy, the coordination number of Cl_2SnL complexes was not unambiguously determined. The tridenicity of 1,3,5-triketones in SnL_2 to form six-coordinate octahedral tin(IV) complexes were also based on IR and Mössbauer spectroscopic data.

(iii) Five-coordinate tin(IV) complexes

Several independent groups [155–159] have reported complexes of the type R_2SnL (**51**), where H_2L = saturated diol. Bornstein et al. [155] first proposed two bridging ethylene glycol ligands to form a dimetallic tin(IV) complex **52** (Fig. 32) yet the propylene glycol adduct remains monometallic (Fig. 33). Mehrotra and Gupta [156] suggested a polymeric structure for similar **51** species based on molecular weight determinations.

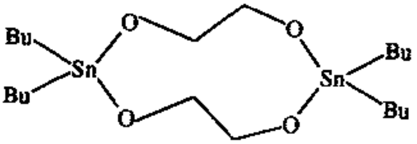


Fig. 32. Proposed dimetallic structure of **52**.

Other 1,2-diols were later re-examined showing monometallic **51** complexes, with the exception of **52** [157]. Pommier and Valade [158] supported the dimetallic structure **52**, rejecting the possibility of intermolecular Sn···O interactions to form dimeric five-coordinate **51** species (Fig. 34). More recent studies [159] using ^{119}Sn NMR and ^{119m}Sn Mössbauer spectroscopy indicated that these complexes have monometallic structures with extra coordination provided by intermolecular interactions as shown in Fig. 34. The evidence was based on the ^{119}Sn NMR chemical shift range and Mössbauer data, both of which indicated five-coordinate tin(IV) species.

Certain tricyclohexyltin(IV) complexes, Cy_3SnX, are known to possess good acaricidal activity, where X = monodentate ligand [160]. However, when X is replaced by a bidentate ligand such as tropolone, the five-coordinate complex often displays a significant reduction in biological activity. The elucidation of the five-coordinate $Cy_3Sn(trop)$ (**53**) complex [161] was based on ^{119}Sn NMR data which show a significant shift to a high field resonance corresponding to a change in coordination number from four to five (e.g. Cy_3SnOH, δ 1.5; **53**, δ –62.8). Other tropolonato derivatives, $Ph_3Sn(trop)$, $Me_2SnCl(trop)$ and $Me_2SnBr(trop)$ have been reported [162]. Molecular weight determinations, IR and ^{1}H NMR spectroscopy indicated a monomeric, five-coordinate TBP geometry for these complexes. The 3-hydroxyflavone (Hhfo, Fig. 35) derivative, $Cy_3Sn(hfo)$, showed a reduced carbonyl stretching frequency in the IR spectrum which indicated intramolecular interaction and the analogous five-coordinate species has been proposed [163]. The ^{119}Sn NMR chemical shift, δ –27.4, however, indicated a much weaker Sn···O=C interaction than in **53** [161]. $Ph_3Sn(hfo)$, $Np_3Sn(hfo)$ and $Ph_2SnCl(hfo)$, where Np = $PhMe_2CCH_2$–, show ^{119}Sn NMR resonances which are consistent with a five-coordinate tin. The Mössbauer data also support a *cis*-diphenyl configuration for the latter complex [163]. The strong fluorescence character of organotin complexes of Hhfo has been associated with the five-coordination at the tin(IV) centre [163].

Acetylacetonatotriethyltin(IV), $Et_3Sn(acac)$ (**54**), was synthesized by the reaction between triethyltin ethoxide with Hacac in equimolar ratio in benzene (eqn. (41)) [164].

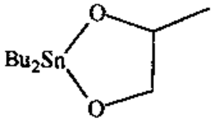


Fig. 33. Proposed monometallic structure of (propylene glycolato)butyltin(IV).

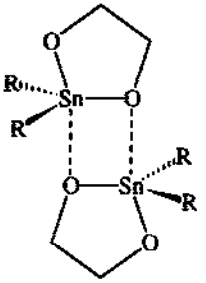


Fig. 34. Proposed polymeric structure of glycolatodialkyltin(IV).

$$Et_3SnOEt + Hacac \rightarrow Et_3Sn(acac) + EtOH \qquad (41)$$

Molecular weight determinations indicated that **54** are monomeric in solution. Subsequently, Cauletti et al. [165] investigated the electronic structures of **54** and $Me_3Sn(acac)$ (**55**) by UV photoelectron spectroscopy. The spectra show three bands in the low ionization energy region: 8.51, 8.93, 10.26 and 9.14, 9.64, 10.72 eV for **54** and **55**, respectively. These have been assigned by analogy with other 1,3-diketonato complexes to π_3, n^--Sn–O bonding and σ bonding Sn–C orbitals, respectively.

Various other R_3SnL complexes, where R = Me or Ph and HL = Hacac, Hbzac or Hdbzm, have been synthesized by reaction of R_3SnCl with the thallium(I) 1,3-diketonato salts [166]. A comparison of the Mössbauer quadrupole splittings to R_2SnL_2 analogues (see below), Ph_3SnL and Me_3SnL were assigned as the *cis*-diphenyl and the *trans*-dimethyl configurations, respectively (Fig. 36). The crystal structure of $Ph_3Sn(dbzm)$ show a slightly distorted TBP geometry with a *cis*-diphenyl configuration consistent with the Mössbauer data (Fig. 37).

The reactions of mono- and disodium 1,3,5-triketones with triorganotin(IV) chloride, R_3SnCl, have been reported, where R = Me, Et, ^nPr, ^nBu and Ph (eqns. (42) and (43)) [167].

$$R_3SnCl + NaHL \rightarrow R_3Sn(HL) \qquad (42)$$

$$2R_3SnCl + Na_2L \rightarrow (R_3Sn)_2L \qquad (43)$$

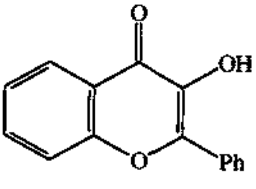


Fig. 35. 3-Hydroxyflavone.

Ring = 1,3-diketonate

Fig. 36. Proposed structures of *cis*-diphenyl and *trans*-dimethyl configurations in 1,3-diketonatotriphenyltin(IV) and 1,3-diketonatotrimethyltin(IV) complexes.

In the monometallic complexes, ^{1}H NMR spectroscopy indicated the presence of tautomeric forms in solution (Fig. 38). However, in the bimetallic complexes, two structures have been proposed based on the ^{1}H NMR data and depend on the R group: (a) two five-coordinate triphenyltin(IV) centres where the central oxygen atom is three-coordinate or (b) one five-coordinate and one four-coordinate trialkyltin(IV) centre (Fig. 39).

Harrison and co-workers [168–171] have reported the synthesis of a series of R_3SnL complexes, where HL = hydroxamic acids (see Fig. 15). In most cases, the reaction was carried out by azeotropic removal of water from the acid and either the triorganotin(IV) oxide or hydroxide (eqn. (44)) [168].

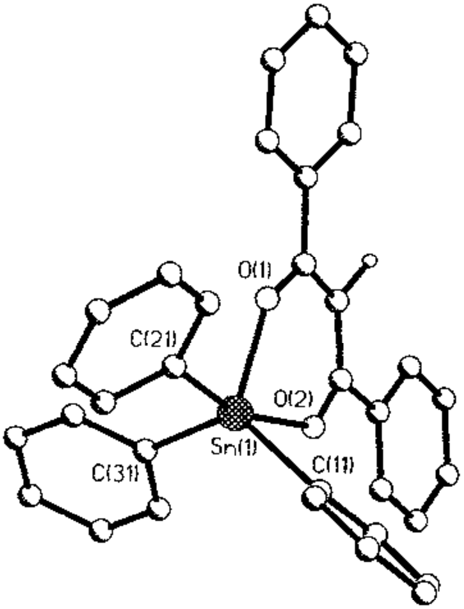


Fig. 37. The crystal structure of dibenzoylmethanatotriphenyltin(IV).

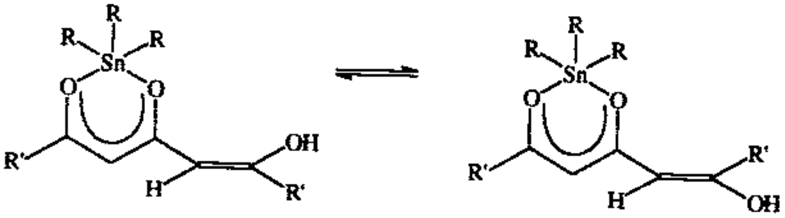
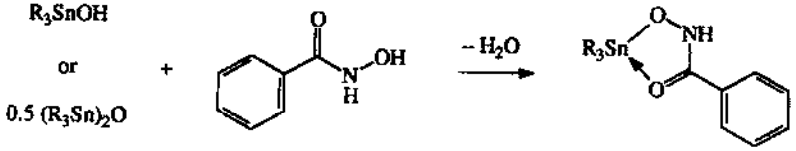
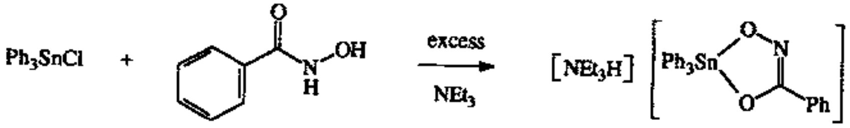


Fig. 38. Tautomeric forms of 1,3,5-triketonatotriorganotin(IV) complexes.



(44)

The crystal structures of *N*-phenylbenzohydroxamatotriphenyltin(IV) (**56**) and the trimethyl analogue have been determined [169–171]. The complexes possess a distorted TBP geometry with two equatorial and one axial R groups (Figs. 40 and 41). Inspection of the bond distances within the chelates reveal significant contribution of the canonical resonance isomer as shown in Fig. 42. The reaction shown in eqn. (44) did not, however, proceed with Ph_3SnOH which yielded Ph_4Sn only. The reaction with Ph_3SnCl with excess NEt_3 yielded the triethylammonium salt (eqn. (45)).



(45)

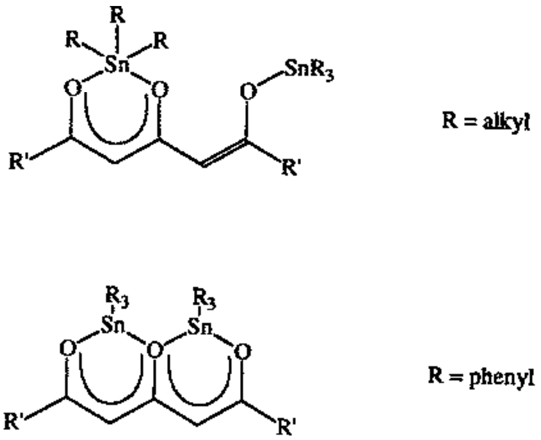


Fig. 39. Proposed structures of bis{triorganotin(IV)}-1,3,5-triketonato complexes.

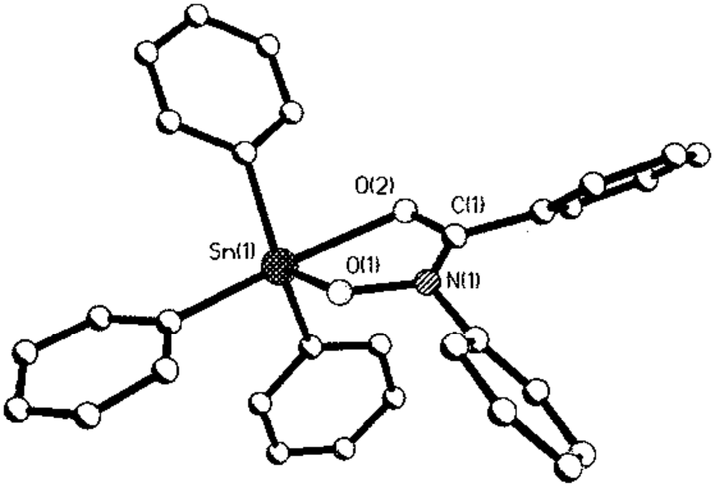


Fig. 40. The crystal structure of **56**.

Assignment of this five-coordinate anion was consistent with previous structural assignments made on the basis of Mössbauer spectroscopy data [168].

Das et al. [172] have also described the synthesis and characterization of various R_3SnL complexes derived from substituted hydroxamic acids. The compounds were characterized by UV, IR, NMR and Mössbauer spectroscopy and a distorted TBP structure was proposed. The stereochemistry proposed was also consistent with the work of Harrison and co-workers as described above.

