Reactions of M[CH(SiMe$_3$)$_2$] (M = Na or K) with PhCN, and related chemistry

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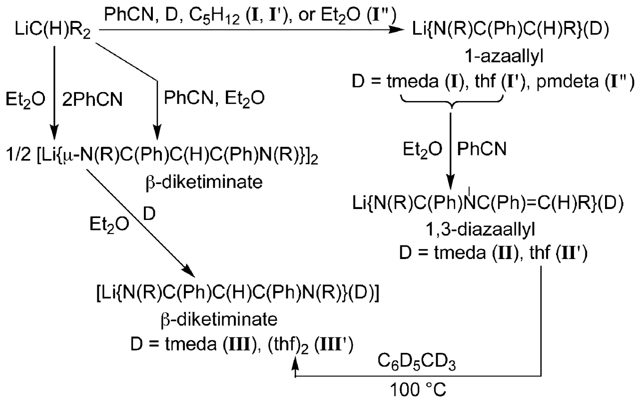
A number of metal complexes containing one of the following ligands: the 1-azaallyl [N(R)C(Ph)C(H)R]$^-$ (≡L$^-$), the 1,3-diazaallyl[N(R)C(Ph)$\overset{|}{\mathrm{N}}$C(Ph) = C(H)R]$^-$ (≡ LL$'^-$) and the isomeric β-diketiminate [{N(R)C(Ph)}$_2$CH]$^-$ (≡ LL$^-$) have been prepared (R = SiMe$_3$). These are the crystalline compounds H(LL) (**2**), Na(LL) (**3**), [Na(LL)(thf)$_2$] (**4**), Na(L) (**6**), [Na(μ-LL′)]$_8$ (**7**), [K(μ-L)(η^6-C$_6$H$_6$)]$_2$ (**8**), [K(μ-LL′)(thf)]$_2$ (**9**), [K(thf)$_2$(μ-LL)]$_\infty$ (**10**) and [Ni(LL′)$_2$] (**11**). A new synthesis of Na[C(H)R$_2$] (**1**) involved Hg[C(H)R$_2$]$_2$ and Na/Hg as reagents. The β-diketimine **2** was obtained from Li(LL) and cyclopentadiene. Under different conditions compounds **3**, **6** and **7** were isolated from **1** and benzonitrile, and compounds **8**, **9** and **10** from K[C(H)R$_2$] and PhCN. Complex **11** was derived from [Li(LL′)]$_2$ and [NiBr$_2$(dme)]. The solution obtained from **1** + 2 PhCN in Et$_2$O at ambient temperature was a mixture (**5**) of **3** (predominantly) and **7**. The 1-azaallyl complex **8** has the ligand bound to the metal as the enamide, and this is also probably (NMR) the case for **6**. The molecular structures of the crystalline complexes **7**, **8** and **11** are presented; that of **10** was published earlier. Compound **7**, a cyclooctamer, is particularly interesting, in that each LL$'^-$ ligand is bridging *via* one of its N atoms to two neighbouring sodium ions and is not only N,N′- but also (η^2-C=C)-chelating to one of them.

Introduction

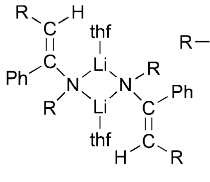
We have previously shown that from LiCH(SiMe$_3$)$_2$ and PhCN a diversity of products is obtained: a lithium 1-azaallyl (**I**), 1,3-diazaallyl (**II**) or the isomeric β-diketiminate (**III**) and each coordinated ligand may be terminal or bridging. The outcome of such reactions depends on stoichiometry, reaction conditions and the presence or absence of a strong neutral coligand D.[1] The principal focus of the present study was to investigate the corresponding system using the heavier alkali metal alkyl MC(H)R$_2$ (M = Na or K, R = SiMe$_3$).

