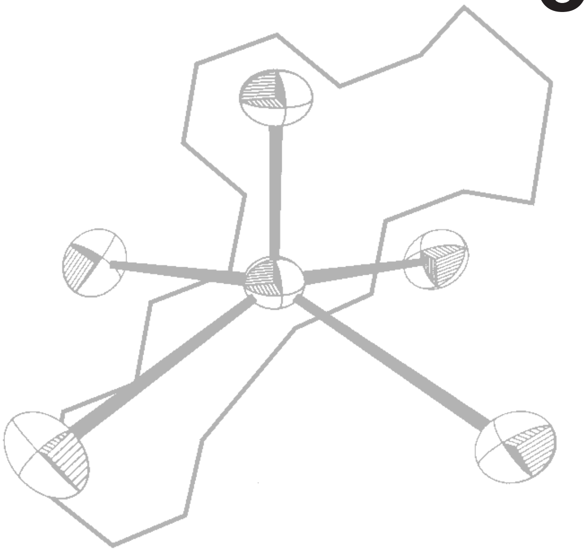
CSIRO PUBLISHING

Australian Journal of Chemistry



Volume 52, 1999

A journal for the publication of original research
in all branches of chemistry and chemical technology

www.publish.csiro.au/journals/ajc

All enquiries and manuscripts should be directed to
The Managing Editor
Australian Journal of Chemistry
CSIRO PUBLISHING
PO Box 1139 (150 Oxford St)
Collingwood
Vic. 3066
Australia
Telephone: 61 3 9662 7630
Facsimile: 61 3 9662 7611
Email: john.zdysiewicz@publish.csiro.au

Published by **CSIRO** PUBLISHING
for CSIRO Australia and
the Australian Academy of Science

Aust. J. Chem., 1999, **52**, 733–739

Main Group Pyrazolates—the X-Ray Structures of $[\mathrm{Al}(\eta^2\text{-}\mathrm{Bu^t{}_2pz})_3]$, $[\mathrm{SnMe_3}(\eta^1\text{-}\mathrm{Ph_2pz})]$ and $[\mathrm{GePh_3}(\eta^1\text{-}\mathrm{Bu^t{}_2pz})]$ ($\mathrm{R_2pz}$ = 3,5-Disubstituted Pyrazolate)†

Glen B. Deacon,[A] *Ewan E. Delbridge,*[A] *Craig M. Forsyth,*[A]
Peter C. Junk,[B] *Brian W. Skelton*[C] *and Allan H. White*[C]

[A] Department of Chemistry, Monash University, Clayton, Vic. 3168.
[B] Department of Chemistry, James Cook University, Townsville, Qld. 4811.
[C] Department of Chemistry, The University of Western Australia, Nedlands, W.A. 6907.

From metathesis reactions between $\mathrm{AlCl_3}$, $\mathrm{SnMe_3Cl}$, or $\mathrm{GePh_3Br}$ and the appropriate potassium 3,5-disubstituted pyrazolate $[\mathrm{K(R_2pz)}]$ the complexes $[\mathrm{Al(Bu^t{}_2pz)_3}]$, $[\mathrm{SnMe_3(Ph_2pz)}]$, $[\mathrm{SnMe_3(Bu^t{}_2pz)}]$, and $[\mathrm{GePh_3(Bu^t{}_2pz)}]$ have been obtained. The X-ray structure of $[\mathrm{Al(Bu^t{}_2pz)_3}]$ shows the complex to be monomeric with η^2-pyrazolate groups, in a quasi-trigonal prismatic array: the first monomeric homoleptic tris(pyrazolato) complex of any element. X-Ray structures of $[\mathrm{SnMe_3(Ph_2pz)}]$ and $[\mathrm{GePh_3(Bu^t{}_2pz)}]$ reveal mononuclear species with distorted tetrahedral stereochemistries and η^1-pyrazolate groups. Comparisons of spectroscopic data between $[\mathrm{SnMe_3(Ph_2pz)}]$ and $[\mathrm{SnMe_3(Bu^t{}_2pz)}]$ suggest the latter is also four-coordinate with an η^1-$\mathrm{Bu^t{}_2pz}$ ligand.

Introduction

Prior to 1997, the crystallographically established modes for coordination[1–5] of pyrazolate ions were (i) μ-$\eta^1\!:\!\eta^1$, (ii) η^1 and (iii) η^2 (chelating). The first is commonly observed for d-block metals but known for f-block, the second is best known for precious metals, though the ubiquitous pyrazolylborates can be regarded as such, and the third was restricted to f-block elements for some 16 years following its somewhat fortuitous discovery.[6] Since 1997, the situation has been dramatically transformed with the (initially surprising) observation of η^2-coordination for both d-block and main group elements,[7–10] and the first homoleptic pyrazolate complexes (viz. $\mathrm{Ti}(\eta^2\text{-}\mathrm{Me_2pz})_4$[7] and $\mathrm{Ta}(\eta^2\text{-}\mathrm{Me_2pz})_3(\eta^1\text{-}\mathrm{Me_2pz})_2$[8] ($\mathrm{Me_2pz}$ = 3,5-dimethylpyrazolate)). Furthermore, five new modes of pyrazolate coordination have been observed.[9,11–14] Thus μ-$\eta^2\!:\!\eta^2$ coordination[11] with the pyrazolate group normal to the metal···metal axis in contrast to parallel with μ-$\eta^1\!:\!\eta^1$ bonding,[1–5] μ-$\eta^1\!:\!\eta^2\!:\!\eta^1$ (to $\mathrm{K^+}$),[9] π-η^1 (to $\mathrm{Ag^+}$),[12] π-η^3 (to $\mathrm{K^+}$),[13] and the long elusive η^5-pyrazolate (i.e. η^5-1,2-diazacyclopentadienyl) coordination (to $\mathrm{Ru^{2+}}$)[14] have been established.