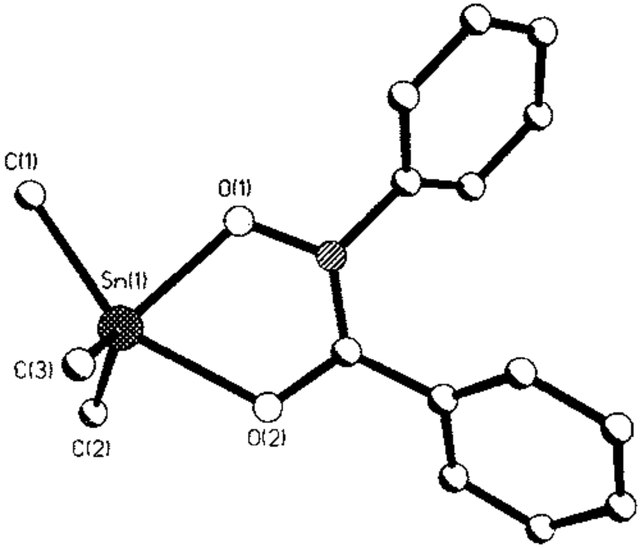


Fig. 41. The crystal structure of *N*-phenylbenzohydroxamatotrimethyltin(IV).

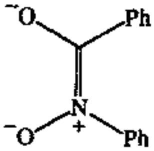
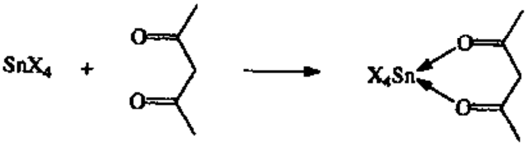


Fig. 42. A canonical form of the *N*-phenylbenzohydroxamate chelate.

(iv) Six-coordinate tin(IV) complexes with one O_2-bidentate ligand

In 1960, Muetterties reported ^{19}F NMR evidence to suggest formation of octahedral six-coordinate $SnF_4 \cdot Hacac$ [173]. Subsequently, Allred and Thompson [174] were able to confirm the formation of un-enolized 1,3-diketone adducts of tin(IV) halides by direct reaction at low temperature (eqn. (46)).



(46)

The reactions were carried out using acetylacetone, the 3-methyl and the 3,3-dimethyl analogues. The latter 1,3-diketone does not contain readily enolizable hydrogen atoms and was used to compare with the former 1,3-diketones. IR and ^1H NMR spectroscopic data indicated that the adducts partially dissociate in dichloromethane and, if enolization was possible, there is some hydrogen chloride lost due to complexation. Further, the equilibrium between adduct and complexation can be shifted towards the adduct by the addition of hydrogen chloride. On the basis of the quadrupole splittings in the Mössbauer spectra, the complexes, $SnCl_4 \cdot Hacac$ and $SnCl_4 \cdot Hbzac$ were assigned a *cis* configuration [175]. The enolized complexes, $[HB][X_4Sn(acac)]$ (**57**) and $(^nBu)Cl_2Sn(acac) \cdot C_5H_5N$ (**58**), where HB = pyridinium or tetraethylammonium cations and X = Cl, Br or I, were later reported by Thompson and co-workers [176,177]. Evidence for **57** type complexes were based on ^1H NMR, Mössbauer, conductivity, melting point and microanalytical data. When the authors attempted the reaction using $^nBuSnCl_3$, in place of $SnCl_4$, they expected the analogous product, $[C_5H_5NH]$ $[(^nBu)Cl_3Sn(acac)]$ but the pyridine-coordinated complex **58** was isolated instead.

Equilibrium studies of the dimethyltin(IV) cation, $[Me^2Sn]^{2+}$, with acetylacetone have been reported [178]. The formation of Me_2SnL at 25°C was found to be most successful for $acac^-$ compared to picolinate and phenanthroline with N, O and N_2 donors, respectively ($\log K_1 = 6.6$, 5.1 and 4.2, respectively).

Complexes of the type, $[(MeO)X_2Sn(acac)]_2$ (Fig. 43), where X = Cl, Br or I, have been reported [179]. The dimeric nature and configuration were based on IR spectroscopy and molecular weight determinations. The apparent hydrolytic stability was consistent with the proposed structure. The stereochemistry and lability of $[(MeO)Cl_2Sn(acac)]_2$ and

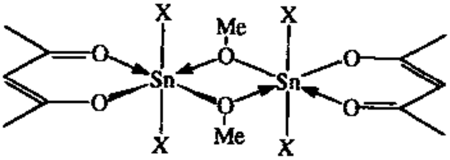


Fig. 43. Proposed structures of $[(MeO)X_2Sn(acac)]_2$, where X = Cl, Br or I.

$[(MeO)Cl_2Sn(dpm)]_2$, where Hdpm = dipivalomethane, have been described using VT ^1H NMR spectroscopy [180]. A ^{13}C NMR analysis of various organotin complexes suggest a similar dimeric structure for $[(MeO)Bu_2Sn(acac)]_2$ (Fig. 44) [181].

Westlake and Martin [182] treated $Ph_2SnCl(hq)$ and $Me_2SnCl(hq)$ with thallium(I) salts of 1,3-diketones in an attempt to form mixed chelates, $R_2Sn(hq)(diket)$, where Hhq = 8-hydroxyquinoline. The melting point range suggested a pure $Ph_2Sn(hq)(dbzm)$ complex but $Ph_2Sn(hq)(bzac)$ and $Me_2Sn(hq)(dbzm)$ disproportionated to form $R_2Sn(hq)_2$ and $R_2Sn(diket)_2$. Subsequently, Komura et al. [183] described the synthesis of the analogous mixed chelate using tropolone, thus reaction of $Me_2Sn(hq)_2$ (**59**) and $Me_2Sn(trop)_2$ (**60**) in ethanol yielded $Me_2Sn(hq)(trop)$ (**61**). Here, the evidence for a genuine mixed chelate **61** as opposed to a mixture of **59** and **60** was provided by IR, X-ray powder pattern, melting point determination and ^1H NMR spectroscopy. Three methyl resonances were observed in the NMR spectrum, corresponding to the equilibrium (eq. (47))

$$2Me_2Sn(hq)(acac) \rightleftharpoons Me_2Sn(hq)_2 + Me_2Sn(trop)_2 \qquad (47)$$

The high and low field resonances were assigned to **59** and **60**, respectively. The intermediate resonance was assigned to **61**.

(v) Six-coordinate bis(1,3-diketonato)tin(IV) complexes

(a) $X_2Sn(diket)_2$ complexes

Bis(acetylacetonato)tin(IV) dichloride, $Cl_2Sn(acac)_2$ (**62**), was first synthesized by Dilthey and Rosenheim et al. in 1903 [62]. Microanalytical data were in accord with the empirical formula for **62**. Subsequently, Morgan and Drew in 1924 [184] reported molecular weight determinations of **62** to confirm its monomeric nature. In addition, the complexes: $Br_2Sn(acac)_2$, $Br_2Sn(bzac)_2$, $Br_2Sn(dbzm)_2$ and $Br_2Sn(3\text{-}Etacac)_2$, where H(3-

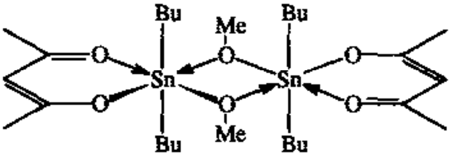


Fig. 44. Proposed structure of $[(MeO)Bu_2Sn(acac)]_2$.

Etacac) = 3-ethylacetylacetone were prepared from copper(I) salts of the respective 1,3-diketone. The publication of the three papers in 1965 [185–187] has undoubtedly contributed to the resurgence of the chemistry of **62**. Nelson and Martin [185] reported the synthesis of **62**, $Cl_2Sn(bzac)_2$ (**63**) and $Cl_2Sn(dbzm)_2$ (**64**) using a novel method by cleavage of Sn–Ph bonds from Ph_2SnCl_2 as the starting material (eqn. (48)).

$$Ph_2SnCl_2 \quad + \quad 2\,\mathrm{Hdiket} \quad \xrightarrow[\substack{\text{excess} \\ \text{Hdiket}}]{> 100^{\circ}\mathrm{C}} \quad Cl_2Sn(\mathrm{diket})_2 \quad + \quad 2\,C_6H_6 \tag{48}$$

The controversy surrounding the *cis* or *trans* nature of these complexes was initiated by Cox et al. [111] and Smith and Wilkins [112,186] who proposed a *cis* configuration for **62** based on dipole moment measurements and ^1H NMR chemical shifts/heteronuclear spin-spin coupling between the tin and the protons in the methyl groups, respectively. The *cis* configuration was based on the observation of a large dipole moment and two methyl resonances in the ^1H NMR spectra (see Fig. 23). However, Kawasaki and co-workers [187–189] proposed a distorted *trans* structure containing partially localized double bonds in the 1,3-diketonate ligand based on ^1H NMR, IR and VT ^1H NMR spectroscopy, respectively.

Douek et al. [190] studied $X_2Sn(acac)_2$, where X = Cl, Br and I, using far IR spectroscopy, but due to the complexity of the spectra and other factors discussed, the configuration was not established unequivocally.

The fact that a larger dipole moment is expected for the *cis* configuration has been utilized by several groups [191–195]. All reports indicated a *cis* configuration for the complexes, although there has been some discrepancy as to the exact value of the dipole moment and range from 2 to 6–7 D. Doron and Fischer [191] have also proposed a *cis-cis* racemization process in solution based on VT dipole moment studies. Further support for the *cis* configuration by ^1H NMR spectroscopy were provided by Nelson [192] and Faller and Davison [193]. In addition, Faller and Davison attributed the coalescence of the two methyl resonances to enantiomerization of the *cis* stereomers as opposed to geometrical isomerism of the *cis* and *trans* isomers. An intramolecular "twist" mechanism was proposed based on the preservation of ^4J(Sn–H) at various temperatures with an averaged coupling constant after coalescence. The intermolecular rate of ligand exchange of **62** was found to be the slowest when compared with $MeClSn(acac)_2$ and $Me_2Sn(acac)_2$ [196]. It was suggested that these intermolecular exchange processes were appreciably slower than the intramolecular racemization processes described by Faller and Davison.

Muetterties [197] suggested that intramolecular non-bond-breaking mechanisms can not be easily confirmed. With reference to the work of Faller and Davison, Muetterties suggested that dissociative mechanisms such as Sn–Cl cleavage were not eliminated as possibilities. A comprehensive VT ^1H NMR and IR spectroscopic analysis of $X_2Sn(acac)_2$, where X = F, Cl, Br and I, have been reported by Jones and Fay [198].

(Note, the pure difluoro derivative was isolated for the first time). The NMR analysis revealed the rate of exchange between two non-equivalent sites in the *cis*-$X_2Sn(acac)_2$ complexes. In general, the halogen had only a relatively small effect on the rates (which is also in support of an intramolecular, non-Sn–X dissociative mechanism), and that the rate increases in the order Cl < Br < I < F. The preservation of the heteronuclear Sn–H coupling constants in both slow and fast exchange support non-bond-breaking mechanism in accord with previous studies [193]. Rearrangement by an intermolecular mechanism involving Sn–X cleavage was eliminated by observation of spectra derived from a mixture of two $X_2Sn(acac)_2$ complexes. The IR assignments were reported for Sn–X and Sn–O bonds and these suggest that the *cis* configuration is maintained in the solid state as well as in solution.

Other NMR studies include the correlation of the chemical shift of the 3-proton with the inductive effect of the substituents on the tin atom (quantified by the sum of the Hammett factors, i.e. $\delta \propto \Sigma\sigma$) [199]. Wilkie et al. [200] used ^{13}C NMR and IR spectroscopy to suggest a bond rupture mechanism for the complexes. The proposed mechanism was based on a strong *trans* effect exerted by the halogen such that the strength of the Sn–O bonds *cis* and *trans* to the halogen differ as reflected in the spectra.

