ELSEVIER

Coordination Chemistry Reviews
145 (1995) 157–200

COORDINATION CHEMISTRY REVIEWS

The molecular structure of organogermanium compounds

Kim M. Baines *, William G. Stibbs

Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada

Received 9 December 1994; accepted 22 December 1994

Contents

Abstract 157
1. Introduction 157
2. Organogermanium derivatives of Group 1, 2 and 13 elements 158
3. Organogermanium derivatives of Group 14 elements 158
4. Organogermanium derivatives of Group 15 elements 167
5. Organogermanium derivatives of Group 16 elements 173
6. Organogermanium derivatives of Group 17 elements 182
7. Low-coordinate germanium compounds 187
    7.1 Tricoordinate germanium compounds 187
    7.2 Dicoordinate germanium compounds 190
8. Hypercoordinated germanium compounds 193
9. Summary 194
Acknowledgements 195
References 196

Abstract

The molecular structures, as determined by X-ray crystallography, of organogermanium compounds of the main group elements, excluding carboranes, are reviewed.

Keywords: Organogermanium compounds; Polygermanes; Heterocycles

---

1. Introduction

The relationship between the structure of a compound and its reactivity is a central theme in the study of chemistry. In the field of organogermanium chemistry, to our knowledge, only one review has been published in this area concerning the structural

---

* Corresponding author.

0010-8545/95/$29.00 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0010-8545(95)09106-8

investigations of polygermanes and heterocycles rich in germanium [1]. The review also details the synthesis and spectroscopy of compounds of this type. The present review surveys the molecular structures of a variety of functional organogermanium compounds, including low- and hypercoordinate compounds as determined by X-ray crystallography. Only compounds containing main group elements have been considered, excluding carborane structures. We have deliberately focused only on compounds containing a germanium–carbon bond to provide a precise definition of the scope of the review and to limit the material covered to a manageable amount. Inevitably, this led to the exclusion of some seemingly relevant compounds; however, we believe this was unavoidable. The review is based on the results obtained from a search of the Cambridge Structural Database [2] conducted in February 1994; however, we have attempted to cover the literature up to the end of 1994. Any omissions are unintentional.

2. Organogermanium derivatives of Group 1, 2 and 13 elements

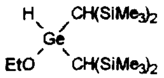
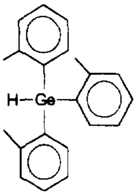
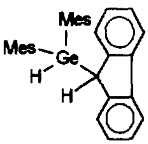
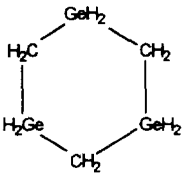
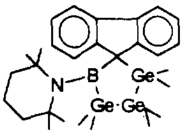
Cyclo(GeH_2CH_2)$_3$ (Entry 4, Table 1) has an almost ideal chair conformation with angles at germanium of 110.3(2)° and 109.5(2)° [3]. All the other structures of germanium hydrides reported have the germanium in a distorted tetrahedral environment (Entries 1–3 and 5, Table 1); the degree of distortion is determined by steric factors and non-bonding intramolecular interactions. The H—Ge—C angles in $H(EtO)Ge[CH(SiMe_3)_2]_2$ (108(2)° and 120(2)°) [4], (*o*-MeC_6H_4)$_3$GeH (102.0°, 120.0° and 116.0°) [5] and $(Mes)_2Ge$(fluorenyl)H (113.4(2)°) [6] (Entries 1–3, Table 1) all exhibit significant distortions from tetrahedral geometry due to, respectively, different non-bonding $H\cdots CH_3$ contacts with the $SiMe_3$ groups, different non-bonding contacts between H and the *o*-Me groups, all of which are on the same side of the molecule, and steric crowding. A limited number of Ge—H bond lengths have been determined; a shorter distance is found when there is an ethoxy substituent (1.46 Å, Entry 1, Table 1) than when there are only alkyl and silyl substituents (1.70 Å, Entries 2 and 5, Table 1).

The only structure examined containing a Ge—Group 2 element bond is that of $Mg(GeMe_3)_2 \cdot 2DME$ (Entry 6, Table 1), in which the coordination polyhedron is octahedral about magnesium and the germanium atoms are neighbours; the germanium atoms show distorted tetrahedral geometry [7]. The boron-containing five-membered ring species (Entry 7, Table 1) has an envelope conformation with the germanium atom adjacent to the carbon atom out of the Ge—Ge—B—C plane [8]. The two germanium–germanium bond lengths are different [2.402(2) versus 2.435(2) Å] owing to the inductive effect of boron, the longer bond being adjacent to boron.

3. Organogermanium derivatives of Group 14 elements

Because of the large number of compounds containing a Ge—C bond, each compound is not reviewed individually, but rather a histogram of the distribution

Table 1
Selected bond lengths and angles of compounds containing a Ge—Group 1, 2 or 13 element bond

Entry	Compound	Ge—E (Å)	X—Ge—E (°)	Ref.
1		1.46(6)	C—Ge—H: 108(2), 120(2) O—Ge—H: 98(2)	[4]
2		1.700	C—Ge—H: 102.0, 120.0, 116.0	[5]
3[a]		Not located	113.4(2)	[6]
4		Not located	C—Ge—C: 110.3(2), 109.5(2)	[3]
5[a]	$Mes_3GeGeMes(SiEt_3)H$	1.70(10)		[134]
6[b]	$Mg(GeMe_3)_2 \cdot 2DME$	Molecule 1: 2.727(7), 2.717(7) Molecule 2: 2.712(6), 2.718(6)	C—Ge—C: 95(1)-101(2) 94(1)-100(1)	[7]
7		2.165(10)	Ge—Ge—B: 103.5(3)	[8]

[a] Mes = 2,4,6-trimethylphenyl.
[b] DME = 1,2-dimethoxyethane.

of Ge—C bond lengths in the Cambridge Structural Database is given in Fig. 1. Examination of Fig. 1 reveals that most compounds have a Ge—C bond length in the range of 1.9–2.05 Å; however, most of these fall in the narrow range of 1.95–2.00 Å. The shorter Ge—C bonds tend to be found either in compounds in which the germanium atom is attached to an unsaturated carbon atom (where there is the possibility of some delocalization occurring) or in simple compounds in which the

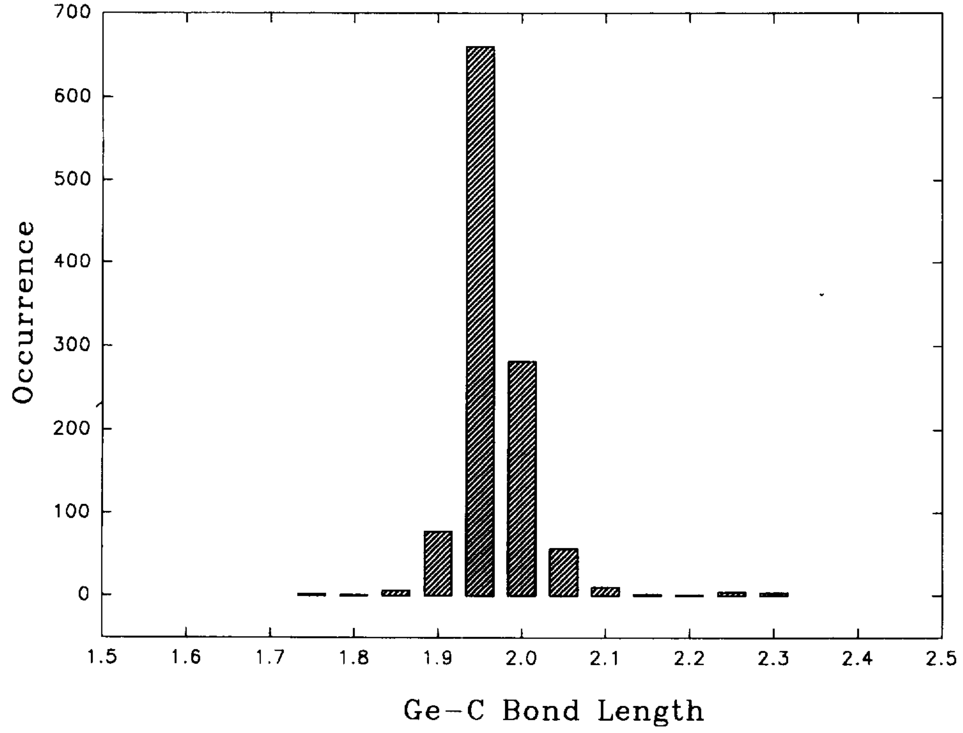


Fig. 1. Histogram of Ge—C bond lengths.

electronic and steric effects which cause elongation are minimized; for example, 2,3,4,5-tetraphenyl-1,1-diethynyl-1-germacyclopentadiene has a Ge—C_{sp} bond length of 1.88 Å [9], the Ge—C bonding distance of $Ph_3GeSSSGePh_3$ (Entry 5, Table 13) varies from 1.85 to 1.92 Å and that of $Ph_3SiOGePh_3$ from 1.89 to 1.90 Å [10]. The longer Ge—C bonds occur in extremely sterically congested molecules such as ClGe(9-triptycyl)$_3$ (Entry 14, Table 16) with a value of 2.16 Å and for the germylenes (see Table 18) in which the Ge—C bond length can be as long as 2.36 Å.

The highly strained nature of three- and four-membered hydrocarbon rings containing one or two germanium atoms leads to some interesting structural features. The two reported germiranes (Entries 1 and 2, Table 2) exhibit Ge—$C_{(endo)}$ bond lengths within the normal ranges. The germirenes (Entries 3 and 4, Table 2), like the germiranes, show significant deviation of the configuration about the germanium atom from ideal tetrahedral geometry (for example $C_{(endo)}$—Ge—$C_{(endo)}$ 40.5(3)°, $C_{(endo)}$—Ge—$C_{(exo)}$ 113.9(3)° for Entry 4). The endocyclic Ge—C bond lengths of the germirenes are shorter than the standard Ge—C bond lengths (1.88–1.93 versus 1.95–2.00 Å). The bond shortening suggests that the germirene may be aromatic; however, the C=C bond does not deviate significantly from the typical value (1.331(9) and 1.339(1) versus 1.337 Å) [11,12]. The digermirane (Entry 5, Table 2) also shows significant distortion of the germanium atom from tetrahedral geometry,

Table 2
Selected bond lengths and angles of compounds containing a germanium atom in a three- or four-membered hydrocarbon ring

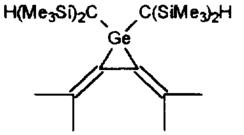
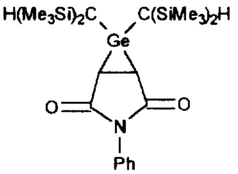
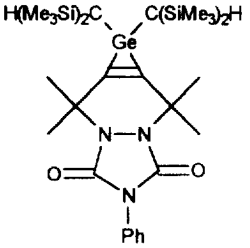
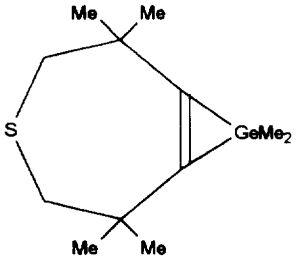
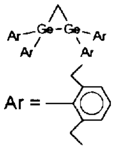
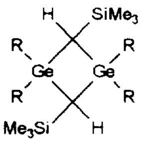
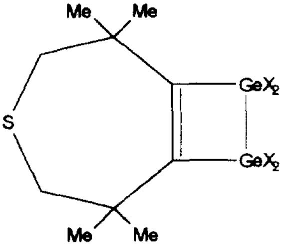
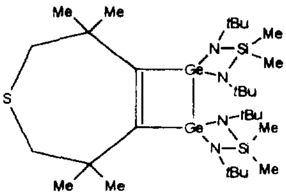
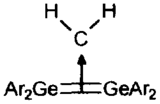
Entry	Compound	Ge—$C_{(ring)}$ (Å)	$C_{(ring)}$—Ge—E (°)	Ge—C—E (°)	Ref.
1		1.95(1), 1.96(1)	44.0(5)	68.3(7), 67.7(7)	[11]
2		Molecule 1: 1.92(2), 1.98(2) Molecule 2: 1.97(2), 2.07(2)	45.0(8) 47.7(8)	68(1), 61.4(9) 71(1), 67(1)	[11]
3		1.88(1)	43.2(2)	68.4(2)	[11]
4		1.929(6), 1.915(6)	40.5(3)	70.3(4), 69.2(4)	[12]
5		1.970(1), 1.984(3)	52.9(1)	74.3(1)	[13]
6		R = Ph: 1.987, 1.990 R = Cl: 1.982, 1.975	R = Ph: 91.4	R = Ph: 88.6	R = Ph: [135] R = Cl: [136]

Table 2 (*continued*)

Entry	Compound	Ge—C$_{(ring)}$ (Å)	C$_{(ring)}$—Ge—E (°)	Ge—C—E (°)	Ref.
7		X=Cl: 1.998(6), 2.002(6) X=I: 2.003, 2.009	X=Cl: 74.6(2), 74.7(2)	X=Cl: 105.7(4), 105.1(4)	X=Cl: [137] X=I: [138]
8		2.030(7), 2.028(6)	73.3(1)	105.0(1)	[14]

and the Ge—Ge bond is also relatively short (2.379(1) versus 2.44 Å), suggesting that the π-complex shown below may contribute to the structure [13].

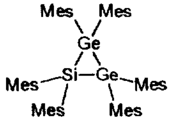
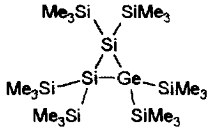
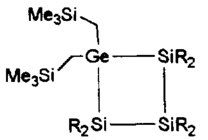


The 1,3-digermacyclobutanes (Entry 6, Table 2) are planar with no unusual bond lengths and angles, whereas the 1,2-digermacyclobutenes (Entries 7 and 8, Table 2) exhibit distorted bond angles owing to the difference in length between the Ge—Ge bond and the C=C bond. The angle at germanium (73.3–74.7°) is much smaller than that at carbon (105°). The introduction of bulky substituents at Ge leads to a slight puckering of the four-membered ring [14].

The structures of an isomeric pair of silylgermanes, $Ph_3GeSiMe_3$ [15] and $Ph_3SiGeMe_3$ [16], have been examined. The Ge—Si bond length in the two isomers, 2.384 and 2.394 Å, respectively, varies only slightly (Entries 1 and 2, Table 3) and is comparable to the Ge—Si bond length in the simplest silylgermane, H_3SiGeH_3, determined by microwave spectroscopy [2.36(2) Å] [17]. With increasing substitution, the Ge—Si bond appears to elongate (Entries 3–8, Table 3) to 2.40–2.45 Å. With the exception of the large M—M′—M angles noted in the perphenylated propane analogues (Entries 3 and 4, Table 3: Ge—Si—Ge 116.5(1)° and Si—Ge—Si 123.3(1)°) [18], no unusual angles were noted in linear silylgermanes.

The two three-membered ring systems, the siladigermirane (Entry 7, Table 3) [19] and the disilagermirane (Entry 8, Table 3) [20], show a similar disorder in the

Table 3
Selected bond lengths of compounds containing a Ge—Si bond

Entry	Compound	Ge—Si (Å)	Ref.
1	$Ph_3GeSiMe_3$	2.384(1)	[15]
2	$Ph_3SiGeMe_3$	2.394(1)	[16]
3	$Ph_3GeSiPh_2GePh_3$	2.401(2), 2.406(1)	[18]
4	$Ph_3SiGePh_2SiPh_3$	2.418(4), 2.425(4)	[18]
5	$Ph_3GeSi(SiMe_3)_3$	2.416(1)	[139]
6[a]	$Mes_3GeGeHMesSiEt_3$	2.440(4)	[134]
7[a]		M(1)—M(2), 2.510(2) M(2)—M(2) 2.505(2)	[19]
8		Exocyclic: 2.356(4) Endocyclic: 2.391(1)	[20]
9		R = ^{i}Pr: 2.457 (av.) R = neopentyl: 2.444 (av.)	[21]

[a] Mes = 2,4,6-trimethylphenyl.

crystal. The single metal atom (i.e. Si or Ge, respectively) of the central ring appears to be disordered equally over three sites for each molecule. In the siladigermirane, the Ge—Si bond length was estimated to be 2.493 Å, whereas in the disilagermirane, the disorder was successfully resolved and the two different bond lengths were refined.