This burgeoning development has led us to extend our interests from lanthanoid pyrazolates to the structural chemistry of main group pyrazolates. We now report the preparations of $[\mathrm{Al(Bu^t{}_2pz)_3}]$ ($\mathrm{Bu^t{}_2pz}$ = 3,5-di-t-butylpyrazolate), $[\mathrm{SnMe_3(R_2pz)}]$ ($\mathrm{R_2pz}$ = 3,5-disubstitued pyrazolate, R = $\mathrm{Bu^t}$ or Ph) and $[\mathrm{GePh_3(Bu^t{}_2pz)}]$ together with the X-ray structures of the aluminium complex, $[\mathrm{SnMe_3(Ph_2pz)}]$, and the germanium complex. Interest in the aluminium complex arose from an inability to prepare monomeric homoleptic $\mathrm{Ln}(\eta^2\text{-}\mathrm{R_2pz})_3$ complexes which invariably crystallize with coligands, e.g. $[\mathrm{Ln}(\eta^2\text{-}\mathrm{Bu^t{}_2pz})_3(\mathrm{thf})_2]$[15] and $[\mathrm{Ln}(\eta^2\text{-}\mathrm{Ph_2pz})_3(\mathrm{thf})_3]$,[16] owing to the large size of $\mathrm{Ln^{3+}}$. The small $\mathrm{Al^{3+}}$ ion was considered to offer better prospects for the formation of a neutral monomeric homoleptic tris(η^2-pyrazolato) metal complex. The sole crystallographically characterized aluminium pyrazolate hitherto recorded is $[\mathrm{AlMe_2}(\mu\text{-pz})]_2$[17] which has μ-$\eta^1\!:\!\eta^1$-pyrazolate ligands. Several structures have been proposed for triorganotin(IV) pyrazolates, e.g. polymeric with μ-$\eta^1\!:\!\eta^1$-bridging[18] and dimeric with μ-$\eta^1\!:\!\eta^1$-ligands,[19] but X-ray validation is lacking. However, η^1-(N)-coordination has been crystallographically established in a complex with the rather more esoteric ligand 3-dimethylarsino-4,5-di(methoxycarbonyl)pyrazolate.[20] A few organogermanium pyrazolates are known (e.g. $[\mathrm{GeMe_3(Me_2pz)}]$),[21] but none with the bulky $\mathrm{Bu^t{}_2pz}$ ligand, and no structure has been determined. Thus the derivative $[\mathrm{GePh_3(Bu^t{}_2pz)}]$ was chosen to provide an organogermanium pyrazolate that could be crystallized for X-ray examination. Recently, a remarkable cationic germanium(II) trichlorogermate(II) complex $[\mathrm{Ge^{II}{}_2}(\mu\text{-}\eta^1\!:\!\eta^1\text{-}\mathrm{Me_2pz})_3][\mathrm{Ge^{II}Cl_3}]$ has been prepared and its structure obtained.[22]

† Dedicated to Professor M. N. Bochkarev on the occasion of his 60th birthday.

Manuscript received 7 June 1999

10.1071/CH98068 0004-9425/99/080733$05.00

Results and Discussion

Preparations and Properties

Air- and moisture-sensitive tris(3,5-di-t-butylpyrazolato)aluminium (1), 3,5-diphenylpyrazolatotrimethyltin (2), 3,5-di-t-butylpyrazolatotrimethyltin (3), and 3,5-di-t-butylpyrazolatotriphenylgermanium (4) were obtained by metathesis reactions *(1)* and *(2)*:

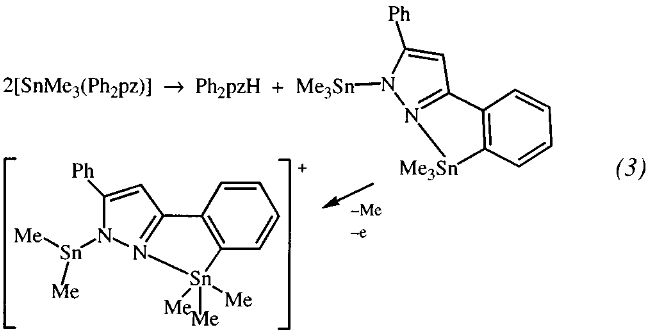
$$AlCl_3 + 3K(Bu^t{}_2pz) \rightarrow \underset{(1)}{[Al(Bu^t{}_2pz)_3]} + 3KCl \qquad (1)$$

$$ER'_3X + K(R_2pz) \rightarrow [ER'_3(R_2pz)] + KX \qquad (2)$$

	E	R′	R	X
(2)	Sn	Me	Ph	Cl
(3)	Sn	Me	Bu^t	Cl
(4)	Ge	Ph	Bu^t	Br

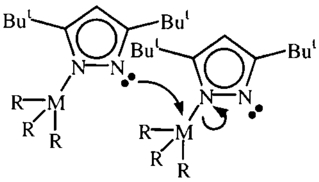
Microanalysis of aluminium 3,5-di-t-butylpyrazolate (1) indicated that the complex was obtained unsolvated from tetrahydrofuran, by contrast with the isolation of solvent-complexed $[Ln(Bu^t{}_2pz)_3(thf)_2]$ [15] for the larger lanthanoid ions. The highest peak in the mass spectrum was assignable to the monomeric $[Al(Bu^t{}_2pz)_3]^+$ ion. The absence of any ν(NH) infrared absorption was consistent with pyrazolate formation and eliminated the possibility of an $[Al(Bu^t{}_2pz)_3(Bu^t{}_2pzH)_n]$ complex. The ^{27}Al n.m.r. chemical shift (δ 0·0), coincidentally corresponding to that of the standard $(Al(H_2O)_6{}^{3+})$, lies in the normal range (from −46 to 40 ppm) for octahedral aluminium(III) complexes.[23] This is consistent with the observed formal six-coordination determined by X-ray crystallography (below), though the stereochemistry is far from the octahedral norm.

The organotin pyrazolates $[SnMe_3(R_2pz)]$ (R = Ph or Bu^t) (2) and (3) each show features attibutable[24] to ν_{as}(Sn–C) and ν_s(Sn–C) at *c.* 540 and 515 cm^{-1} respectively in both their infrared and Raman spectra. In agreement with this assignment, the former absorption was more intense in the infrared and the latter in the Raman spectrum. This rules out a polymeric structure with planar SnMe$_3$ units bridged by μ-$\eta^1:\eta^1$-pyrazolate groups, but is consistent with a four-coordinate monomer with unidentate R$_2$pz groups and tetrahedral SnC$_3$N stereochemistry as observed for solid $[SnMe_3(Ph_2pz)]$ from the following X-ray study. In addition, the magnitude of the ^2J(Sn–Me) coupling constants are as expected[25,26] for tetrahedral $[SnMe_3X]$ complexes, whilst ^{119}Sn n.m.r. chemical shifts are in the range for monomeric $[SnMe_3NR_2]$ compounds.[23,25] The tin complexes and the germanium compound (4) show monomer parent ions in their electron impact mass spectra, but, surprisingly in view of the monomeric solid-state structure, $[SnMe_3(Ph_2pz)]$ also gives $[Sn_2Me_5(Ph_2pz) - H]^+$ and $[Sn_2Me_3(Ph_2pz) - H]^+$ ions which have significant intensity. It is unlikely that $[SnMe_3(Ph_2pz)]$ monomers from the solid state would give species linked by μ-$\eta^1:\eta^1$-Ph$_2$pz groups in the less condensed vapour state at an elevated temperature. Moreover, the dinuclear ions have only one Ph$_2$pz group, suggesting they result from a process which eliminates a Ph$_2$pz ligand. A thermally induced cyclometallation *(3)* provides a possible explanation:



(3)

The ^{1}H n.m.r. spectrum of (4) shows two Bu^t resonances, consistent with the inequivalent Bu$^t{}_2$pz substituents of the η^1-bonded monomer established crystallographically (below). On warming, the peaks coalesce and then sharpen to give, at 328 K, a Bu^t resonance of similar form to that exhibited by $[SnMe_3(Bu^t{}_2pz)]$ at room temperature. Plausibly an exchange process rendering the nitrogens equivalent is inhibited for (4) by the smaller size of germanium than tin and by the bulkier substituents (Ph > Me) on germanium. An intermolecular exchange process involving μ-$\eta^1:\eta^1$ coordination and displacement of Bu$^t{}_2$pz$^-$ (Scheme 1) seems more likely to be adversely affected by steric factors than an intramolecular exchange via an η^2-bonded species, or unimolecular ionization (which could even be aided by increased crowding in $[MR_3(Bu^t{}_2pz)]$).