The X-ray crystal structure of **62** was determined by Miller and Schlemper in 1978 [201]. The structure consists of discrete molecules with the tin atom in a distorted octahedral geometry. The chloro groups are *cis* and the molecule has C_2 symmetry (Fig. 45). Later, the characterization of "TiOCl(acac)" [202] by X-ray diffraction revealed that the compound was in fact crystals of **62**, where the tin source was introduced during synthesis. The structure determination proceeded to final atomic coordinates analogous to those reported by Miller and Schlemper, where again, discrete *cis* distorted octahedral mole-

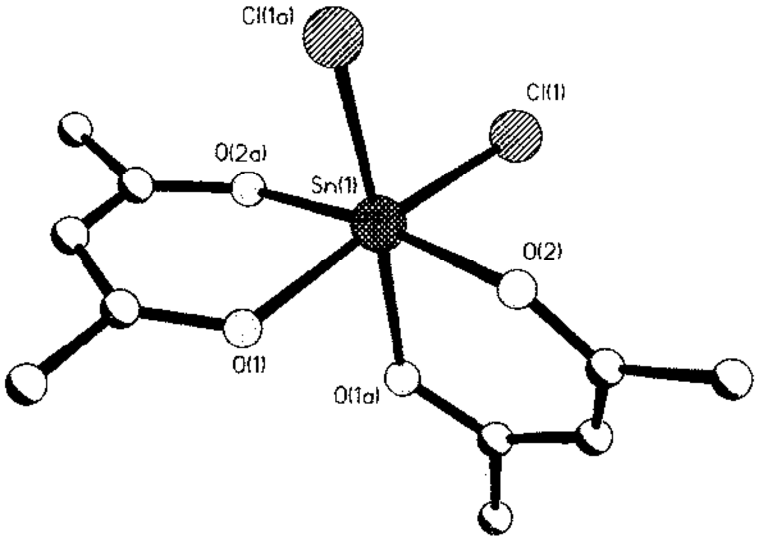


Fig. 45. The crystal structure of **62**.

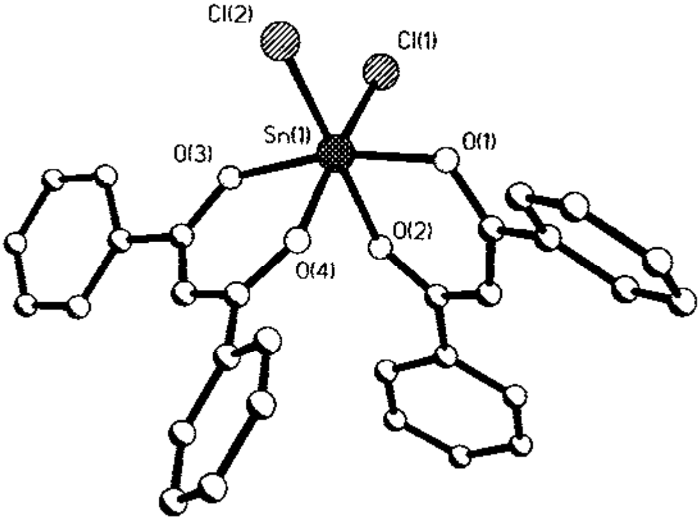


Fig. 46. The crystal structure of **64**.

cules were confirmed. The X-ray crystal structure of **64** has recently been determined [131]. The structure was found to share the same geometry as **62**, consisting of discrete *cis*-**64** molecules (Fig. 46).

The possibility of an unusual bridging action of the 3-cyanopentane-2,4-dionate anion (Fig. 47) was investigated with tin, however, only the dioxygen bidentate function complexed with tin to form X_2SnL_2 species. IR studies revealed lower Sn–O stretches due to the electronegative cyano group [203].

Greenwood and Ruddick [204] used Mössbauer spectroscopy to establish a trend between the isomer shift and the electronegativity of the halogen attached to tin. It was observed that six-coordinate tin(IV) compounds, even when the tin atom deviated appreciably from a true octahedron, the quadrupole splitting was effectively zero. In addition, there was an appreciable isomer shift difference between **62** and **63** (δ 0.25 and 0.18 mm^{-1}, respectively). In contrast, a later study by Searle et al. [131] suggested similar isomer shifts for **63** and **64** (δ 0.23 and 0.21 mm^{-1}), respectively). The paper also describes the results of anti-tumour tests for **63** and **64** which showed successful inhibition of cell growth in vitro but unsuccessful in vivo tests in mice.

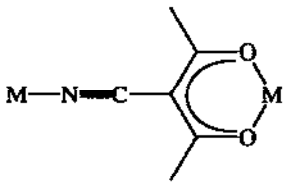


Fig. 47. Bridging action of the 3-cyanopentane-2,4-dionate chelate.

(b) $R_2Sn(diket)_2$ complexes

In 1964, Kawasaki et al. [205] reported the IR and Raman spectra of $Me_2Sn(acac)_2$ (**65**) and concluded that the most probable configuration is a *trans*-**65** isomer, however, synthesis of **65** was not described. In the following year, Nelson and Martin [206], McGrady and Tibias [207] and Mehrotra and Gupta [164] reported the syntheses and characterization of various bis(1,3-diketonato)dialkyl- and diaryltin(IV) complexes. Nelson and Martin [206] prepared $Ph_2Sn(diket)_2$, where Hdiket = Hacac, Hbzac and Hdbzm, by two methods (eqns. (49) and (50)).

$$Ph_2SnCl_2 + 2Tl(diket) \xrightarrow{C_6H_6} Ph_2Sn(diket)_2 + 2TlCl \qquad (49)$$

The preparation according to eqn. (50) was only partially successful since it often yielded a mixture of products due to cleavage of Sn–Ph bonds. They concluded that the complexes are monomeric in benzene solution. The *trans* isomer was proposed based on dipole moment measurements and the failure to resolve the compounds by stereomeric chromatography.

McGrady and Tobias [207] reported the synthesis of both the dimethyl and the diphenyl derivatives of $R_2Sn(diket)_2$ by two different methods (eqns. (51) and (52)).

$$Me_2SnO + 2Hacac \rightarrow Me_2Sn(acac)_2 + H_2O \qquad (51)$$

$$Ph_2SnCl_2 + 2Na(acac) \rightarrow Ph_2Sn(acac)_2 + 2NaCl \qquad (52)$$

The ^1H NMR, IR and Raman spectra of **65** indicated a *trans* isomer in general. ^1H NMR spectra also indicated a *trans* isomer for $Ph_2Sn(acac)_2$ (**66**) by a comparison of the heteronuclear Sn–H spin-spin coupling constants with known *trans*-tin(IV) complexes.

Mehrotra and Gupta [164] reported the synthesis of $Bu_2Sn(diket)_2$ using dibutyltin(IV) diethoxide (eqn. (53)).

$$Bu_2Sn(OEt)_2 + 2MeCOCH_2COR \rightarrow Bu_2SnL_2 + 2EtOH, \quad R = Me, OMe \text{ or } OEt \qquad (53)$$

The complexes were characterized by microanalytical and molecular weight studies. Kawasaki and co-workers [188,208] reported the synthesis using the analogous $R_2Sn(OMe)_2$ synthons and subsequently reported an IR spectroscopic study of $R_2Sn(diket)_2$ complexes. As noted earlier, Kawasaki et al. [199], correlated the ^1H NMR chemical shift with the inductive effect for various halogens; different alkyl and aryl derivatives also show the same correlation (i.e. $\delta \propto \Sigma\sigma$).

The use of Mössbauer spectroscopy to establish six-coordinate tin(IV) complexes by observation of a zero quadrupole splitting has already been discussed [204]. However, a non-zero quadrupole splitting is observed for C–Sn–C systems. Fitzsimmons et al. [209] assigned the geometries as *trans*-**65** and *cis*-**66** by correlating the quadrupole splitting with the geometry. Subsequently, Bancroft and co-workers [175,210] extended the series with the following assignments based on the Mössbauer quadrupole splitting values: *trans*-$Me_2Sn(diket)_2$ and *cis*-$Ph_2Sn(diket)_2$, where Hdiket = Hacac, Hbzac, Hdbzm, Htfac, Hhfac, and cis-MePhSn(diket)2, where Hdiket = Hacac, Hbzac and Hdbzm. Thus, it was concluded that the preference for a *cis* configuration decreases in the order Ph_2Sn > MePhSn > Me_2Sn, which parallels the σ-donating series as Me > Ph.

Dipole moment measurements for $R_2Sn(diket)_2$ complexes, where R = Me, Et, Bu or Ph and Hdiket = Hacac, Hdbzm or Hhfac, have been studied in benzene and cyclohexane solutions [211]. In all cases, the dipole moments were found to be in the range ~ 2–4 D, in accord with the polarized *cis* geometry. The conclusions were substantiated by dielectric absorption measurements on **66** in benzene, although the existence of a mixture of *cis* and *trans* forms (with predominantly the former) was not precluded [212]. Dipole moments and relaxation times determined by dielectric loss measurements were reported for **65** which show true orientation polarization in accord with the *cis* isomer assignment [213].

VT ^1H NMR analysis by Serpone and Hersh [214] indicated a *cis*-**66** isomer at low temperature (–60°C) which coalesces at higher temperatures due to exchange of the methyl protons between the two non-equivalent sites of the *cis* isomer. The intermolecular ligand exchange rate between Hacac and the complexes have been previously determined [196]. Serpone and co-workers [215–217] made a more comprehensive kinetic study by VT ^1H NMR spectroscopy and suggested a mechanism involving Sn–O bond rupture in **66** to yield an intermediate five-coordinate tin species with an unidentate acac ligand during the intermolecular exchange [215]. The configuration of **65** could not be unequivocally determined from VT ^1H NMR spectroscopy [216]. Permutational and mechanistic analysis suggest environmental averaging of *cis*-**66** proceed via a twist mechanism on the basis of the activation parameters. Cauletti et al. [165] investigated the electronic structures of **65**, $Me_2Sn(tfac)_2$ (**67**) and $Bu_2Sn(acac)_2$ (**68**) by UV photoelectron spectroscopy. The bands in **67** show a shift to higher ionization energy compared with **65** in accord with the increased electronegativity of the fluorine atoms. The spectrum for **68** was less well resolved due to the greater number of σ(C–H) and σ(C–C) bonding orbitals with respect to the dimethyl analogues.

In 1973, Miller and Schlemper [218] reported the X-ray crystal structure of **65** (Fig. 48). The molecule is arranged in distorted octahedral geometry with *trans*-methyl isomerization. Raman spectra have been recorded with benzene solutions, non-oriented crystalline samples, and with oriented single crystals for **65** [219]. Both the frequency and the intensity data suggest a *trans* isomer in solution and in the solid state. The non-zero dipole moment is consistent with previous reports (see above) and was accounted for by bending of the acetylacetonate ring in solution such that a permanent dipole moment was established. However, LeBlanc and Nelson [220] reported the carbon disulphide solution IR spectra of **65** and $(CD_3)_2Sn(acac)_2$ which indicated the coexistence of *cis* and *trans* isomers of **65** in solution.

Nelson and co-workers [221–223] reported the molecular optical anisotropy of various $R_2Sn(diket)_2$ complexes in cyclohexane by means of a depolarized Rayleigh light-

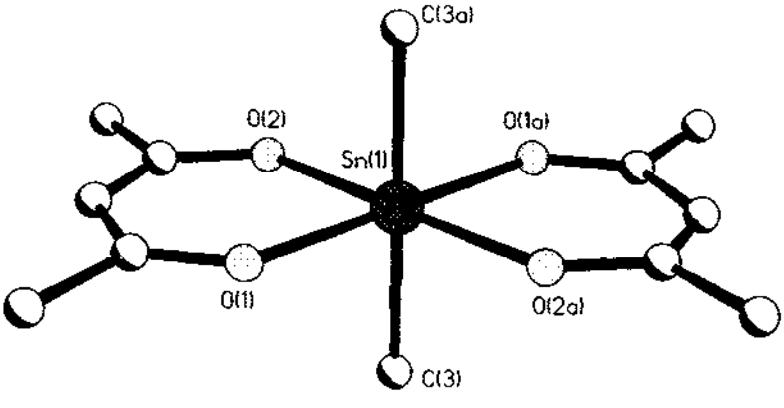


Fig. 48. The crystal structure of **65**.

scattering method. It was found that the *cis-trans* isomer distribution of compounds can be measured most effectively with highly anisotropic ligands such as dibenzoylmethane. $Me_2Sn(dbzm)_2$ (**69**) and $Et_2Sn(dbzm)_2$ (**70**) have been characterized as being composed of approximately two-thirds *trans* and one-third *cis* isomers [221]. Rayleigh intensities and line shapes for $Bu_2Sn(dbzm)_2$, $Cy_2Sn(dbzm)_2$ and $Oct_2Sn(dbzm)_2$ support the conclusion that the complexes are monomeric and predominantly of *trans* or distorted *trans* isomer [222,223]. By use of the Kerr effect, Brahma and Nelson [224] were finally able to reconcile the IR, Raman and dipole moment data by proposing a skew-trapezoidal-bipyramid (*skew*) structure which accounted for a near linear Me–Sn–Me moiety which may be active in both Raman and IR spectroscopy and possess a permanent dipole moment. In fact, such large Kerr constants in *skew-69* and *skew-70* may rule out the *cis* configuration entirely for these complexes.

