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FULL PAPER

Metal (Li, K, Sn^{II} and Hg^{II}) complexes of the 1,3-diazaallyl $[N(R)C(Ph)NC(Ph){=}CR_2]^-$ ($R = SiMe_3$)

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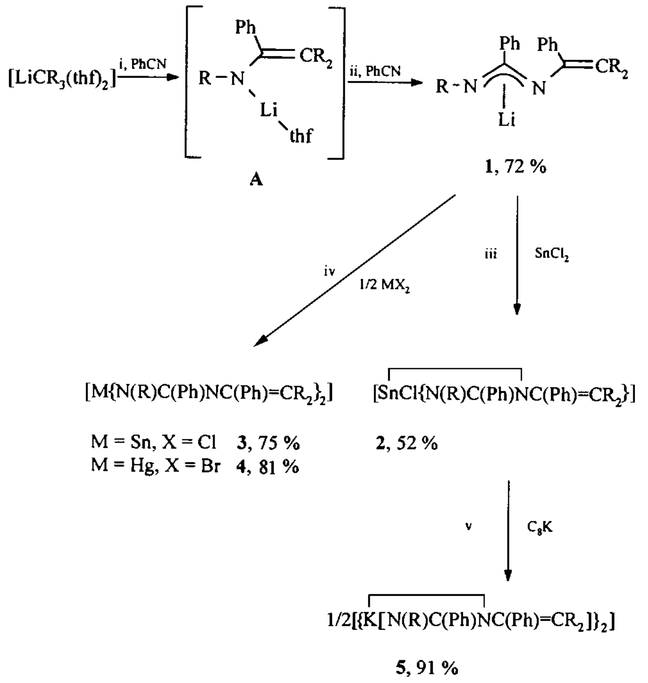
The new lithium 1,3-diazaallyl $[Li\{N(R)C(Ph)NC(Ph){=}CR_2\}]$ **1** [abbreviated as Li(L–L′)] has been prepared from $[Li(CR_3)(thf)_2]$ and 2 equivalents of benzonitrile ($R = SiMe_3$, thf = C_4H_8O). Compound **1** was shown to be a suitable precursor for the synthesis of the metal complexes [SnCl(L–L′)] **2**, $[Sn(L–L')_2]$ **3** and $[Hg(L–L')_2]$ **4** from the appropriate metal(II) chloride, while the reduction of **2** with potassium–graphite led in high yield to $[\{K(\mu\text{-}L–L')\}_2]$ **5**. Each of the compounds was fully characterised by multinuclear NMR spectroscopy, mass spectrometry and for **3**–**5** by X-ray diffraction.

We have reviewed initial progress on the synthesis, structures and reactions of alkali metal α,ω-bis(trimethylsilyl)-1-azaallyls and -β-diketiminates, including their role as precursors for preparing unusual transition metal and main group element complexes.[1] Recently we described the new lithium 1-azaallyl $[Li\{N(R)C(Ph){=}CR_2\}(thf)]$ **A** ($R = SiMe_3$), obtained by treatment of $[Li(CR_3)(thf)_2]$[2] with 1 equivalent of benzonitrile [(i) in Scheme 1], and its application in the context of low valent Group 14 metal chemistry.[3] We also drew attention to the diversity of bonding modes in 1-azaallyl metal compounds in which the ligand functioned in an η^1-enamido,[4] η^3-chelating[4] or μ,η^2 mode.[5]

Now we report the synthesis of the new unsymmetrical lithium 1,3-diazaallyl $[Li\{N(R)C(Ph)NC(Ph){=}CR_2\}]$ [≡ Li(L–L′)] **1** from $[Li(CR_3)(thf)_2]$ and 2 equivalents of benzonitrile [(ii) in Scheme 1] and the use of **1** as a source of L–L′ derivatives of K, Sn and Hg.

While symmetrical 1,3-diazaallyls, and in particular metal benzamidinates based on the $[N(R)C(Ph)N(R)]^-$ ligand, have been extensively studied and recently reviewed,[6] their unsymmetrical analogues have received less attention.



Scheme 1 Preparation and some reactions of the 1,3-diazaallyl lithium compound **1** ($R = SiMe_3$).