Scheme 1

X-Ray Crystal Structures

Atomic coordinates for the structures of (1), (2) and (4) are given in Table 1, whilst the structures are displayed in Figs 1–3 with selected bond lengths in Tables 2–4.

(i) *[Al(Bu$^t{}_2$pz)$_3$] (1)*

Tris(3,5-di-t-butylpyrazolato)aluminium(III) (1) has a monomeric structure with three chelating pyrazolate ligands and formal six-coordination for aluminium. The combination of the small ionic radius of the metal[27] and the bulkiest 3,5-disubstituted pyrazolate available to us has enabled the isolation of the first neutral homoleptic *tris*(pyrazolato) complex of any element. It is thus consistent with the isolation of homoleptic tetrakis(η^2-

pyrazolato) complexes of the larger Ti^{4+},[7,28] and contrasts formation of $[Ln(\eta^2\text{-}R_2pz)_3L_2]$ complexes by the much larger lanthanoid ions.[15,16] The sole structurally characterized homoleptic tris(pyrazolato)lanthanoid(III) complex attains a higher coordination number by dimerization, viz. $[Nd(\eta^2\text{-}Bu^t{}_2pz)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bu^t{}_2pz)]_2$.[29] The molecule lies disposed with the aluminium on a site of crystallographic *3* symmetry; one-third of the molecule, inclusive of one complete/independent ligand about the aluminium, constitutes the asymetric unit of the structure. The two Al–N distances do not differ non-trivially (also true of N(1)–Al–N(1′) and N(2)–Al–N(2′)) so that the molecular symmetry, particularly that local to the aluminium, is a good approximation to $\bar{6}2m$ or D_{3h}. The arrangement of the six nitrogen atoms lies much nearer the trigonal prismatic rather than the octahedral extreme, consistent with the small ligand 'bite'.[30] The two parallel triangular faces of the trigonal prism exhibit a torsional deformation so that the N(1)–N(2) bond (corresponding to a longitudinal edge) makes an angle of 10·1(5)° to the normal of the triangular faces. The centres of the N–N bonds are coplanar with aluminium with a (necessarily) regular triangular arrangement about the metal which lies 0·058(4) Å out of the C_3N_2 ligand plane.

Table 1. Non-hydrogen positional and equivalent isotropic displacement parameters for $[Al(\eta^2\text{-}Bu^t{}_2pz)_3]$ (1), $[SnMe_3(Ph_2pz)]$ (2) and $[GePh_3(Bu^t{}_2pz)]$ (4)

Complex	Atom	x	y	z	U_{eq} (Å^2)
(1)	Al	2/3	1/3	0·8800(1)	0·0134(3)
	N(1)	0·5381(2)	0·2175(2)	0·9463(2)	0·017(1)
	N(2)	0·5306(2)	0·2294(2)	0·8135(2)	0·016(1)
	C(1)	0·4468(2)	0·1328(2)	0·9853(2)	0·015(1)
	C(2)	0·3790(2)	0·0895(2)	0·8793(2)	0·019(2)
	C(3)	0·4352(2)	0·1522(2)	0·7734(2)	0·016(2)
	C(4)	0·4274(2)	0·0985(2)	1·1251(2)	0·019(2)
	C(5)	0·5332(3)	0·1473(3)	1·1975(3)	0·028(3)
	C(6)	0·3561(3)	0·1372(3)	1·1847(3)	0·029(3)
	C(7)	0·3727(3)	−0·0233(3)	1·1329(3)	0·032(3)
	C(8)	0·4023(2)	0·1391(2)	0·6340(2)	0·019(2)
	C(9)	0·4784(3)	0·2390(3)	0·5583(3)	0·025(3)
	C(10)	0·4078(3)	0·0431(3)	0·5797(3)	0·032(3)
	C(11)	0·2881(3)	0·1159(4)	0·6219(3)	0·036(3)
(2)	Sn	0·63116(5)	0·53869(3)	0·59825(2)	0·0497(3)
	N(1)	0·5358(5)	0·6445(3)	0·5577(2)	0·045(3)
	N(2)	0·5906(5)	0·6762(4)	0·5076(2)	0·045(3)
	C(1)	0·4226(6)	0·6884(4)	0·5684(3)	0·044(4)
	C(2)	0·4062(6)	0·7476(5)	0·5230(3)	0·045(4)
	C(3)	0·5134(6)	0·7391(4)	0·4865(3)	0·039(4)
	C(11)	0·3406(6)	0·6695(5)	0·6204(3)	0·051(4)
	C(12)	0·3897(7)	0·6632(6)	0·6769(3)	0·069(6)
	C(13)	0·308(1)	0·6477(7)	0·7251(4)	0·100(8)
	C(14)	0·178(1)	0·6412(7)	0·7162(5)	0·107(8)
	C(15)	0·1275(8)	0·6485(6)	0·6593(4)	0·088(7)
	C(16)	0·2083(7)	0·6638(5)	0·6121(3)	0·059(5)
	C(31)	0·5446(6)	0·7875(4)	0·4335(3)	0·045(4)
	C(32)	0·6524(7)	0·7664(5)	0·3986(3)	0·063(5)
	C(33)	0·6783(8)	0·8141(6)	0·3477(3)	0·077(6)
	C(34)	0·6015(9)	0·8821(6)	0·3289(3)	0·083(6)
	C(35)	0·4993(9)	0·9041(5)	0·3616(3)	0·072(5)
	C(36)	0·4688(7)	0·8577(5)	0·4136(3)	0·059(5)
	C(111)	0·7363(9)	0·4871(6)	0·5282(4)	0·081(6)
	C(121)	0·7397(9)	0·5985(5)	0·6670(4)	0·079(6)
	C(131)	0·4874(9)	0·4528(5)	0·6304(5)	0·083(6)
(4)	Ge	0·77475(4)	0·19346(3)	0·12669(1)	0·0195(2)
	N(1)	0·7103(4)	0·3651(3)	0·1274(1)	0·021(1)
	N(2)	0·8280(4)	0·4306(3)	0·1035(1)	0·022(1)
	C(1)	0·5945(5)	0·4445(3)	0·1446(1)	0·022(2)
	C(2)	0·6372(4)	0·5627(3)	0·1300(1)	0·023(2)
	C(3)	0·7819(5)	0·5508(3)	0·1049(1)	0·023(2)
	C(4)	0·4463(5)	0·4077(4)	0·1727(1)	0·027(2)
	C(5)	0·4919(5)	0·3169(5)	0·2117(1)	0·034(2)
	C(6)	0·3181(6)	0·3495(5)	0·1412(2)	0·036(2)
	C(7)	0·3740(6)	0·5267(5)	0·1951(2)	0·040(3)
	C(8)	0·8756(5)	0·6507(4)	0·0797(1)	0·027(2)
	C(9)	1·0262(8)	0·5969(5)	0·0470(2)	0·052(3)
	C(10)	0·7655(7)	0·7088(4)	0·0428(2)	0·046(3)
	C(11)	0·9237(7)	0·7538(5)	0·1138(2)	0·040(3)
	C(111)	0·8930(5)	0·1587(3)	0·0699(1)	0·022(2)
	C(112)	0·8458(6)	0·0615(4)	0·0411(1)	0·029(2)
	C(113)	0·9325(6)	0·0340(4)	0·0008(1)	0·036(2)
	C(114)	1·0677(6)	0·1036(4)	−0·0107(1)	0·036(2)
	C(115)	1·1186(6)	0·1989(4)	0·0185(1)	0·035(2)
	C(116)	1·0323(5)	0·2270(4)	0·0584(1)	0·029(2)
	C(121)	0·5941(4)	0·0756(3)	0·1286(1)	0·023(2)
	C(122)	0·5888(5)	−0·0160(4)	0·1629(1)	0·026(2)
	C(123)	0·4736(5)	−0·1109(4)	0·1611(1)	0·030(2)
	C(124)	0·3632(5)	−0·1153(4)	0·1250(2)	0·035(2)
	C(125)	0·3652(5)	−0·0237(4)	0·0908(1)	0·034(2)
	C(126)	0·4815(5)	0·0710(4)	0·0923(1)	0·028(2)
	C(131)	0·9185(4)	0·1744(3)	0·1797(1)	0·022(2)
	C(132)	0·9243(5)	0·2608(4)	0·2153(1)	0·029(2)
	C(133)	1·0263(6)	0·2436(4)	0·2532(1)	0·035(2)
	C(134)	1·1247(5)	0·1384(4)	0·2550(1)	0·034(2)
	C(135)	1·1250(6)	0·0547(4)	0·2190(1)	0·033(2)
	C(136)	1·0224(5)	0·0716(4)	0·1814(1)	0·028(2)

