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Dilithium diamides [{Li(OC_4H_8)}$_2${$C_{20}H_{12}(NR)_2$}] (R = $SiMe_3$ or CH_2Bu^t) derived from *R*-, *S*- or *R,S*-2,2′-diamino-1,1′-binaphthyl derivatives *

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The dilithium diamides [{Li(thf)}$_2${$C_{20}H_{12}(NR)_2$}] (R = $SiMe_3$ **1** or CH_2Bu^t **2**, thf = tetrahydrofuran) were prepared from *R,S*-2,2′-diamino-1,1′-binaphthyl, $C_{20}H_{12}(NH_2)_2$, *via* $C_{20}H_{12}[N(H)SiMe_3]_2$ or $C_{20}H_{12}[NHC(O)Bu^t]_2$ and $C_{20}H_{12}[N(H)CH_2Bu^t]_2$, respectively, and were transformed into $SiCl_2[C_{20}H_{12}(NR)_2]$ by treatment with $SiCl_4$. The crystal structures of **1** and **2** were determined. They are monomers, having a Li(1)N(1)Li(2)N(2) buckled ring, with Li(1)–N(2) *ca.* 0.2 Å shorter than Li(1)–N(1), the two groups R *cis* to one another, and N(1)–C(1) η^2 bonded to Li(1). The *R* and *S* enantiomers were similarly prepared and their optical stability was demonstrated by their hydrolysis to *R*- and *S*-$C_{20}H_{12}(NH_2)_2$, respectively. Evidence is provided for the structures of [M{$C_{20}H_{12}[N(SiMe_3)]_2$}] (M = Ge or Sn), obtained by conversion of the stannylene into the crystallographically characterised [{Sn[$(NSiMe_3)_2C_{20}H_{12}$](μ-O)}$_3$].

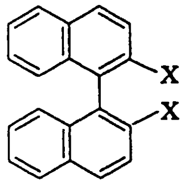
This paper has a bearing on two diverse topics of current interest: novel, lipophilic, organic compounds of the alkali metals and C_2-symmetric chiral auxiliaries.

Organic lithium compounds, with or without a neutral coligand [such as OEt_2, tetrahydrofuran (thf), $(Me_2NCH_2)_2$ (tmen) or $NMe(CH_2CH_2NMe_2)_2$ (pmdien)], are important as reagents.[1] Their structures, both in solution and the crystalline state, have also attracted much attention.[2] The role of the coligand, which lowers the state of aggregation of the lithium compound, has been to change the reactivity of the reagent. Chiral lithium amides have been shown to undergo intermolecular chirality transfer in a wide variety of applications.[3]

The structures of crystalline lithium amides have been reviewed.[4] Those having an ether as coligand are at least binuclear, as in [{Li[μ-N($SiMe_3$)]L}$_2$] {L = OEt_2[5a] [Li–N 2.06(1), Li–O 1.95(2)] or L = thf[5b] [Li–N 2.03(9), Li–O 1.88(1) Å]}, but mononuclear analogues with a bidentate coligand are known, *e.g.* [Li(NRR′)(tmen)] {R = R′ = $SiMe_3$ [Li–N 1.79(1)] or R(R′) = H($C_6H_2Bu^t_3$-2,4,6) [Li–N 1.89(8) [Å]}.[6] Only one example of a lithium bis(amide) appears to have been described previously, the dimer {$Me_2Si[N(Li)Bu^t]_2$}$_2$.[7] A small number of dimeric tris(amides) has been reported, {$RSi[N(Li)SiMe_3]_3$}$_2$ (R = Me, Bu^t or Ph),[8] {$PhSi[N(Li)Bu^t]_3$}$_2$[7] and {$MeC[CH_2N(Li)R]_3$}$_2$ (R = Pr^i or $SiMe_3$),[9] as well as the monomeric $CH[SiMe_2N(Li)Bu^t]_3$ and its bis(thf) adduct.[10] In $CH[SiMe_2N(Li)Bu^t]_3$ each Li atom is two-co-ordinate with an average Li–N distance of 1.92 Å (*cf.* 2.00 Å in the thf adduct in which the four-co-ordination of Li is completed by bonds to oxygen, average 2.03 Å).

Lithium salts of dianionic ligands which we have previously crystallographically characterised include the monomeric dialkyls and diphosphides [{Li(tmen)}$_2${*o*-$C_6H_4[E(SiMe_3)]_2$}] (E = CH[11] or P[12]) in which each Li atom is equidistant from the two dianionic centres; the related bis(amide) has only been structurally studied as its dimeric magnesium salt [{$Mg(OEt_2)$[*o*-C_6H_4{$N(SiMe_3)$}$_2$]}$_2$].[13] *R,S*-2,2′-Dimethyl-1,1′-binaphthyl, isoelectronic with $C_{20}H_{12}(NH_2)_2$, has been converted into crystalline [{Li(tmen)}$_2${$C_{20}H_{12}(CHSiMe_3)_2$}] having a dihedral angle between the two naphthyl planes of 82°.[14]

The synthesis and applications of *R*- and *S*-binaphthylic C_2 derivatives have been reviewed.[15] Many of these have been the neutral molecules $C_{20}H_{12}X_2$, including those with X = PPh_2 (binap), OH (binol) {*cf.* Li[($C_{20}H_{10}O_2$)Al(OR)H]}, SH or NH_2.[16] Compounds having X = NHR (R = Me, Et, Bu^i or CH_2Ph) have been obtained from the parent diamine $C_{20}H_{12}(NH_2)_2$.[17,18] One of these, *R*-$C_{20}H_{12}(NHEt)_2$ upon treatment with Li[AlH_4] in thf, yielded a solution believed to contain [Li{$C_{20}H_{12}(NEt)_2AlH_2$}], which was used for enantioselective reduction of alkyl phenyl ketones.



$C_{20}H_{12}X_2$

Results and Discussion

The parent diamine $C_{20}H_{12}(NH_2)_2$ **I** was synthesised by the reaction of 2-naphthol and hydrazine hydrate (98%) in a sealed glass cylinder at 180–190 °C.[19] Careful purification was advantageous with respect to the subsequent resolution and reactions. Both enantiomers were readily obtained using (+)-camphor-10-sulfonic acid (7,7-dimethyl-2-oxobicyclo[2.2.1]-heptane-1-methanesulfonic acid) as the resolving agent.[20] The snow-white diamine was stored for long periods under argon at room temperature, without deteriorating.