Results and discussion

Whereas the reaction of $[Li(CR_3)(thf)_2]$ with 1 equivalent of PhCN in Et_2O led to the hydrocarbon-soluble lithium 1-azaallyl **A** [(i) in Scheme 1],[3] the addition of 2 equivalents of PhCN gave the lithium 1,3-diazaallyl **1** [(ii) in Scheme 1]. It is assumed that in the latter reaction **A** is formed as an intermediate which then behaves as an *N*-centred nucleophile towards a second equivalent of PhCN. The 1,3-diazaallyl **1** was obtained from the reaction mixture as a yellow, air-sensitive powder by removing all volatiles, washing the residue with C_5H_{12} and drying it *in vacuo*.

Treatment of a halide of tin(II) or mercury(II) with $[Li\{N(R)C(Ph)NC(Ph){=}CR_2\}]$ **1** in diethyl ether gave the complexes [SnCl(L–L′)] **2**, $[Sn(L–L')_2]$ **3** or $[Hg(L–L')_2]$ **4** in high yield [(iii) or (iv) in Scheme 1]. The attempted potassium–graphite reduction of **2** led, not as expected, to a tin(I) species but to tin metal and $[\{K(L–L')\}_2]$ **5** [(v) in Scheme 1].

Compound **2**, unlike **3**–**5**, was very soluble in hydrocarbons; **3**–**5** were purified by recrystallisation from diethyl ether (**3**) or benzene (**3**–**5**). Compounds **2**–**4** showed the molecular ion peaks in high intensities in their EI mass spectra, which may indicate a considerable degree of covalency in these compounds. In the case of the more ionic alkali metal compounds **1** and **5**, in contrast, only fragments of the ligand were observed.

Crystal structures of the metal 1,3-diazaallyls 3, 4 and 5

The molecular structures of crystalline compounds **3**, **4** and **5** with the atom numbering schemes are illustrated in Figs. 1–3, respectively. Selected bond distances and angles are listed in Tables 1–3.

The crystalline compound $[Hg(L–L')_2]$ **4** is a monomer in which the metal atom is bonded in a linear fashion to the terminal nitrogen atoms of two different 1,3-diazaallyl ligands [N(1)–Hg–N(3) 176.6(4)]; the Hg–N bond distances to these nitrogen atoms, of 2.07(1) and 2.08(1) Å, are within the range for typical covalent Hg–N single bonds as observed in $[Hg_2N]Br$,[7] $[Hg\{N(H)C(O)Me\}_2]$[8] or $[Hg\{NC(O)(CH_2)_2C(O)\}_2]$,[9] while the contacts to the internal nitrogen atoms N(2) and N(4) are much longer, 2.70(1) and

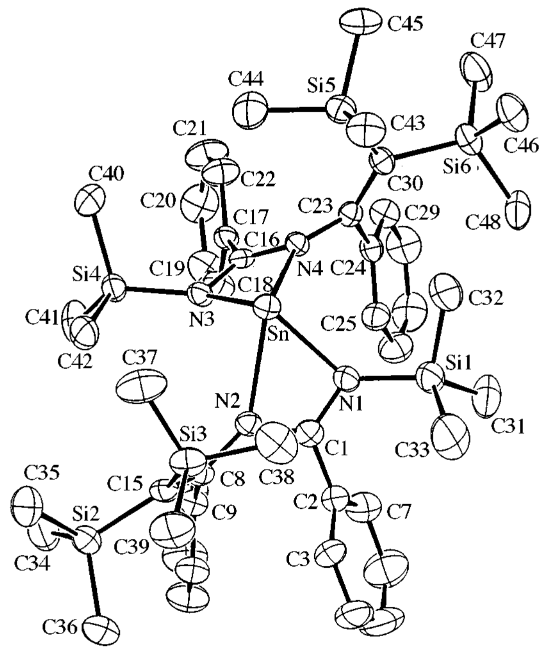


Fig. 1 Molecular structure of compound **3**.