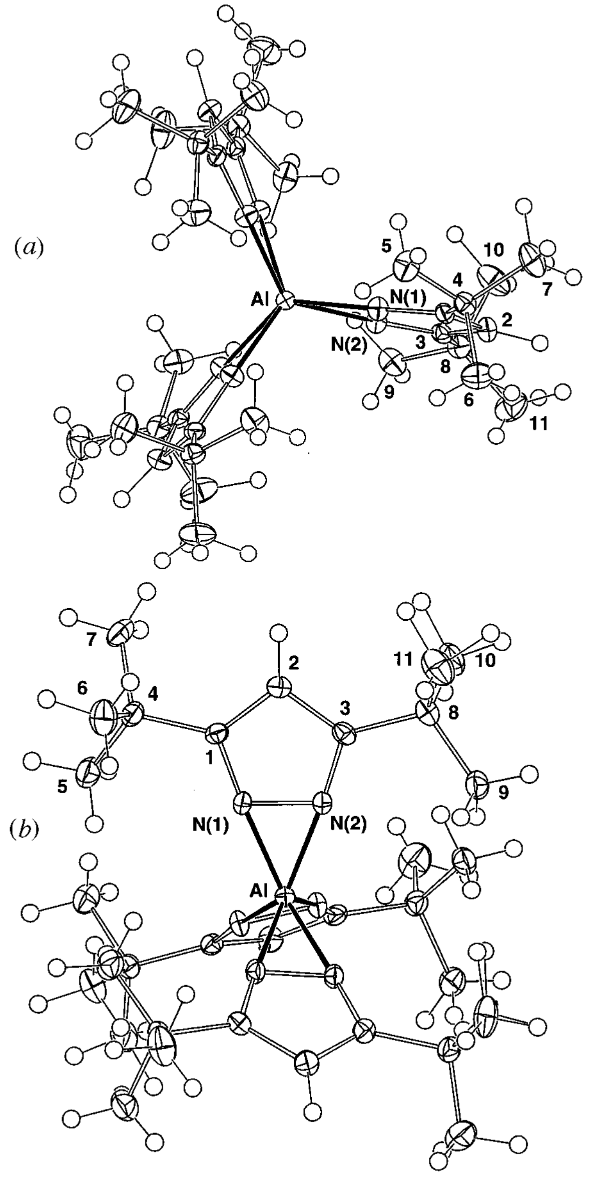


Fig. 1. Molecular projection of $[Al(Bu^t{}_2pz)_3]$ (1): (*a*) down; (*b*) normal to the (quasi-)*3* molecular axis showing 50% thermal ellipsoids for the non-hydrogen atoms, with hydrogen atoms having arbitrary radii of 0·1 Å.

The Al–N distances (Table 2) are somewhat shorter (*c.* 0·05 Å) than those of other six-coordinate aluminium amides, viz. tris(1,3-disubstituted triazenido)aluminium(III) complexes[31] and tris(di(2-pyridyl)amido)aluminium(III),[32] perhaps reflecting less crowding about the aluminium in (1). Terminal Al–N(amide) bonds in four-coordinate complexes average 1·80 Å,[33] and addition of the difference[27] between the ionic radii of six- and four-coordinate Al^{3+} gives a value of 1·94 Å, midway between values for (1) and those of the triazenide[31] and di(2-pyridyl)amide complexes.[32] The Al–N bond distances in (1) are comparable with those found in four-coordinate $[AlMe_2(\mu\text{-}pz)]_2$.[17] This demonstrates that any lengthening of the Al–N distances, because of the increased coordination number in (1), is offset by terminal Al–N bonding. The largest N–Al–N angle is 131·6(1)°, cf. the tris(triazenido)aluminium(III) complexes where angles in the range 145–163° are observed, the difference being attributable to the adoption of essentially trigonal prismatic stereochemistry in (1). Because of the small size of the aluminium, the η^2-pyrazolate bite angle (43·18(9)°) is larger than those of $[Ti(\eta^2\text{-}Me_2pz)_4]$ (38–41°)[28] and much larger than is found in $[Ln(\eta^2\text{-}R_2pz)_3L_2]$ complexes (31–35°)[15,16,34] as well as $[Ln(\eta^2\text{-}Bu^t{}_2pz)_4]^-$ (*c.* 34°).[13]

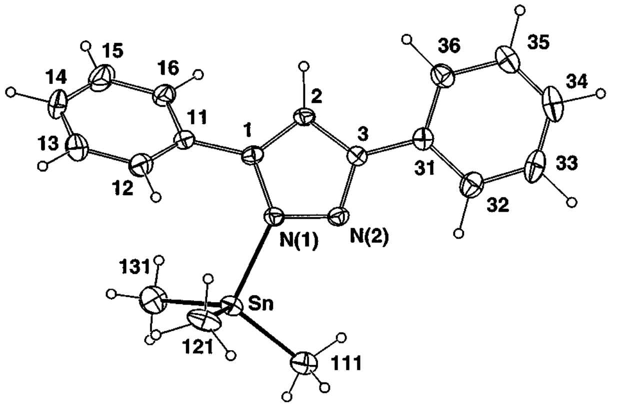


Fig. 2. Molecular projection of $[SnMe_3(Ph_2pz)]$ (2).