Otera and co-workers [225–227] reported the use of ^{119}Sn NMR spectroscopy to elucidate the coordination about tin in various organotin(IV) compounds including $R_2Sn(diket)_2$ type complexes. Thus, five- and six-coordinate organotin complexes have different ^{119}Sn chemical shift ranges, although these are less well defined than with the ^{29}Si nucleus due to the diversity of Sn–C bonded systems [225]. However, the effect of the chelate ring size in Me_2SnL_2 complexes from six (e.g. 1,3-diketones) to five (e.g. tropolones) parallels that of the ^{29}Si nucleus, i.e. a higher field is observed for six-membered chelate rings than five [226]. The differences of the di-t-butyltin(IV) analogues were reported using ^1H and ^{119}Sn NMR spectroscopy [227]. The reduced acceptor property of the tin nucleus in these compounds were primarily attributed to the inductive effect of the t-butyl groups but the steric factors were also considered in some cases. Howard et al. [228] reported solution studies by ^{13}C and ^{119}Sn NMR spectroscopy of various $R_2Sn(diket)_2$ complexes, where R = Me, Et or ^nBu and Hdiket = Hbzac or Hdbzm. The relationship between J (both ^1H and ^{13}C) and the C–Sn–C angle was discussed.

In the course of a ^{13}C NMR spectroscopy investigation of organotin compounds, Mitchell [181] recorded the ^{13}C NMR spectra of **65** and **68** (with respectively δ 7.8 ppm

(C1), ^1J(Sn–C) = 966 Hz; δ 27.7 (C1), 27.4 (C2), 26.5 (C3), 13.9 (C4) ppm, ^1J(Sn–C) = 914, ^2J(Sn–C) = 41 and ^3J(Sn–C) = 130 Hz). Correlations were made between the magnitude of ^1J(Sn–C) and the hybridization state and coordination number of the tin atom. Subsequently, Lockhart and co-workers [229–231] applied solution and solid state (CPMAS) ^{13}C NMR spectroscopy to elucidate some structural aspects of various $R_2Sn(diket)_2$ complexes. The CPMAS $^{13}C\{^1H\}$ NMR spectrum of **65** gave $^1J(^{117}Sn–C)$ and $^2J(^{119}Sn–C)$ equal to 1125 and 1175 Hz, respectively. The 200 Hz difference between the solid and solution [181] ^1J(Sn–C) values reflect a decrease in s character in the Sn–C bond which is directly related to $|J|$ and has been attributed to a decrease in the Me–Sn–Me bond angle from the solid (180°) [229]. Thus, a linear relationship was reported between $|J|$ and the Me–Sn–Me angle in various methyltin(IV) complexes [230]. For **65**, the 966 Hz coupling in solution was extrapolated to give an Me–Sn–Me angle of 161° in $CDCl_3$ and 158° in C_6D_6 [231] in support of the non-linear structure indicated by other studies (see above). Lockhart and Manders [232] then extended the use of J by correlating new and published ^1J(Sn–C) and ^2J(Sn–H) data with the Me–Sn–Me angle. A plot of ^2J(Sn–H) and Me–Sn–Me was fitted to two curves, one exclusively for Me_2SnX_2 and the other for other coordination complexes including $Me_2Sn(diket)_2$.

Chandler et al. [233] have reported dimerization of $(^iPrO)_3Sn(acac)$ in the solid state to form six-coordinate tin(IV) species bridged by two alkoxide moieties (Fig. 49). The structure show considerable distortion from a regular octahedron with the acetylacetonates *trans* to each other. In solution, the ^{119}Sn NMR data indicated disproportionation to *cis*-$(^iPrO)_2Sn(acac)_2$ and $Sn(O\text{-}^iPr)_4$. The *cis* configuration was assigned on the basis of two methyl ^{1}H NMR resonances in the spectrum. Solution NMR studies were also described for other *cis*-$(RO)_2Sn(acac)_2$ complexes, where R = Me, ^{n}Bu or ^{t}Bu.

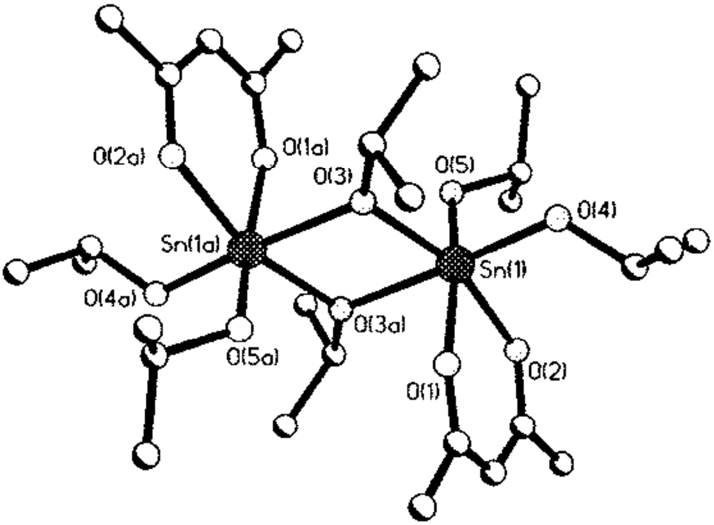


Fig. 49. The crystal structure of $[(^iPrO)_3Sn(acac)]_2$.

(c) RXSn(diket)$_2$ complexes

The preparation and characterization of RXSn(diket)$_2$ (**71**) complexes are briefly described since much of the data refer to references already mentioned. Ueeda et al. [208] prepared **71** complexes using $RSnX_3$ and 2 equiv. of Hacac (eqn. (54)).

$$RSnX_3 + 2Hacac \rightarrow RXSn(acac)_2 + 2HX \qquad (54)$$

An alternative but less general method was later described by Bos et al. [144] by oxidative addition of :Sn(acac)$_2$ with MeI (eqn. (55)).

$$:Sn(acac)_2 + MeI \rightarrow MeISn(acac)_2 \qquad (55)$$

Kawasaki and Tanaka [187] ascribed the missing ^{115}Sn, ^{117}Sn and ^{119}Sn satellites in the ^{1}H NMR spectra of **71**, where Hdiket = Hacac, R = Ph and X = Cl or Br, to weaker Sn–O bonds compared to $X_2Sn(diket)_2$ analogues, as indicated by their stretching frequencies. Further IR studies were subsequently reported with more detailed assignments [188]. VT ^{1}H NMR data indicated a *cis* configuration at –30°C, *cis-trans* equilibrium 0–15°C and a *trans*-**71** configuration at 20°C, where Hdiket = Hacac or Hbzac, R = Me or Et and X = Cl or Br [234]. The long range Sn–H spin-spin coupling (^4J) in **71** has been analyzed by Kawasaki [235] using ^{1}H NMR at high temperatures (50–75°C). Results indicate that the couplings decrease in the order $X_2Sn(acac)_2 > RXSn(acac)_2 > R_2Sn(acac)_2$, consistent with the reduction in covalent character of the Sn–O bond.

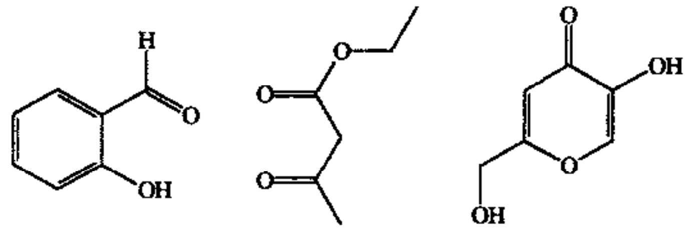
Serpone and co-workers [216,217] reported VT ^{1}H NMR analysis of various **71** complexes, where Hdiket = Hacac, R = Me or Ph and X = Cl, and concluded a predominantly *cis* configuration for the complexes, thus reassigning the configurations made earlier by Kawasaki and co-workers as described above. Kinetic studies indicated that the lability of the acetylacetonate decrease in the order $Ph_2Sn(acac)_2 > MeClSn(acac)_2 > PhClSn(acac)_2 > Cl_2Sn(acac)_2$. Permutational and mechanistic analysis support a twist mechanism for the configurational rearrangement.

Finally, Sharma et al. [236] reported the synthesis of ClYSn(diket)$_2$, where Hdiket = Hacac, Hbzac or Hdbzm and Y = S_2COMe, S_2CO-^{i}Pr or S_2CO-^{n}Bu. The complexes were characterized by elemental analysis, molecular weight determination, IR and ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. Results suggested a distorted *cis*-octahedral geometry with monodentate xanthate ligands.

(vi) Six-coordinate bis(bidentate ligand)tin(IV) complexes

(a) X_2SnL_2 complexes (L = bidentate chelate)

A bidentate ligand related to acetylacetone, the 1,3-diketoester, ethylacetoacetate (Hetac, Fig. 50) has been used to compare with $X_2Sn(acac)_2$ in terms of stereochemistry. Thus, the X-ray structure of $Cl_2Sn(etac)_2$ (**72**) (Fig. 51) show a distorted octahedral monomeric **72** unit analogous to **62** with the chlorine atoms in *cis* configuration (Fig. 45) [237]. The far IR analysis of X_2SnL_2 complexes by Douek et al. [190] involving the



Salicyaldehyde Ethylacetoacetate Kojic acid

Fig. 50. The structures of salicyaldehyde, ethylacetoacetate and kojic acid.

bis(acetylacetonato) derivatives have already been discussed. They also investigated the analogous complexes with HL = salicylaldehyde (Fig. 50) and again the configuration was not unequivocally established. Harrison et al. [238] reported the X-ray crystal structure of bis(*N*-phenylbenzohydroxamato)tin(IV) dichloride (Fig. 52). The structure possesses a distorted octahedral geometry with *cis*-chloride configuration. The Sn–O bond lengths and angles have been compared with **56** and the dimethyl analogue (see below).

The synthesis of a range of X_2SnL_2 complexes, where X = Cl, Br or I and HL = maltol, 3-hydroxypyridin-4-ones, tropolone, 3-hydroxypyridin-2-one and kojic acid (see Figs. 15 and 50) has recently been reported by Denekamp et al. [239]. The complexes were characterized by microanalysis, mass spectrometry, IR, ^{1}H, VT ^{1}H, ^{119}Sn

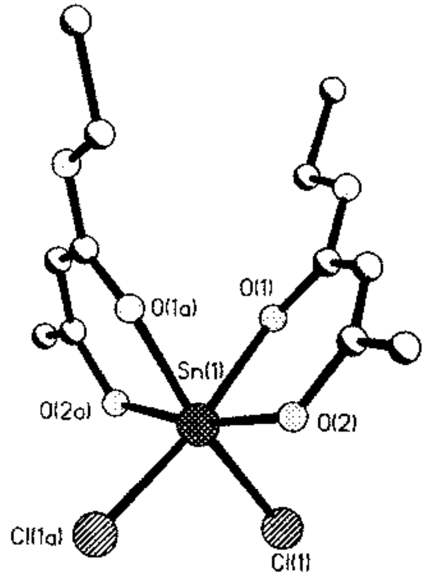


Fig. 51. The crystal structure of **72**.

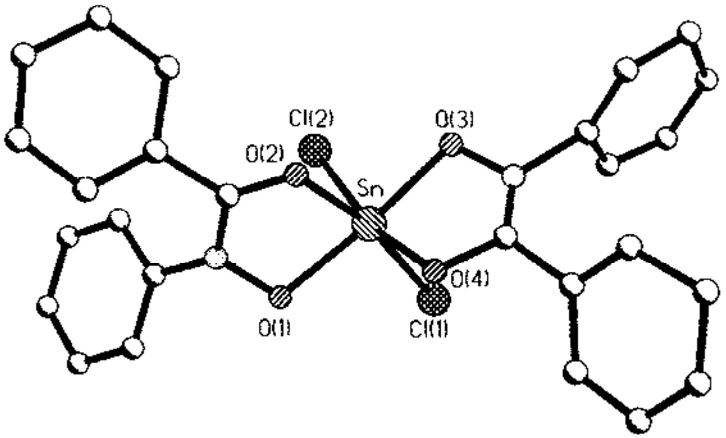


Fig. 52. The crystal structure of bis(*N*-phenylbenzohydroxamato)tin(IV) dichloride.