The diamine **I** proved to be surprisingly resistant to silylation, *e.g.* using $SiMe_3Cl$ and a base or hexamethyldisilazane and a catalytic amount of $SiMe_3Cl$. However, the *N,N′*-bis(trimethylsilyl)diamine **II** was obtained (90%) from *R,S*-**I** and *N,N*-bis(trimethylsilyl)acetamide in the presence of a trace of $SiMe_3Cl$ [(*i*) in Scheme 1]. Acylation of *R,S*-**I** with $Bu^tC(O)Cl$–NEt_3, yielding the *N,N′*-bis(pivaloyl)diamine $C_{20}H_{12}[NHC(O)Bu^t]_2$ **III** [(*ii*) in Scheme 1], was more facile; **III** was readily reduced [(*iii*) in Scheme 1] to give the *N,N′*-bis(neopentyl)-diamine **IV**. Similar reactions of *R*(+)- or *S*(−)-**I** gave the corresponding *R* and *S* derivatives **II**–**IV**. Each of **II** and **IV** was transformed into the appropriate dilithium diamide [{Li(thf)}$_2${$C_{20}H_{12}(NR)_2$}] **1** and **2** using $LiBu^n$–hexane–thf [(*iv*)

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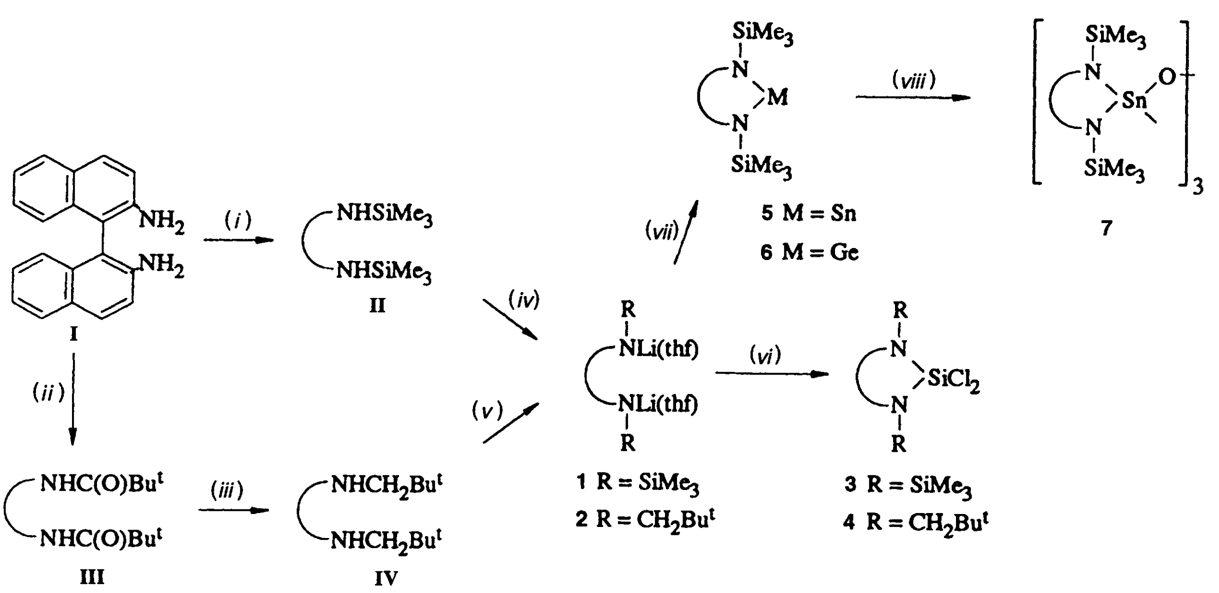
* No reprints available.



Scheme 1 Synthesis of the *N*,*N'*-substituted derivatives **II** and **IV** of 2,2'-diamino-1,1'-binaphthyl **I** and their conversions into lithium salts, silanes and germanium and tin compounds. (*i*) MeC(O)N(SiMe$_3$)$_2$, SiMe$_3$Cl, 140–150 °C, 4 h; (*ii*) Bu^{t}C(O)Cl, NEt$_3$, thf, 4 h reflux; (*iii*) Li[AlH$_4$], thf, 1.5 d reflux; (*iv*) LiBu^n, C$_6$H$_{14}$, 5 h; (*v*) LiBu^n, C$_6$H$_{14}$, 4 h, 25 °C; (*vi*) SiCl$_4$, C$_6$H$_{14}$, thf, 2 h relux; (*vii*) SnCl$_2$ or GeCl$_2$·diox, C$_6$H$_{14}$, thf, 5 h reflux; (*viii*) C$_5$H$_{12}$, O$_2$, 4 weeks

and (*v*) in Scheme 1]. Hydrolysis of the silylated *R*-**II** and the lithiated *R*-**II** afforded in both cases optically pure *R*(+)-**I**, $[\alpha]^{25}_{589} = +164.5$ (c = 1.89, thf); therefore no racemisation occurred during any of the transformations **I**→**II**→**1** or **I**→**III**→**IV**→**2**. Treatment of **1** or **2** with an equimolar portion of SiCl$_4$ afforded [(*vi*) in Scheme 1] the appropriate diaminodichlorosilane $\overline{\mathrm{SiCl_2[C_{20}H_{12}(N}}\mathrm{R)_2]}$ **3** or **4**.

The reaction of the dilithium diamide [{Li(thf)}$_2${C$_{20}$H$_{12}$(NR)$_2$}] **1** (R = SiMe$_3$) with SnCl$_2$ or GeCl$_2$·diox (diox = 1,4-dioxane) in hexane–thf yielded coloured solutions from which the corresponding tin(II) (**5**) or germanium(II) (**6**) amide was obtained, but not in a pure, crystalline form. (The orange-yellow foamy mass, obtained in both cases after the usual work-up, resisted crystallisation from various solvents.) Since purification of **5** or **6** was not achieved, their identification rests on their electron-impact (EI) mass spectra (giving parent molecular ions), and for **5** the ^{119}Sn-{^{1}H} NMR spectrum and its derivatisation to produce the crystallographically characterised complex **7**. Compound **5** showed as the major ^{119}Sn NMR signal a peak at δ +512. This highly deshielded value is characteristic for a homoleptic monomeric tin(II) amide.[21]

An attempted synthesis of the stannylene **5** from Sn[N(SiMe$_3$)$_2$]$_2$ and C$_{20}$H$_{12}$[NH(SiMe$_3$]$_2$ **II** proved to be unsuccessful, and the lack of the reaction is attributed to the high steric demands of **II**. This result may be compared with the ready formation of [Sn{*o*-C$_6$H$_4$[N(SiMe$_3$)]$_2$}] from *o*-C$_6$H$_4$[NH(SiMe$_3$)]$_2$ and Sn[N(SiMe$_3$)$_2$]$_2$.[22]