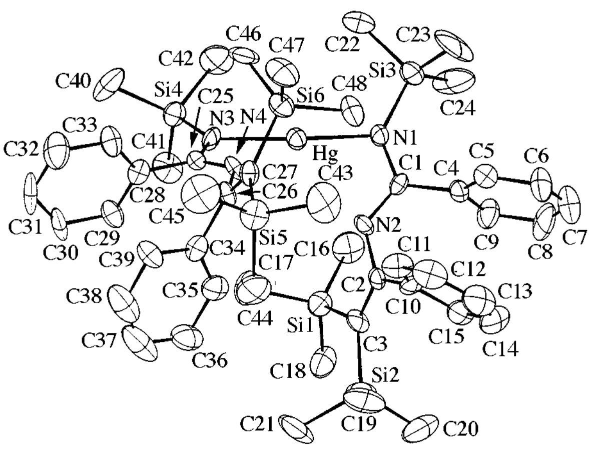


Fig. 2 Molecular structure of compound **4**.

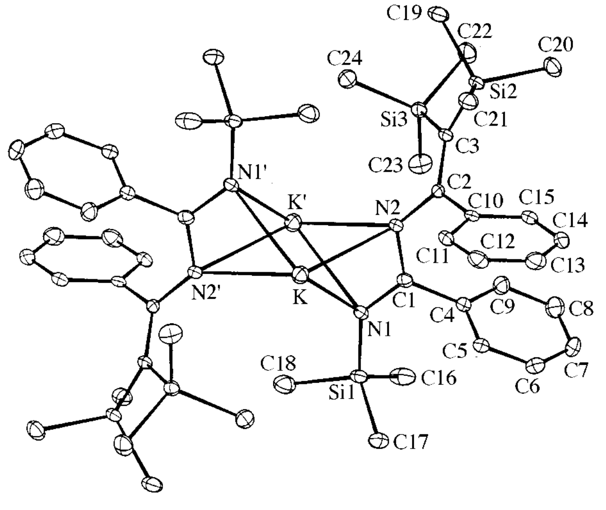


Fig. 3 Molecular structure of compound **5**.

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for compound **3**

Sn–N(1)	2.267(3)	Sn–N(3)	2.271(3)
Sn–N(2)	2.391(3)	Sn–N(4)	2.393(3)
Si(1)–N(1)	1.760(3)	Si(4)–N(3)	1.758(3)
N(1)–C(1)	1.336(5)	N(2)–C(1)	1.314(5)
N(2)–C(8)	1.428(5)	N(3)–C(16)	1.336(5)
N(4)–C(16)	1.319(5)	N(4)–C(23)	1.415(5)
C(8)–C(9)	1.494(6)	C(8)–C(15)	1.343(5)
C(23)–C(30)	1.360(5)	C(23)–C(24)	1.486(5)
N(1)–Sn–N(3)	107.75(12)	N(1)–Sn–N(2)	57.49(11)
N(3)–Sn–N(2)	86.37(11)	N(1)–Sn–N(4)	87.07(11)
N(3)–Sn–N(4)	57.65(11)	N(2)–Sn–N(4)	119.56(11)
C(1)–N(1)–Si(1)	125.4(3)	C(1)–N(1)–Sn	95.9(3)
Si(1)–N(1)–Sn	129.2(2)	C(1)–N(2)–C(8)	123.3(3)
C(1)–N(2)–Sn	90.9(2)	C(8)–N(2)–Sn	145.0(3)
C(16)–N(3)–Si(4)	125.5(3)	C(16)–N(3)–Sn	95.6(2)
Si(4)–N(3)–Sn	129.3(2)	C(16)–N(4)–C(23)	124.4(3)
C(16)–N(4)–Sn	90.6(2)	C(23)–N(4)–Sn	143.3(2)
N(2)–C(1)–N(1)	115.6(4)	N(2)–C(1)–C(2)	122.7(4)
N(1)–C(1)–C(2)	121.6(4)	N(4)–C(16)–N(3)	116.0(3)
N(4)–C(16)–C(17)	122.7(3)	N(3)–C(16)–C(17)	121.3(3)