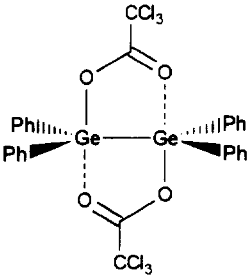
The trisilagermetane rings (Entry 9, Table 3) are both folded (R = ^{i}Pr, 24°; R = neopentyl, 36°) [21]. The reduction in the degree of puckering in comparison with the corresponding cyclotetrasilanes (37° in $(^{i}Pr_2Si)_4$ [22] and 39° in $[(^{t}BuCH_2)_2Si]_4$ [23]) is believed to be the result of the introduction of a germanium atom into the ring which has a larger atomic radius than the silicon atom. The considerably smaller puckering of the ring when R = ^{i}Pr has been attributed to the less bulky nature of the isopropyl groups compared with the neopentyl groups.

In digermane, the central Ge—Ge bond has been found to be 2.404(3) Å by electron diffraction [24]; however, in perphenylated di- and polygermanes the Ge—Ge bond length typically varies from 2.42 to 2.47 Å (Table 4). Replacement of one or more phenyl groups with chlorine or methyl significantly shortens the bond to 2.41 Å, which is comparable to the bond length in the parent digermane. The increase in the bond length on substitution with phenyl has been attributed solely to a steric effect. The shortest Ge—Ge bond length has been found in 1,2-bis(trichloroacetate)tetraphenyldigermane (Entry 5, Table 4), 2.393 Å [25]. The

Table 4
Selected bond lengths in digermanes and linear polygermanes

Entry	Compound	Ge—Ge (Å)	Ge—Ge—Ge (°)	Ref.
1	$Ph_3GeGePh_3$	2.437(2)	–	[140], see also [1]
2	$Me_3GeGePh_3$	2.418(1)	–	[39]
3	$(^tBu)_3GeGe(^tBu)_3$	Molecule 1: 2.705(1) Molecule 2: 2.714(1)	– –	[27]
4	$PhCl_2GeGePhCl_2$	2.413(1)	–	[141]
5	$[GePh_2OCOCCl_3]_2$	2.393(2)	–	[25]
6	$Ph_3GeGePh_2GePh_3$	2.438(2), 2.441(2)	121.3(1)	[29], see also [1]
7	$Ph_3GeGeMe_2GePh_3$	2.429(1)	120.3(1)	[142], see also [1]
8	$ClPh_2GeGePh_2GePh_2Cl$	Molecule 1: 2.437(2), 2.419(1) Molecule 2: 2.413(2), 2.423(2)	110.4(1) 116.7(1)	[143]
9	$Ph_3GeGePh_2GePh_2GePh_3$	2.463(2), 2.461(3)	117.8(1)	[29], see also [1]
10	$IPh_2GeGePh_2GePh_2GePh_2I$	IGe—Ge: 2.451(1), Ge—Ge (central): 2.450(2)	114.2(1)	[28], see also [1]
11	$Ph_3Ge(GePh_2)_3GePh_3$	2.447(4), 2.485(4), 2.468(4), 2.439(4)	116.7(2), 114.0(2), 116.0(2)	[26]

bridging carboxylate group is believed to be responsible for shortening the Ge—Ge bond.



The Ge—Ge bond can be stretched with increasing steric repulsions between the substituents. For example, the central Ge—Ge bonds in Ge_5Ph_{12} are significantly longer than the peripheral Ge—Ge bonds: 2.48 versus 2.44 Å, respectively [26] (Entry 11, Table 4). A rather dramatic lengthening of the Ge—Ge bond was found in $(^tBu)_3GeGe(^tBu)_3$, where the Ge—Ge bond length is 2.71 Å [27]. This is the longest Ge—Ge bond reported to date.

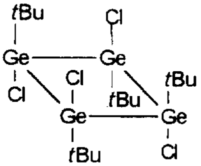
The Ge—Ge—Ge bond angles in polygermanes with bulky substituents (i.e. Ph versus Cl or Me) are typically larger than the normal tetrahedral angle, ranging from

114° in $I(GePh_2)_4I$ [28] to 121° in Ge_3Ph_8 [29]. The phenyl groups in the phenylated di- and polygermanes, both linear and cyclic, often form a propeller-type arrangement about the Ge—Ge bonds. The arrangements have been discussed in a previous review [1].

Cyclotrigermanes, the smallest members of the cyclopolygermane series, are isolable provided that they are substituted with bulky ligands which serve to stabilize kinetically the three-membered ring. Three structure determinations of cyclotrigermanes have been reported to date. Because of the bulky substituents, not surprisingly, the Ge—Ge bond is elongated in the ring to 2.53–2.56 Å (Entries 1–3, Table 5). Unlike the planar four-membered ring in $(GePh_2)_4$ [30] (mean deviation from the least-squares plane ±0.003 Å), the four-membered ring in $(Ge^tBuCl)_4$ is puckered by 21° [31]. The Ge—Ge—C angles are expanded to 125° and the Ge—Ge—Cl angles are contracted to 105° because of the steric repulsion between the substituents.

The Ge—Ge bond lengths in perphenylated cyclopolygermanes (Entries 5–7, Table 5) do not differ from those found in linear perphenylated polygermanes (2.42–2.47 Å). Because of the considerable decomposition of the crystal which occurred during measurement and the shortness of the Ge—Ge bond in comparison with the Ge—Ge bond in the perphenylated analogue [32], the accuracy of the short bond length observed in $(GeMe_2)_6$, 2.374(8) Å [33], has been questioned. The

Table 5
Selected Ge—Ge bond lengths in cyclic polygermanes

Entry	Compound	Ge—Ge (Å)	Ref.
1	$(Ge^tBu_2)_3$	2.563(1)	[27]
2^a	$(GeMes_2)_3$	2.535(2), 2.539(2)	[19]
3^b	$(GeDmp_2)_3$	2.537(1), 2.543(1)	[51]
4		2.471(2), 2.455(2)	[31]
5	$(GePh_2)_4$	2.458(2), 2.472(2), 2.471(2), 2.461(2)	[30], see also [1]
6	$(GePh_2)_5$	Molecule 1: 2.449(2), 2.455(2), 2.449(2), 2.454(2), 2.473(2) Molecule 2: 2.445(2), 2.462(2), 2.450(2), 2.440(2), 2.455(2)	[144], see also [1]
7	$(GePh_2)_6 \cdot 7C_6H_6$	2.458(2), 2.456(2), 2.458(2)	[32], see also [1]
8	$(GeMe_2)_6$	2.366(7), 2.377(9), 2.378(6)	[33]

[a] Mes = 2,4,6-trimethylphenyl.
[b] Dmp = 2,6-dimethylphenyl.

structures of this class of polygermanes have been discussed in detail in a previous review [1].

Four interesting structures of polyhedral polygermanes have been reported. The molecular structures of two examples of tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octagermanes (Entry 1, Table 6) have been determined. Each tertiary germanium atom is substituted with a ^{t}Bu group and the secondary germanium atoms are substituted with a halogen, either bromine [34] or chlorine [35], in addition to the alkyl group. The dimensions in the core germanium rings are essentially identical and range from 2.442 to 2.542 Å. A hexagermaprismane [36] (Entry 2, Table 6) and an octagermacubane [37] (Entry 3, Table 6) have also been synthesized and their structures determined. The prismane consists of two regular triangles and two regular squares. The bond lengths in the triangles at 2.578–2.584 Å are longer than in the squares (2.516–2.526 Å). This

Table 6
Selected bond lengths in polycyclic compounds containing a Ge—Ge bond

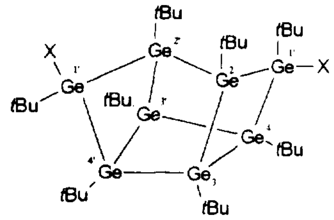
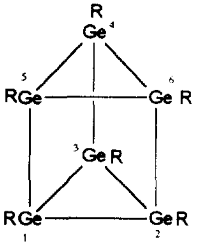
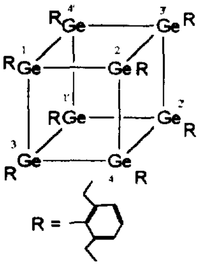
Entry	Compound	Ge—Ge (Å)			Ref.
		Ge—Ge	X=Cl	X=Br	
1		1–2	2.470(6)	2.478(1)	X=Cl: [35] X=Br: [34]
		1–4	2.442(6)	2.443(1)	
		2–3	2.537(6)	2.542(1)	
		2–2′	2.466(6)	2.461(1)	
		3–4′	2.481(6)	2.495(1)	
		3–4	2.473(6)	–	
2	 R = CH(SiMe$_3$)$_2$	1–2	2.584(6)		[36]
		1–3	2.580(6)		
		2–3	2.580(5)		
		4–5	2.579(6)		
		4–6	2.579(5)		
		5–6	2.578(6)		
		1–5	2.526(6)		
		2–6	2.516(6)		
		3–4	2.523(4)		
3		1–2	2.478(1)		[37]
		1–4	2.492(1)		
		2–3	2.486(1)		
		3–4	2.503(1)		
		1–4′	2.500(1)		
		2–3′	2.482(1)		

Table 7
Selected bond lengths of compounds containing a Ge—Sn or a Ge—Pb bond

Entry	Compound	Ge—Sn/Pb (Å)	Ref.
1	$Me_3GeSnPh_3$	2.601(3)	[38,39]
2	$Me_3SnGePh_3$	2.611(1)	[38,39]
3[a]	$Ph_3GePbPh_3$	2.623(5)	[40]
4[b]	$Ph_3GePb(p\text{-}Tol)_3$	2.642(1)	[41]
5[a,b]	$(p\text{-}Tol)_3GePb(p\text{-}Tol)_3$	2.599(2)	[41]

[a] Oppositely placed Ge—Pb orientations.
[b] p-Tol = p-tolyl.

is opposite to the trend found in the carbon analogues. The Ge—Ge bond lengths found in the squares are comparable to those found in bulky substituted cyclotrigermanes; the Ge—Ge bond lengths in the triangles are only slightly longer.

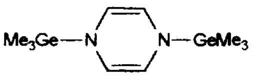
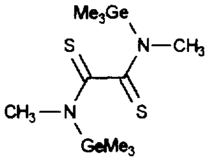
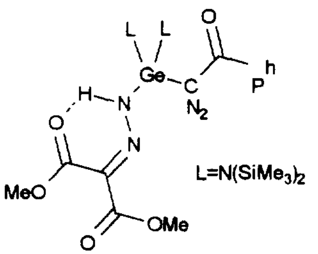
Only a limited numbers of compounds containing a germanium–tin or germanium–lead bond have had their structures determined by X-ray crystallography (Table 7). The pair of germylstannanes $Me_3GeSnPh_3$ and $Me_3SnGePh_3$ were found to have essentially identical Ge—Sn bond lengths, 2.601 and 2.611 Å, respectively [38], after a correction [39].

Although three germylplumbanes, $R_3GePbR'_3$, have been structurally characterized, in two cases there are two different orientations of the Ge—Pb vector in the unit cell because of the presence of identical substituents (R = R′ = Ph [40] and R = R′ = p-tolyl [41]). The Ge—Pb length in an unsymmetrically substituted molecule, R = Ph, R′ = p-tolyl, is 2.642 Å, consistent with the sum of the covalent radii (Ge 1.22; Pb 1.42) [41].

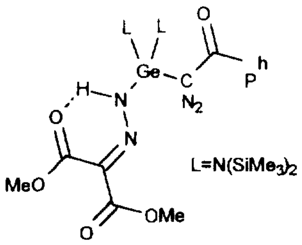
4. Organogermanium derivatives of Group 15 elements

In organogermanium compounds with an acyclic Ge—N bond, the length of the Ge—N bond ranges from 1.85 to 1.86 Å (Entries 1, 2 and 4, Table 8), comparable to the value of 1.836(5) Å found in trigermylamine, $N(GeH_3)_3$ [42]. Mes_3GeNH_2 (Entry 1, Table 8), the only primary amine to have its structure determined by X-ray methods, has a propeller arrangement of the mesityl groups [43]. The germyl-substituted dithiooxamide (Entry 3, Table 8) has elongated Ge—N bond distances of 1.917–1.924 Å [44] for no obvious reason. The dithiooxamide molecule can be divided up into two planes, each containing the $(Ge)(N)(C_{Me})(C_{=S})$ skeleton. The two planes are twisted by 78.6°. As has been observed in other compounds containing the [bis(trimethylsilyl)amino]germyl moiety [45], the Ge—N bonds are slightly shortened and the $N(Si_2)$—Ge—$N(Si_2)$ angle is enlarged in the compound shown [46] (Entry 4, Table 8) in comparison with the free germylene, $Ge[N(SiMe_3)_2]_2$ [47].

Table 8
Selected bond lengths of compounds containing an acyclic Ge—N bond

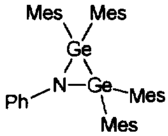
Entry	Compound	Ge—N (Å)	Ref.
1[a]	Mes_3GeNH_2	1.854(3)	[43]
2	 	1.859(4)	[145]
3	 	1.924(8), 1.917(8)	[44]
4	 	Ge—N: 1.859(4) Ge—N(Si_2): 1.821(5), 1.829(5)	[46]
5[a]	$Mes_3GeNHCO^tBu$	1.899(6)	[48]

[a] Mes = 2,4,6-trimethylphenyl.



The Ge—N bond length in $Mes_3GeNHCO^tBu$ (Entry 5, Table 8) is elongated to 1.899 Å [48]; however, this is probably a consequence of the weak coordination between the carbonyl oxygen atom and the germanium atom.

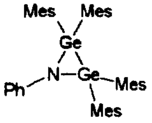
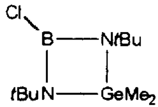
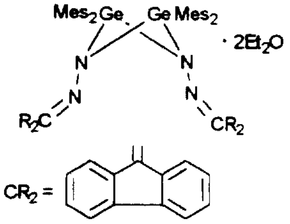
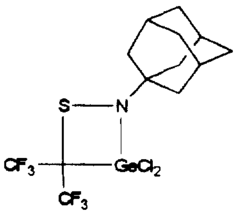
In cyclic germylamines, the endocyclic Ge—N bond elongates only slightly, to 1.895 Å, on substitution with bulky substituents, such as mesityl groups (Entries 1 and 3, Table 9). The Ge—N bond in the (—C—S—N—Ge—) four-membered ring (Entry 4, Table 9) has a significantly shortened length (1.813 Å) [49]. The structure of the azadigermiridine (Entry 1, Table 9) shown is interesting [50]. Unlike the corresponding hexakis(2,6-dimethylphenyl)cyclotrigermane [51], the bulky aryl-substituted Ge—Ge bond is short (2.379 versus 2.54 Å).



In addition, there is a nearly planar arrangement of the Ge atoms and the carbon atoms directly bonded to them (sum of the angles about Ge = 358.2°). The structure suggests that the compound may have considerable π-complex character, as has been observed in some three-membered disilaheterocycles [52].