The stannylene **5** was converted into the cyclotristannoxane $[\{\mathrm{Sn}[\overline{\mathrm{(N}}\mathrm{SiMe_3)_2}\overline{\mathrm{C}}\mathrm{_{20}H_{12}](\mu\text{-}O)\}_3]$ **7**. Only a very few pale yellow crystals were obtained after slow (4 weeks) diffusion of molecular oxygen into a solution of **5** in pentane at room temperature. Cyclostannoxanes [{SnR$_2$(μ-O)}$_x$] (x = 2 or 3) are extremely rare. The sole structurally authenticated cyclo-2,4-distannoxane is [{Sn(CHR$_2$)$_2$(μ-O)$_2$}] (R = SiMe$_3$),[23] synthesised by oxidation of the stannylene Sn(CHR$_2$)$_2$ with Me$_3$NO. Access to the less strained Sn$_3$O$_3$ six-membered ring compounds having alkyl or aryl groups bonded to the tin has been by treatment of a di(hydrocarbyl)tin(IV) chloride (*e.g.* SnBu$^t_2$Cl$_2$) with NaOH. There are several examples of such cyclotristannoxanes which have been characterised by X-ray studies.[24] In contrast to these, amido-ligated cyclostannoxanes are even more rare. Treatment of the stannylene Sn(NR$_2$)$_2$ (R = SiMe$_3$) with molecular oxygen gave the remarkable bis(μ-peroxo)-bridged tin(IV) complex [{Sn(NR$_2$)$_2$(μ-O$_2$)}$_2$],[25] while the cyclic stannylene $[\mathrm{Sn}\{\overline{\mathrm{(NBu^t)_2Si}}\mathrm{Me_2}\}]$ and molecular oxygen gave an adduct of a compound containing an Sn$_2$O$_2$ four-membered ring, $[\{\mathrm{Sn}[\overline{\mathrm{(NBu^t)_2Si}}\mathrm{Me_2}](\mu\text{-}O)\}_2]\cdot[\{\mathrm{Sn_2O}[\overline{\mathrm{(NBu^t)_2Si}}\mathrm{Me_2}]\}_2]$.[26] Thus, complex **7** is the first cyclotri(diamino)stannoxane, although a germanium analogue [{Ge(NR$_2$)$_2$(μ-O)}$_3$] is known.[27]

Each of the compounds **1**–**4** and **II**–**IV** gave satisfactory C, H and N microanalyses (Table 1, which also documents their m.p.s) and NMR spectra (see Experimental section). Some data on the optically active compounds **II**–**IV** are listed in Table 2. Compounds **3**–**7** and **II**–**IV** showed parent molecular ions (Table 3, which also summarises their fragmentation) in their EI mass spectra.

The structures of crystalline compounds **1** and **2** (data for **2** in parentheses) are very similar, as shown in outline, together with atom labelling, in Fig. 1. Selected intramolecular bond lengths and angles are in Tables 4 (**1**) and 5 (**2**). There is a central Li(1)N(1)Li(2)N(2) buckled ring; this is certainly not due to intermolecular effects, as evident from the packing diagrams for **1** (Fig. 2) and **2** (Fig. 3), but is believed to be a consequence of the nature of the Li–N bonding (see below). (Another buckled NMNM ring was reported for [{Na[μ-N(Me)Ph](tmen)}$_2$].[28]) The Li(1)–N(2) at 1.85(3) [1.92(3)] and Li(2)–N(1) 1.97(3) [1.94(3)] Å bonds are shorter than Li(1)–N(1) at 2.20(3) [2.13(3)] and Li(2)–N(2) 2.25(3) [2.24(3)] Å. The pairs of SiMe$_3$ (**1**) or CH$_2$Bu^t (**2**) substituents at N(1) and N(2) are *cis* to one another. Each C(sp^2)–N bond of one unit, *e.g.* N(1)–C(1), is related in an η^2 fashion to the lithium atom of the neighbouring unit, *e.g.* Li(1)–C(1) 2.26(3) [2.23(3)] Å. Each nitrogen atom lies in a trigonal-planar environment with respect to the attached C(sp^2), Si[C(sp^3)], and Li atoms: *e.g.* Li(2)–Si(1)–C(1) have N(1) as their coplanar centroid: C(1)–N(1)–Si(1)[C(21)] 130(1) [119(1)], C(1)–N(1)–Li(2) 118(1) [122(1)] and Si(1)[C(21)]–N(1)–Li(2) 111(1) [117(1)]°, with C(1)–N(1) 1.37(2) [1.39(2)] and Si(1)[C(21)]–N(1) 1.71(1) [1.46(2)] Å. The atom Li(1) tends towards being orthogonal to the Li(2)Si(1)C(1)N(1) plane [and conversely Li(2) with respect to Li(1)Si(2)C(2)N(2)]; *cf.* Li(1)–N(1)–Li(2) 81(1), Li(1)–N(1)–Si(1) 123(1) and Li(1)–N(1)–C(1) 75(1)°. This, together with the shorter Li(2)–N(1) bond compared with Li(1)–N(1), suggests that N(1) uses sp^2 hybrid orbitals in its bonds to Li(2), Si(1) and C(1) and its orthogonal p orbital to bind to Li(1); similarly, N(2) uses sp^2

Table 1 Melting points and analytical data for the *R*,*S* compounds **1**–**4** and **II**–**IV**

Compound	M.p. (°C)	Analysis (%)*		
		C	H	N
1 $[\{Li(thf)\}_2\{C_{20}H_{12}(NSiMe_3)_2\}]$	≈150 (decomp.)	68.6 (69.8)	8.50 (7.95)	4.00 (4.80)
2 $[\{Li(thf)\}_2\{C_{20}H_{12}(NCH_2Bu^t)_2\}]$	≈130 (decomp.)	78.1 (77.5)	8.60 (9.95)	4.80 (4.75)
3 $SiCl_2[C_{20}H_{12}(NSiMe_3)_2]$	149–154	59.0 (59.4)	5.45 (5.75)	5.20 (5.35)
4 $SiCl_2[C_{20}H_{12}(NCH_2Bu^t)_2]$	≈210 (decomp.)	68.6 (69.1)	6.00 (6.55)	5.25 (5.35)
II $C_{20}H_{12}(NHSiMe_3)_2$	147–149	79.5 (79.6)	7.50 (7.15)	6.10 (6.20)
III $C_{20}H_{12}(NHCOBu^t)_2$	171–174	84.7 (84.9)	8.60 (8.55)	6.50 (6.60)
IV $C_{20}H_{12}(NHCH_2Bu^t)_2$	116–117	72.8 (72.8)	7.50 (7.50)	6.50 (6.55)

* Calculated values in parentheses.