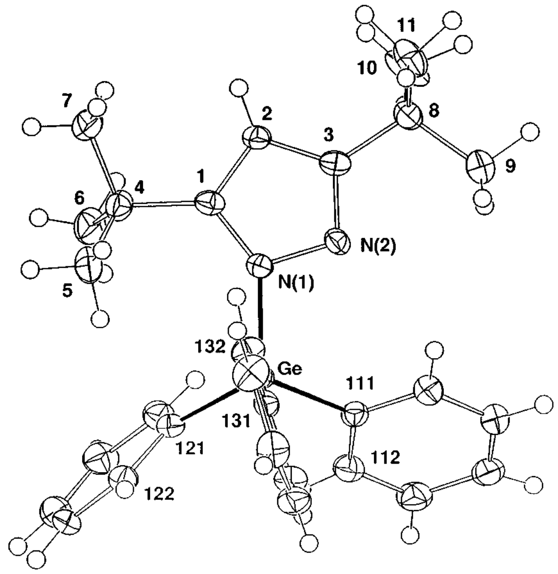


Fig. 3. Molecular projection of $[GePh_3(Bu^t{}_2pz)]$ (4).

Table 2. Selected geometries in $[Al(Bu^t{}_2pz)_3]$ (1)

Distances (Å)				Angles (degrees)			
Al–N(1)	1·903(2)	Al–N(2)	1·911(2)	N(1)–Al–N(1′)	107·7(1)	N(1)–Al–N(2)	43·18(9)
Al–cen[A]	$1\cdot77_6$			N(1)–Al–N(2′)	117·3(1)	N(1)–Al–N(2″)	131·6(1)
				N(2)–Al–N(2″)	107·7(1)		

[A] cen = centre of the N(1)–N(2) bond.

Table 3. Selected geometries in $[SnMe_3(Ph_2pz)]$ (2)

Distances (Å)				Angles (degrees)			
Sn–N(1)	2·102(5)	Sn···N(2)[A]	2·950(5)	N(1)–Sn···N(2)[B]	24·3(4)	N(1)–Sn–C(111)	102·2(3)
Sn–C(111)	2·072(9)	Sn–C(121)	2·119(9)	N(1)–Sn–C(121)	103·9(3)	N(1)–Sn–C(131)	106·3(6)
Sn–C(131)	2·117(9)			C(111)–Sn–C(131)	113·6(4)	C(111)–Sn–C(121)	115·6(4)
				C(121)–Sn–C(131)	113·3(4)	Sn–N(1)–N(2)	115·7(4)
				Sn–N(1)–C(1)	134·5(4)		

[A] Non-bonding separation. [B] Non-bonding to tin.

Table 4. Selected geometries in $[GePh_3(Bu^t{}_2pz)]$ (4)

Distances (Å)				Angles (degrees)			
Ge–N(1)	1·909(3)	Ge···N(2)[A]	2·656(3)	N(1)–Ge···N(2)[B]	29·9(1)	N(1)–Ge–C(111)	109·4(1)
Ge–C(111)	1·945(3)	Ge–C(121)	1·952(3)	N(1)–Ge–C(121)	114·0(1)	N(1)–Ge–C(131)	105·2(1)
Ge–C(131)	1·948(3)			C(111)–Ge–C(121)	106·5(2)	C(111)–Ge–C(131)	109·7(2)
				C(121)–Ge–C(131)	112·0(2)	Ge–N(1)–N(2)	106·5(2)
				Ge–N(1)–C(1)	142·4(2)		

[A] Non-bonding separation. [B] Non-bonding to germanium.

(ii) *[$SnMe_3(Ph_2pz)$] (2) and [$GePh_3(Bu^t{}_2pz)$] (4)*

Both complexes have monomeric structures devoid of crystallographic symmetry with a distorted tetrahedral arrangement of one nitrogen and three carbon donor atoms about the metal (Figs 2 and 3). The pyrazolate ligands are η^1-(N)-bonded, as observed in the trisubstituted pyrazolato complex [$SnMe_3(Me_2As(MeO_2C)_2C_3N_2)$],[20] but this latter complex has additional weak inter- and intra-molecular Sn–O interactions. The M$\cdots$N(2) separations are 0·75 (Ge) and 0·85 Å (Sn) longer than the M–N(1) bond distances, cf. $\leq$ 0·2 Å for the most unsymmetrical η^2-R_2pz binding,[9*] so that N(2) is not regarded as attached to Sn (Ge). Although N(2) is closer to Ge or Sn than the sum of the corresponding van der Waals radii (3·4 (Ge), 3·6 Å (Sn)),[36] their proximity is solely due to the N–N connectivity of the pyrazolate ions. The non-bonded status of N(2) is even more evident from bond angle considerations. Thus, Ge–N(1)–N(2) (106·5(2)°), Ge–N(1)–C(1) (142·4(2)°), Sn–N(1)–N(2) (115·7(4)°) and Sn–N(1)–C(3) (142·4(2)°) angles are totally different from those of complexes with η^2-coordination, e.g. for (1) Al–N(1)–N(2) 68·6(1)° and Al–N(1)–C(1) 176·2(2)°, and, for [$Er(Bu^t{}_2pz)_4$]$^-$, Er–N–N 70–75° and Er–N–C 168–172°.[13] Furthermore, the pseudo 'bite' angles of (2) and (4) (Tables 3 and 4) are less than 30°, whereas, even for large Ln^{3+} ions, the 'bite' angles for η^2-R_2pz–Ln binding are 31–35° ('bite' angles decrease with increased M^{n+} size, see above). Both the Sn–C (average 2·10 Å) and Sn–N (2·102(5) Å) distances are shorter than those found in [$SnMe_3(Me_2As(MeO_2C)_2C_3N_2)$], consistent with the observation of Sn–O interactions additional to four-coordination in the latter and with the absence of M$\cdots$N(2) binding in (2). The Sn–N distance is close to that (2·114 Å) of four-coordinate tris(2-methyl-2-phenylpropyl)(1,2,4-triazol-1-yl)tin,[37] but the Sn–C distances of (2) also average some 0·06 Å shorter than those of the 2-methyl-2-phenylpropyl species. In (4), the Ge–C and Ge–N distances are closely comparable with those of four-coordinate 1,4-diphenyl-1,4-bis(trimethylgermyl)tetrazene.[38] It is thus clear from the relatively short M–N and M–C distances in (2) and (4) that there are *no* M$\cdots$N(2) interactions. The similarity of the Sn–C stretching frequencies, ^{119}Sn n.m.r. chemical shifts and ^{117,119}Sn–H coupling constants of (3) to those of (2) indicates that [$SnMe_3(Bu^t{}_2pz)$] has four-coordination for tin and a unidentate 3,5-di-t-butylpyrazolate ligand.