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for compound **4**

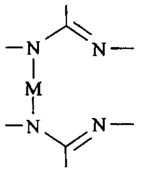
Hg–N(1)	2.065(10)	Hg···N(2)	2.698(11)
Hg–N(3)	2.080(10)	Hg···N(4)	2.614(9)
N(1)–C(1)	1.313(14)	N(2)–C(1)	1.320(14)
N(2)–C(2)	1.40(2)	N(3)–C(25)	1.34(2)
N(4)–C(25)	1.29(2)	N(4)–C(26)	1.415(14)
C(1)–C(4)	1.50(2)	C(2)–C(3)	1.35(2)
C(2)–C(10)	1.50(2)	C(25)–C(28)	1.49(2)
C(26)–C(27)	1.36(2)		
N(1)–Hg–N(3)	176.6(4)	N(3)–Hg–N(4)	56.1(4)
N(1)–Hg–N(2)	54.3(3)	C(1)–N(1)–Si(3)	131.3(9)
C(1)–N(1)–Hg	108.5(8)	Si(3)–N(1)–Hg	120.1(6)
C(1)–N(2)–C(2)	125.2(11)	C(25)–N(3)–Si(4)	133.8(9)
C(25)–N(3)–Hg	104.2(8)	Si(4)–N(3)–Hg	122.0(6)
C(25)–N(4)–C(26)	125.0(10)	N(1)–C(1)–N(2)	117.2(12)
N(1)–C(1)–C(4)	118.1(12)	N(2)–C(1)–C(4)	124.3(12)
C(3)–C(2)–N(2)	123.4(12)	C(3)–C(2)–C(10)	122.5(12)
N(2)–C(2)–C(10)	114.0(11)	C(2)–C(3)–Si(2)	123.8(10)
C(2)–C(3)–Si(1)	116.0(10)	Si(2)–C(3)–Si(1)	119.8(7)
N(4)–C(25)–N(3)	117.7(11)	N(4)–C(25)–C(28)	124.2(13)
N(3)–C(25)–C(28)	118.1(13)	C(27)–C(26)–N(4)	121.5(11)
C(27)–C(26)–C(34)	124.8(11)	N(4)–C(26)–C(34)	113.5(11)
C(26)–C(27)–Si(6)	117.3(10)	C(26)–C(27)–Si(5)	121.9(10)

2.61(1) Å respectively, and thus represent at best only weak interactions. Similar bond lengths [Hg–N 2.069(6), 2.071(7) and 2.721(7), 2.717(7) Å, respectively] have been reported for the related benzamidinate $[\text{Hg}\{\text{N(R)C(Ph)NR}\}_2]$.[10] A corollary of the observed close contacts between only one nitrogen atom in each ligand and the mercury atom is the presence of two distinctly different C–N bond distances in the backbone of the ligands, as illustrated in structure **I** [a homoleptic metal(II) η^1-iminoamide]; these values are similar to those observed in H(R)NC(Ph)=NR,[11] 1.263(3) and 1.410(3) Å, appropriate for CN double or single bonds, respectively. While the bond distances C=N 1.28(1) and C–N 1.36(1) Å found in $[\text{Hg}\{\text{N(R)C(Ph)N(R)}\}_2]$ are in good agreement with this view, indicating only a small degree of delocalisation in the backbone of the amidinate ligand, the corresponding values in **4** are rather closer to one another: 1.29(2), 1.34(2), 1.31(1) and 1.32(1) Å. These are, however, in the same range as in compounds where the π-electron density in the ligand is delocalised (structure **II**) with both nitrogen atoms of each ligand binding more or less equally to the metal as in $[\overline{\text{Au}\{\text{N(R)C(Ph)N}}\text{R}\}\text{Cl}_2]$,[12] $[\overline{\text{Al}\{\text{N(R)C(Ph)N}}\text{R}\}\text{Cl}_2]$,[13a] $[\overline{\text{Al}\{\text{N(R)C(Ph)N}}\text{R}\}_2\text{H}]$,[13b] $[\overline{\text{Cr}\{\text{N(R)C(Ph)N}}\text{R}\}_2]$,[14] $[\overline{\text{Mg}\{\text{N(R)C(Ph)N}}\text{R}\}_2(\text{NCPh})]$,[15] $[\overline{\text{Sn}\{\text{N(R)C(Ph)N}}\text{C(Ph)=CR}_2\}_2]$ **3** (see below) or $[\overline{\text{Ge}\{\text{N(Pr}^i\text{)C(Me)N}}\text{Pr}^i\}_2]$.[16] Another interesting feature of the two related mercury compounds is the very different arrangement of the ligands relative to one another, as evident from the torsion angles C–N(–Hg–)N–C across the linear HgN_2 fragment of −147.5° in $[\text{Hg}\{\text{N(R)C(Ph)NR}\}_2]$ and 55.4° in **4**.