The various reactions between LiC(H)R$_2$ and PhCN are summarised in Scheme 1 and typical structures of crystalline **I–III** are shown schematically in **I′**, **II′** and **III′**, respectively.[1]

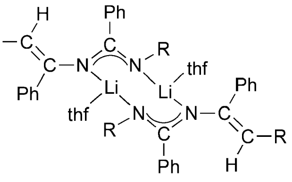
The reaction pathway from LiC(H)R$_2$ and PhCN to **I**, **II** and **III** was proposed to implicate successive intermediates: the donor–acceptor adduct Li{C(H)R$_2$}(NCPh) and the Li imide LiN=C(Ph)C(H)R$_2$, which by a Brook 1,3-Me$_3$Si migration (C → N) gave the Li 1-azaallyl **I**. The latter, in the presence of a strong donor (including thf), behaved as an N-centred nucleophile towards PhCN, affording (*via* Li{N=C(Ph)N(R)C(Ph)=C(H)R} and a 1,3-Me$_3$Si (N → N) shift) the Li 1,3-diazaallyl **II**. In the absence of such a strong donor (as in an Et$_2$O solution), **I** behaved as a C-centered nucleophile yielding (*via* the imide Li{N=C(Ph)C(H)(R)C(Ph)N(R)} and a final 1,3-Me$_3$Si (C → N) shift) the Li β-diketiminate **III**.[1] In order to account for the thermal isomerisation of **II′** to the thermodynamically preferred **III′**, it was suggested that each of the final two steps from **I′** → **II′** and **I′** → **III** was reversible. The above proposal[1] for the pathway from LiC(H)R$_2$ + PhCN → Li{N(R)C(Ph)C(H)C(Ph)N(R)} is also reproduced in ref. 2 as is that of a related Zr(IV) 1,3-diazaallyl to the isomeric Zr(IV) β-diketiminate. In the light of the above proposals, it is unsurprising that in a further paper by Eisen *et al.*,[3] it was shown (by NMR observations in the −25 to 20 °C range) that the Li β-diketiminate Li{N(R)C(Ph)C(H)C(Ph)N(R)} did not rearrange to the 1,3-diazaallyllithium isomer.



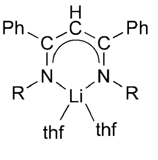
Scheme 1 (R = SiMe$_3$).



I′ (1-azaallyl)



II′ (1,3-diazaallyl)



III′ (β-diketiminate)

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Results and discussion

A new synthesis of bis(trimethylsilyl)methylsodium (1)

Compound **1** was originally prepared, in 1993, from LiC(H)R$_2$ by a metathetical exchange reaction in hexane with LiOBu^t,[4a] and **1** was used *in situ* to prepare the ytterbium(II) 1-azaallyl [Yb{κ^2-N(R)C(Bu^t)C(H)R}$_2$] from YbI$_2$(OEt$_2$)$_2$, 2(**1**) and Bu^{t}CN.[5] A full report on this synthesis of **1** revealed that a significant problem was the separation of the products, both **1** and LiOBu^t being hexane soluble (**1** < LiOBu^t).[4b] The X-ray structure showed pure **1** to crystallise as a chain polymer having singly-bridging $^-$C(H)R$_2$ ligands, [Na{μ-C(H)R$_2$}]$_\infty$.[4a]

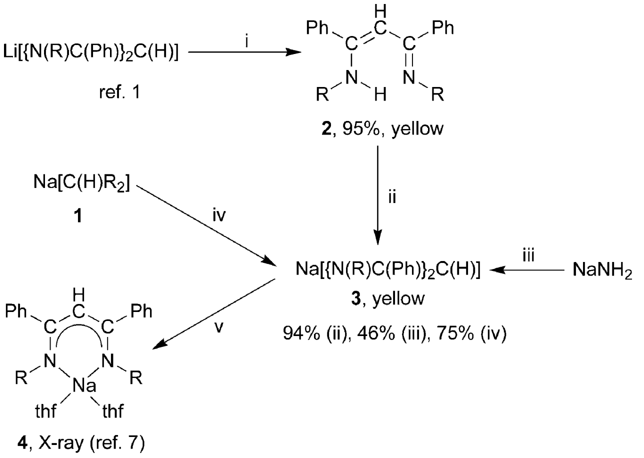
An alternative strategy to **1** was modelled on a procedure which had been used to prepare Li(CH$_2$)$_3$Li from Bu^{t}Hg(CH$_2$)$_3$HgBu^t and 2 LiBu^t.[6] Thus, Hg[C(H)R$_2$]$_2$ was treated with 2 NaBu^n; this method proved to be unsatisfactory due to the difficulty of separating **1** from HgBu$^n{}_2$.[4b]