NMR spectroscopy. In addition, the X-ray crystal structures of both $Cl_2Sn(mal)_2$ and $Cl_2Sn(trop)_2$ (73) were reported (Figs. 53 and 54). Both structures show *cis*-chloride configurations in the solid state. The use of ^{119}Sn NMR spectroscopy to study the *cis-trans* isomerization showed partial separation of the five isomers produced by asymmetric HL ligands (Fig. 55). It was interesting to note the observation of both *cis* and *trans*-halide isomers in the 3-hydroxypyridin-4-onato analogues which reflect the strong Sn–O bonds in these examples. Different chemical shifts were assigned to *cis* and *trans*-halide isomers and in some cases, the tentative *cis-cis-cis* isomer was also separated. The effect of different halogens on the ^{119}Sn chemical shift has also been discussed.

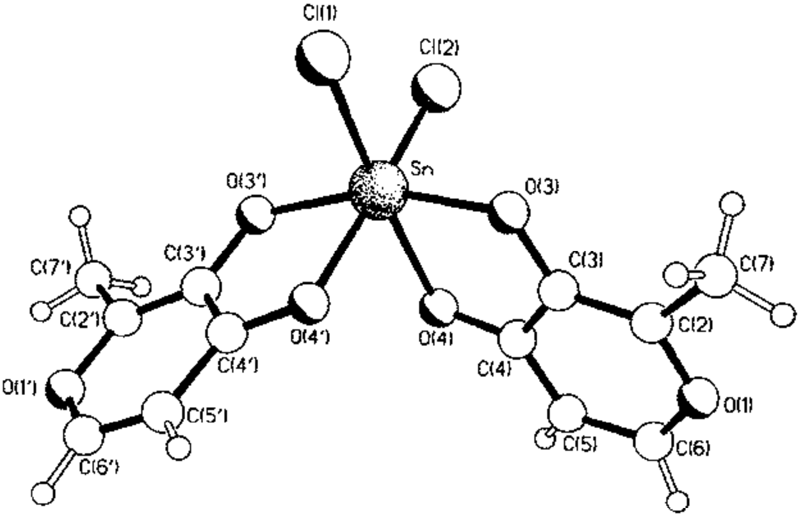


Fig. 53. The crystal structure of bis(maltolato)tin(IV) dichloride.

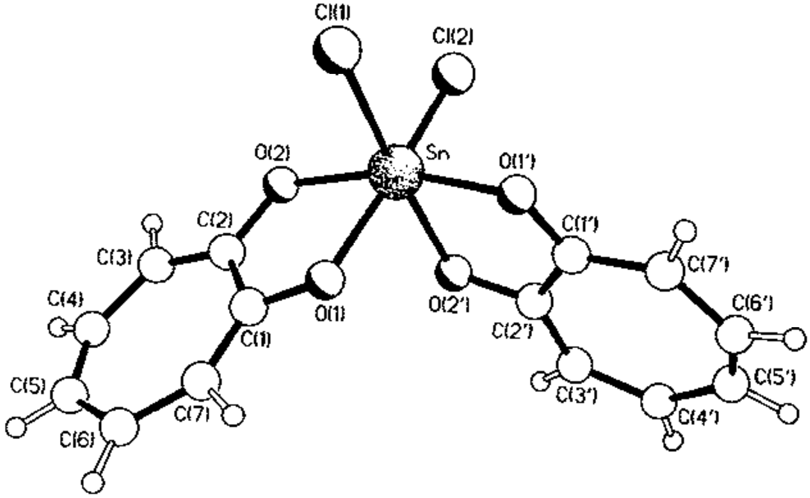
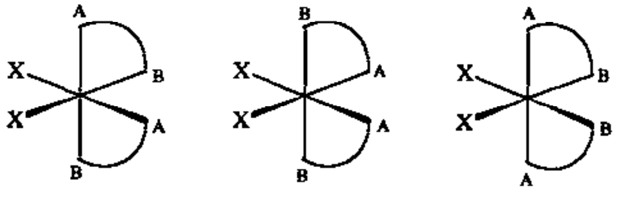
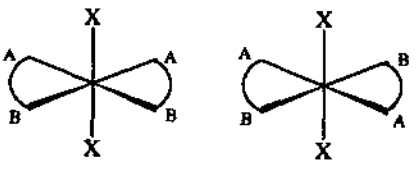


Fig. 54. The crystal structure of 73.

An alternative method for the synthesis of $I_2Sn(mal)_2$ was reported by Annan et al. [150] by oxidative addition of $:Sn(mal)_2$ with I_2. $X_2Sn(trop)_2$, where X = Cl, Br or I, have been previously prepared by Komura et al. [162]. Dipole moments and Kerr constants have been measured for 73 in solution [240]. The results also indicate a *cis*-chloride configuration and the dipole moments are in general larger than the acetylacetonato analogue.



cis-cis-cis *cis-cis-trans* *cis-trans-cis*



trans-cis-cis *trans-trans-trans*

Fig. 55. Geometrical isomers of six-coordinate bis(asymmetric bidentate ligand)dihalogeno complexes.

The kojic acid derivatives, $Cl_2Sn(koj)_2$ and $Br_2Sn(koj)_2$, where Hkoj = kojic acid, have been previously reported [241]. Long range ^4J(Sn–H) coupling was observed for the 3-proton and not the 6-proton. This observation suggested long range spin-spin couplings occur more strongly through the π-electron system of the C=O than through the σ-electron C–O bond in the kojate systems.

(b) R_2SnL_2 complexes

The chemistry of $R_2Sn(trop)_2$ complexes has been the subject of much research due to the similarities with the analogous $R_2Sn(acac)_2$ complexes. The principal difference between acetylacetone and tropolone as ligands is that the former chelates form six-membered rings and the latter chelates form five-membered rings. The work for the acetylacetonato derivatives have already been discussed (see above) and in many cases similar tropolonato derivatives were also reported: Komura et al. [162] prepared $R_2Sn(trop)_2$ complexes by reaction of dialkyl- or diphenyltin dichloride with the sodium salt of tropolone (eqn. (56)).

$$R_2SnCl_2 + 2Na(trop) \rightarrow R_2Sn(trop)_2 + 2NaCl, \quad R = Me, Et, {}^nPr, {}^nBu, Ph \tag{56}$$

Sage and Tobias [242] used ^1H NMR spectroscopy and utilized the heteronuclear Sn–H spin-spin couplings to assign a *cis* configuration for the complex, $Me_2Sn(trop)_2$ (74). Nelson and co-workers used IR, Raman spectroscopy [220], dipole moment measurements [213,240] and Kerr constants [240] to assign a *cis* geometry to **74**. They then used Rayleigh light scattering techniques [224] and refined Kerr constant calculations [221] to show the possibility of a *skew* geometry to account for the IR, Raman and dipole moment data in $Et_2Sn(trop)_2$. Otera and co-workers [226,227] used multinuclear ^1H, ^{13}C, ^{119}Sn NMR spectroscopy and the heteronuclear spin-spin couplings to relate to the

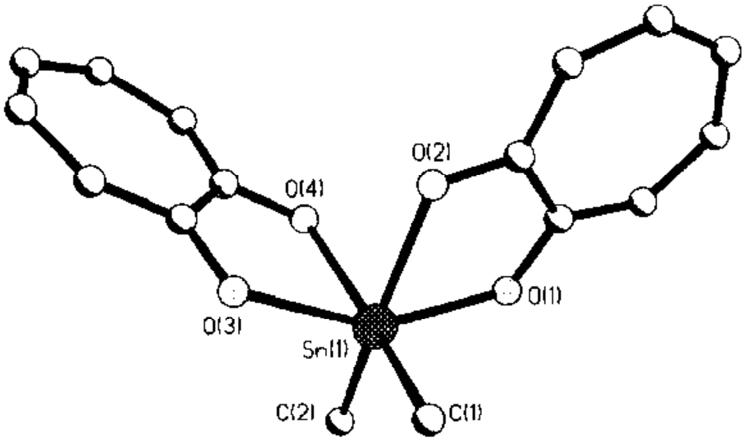


Fig. 56. The crystal structure of 74.

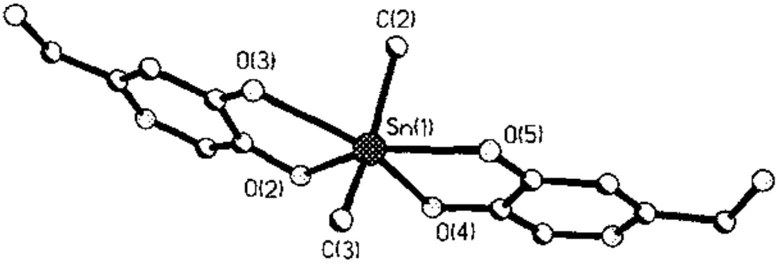


Fig. 57. The crystal structure of **75**.

C–Sn–C angle and thus the isomerization in **74** and ${}^{t}Bu_2Sn(trop)_2$. Later, Nelson and co-workers [228] using similar NMR studies backed other techniques described above, assigned the $R_2Sn(trop)_2$ complexes to the *skew* geometry in solution. Subsequently, Lockhart and co-workers used the spin-spin coupling results to accurately calculate the C–Sn–C angle [232]. They also determined the X-ray crystal structure of **74** (Fig. 56), which suggest a *cis* configuration for the complex [243].

On the basis of the long range ${}^{4}J$(Sn–H) coupling values in the ${}^{1}H$ NMR and the IR spectra, the geometry of $Me_2Sn(koj)_2$ (**75**) has been assigned as a distorted octahedron with a *trans* configuration in solution [241]. The X-ray crystal structure of **75** shows that the molecule adopts a *skew* geometry in the solid state (Fig. 57) [243].

Harrison and co-workers [244,245] have reported the X-ray crystal structures of bis(*N*-methylacetohydroxamato)dimethyltin(IV) (**76**) (Fig. 58) and bis(acetohydroxamato)dimethyltin(IV) (**77**) (Fig. 59). The structure of **76** is that of a distorted octahedron and an overall symmetry approximating C_{2v}, *skew* (C–Sn–C = 145.8°). The structure of **77** is also of a distorted octahedron but the stereochemistry of the anhydrous molecule (Fig. 59(a)) differs significantly from that of the monohydrated molecule (Fig. 59(b)). The anhydrous **77** molecule possesses a *cis* configuration (C–Sn–C = 109.1°) but the monohydrated **77** molecule is *skew* (mean C–Sn–C = 156.8°). The intermolecular

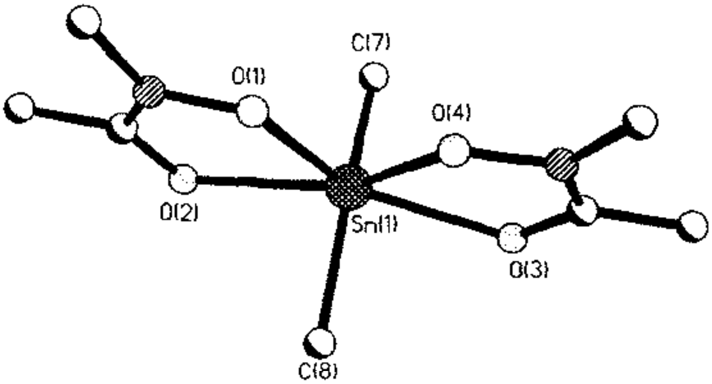


Fig. 58. The crystal structure of **76**.

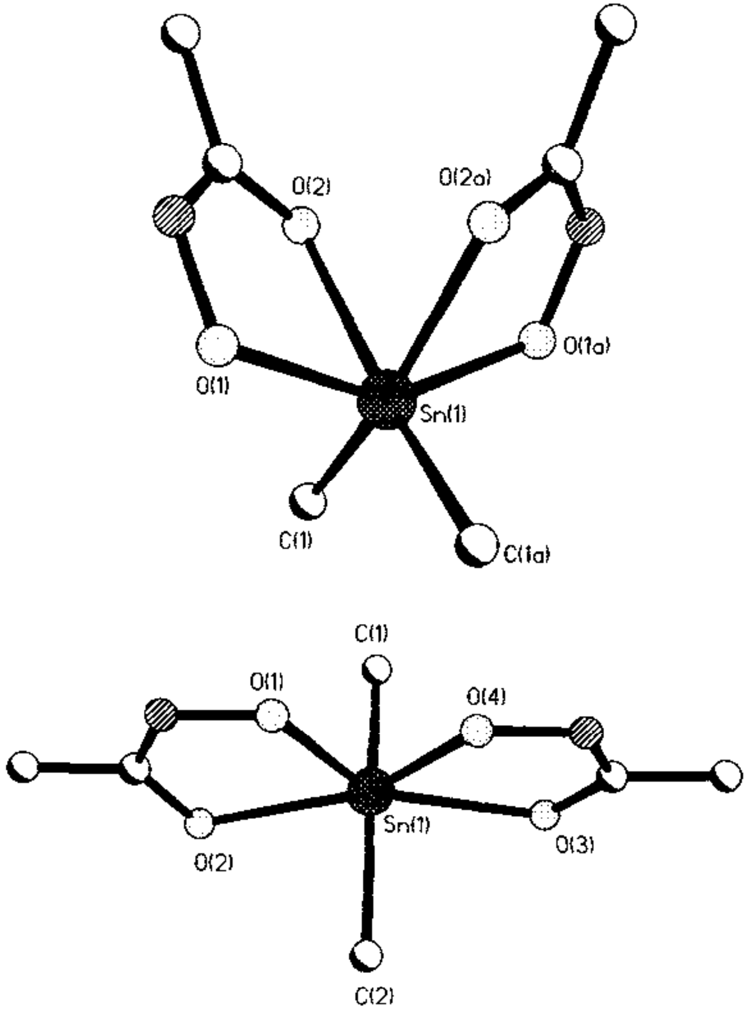


Fig. 59. (a) The crystal structure of *cis*-77. (b) The crystal structure of *skew*-77.

interactions are also very different between anhydrous and monohydrated forms. Das et al. [172] reported various R_2SnL_2 complexes derived from substituted hydroxamic acids. The complexes were characterized by UV, IR, NMR and Mössbauer spectroscopy. For $R = {}^nBu$, a distorted *trans*-octahedral geometry was proposed and for R = Ph, the *cis* configuration was proposed.