Table 2 Some properties of the optically active compounds

Compound	M.p. (°C)	Optical data*	
		$[\alpha]^T_{589}$	T/°C
II R-$C_{20}H_{12}(NHSiMe_3)_2$	59	−43.6	25
S-$C_{20}H_{12}(NHSiMe_3)_2$	59	+48.5	23
III R-$C_{20}H_{12}(NHCOBu^t)_2$	102–106	+86.6	25
S-$C_{20}H_{12}(NHCOBu^t)_2$	102–106	−92.2	25
IV R-$C_{20}H_{12}(NHCH_2Bu^t)_2$	112–115	+6.5	27
S-$C_{20}H_{12}(NHCH_2Bu^t)_2$	112–115	−6.1	20

* Optical rotations were measured in thf.

Table 3 Principal mass spectral features with relative intensities and assignments (M^+ = parent molecular ion)

Compound	m/z (%, assignment)
3	524 (62, M^+), 509 (100, $[M - Me]^+$), 451 (4, $[M - SiMe_3]^+$)
4	520 (15, M^+), 463 (100, $[M - CMe_3]^+$)
II	428 (82, M^+), 413 (18, $[M - Me]^+$), 355 (16, $[M - SiMe_3]^+$), 340 (40, $[M - SiMe_3]^+$), 325 (68, $[M - SiMe_3 - Me]^+$)
III	453 (8, M^+), 396 (1, $[M - CMe_3]^+$)
IV	424 (12, M^+), 367 (16, $[M - CMe_3]^+$)
5	564 (32, M^+), 531 (25, $[M - Me]^+$)
6	500 (40, M^+), 548 (21, $[M - Me]^+$)
7	1684 (2, M^+)

Table 4 Selected intramolecular distances (Å) and angles (°) for $[\{Li(thf)\}_2\{C_{20}H_{12}(NR)_2\}]$ **1** (R = $SiMe_3$)

Si(1)–N(1)	1.711(15)	N(1)–C(1)	1.37(2)
Si(2)–N(2)	1.713(12)	N(2)–C(20)	1.38(2)
O(1)–Li(2)	1.85(3)	C(1)–Li(1)	2.26(3)
O(2)–Li(1)	1.92(3)	C(20)–Li(2)	2.25(3)
N(1)–Li(2)	1.97(3)	N(1)–Li(1)	2.20(3)
N(2)–Li(1)	1.85(3)	N(2)–Li(2)	2.25(3)
Si(1)–N(1)–C(1)	130(1)	Si(2)–N(2)–C(20)	129.3(9)
Si(1)–N(1)–Li(2)	111(1)	Si(2)–N(2)–Li(1)	113(1)
C(1)–N(1)–Li(2)	118(1)	C(20)–N(2)–Li(1)	117(1)
C(1)–N(1)–Li(1)	75(1)	C(20)–N(2)–Li(2)	72(1)
N(1)–Li(1)–N(2)	100(1)	N(1)–Li(2)–N(2)	94(1)
N(1)–C(1)–C(10)	121(1)	N(2)–C(20)–C(11)	122(1)
C(30)–O(1)–Li(2)	136(1)	C(30)–O(2)–Li(1)	121(1)
C(34)–O(2)–Li(1)	134(1)	Si(1)–N(1)–Li(1)	123(1)
Si(2)–N(2)–Li(2)	108.8(8)	Li(1)–N(1)–Li(2)	81(1)
Li(1)–N(2)–Li(2)	82(1)	N(2)–C(20)–Li(2)	72(1)
C(11)–C(20)–Li(2)	84(1)	C(19)–C(20)–Li(2)	112(1)
O(2)–Li(1)–N(1)	126(1)	O(2)–Li(1)–N(2)	134(2)
O(2)–Li(1)–C(1)	109(1)	N(2)–Li(1)–C(1)	108(1)
N(1)–Li(1)–N(2)	100(1)	N(1)–Li(1)–C(1)	35.8(6)
O(1)–Li(2)–N(1)	127(2)	O(1)–Li(2)–N(2)	136(2)
O(1)–Li(2)–C(20)	110(1)	N(2)–Li(2)–C(20)	35.6(7)
N(1)–Li(2)–N(2)	94(1)	N(1)–Li(2)–C(20)	104(1)

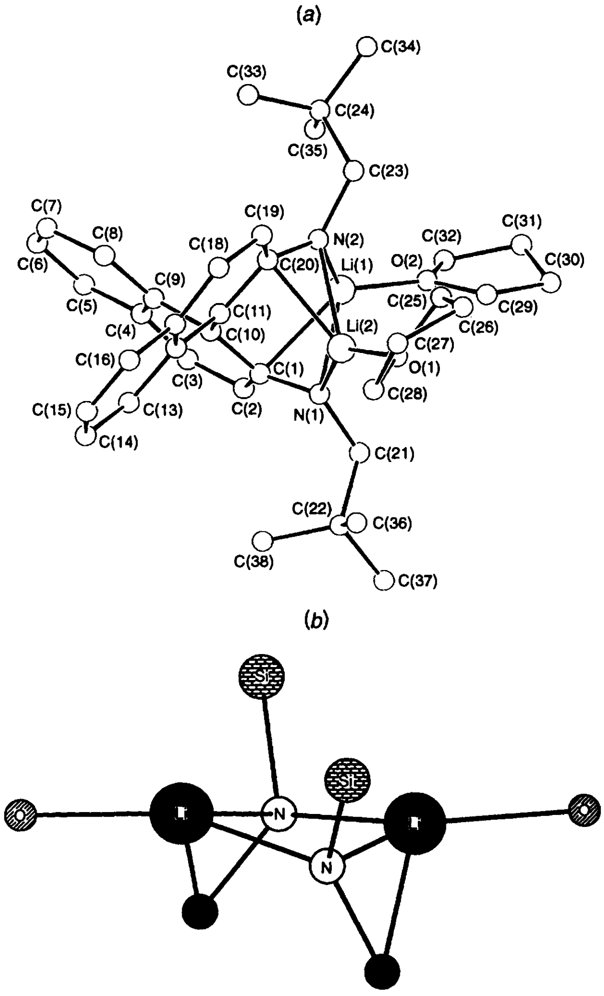


Fig. 1 Molecular structure of (*a*) $[\{Li(thf)\}_2\{C_{20}H_{12}(NR)_2\}]$ **2** (R = CH_2Bu^t) and the atom numbering scheme; (*b*) the central skeletal arrangement for $[\{Li(thf)\}_2\{C_{20}H_{12}(NR)_2\}]$ (R = $SiMe_3$ **1** or CH_2Bu^t **2**)

hybrids in bonding to Li(1), Si(2) and C(2) and the remaining p orbital to bind to Li(2), and a similar picture may apply to **2**; we thank a referee for this suggestion. Each lithium atom has four near neighbours: two nitrogens, one oxygen {Li(2)–O(1) 1.85(3) [1.85(3)], Li(1)–O(2) 1.92(3) [1.90(3)] Å} and an *ipso*-carbon, Li(2)–C(20) 2.25(3) [2.22(3)] Å. The dihedral angle between the two naphthyl planes is 81° in **2**, 78° in **1**. The distance of the nitrogen atoms from the least-squares plane of each naphthyl unit is 0.31 [0.18] Å for N(1) and 0.37 [0.31] Å for N(2). The carbon atoms of each naphthyl group are coplanar with a maximum deviation of 0.08 [0.054] Å.