We now report that this dialkylmercury was a convenient substrate, when reacted with sodium amalgam in hexane, eqn (1). The separation of **1** in 78% yield from the coproduct mercury was straightforward. A similar procedure had been used for NaCH$_2$R.[4c]

$$\mathrm{Hg[C(H)R_2] + 2Na/Hg \xrightarrow[-Hg]{C_6H_{14}} NaC(H)R_2\,\mathbf{1}} \qquad (1)$$

Routes to a sodium β-diketiminate and its characterisation

Three alternative pathways to the sodium analogue of the lithium β-diketiminate **III** were explored, Scheme 2, using as precursor Na[C(H)R$_2$] **1** or the β-diketimine **2**, which had previously been obtained from K[{N(R)C(Ph)}$_2$CH][8] and 1,2-dibromoethane or, for a close analogue H[{N(R)C(C$_6$H$_4$Me-4)}$_2$CH], by the carefully controlled hydrolysis of the lithium β-diketiminate.[1] This is not straightforward because of the hydrolytic sensitivity of the N–Si bonds. It is now shown that the pentane soluble **2** is conveniently accessible (i in Scheme 1) from the latter and cyclopentadiene in pentane, the precipitated coproduct LiCp being readily separated. Treatment of **2** with Na[N(SiMe$_3$)$_2$] in toluene gave (ii in Scheme 2) the sodium β-diketiminate **3** almost quantitatively, while use of NaNH$_2$ in Et$_2$O as the base was rather less satisfactory (iii in Scheme 2). A good yield of the yellow hexane-insoluble solid **3** was obtained (iv in Scheme 2) from the sodium alkyl **1** and two equivalents of PhCN in Et$_2$O.

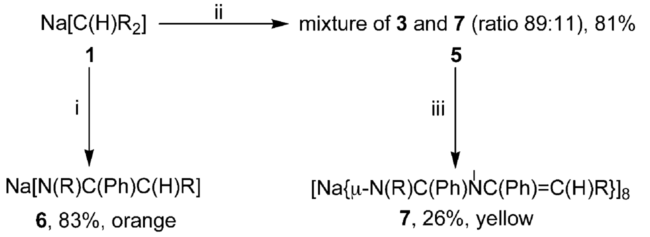


Scheme 2 (R = SiMe$_3$). *Reagents and conditions* at *ca.* 25 °C: i, C$_5$H$_6$, C$_5$H$_{12}$, 12 h; ii, Na[N(SiMe$_3$)$_2$], PhMe, 20 h; iii, **2**, Et$_2$O, 12 h; iv, 2 PhCN, Et$_2$O, 0 °C; v, crystallisation from thf.

The sodium β-diketiminate **3** was used in previous studies, as a precursor to some lanthanoid,[9a] actinoid,[9b] and thallium(I)[7] β-diketiminates. The earlier route to **3** was from the reaction of the lithium compound **III** and NaOBu^t in hexane, and **3** was characterised by elemental analysis, NMR solution spectra in pyridine-d$_5$ and by an X-ray structure of its bis(thf) adduct **3**[7] (see also v of Scheme 2).

Routes to a sodium 1-azaallyl, 1,3-diazaallyl and their characterisation

Whereas addition of two equivalents of benzonitrile to the sodium alkyl **1** in Et$_2$O yielded (iv in Scheme 2) the sodium β-diketiminate **3**, use of one equivalent of PhCN at low temperature afforded (i in Scheme 3) the orange crystalline sodium 1-azaallyl **6** in good yield. This situation differs from that in the corresponding Li[C(H)R$_2$]$_2$/PhCN system, in which even use of equivalent portions of the two reagents led to the β-diketiminatolithium product; and the lithium 1-azaallyl (**I**) was obtained only in the presence of a stronger neutral donor such as tmeda (see **III**).[1] It is clearly the case that [N(R)C(Ph)C(H)R]$^-$ is a more powerful nucleophile than [C(H)R$_2$]$^-$ for Li$^+$, but not Na$^+$, as counter cation, *i.e.*, nucleophilicity decreases for Li(1-azaallyl) > LiC(H)R$_2$, but NaC(H)R$_2$ > Na(1-azaallyl). The main factor may be the greater covalent character of the Li rather than the Na bis(trimethylsilyl)methyl.