The 3-hydroxyflavone (Fig. 35) derivatives, $R_2Sn(hfo)_2$, where R = Me, Bu and Ph, have been characterized by ^{119}Sn NMR and Mössbauer spectroscopy [163]. The six-coordinate tin(IV) nucleus was evident from the ^{119}Sn NMR data and *cis*-phenyl, *trans*-alkyl configurations were assigned on the basis of the Mössbauer data.

Matsubayashi et al. [246] reported several tetrathiafulvalene and tetraselenafulvalene salts with the tin complexes, $[R_2Sn(ox)_2]^{2-}$, where R = Me or Et. The *cis* configuration was assigned based on the correlation of ^2J(Sn–C) with the C–Sn–C angles.

(vii) Tris(bidentate ligand)tin(IV) complexes

The formation of tris(catecholato)tin(IV) complexes was first reported by Weinland and Maier in 1926 [247]. The dianionic complex, $[Sn(cat)_3]^{2-}$ (78) was synthesized using tin tetrachloride and catechol in water, in the presence of a base, e.g. eqn. (57).

$$SnCl_4 + 3H_2cat + 2NH_3 \rightarrow [NH_4]_2[Sn(cat)_3] + 4HCl \qquad (57)$$

Surprisingly, there has been little development of the chemistry of these complexes since this early report. Parr [126] has synthesized a range of tris(catecholato)tin(IV) complexes derived from catechol and substituted catechols (e.g. 4-cyano-, 4-methyl-, 4-nitro-, 4,5-dinitro-, 4-chloro- and 4,5-dichlorocatechol). The complexes were characterized by microanalysis, IR, ^1H and ^{119}Sn NMR spectroscopy. Asymmetric catechols complex to give *fac* and *mer* isomers in solution as observed for the analogous silicon(IV) and germanium(IV) complexes (see above). The existence of this isomerization alone is evidence for six-coordinate tin in solution. Further support for the regular six-coordinate geometry was given by the proton-coupled ^{119}Sn NMR spectrum of 78, which shows the presence of ^4J(Sn–H) and ^5J(Sn–H) with values that overlap ($^4J \sim 3 \times {}^5J$) and thus simplify the otherwise complicated heptuplet of heptuplets (Fig. 60). Both the analogous silicon [34] and the tin complexes show linear relationships between the NMR chemical shift and the sum of the Hammett factors due to substituents on the catechol. Thus, a plot of the ^{119}Sn versus ^{29}Si NMR chemical shifts also shows a linear relationship for analogous catecholates.

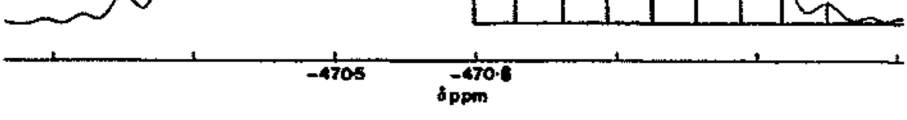


Fig. 60. Proton-coupled ^{119}Sn NMR spectrum (93.28 MHz, D_2O) of 78 with superimposed stick diagram showing the expected intensities for a heptuplet of heptuplets normalized to the central peak as unity ($^4J = 3 \times {}^5J$).

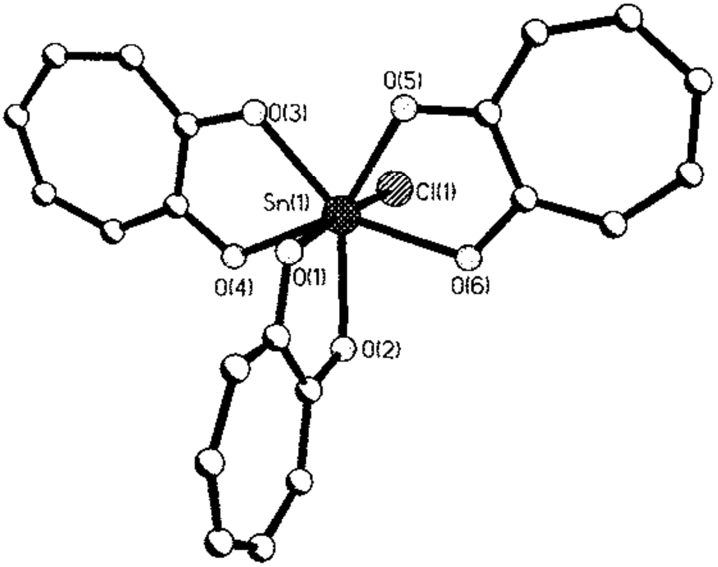


Fig. 61. The crystal structure of 79.

The tris(tropolonato)tin(IV) derivatives, ClSn(trop)$_3$ (**79**) and PhSn(trop)$_3$ (**80**), were first reported by Muetterties and Wright in 1964 [85]. The complex **79** was synthesized by reaction of tin tetrachloride with sodium tropolonate. Similarly, phenyltin trichloride and tropolone reacted to give PhClSn(trop)$_2$, which was converted to PhSn(trop)$_3$ (**80**) by subsequent reaction with sodium tropolonate. The non-electrolytic character, solubility and the molecular weight determination of **80** led them to suggest a seven-coordinated tin atom for both **79** and **80**. The eight-coordinate Sn(trop)$_4$ complex was also proposed based on comparative IR spectra (with Ce(trop)$_4$ and Zr(trop)$_4$). The X-ray crystal structures of the seven-coordinate complexes, **79** and HOSn(trop)$_3$, reveal similar geometries approximating to pentagonal-bipyramid (Fig. 61) [248]. The structures are almost iso-dimensional with the exception of the Sn–X bond length, where X = OH or Cl. ^{119}Sn NMR resonances of these seven-coordinate complexes show chemical shifts appreciably upfield (ca. 200 ppm) from typical six-coordinate oxygen donor complexes and the mass spectra indicate fragments with preservation of Sn–Cl bonds [127].

The 3-hydroxypyridin-4-onato derivatives (see Fig. 15), [SnL3]$^+$, were described as salts on evidence from ^{119}Sn NMR and mass spectrometry analysis [127]. For coordinated Sn–X, where X = Cl, Br or I, the chemical shift of the ^{119}Sn would be expected to change appreciably as observed for the tropolonato derivatives. Absence of Sn–X bonded fragments in the mass spectra as observed for the tropolonato derivatives also indicate ion-separated species.

Mixed SnL$_2$L' neutral complexes, where L = monobasic ligand (e.g. kojic acid) and L' = dibasic ligand (e.g. catechol), have been prepared by three methods (eqns. (58) [150], (59) and (60) [127]).

$$:SnL_2 + Q \rightarrow SnL_2(cat), \quad Q = \text{orthoquinone} \tag{58}$$

$$I_2SnL_2 + H_2L \rightarrow SnL_2L' + 2HI \tag{59}$$

$$SnI_4 + 2HL + H_2L' \rightarrow SnL_2L' + 4HI \tag{60}$$

ACKNOWLEDGEMENTS

C.Y.W. thanks the SERC for a grant.

REFERENCES

1 See for example: A.R. Siedle, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 2., Pergamon Press, Oxford, 1987, p. 365; C. G. Pierpont and R. M. Buchanan, Coord. Chem. Rev., 38 (1981) 45; D.A. Thornton, Coord. Chem. Rev., 104 (1990) 173.

2 P.G. Harrison, Coord. Chem. Rev., 102 (1990) 234; 85 (1988) 193; 75 (1986) 200; 66 (1985) 190; 56 (1984) 189; 49 (1983) 193; 40 (1982) 179; 34 (1981) 154; 30 (1979) 137.

3 L. Addadi and S. Weiner, Angew. Chem., Int. Ed. Engl., 31 (1992) 153.

4 R.J.P. Williams, J. Chem. Soc., Dalton Trans., (1991) 539; Coord. Chem. Rev., 100 (1990) 573.

5 S. Mann, New Scientist, 125(1707) (1990) 42.

6 J.D. Birchall, Chem. Ber., 26 (1990) 141.

7 S. Mann, J. Webb and R.J.P. Williams (Eds), Biomineralization, Chemical and Biochemical Perspectives, VCH, New York, 1989.

8 G. Bendz and I. Lindquist (Eds), Biochemistry of Silicon and Related Problems, Plenum Press, New York, 1978.

9 T.L. Simpson and B.E. Volcani (Eds), Silicon and Siliceous Structures in Biological Systems, Springer-Verlag, New York, 1981.

10 R.K. Iler, The Chemistry of Silica, Wiley, New York, 1979.

11 L.H. Sommer, Stereochemistry and Mechanisms in Silicon. McGraw-Hill, New York, 1965.

12 H. Meyer and G. Nargorsen, Angew. Chem., Int. Ed. Engl., 18 (1979) 551.

13 E.H. Würthwein and P.V.R. Schleyer, Angew. Chem., Int. Ed. Engl., 18 (1979) 553.

14 J.D. Dunitz, Angew. Chem., Int. Ed. Engl., 19 (1980) 1034.

15 G. Nargorsen and H. Meyer, Angew. Chem., Int. Ed. Engl., 19 (1980) 1034.

16 D. Schomburg, Angew. Chem., Int. Ed. Engl., 22 (1983) 65.

17 J.J. Zuckerman, W. Bibber, C.L. Barnes, D.V.D. Helm, Angew. Chem., Int. Ed. Engl., 22 (1983) 501.

18 W. Hönle, U. Dettlaff-Weglikowska, L. Walz and H. G. V. Schnering, Angew. Chem., Int. Ed. Engl., 28 (1989) 623.

19 S.N. Tandura, M.G. Voronkov and N.V. Alekseev, Top. Curr. Chem., 131 (1986) 99.

20 R.J.P. Corriu and C. Guerin, Adv. Organomet. Chem., 20 (1982) 265 and refs. therein.

21 R.J.P. Corriu, C. Guerin and J.J.E. Moreau, Top. Stereochem., 15 (1984) 48; R.J.P. Corriu, C. Guerin and J.J.E. Moreau, in S. Patai and Z. Rappoport (Eds.), Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, Part I, p. 305.