The structure of the crystalline *R*,*S*-cyclotristannoxane **7**, with atom labelling, is shown in Fig. 4. Selected bond lengths and angles are given in Table 6. The molecular structure has a planar $(SnO)_3$ core, each tin(IV) centre being attached to the chelating $C_{20}H_{12}[N(SiMe_3)]_2$ ligand. The pairs of $SiMe_3$

Table 5 Selected intramolecular distances (Å) and angles (°) for $[\{Li(thf)\}_2\{C_{20}H_{12}(NR)_2\}]$ **2** (R = CH_2Bu^t)

O(1)–Li(2)	1.85(3)	N(2)–Li(2)	2.24(3)
O(2)–Li(1)	1.90(3)	N(1)–C(1)	1.39(2)
N(1)–Li(1)	2.13(3)	N(2)–C(20)	1.38(2)
N(1)–Li(2)	1.94(3)	C(1)–Li(1)	2.23(3)
N(2)–Li(1)	1.92(3)	C(20)–Li(2)	2.22(3)
C(1)–N(1)–C(21)	119(1)	C(20)–N(2)–C(23)	117(1)
C(1)–N(1)–Li(2)	122(1)	C(20)–N(2)–Li(1)	125(1)
C(21)–N(1)–Li(2)	117(1)	C(23)–N(2)–Li(1)	118(1)
C(1)–N(1)–Li(1)	75(1)	C(20)–N(2)–Li(2)	71.3(9)
N(1)–Li(1)–N(2)	99(1)	N(1)–Li(2)–N(2)	95(1)
N(1)–C(1)–C(10)	119(1)	N(2)–C(20)–C(11)	117(1)
C(28)–O(1)–Li(2)	124(1)	C(25)–O(1)–Li(2)	119(1)
C(29)–O(2)–Li(1)	117(1)	C(21)–N(1)–Li(1)	121(1)
Li(1)–N(1)–Li(2)	78(1)	C(23)–N(2)–Li(2)	132(1)
Li(1)–N(2)–Li(2)	76(1)	N(1)–C(1)–Li(1)	68(1)
C(10)–C(1)–Li(1)	92(1)	N(2)–C(20)–Li(2)	72.7(9)
C(11)–C(20)–Li(2)	80(1)	C(19)–C(20)–Li(2)	112(1)
O(2)–Li(1)–N(1)	114(1)	O(2)–Li(1)–N(2)	124(2)
O(2)–Li(1)–C(1)	131(1)	O(2)–Li(1)–Li(2)	118(1)
N(1)–Li(1)–C(1)	37.0(6)	N(1)–Li(1)–Li(2)	47.4(8)
N(2)–Li(1)–C(1)	102(1)	N(2)–Li(1)–Li(2)	57.4(9)
C(1)–Li(1)–Li(2)	73(1)	O(1)–Li(2)–N(1)	142(1)
O(1)–Li(2)–N(2)	117(1)	O(1)–Li(2)–C(20)	112(1)
N(1)–Li(2)–C(20)	106(1)	N(2)–Li(2)–C(20)	36.0(6)

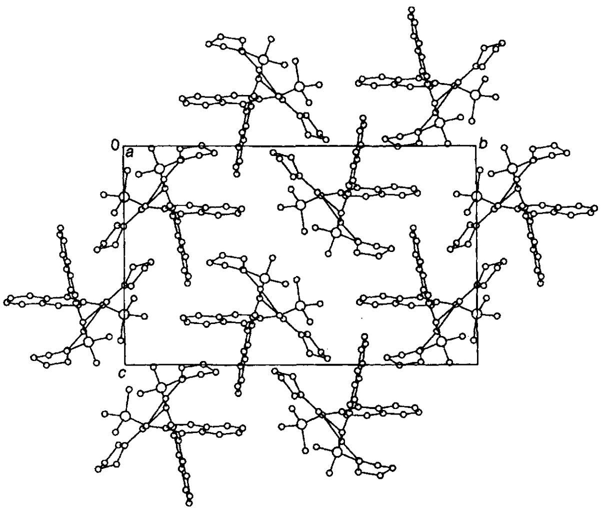


Fig. 2 Crystal packing of complex **1**

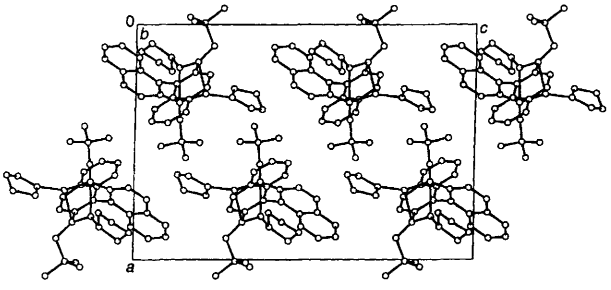


Fig. 3 Crystal packing of complex **2**

Table 6 Selected intramolecular distances (Å) and angles (°) for $[\{Sn[(\overline{NSiMe_3)_2C}_{20}H_{12}](\mu\text{-}O)\}_3]$ **7**

Sn(1)–O(2)	1.76(4)	Sn(1)–O(1)	1.90(2)
Sn(1)–N(1)	2.07(3)	Sn(1)–N(2)	2.02(3)
Sn(2)–O(2)	1.76(4)	Sn(2)–O(3)	1.79(3)
Sn(2)–N(3)	1.91(2)	Sn(2)–N(4)	2.03(3)
Sn(3)–O(1)	1.87(2)	Sn(3)–O(3)	1.93(3)
Sn(3)–N(5)	2.03(2)	Sn(3)–N(6)	1.99(2)
O(2)–Sn(1)–O(1)	118.7(14)	N(2)–Sn(1)–N(2)	101.6(11)
O(2)–Sn(2)–O(3)	119.4(14)	N(3)–Sn(2)–N(4)	100.5(10)
O(1)–Sn(3)–O(3)	111.2(9)	N(6)–Sn(3)–N(5)	103.1(10)
N(1)–C(1)–C(10)	124(3)	N(2)–C(20)–C(11)	122(3)
Sn(1)–O(1)–Sn(3)	122.8(12)	Sn(2)–O(3)–Sn(3)	124.5(14)
Sn(1)–O(2)–Sn(2)	123(2)		