Two of the three four-membered rings containing a Ge—N linkage in Table 9 are planar, whereas the third, the cyclodigermazane shown below, deviates significantly from planarity. There is a fold angle of 34° between the two planes containing the Ge—N—N atoms of the cyclodigermazane [53] and a fold angle of 38° between the two Ge—Ge—N planes. This large fold angle is unique in comparison with related cyclodigermazanes [54] and cyclodisilazanes [55], which are all planar. The

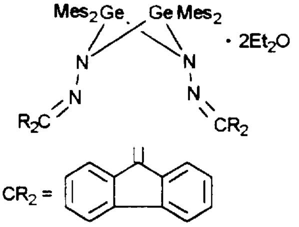
Table 9
Selected bond lengths and angles of compounds containing a cyclic Ge—N bond

Entry	Compound	Ge—N (Å)	X—Ge—N (°)	Ref.
1[a]		1.876(1)	50.6(1)	[50]
2		1.862(3), 1.865(3)	75.1(1)	[146]
3[a]		1.894(3), 1.895(3)	79.6(2)	[53]
4		1.813(3)	82.9(2)	[49]

---

[a] Mes = 2,4,6-trimethylphenyl.

bulky substituents, however, on both the germanium and the nitrogen ring atoms and the pyramidalized nitrogen ring atom may account for this unexpected fold.



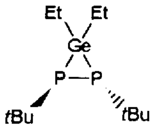
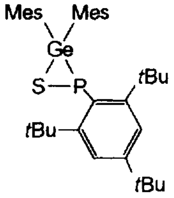
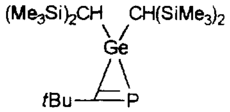
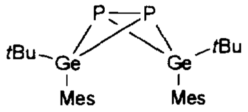
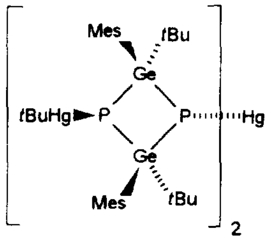
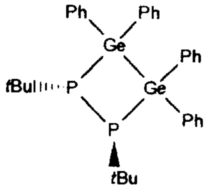
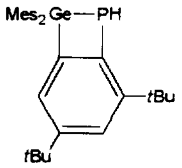
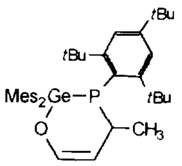
It is well known that in germylamines, the three-coordinate nitrogen is most often planar [56]. It is interesting that the majority of the structures in Tables 8 and 9 (Entries 2, 3 and 4 in Table 8 and Entries 1, 2 and 4 in Table 9) are indeed planar, or nearly planar, about the nitrogen atoms attached to germanium. In the cyclic compounds, the endocyclic angle at germanium is significantly compressed (75.1–82.9°), probably as a result of the planar-coordinated nitrogen atom, although the same trend is still observed in the cyclodigermazane where the ring nitrogen atoms are pyramidalized.

The Ge−P bond length in trigermylphosphine, $P(GeH_3)_3$, is 2.308(3) Å [57], essentially identical with the distance observed in three-membered rings containing the Ge−P linkage, 2.291–2.316 Å (Entries 1–4, Table 10). The Ge−P distance is remarkably constant in these compounds despite a variety of substituents and types of atoms in the ring. In four-membered rings, the length of the Ge−P bond increases significantly to 2.332–2.369 Å (Entries 5–7, Table 10) and is the longest (2.731 Å) in the six-membered germaoxaphosphorinene ring (Entry 8, Table 10) [58]. For the adamantane-like, edge-substituted tetraphosphide $(Me_2Ge)_6P_4$ (Entry 1, Table 11), the Ge−P distance, at 2.322 Å, falls between the two ranges observed for the three- and four-membered rings [59] and the germyl-substituted heptaphosphanortricyclenes, $P_7(GeR_3)_3$, R = Me [60], R = Ph [61] (Entry 2, Table 11), have bond lengths of the same order as the four-membered rings.

The endocyclic bond angles at germanium in the three- and four-membered rings are not remarkable except to note that the most extreme compression occurs when there is an inflexible first-row atom also in the ring, such as in the germaphosphirene, C−Ge−P = 45.6° (av.) and Ge−C−P = 78.9° (av.) [62], and the planar germaphosphetane, C−Ge−P = 75.0 (av.), Ge−C−C = 101.1° (av.) [63]. Both the 1,2- (Entry 6, Table 10) [64] and the 1,3-digermadiphosphetanes (Entry 5, Table 10) [65] are puckered, the former by 32°. The six-membered germaoxaphosphorinene ring is in a distorted boat conformation. The bulky substituents on both the germanium and the phosphorus atoms result in some distortion about the germanium atom. The endocyclic O−Ge−P angle is compressed to 100.1°, as is one of the O−Ge−C(Mes) angles (to 100.0°), and the two P−Ge−C angles are expanded (115.9° and 118.6°) [58].

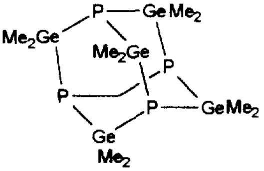
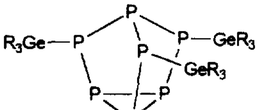
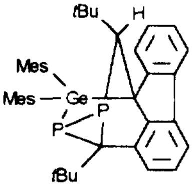
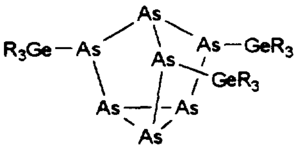
The germathiaphosphirane [66] (Entry 2, Table 10) exhibits structural features that are very similar to those in the previously discussed azadigermirane [50]. The

Table 10
Selected bond lengths and angles of compounds containing a cyclic Ge—P bond

Entry	Compound	Ge—P (Å)	X—Ge—P (°)	Ref.
1		Molecule 1: 2.301(2) Molecule 2: 2.300(2), 2.296(2)	58.0(1) av.	[147]
2[a]		2.316(1) Ge—S: 2.227(1)	57.2(1)	[66]
3		Molecule 1: 2.298(4) Molecule 2: 2.291(4)	Molecule 1: 45.2(3) Molecule 2: 45.9(3)	[62]
4[a]		2.312(2), 2.310(2)	62.1(1)	[65]
5[a]		2.343(5), 2.368(4), 2.342(4), 2.364(5)	91.6(1), 91.7(1)	[65]
6		2.332(2), 2.347(2) Ge—Ge: 2.421(1)	83.16(6), 82.79(7)	[64], see also [1]
7[a]		Molecule 1: 2.354(3) Molecule 2: 2.369(3)	Molecule 1: 75.0(3) Molecule 2: 74.9(3)	[63]
8[a]		2.371(1) Ge—O: 1.832(3)	100.1(1)	[58]

[a] Mes = 2,4,6-trimethylphenyl.

Table 11
Selected bond lengths and angles of polycyclic compounds containing Ge—P bonds and of compounds containing Ge—As and Ge—Sb bonds

Entry	Compound	Ge—X (Å)	X—Ge—X (°)	Ref.
1		2.32(8)	120.7(2)	[59], see also [1]
2		R = Me: 2.362(8), 2.351(8), 2.348(8) R = Ph: 2.349(1) av.	-	R = Me: [60] R = Ph: [61]
3[a]		2.308(2)	94.7(2)	[148]
4		R = Me: 2.450(1)	-	[67]
5	$(Me_3Ge)_2Sb$-$Sb(GeMe_3)_2$	2.636(1), 2.624(1)	-	[68]

[a] Mes = 2,4,6-trimethylphenyl.

Ge—P bond is not elongated for a bond between a bulky-substituted germanium atom and a bulky-substituted phosphorus atom. The germanium, the phosphorus and the three *ipso* carbon atoms of the aryl groups lie nearly in the same plane (sum of angles about Ge = 358.1°). Again, because of the short Ge—P bond length and the planarity of the $GePC_3$ skeleton, the hybridization at germanium may be better represented as sp^2-hybridized and the bonding may be intermediate between that of a normal three-membered ring and that of a π-complex.

Only one molecular structure of an organogermanium compound containing a Ge—As bond has been reported, and one containing a Ge—Sb bond. The trimethylgermyl-substituted heptaarsanortricyclene $As_7(GeMe_3)_3$ (Entry 4, Table 11) has a Ge—As bond length of 2.450 Å [67] and tetrakis(trimethylgermyl)distibane has a Ge—Sb bond length of 2.630 Å [68], in close agreement with the values obtained from addition of the covalent radii. The bond angles about germanium in both compounds are not particularly notable.

5. Organogermanium derivatives of Group 16 elements

Fig. 2 shows the distribution of Ge—O bond lengths in organogermanium compounds in the Cambridge Structural Database. Most compounds have a Ge—O bond length of 1.75–1.85 Å. For the most part, the longer Ge—O bonds in Fig. 2 (>2.0 Å) are found in hypercoordinate compounds of germanium (see Section 8). The shorter Ge—O bonds (≤1.75 Å) tend to be found in simple, linear compounds such as $(PhCH_2)_3GeOGe(CH_2Ph)_3$, $Ph_3SiOGePh_3$ and $-[(CF_3)_2GeO]-_n$ with Ge—O distances of 1.73 [69], 1.70 [10] and 1.73–1.75 Å [70], respectively. The structures of compounds with Ge—O bonds are too numerous for them all to be discussed here; instead, an interesting subgroup, namely the four-membered rings, are covered, in addition to some five- and six-membered rings for comparison.

Four-membered rings containing endocyclic Ge—O bonds have highly strained structures (Entries 1–4, Table 12). The germaoxetanes (Entry 1, Table 12) are folded by 8–24° in order to relieve the steric strain [71]; this degree of folding is higher than that found in $(Ph_2Ge)_4$ but less than that of a 1,3-digermazane [53]. A 1,3-cyclodigermoxane (Entry 2, Table 12) exhibits an almost square ring which is puckered with a fold angle of 8–9° [72]. These three compounds all have endocyclic bonds within the normal ranges. On the other hand the 1,2-digermadioxetane (Entry 3, Table 12) has a trapezoidal ring with a normal Ge—Ge bond [2.441(2) Å] and an elongated Ge—O bond [1.857(5) versus 1.82 Å] [72]. The ring is puckered

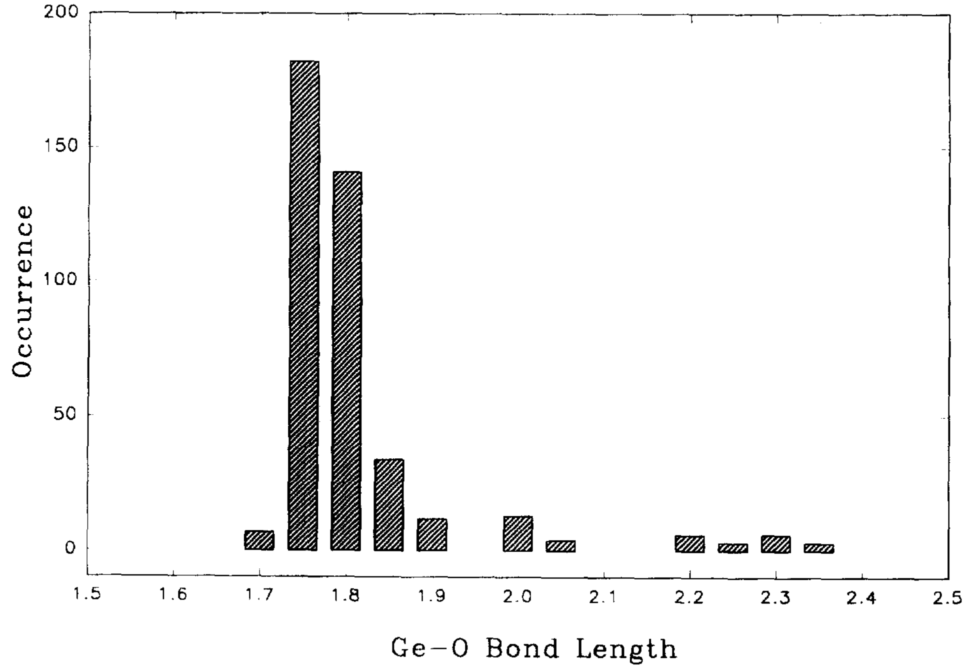


Fig. 2. Histogram of Ge—O bond lengths.

Table 12
Selected bond lengths and angles of four-, five- and six-membered rings containing endocyclic Ge—O bonds

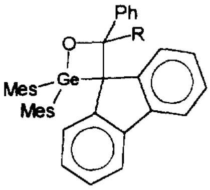
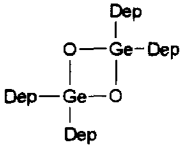
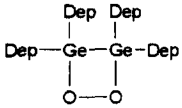
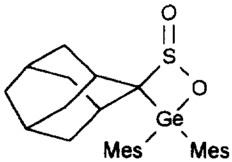
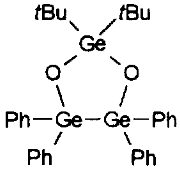
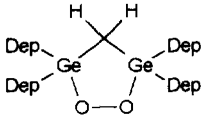
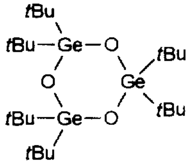
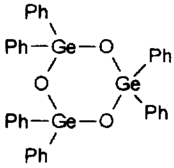
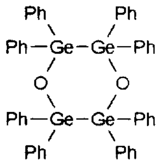
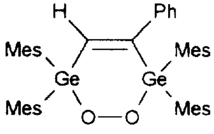
Entry	Compound	Ge—O (Å)	O—Ge—E (°)	Ref.
1[a]		R = H: 1.827(3) R = Ph: Molecule 1: 1.83(1) Molecule 2: 1.82(1)	R = H: 93.7(2) R = Ph: Molecule 1: 99(1) Molecule 2: 98(1)	[71]
2[b]		1.820(2), 1.814(2)	87.6(1)	[72]
3[b]		1.857(5)	74.1(1)	[72]
4[a]		1.876(3)	77.9(1)	[73]
5		1.783(10), 1.789(10), 1.800(10), 1.786(11)	Ge—Ge—O: 95.7(3), 97.1(3) O—Ge—O: 105.1(5)	[149]
6[b]		1.80(1), 1.76(1)	94.2(4), 97.2(5)	[150]
7		1.781(1)	107.0(1)	[151]
8		1.765(4), 1.775(4), 1.768(4)	107.0(2), 108.1(2), 107.0(2)	[152]

Table 12 (*continued*)

Entry	Compound	Ge–O (Å)	O–Ge–E (°)	Ref.
9		1.786(1), 1.781(1)	106.7(1), 106.7(1)	[153]
10[a]		1.79(1), 1.81(1)	O–Ge–C(Ph): 101.0(4) O–Ge–C(H): 102.9(7)	[74]

[a] Mes = 2,4,6-trimethylphenyl.

[b] Dep = 2,6-diethylphenyl.

with a torsion angle between the two Ge–O moieties of 19.5°. The ring of the 1,2,4-oxathiagermetane *S*-oxide (Entry 4, Table 12) also deviates significantly from planarity with a dihedral angle of 24.3(3)° between the Ge–S–C and Ge–S–O planes. The Ge–O and endocyclic Ge–C bonds are both elongated, the latter presumably owing to steric repulsion between the bulky adamantyl and mesityl groups [73].