Scheme 3 (R = SiMe$_3$). *Reagents and conditions*: i, PhCN, Et$_2$O, −78 °C, and crystallisation from C$_6$H$_{14}$; ii, 2 PhCN, Et$_2$O, 23 °C, removal of volatiles, and washing C$_6$H$_{14}$; iii, crystallisation from C$_5$H$_{12}$.

Addition of two equivalents of benzonitrile to **1** in Et$_2$O at ambient temperature, followed by removal of volatiles and crystallisation from pentane gave (ii followed by iii in Scheme 3) yellow crystals of the 1,3-diazaallylsodium compound **7** in modest yield. In another experiment (ii of Scheme 3), the ether-free residue was dissolved in C$_6$D$_6$ and was shown by ^{1}H NMR spectroscopy to correspond to an 81% conversion of **1** and 2 PhCN into a mixture of the two isomers: the sodium β-diketiminate **3** and the diazaallyl **7**, in a ratio of 89 : 11, respectively.

Compound **6** has been used extensively as a 1-azaallyl ligand transfer reagent; its characterisation herein rests solely on its NMR solution and EI-mass spectra. As for the latter, this simply revealed signals of the metal-free ligand. The ^{1}H NMR spectra in C$_6$D$_6$ showed the appropriate signals and relative intensities of the 1-azaallyl ligand [N(R)C(Ph)C(H)R]$^-$. From the chemical shifts characteristic of the *C*(*H*)R group it is likely that in **6** the ligand is present in the enamido (κ^1) form [N(R)C(Ph)=C(H)R]$^-$, rather than the delocalised (η^3) form. This is based on data on various lithium compounds of the same ligand, in which the κ^1- was identified from $\delta(^1H)$ at 3.5–4.0 ppm and $\delta[^{13}C\{^1H\}]$ at 83–85 ppm, compared with $\delta(^1H)$ at 4.8 and $\delta^{13}[C\{^1H\}]$ at 95–97 ppm.[1]

The crystalline sodium 1,3-diazaallyl **7**, a benzamidinate, was characterised by satisfactory microanalytical data (C, H, N), its ^{1}H and $^{13}C\{^1H\}$ solution NMR and EI-mass spectra and finally by a single-crystal X-ray diffraction study. The latter reveals the molecule to have the Na[N(R)C(Ph)NC(Ph) = C(H)R] monomers associated into a cyclo-octamer lying across the four-fold rotation axis, in which successive sodium ions are joined by an N,N′-bridging ligand. Thus, the structure of **7** is that of a 32-membered macrocycle containing eight NaNCN repeating units, as shown in the ball-and-stick model of Fig. 1. An ORTEP representation is in Fig. 2, geometrical parameters are in Table 1, while the space-filling model of Fig. 3 shows that the sodium ions are well protected and the internal cavity is very small. Selected geometrical parameters are conveniently described in the context of the dimeric fragment of Fig. 4.

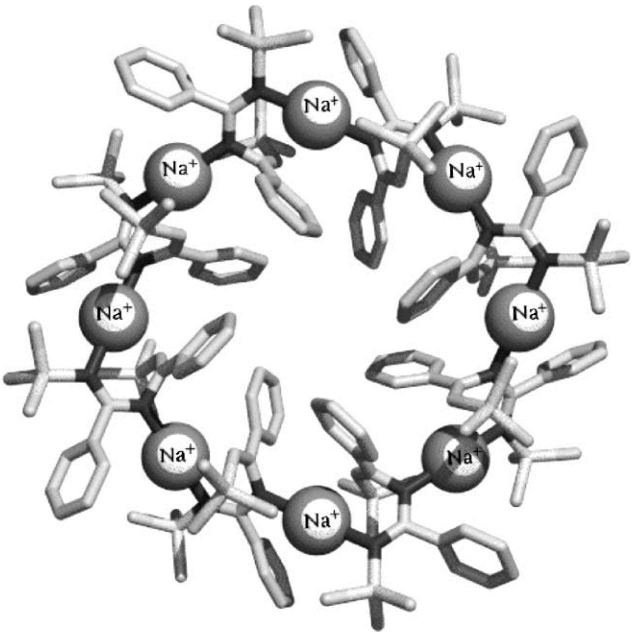


Fig. 1 Ball-and-stick model of crystalline **7**.