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for compound **5**

K–N(1′)	2.796(3)	K–N(1)	2.804(3)
K–N(2′)	2.857(3)	K···N(2)	3.067(3)
K···C(1)	3.176(4)	K···C(1′)	3.208(4)
K···K′	3.343(2)	Si(1)–N(1)	1.717(3)
N(1)–C(1)	1.335(4)	N(2)–C(1)	1.336(4)
N(2)–C(2)	1.402(4)	C(1)–C(4)	1.500(5)
C(2)–C(3)	1.383(5)		
N(1′)–K–N(1)	106.68(8)	N(1′)–K–N(2′)	47.85(9)
N(1)–K–N(2′)	92.82(9)	N(1′)–K–N(2)	88.62(9)
N(1)–K–N(2)	45.71(8)	N(2′)–K–N(2)	111.39(7)
C(1)–N(1)–Si(1)	129.0(3)	C(1)–N(1)–K′	95.3(2)
Si(1)–N(1)–K′	119.3(3)	C(1)–N(1)–K	93.4(2)
Si(1)–N(1)–K	130.1(2)	K′–N(1)–K	73.32(8)
C(1)–N(2)–C(2)	121.9(3)	C(1)–N(2)–K′	92.6(2)
C(2)–N(2)–K′	143.8(2)	C(1)–N(2)–K	82.3(2)
C(2)–N(2)–K	122.5(2)	K′–N(2)–K	68.61(7)
N(1)–C(1)–N(2)	118.3(3)	N(1)–C(1)–C(4)	120.4(3)
N(2)–C(1)–C(4)	121.3(3)	C(3)–C(2)–C(10)	119.8(3)
C(3)–C(2)–N(2)	122.7(3)	C(2)–C(3)–Si(3)	119.8(3)
N(2)–C(2)–C(10)	117.3(3)	Si(3)–C(3)–Si(2)	119.0(2)
C(2)–C(3)–Si(2)	121.1(3)		

Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, $-z$.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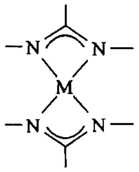
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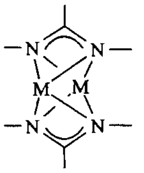
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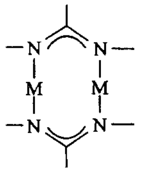
IV

Crystalline [Sn{N(R)C(Ph)NC(Ph)=CR$_2$}$_2$] **3** shows, in contrast to **4**, a severely distorted ψ-trigonal bipyramidal co-ordination at Sn with a stereochemically active lone electron pair occupying an equatorial site. The atoms N(2) and N(4) may be regarded as being approximately axial; however, the N(2)–Sn–N(4) bond angle of *ca.* 120° is well removed from 180°. The Sn–N distances are 2.267(3), 2.391(3), 2.271(3) and 2.393(3) Å, the equatorial bonds being the shorter. The two ligands are tilted against one another with an angle of 79.1° between the N(1)–C(1)–N(2) and N(3)–C(16)–N(4) planes. The Sn–N distances, average 2.269(3) Å, are much longer than in simple tin(II) amides such as Sn(NR$_2$)$_2$ [2.092(6) Å],[17] but are in the same range as in compounds with related monoanionic chelating ligands as in [Sn(NC$_5$H$_4$CR$_2$-2)$_2$][18] or [Sn{N(R)C(Ph)CR$_2$}{N(R)C(Ph)=CR$_2$}] (ref. 3, and literature cited therein). The C–N bond distances in **3** [1.336(5), 1.314(5), 1.336(5) and 1.319(5) Å] are essentially identical within the standard deviations, as appropriate for a type **II** structure, with each ligand co-ordinating in a chelating fashion to the metal. The structure of crystalline **3** is thus similar to that of [Ge{N(Pr^i)C(Me)NPr^i}$_2$],[16] having the amidinate bite angle of 61.0° compared with average 57.6(1)° in **3**.