Five- and six-membered rings containing a Ge–O bond, as a result of being less strained than the four-membered rings, generally have shorter Ge–O bond lengths (the averages values are 1.78 versus 1.83 Å). Examples of five-membered rings which have both planar (Entry 5, Table 12) and half-chair conformations (Entry 6, Table 12) have been reported. Six-membered rings of the type $[R_2GeO]_3$ (Entries 7 and 8, Table 12) have planar conformations whereas $[Ph_2GePh_2GeO]_2$ (Entry 9, Table 12) adopts a chair conformation. The unsaturated ring $[Mes_2GeOOMes_2GePhC{=}CH]$ (Entry 10, Table 12) deviates significantly from planarity with a Ge–O–O–Ge torsion angle of 94.5(5)° [74].

The parent digermyl sulphide, $(H_3Ge)_2S$, has been studied in the gas phase by electron diffraction (Entry 1, Table 13) [75]. The Ge–S bond length is consistent with a Ge–S single bond (2.209(4) Å) and the geometry about germanium is essentially tetrahedral. The structures of two other digermyl sulphides have been reported (Entries 2 and 3, Table 13); $(Ph_3Ge)_2S$, which has previously been reviewed [1], crystallizes in two forms which have different conformeric structures with respect to the rotation of the Ph_3Ge groups around the Ge–S bonds; one of the forms has significantly different Ge–S bond lengths, giving rise to an unsymmetrical S bridge for no obvious reason [76]; $(PhCH_2Ge)_2S$ has symmetrical Ge–S bond lengths which do not indicate significant π-bond contributions [77].

Molecules with a trithio bridge between two germanium atoms (Entries 4 and 5, Table 13) have a coiled conformation with the central S atom being 1.14–1.19 Å out of the plane formed by the two Ge–S moieties [78]. The organic groups have a

Table 13
Selected bond lengths of compounds containing an acyclic Ge—S bond

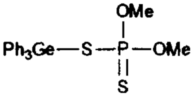
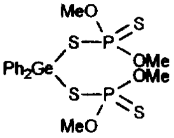
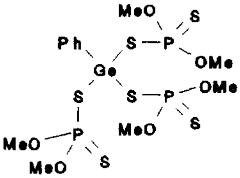
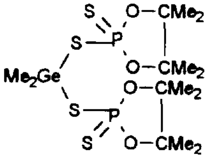
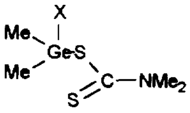
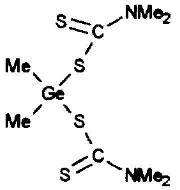
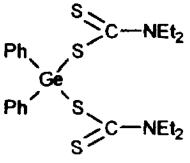
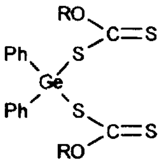
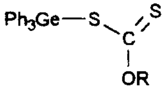
Entry	Compound	Ge—S (Å)	Ref.
1	$H_3GeSGeH_3$	2.209(4)	[75]
2	$Ph_3GeSGePh_3$	Molecule 1: 2.212(1), 2.261(1) Molecule 2: 2.227(1), 2.240(2)	[76]
3	$(PhCH_2)_3GeSGe(CH_2Ph)_3$	2.233(4)	[77]
4[a]	$Cy_3GeSSSGeCy_3$	2.278(5), 2.286(5)	[78]
5	$Ph_3GeSSSGePh_3$	2.254(11), 2.263(11)	[78]
6[a]	Cy_3GeSH	2.253(2)	[79]
7	Ph_3GeSMe	2.224(1)	[80]
8	$Ph_3GeS(p\text{-}C_6H_4{}^tBu)$	2.229(2)	[81]
9	 $Ph_3Ge{-}S{-}P(OMe)(=S){-}OMe$	2.285(1)	[82]
10		2.257(2), 2.253(2)	[82]
11		2.25	[83]
12		2.268(4), 2.275(4)	[84]
13		X = Cl: 2.254(1) X = Br: 2.222(4), 2.252(4) X = I: 2.255(2)	X = Cl: [85] X = Br, I: [86]
14		2.275(2), 2.281(2)	[87]
15		2.271(1)	[88]

Table 13 (*continued*)

Entry	Compound	Ge—S (Å)	Ref.
16		R = Me: 2.262(3) R = ^{i}Pr: 2.251(3), 2.252(3)	R = Me: [89] R = ^{i}Pr: [90]
17		R = Me: 2.249(4) R = ^{i}Pr: 2.270(2)	[90]

[a] Cy = cyclohexyl.

staggered propeller-like arrangement about the germanium atoms. In the case of $(Cy_3Ge)_2S_3$ the Ge—S bond distances were found to be significantly longer than in digermyl sulphides. Compounds of the type R_3GeSR' (Entries 6–8, Table 13) all exhibit distorted tetrahedral geometry about the germanium atom with Ge—S bond lengths from 2.22 to 2.25 Å [79–81].

Mono-, di- and tri-*O,O'*-dimethyldithiophosphato compounds of germanium show monodentate coordination of the ligand with tetrahedral geometry about the germanium atom (Entries 9–11, Table 13). The Ge—S bond length in diphenylbis(*O,O'*-dimethyldithiophosphato)germanium is shorter than in the triphenyl derivative [2.255(2) versus 2.285(1) Å] because of the replacement of a phenyl with the more electronegative dithiophosphate group [82]. There is no indication of any anisobidentate coordination for the sulphur ligand, the smallest non-bonding Ge···S distances being 5.253(1) and 5.363(2) Å for the triphenyl and diphenyl derivatives, respectively (compared with the sum of the van der Waals radii of 3.75 Å). Only partial solution of the structure of the monophenyl derivative was possible owing to deterioration of the crystal during data collection; the data are consistent with the structures discussed above [83]. In contrast, the structure of dimethylbis(*O,O*-2,3-dimethylbutylenedithiophosphato)germane (Entry 12, Table 13) has the terminal sulphur atoms oriented towards the germanium atom with an average Ge···S distance of 3.49(3) Å; however, this distance is still too great to consider the ligand to be anisobidentate [84].

The structures of chloro-, [85] bromo- [86] and iodo(*N,N*-dimethyldithiocarbamato)dimethylgermanium [86] have been reported (Entry 13, Table 13). In all three cases the germanium atom is at the centre of a distorted trigonal bipyramid with the halogen and a sulphur atom occupying the axial positions. The molecule is "frozen" in this anisobidentate coordination. The axial Ge—S distance is much greater than that of a normal Ge—S covalent bond (2.68–2.90 versus 2.25 Å) whilst being much less than the sum of the van der Waals radii (3.75 Å) and the S—Ge—S angle is about 160° rather than 180°. The Ge—S_{axial} bond length increases in the order X = I < X = Br < X = Cl; this is accompanied by a decrease in the Ge—X distance

Table 14
Selected bond lengths and angles of compounds containing a cyclic Ge—S bond

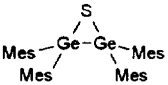
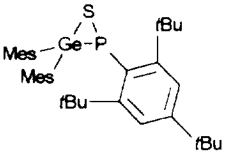
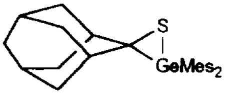
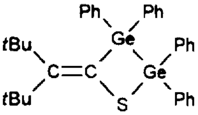
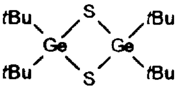
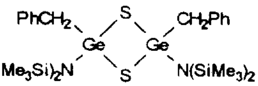
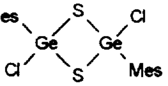
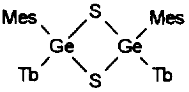
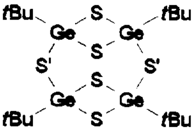
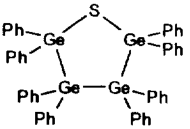
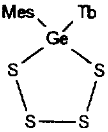
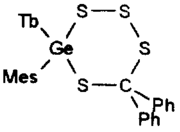
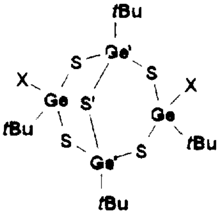
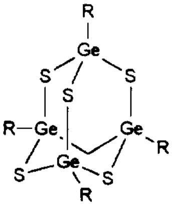
Entry	Compound	Ge—S (Å)	X—Ge—S (°)	Ref.
1[a]		2.263(3), 2.277(3)	58.2(1), 58.7(1)	[91]
2[a]		2.227(1)	57.2(1)	[66]
3[a]		2.222(1)	52.9(1)	[73]
4		2.242(6)	78.7(2)	[92]
5		2.246(3), 2.254(3)	94.5(1)	[154]
6		2.230(5), 2.248(6), 2.254(6), 2.241(5)	95.5(3)	[155]
7[a]		2.226(2), 2.210(2)	95.3(1)	[98]
8[a,b]		2.274(4), 2.250(5), 2.259(5), 2.275(4)	84.6(2), 84.8(2)	[93]
9		Ge—S: 2.243(8) Ge—S′: 2.216(3)	S—Ge—S′: 114.2(2) S—Ge—S: 96.7	[94]
10		2.230(4), 2.250(4)	109.5(1)	[95], see also [1]
11[a,b]				[96]

Table 14 (*continued*)

Entry	Compound	Ge—S (Å)	X—Ge—S (°)	Ref.
12[a,b]		2.290(2), 2.251(2)		[97]
13		X = Cl: Ge′—S: 2.227(4), 2.221(4); Ge—S: 2.212(4), 2.214(4)	X = Cl: S—Ge′—S: 104.3(2) S—Ge—S′: 112.2(1), 113.3(1) S—Ge—S: 115.3(2)	X = SH: [94] X = Cl: [98]
14		R = Me: 2.218(3) R = CF_3: 2.210(2)	111.8(3) 113.8(1)	R = Me: [156], see also [1] R = CF_3: [157]

[a] Mes = 2,4,6-trimethylphenyl.

[b] Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl.

and a narrowing of the S—Ge—S angle [X = I, 71.6(1)°; X = Br, 69.7(2)°; X = Cl, 68.5(1)°]. The bis(dithiocarbamato) germanium compounds (Entries 14 and 15, Table 13) show pseudotetrahedral geometry about germanium with the non-bonding sulphur atoms occupying open positions; the Ge···S non-bonding distances are long enough (3.08–3.18 Å) for the ligands to be considered as monodentate rather than anisobidentate. The Ge—S bond lengths of dimethylbis(*N*,*N*-dimethyldithiocarbamato)germanium [87] are longer than those of the monoderivative because of the increased steric crowding. The diphenyl derivative has a similar value [88]. In both cases the dithiocarbamate groups are pseudocoplanar.

The structures of several dithiocarbonate derivatives of di- and triphenylgermane have been reported (Entries 16 and 17, Table 13). All exhibit distorted tetrahedral geometry about the germanium atom and the dithiocarbonate ligands are clearly monodentate; if any secondary interaction does occur it is through the oxygen atom of the ligand, the Ge···O distance varies from 2.92 to 3.15 Å (the sum of the covalent radii is 1.88 Å and that of the van der Waals radii 3.47 Å). The S—Ge—S angle is significantly smaller for $Ph_2Ge[S_2COMe]_2$ [89] than that of $Ph_2Ge[S_2CO(^iPr)]_2$ [90] because the isopropyl groups prevent the dithiocarbonate ligands from coming as close as they can in the methyl-substituted case. From the structures reported, neither an increase in the number of phenyl substituents nor a change in the bulk

Table 15
Selected bond lengths of compounds containing a Ge−Se or Ge−Te bond

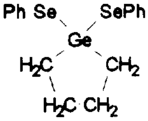
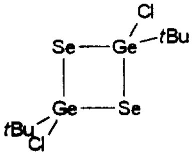
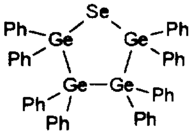
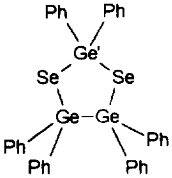
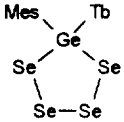
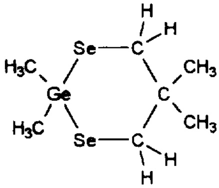
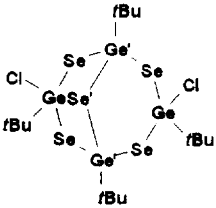
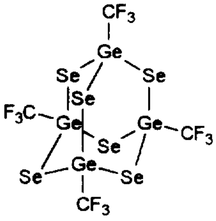
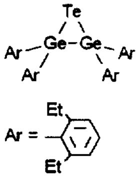
Entry	Compound	Ge−X (Å)	X−Ge−X (°)	Ref.
1	$Ge(SePh)_4$	2.347(1), 2.344(1)		[158]
2	$EtGe(SePh)_3$	2.353(1), 2.356(1), 2.348(1)		[158]
3		2.362(5)		[159]
4		2.351(2), 2.350(2)	99.0, 99.1	[98]
5		2.373(1)	110.4(1)	[99], see also [1]
6		Ge'−Se: 2.368(1), 2.363(1) Ge−Se: 2.370(1), 2.359(1)	Se−Ge'−Se: 113.1(1) Se−Ge−Ge: 103.0(1), 101.3(1)	[100]
7[a,b]		2.421(2), 2.409(2)	101.23(7)	[101]
8		2.349, 2.352	103.2	[102]
9		Ge'−Se: 2.359(1), 2.358(1) Ge'−Se': 2.347(1) Ge−Se: 2.336(1), 2.337(2)	Se−Ge'−Se: 103.9(1) Se−Ge'−Se': 112.7(1), 114.8(1) Se−Ge−Se: 116.6(1)	[98]

Table 15 (*continued*)

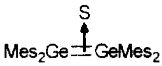
Entry	Compound	Ge—X (Å)	X—Ge—X (°)	Ref.
10		2.344(1)	114.8(1)	[157]
11		2.597(2)	62.04(4), 62.05(4)	[111]

[a] Mes = 2,4,6-trimethylphenyl.

[b] Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl.

of the R group in the dithiocarbonate ligand has any significant effect on the arrangement about germanium.

The structure of a thiadigermirane has been examined (Entry 1, Table 14) [91]. The Ge—Ge bond is shorter than normal [2.376(2) versus 2.44 Å] and the angles about the germanium atoms are almost planar (357.3° and 356.7°), suggesting that the compound has some of the character of the π-complex shown. It has been postulated that partial π-bonding also occurs in a germathiaphosphirane (Entry 2, Table 14), although the Ge—P bond length is not unusually short [66]. The structure of the only reported thiagermirane is unremarkable (Entry 3, Table 14) [73].



$$Mes_2Ge \overset{S \atop \uparrow}{=} GeMes_2$$

Compounds containing a four-membered ring with a Ge—S linkage all have bond lengths which are consistent with single Ge—S bonds (Entries 4–8, Table 14). The ring of an alkylidenedigermathietane (Entry 4, Table 14) has a puckered structure with a dihedral angle of 15.4° formed by the Ge—Ge—S and Ge—C—S planes [92]. In contrast to the other planar 1,3-dithia-2,4-digermetanes, the ring with an extremely congested *cis* configuration of four bulky aryl groups (Entry 8, Table 14) has a folded structure with large torsion angles of 36° and 38° [93]. The germanium sesquisulphide $(^tBuGe)_4S_6$ has a "double-decker"-type structure with two four-membered rings and two eight-membered rings (Entry 9, Table 14). The two four-membered rings are almost planar and are perpendicular to the common plane of the two eight-membered rings [94].

The two compounds containing a five-membered ring with a Ge—S bond (Entries 10 and 11, Table 14) both show envelope conformations. $(Ph_2Ge)_4S$ (Entry 10,

Table 14) has been reviewed previously [1] and shows no unusual features [95]. In MesTbGeS$_4$, the S$_4$ unit is asymmetrically bound with two unequal Ge—S lengths [96]. The only six-membered ring reported (Entry 12, Table 14) adopts a chair conformation in which the germanium-containing moiety is significantly flatter than the carbon-containing moiety (51° versus 78°) [97].