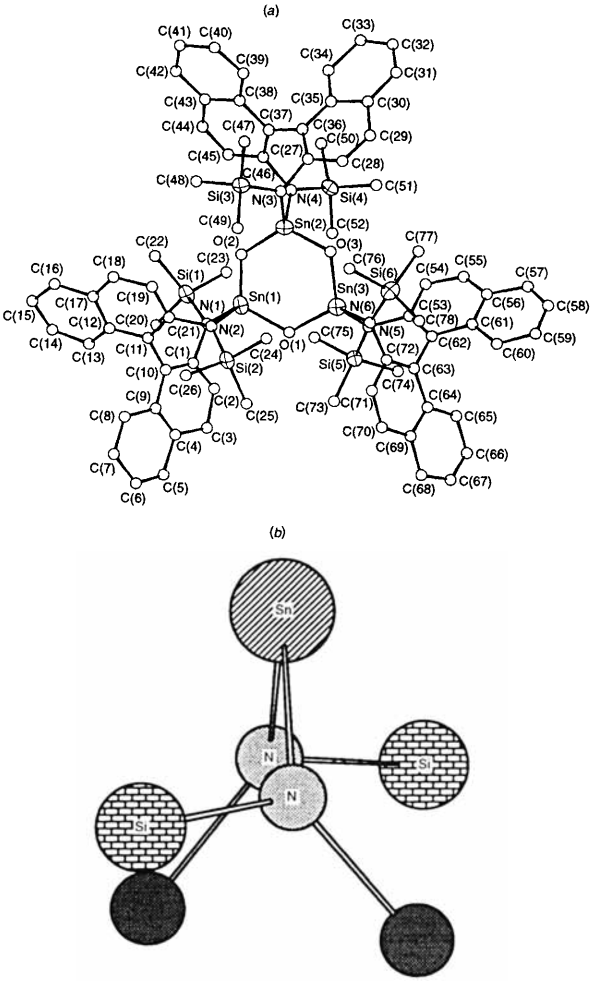


Fig. 4 Molecular structure of (*a*) $[\{Sn[(\overline{NSiMe_3)_2C}_{20}H_{12}](\mu\text{-}O)\}_3]$ **7** and the atom numbering scheme; (*b*) the central skeletal arrangement for one unit Sn(2)N(3)N(4)Si(3)Si(4)C(46)C(27)

substituents are now, in contrast to compounds **1** and **2**, *trans* to one another. Also, unlike in **1** or **2**, there is no evidence of a close M • • • C(sp^2) contact. The sum of angles at the N atoms is approximately 358°, with respect to the attached C(sp^2), Si[C(sp^3)], and Sn atoms, consistent with there being a trigonal-planar environment at the nitrogens, with N(3)–C(27) 1.45(3) and N(3)–Si(3) 1.82(3) Å. The Sn–O bond lengths, which are within the range 1.76(4)–1.93(3) Å, are shorter than typical for related tin(IV) complexes; *e.g.* ⟨Sn–O⟩ 1.987(7) Å for $[\{Sn(NR_2)_2(\mu\text{-}O_2)\}_2]$ [25] or 1.96–1.99 Å for the cyclotristannoxane $[\{SnR_2(\mu\text{-}O)\}_3]$ (R = $C_6H_2Me_3$-2,4,6).[24] The O–Sn–O angles [111.2(9)–119.4(14)°], are somewhat larger than a tetrahedral value, while the N–Sn–N angles are considerably smaller [100.5(10)–103.1(10)°]. The Sn–O–Sn angles range from 122.8(12) to 124.5(14)°; thus the endocyclic angles at tin are narrower than those at oxygen. The Sn–N bond lengths, 1.91(2)–2.07(3) Å, are significantly shorter than in amidostannylenes, *e.g.* 2.096(1) and 2.088(6) Å in $Sn(NR_2)_2$ (R = $SiMe_3$)[29] or 2.098(5) and 2.093(5) Å in [{Sn[*o*-

$C_6H_4\{N(SiMe_3)\}_2]\}_2]$·tmen.[22] The N–Si bond lengths range from 1.69(2) to 1.82(3) Å. The dihedral angles of all three binaphthalene groups attached to Sn(1), Sn(2) and Sn(3) are 72° for Sn(1) and Sn(2) but 69° for Sn(3), and therefore clearly smaller than those observed for the lithium derivatives **1** (78) and **2** (81°).

Experimental

All synthetic work was carried out under argon using standard Schlenk techniques. Tetrahydrofuran, pentane and hexane were predried over sodium wire, distilled from sodium–potassium alloy and stored over molecular sieves (4 Å). Triethylamine was dried over sodium wire. Deuteriated solvents (C_6D_6 and $CDCl_3$) were stored over molecular sieves (4 Å). Triethylamine, chlorotrimethylsilane, lithium aluminium hydride, (+)-camphor-10-sulfonic acid, 2-naphthol, pivaloyl chloride and tetrachlorosilane (Aldrich), *N*,*N*-bis(trimethylsilyl)acetamide (Lancaster) and 1.6 mol dm^{-3} $LiBu^n$ in hexane (FMC Corporation) were used without further purification. The racemic *R*,*S*-2,2′-diamino-1,1′-binaphthyl **I** was prepared by a literature procedure.[5] The NMR spectra were recorded on a Bruker AC 250 at 250 (^1H), 62.86 (^{13}C-$\{^1H\}$) and 97.16 MHz (^7Li-$\{^1H\}$) or AMX 500 spectrometer at 99.33 MHz (^{29}Si-$\{^1H\}$) and referenced internally to residual solvent resonances, EI mass spectra on solid samples using a Kratos MS80RF spectrometer. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed by Medac Ltd., Brunel University. Melting points were determined in sealed capillaries and are uncorrected.