The solvent-free, crystalline [K(L–L′)]$_2$ **5** is a centrosymmetric dimer, the two potassium atoms being bridged by two ligands, each of which is thus of μ-η^2:η^2 type, the overall structure being represented schematically in **III** rather than **IV** (μ-η^2). The four nitrogen atoms of the ligands are coplanar, this plane being the common base for the two distorted pyramids having an axial potassium atom. The rather short K–N(1) 2.804(3), K–N(1′) 2.796(3) and K–N(2′) 2.857(3) Å bonds are in the same range as in [{K(μ-NR$_2$)}$_2$],[19a] [K(NR$_2$)]·C$_6$H$_5$Me,[19b] [K(NC$_5$H$_4$NPh-2)(tmen)],[20] [K{N(R)P(Ph)$_2$NR}(thf)$_4$],[21] [K{N(Bu^t)S(Ph)NR}(thf)][22] and [K{N(R)C(R′)NC(R′)=CH(R)}(NCR′)] (R = SiMe$_3$, R′ = C$_6$H$_3$Me$_2$-2,5),[23] while the K···N(2) contact of 3.067(3) Å is only slightly longer. The C–N distances of 1.335(4) and 1.336(4) Å in the backbone of the ligand are identical. The overall geometry of **5** is similar to that of the above nitrile-co-ordinated potassium 1,3-diazaallyl [K{N(R)C(R′)NC(R′)=CH(R)}(NCR′)], which likewise belongs to type **III**. Both compounds show close K···K contacts of 3.343(2) (**5**) and 3.299(5) Å, which are shorter than in potassium metal, 4.54 Å.[24]

The related coinage metal complexes [{M[μ-η^2-N(R)C(Ph)NR]}$_2$] (M = Cu[25] or Ag[26]), in contrast to these potassium compounds, while also dimeric in the solid state, show a linear co-ordination at the metal with only two short M–N contacts and equidistant C–N bond lengths. This bonding mode, **IV**, may be described as μ-η^2-bridging.

Experimental

General procedures

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in C$_6$D$_6$ or CDCl$_3$ at 298 K using the following Bruker instruments: AC-P 250 (^{1}H, 250.1; ^{13}C, 62.9), DPX 300 (^{1}H, 300.1; ^{13}C, 75.5) and AMX 500 (^{1}H, 500.1; ^{13}C, 125.7; ^{119}Sn, 186.5 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ) in the case of ^{1}H and ^{13}C spectra. The ^{119}Sn spectra were referenced externally to SnMe$_4$. Unless otherwise stated, all NMR spectra other than ^{1}H were proton-decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected.

Preparations

[Li{N(R)C(Ph)NC(Ph)=CR$_2$}] 1. Benzonitrile (1.91 cm^3, 19 mmol) was added to a solution of [Li(CR$_3$)(thf)$_2$] (3.58 g, 9.4 mmol) in diethyl ether (30 cm^3) at room temperature. The reaction mixture was stirred for 18 h. Volatiles were removed *in vacuo*, the residue 'stripped' with pentane and then heated *in vacuo* for 2.5 h at 60 °C. The residue was washed with pentane (10 cm^3) and dried *in vacuo* to give the yellow powder **1** (3.0 g, 72%), mp (decomp.) 224 °C. MS: *m*/*z* (%) 438 (20, [HL–L′]$^+$), 423 (4, [HL–L′ − Me]$^+$), 365 (12 [HL–L′ − SiMe$_3$]$^+$) and 335 (22, [HL–L′ − PhCN]$^+$). ^{1}H NMR (C$_6$D$_6$–C$_5$D$_5$N): δ 0.01, 0.05, 0.57 (s, SiMe$_3$), 6.87–6.73, 6.81–6.88, 6.98–7.01 (m, Ph, 10 H). ^{7}Li NMR (C$_6$D$_6$–C$_5$D$_5$N): δ 3.0. ^{13}C NMR (C$_6$D$_6$–C$_5$D$_5$N): δ 3.2, 3.6, 4.0 (s, SiMe$_3$), 108.0 (s, CSi$_2$), 126.9–132.4 (s, *o*,*m*-C of Ph), 146.1 (s, *ipso*-C), 175.3 and 177.5 (s, CN).