The two substituted sesquichalcogenides are bicyclic compounds with two six-membered rings and a Ge—S—Ge bridge (Entry 13, Table 14). The dichloro-derivative has a twist-boat conformation for both rings and the chloro substituents are both axial and hence on the same side of the rings as the sulphur atom of the bridge. This steric situation prevents conversion to the corresponding sesquichalcogenide [98]. The tetragermanium hexasulphides (Entry 14, Table 14) both have adamantane structures with unremarkable bond lengths and angles. The methyl-substituted compound has been reviewed previously [1].

The Ge—Se bond lengths in acyclic compounds vary from 2.34 to 2.36 Å (Entries 1–3, Table 15). The distortion from tetrahedral geometry about the germanium atoms is caused by steric effects.

Compounds containing four-, five- and six-membered rings generally have similar Ge—Se bond lengths compared with the linear compounds and bond angles consistent with a distorted tetrahedral geometry about germanium (Entries 4–8, Table 15). The four-membered ring (^{t}BuClGeSe)$_2$ is folded along the Se···Se axis. Both ^{t}Bu groups are on the same side of the ring as the selenium atoms [98]. (Ph$_2$Ge)$_4$Se [99], which has been reviewed previously [1], exhibits a twist conformation and approximates planarity, whereas both (Ph$_2$Ge)$_2$Se(Ph$_2$Ge)Se [100] and TbMesGeSe$_4$ [101] exhibit half-chair conformations. The Ge—Ge bond length in (Ph$_2$Ge)$_2$Se(Ph$_2$Ge)Se is shorter than found in a perphenylated cyclopolygermane [2.415(1) versus 2.42–2.47 Å]. A 1,3-diselena-2-germacyclohexane (Entry 8, Table 15) surprisingly shows a 2,5-twist-boat conformation, which results in an intramolecular non-bonding distance of ca. 3.21 Å between selenium and the methylene carbon, which is much less than the sum of the van der Waals radii (3.6 Å), which may suggest attractive interactions due to the hypervalent nature of selenium [102].

(^{t}BuGe)$_4$Se$_5$Cl$_2$ (Entry 9, Table 15) has a bicyclic structure with two twisted six-membered rings, which results in both chlorine atoms being on the same side of the rings as the Ge—Se—Ge bridge [98]. (CF$_3$Ge)$_4$Se$_6$ (Entry 10, Table 15) has an adamantane structure. The tellurium-containing three-membered ring (Entry 11, Table 15) has an unusually long Ge—Ge bond [2.435(2) versus 2.38–2.40 Å] for a Ge$_2$X ring system [103].

6. Organogermanium derivatives of Group 17 elements

A large number of compounds containing germanium–halogen bonds have had their structures determined by X-ray crystallography (Table 16). Typical Ge—Cl bond lengths are 2.08–2.15 Å; far fewer values are available for the other halogens. Longer bond lengths occur when the germanium atom has a coordination number greater than four.

Simple four-coordinate compounds have a distorted tetrahedral arrangement about the germanium atom, the deviation from tetrahedral geometry being dependent on the relative sizes of the halogen atom and the organic substituents. The simplest structures reported (Entries 1–13, Table 16) show clearly that, as expected, the Ge—X bond length increases in the order $Cl < Br < I$, the average values being 2.15, 2.32 and 2.51 Å, respectively.

Tris(9-triptycyl)chlorogermane (Entry 14, Table 16) has a slightly elongated Ge—Cl bond owing to the steric crowding caused by the bulky 9-triptycene groups [104]. On the other hand, electronic effects result in long Ge—Cl bond lengths in the complex $\{HCP[N(CH_3)_2]_2\}_2 \cdot GeCl_2$ (Entry 16, Table 16), the bonding between the germanium atom and the ligand having some ionic character [105].

The four-membered ring compound $(CF_3)_2CSN$(adamantyl)$GeCl_2$ (Entry 19, Table 16) has a surprisingly short Ge—Cl bond length [2.008(4) Å] for no immediately obvious reason [49]. All the other four-membered rings surveyed have typical Ge—X bond distances. The bicyclic compounds (Entries 23 and 24, Table 16) have the chlorine atoms in axial positions and, therefore, on the same side of the rings as the sulphur or selenium bridge, which prevents ring closure from occurring which would lead to an adamantane-type structure [98].

A series of carboxylic acids and carboxylic acid derivatives with terminal trihalogermyl groups have been reported (Entries 25–32, Table 16). In the amino derivatives, an intramolecular interaction between the oxygen of the carbonyl group and the germanium atom can occur, resulting in the germanium becoming pentacoordinate with a distorted trigonal bipyramidal coordination polyhedron and lengthening of the Ge–halogen bond *trans* to the oxygen atom. For example, in $Cl_3GeCH_2CH_2CONH_2$ (Entry 31, Table 16), the Ge···O distance is 2.166(9) Å (the sum of the covalent radii is 1.88 Å), the germanium atom is in a trigonal bipyramidal environment and the axial Ge—Cl bond is ca. 0.1 Å longer than the equatorial Ge—Cl bonds [2.253(6) versus 2.156(4) and 2.138(6) Å] [106]. On the other hand, the corresponding acid, $Cl_3GeCH_2CH_2COOH$ (Entry 25, Table 16), has a Ge···O distance of 3.228 Å (close to the sum of the van der Waals' radii of 3.3 Å), the environment around the germanium atom is tetrahedral and there is no *trans* influence of the O atom on one of the Ge—Cl bond lengths [2.134(2), 2.123(2) and 2.121(2) Å] [106, 107]. The examined pyrrolidines (Entries 34 and 35, Table 16), piperidone-2 (Entry 36, Table 16) and δ-valerolactam (Entry 37, Table 16) all have a distorted [3+2] trigonal bipyramidal geometry about germanium with either oxygen or nitrogen as the second axial atom, and this is accompanied by long Ge—Cl bonds of 2.32–2.57 Å [108]. The chloro-, bromo- and iodo(*N*,*N*-dimethyldithiocarbamato)dimethylgermanium structures (Entry 39, Table 16) also exhibit this geometry with sulphur as the internally coordinated atom; all the Ge—X bonds are elongated [85,86].

The structure of the pentacoordinate compound *o*-$(Me_2NCH_2)C_6H_4GeMePhCl$ (Entry 41, Table 16) is similar to that of those above which involve internal coordination [109]. The only structures of compounds containing Ge—F bonds which have been reported are penta- and hexacoordinate anions (Entries 43 and 44, Table 16); in both cases the Ge—F bond length is approx. 1.83 Å [110,111].

Table 16
Selected bond lengths of compounds with Ge—halogen bonds

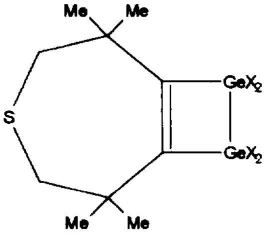
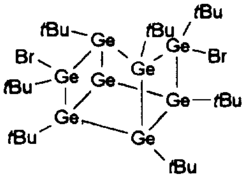
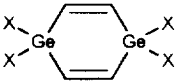
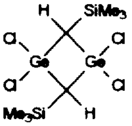
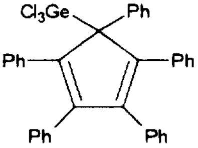
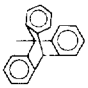
Entry	Compound	Ge—X (Å)	Ref.
1	Ph_3GeBr	2.318(3), 2.322(3)	[160]
2	$MeGeI_3$	2.502(2), 2.497(2)	[161]
3	$(Cl_2PhGe)_2$	2.156(2), 2.147(2)	[141]
4	$Cl(Ph_2Ge)_3Cl$	Molecule 1: 2.187(6), 2.194(4) Molecule 2: 2.192(6), 2.196(6)	[143]
5	$Cl(Ph_2Ge)_4Cl$	2.132(8)	[143]
6	$I(Ph_2Ge)_4I$	2.559(1)	[28], see also [1]
7	$(C_6Cl_5)_3GeCl$	2.158(2)	[162]
8	$(C_6Cl_5)_2GeI_2$	2.518(2), 2.502(2)	[163]
9		X=Cl: 2.146(2), 2.150(2), 2.146(2), 2.145(2) X=I: 2.522, 2.511, 2.515, 2.526	X=Cl: [137] X=I: [138]
10		2.378	[34]
11		X=Cl: 2.144, 2.138 X=I: 2.490, 2.483	X=Cl: [164] X=I: [165]
12		2.142, 2.127	[136]
13		2.1240(6), 2.1335(6), 2.1374(6)	[166]
14[a]	$ClGeTp_3$ Tp= 	2.204(2)	[104]

Table 16 (*continued*)

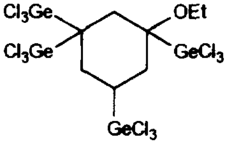
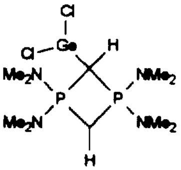
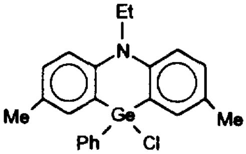
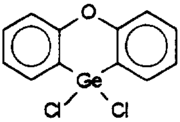
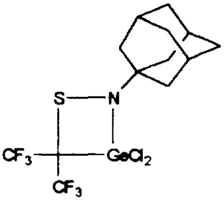
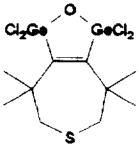
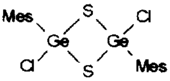
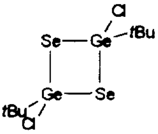
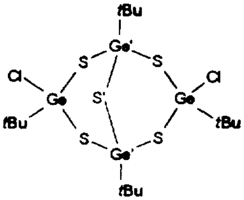
Entry	Compound	Ge–X (Å)	Ref.
15		2.110(2), 2.110(2), 2.126(2), 2.111(2), 2.128(2), 2.110(2), 2.134(2), 2.115(2), 2.115(3), 2.118(2), 2.108(3), 2.128(2)	[167]
16		2.323(1), 2.297(1)	[105]
17		2.212	[168]
18		2.144, 2.152	[169]
19		2.008(4)	[49]
20		2.129, 2.130, 2.130, 2.123	[170]
21[b]		2.183(2)	[98]
22		2.159(7), 2.181(9)	[98]
23		2.180(5)	[98]

Table 16 (*continued*)

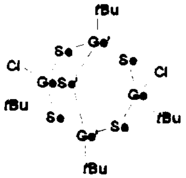
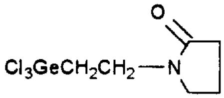
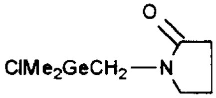
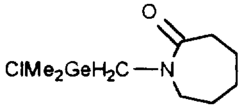
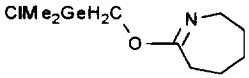
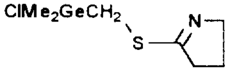
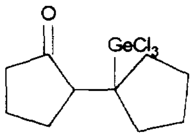
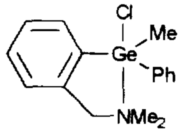
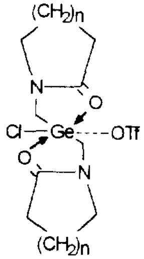
Entry	Compound	Ge–X (Å)	Ref.
24		2.174(3)	[98]
25	$Cl_3GeCH_2CH_2COOH$	2.134(2), 2.123(2), 2.121(2), 2.128, 2.125, 2.141	[106] [107]
26	$Cl_3GeCH_2CH(Me)COOH$	2.141, 2.127, 2.122	[171]
27	$(Br_3Ge)_2CHCH_2COOH$	2.272, 2.271, 2.267, 2.261, 2.250, 2.273	[172]
28	$Cl_3GeCH_2CH(Me)COOMe$	2.120, 2.133, 2.152	[173]
29	$Cl_3GeCH_2CH_2COOPh$	Molecule 1: 2.122, 2.123, 2.109 Molecule 2: 2.107, 2.123, 2.117	[174]
30	$Cl_3GeC(Ph)(Me)CH_2COPh$	2.138, 2.143, 2.181	[175]
31	$Cl_3GeCH_2CH_2CONH_2$	2.156(4), 2.138(6), 2.253(6)	[106]
32	$Cl_3GeCH(Me)CH_2CONMe_2$	2.263, 2.143, 2.135	[176]
33		2.253, 2.134, 2.138	[176]
34		2.324(2)	[108]
35		2.354(2)	[108]
36		2.458(8)	[108]
37		2.566(2)	[108]
38	$Cl_3GeN(Me)CO(p\text{-}C_6H_4\text{-}Me)$	Molecule 1: 2.149, 2.251, 2.133 Molecule 2: 2.142, 2.238, 2.149	[177]
39	$XMe_2GeSCSNMe_2$	X=Cl: 2.251(1) X=Br: Molecule 1: 2.418(3) Molecule 2: 2.430(3) X=I: 2.712(1)	X=Cl: [85] X=Br, I: [86]

Table 16 (*continued*)

Entry	Compound	Ge–X (Å)	Ref.
40		2.148, 2.168, 2.139	[178]
41		Molecule 1: 2.327(5) Molecule 2: 2.301(4)	[109]
42[c]		$n=1:2.159(1)$ $n=2:2.129(2)$ $n=3:2.165(1)$	[179]
43	$[F_2Ge(CF_3)_3]\ NMe_4^-$	1.835(8)	[110]
44	$[F_4Ge(CF_3)_2]^{2-}\ 2K^+$	1.824, 1.833	[111]

[a] Tp = 9-triptycyl.

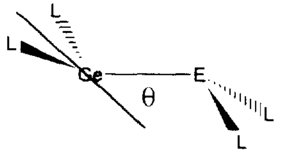
[b] Mes = 2,4,6-trimethylphenyl.

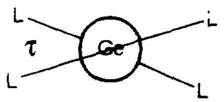
[c] OTf = trifluoromethanesulphonate.

7. Low coordinate germanium compounds

7.1. Tricoordinate germanium compounds

Several compounds containing a tricoordinate germanium atom have had their structures determined by X-ray crystallography; they are listed in Table 17. The fold angle, θ, is defined as the angle between the Ge–E vector and the GeL_2 plane. The twist angle, τ, is defined as the angle between the GeL_2 and the EL_2 planes about the Ge–E vector.