22 R.R. Holmes, Chem. Rev., 90 (1990) 17 and refs. therein.

23 J.J. Harland, R.O. Day, J.F. Vollano, A.C. Sau and R.R. Holmes, J. Am. Chem. Soc., 103 (1981) 5269.

24 R.R. Holmes, R.O. Day, J.J. Harland, A.C. Sau and J.M. Holmes, Organometallics, 3 (1984) 341.
25. R.R. Holmes, R.O. Day, J.J. Harland and J.M. Holmes, Organometallics, 3 (1984) 347.
26 R.R. Holmes, R.O. Day, V. Chandrasekhar and J.M. Holmes, Inorg. Chem., 24 (1985) 2009.
27 R.R. Holmes, R.O. Day, V. Chandrasekhar, J.J. Harland and J.M. Holmes, Inorg. Chem., 24 (1985) 2016.
28 K.C.K. Swarmy, V. Chandrasekhar, J.J. Harland, J.M. Holmes and R.R. Holmes, J. Am. Chem. Soc., 112 (1990) 2341.
29 R.R. Holmes, R.O. Day and J.S. Payne, Phosphorus Sulfur, 42 (1989) 1.
30 K.C.K. Swarmy, C. Sreelatha, R.O. Day, J.M. Holmes and R.R. Holmes, Inorg. Chem., 30 (1991) 3126.
31 J.A. Cella, J.D. Cargioli and E.A. Williams, J. Organomet. Chem., 186 (1980) 13.
32 E.A. Williams and J.D. Cargioli, Annu. Rep. N.M.R. Spectrosc., 9 (1979) 221.
33 E.A. Williams, Annu. Rep. N.M.R. Spectrosc., 15 (1983) 235.
34 D.F. Evans, J. Parr and E.N. Coker, Polyhedron, 9 (1990) 813.
35 D.F. Evans and C.Y. Wong, Polyhedron, 10 (1991) 1131.
36 D.F. Evans, J. Parr and C.Y. Wong, Polyhedron, 11 (1992) 567.
37 D.F. Evans, A.M. Z. Slawin, D.J. Williams, C.Y. Wong and J.D. Woollins, J. Chem. Soc., Dalton Trans., (1992) 2383.
38 S. Sjöberg, N. Ingri, A.M. Nenner and L.O. Öhman, J. Inorg. Biochem., 24 (1985) 267.
39 C.L. Frye, J. Org. Chem., 34 (1969) 2496.
40 R. Müller and L. Heinrich, Chem. Ber., 94 (1961) 1943.
41 W. Ando and M. Ikeno, J. Chem. Soc., Chem. Commun., (1979) 655.
42 R. Schwarz and W. Kuchen, Z. Anorg. Allg. Chem., 266 (1951) 185.
43 H.R. Allcock, T.A. Nugent and L.A. Smeltz, Synth. Inorg. Met.-Org. Chem., 2 (1972) 97.
44 R. Schwarz and W. Kuchen, Z. Anorg. Allg. Chem., 279 (1955) 84.
45 J.J. Zuckerman, J. Chem. Soc., (1962) 873.
46 F.A. Gianturco, J. Chem. Soc. A, (1969) 1293.
47 C.L. Frye, J. Am. Chem. Soc., 92 (1970) 1205.
48 D. Schomburg, Z. Naturforsch., 37B (1982) 195.
49 D. Schomburg, Z. Naturforsch., 38B (1983) 938.
50 R.M. Laine, K.Y. Blohowiak, T.R. Robinson, M.L. Hoppe, P. Nardi, J. Kampf and J. Uhm, Nature, 353 (1991) 642.
51 G. Schott and K. Golz, Z Anorg. Allg. Chem., 383 (1971) 314.
52 C.L. Frye, J. Am. Chem. Soc., 86 (1964) 3170.
53 F.P. Boer, J.J. Flynn and J.W. Turley, J. Am. Chem. Soc., 90 (1968) 6973.
54 R.R. Holmes and J.A. Deiters, J. Am. Chem. Soc., 99 (1977) 3318.
55 R.R. Holmes, Acc. Chem. Res., 2 (1979) 257.
56 R.R. Holmes, Pentacoordinated Phosphorus – Structure and Spectroscopy, ACS Monograph 175, ACS, Washington, DC, 1980, Vol. 1.
57 R.R. Holmes, Prog. Inorg. Chem., 32 (1984) Ch. 2.
58 E. Hey-Hawkins, U. Dettlaff-Weglikowska, D. Thiery and H.G.V. Schnering, Polyhedron, 11 (1992) 1789.
59 R.S. Berry, J. Chem. Phys., 32 (1960) 933.
60 R.O. Day, C. Sreelatha, J.A. Deiters, S.E. Johnson, J.M. Holmes, L. Howe and R.R. Holmes, Organometallics, 10 (1991) 1758.
61 A. Boudin, G. Cerveau, C. Chuit, R.J.P. Corriu and C. Reye, Angew. Chem., Int. Ed. Engl., 25 (1986) 473.

62 W. Dilthey, Chem. Ber., 36 (1903) 923, 1595, 3207; W. Dilthey, Ann. Chem., 344 (1906) 300; A. Rosenheim, W. Loewenstamm and L. Singer, Chem. Ber., 36 (1903) 1833.
63 R.M. Pike, Coord. Chem. Rev., 2 (1967) 163.
64 R. West, J. Am. Chem. Soc., 80 (1958) 3246.
65 R.E. Harter, Chem. Ind. (London), (1963) 1397.
66 S.K. Dhar, V. Doron and S. Kirschner, J. Am. Chem. Soc., 80 (1958) 753; 81 (1959) 6372.
67 E. Larsen, S.F. Mason and G.H. Searle, Acta. Chem. Scand., 20 (1966) 191.
68 T. Inoue and K. Saito, Bull. Chem. Soc. Jpn., 46 (1973) 2417.
69 T. Shimizutani and Y. Yoshikawa, Inorg. Chem., 30 (1991) 3236.
70 R.G. Pearson, D.N. Edginton and F. Basolo, J. Am. Chem. Soc., 84 (1962) 3234.
71 E.L. Muetterties and C.M. Wright, J. Am. Chem. Soc., 87 (1965) 21.
72 R.M. Pike and R.R. Luongo, J. Am. Chem. Soc., 87 (1965) 1403; 88 (1966) 2972.
73 C.E. Holloway, R.R. Luongo and R.M. Pike, J. Am. Chem. Soc., 88 (1966) 2060.
74 D.W. Thompson, Inorg. Chem., 8 (1969) 2015.
75 N. Serpone and K.A. Hersh, J. Organomet. Chem., 84 (1975) 177.
76 D.T. Haworth, G.Y. Lin and C.A. Wilkie, Inorg. Chem. Acta, 40 (1980) 119.
77 A. Rosenheim and O. Sorge, Chem. Ber., 53 (1920) 932.
78 J.J. Flynn and F.P. Boer, J. Am. Chem. Soc., 91 (1969) 5756.
79 A. Rosenheim, B. Raibmann and G. Schendel, Z. Anorg. Allg. Chem., 96 (1931) 160.
80 H. Bartels, Helv. Chim. Acta, 47 (1964) 1605.
81 H. Baumann, Bietr. Silikose Forch. Sonderb., 5 (1960) 11.
82 L.O. Öhman, A. Nordin, I.F. Sedeh and S. Sjöberg, Acta Chem. Scand., 45 (1991) 335.
83 A. Boudin, G. Cerveau, C. Chuit, R.J.P. Corriu and C. Reye, Angew. Chem., Int. Ed. Engl., 25 (1986) 474.
84 A. Boudin, G. Cerveau, C. Chuit, R.J.P. Corriu and C. Reye, Organometallics, 7 (1988) 1165.
85 E.L. Muetterties and C.M. Wright, J. Am. Chem. Soc., 86 (1964) 5132.
86 E.L. Muetterties and C.W. Alegrati, J. Am. Chem. Soc., 91 (1969) 4420.
87 T. Ito, N. Tanaka, I. Hanazaki and S. Nagakura, Inorg. Nucl. Chem. Lett., 5 (1969) 781.
88 T. Inoue, Inorg. Chem., 22 (1983) 2435.
89 P.A.W. Dean, D.F. Evans and R.F. Phillips, J. Chem. Soc. A, (1969) 363.
90 G. Schott and D. Lange, Z. Anorg. Allg. Chem., 391 (1972) 27.
91 A. Weiss and D.R. Harvey, Angew. Chem., Int. Ed. Engl., 3 (1964) 698.
92 D.F. Evans and C.Y. Wong, unpublished work.
93 A. Reisman, M. Berkenblit, S.A. Chen, F.B. Kaufman and D.C. Green, J. Electrochem. Soc., 126 (1979) 1406.
94 F. Glocking, The Chemistry of Germanium, Academic Press, London, 1969.
95 S.R. Stobart, M.R. Churchill, F.J. Hollander and W.J. Youngs, J. Chem. Soc., Chem. Commun., (1979) 911.
96 H. Lavayssiere, G. Dousse and J. Satge, J. Organomet. Chem., 137 (1977) C37.
97 H. Lavayssiere and G. Dousse, J. Organomet. Chem., 297 (1985) C17 and refs. therein.
98 E. Michels and W.P. Neumann, Tetrahedron Lett., 27 (1986) 2455.
99 P. Rivière, A. Castel, J. Satgé and D. Guyot, J. Organomet. Chem., 315 (1986) 157.
100 R.H. Cragg and M. Nazery, J. Organomet. Chem., 71 (1974) 225.
101 R. Müller and L. Heinrich, Chem. Ber., 95 (1962) 2276.
102 C.M.S. Yoder and J.J. Zuckerman, Inorg. Chem., 6 (1967) 163.
103 A.C. Sau, R.O. Day and R.R. Holmes, J. Am. Chem. Soc., 102 (1980) 7973.
104 A.C. Sau and R.R. Holmes, Inorg. Chem., 20 (1981) 4129.

105 R.O. Day, J.M. Holmes, A.C. Sau and R.R. Holmes, Inorg. Chem., 21 (1982) 281.
106 R.R. Holmes, R.O. Day, A.C. Sau, C.A. Poutasse and J.M. Holmes, Inorg. Chem., 24 (1985) 193.
107 P. Bévillard, Bull. Soc. Chim. Fr., (1954) 304.
108 G.I. Kurnevich and V.B. Vishnevskii, J. Appl. Spectrosc. (Engl. transl.), 13 (1970) 1201.
109 G.A. Shagisultanova, G.I. Kurnevich, V.B. Vishnevskii and I.V. Bogdanova, Russ. J. Inorg. Chem. (Engl. transl.), 15 (1970) 1647.
110 G.T. Morgan and H.D.K. Drew, J. Chem. Soc., (1924) 1261.
111 M. Cox, J. Lewis and R.S. Nyholm, J. Chem. Soc., (1964) 6113.
112 J.A.S. Smith and E.J. Wilkins, J. Chem. Soc. A, (1966) 1749.
113 T.J. Pinnavalia, L.J. Matienzo and Y.A. Peters, Inorg. Chem., 9 (1970) 993.
114 R.C. Mehrotra and S. Mathur, J. Organomet. Chem., 6 (1966) 11.
115 N. Jorgensen and T.J.R. Weakley, J. Chem. Soc., Dalton Trans., (1980) 2051.
116 W.K. Ong and R.H. Prince, J. Inorg. Nucl. Chem., 27 (1965) 1037.
117 A. Nagasawa and K. Saito, Bull. Chem. Soc. Jpn., 47 (1974) 131.
118 F.B. Ueno, A. Nagasawa and K. Saito, Inorg. Chem., 20 (1981) 3504.
119 A. Nagasawa and K. Saito, Bull. Chem. Soc. Jpn., 51 (1978) 2015.
120 T. Ito, K. Toriumi, F.B. Ueno and K. Saito, Acta Crystallogr., Sect B, 36 (1980) 2998.
121 P. Bévillard, Bull. Soc. Chim. Fr., (1954) 296.
122 A.M. Andrianov and V.A. Nazarenko, Russ. J. Inorg. Chem. (Engl. transl.), 8 (1963) 1194.
123 P.J. Antikainen and V.M.K. Rossi, Suomen Kem., B32 (1959) 185.
124 P. Pichet and R.L. Benoit, Inorg. Chem., 6 (1967) 1505.
125 P.J. Antikainen and H. Oksanen, Acta Chem. Scand., 22 (1968) 2867.
126 J. Parr, PhD thesis, University of London, London, 1989.
127 C.I.F. Denekamp, PhD thesis, University of London, London, 1992.
128 P.G. Harrison (Ed.), Chemistry of Tin, Chapman and Hall, New York, 1989.
129 WHO, Reports and Studies 22: Review of Potentially Harmful Substances – Cadmium, Lead and Tin, World Health Organization, Geneva, 1983.
130 N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984.
131 D. Searle, P.J. Smith, N.A. Bell, L.A. March, I.W. Nowell and J.D. Donaldson, Inorg. Chim. Acta, 162 (1989) 143 and refs. therein.
132 M. Veith and O. Recktenwald, Top. Curr. Chem., 104 (1982) 1.
133 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251.
134 R. Merten and G. Loew, U.S. Patent No. 3,055,845 (1962); Chem. Abstr., 58 (1963) 11548.
135 J.J. Zuckerman, Adv. Organomet. Chem., 9 (1970) 21.
136 J.J. Zuckerman, J. Chem. Soc., (1963) 1322.
137 J.C. Maire, Ann. Chim. (Paris), 6 (1961) 969.
138 E. Amberger and M.R. Kula, Chem. Ber., 96 (1963) 2562.
139 H.J. Emeléus and J.J. Zuckerman, J. Organomet. Chem., 1 (1964) 328.
140 G.T. Cocks and J.J. Zuckerman, Inorg. Chem., 4 (1965) 592.
141 D.E. Fenton, R.R. Gould, P.G. Harrison, T.B. Harvey, III, G.M. Omietanski, K.C.T. Sze and J.J. Zuckerman, Inorg. Chim. Acta, 4 (1970) 235.
142 W.D. Honnick and J.J. Zuckerman, Inorg. Chem., 17 (1978) 501.
143 A.D. Christie, R.A. Howie and W. Moser, Inorg. Chim. Acta, 36 (1979) L447.
144 K.D. Bos, H.A. Budding, E.J. Bulten and J.G. Noltes, Inorg. Nucl. Chem. Lett., 9 (1973) 961.
145 P.G. Harrison, J. Chem. Soc., Chem. Commun., (1972) 544.
146 P.F.R. Ewings, D.E. Fenton and P.G. Harrison, J. Chem. Soc., Dalton Trans., (1975) 821.