Experimental

The compounds described here are air- and moisture-sensitive. All manipulations were carried out under purified (BASF R3/11 oxygen removal catalyst and activated 4A molecular sieves) nitrogen or argon using standard Schlenk techniques or in a Miller Howe or Vacuum Atmospheres dry box. Solvents (thf, dme, toluene and light petroleum—b.p. 60–70°C) were dried and deoxygenated by refluxing over blue sodium benzophenone ketyl under purified nitrogen. Tetraethylene glycol dimethyl ether was added to the light petroleum to dissolve the benzophenone ketyl. Solvents were distilled directly into storage flasks equipped with Teflon taps and stored under nitrogen. Elemental analyses (C, H, N) were performed by The Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, Dunedin, New Zealand. I.r. spectra were obtained as Nujol mulls with a Perkin Elmer 1600 FTIR instrument. Raman data were obtained with a Renishaw Ramascope, near-infrared diode laser operating at 780 nm for samples (solid or liquid) sealed in glass capillaries, and were recorded for the range 1100–100 cm^{-1}. The n.m.r. spectra were recorded on either Bruker AC200 or AM300 spectrometers, and data were referenced to either the residual protonated solvent signals (C_4D_8O δ^1H 1·74, C_6D_6 δ^1H 7·15 or C_7D_8 δ^1H 2·09) or a solution of an external standard ($Al(NO_3)_3$, 0·67 M (aq), ^{27}Al $\delta = 0{\cdot}0$; $SnMe_4$, neat, ^{119}Sn $\delta = 0{\cdot}0$). Mass spectra (e.i.) were obtained with a VG Trio-1 GC mass spectrometer; a sample probe designed for air-sensitive materials was used. Only the most intense peak of a cluster with the correct isotope pattern is given. The vapour pressure of (3) was determined under dynamic vacuum ($>10^{-5}$ Torr) by monitoring rate of mass loss (using a Cahn C1000 electrobalance).[39] $GePh_3Br$ was obtained from Research Organic and Inorganic Chemicals. $SnMe_3Cl$ and $AlCl_3$ were purchased from Aldrich, and the latter was sublimed under vacuum before use. Pyrazole syntheses have been described previously.[40]

Tris(η^2-3,5-di-t-butylpyrazolato)aluminium(III) *(1)*

3,5-Di-t-butylpyrazole (1·22 g, 6·8 mmol) was treated with a thf solution (30 ml) of potassium hydride (0·27 g, 6·8 mmol) at room temperature. Gas evolution was observed and a slightly pale yellow solution formed. $AlCl_3$ (0·30 g, 2·3 mmol) was slowly added causing formation of a white precipitate. The reaction mixture was stirred for 12 h after which time the thf was removed under vacuum yielding an off-white solid which was extracted with light petroleum (50 ml). Concentration and cooling (−20°C) yielded large colourless *crystals* of (1) (yield 94%), m.p. 182–184°C (Found: C, 70·6; H, 10·5; N, 14·0. $C_{33}H_{57}AlN_6$ requires C, 70·2; H, 10·2; N, 14·9%). I.r. absorption: 1526m, 1507s, 1484m, 1417w, 1364s, 1325m, 1253s, 1233s, 1205m, 1112w, 1070w, 1028m, 1001w, 986vs, 926w, 824w, 798vs, 718m cm^{-1}. ^{1}H n.m.r. δ (C_4D_8O) 1·17, s, 54H, Bu^t; 5·94 s, 3H, H 4. ^{27}Al n.m.r. δ (C_7D_8) 0·0. Mass spectrum: *m/z* 564 (35%, M^+), 549 (15, $(M-Me)^+$), 385 (50, $(M-L)^+$), 369 (50, $(M-L-Me)^+$), 165 (100, $(LH-Me)^+$), 57 (90, $C_4H_9{}^+$).

(η^1-3,5-Diphenylpyrazolato)trimethyltin(IV) *(2)*

3,5-Diphenylpyrazole (1·10 g, 5·0 mmol) was treated with a diethyl ether solution (30 ml) of potassium hydride (0·20 g, 5·0 mmol) at room temperature. Gas evolution was observed and a pale yellow solution formed. $SnMe_3Cl$ (1·19 g, 5·0 mmol) was added causing formation of a white precipitate. The reaction mixture was stirred for 12 h after which time the diethyl ether was removed under vacuum yielding a white solid which was extracted with toluene (50 ml). The toluene solution was concentrated and cooled to −20°C and afforded large colourless *crystals* of (2) (yield 74%), m.p. 95–97°C (Found: C, 56·7; H, 5·5; N, 7·3. $C_{18}H_{20}N_2Sn$ requires C, 56·4; H, 5·3; N, 7·3%). I.r. absorption: 3102w, 1602w, 1541w, 1513w, 1320vw, 1295w, 1272m, 1190m, 1155w, 1120s, 1072s, 1024m, 1002w, 986m, 957m, 918m, 846w, 821m, 774s, 763vs, 708w, 697vs, 682vs, 669w, 550w, 541m, 517w, 438m cm^{-1}.

---

[*] In the triazenido complex [$SnMe_3(1,3\text{-}(Bu^t{}_3Si)_2N_3)$], where a *weak* Sn$\cdots$N interaction is proposed in addition to the main Sn–N bond, the difference is 0·35 Å.[35]

Raman lines (solid sample): 1029w, 1002s, 985w, 957m, 848w, 768w, 708w, 668mw, 618mw, 543m, 518vs, 438m, 413m, 349w, 271w, 244w, 202m, 181m, 165m cm^{-1}. ^{1}H n.m.r. δ (C_4D_8O) 0·49, s, $^2J_{H,^{117}Sn}$ 60 Hz, $^2J_{H,^{119}Sn}$ 63 Hz, 9H, Me; 6·67, s, 1H, H 4; 7·35, m, 6H, *m*- and *p*-H; 7·66, s, 4H, *o*-H; ^{119}Sn n.m.r. δ (0·06 M in PhMe/10% C_6D_6) 87·7 ($\Delta\nu_{1/2}$ 28 Hz). Mass spectrum: *m/z* 531 (10%, $((Sn_2Me_5Ph_2pz)-H)^+$), 501 (10, $((Sn_2Me_3Ph_2pz)-H)^+$), 384 (50, M^+), 369 (85, $(^{120}Sn)(M-Me)^+$), 354 (10, $(^{120}Sn)(M-2Me)^+$), 339 (80, $(^{120}Sn)(M-3Me)^+$), 220 (35, $(Ph_2pzH)^+$), 191 (100, $(C_{15}H_{11})^+$), 165 (55, $(^{120}SnMe_3)^+$), 150 (15, $(^{120}SnMe_2)^+$), 135 (30, $(^{120}SnMe)^+$), 120 (10, $^{120}Sn^+$).