There are some general trends of note. Except for the digermenes, the tricoordinate germanium atom is trigonal planar. Although the degree of shortening of the Ge–E double bond length varies from 4% to 10%, the majority are shortened by 7–9%

Table 17
Selected bond lengths and angles in double bonded germanium compounds

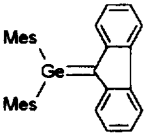
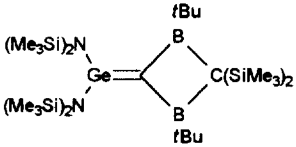
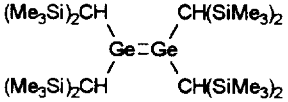
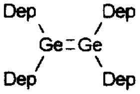
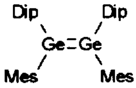
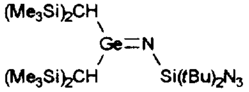
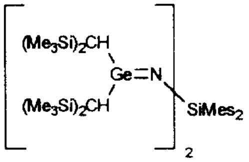
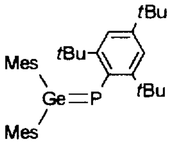
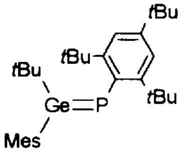
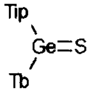
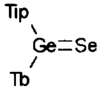
Entry	Compound	Ge=E (Å)	C–Ge–C (°)	C–Ge–E (°)	Fold (°)	Twist (°)	Ref.
1[a]		1.803(4)			0	6	[6]
2		1.827(4)	N–Ge–N: 110.5(2)	N–Ge–E: 125.3(2), 124.1(2)	1.7	36	[114]
3		2.347(2)	112.5(2)	113.7(3), 122.3(2)	32	0	[115]
4[b]		2.213(2)	115.4(2)	118.7(1), 124.3(1)	12	10	[116]
5[a,c]		2.301(1)	109.9(2)	111.6(2), 124.0(2)	36	7	[117]
6		1.704(5)	122.9(3)	121.8(3), 115.2(3)			[118]
7[a]		1.681(8)	116.3(5)	N–Ge–C: 119.1(5), 124.6(4)			[118]
8[a]		2.138(3)	112.9(4)	111.8(3), 135.2(4)		*cis*: 10 *trans*: 13	[180]
9[a]		2.144(3)	110.9(5)	114.4(3), 134.7(4)			[181]

Table 17 (*continued*)

Entry	Compound	Ge=E (Å)	C–Ge–C (°)	C–Ge–E (°)	Fold (°)	Twist (°)	Ref.
10[d,e]	 $\mathrm{Tip(Tb)Ge{=}S}$	2.049(3)	118.4(4)	124.8(3), 116.2(3)			[120]
11[d,e]	 $\mathrm{Tip(Tb)Ge{=}Se}$	2.180(2)	119.1(4)	126.4(3), 113.8(3)			[121]

---

[a] Mes = 2,4,6-trimethylphenyl.

[b] Dep = 2,6-diethylphenyl.

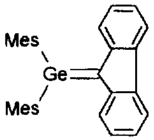
[c] Dip = 2,6-diisopropylphenyl.

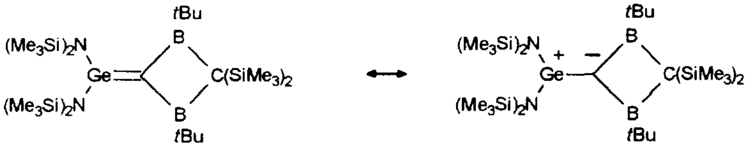
[d] Tip = 2,4,6-triisopropylphenyl.

[e] Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl.

compared with the average Ge—E single bond length. This is slightly smaller than the degree of shortening observed for C—C to C=C (12%), but not surprising considering the relative weakness of Ge—E π bond strengths [112,113].

The molecular structures of two germenes have been determined (Entries 1 and 2, Table 17) by X-ray methods. In both, the germanium atom is essentially trigonal planar and there is a shortening of 8–9% (Ge—C 1.98 Å) of the Ge—C bond. In the fluorenylidene substituted germene shown, 16 atoms (those of the fluorenylidene group, the germanium atom and the *ipso* carbon atoms of the mesityl groups) all lie in the same plane which is consistent with stabilization of the Ge=C by electronic interactions between Ge=C and the fluorenylidene moiety [6]. From the chemical shifts of the carbon atom of the double bond and the directly substituted boron atoms, the bis[bis(trimethylsilyl)amino]-substituted germene shown appears to have significant ylid character [114]. This molecule is also significantly twisted by 36° about the Ge—E axis.





The molecular structures of three digermenes, RR′Ge=GeRR′, have been determined (Entries 3 [R = R′ = $CH(SiMe_3)_2$], 4 (R = R′ = 2,6-diethylphenyl) and 5 [(*Z*) R = mesityl, R′ = 2,6-diisopropylphenyl], Table 17}. All three have *trans*-bent double bonds. The *trans*-bent geometry has been calculated to have the lowest energy of all the Ge_2H_4 isomers [112] and lies 3.2 kcal mol^{-1} below the planar form. The fold angle (as defined above) appears to increase with steric congestion and, as the germanium atom becomes more pyramidalized, the degree of bond shortening decreases {9% for RR'Ge=GeRR'(R = R' = 2,6-diethylphenyl) [115] and 4% for RR'Ge=GeRR'[R = R' = $CH(SiMe_3)_2$} [116]; Ge—Ge 2.44 Å}. The digermene with the longest Ge=Ge double bond length [Entry 3, R = R' = $CH(SiMe_3)_2$] dissociates readily in solution to two germylenes, although this does not appear to be related to the conformation of the digermene since the bulky substituted (*Z*)-1,2-bis(2,6-diisopropyl)-1,2-dimesityldigermene does not appear to dissociate under the same conditions [117]. The small twist observed about the Ge—E vector also may relieve some steric strain.

The structures of two germanimines containing a Ge—C bond have been examined by X-ray crystallography (Entries 6 and 7, Table 17) [118]. In each case, the germanium atom is trigonal planar and an 8–10% shortening of the Ge—N bond is observed. The Ge—N—L (L = silyl ligand) angle is enlarged to 136–137° from the expected 120°.

The molecular structures of germaphosphenes (Entries 8 and 9, Table 17) show much the same characteristics as germanimines. They are planar about the germanium atom and the Ge=P double bond is about 8% shorter than its single-bond analogue. The angle at phosphorus is smaller than in germanimines (102.6–107.5°), reflecting the increased p-character used in bonding to the phosphorus. The same trend has been observed on going from diimines to diphosphenes to diarsenes [119].

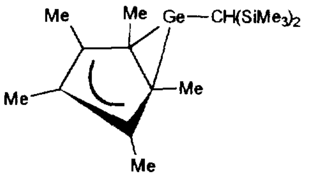
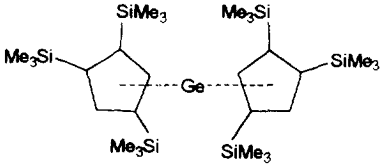
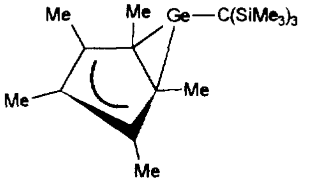
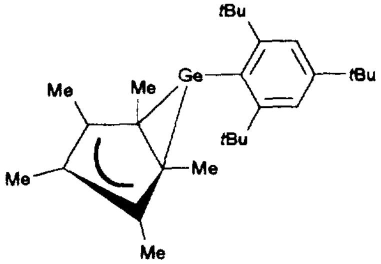
One example of a diarylgermanethione, with a germanium–sulphur double bond [120], and one example of a diarylgermaneselone, with a germanium–selenium double bond [121], have been examined (Entries 10 and 11, Table 17). Both compounds are kinetically stabilized by the extremely bulky 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl and the 2,4,6-triisopropylphenyl groups. Again, the germanium is trigonal planar in each case. The Ge—S bond is shortened by 8% and the Ge—Se bond is shortened by approximately 7%.

7.2. *Dicoordinate germanium compounds*

The molecular structures of the germylene species which have been carried out to date can be classified into two groups. There is one example of a dialkylgermylene; all other examples have at least one cyclopentadienyl derivative as a ligand (see Table 18). By substitution of a trimethylsilyl group for one hydrogen attached to the central carbon atom in one of the bis(trimethylsilyl)methyl ligands in $Ge[CH(SiMe_3)_2]_2$, the structure of $(Me_3Si)_3C—Ge—CH(SiMe_3)_2$ (Entry 5, Table 18) becomes monomeric in the solid state [122]. Presumably, the extra steric bulk of the silyl group prevents dimerization of the germylene as was observed in the X-ray determination of the structure of $Ge[CH(SiMe_3)_2]_2$ [115]. The Ge—C bond lengths in $(Me_3Si)_3C—Ge—CH(SiMe_3)_2$ are elongated and the angle at germanium is compressed (111.3° compared with the expected 120°), indicating the presence of a stereochemically active lone pair and steric crowding within the molecule.

Within the cyclopentadienyl-substituted low-valent germanium compounds, there

Table 18
Selected bond lengths and angles in germylenes

Entry	Compound	Ge—C (Å)	C—Ge—C (°)	Ref.
1[a]	Cp_2Ge	2.347(7), 2.359(6)	50.4[b]	[125]
2[c]	$(C_5Bn_5)_2Ge$	2.429(3)–2.723(4) Ge—[centroid of C_5 ring]: 2.240(4), 2.288(4)	31[b] (Centroid of ring) —Ge—(centroid of ring): 163.1(1)	[124]
3[d]		Ge—CSi_2: 2.044(7) Ge—C(Cp*): 2.243(8), 2.250(9)	$(Si_2)C$—Ge—[vector to mid-point of C(Cp*)—C(Cp*) bond]: 106.9	[182]
4		2.46(1)–2.66(2) Ge—[centroid of C_5 ring]: 2.250–2.261	(Centroid of ring) —Ge—(centroid of ring): Molecule 1: 169.48 Molecule 2: 177.77	[123]
5	$(Me_3Si)_3C$—Ge—$CH(SiMe_3)_3$	Ge—CSi_3: 2.067(4) Ge—CSi_2: 2.012(6)	111.3(2)	[122]
6[d]		Ge—CSi_3: 2.14(2) Ge—C(Cp*): 2.25(2), 2.29(2)	$(Si_2)C$—Ge—[vector to mid-point of C(Cp*) —C(Cp*) bond]: 118.9	[183]
7[d]		Ge—C(Ar): 2.087(7) Ge—C(Cp*): 2.304(7), 2.325(7)	(Ar)C—Ge—[vector to mid-point of C(Cp*) —C(Cp*) bond]: 101.0	[183]

[a] Cp = cyclopentadienyl.
[b] The angle of aperture of the cyclopentadienyl ring planes.
[c] Bn = benzyl.
[d] Cp* = pentamethylcyclopentadienyl.

appear to be two different modes of bonding in the solid state, although all compounds are fluxional in solution. In bis[tris(trimethylsilyl)cyclopentadienyl]germylene (Entry 4, Table 18) [123] and decabenzylgermanocene (Entry 2, Table 18) [124], the cyclopentadienyl unit is η^5 in character and there is only a slight deviation

Table 19
Selected bond lengths and angles in hypercoordinated germanium compounds

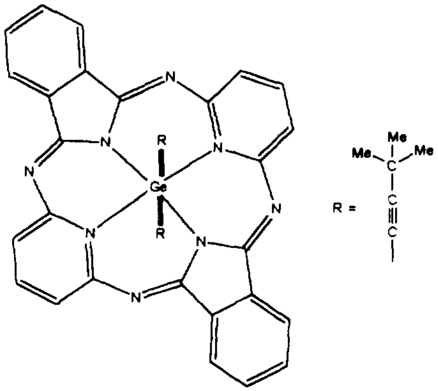
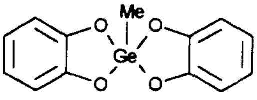
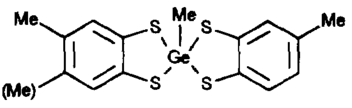
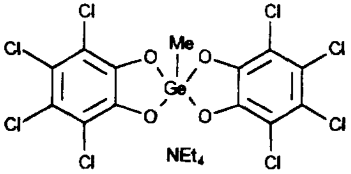
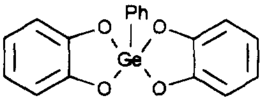
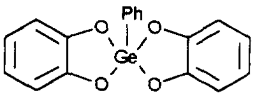
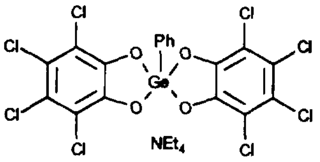
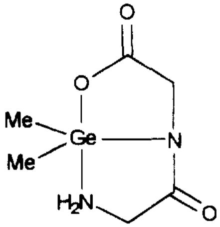
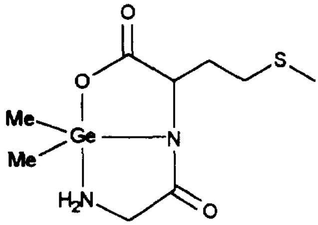
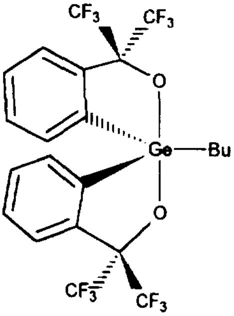
Entry	Compound	Ge—X (Å)	Coordination	Ref.
1		Ge—N: 1.956(2), 2.172(3) Ge—C: 1.938(3)	Octahedral	[127]
2	 NEt$_4$	Ge—C: 1.946(6) Ge—O: 1.920(5), 1.834(5)	Displaced 21.3% from trigonal bipyramidal to rectangular pyramid[a]	[128]
3	 NEt$_4$	Ge—C: 1.97(1) Ge—S: 2.413(4), 2.383(4), 2.278(4), 2.269(4)	Displaced 41.3% from trigonal bipyramidal to rectangular pyramid[a]	[128]
4	 NEt$_4$	Ge—C: 1.901(6) Ge—O: 1.874(4), 1.884(4), 1.872(4), 1.890(4)	Displaced 85% from trigonal bipyramidal to rectangular pyramid[a]	[128]
5	 NEt$_4$	Ge—C: 1.936(3) Ge—O: 1.897(2), 1.883(2), 1.847(2), 1.845(2)	Displaced 50.5% from trigonal bipyramidal to rectangular pyramid[a]	[129]
6	 NHEt$_3$·1/6 CH$_3$CN	Ge—C: 1.937(7) Ge—O: 1.874(5), 1.858(5), 1.832(5), 1.870(5)	Displaced 80.7% from trigonal bipyramidal to rectangular pyramid[a]	[129]
7	 NEt$_4$	Ge—C: 1.930(6) Ge—O: 1.879(4), 1.870(4), 1.859(4), 1.884(4)	Displaced 84.2% from trigonal bipyramidal to rectangular pyramid[a]	[129]

Table 19 (*continued*)

Entry	Compound	Ge–X (Å)	Coordination	Ref.
8		Ge–N$_{peptide}$: 1.888(4) Ge–N$_{amino}$: 2.110(5) Ge–O: 2.025(4) Ge–C: 1.907(7), 1.905(7)	Distorted trigonal bipyramid	[131]
9		Ge–N$_{peptide}$: 1.889(4) Ge–N$_{amino}$: 2.103(4) Ge–O: 2.008(3) Ge–C: 1.921(5), 1.908(5)	Distorted trigonal bipyramid	[132]
10		Ge–O: 1.984(5), 1.994(5) Ge–C: 1.930(6), 1.972(8) Ge–C(Bu): 1.947(9)	Distorted trigonal bipyramid	[130]

---

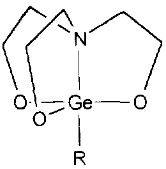
[a] By the dihedral angle method to access displacement, see [128,129].

from linearity. These structures most closely resemble the well known metallocene sandwich-type structure. In Entries 3, 6 and 7 (Table 18), the pentamethylcyclopentadienyl ligands are all η^2-substituted and there is a significant bending observed at the germanium atom (101.0° to 118.9°). The reported Ge–C bond lengths in Cp_2Ge (Entry 1, Table 18) are similar to those in the η^2-bonded cyclopentadienyl ligands in Entries 3, 6 and 7 [125]. The germanium atom is described as being displaced towards the apex at which the cyclopentadienyl rings touch.

8. Hypercoordinated germanium compounds

The structures of several penta- and hexacoordinate organogermanium compounds have already been discussed in previous sections (in particular, Sections 5 and 6) and the reader is also referred there.

Organogermatranes, of the general structure shown, are an important class of pentacoordinated organogermanium compounds; however, the structural features of these molecules have already been reviewed [126] and will not be discussed in detail here. The coordination about the germanium atom is trigonal bipyramidal and the Ge—N intramolecular distance varies from 2.1 to 2.4 Å.