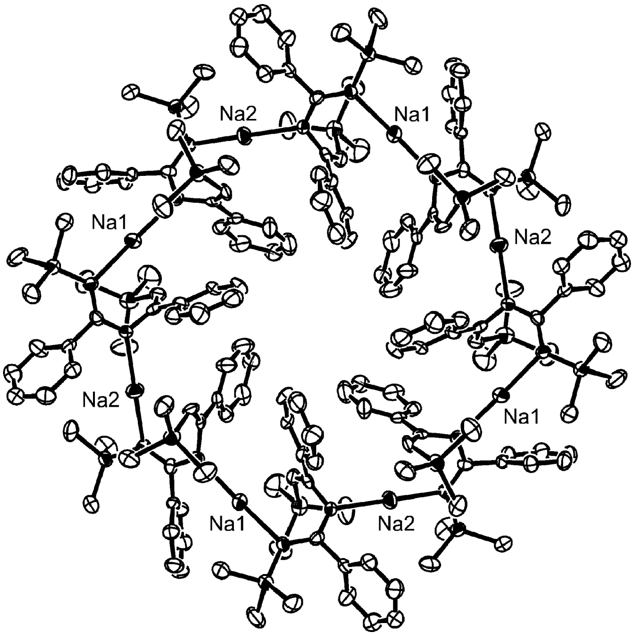


Fig. 2 ORTEP representation of crystalline **7** with selected labelling of a dimeric fragment.

Table 1 Selected bond lengths (Å) and angles (°) of **7**

Na(1)–N(4)	2.417(8)	Na(1)–N(1)	2.431(8)
Na(1) · · · C(2)	2.722(9)	Na(1) · · · C(3)	2.728(9)
Na(2)–N(2)[a]	2.376(7)	Na(2)–N(3)	2.420(8)
Na(2) · · · C(23)	2.813(9)	Na(2) · · · C(24)	2.748(9)
Si(1)–N(1)	1.714(7)	Si(2)–C(3)	1.847(10)
Si(3)–N(3)	1.718(7)	Si(4)–C(24)	1.863(10)
N(1)–C(1)	1.333(11)	N(2)–C(1)	1.328(11)
N(2)–C(2)	1.418(11)	N(3)–C(22)	1.335(10)
N(4)–C(22)	1.299(10)	N(4)–C(23)	1.425(11)
C(1)–C(4)	1.501(12)	C(2)–C(3)	1.352(12)
C(2)–C(10)	1.506(13)	C(4)–C(9)	1.383(12)
C(22)–C(25)	1.507(12)	C(23)–C(24)	1.348(12)
C(23)–C(31)	1.489(12)	C(25)–C(26)	1.374(12)
N(4)–Na(1)–N(1)	174.7(3)	N(2)[a]–Na(2)–N(3)	173.5(3)
C(1)–N(1)–Si(1)	125.9(6)	C(1)–N(1)–Na(1)	117.9(5)
Si(1)–N(1)–Na(1)	115.7(4)	C(1)–N(2)–C(2)	117.8(7)
C(1)–N(2)–Na(2)[b]	127.2(6)	C(2)–N(2)–Na(2)[b]	115.0(5)
C(22)–N(3)–Si(3)	129.2(6)	C(22)–N(3)–Na(2)	120.2(6)
Si(3)–N(3)–Na(2)	107.9(4)	C(22)–N(4)–C(23)	117.0(7)
C(22)–N(4)–Na(1)	120.4(6)	C(23)–N(4)–Na(1)	122.6(5)
N(2)–C(1)–N(1)	127.3(8)	N(2)–C(1)–C(4)	111.5(8)
N(1)–C(1)–C(4)	121.1(8)	C(3)–C(2)–N(2)	120.4(9)
C(3)–C(2)–C(10)	123.9(9)	N(2)–C(2)–C(10)	115.5(8)
C(2)–C(3)–Si(2)	127.3(8)	C(5)–C(4)–C(1)	119.7(9)
C(9)–C(4)–C(1)	122.4(9)	C(11)–C(10)–C(15)	117.8(10)
C(11)–C(10)–C(2)	121.4(9)	C(15)–C(10)–C(2)	120.7(9)
N(4)–C(22)–N(3)	127.5(8)	N(4)–C(22)–C(25)	111.9(8)
N(3)–C(22)–C(25)	120.5(8)	C(24)–C(23)–N(4)	121.0(8)
C(24)–C(23)–C(31)	123.5(9)	N(4)–C(23)–C(31)	115.4(8)
C(23)–C(24)–Si(4)	125.6(7)	C(26)–C(25)–C(22)	119.8(8)
C(36)–C(31)–C(23)	122.6(9)	C(32)–C(31)–C(23)	120.7(8)

Symmetry transformations to generate equivalent atoms: [a] $-y + 1/2, x + 1, z$. [b] $y - 1, x + 1/2, z$.