Preparations

***R*,*S*-2,2′-Diamino-1,1′-binaphthyl and the *R* and *S* enantiomers.** In a typical experiment, 2-naphthol (35 g) and hydrazine hydrate (6.08 g, 98%) were sealed under argon in a Carius tube and heated at 180–190 °C for 5 d. After cooling and carefully opening the tube, the orange-yellow gummy mass was treated with ethyl acetate–hexane (1 : 1, 100 cm^3), whereupon the product precipitated. The supernatant orange solution was removed and the washing procedure repeated until the gummy mass disappeared and the washings remained colourless to slightly yellow. The crude residual diamine was filtered off, dissolved in tetrahydrofuran and filtered again. Concentration and cooling the filtrate to −30 °C yielded the crystalline product, which was isolated and dried *in vacuo*. Finally the diamine was washed by stirring in pentane, yielding a free-flowing, white powder (20–27%) after filtration and evaporation to dryness, m.p. 192–193 °C. Optical resolution was effected with (+)-camphor-10-sulfonic acid according to the literature: $[\alpha]_{589}^{25}$ +164.2 (c = 1.75, thf) for *R*-**I**, −167.2 (c = 1.72, thf) for *S*-**I**; $[\alpha]_{589}^{22}$ +157.4 (c = 0.712, pyridine) for *R*-**I**, $[\alpha]_{589}^{23}$ −153.0 (c = 0.758, pyridine) for *S*-**I**.[17]

***R*,*S*-2,2′-Bis(trimethylsilylamino)-1,1′-binaphthyl II and its *R* and *S* enantiomers.** *N*,*N*-Bis(trimethylsilyl)acetamide (8.58 g, 42.6 mmol) was added at room temperature to racemic compound **I** (2.0 g, 7.0 mmol) and a few drops of $SiMe_3Cl$. The stirred reaction mixture was rapidly warmed to reflux temperature until **I** had dissolved. After refluxing for 4 h at 150 °C to ensure complete silylation, the volatiles were removed under vacuum. The residue was extracted into hexane (20 cm^3). Cooling the extract to −20 °C afforded colourless crystals of compound **II** (2.71 g, 90%). NMR ($CDCl_3$): ^1H, δ 0.18 [s, 18 H, $Si(CH_3)_3$], 3.53 (s, 2 H, NH) and 7.23–7.92 (m, 12 H, H of naphthyl); ^{13}C, δ 1.92 (SiC_3) and 112.58–142.64 (C of naphthyl); ^{29}Si, δ 3.48.

Similar treatment of *R*(+)- or *S*(−)-**I** with bis(trimethylsilyl)-acetamide afforded the corresponding optically active compounds *R*- and *S*-**II** in comparable yields, purified by distillation at 175 °C (10^{-6} mmHg, *ca.* 1.33 × 10^{-4} Pa) to yield the glassy solids.

***R*,*S*-2,2′-Bis(pivaloylamino)-1,1′-binaphthyl III and its *R* and *S* enantiomers.** Pivaloyl chloride (2.54 g, 21.1 mmol) was added dropwise at room temperature to a stirred solution of racemic compound **I** (3.0 g, 10.5 mmol) in thf (50 cm^3) and NEt_3 (4.27 g, 42.2 mmol). The mixture was refluxed for 4 h then stirred for 3 h. The precipitate was filtered off and washed with thf (20 cm^3). The volatiles were removed from the filtrate under vacuum. The foamy residue was treated with EtOH (10 cm^3) whereupon **III** began to crystallise. Recrystallisation from EtOH yielded colourless crystals (4.58 g, 96%). NMR ($CDCl_3$): ^1H, δ 0.76 [s, 18 H, $C(CH_3)_3$] and 7.17–8.07 (m, 12 H, H of naphthyl); ^{13}C, δ 26.79 [$C(\mathit{C}H_3)_3$], 39.27 [$\mathit{C}(CH_3)_3$], 121.12–135.06 (C of naphthyl) and 177.01 (CO).

The corresponding *R* and *S* enantiomers were prepared similarly from the appropriate *R*- and *S*-diamine **II**.

***R*,*S*-2,2′-Bis(neopentylamino)-1,1′-binaphthyl IV and its *R* and *S* enantiomers.** A solution of compound *R*,*S*-**III** (4.0 g, 8.8 mmol) in thf (50 cm^3) was added dropwise to a stirred suspension of $Li[AlH_4]$ (2.0 g, 52.7 mmol) in thf (100 cm^3). The mixture was heated under reflux for 1.5 d. The cooled (0 °C) reaction mixture was carefully quenched by addition of water (20 cm^3). The precipitate was filtered off and washed with Et_2O (2 × 20 cm^3). The combined filtrate and washings were evaporated under reduced pressure, and extracted into pentane (20 cm^3); the extract was concentrated and cooled (−20 °C) yielding colourless crystals of compound **IV** (3.60 g, 96%). NMR ($CDCl_3$): ^1H, δ 0.68 [s, 18 H, $C(CH_3)_3$], 2.92 (d, 2 H, *J* 12.6, CH_2Bu^t), 2.99 (d, 2 H, *J* 12.6 Hz, CH_2Bu^t), 3.83 (br s, 2 H, NH) and 7.04–7.91 (m, 12 H, H of naphthyl); ^{13}C, δ 27.22 [$C(\mathit{C}H_3)_3$], 32.32 [$\mathit{C}(CH_3)_3$], 55.72 ($\mathit{C}H_2Bu^t$) and 111.65–144.69 (C of naphthyl).

The analogous *R* and *S* compounds were prepared similarly.

***R*,*S*-Dilithiodiamides $[\{Li(thf)\}_2\{C_{20}H_{12}(NR)_2\}]$ (R = $SiMe_3$ 1 or CH_2Bu^t 2).** n-Butyllithium (1.46 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 2.3 mmol) was added dropwise to a stirred solution of the *R*,*S*-diamine **II** or **IV** (0.5 g, 1.2 mmol) in hexane (50 cm^3). The mixture was stirred for 5 h, then heated to gentle reflux while thf was slowly added by a syringe until the precipitate had dissolved. Slow cooling to room temperature afforded yellow-orange crystals of **2** (0.62 g, 91%) or yellow crystals of **1** (0.58 g, 85%). Complex **1**: NMR (C_6D_6), ^1H, δ 0.41 [s, 18 H, $Si(CH_3)$], 0.85 (m, 8 H, thf), 2.95 (m, 8 H, thf) and 6.72–7.56 (m, 12 H, H of naphthyl); ^{13}C, δ 2.76 (SiC_3), 25.14 (thf), 68.07 (thf) and 120.06–155.03 (C of naphthyl); ^{29}Si, δ −11.68; ^7Li, δ 0.38. Complex **2**: NMR (C_6D_6), ^1H, δ 1.01 [s, 18 H, $C(CH_3)_3$], 1.07 (m, 8 H, thf), 2.90 (m, 8 H, thf), 3.03 (d, 2 H, *J* 12.4, CH_2Bu^t), 3.47 (d, 2 H, *J* 12.6 Hz, CH_2Bu^t) and 6.80–7.71 (m, 12 H, H of naphthyl); ^{13}C, δ 25.01 (thf), 28.99 [$C(\mathit{C}H_3)_3$], 33.71 [$\mathit{C}(CH_3)_3$], 62.48 ($\mathit{C}H_2Bu^t$), 67.86 (thf) and 113.43–157.53 (C of naphthyl); ^7Li, δ 0.14.