(η^1-3,5-Di-t-butylpyrazolato)trimethyltin(IV) *(3)*

3,5-Di-t-butylpyrazole (1·48 g, 8·2 mmol) was treated with a diethyl ether solution (30 ml) of potassium hydride (0·33 g, 8·2 mmol) at room temperature. Gas evolution was observed and a pale yellow solution formed. $SnMe_3Cl$ (1·00 g, 8·4 mmol) was added causing formation of a white precipitate. The reaction mixture was stirred for 12 h after which time the diethyl ether was removed under vacuum yielding a white solid which was extracted with light petroleum (50 ml). The light petroleum solution was concentrated and cooled to −20°C, and afforded large colourless *crystals* of (3) (yield 75%), m.p. 30°C (Found: C, 49·5; H, 8·2; N, 8·5. $C_{14}H_{28}N_2Sn$ requires C, 49·0; H, 8·2; N, 8·2%). I.r. absorption: 1527m, 1418w, 1361s, 1307m, 1250m, 1224w, 1205m, 1113w, 1081m, 1043w, 1019w, 993m, 786vs, 724s, 632w, 534s, 514m, 464m cm^{-1}. Raman lines (liquid sample): 1527m, 1042w, 1025w, 993w, 927w, 823m, 565w, 537m, 514vs, 260w, 220w, 163m cm^{-1}. ^{1}H n.m.r. δ (C_6D_6) 0·42, s, $^2J_{H,^{117}Sn}$ 55 Hz, $^2J_{H,^{119}Sn}$ 58 Hz, 9H, Me; 1·38, s, 18H, Bu^t; 6·16, s, 1H, H 4. ^{119}Sn n.m.r. δ (0·06 M in PhMe/10% C_6D_6) 72·1 ($\Delta\nu_{1/2}$ 26 Hz). Mass spectrum *m/z*: 344 (10%, $(^{120}Sn)M^+$), 329 (70, $(^{120}Sn)(M-Me)^+$), 299 (40, $(^{120}Sn)(M-3Me)^+$), 180 (35, $Bu^t{}_2pzH^+$), 165 (100, $(^{120}SnMe_3)^+$), 150 (30, $(^{120}SnMe_2)^+$), 135 (30, $(^{120}SnMe)^+$), 120 (10, $^{120}Sn^+$), 57 (90, Bu^{t+}). Vapour pressure $P = 6{\cdot}33\times10^{-3}$ Pa (298 K).

(η^1-3,5-Di-t-butylpyrazolato)triphenylgermanium(IV) *(4)*

3,5-Di-t-butylpyrazole (0·36 g, 2·0 mmol) was treated with a thf solution (30 ml) of potassium hydride (0·08 g, 2·0 mmol) at room temperature. Gas evolution was observed and a pale yellow solution formed. Ph_3GeBr (0·77 g, 2·0 mmol) was added, causing formation of a white precipitate. The reaction mixture was stirred for 2 h after which time the thf was removed under vacuum yielding a white solid which was extracted with light petroleum (50 ml). The light petroleum solution was concentrated and cooled to −20°C and afforded fluffy colourless *crystals* of (4) (yield 49%), m.p. 135°C (Found: C, 73·1; H, 7·2; N, 5·7. $C_{29}H_{34}GeN_2$ requires C, 72·1; H, 7·1; N, 5·8%). I.r. absorption: 1530m, 1433s, 1364s, 1298m, 1248m, 1225w, 1200m, 1188m, 1120w, 1113w, 1092s, 1027m, 993s, 920w, 797vs, 744vs, 697vs, 676vs, 633w cm^{-1}. ^{1}H n.m.r. δ (C_4D_8O) (298 K) 1·04 and 1·28, vbr s (coalescence at 303 K, 1·15, br s), 18H, Bu^t; 6·10, s, 1H, H 4; 7·37, m, 9H, *m*- and *p*-H; 7·60, dd, 6H, *o*-H; (328 K) 1·15, s, 18H, Bu^t; 6·08, s, 1H, H 4; 7·35, m, 9H, *m*- and *p*-H; 7·59, dd, 6H, *o*-H (a spectrum of (4) in C_7D_8 at 298 K was similar to that in C_4D_8O at the same temperature). Mass spectrum: *m/z* 484 (20%, $(^{74}Ge)M^+$), 469 (10, $(^{74}Ge)(M-Me)^+$), 442 (40, $(^{74}Ge)(M-Bu^t)+2CH_3)^+$), 427 (20, $(^{74}Ge)(M-Bu^t)^+$), 305 (100, $(^{74}GePh_3)^+$), 227 (40, $(^{74}GePh_2)^+$), 151 (95, $(^{74}GePh)^+$), 57 (70, Bu^{t+}).

X-Ray Determinations

A single crystal of (1) was mounted under viscous oil on a glass fibre and immediately placed in a cold (*c.* 123 K) nitrogen stream on an Enraf Nonius CCD area detector instrument. A hemisphere of data was measured ('COLLECT') (monochromatic Mo Kα radiation, λ 0·7107$_3$ Å) yielding $N_{\rm tot}$ reflections after integration ('DENZO-SMN') which merged to N unique data ($R_{\rm int}$ 0·039). No absorption correction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined by full matrix least squares on F ('teXsan'), with anisotropic displacement parameters. Hydrogen atoms were located in the difference-Fourier map and refined isotropically. The weighting scheme was based on counting statistics ($w = \sigma^2(F_{\rm o})^{-1}$).

For (2), room-temperature single-counter/four-circle diffractometer (Enraf–Nonius CAD4) data sets were measured on a capillary-mounted specimen ($2\theta/\theta$ scan mode; graphite monochromatized radiation, λ 0·7107$_3$ Å; temperature *c.* 296 K). For (4), a sphere of data was measured at *c.* 153 K on a Bruker AXS CCD area detector diffractometer (monochromatic Mo Kα radiation, λ 0·7107$_3$ Å) using the proprietary software SMART/SAINT. Both data sets yielded $N_{\rm tot}$ reflections which reduced to N unique data ($R_{\rm int}$ 0·046 (4)) after absorption correction ((2) Gaussian, (4) empirical ('SADABS')). $N_{\rm o}$ with $I > 3\sigma(I)$ were considered 'observed' and used in full-matrix least-squares refinement (anisotropic displacement parameters for the non-hydrogen atoms, $(x, y, z, U_{\rm iso})_{\rm H}$ constrained at estimates) after structure solution by conventional methods; statistical weights were employed throughout. An Accessory Publication, consisting of anisotropic displacement parameters, hydrogen atom parameters, bond distances and angles, and lists of structure factors, is available (until 31 December 2004) from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066.

Crystal/Refinement Data

(1). $C_{33}H_{57}AlN_6$, M 564·83. Trigonal, space group $P\bar{3}$ (C_{3i}^1, No. 147), a 14·4582(4), c 10·4065(2) Å, V 1883·92(7) Å^3. $D_{\rm c}(Z = 2)$ 0·99$_6$ g cm^{-3}; $F(000)$ 620. $\mu_{\rm Mo}$ 0·081 mm^{-1}; specimen: 0·25 by 0·25 by 0·25 mm. $2\theta_{\rm max}$ 60·0°; $N_{\rm tot}$ 13872, N 3510, $N_{\rm o}$ 2598; R 0·067, R_w 0·097.

(2). $C_{18}H_{20}N_2Sn$, M 383·08. Orthorhombic, space group *Pcan* (D_{2h}^{14}, No. 60 (variant)), a 10·4372(9), b 15·223(4), c 22·455(3) Å, V 3568(1) Å^3. $D_{\rm c}(Z = 8)$ 1·42$_6$ g cm^{-3}; $F(000)$ 1536. $\mu_{\rm Mo}$ 1·43 mm^{-1}; specimen: 0·36 by 0·44 by 0·20 mm; $T_{\rm min,max}$ 0·61, 0·75. $2\theta_{\rm max}$ 50°; N 3558, $N_{\rm o}$ 1845; R 0·042, R_w 0·052.