Whereas one sodium ion, say Na1, has adjacent N(R) moieties belonging to neighbouring 1,3-diazaallyl ligands, the next sodium ion, say Na(2)″, is attached to two N{C(Ph)} moieties one of which is the partner of one of the ligands joined to Na(1). Each sodium ion is only just outside the N–N′ vector, the N(1)–Na(1)–N(4) and N(2)–Na(2)″–N(3)″ bond angles being almost identical, 174.1 ± 0.6°. A 1,3-diazaallyl ligand, say of skeletal arrangement N(1)C(1)N(2)C(2)C(3), not only acts as a bridge between Na(1) and Na(2)″, but is also chelating to Na(1) *via* an η^2-alkene-contact. The coordination environment around Na(1) is shown schematically in Fig. 5. In support of this unusual (η^2-alkene)–Na$^+$ contact, it is noted that the Na(1)–C(2), Na(1)–C(3), Na(2)′–C(23) and Na(2)″–C(24) distances of 2.75 Å (mean) are only slightly longer than the 2.56 ± 0.02 Å for the Na–C distance in $[Na\{\mu\text{-}C(H)R_2\}]_\infty$,[4a] and are close to the 2.72 Å cited for side-on Na$^+$–(π-olefin) systems.[10] The Na–N(R) and Na–N{C(H)Ph} bond lengths are closely similar not only to one another but also to the Na–N bond distances of 2.358(6) Å of the β-diketiminate **4**.[7] Each of the three-coordinate N(1), C(1), N(2) and C(2) atoms is in a distorted trigonal planar environment, with the endocyclic bond

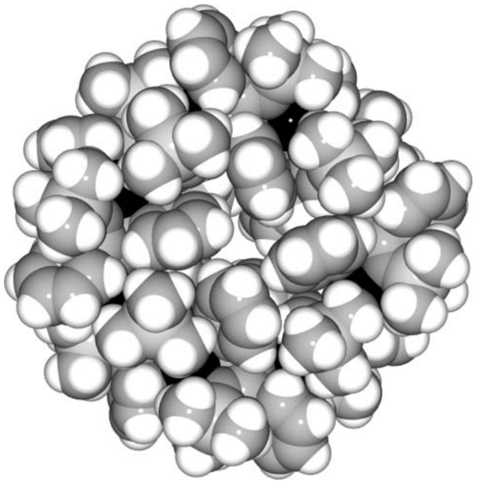


Fig. 3 Space-filling model of crystalline **7**.

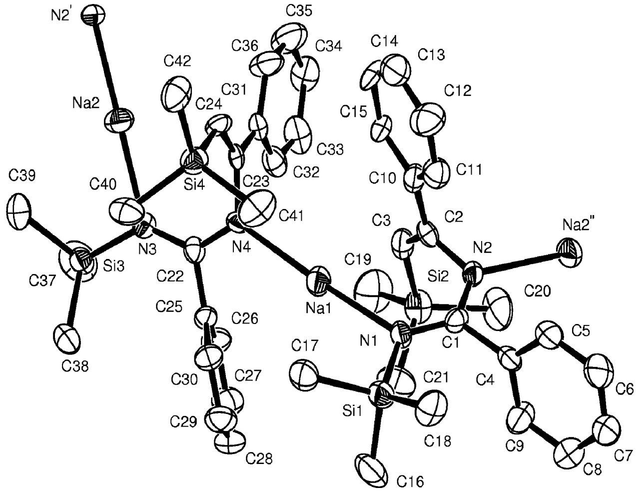


Fig. 4 ORTEP representation of a dimeric fragment of **7** (50% ellipsoids).