[SnCl{N(R)C(Ph)NC(Ph)=CR$_2$}] 2. Tin(II) chloride (0.23 g, 1.24 mmol) was added to a stirred solution of compound **1** (0.55 g, 1.24 mmol) in diethyl ether (25 cm^3) at room temperature. The reaction mixture was stirred overnight and volatiles were then removed *in vacuo*. Extracting with pentane (40 cm^3) gave colourless crystals of **2** (0.38 g, 52%). MS: *m*/*z* (%) 592 (12, M$^+$), 557 (20, [M − Cl]$^+$), 519 (18, [M − SiMe$_3$]$^+$) and 437 (60, [L–L′]$^+$). ^{1}H NMR (C$_6$D$_6$): δ −0.15, −0.11, 0.53 (s, SiMe$_3$), 6.68–6.83 (m, Ph, 10 H). ^{119}Sn NMR (C$_6$D$_6$): δ −35.1. ^{13}C NMR (C$_6$D$_6$): δ 1.3, 2.9, 4.4 (s, SiMe$_3$), 126.4, 127.2, 127.7, 127.9, 128.1, 128.3, 129.1, 129.7 (s, *o*,*m*-C of Ph), 130.2 (s, CSi$_2$), 139.1, 145.4 (s, *ipso*-C), 162.6 (s, CN) and 179.3 (s, CN$_2$).

[Sn{N(R)C(Ph)NC(Ph)=CR$_2$}$_2$] 3. Tin(II) chloride (0.17 g, 0.88 mmol) was added to a stirred solution of compound **1** (0.79 g, 1.77 mmol) in diethyl ether (30 cm^3) at room temperature. The reaction mixture was stirred overnight and then filtered. Cooling of the filtrate gave colourless crystals of **3** (0.47 g, 53%). A second crop of crystals was isolated from the

Table 4 Crystal data and refinement for compounds **3**, **4** and **5**

	3	**4**	**5**
Formula	$C_{48}H_{74}N_4Si_6Sn\cdot C_6H_6$	$C_{48}H_{74}HgN_4Si_6$	$C_{48}H_{74}K_2N_4Si_6$
M	1072.5	1076.2	953.9
T/K	293(2)	293(2)	173(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (non-st. no. 14)	$P2_1/n$ (no. 14)
a/Å	12.307(3)	12.995(6)	9.227(3)
b/Å	13.096(2)	35.21(2)	18.050(8)
c/Å	19.767(3)	13.391(3)	16.192(11)
α/°	101.84(1)		
β/°	103.25(2)	114.69(2)	96.09(4)
γ/°	94.27(2)		
U/Å^3	3010(1)	5567(4)	2682(2)
Z	2	4	2
D_c/g cm^{-3}	1.18	1.28	1.18
F(000)	1132	2216	1024
μ/mm^{-1}	0.58	2.93	0.35
Crystal size/mm	0.70 × 0.60 × 0.60	0.2 × 0.2 × 0.1	0.3 × 0.3 × 0.2
θ_{min}, θ_{max}/°	2, 25	2, 25	2, 25
Index ranges	$0 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 15$, $-23 \leqslant l \leqslant 22$	$0 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 41$, $-15 \leqslant l \leqslant 14$	$0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 21$, $-19 \leqslant l \leqslant 19$
Reflections collected	10 592	10 217	4991
Independent reflections	10 592	9768 (R_{int} = 0.0841)	4691 (R_{int} = 0.0478)
Reflections with $I > 2\sigma(I)$	7536	4409	3332
No. variables	597	532	271
$R1$ $[I > 2\sigma(I)]^a$	0.050	0.080	0.056
$wR2$ (all data)^b	0.111	0.156	0.153
Largest difference peak/e Å^{-3}	0.37	0.72	0.39
Absorption correction from ψ scans	T_{max} = 1.00, T_{min} = 0.90	T_{max} = 1.00, T_{min} = 0.58	Not applied
Maximum shift/e.s.d.	0.001	0.001	0.002

^{a} $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$.