(4). $C_{29}H_{34}GeN_2$, M 483·20. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a 8·2525(8), b 10·680(1), c 28·895(3) Å, V 2546·6(7) Å^3. $D_{\rm c}(Z = 4)$ 1·26$_0$ g cm^{-3}; $F(000)$ 1016. $\mu_{\rm Mo}$ 122·1 mm^{-1}; specimen: 0·55 by 0·25 by 0·15 mm; 'T'$_{\rm min,max}$ 0·46, 0·86. $2\theta_{\rm max}$ 58°; $N_{\rm tot}$ 28148, N 3661, $N_{\rm o}$ 3461; R 0·035, R_w 0·043 (preferred chirality; $x_{\rm abs} = 0{\cdot}01(1)$).

Acknowledgments

We are grateful to the Australian Research Council for financial support and for an Australian Postgraduate Award (E.E.D.).

References

[1] Trofimenko, S., *Chem. Rev.*, 1972, **72**, 497.
[2] Trofimenko, S., *Prog. Inorg. Chem.*, 1986, **34**, 115.
[3] Sadimenko, A. P., and Basson, S. S., *Coord. Chem. Rev.*, 1996, **147**, 247.
[4] La Monica, G., and Ardizzoia, G. A., *Prog. Inorg. Chem.*, 1997, **46**, 151.
[5] Cosgriff, J. E., and Deacon, G. B., *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 286.
[6] Eigenbrot, C. W., and Raymond, K. N., *Inorg. Chem.*, 1981, **20**, 1553; 1982, **21**, 2653.
[7] Guzei, I. A., Yap, G. P. A., Rheingold, A. H., Schlegel, H. B., and Winter, C. H., *J. Am. Chem. Soc.*, 1997, **119**, 3387.

[8] Guzei, I. A., Yap, G. P. A., and Winter, C. H., *Inorg. Chem.*, 1997, **36**, 1738.

[9] Yélamos, C., Heeg, M. J., and Winter, C. H., *Inorg. Chem.*, 1998, **37**, 3892.

[10] Pfeiffer, D., Heeg, M. J., and Winter, C. H., *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2517.

[11] Deacon, G. B., Delbridge, E. E., Skelton, B. W., and White, A. H., *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2251.

[12] Falvello, L. R., Forniés, J., Martin, A., Navarro, R., Sicilia, V., and Villarroya, P., *Chem. Commun.*, 1998, 2429.

[13] Deacon, G. B., Delbridge, E. E., and Forsyth, C. M., *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1766.

[14] Perera, J. R., Heeg, M. J., Schlegel, H. B., and Winter, C. H., *J. Am. Chem. Soc.*, 1999, **121**, 4536.

[15] Cosgriff, J. E., Deacon, G. B., Gatehouse, B. M., Hemling, H., and Schumann, H., *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 874; *Aust. J. Chem.*, 1994, **47**, 1223.

[16] Cosgriff, J. E., Deacon, G. B., and Gatehouse, B. M., *Aust. J. Chem.*, 1993, **46**, 1881.

[17] Chang, C. C., Her, T.-Y., Hsieh, F.-Y., Yang, C.-Y., Chiang, M. Y., Lee, G.-H., Wang, Y. J., and Peng, S. M., *J. Chin. Chem. Soc. (Taipei)*, 1994, **41**, 783.

[18] Gassend, R., Delmas, M., Maire, J.-C., Richard, Y., and More, C., *J. Organomet. Chem.*, 1972, **42**, C29.

[19] Hillman, J., Hausen, H.-D., Schwarz, W., and Weidlein, J., *Z. Anorg. Allg. Chem.*, 1995, **621**, 1785.

[20] Gassend, R., Maire, J. C., and Pommier, J. C., *J. Organomet. Chem.*, 1977, **132**, 69.

[21] Elguero, J., Rivière-Baudet, M., and Satgé, J., *C. R. Acad. Sci., Paris, Ser. C*, 1968, **266**, 44; Marchand, A., Rivière-Baudet, M., Satgé, J., and Soulard, M.-H., *J. Organomet. Chem.*, 1976, **107**, 33.

[22] Steiner, A., and Stalke, D., *J. Chem. Soc., Chem. Commun.*, 1993, 1703; *Inorg. Chem.*, 1995, **34**, 4846.

[23] Mason, J., 'Multinuclear NMR' Chs 9, 11 (Plenum: New York 1989).

[24] Edgell, W. F., and Ward, C. H., *J. Mol. Spectrosc.*, 1962, **8**, 343.

[25] Harris, R. K., and Mann, B. E., 'NMR and the Periodic Table' p. 342 (Academic: London 1978).

[26] 'Gmelin Handbook of Inorganic Chemistry, Tin Organic Compounds' Part 7, p. 15 (Springer: Berlin 1980); Schumann, H., and Schumann, I., 'Organotin Bromides' (Ed. H. Bitterer) (Gmelin-Institut: Frankfurt am Main).

[27] Shannon, R. D., *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

[28] Guzei, I. A., and Winter, C. H., *Inorg. Chem.*, 1997, **36**, 4415.

[29] Deacon, G. B., Gitlitz, A., Skelton, B. W., and White, A. H., *Chem. Commun.*, 1999, 1213.

[30] Kepert, D. L., 'Inorganic Stereochemistry' Ch. 8 (Springer: Heidelberg 1982).

[31] Leman, J. T., Barron, A. R., Ziller, J. W., and Kren, R. M., *Polyhedron*, 1989, **8**, 1909; Leman, J. T., Braddock-Wilking, J., Coolong, A. J., and Barron, A. R., *Inorg. Chem.*, 1993, **32**, 4324; Braddock-Wilking, J., Leman, J. T., Farrer, C. T., Larsen, S. C., Singel, D. J., and Barron, A. R., *J. Am. Chem. Soc.*, 1995, **117**, 1736.

[32] Engelhardt, L. M., Gardiner, M. G., Jones, C., Junk, P. C., Raston, C. L., and White, A. H., *J. Chem. Soc., Dalton Trans.*, 1996, 3053.

[33] Taylor, M. J., 'Aluminium and Gallium' in 'Comprehensive Coordination Chemistry' (Eds G. Wilkinson, R. D. Gillard and J. A. McCleverty) Vol. 3, Ch. 25.1 (Pergamon: Oxford 1987).

[34] Cosgriff, J. E., Deacon, G. B., Fallon, G. D., Gatehouse, B. M., Schumann, H., and Weimann, R., *Chem. Ber.*, 1996, **129**, 953.

[35] Wiberg, N., Karampatses, P., Kühnel, E., Veith, M., and Huch, V., *Z. Anorg. Allg. Chem.*, 1988, **562**, 91.

[36] Bondi, A., *J. Phys. Chem.*, 1964, **68**, 441; Pauling, L. C., 'The Nature of the Chemical Bond' (Cornell University Press: Ithaca, New York, 1960).

[37] Schomburg, D., Link, M., Linoh, H., and Tacke, R., *J. Organomet. Chem.*, 1988, **339**, 69.

[38] Miller, G. A., Lee, S. W., and Trogler, W. C., *Organometallics*, 1989, **8**, 738.

[39] Bradley, D. C., Faktor, M. M., Frigo, D. M., and Young, K. V., *Chemtronics*, 1988, **3**, 50.

[40] Deacon, G. B., Delbridge, E. E., Skelton, B. W., and White, A. H., *Eur. J. Inorg. Chem.*, 1998, 543; 1999, 751.