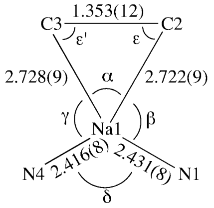
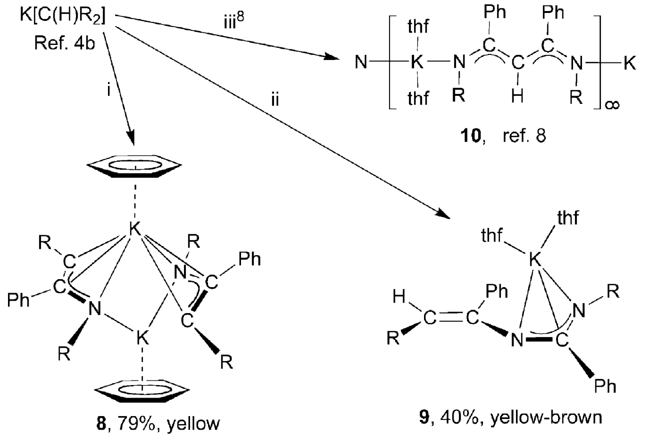


Fig. 5 The environment of Na in **7**: angles (°): $\alpha = 28.74(25)$, $\beta = 65.62(26)$, $\gamma = 96.78(28)$, $\delta = 174.7(3)$, $\varepsilon = 75.84(51)$, $\varepsilon' = 75.42(51)$.

angles of 117.9(6), 127.3(8), 117.8(7) and 120.4(9)° at these atoms, respectively.



Scheme 4 ($R = SiMe_3$). *Reagents and conditions*: i, PhCN, Et_2O, −78 °C, 1 h, crystallisation from C_6H_6; ii, PhCN, Et_2O, −78 °C, removal of volatiles, reflux thf, then PhCN, 2 min; iii, 2 PhCN, thf–C_5H_{12}.

The bis(trimethylsilyl)methylpotassium–benzonitrile system: synthesis and structures of the derived potassium 1-azaallyl, 1,3-diazaallyl and the isomeric β-diketiminate

The yellow, crystalline, dimeric 1-azaallylpotassium compound **8** was obtained (i in Scheme 4) in good yield from $K[C(H)R_2]$[4b] and an equimolar portion of benzonitrile in diethyl ether and recrystallisation from benzene. In another experiment, removal of Et_2O followed successively by heating a thf solution under reflux, addition of a second equivalent of PhCN, removal of thf, addition of hexane, and crystallisation of the hexane-insoluble solid from thf furnished (ii in Scheme 4) the yellow–brown, crystalline 1,3-diazaallylpotasium–thf adduct **9** in modest yield. The isomeric, crystalline, polymeric β-diketiminatopotassium–bis(thf) adduct **10** was obtained (iii in Scheme 4) as shown earlier.[8]

In a preliminary communication it was reported that the β-diketiminate $K[\{N(R)C(Ph)\}_2CH]$ (**IV**) was accessible in good yield from either $K[C(H)R_2]$ + 2 PhCN in Et_2O, or $Li[\{N(R)C(Ph)\}_2CH]$ + $KOBu^t$ in hexane. For example, reaction between $K[C(H)R_2]$ + 2 PhCN in Et_2O at −78 °C afforded a mixture of **IV**,$K[N(R)C(Ph)NC(Ph){=}C(H)R]$, and $H[\{N(R)C(Ph)\}_2CH]$ in a ratio of 87 : 7 : 6 (from ^1H NMR). Later it was shown that **IV** was convertible into the X-ray-characterised derivative **10**.[8]

Each of the crystalline potassium salts **8–10** gave satisfactory microanalyses (C, H, N), NMR solution and EI-mass spectra. Single-crystal X-ray diffraction data were obtained for **8**, but for crystalline **9** these were adequate solely to confirm its structure to be as shown in Scheme 4; the structure of crystalline **10** has been published.[8]