mother-liquor (0.19 g, 22%) (Found: C, 59.2; H, 7.48; N, 5.63. $C_{48}H_{74}N_4Si_6Sn$ requires C, 58.0; H, 7.50; N, 5.63%), mp (decomp.) 230 °C. MS: m/z (%) 993 (0.2, $[M - H]^+$), 979 (0.4, $[M - Me]^+$), 921 (11, $[M - SiMe_3]^+$) and 557 (28, $[M - L\text{–}L']^+$). ^{1}H NMR (C_6D_6): δ 0.08 (s, $SiMe_3$), 0.71 (s, $NSiMe_3$) and 6.87 (s, broad, Ph, 10 H). ^{119}Sn NMR (C_6D_6): δ −141.4. ^{13}C NMR ($CDCl_3$): δ 3.6, 3.7 (s, $SiMe_3$), 4.8 (s, $NSiMe_3$), 124.4 (s, CSi_2), 126.8, 127.5, 127.6, 128.9, 130.8 (s, *o*,*m*-C of Ph), 139.9 and 147.0 (s, *ipso*-C), 176.0 (s, CN_2).

[Hg{N(R)C(Ph)NC(Ph)=CR$_2$}$_2$] 4. Mercury(II) bromide (0.19 g, 0.54 mmol) was added to a solution of compound **1** in diethyl ether (80 cm^3) at room temperature. The originally pale yellow solution was immediately decolorised and the $HgBr_2$ dissolved in the reaction mixture. After stirring for 15 h at room temperature, filtration from a small amount of precipitate and cooling of the filtrate gave colourless crystals of **3** (0.27 g, 45%). A second crop was obtained from the mother-liquor after partial removal of the solvent (0.21 g, 36%) (Found: C, 53.2; H, 6.82; N, 5.47. $C_{48}H_{74}HgN_4Si_6$ requires C, 53.6; H, 6.93; N, 5.21%), mp (decomp.) 182 °C. MS: m/z (%) 1075 (37, $[M - H]^+$), 1061 (4, $[M - Me]^+$) and 1003 (21, $[M - SiMe_3]^+$). ^{1}H NMR (C_6D_6–C_5D_5N): δ −0.06, −0.04, 0.60 (s, $SiMe_3$) and 6.86–7.15 (Ph, 10 H). ^{13}C NMR ($CDCl_3$): δ 2.7, 2.9, 3.2 (s, $SiMe_3$), 119.8 (s, CSi_2), 125.9–128.9 (s, Ph), 139.2 and 146.8 (s, *ipso*-C), 166.9 and 167.7 (s, CN).

[{K[N(R)C(Ph)NC(Ph)=CR$_2$]}$_2$] 5. A solution of compound **2** (0.30 g, 0.51 mmol) in diethyl ether (20 cm^3) was added to a suspension of freshly prepared potassium–graphite (0.8 mmol; 0.03 g K and 0.08 g C) in diethyl ether (10 cm^3) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The residue, after removal of volatiles *in vacuo*, was extracted with hot benzene and the extract stored at room temperature to give colourless crystals of **5** (0.22 g, 91%), mp (decomp.) 145–195 °C. MS: m/z (%) 438 (15, $[HL\text{–}L']^+$) and 365 (12, $[HL\text{–}L' - SiMe_3]^+$). ^{1}H NMR ($C_6D_6$): δ −0.03, 0.01, 0.48 (s, $SiMe_3$), 6.70 (d, Ph, 2 H), 6.87–6.97 (m, Ph, 8 H). ^{13}C NMR (C_6D_6): δ 3.5, 3.6, 4.0 (s, $SiMe_3$), 111.5 (s, CSi_2), 126.2, 126.3, 127.3, 128.3, 129.0 (s, *o*,*m*-C of Ph), 145.8, 149.8 (s, *ipso*-C), 172.7 and 174.7 (s, CN).

Crystallography

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromatic Mo-Kα radiation (λ 0.710 73 Å). For compounds **3** and **4** the crystals were sealed in a capillary under argon, whilst for **5** the crystal was enclosed in an oil drop and frozen in a stream of cold nitrogen gas. Cell dimensions were calculated from the setting angles for 25 reflections with $7 < \theta < 10°$. Intensities were measured by an ω–2θ scan. Corrections were made for Lorentz-polarisation effects and also for absorption by ψ scans. There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods using SHELXS 86[27] and refined on F^2 with anisotropic thermal parameters, by full-matrix, least squares using SHELXL 93.[28] Further details are in Table 4.

CCDC reference number 186/1085.

See http://www.rsc.org/suppdata/dt/1998/3113/ for crystallographic files in .cif format.

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