The structure of a bis-substituted tert-butylalkynyl-substituted germanium hemiporphyracine has been reported (Entry 1, Table 19) [127]. The geometry about the germanium atom is that of a distorted octahedron. The Ge—N bond lengths are unequal (1.956 and 2.172 Å) and longer than Ge—N bond lengths found in tetracoordinated germylamines (1.85–1.92 Å). The Ge—C bond length, on the other hand, is not lengthened.

Several structures of anionic pentacoordinated germanates have been determined (Entries 2–7 and 10, Table 19). The sulphur-substituted germanate (Entry 3, Table 19) is apparently a 50:50 mixture of the *cis* and *trans* isomers with respect to the position of the methyl substituent on the aromatic ring. The position along the coordinate between a trigonal bipyramidal and a rectangular pyramidal (with four basal chalcogen atoms and an apical organic moiety) structure about germanium in Entries 2–7 was determined by the dihedral angle method and was rationalized in terms of ligand effects on germanium, substituent effects on the aromatic rings, hydrogen bonding to the cation and the nature of the acyclic ligand [128,129]. The butyl-substituted germanate (Entry 10, Table 19) shows only slight distortion from trigonal bipyramidal geometry about the germanium and lengthened Ge—O and Ge—C bonds, as expected [130].

The molecular structures of two dimethylgermanium derivatives of dipeptides have been reported (Entries 8 and 9, Table 19) [131,132]. Both show a distorted trigonal bipyramidal arrangement of the ligands about germanium with the two methyl groups and the peptide nitrogen atom in the equatorial positions and the oxygen of the carboxylate group and the amino nitrogen atom in the apical positions. The apical Ge—N and Ge—O bond lengths are significantly elongated compared with the corresponding four-coordinate values; however, the Ge—$N_{(amino)}$ bond is not as long as those reported in organogermatranes [133]. Intermolecular hydrogen bonds are apparently present in the Me_2GeGlyMet derivative but absent in the analogous Me_2GeGlyGly.

9. Summary

Table 20 summarizes the typical ranges of Ge—X bond lengths found in this review; unusually short or long bond lengths are not included in the ranges. These

Table 20
Typical bond lengths in organogermanium compounds

Ge–X	Range	
	Linear	Cyclic
Ge–H	1.46–1.70	
Ge–B	2.17	
Ge–Mg	2.72	
Ge–C	1.90–2.05	
Ge=C	1.80–1.83	
Ge–Si	2.38–2.46	
Ge–Ge	2.41–2.48	2.44–2.54
Ge=Ge	2.21–2.30	
Ge–Sn	2.60–2.61	
Ge–Pb	2.64	
Ge–N	1.85–1.86	1.86–1.90
Ge=N	1.68–1.70	
Ge–P	2.35–2.36	2.29–2.37
Ge=P	2.14	
Ge–As	2.45	
Ge–Sb	2.62–2.64	
Ge–O	1.75–1.85	
Ge–S	2.21–2.29	2.21–2.29
Ge=S	2.05	
Ge–Se	2.34–2.36	2.34–2.42
Ge=Se	2.18	
Ge–Te		2.60
Ge–F	1.82–1.84	
Ge–Cl	2.09–2.21	
Ge–Br	2.25–2.38	
Ge–I	2.48–2.56	

values were derived from a close examination of the material surveyed herein and it is hoped that this table will be useful in providing the reader with a convenient source of standard bond lengths found in organogermanium compounds.

Acknowledgements

Useful discussions with and the assistance of Dr. J.J. Vittal, Professor N.C. Payne and Professor R.H. Lipson, all of the Department of Chemistry, University of Western Ontario, and Dr. A.J. Lough of the Department of Chemistry, University of Toronto, are gratefully acknowledged. Financial assistance in the form of a grant to K.M.B. from NSERC (Canada) and a NATO Postdoctoral Fellowship to W.G.S. is also acknowledged.

References

[1] M. Dräger, L. Ross and D. Simon, Rev. Si Ge Pb Compd., 7 (1983) 299.
[2] F.H. Allen, O. Kennard and R. Taylor, Acc. Chem. Res., 16 (1983) 146.
[3] H. Schmidbaur, J. Rott, G. Reber and G. Müller, Z. Naturforsch., Teil B, 43 (1988) 727.
[4] M.F. Lappert, S.J. Miles, J.L. Attwood, M.J. Zaworotko and A.J. Carty, J. Organomet. Chem., 212 (1981) C4.
[5] T.S. Cameron, Kh.M. Mannan and S.R. Stobart, Cryst. Struct. Commun., 4 (1975) 601.
[6] M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Dräger and R. Dammel, Angew. Chem., Int. Ed. Engl., 27 (1988) 828.
[7] L. Rösch, C. Krüger and A.-P. Chiang, Z. Naturforsch., Teil B, 39 (1984) 855.
[8] E.P. Mayer, H. Nöth, W. Rattay and U. Wietelmann, Chem. Ber., 125 (1992) 401.
[9] S.V. Lindeman, V.E. Shklover, Yu.T. Struchkov, N.A. Vasnyova and A.M. Sladkov, Cryst. Struct. Commun., 10 (1981) 827.
[10] B. Morosin and L.A. Harrah, Acta Crystallogr., Sect. B, 37 (1981) 579.
[11] W. Ando, H. Ohgaki and Y. Kabe, Angew. Chem., Int. Ed. Engl., 33 (1994) 659.
[12] M.P. Egorov, S.P. Kolesnikov, Yu.T. Struchkov, M.Yu. Antipin, S.V. Serada and O.M. Nefedov, J. Organomet. Chem., 290 (1985) C27.
[13] T. Tsumuraya, S. Sato and W. Ando, Organometallics, 9 (1990) 2061.
[14] A. Krebs, A. Jacobsen-Bauer, E. Haupt, M. Veith and V. Huch, Angew. Chem., Int. Ed. Engl., 28 (1989) 603.
[15] L. Párkányi, C. Hernandez and K.H. Pannell, J. Organomet. Chem., 301 (1986) 145.
[16] K.H. Pannell, R.N. Kapoor, R. Raptis, L. Párkányi and V. Fülöp, J. Organomet. Chem., 384 (1990) 41.
[17] A.P. Cox and R. Varma, J. Chem. Phys., 46 (1967) 2007.
[18] M. Charissé, M. Mathes, D. Simon and M. Dräger, J. Organomet. Chem., 445 (1993) 39.
[19] K.M. Baines, J.A. Cooke, N.C. Payne and J.J. Vittal, Organometallics, 11 (1992) 1408.
[20] A. Heine and D. Stalke, Angew. Chem., Int. Ed. Engl., 33 (1994) 113.
[21] H. Suzuki, K. Okabe, R. Kato, N. Sato, Y. Fukuda, H. Watanabe and M. Goto, Organometallics, 12 (1993) 4833.
[22] H. Watanabe, M. Kato, T. Okawa, Y. Kougo, Y. Nagai and M. Goto, Appl. Organomet. Chem., 1 (1987) 157.
[23] H. Matsumoto, M. Minemura, K. Takatsuna, Y. Nagai and M. Goto, Chem. Lett., (1985) 1005.
[24] B. Beagley and J.J. Monaghan, Trans. Faraday Soc., 66 (1970) 2745.
[25] D. Simon, K. Häberle and M. Dräger, J. Organomet. Chem., 267 (1984) 133.
[26] S. Roller and M. Dräger, J. Organomet. Chem., 316 (1986) 57.
[27] M. Weidenbruch, F.-T. Grimm, M. Herrndorf, A. Schäfer, K. Peters and H.G. von Schnering, J. Organomet. Chem., 341 (1988) 335.
[28] M. Dräger and D. Simon, Z. Anorg. Allg. Chem., 472 (1981) 120.
[29] S. Roller, D. Simon and M. Dräger, J. Organomet. Chem., 301 (1986) 27.
[30] L. Ross and M. Dräger, J. Organomet. Chem., 199 (1980) 195.
[31] A. Sekiguchi, T. Yatabe, H. Naito, C. Kabuto and H. Sakurai, Chem. Lett., (1992) 1697.
[32] M. Dräger, L. Ross and D. Simon, Z. Anorg. Allg. Chem., 466 (1980) 145; M. Dräger and L. Ross, Z. Anorg. Allg. Chem., 476 (1981) 95.
[33] W. Jensen, R. Jacobson and J. Benson, Cryst. Struct. Commun., 4 (1975) 299.
[34] M. Weidenbruch, F.-T. Grimm, S. Pohl and W. Saak, Angew. Chem., Int. Ed. Engl., 28 (1989) 198.
[35] A. Sekiguchi, H. Naito, H. Nameki, K. Ebata, C. Kabuto and H. Sakurai, J. Organomet. Chem., 368 (1989) C1.
[36] A. Sekiguchi, C. Kabuto and H. Sakurai, Angew. Chem., Int. Ed. Engl., 28 (1989) 55.
[37] A. Sekiguchi, T. Yatabe, H. Kamatani, C. Kabuto and H. Sakurai, J. Am. Chem. Soc., 114 (1992) 6260.
[38] K.H. Pannell, L. Párkányi, H. Sharma and F. Cervantes-Lee, Inorg. Chem., 31 (1992) 522.
[39] L. Párkányi, A. Kálmán, S. Sharma, D.M. Nolen and K.H. Pannell, Inorg. Chem., 33 (1994) 180.

[40] N. Kleiner and M. Dräger, J. Organomet. Chem., 270 (1984) 151.

[41] H.-J. Koglin, K. Behrends and M. Dräger, Organometallics, 13 (1994) 2733.

[42] C. Glidewell, D.W.H. Rankin and A.G. Robiette, J. Chem. Soc. A, (1970) 2935.

[43] M. Rivière-Baudet, A. Morère, J.F. Britten and M. Onyszchuk, J. Organomet. Chem., 423 (1992) C5.

[44] T. Halder, W. Schwarz, J. Weidlein and P. Fischer, J. Organomet. Chem., 246 (1983) 29.

[45] C. Glidewell, M.B. Hursthouse, D. Lloyd, K.W. Lumbard and R.L. Short, J. Chem. Res. (S), (1986) 434, (M) 3501; C. Glidewell, M.B. Hursthouse, D. Lloyd, K.W. Lumbard and R.L. Short, J. Chem. Res. (S), (1986) 400, (M) 3319.

[46] C. Glidewell, D. Lloyd, K.W. Lumbard, J.S. McKechnie, M.B. Hursthouse and R.L. Short, J. Chem. Soc., Dalton Trans., (1987) 2981.

[47] T. Fjeldberg, H. Hope, M.F. Lappert, P.P. Power and A.J. Thorne, J. Chem. Soc., Chem. Commun., (1983) 639.

[48] A. Morère, M. Rivière-Baudet, J.F. Britten and M. Onyszchuk, Main Group Met. Chem., 15 (1992) 141.

[49] A. May, H.W. Roesky, R. Herbst-Irmer. S. Freitag and G.M. Sheldrick, Organometallics, 11 (1992) 15.

[50] T. Tsumuraya, S. Sato and W. Ando, Organometallics, 9 (1990) 2061.

[51] S. Masamune, Y. Hanzawa and D.J. Williams, J. Am. Chem. Soc., 104 (1982) 6136.

[52] S. Masamune, S. Murakami, H. Tobita and D.J. Williams, J. Am. Chem. Soc., 105 (1983) 7776; R. West, D.J. DeYoung and K.J. Haller, J. Am. Chem. Soc., 107 (1985) 4942; H. Yokelson, A.J. Millivolte; G.R. Gillette and R. West, J. Am. Chem. Soc., 109 (1987) 6865.

[53] M. Lazraq, C. Couret, J.P. Declercq, A. Dubourg, J. Escudie and M. Riviere-Baudet, Organometallics, 9 (1990) 845.

[54] W.S. Sheldrick, D. Schomburg and W. Wolfsberger, Z. Naturforsch., Teil B, 33 (1978) 493; J. Pfeiffer, W. Maringgele, M. Noltemeyer and A. Meller, Chem. Ber., 122 (1989) 245.

[55] W. Clegg, U. Klingebiel, C. Krampe and G.M. Sheldrick, Z. Naturforsch., Teil B, 35 (1980) 275; D. Stalke, N. Keweloh, U. Klingebiel, M. Noltemeyer and G.M. Sheldrick, Z. Naturforsch., Teil B, 42 (1987) 1237; S. Walter, U. Klingebiel and M. Noltemeyer, Chem. Ber., 125 (1992) 783.

[56] C. Glidewell. Inorg. Chim. Acta Rev., 7 (1973) 69.

[57] D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick, B. Beagley and T.G. Hewitt, J. Inorg. Nucl. Chem., 31 (1969) 2351.

[58] H. Ranaivonjatovo, J. Escudié, C. Couret, J.-P. Declercq, A. Dubourg and J. Satgé, Organometallics, 12 (1993) 1674.

[59] A.R. Dahl, A.D. Norman, H. Shenav and R. Schaeffer, J. Am. Chem. Soc., 97 (1975) 6364.

[60] G. Fritz, K.D. Hoppe, W. Hönle, D. Weber. C. Mujica, V. Manriquez and H.G. von Schnering, J. Organomet. Chem., 249 (1983) 63.

[61] C. Mujica, D. Weber and H.G. von Schnering, Z. Naturforsch., Teil B, 41 (1986) 991.

[62] A.H. Cowley, S.W. Hall, C.M. Nunn and J.M. Power, J. Chem. Soc., Chem. Commun., (1988) 753.

[63] M. Andrianarison, C. Couret, J.-P. Declercq, A. Dubourg, J. Escudie and J. Satge, J. Chem. Soc., Chem. Commun., (1987) 921.

[64] K.-F. Tebbe and R. Fröhlich, Z. Anorg. Allg. Chem., 506 (1983) 27.

[65] M. Drieß, H. Pritzkow and U. Winkler, Chem. Ber., 125 (1992) 1541.

[66] M. Andrianarison, C. Couret, J.-P. Declercq, A. Dubourg, J. Escudie, H. Ranaivonjatovo and J. Satge, Organometallics, 7 (1988) 1545.

[67] W. Hönle, J. Wolf and H.G. von Schnering, Z. Naturforsch., Teil B, 43 (1988) 219.

[68] S. Roller, M. Dräger, H.J. Breunig, M. Ates and S. Güleç, J. Organomet. Chem., 378 (1989) 327.

[69] C. Glidewell and D.C. Liles, J. Organomet. Chem., 174 (1979) 275.

[70] A. Haas, H.-J. Kutsch and C. Kruger, Chem. Ber., 122 (1989) 271.

[71] M. Lazraq, C. Couret, J. Escudie, J. Satgé and M. Dräger, Organometallics, 10 (1991) 1771.

[72] S. Masamune, S.A. Batcheller, J. Park and W.M. Davis, J. Am. Chem. Soc., 111 (1989) 1888.

[73] T. Tsumuraya, S. Sato and W. Ando, Organometallics, 8 (1989) 161.

[74] W. Ando, M. Kako and T. Akasaka, J. Chem. Soc., Chem. Commun., (1992) 458.

[75] C. Glidewell, D.W.H. Rankin, A.G. Robiette. G.M. Sheldrick, B. Beagley and S. Cradock, J. Chem. Soc. A, (1970) 315.