***R*,*S*-Dichlorosilanes $\overline{SiCl_2[C_{20}H_{12}(N}R)_2]$ (R = $SiMe_3$ 3 or CH_2Bu^t 4).** Addition of $SiCl_4$ (0.33 g, 1.9 mmol for **1**; or 0.46 g, 2.7 mmol for **2**) to a solution of complex **1** (1.16 g, 1.9 mmol) or **2** (1.60 g, 2.7 mmol) in hexane–thf (2 : 1, 30 cm^3) at room temperature and refluxing for 2 h afforded **3** or **4**; **3** was filtered through Celite and obtained as a pale yellow powder (0.88 g, 84%). NMR ($CDCl_3$): ^1H, δ −0.27 [s, 18 H, $Si(CH_3)_3$] and 7.23–7.92 (m, 12 H, H of naphthyl); ^{13}C, δ 1.49 (SiC_3) and 124.96–140.32 (C of naphthyl); ^{29}Si, δ −32.61 ($SiCl_2$) and 10.30. Colourless crystals of **4** (1.27 g, 89%) were obtained after filtration and recrystallisation from hexane. NMR ($CDCl_3$): ^1H, δ 0.34 [s, 18 H, $C(CH_3)_3$], 3.20 (d, 2 H, *J* 14.3, CH_2Bu^t), 3.51 (d, 2 H, *J* 14.3 Hz, CH_2Bu^t) and 7.13–7.97 (m, 12 H, H of naphthyl); ^{13}C, δ 27.61 [$C(\mathit{C}H_3)_3$], 34.07 [$\mathit{C}(CH_3)_3$], 57.22

Table 7 Crystallographic data* and refinement for the complexes $[\{\mathrm{Li(thf)}\}_2\{\mathrm{C_{20}H_{12}(NR)_2}\}]$ (R = $\mathrm{SiMe_3}$ **1** or $\mathrm{CH_2Bu^t}$ **2**) and $[\{\mathrm{Sn}[(\overline{\mathrm{NSiMe_3})_2\mathrm{C}}_{20}\mathrm{H}_{12}](\mu\text{-O})\}_3]$ **7**

	1	**2**	**7**
Formula	$C_{34}H_{46}Li_2N_2O_2Si_2$	$C_{38}H_{50}Li_2N_2O_2$	$C_{78}H_{90}N_6O_3Si_6Sn_3$
M	584.8	580.7	1684.2
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$Pca2_1$
a/Å	10.062(3)	15.002(6)	32.166(11)
b/Å	23.224(7)	10.687(4)	14.109(3)
c/Å	15.005(5)	21.682(7)	19.695(8)
β/°	106.23(3)	91.54(3)	
U/Å^3	3366	3475	8938
D_c/g cm^{-3}	1.15	1.11	1.25
$F(000)$	1256	1256	3432
N (total unique)	4256	4537	5669
N_o [$I > 2\sigma(I)$]	1630	1589	3575
Specimen/mm	0.2 × 0.2 × 0.1	0.4 × 0.2 × 0.1	0.3 × 0.3 × 0.2
R	0.116	0.124	0.091
R'	0.109	0.116	0.276
S	1.8	2.0	1.1
μ/cm^{-1}	1.3	0.6	9.6

* Details in common: $Z = 4$; Mo-Kα radiation ($\lambda = 0.7107$ Å); 173 K; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ for $I > 2\sigma(I)$; for **1** and **2**, $R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$ for $I > 2\sigma(I)$; for **7**, $R' = [\Sigma(|F_o| - |F_c|^2)^2/\Sigma(|F_o|^2)^2]^{\frac{1}{2}}$ for all data. For **1** and **2** $w = \sigma^{-2}(F)$ and for **7** w is as defined in ref. 30.

($C\mathrm{H_2Bu^t}$) and 122.61–143.18 (C of naphthyl); ^{29}Si, δ −31.00 ($\mathrm{SiCl_2}$).

***R*,*S*-Amido-stannylene and -germylene, $[\mathbf{M\{C_{20}H_{12}[N(SiMe_3)]_2\}}]$ (M = Sn 5 or Ge 6).** Addition of $\mathrm{SnCl_2}$ (0.45 g, 2.4 mmol for **5**) or $\mathrm{GeCl_2{\cdot}diox}$ (0.51 g, 2.2 mmol for **6**) to a solution of complex **1** (1.4 g, 2.4 mmol for **5**; or 1.3 g, 2.2 mmol for **6**) in hexane–thf (2:1, 100 cm^3) at room temperature and refluxing for 5 h afforded **5** or **6**. Removal of the solvent *in vacuo* from the filtrate yielded in both cases an orange-yellow foamy mass, which was dissolved in hexane and filtered again. Crystals of **5** or **6** were not obtained from different solvents, at room temperature or at −30 °C.

X-Ray quality single crystals of $[\{\mathbf{Sn}[(\overline{\mathbf{NSiMe_3})_2\mathbf{C}}_{20}\mathbf{H}_{12}](\mu\text{-}\mathbf{O})\}_3]$ 7. A dilute solution of compound **5** in pentane was kept in a Schlenk tube at room temperature for about 4 weeks. During this time complex **7** crystallised in the form of pale yellow crystals, owing to slow diffusion of molecular oxygen into the tube. Only a very few crystals were obtained and these were used for crystallographic studies.

Crystallography

Details are given in Table 7. Data for complexes **1** and **2** were collected on an Enraf-Nonius CAD4 diffractometer. Intensities for $hk \pm l$ reflections with $2 < \theta < 22°$ were measured by θ–2θ scans. Reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$ were considered to be observed. No correction was applied for absorption. The structure was solved *via* direct methods using SHELXS 86,[31] with Si atoms refined anisotropically for **1**, otherwise all non-H isotropically by full-matrix least squares on F using the Enraf-Nonius MOLEN program package.[32] Hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. For both crystals the diffraction was weak at high angle and because of the limited significant reflections anisotropic refinement was not justified.

For complex **7** a unique data set was collected, using a single crystal as above. A correction was made for absorption based on ψ scans; maximum 1.00, minimum 0.82. The structure was solved by direct methods and difference maps using SHELXS 86[31] and refined by full-matrix least squares on F^2 using SHELXL 93[30] with Sn and Si atoms anisotropic, C, N and O isotropic and H atoms in riding mode with $U_{iso}(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$ or $1.5U_{eq}(\mathrm{C})$ for methyl groups. The absolute structure parameter refined to 0.04(8). The combination of rather broad diffraction peaks and a long a axis caused some problems of peak overlap which reduced the accuracy of the data.

Atomic coordinates, thermal parameters, and bond length and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/144.

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