147 P.F.R. Ewings, P.G. Harrison and T.J. King, J. Chem. Soc., Dalton Trans., (1975) 1455.
148 A.B. Cornwell and P.G. Harrison, J. Chem. Soc., Dalton Trans., (1975) 1722.
149 B.P. Bachlas, H. Sharma, J.C. Maire and J.J. Zuckerman, Inorg. Chim. Acta, 71 (1983) 227.
150 T.A. Annan, C. Peppe and D.G. Tuck, Can. J. Chem., 68 (1990) 1598.
151 K. Hillner and W.P. Neumann, Tetrahedron Lett., 27 (1986) 5347.
152 I. Wakeshima and I. Kijima, Bull. Chem. Soc. Jpn., 54 (1981) 2345.
153 K.H. Scherping and W.P. Neumann, Organometallics, 1 (1982) 1017.
154 W.P. Neumann and A. Schwarz, Angew. Chem., Int. Ed. Engl., 14 (1975) 812.
155 J. Bornstein, B.R. LaLiberte, T.M. Andrews and J.C. Montermoso, J. Org. Chem., 24 (1959) 886.
156 R.C. Mehrotra and V.D. Gupta, J. Organomet. Chem., 4 (1965) 145.
157 W.J. Considine, J. Organomet. Chem., 5 (1966) 263.
158 J.C. Pommier and J. Valade, J. Organomet. Chem., 12 (1968) 433.
159 P.J. Smith, R.F.M. White and L. Smith, J. Organomet. Chem., 40 (1972) 341.
160 B. Sugavanam, F.E. Smith, S. Haynes and S. King, Publ. No. 607, Int. Tin Res. Inst., London, 1981.
161 S.J. Blunden and R. Hill, Inorg. Chim. Acta, 98 (1985) L7 and refs. therein.
162 M. Komura, T. Tanaka and R. Okawara, Inorg. Chim. Acta, 2 (1968) 321.
163 S.J. Blunden and P.J. Smith, J. Organomet. Chem., 226 (1982) 157.
164 R.C. Mehrotra and V.D. Gupta, J. Organomet. Chem., 4 (1965) 237.
165 C. Cauletti, C. Furlani and M.N. Piancastelli, J. Organomet. Chem., 49 (1978) 289.
166 G.M. Bancroft, B.W. Davies, N.C. Payne and T.K. Sham, J. Chem. Soc., Dalton Trans., (1975) 973.
167 A. Kumar, B.P. Bachlas and J.C. Maire, Polyhedron, 2 (1983) 907.
168 P.G. Harrison, Inorg. Chem., 12 (1973) 1545.
169 T.J. King and P.G. Harrison, J. Chem. Soc., Chem. Commun., (1972) 815.
170 P.G. Harrison and T.J. King, J. Chem. Soc., Dalton Trans., (1974) 2298.
171 P.G. Harrison, T.J. King and K.C. Molloy, J. Organomet. Chem., 185 (1980) 199.
172 M.K. Das, M. Nath and J.J. Zuckerman, Inorg. Chim. Acta, 71 (1983) 49.
173 E.L. Muetterties, J. Am. Chem. Soc., 82 (1960) 1082.
174 A.L. Allred and D.W. Thompson, Inorg. Chem., 7 (1968) 1196.
175 G.M. Bancroft and T.K. Sham, Can. J. Chem., 52 (1974) 1360.
176 D.W. Thompson, J.F. Lefelhocz and K.S. Wong, Inorg. Chem., 11 (1972) 1139.
177 D.W. Thompson and J.F. Lefelhocz, J. Organomet. Chem., 47 (1973) 103.
178 M. Yasuda and R.S. Tobias, Inorg. Chem., 2 (1963) 207.
179 Y. Kawasaki and R. Okawara, J. Inorg. Nucl. Chem., 27 (1965) 1168.
180 P. Finocchiaro, J. Organomet. Chem., 146 (1978) 229.
181 T.N. Mitchell, J. Organomet. Chem., 59 (1973) 189.
182 A.H. Westlake and D.F. Martin, J. Inorg. Nucl. Chem., 27 (1965) 1579.
183 M. Komura, T. Tanaka, T. Mukai and R. Okawara, Inorg. Nucl. Chem. Lett., 3 (1967) 17.
184 G.T. Morgan and H.D.K. Drew, J. Chem. Soc., (1924) 372.
185 W.H. Nelson and D.F. Martin, J. Organomet. Chem., 4 (1965) 67.
186 J.A.S. Smith and E.J. Wilkins, J. Chem. Soc., Chem. Commun., (1965) 381.
187 Y. Kawasaki and T. Tanaka, J. Chem. Phys., 43 (1965) 3396.
188 Y. Kawasaki, T. Tanaka and R. Okawara, Spectrochim. Acta, 22 (1966) 1571.
189 Y. Kawasaki and T. Tanaka, Inorg. Nucl. Chem. Lett., 3 (1967) 13.
190 I. Douek, M.J. Frazer, Z. Goffer, M. Goldstein, B. Rimmer and H.A. Willis, Spectrochim. Acta, Part A, 23 (1967) 373.
191 V. Doron and C. Fischer, Inorg. Chem., 6 (1967) 1917.

192 W.H. Nelson, Inorg. Chem., 6 (1967) 1509.
193 J.W. Faller and A. Davison, Inorg. Chem., 6 (1967) 182.
194 C.Z. Moore and W.H. Nelson, Inorg. Chem., 8 (1969) 143.
195 N. Serpone and R.C. Fay, Inorg. Chem., 8 (1969) 2379.
196 G.E. Glass and R.S. Tobias, J. Organomet. Chem., 15 (1968) 481.
197 E.L. Muetterties, J. Am. Chem. Soc., 90 (1968) 5097.
198 R.W. Jones, Jr. and R.C. Fay, Inorg. Chem., 12 (1973) 2599.
199 Y. Kawasaki, T. Tanaka and R. Okawara, Bull. Chem. Soc. Jpn., 40 (1967) 1562.
200 C.A. Wilkie, G.Y. Lin, W.R. Snyder and D.T. Haworth, Inorg. Chim. Acta, 33 (1979) L121.
201 G.A. Miller and E.O. Schlemper, Inorg. Chim. Acta, 30 (1978) 131.
202 M. Webster and J.S. Wood, J. Chem. Res. (S), (1981) 40.
203 F.S. Delk and D.W. Thompson, J. Chem. Soc., Dalton Trans., (1981) 1235.
204 N.N. Greenwood and J.N.R. Ruddick, J. Chem. Soc. A, (1967) 1679.
205 Y. Kawasaki, T. Tanaka and R. Okawara, Bull. Chem. Soc. Jpn., 37 (1964) 903.
206 W.H. Nelson and D.F. Martin, J. Inorg. Nucl. Chem., 27 (1965) 89.
207 M.M. McGrady and R.S. Tobias, J. Am. Chem. Soc., 87 (1965) 1909.
208 R. Ueeda, Y. Kawasaki, T. Tanaka and R. Okawara, J. Organomet. Chem., 5 (1966) 194.
209 B.W. Fitzsimmons, N.J. Seeley and A.W. Smith, J. Chem. Soc., Chem. Commun., 55 (1977) 390; J. Chem. Soc. A, (1969) 143.
210 T.K. Sham, J.S. Tse, V. Wellington and G.M. Bancroft, Can. J. Chem., 55 (1977) 3487.
211 C.Z. Moore and W.H. Nelson, Inorg. Chem., 8 (1969) 138.
212 J.W. Hayes, R.J.W. LeFèvre and D.V. Radford, Inorg. Chem., 9 (1970) 400.
213 J.W. Hayes, W.H. Nelson and D.V. Radford, Aust. J. Chem., 26 (1973) 871.
214 N. Serpone and K.A. Hersh, Inorg. Nucl. Chem. Lett., 7 (1971) 115.
215 N. Serpone and R. Ishayek, Inorg. Chem., 13 (1974) 52.
216 N. Serpone and K.A. Hersh, Inorg. Chem., 13 (1974) 2901.
217 D.G. Bickley and N. Serpone, Inorg. Chem., 13 (1974) 2908.
218 G.A. Miller and E.O. Schlemper, Inorg. Chem., 12 (1973) 677.
219 V.B. Ramos and R.S. Tobias, Spectrochim. Acta, Part A, 29 (1973) 953.
220 R.B. LeBlanc, Jr. and W.H. Nelson, J. Organomet. Chem., 113 (1976) 257.
221 N. Asting and W.H. Nelson, Inorg. Chem., 16 (1977) 148.
222 W.F. Howard, Jr. and W.H. Nelson, Inorg. Chem., 21 (1982) 2283.
223 W.H. Nelson, W.F. Howard, Jr. and R. Pecora, Inorg. Chem., 21 (1982) 1483.
224 S.K. Brahma and W.H. Nelson, Inorg. Chem., 21 (1982) 4076.
225 J. Otera, J. Organomet. Chem., 221 (1981) 57.
226 J. Otera, T. Hinoishi, Y. Kawabe and R. Okawara, Chem. Lett., (1981) 273.
227 J. Otera, T. Yano and K. Kusakabe, Bull. Chem. Soc. Jpn., 56 (1983) 1057.
228 W.F. Howard, Jr., R.W. Creceley and W.H. Nelson, Inorg. Chem., 24 (1985) 2204.
229 W.F. Manders and T.P. Lockhart, J. Organomet. Chem., 297 (1985) 143.
230 T.P. Kockhart, W.F. Manders and J.J. Zuckerman, J. Am. Chem. Soc., 107 (1985) 4546.
231 T.P. Lockhart, W.F. Manders, E.O. Schlemper and J.J. Zuckerman, J. Am. Chem. Soc., 108 (1986) 4074.
232 T.P. Lockhart and W.F. Manders, Inorg. Chem., 25 (1986) 892.
233 C.D. Chandler, G.D. Fallon, A.J. Koplick and B.O. West, Aust. J. Chem., 40 (1987) 1427.
234 Y. Kawasaki, T. Tananka and R. Okawara, Inorg. Nucl. Chem. Lett., 2 (1966) 9.
235 Y. Kawasaki, J. Inorg. Nucl. Chem., 29 (1967) 840.
236 S. Sharma, R. Bohra and R.C. Mehrotra, Synth. React. Inorg. Met.-Org. Chem., 22 (1992) 43.
237 J. Angenault, C. Mondi and A. Rimsky, Inorg. Chim. Acta, 37 (1979) 145.

238 P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc., Dalton Trans., (1976) 1414.
239 C.I.F. Denekamp, D.F. Evans, A.M.Z. Slawin, D.J. Williams, C.Y. Wong and J.D. Woollins, J. Chem. Soc., Dalton Trans., (1992) 2375.
240 W.H. Nelson and M.J. Aroney, Inorg. Chem., 12 (1973) 132.
241 J. Otera, Y. Kawasaki and T. Tanaka, Inorg. Chim. Acta, 1 (1967) 294.
242 S.H. Sage and R.S. Tobias, Inorg. Nucl. Chem. Lett., 4 (1968) 459.
243 T.P. Lockhart and F. Davidson, Organometallics, 6 (1987) 2471.
244 P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc., Dalton Trans., (1975) 826.
245 P.G. Harrison, T.J. King and R.C. Phillips, J. Chem. Soc., Dalton Trans., (1976) 2317.
246 G.E. Matsubayashi, K. Miyake, K. Ueyama and T. Tanaka, Inorg. Chim. Acta, 105 (1985) 9.
247 R. Weinland and M. Maier, Z Anorg. Allg. Chem., 150 (1926) 217.
248 J.J. Park, D.M. Collins and J.L. Hoard, J. Am. Chem. Soc., 92 (1970) 3636.