[76] B. Krebs and H.-J. Korte, J. Organomet. Chem., 179 (1979) 13.
[77] C. Glidewell and D.C. Liles, Acta Crystallogr., Sect. B, 38 (1982) 1320.
[78] F. Brisse, M. Vanier, M.J. Olivier, Y. Gareau and K. Steliou, Organometallics, 2 (1983) 878.
[79] F. Brisse, F. Bélanger-Gariépy, B. Zacharie, Y. Gareau and K. Steliou, New J. Chem., 7 (1983) 391.
[80] G.D. Andreetti, G. Bocelli, G. Calestani and P. Sgarabotto, J. Organomet. Chem., 273 (1984) 31.
[81] M.E. Cradwick, R.D. Taylor and J.L. Wardell, J. Organomet. Chem., 66 (1974) 43.
[82] R.K. Chada, J.E. Drake and A.B. Sarkar, Inorg. Chem., 24 (1985) 3156.
[83] R.K. Chada, J.E. Drake and A.B. Sarkar, J. Organomet. Chem., 323 (1987) 271.
[84] J.E. Drake, A.G. Mislankar and R. Ratnani, Can. J. Chem., 72 (1994) 1830.
[85] R.K. Chada, J.E. Drake and A.B. Sarkar, Inorg. Chem., 23 (1984) 4769.
[86] R.K. Chada, J.E. Drake, A.B. Sarkar and M.L.Y. Wong, Acta Crystallogr., Sect. C, 45 (1989) 37.
[87] R.K. Chada, J.E. Drake and A.B. Sarkar, Inorg. Chem., 25 (1986) 2201.
[88] R.K. Chada, J.E. Drake and A.B. Sarkar, Inorg. Chim. Acta, 143 (1988) 31.
[89] J.E. Drake, A.B. Sarkar and M.L.Y. Wong, Inorg. Chem., 29 (1990) 785.
[90] J.E. Drake, A.G. Mislankar and M.L.Y. Wong, Inorg. Chem., 30 (1991) 2174.
[91] T. Tsumuraya, S. Sato and W. Ando, Organometallics, 7 (1988) 2015.
[92] W. Ando, T. Tsumuraya and M. Goto, Tetrahedron Lett., 27 (1986) 5105.
[93] N. Tokitoh, T. Matsumoto, H. Ichida and R. Okazaki, Tetrahedron Lett., 32 (1991) 6877.
[94] W. Ando, T. Kadowaki, Y. Kabe and M. Ishii, Angew. Chem., Int. Ed. Engl., 31 (1992) 59.
[95] L. Ross and M. Dräger, J. Organomet. Chem., 194 (1980) 23.
[96] N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi and R. Okazaki, J. Am. Chem. Soc., 113 (1991) 7047.
[97] N. Tokitoh, T. Matsumoto and R. Okazaki, Tetrahedron Lett., 32 (1991) 6143.
[98] H. Puff, K. Braun, S. Franken, T.R. Kök and W. Schuh, J. Organomet. Chem., 335 (1987) 167.
[99] L. Ross and M. Dräger, Z. Anorg. Allg. Chem., 472 (1981) 109.
[100] M. Dräger and K. Häberle, J. Organomet. Chem., 280 (1985) 183.
[101] N. Tokitoh, T. Matsumoto and R. Okazaki, Tetrahedron Lett., 33 (1992) 2531.
[102] S. Tomoda, M. Shimoda, M. Sanami, Y. Takeuchi and Y. Iitaka, J. Chem. Soc., Chem. Commun., (1989) 1304.
[103] T. Tsumuraya, Y. Kabe and W. Ando, J. Chem. Soc., Chem. Commun., (1990) 1159.
[104] J.M. Chance, J.H. Geiger, Y. Okamoto, R. Aburatani and K. Mislow, J. Am. Chem. Soc., 112 (1990) 3540.
[105] E. Fluck, M. Spahn and G. Heckmann, Z. Anorg. Allg. Chem., 612 (1992) 56.
[106] T.K. Gar, N.A. Viktorov, V.F. Mironov, S.N. Gurkova, A.I. Gusev, D.A. Ivaschchenko, V.S. Nikitin, N.V. Alekseev and V.P. Feshin, Zh. Obshch. Khim., 52 (1982) 1593.
[107] S. Guan, Q. Guo, S.-G. Zhang, Z.-S. Jin and J.-Z. Ni, Jiegou Huaxue, 8 (1989) 177.
[108] A.O. Mozzchukhin, A.A. Macharashvili, V.E. Shklover, Yu.T. Struchkov, A.G. Shipov, V.N. Sergeev, S.A. Artamkin, S.V. Pestunovich and Yu.I. Baukov, J. Organomet. Chem., 408 (1991) 305.
[109] C. Breliere, F. Carre, R.J.P. Corriu, A. de Saxce, M. Poirier and G. Royo, J. Organomet. Chem., 205 (1981) C1.
[110] D.J. Brauer, J. Wilke and R. Eujen, J. Organomet. Chem., 316 (1986) 261.
[111] D.J. Brauer, H. Bürger and R. Eujen, Angew. Chem., Int. Ed. Engl., 19 (1980) 836.
[112] R.S. Grev, Adv. Organomet. Chem., 33 (1991) 125.
[113] J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satge, Coord. Chem. Rev., 130 (1994) 427.
[114] H. Meyer, G. Baum, W. Massa and A. Berndt, Angew. Chem., Int. Ed. Engl., 26 (1987) 798.
[115] J.T. Snow, S. Murakami, S. Masamune and D.J. Williams, Tetrahedron Lett., 25 (1984) 4191.
[116] D.E. Goldberg, P.B. Hitchcock, M.F. Lappert, K.M. Thomas, A.J. Thorne, T. Fjeldberg, A. Haaland and B.E.R. Schilling, J. Chem. Soc., Dalton Trans., (1986) 2387.
[117] S.A. Batcheller, T. Tsumuraya, O. Tempkin, W.M. Davis and S. Masamune, J. Am. Chem. Soc., 112 (1990) 9394.
[118] W. Ando, T. Ohtaki and Y. Kabe, Organometallics, 13 (1994) 434.
[119] A.H. Cowley and N.C. Norman, Prog. Inorg. Chem., 34 (1986) 1.
[120] N. Tokitoh, T. Matsumoto, K. Manmaru and R. Okazaki, J. Am. Chem. Soc., 115 (1993) 8855.
[121] T. Matsumoto, N. Tokitoh and R. Okazaki, Angew. Chem., Int. Ed. Engl., 33 (1994) 2316.

[122] P. Jutzi, A. Becker, H.G. Stammler and B. Neumann, Organometallics, 10 (1991) 1647.
[123] P. Jutzi, E. Schlüter, M.B. Hursthouse, A.M. Arif and R.L. Short, J. Organomet. Chem., 299 (1986) 285.
[124] H. Schumann, C. Janiak, E. Hahn, J. Loebel and J.J. Zuckerman, Angew. Chem., Int. Ed. Engl., 24 (1985) 773.
[125] M. Grenz, E. Hahn, W.-W. du Mont and J. Pickardt, Angew. Chem., Int. Ed. Engl., 23 (1984) 61.
[126] S.N. Gurkova, A.I. Gusev, V.A. Sharapov, N.V. Alekseev, T.K. Gar and N.J. Chromova, J. Organomet. Chem., 268 (1984) 119; P. Hencsei, L. Párkányi, Rev. Si Ge Pb Compd., 8 (1985) 191; P. Hencsei, L. Párkányi and V. Mironov, Main Group Met. Chem., 14 (1991) 13; J.G. Verkade, Coord. Chem. Rev., 137 (1994) 233.
[127] W. Hiller, J. Strähle, K. Mitulla and M. Hanack, Liebigs Ann. Chem., (1980) 1946.
[128] R.R. Holmes, R.O. Day, A.C. Sau and J.M. Holmes, Inorg. Chem., 25 (1986) 600.
[129] R.R. Holmes, R.O. Day, A.C. Sau, C.A. Poutasse and J.M. Holmes, Inorg. Chem., 25 (1986) 607.
[130] S.E. Denmark, R.T. Jacobs, G. Dai-Ho and S. Wilson, Organometallics, 9 (1990) 3015.
[131] M. Vornefeld, F. Huber, H. Preut and H. Brunner, Appl. Organomet. Chem., 3 (1989) 177.
[132] H. Preut, M. Vornefeld and F. Huber, Acta Crystallogr., Sect. C, 45 (1989) 1504.
[133] L.O. Atovmyan, Ya Ya Bleidelis, A.A. Kemme and R.P. Shibaeva, J. Struct. Chem., 11 (1970) 295; S.N. Gurkova, A.I. Gusev, I.R. Segel'man, N.V. Alekseev, T.K. Gar and N.V. Khromova, J. Struct. Chem., 22 (1981) 461; A.A. Kemme, Ya Ya Bleidelis, R.P. Shibaeva and L.O. Atovmyan, J. Struct. Chem., 14 (1973) 90.
[134] K.M. Baines, J.A. Cooke and J.J. Vittal, J. Chem. Soc., Chem. Commun., (1992) 1484.
[135] N.N. Zemlyanskii, I.V. Borisova, V.K. Bel'skii, N.D. Kolosova and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 959.
[136] A.I. Gusev, T.K. Gar, M.G. Los and N.V. Alexeev, Zh. Strukt. Khim., 17 (1976) 736.
[137] A.A. Espenbetov, Yu.T. Struchkov, S.P. Kolesnikov and O.M. Nefedov, J. Organomet. Chem., 275 (1984) 33.
[138] A.V. Polyakov, A.I. Yanovskii, Yu.T. Struchkov, A.M. Gal'minas, M.P. Egorov, S.P. Kolesnikov and O.M. Nefedov, Metalloorg. Khim., 1 (1988) 1257.
[139] S.P. Mallela, M.A. Ghuman and R.A. Geanangel, Inorg. Chim. Acta, 202 (1992) 211.
[140] M. Dräger and L. Ross, Z. Anorg. Allg. Chem., 460 (1980) 207.
[141] K. Häberle and M. Dräger, Z. Naturforsch., Teil B, 42 (1987) 323.
[142] M. Dräger and D. Simon, J. Organomet. Chem., 306 (1986) 183.
[143] K. Häberle and M. Dräger, J. Organomet. Chem., 312 (1986) 155.
[144] L. Ross and M. Dräger, Z. Naturforsch., Teil B, 38 (1983) 665; L. Ross and M. Dräger, Z. Anorg. Allg. Chem., 519 (1984) 225.
[145] H.D. Hausen, O. Mundt and W. Kaim, J. Organomet. Chem., 296 (1985) 321.
[146] K.-H. van Bonn, P. Schreyer, P. Paetzold and R. Boese, Chem. Ber., 121 (1988) 1045.
[147] K.-F. Tebbe and B. Freckman, Acta Crystallogr., Sect. C, 40 (1984) 254.
[148] M. Lazraq, J. Escudié, C. Couret, U. Bergsträsser and M. Regitz, J. Chem. Soc., Chem. Commun., (1993) 569.
[149] H. Puff, H. Heisig, W. Schuh and W. Schwab, J. Organomet. Chem., 303 (1986) 343.
[150] M. Kako, T. Akasaka and W. Ando, J. Chem. Soc., Chem. Commun., (1992) 457.
[151] H. Puff, S. Franken, W. Schuh and W. Schwab, J. Organomet. Chem., 254 (1983) 33.
[152] L. Ross and M. Dräger, Chem. Ber., 115 (1982) 615.
[153] M. Dräger and K. Haberle, J. Organomet. Chem., 280 (1985) 183.
[154] M. Wojnowska, M. Noltemeyer, H.-J. Füllgrabe and A. Meller, J. Organomet. Chem., 228 (1982) 229.
[155] P.B. Hitchcock, H.A. Jasim, R.E. Kelly and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1985) 1776.
[156] R.H. Beno and C.J. Fritchie, Jr., J. Chem. Soc., Dalton Trans., (1973) 543.
[157] A. Haas, H.-J. Kutsch and C. Krüger, Chem. Ber., 120 (1987) 1045.
[158] H.J. Gysling and H.R. Luss, Organometallics, 8 (1989) 363.
[159] S. Tomoda, M. Shimoda, Y. Takeuchi and Y. Iitaka, Chem. Lett., (1988) 535.
[160] H. Preut and F. Huber, Acta Crystallogr., Sect. B, 35 (1979) 83.

[161] R.K. Chadha, J.E. Drake and M.K.H. Neo, J. Cryst. Spectrosc., 15 (1985) 39.
[162] L. Fajarí, L. Juliá, J. Riera, E. Molins and C. Miravitlles, J. Organomet. Chem., 363 (1989) 31.
[163] L. Fajarí, J. Carilla, L. Juliá, J. Riera, A. Párraga, M. Coll and X. Solans, J. Organomet. Chem., 474 (1994) 89.
[164] N.G. Bokii and Yu.T. Struchkov, Zh. Strukt. Khim., 9 (1968) 838.
[165] N.G. Bokii and Yu.T. Struchkov, Zh. Strukt. Khim., 8 (1967) 122.
[166] C. Janiak, M. Schwichtenberg and F.E. Hahn, J. Organomet. Chem., 365 (1989) 37.
[167] S.P. Kolesnikov, S.L. Povarov, A.I. Lutsenko, D.S. Yufit, Yu.T. Struchkov and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 39 (1990), 895.
[168] V.K. Belsky, I.E. Saratov, V.O. Reikhsfeld and A.A. Simonenko, J. Organomet. Chem., 258 (1983) 283.
[169] A.I. Udel'nov, V.E. Shklover, N.G. Bokii, E.A. Cheryshev, T.L. Krasnova, E.F. Schipnova and Yu.T. Struchkov, Zh. Strukt. Khim., 15 (1974) 83.
[170] M. Yu. Antipin, A.V. Polyakov, Yu.T. Struchkov, M.P. Egorov, A.L. Gal'minas, S.P. Kolesnikov and O.M. Nefedov, Metalloorg. Khim., 2 (1989) 593.
[171] S.N. Gurkova, A.I. Gusev, N.V. Alexeev, T.K. Gar and N.A. Viktorov, Zh. Strukt. Khim., 26 (1985) 148.
[172] S.N. Gurkova, A.I. Gusev, N.V. Alexeev, T.K. Gar and N.A. Viktorov, Zh. Strukt. Khim., 25 (1984) 180.
[173] G.M. Apal'kova, A.I. Gusev, S.N. Gurkova and A.E. Feoktistov, Metalloorg. Khim., 1 (1988) 942.
[174] J.W. Cai, Z.-S. Jin and J.-Z. Ni, Jiegou Huaxue, 10 (1991) 16.
[175] S.N. Gurkova, A.I. Gusev, N.V. Alexeev, T.K. Gar and N.A. Viktorov, Zh. Strukt. Khim., 25 (1984) 174.
[176] S.N. Gurkova, A.I. Gusev, N.V. Alexeev, T.K. Gar and N.A. Viktorov, Zh. Strukt. Khim., 25 (1984) 170.
[177] S.N. Gurkova, A.I. Gusev, N.V. Alexeev, O.A. Dombrova and T.K. Gar, Metalloorg. Khim., 1 (1988) 1147.
[178] S.N. Gurkova, A.I. Gusev, N.V. Alexeev, T.K. Gar and O.A. Dombrova, Zh. Strukt. Khim., 26 (1985) 185.
[179] Yu.I. Baukov, A.G. Shipov, L.S. Smirnova, E.P. Kramarova, S.Yu. Bylikin, Yu.E. Ovchinnikov and Yu.T. Struchkov, J. Organomet. Chem., 461 (1993) 39.
[180] M. Dräger, J. Escudie, C. Couret, H. Ranaivonjatovo and J. Satge, Organometallics, 7 (1988) 1010.
[181] H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé and M. Dräger, New J. Chem., 13 (1989) 389.
[182] P. Jutzi, B. Hampel, M.B. Hursthouse and A.J. Howes, Organometallics, 5 (1986) 1944.
[183] P. Jutzi, A. Becker, C. Leue, H.G. Stammler, B. Neumann, M.B. Hursthouse and A. Karaulov, Organometallics, 10 (1991) 3838.