The molecular structure of the crystalline dimeric 1-azaallylpotassium–benzene adduct **8** is illustrated in Fig. 6; the molecules are connected into chains along the 2_1 screw axis by weak intermolecular K(2)···C(10)′ interactions giving rise to a polymeric array, Fig. 7; geometrical parameters are in Table 2. The coordination environment of the two potassium atoms K(1) and K(2) are different. That of K(1) approximates to that of a bis(η^3-1-azaallyl)(η^6-benzene)potassiate, while that of K(2) resembles a (η^6-benzene)potassium cation with close K(2)–N(1) and K(2)–N(2) contacts but more remote (agostic) K(2) distances to C(12) and C(27) [from $Si(2)Me_3$ and $Si(4)Me_3$, respectively] and C(10)′ [from $Si(1)'Me_3$] carbon atoms. The centre of the molecule is the K(1)N(1)K(2)N(2) rhombus, having K–N bond lengths of 2.783 ± 0.008 Å (*cf.*[8] 2.830 ± 0.003 Å in **10**) and endocyclic bond angles of 96.3 ± 0.2° at the potassium and 86.7 ± 0.2° at the nitrogen atoms. The K–C(Ph) and K–C(H)SiMe$_3$ distances are almost equal and closely similar to those in $[K\{\mu\text{-}C(H)R_2\}\{O(Me)Bu^t\}]_\infty$ of 3.000 ± 0.012 Å.[4b] The distance from each K atom to the centroid of the attached η^6-benzene is slightly shorter for K(1) at 2.921(4) Å, but both are unexceptional.[11]

Table 2 Selected bond lengths (Å) and angles (°) of **8**

K(1)–N(1)	2.775(3)	K(1)–N(2)	2.783(3)	K(2)–M(2)	3.039(4)	Si(1)–C(1)	1.835(4)
K(1)–C(1)	3.077(4)	K(1)–C(2)	3.087(3)	Si(2)–N(1)	1.697(3)	Si(3)–C(15)	1.831(3)
K(1)–C(15)	3.002(3)	K(1)–C(16)	3.000(3)	Si(4)–N(2)	1.704(3)	Si(4)–C(27)	1.874(4)
K(1)–M(1)	2.921(4)	K(2)–N(1)	2.767(3)	N(1)–C(2)	1.354(4)	N(2)–C(16)	1.357(4)
K(2)–N(2)	2.776(3)	K(2)–C(12)	3.391(4)	C(1)–C(2)	1.374(5)	C(2)–C(3)	1.512(4)
K(2)–C(27)	3.303(5)	K(2)–C(10)[a]	3.496(4)	C(15)–C(16)	1.377(4)	C(16)–C(17)	1.504(4)
N(1)–K(1)–N(2)	96.12(8)	N(1)–K(1)–M(1)	130.83(9)	C(12)–K(2)–C(2)	74.29(9)	C(10)[a]–K(2)–C(2)	75.34(10)
N(2)–K(1)–M(1)	131.27(9)	N(1)–K(1)–C(16)	106.27(9)	C(1)–Si(1)–C(10)	116.1(2)	N(1)–Si(2)–C(12)	107.5(2)
N(2)–K(1)–C(16)	26.80(8)	M(1)–K(1)–C(16)	121.98(7)	C(13)–Si(2)–C(14)	107.2(2)	C(15)–Si(3)–C(25)	106.0(2)
N(1)–K(1)–C(15)	94.05(9)	N(2)–K(1)–C(15)	49.14(9)	C(24)–Si(3)–C(25)	108.3(2)	C(26)–Si(4)–C(27)	105.6(2)
M(1)–K(1)–C(15)	124.85(7)	C(16)–K(1)–C(15)	26.52(9)	C(2)–N(1)–Si(2)	130.3(2)	C(2)–N(1)–K(2)	111.6(2)
N(1)–K(1)–C(1)	48.71(8)	N(2)–K(1)–C(1)	95.40(9)	Si(2)–N(1)–K(2)	112.04(13)	C(2)–N(1)–K(1)	89.9(2)
M(1)–K(1)–C(1)	105.93(7)	C(16)–K(1)–C(1)	120.93(9)	Si(2)–N(1)–K(1)	117.29(13)	K(2)–N(1)–K(1)	83.85(7)
C(15)–K(1)–C(1)	129.05(10)	N(1)–K(1)–C(2)	26.01(8)	C(16)–N(2)–Si(4)	130.3(2)	C(16)–N(2)–K(2)	114.7(2)
N(2)–K(1)–C(2)	105.39(8)	M(1)–K(1)–C(2)	112.80(7)	Si(4)–N(2)–K(2)	110.54(13)	C(16)–N(2)–K(1)	85.5(2)
C(16)–K(1)–C(2)	124.44(9)	C(15)–K(1)–C(2)	118.68(9)	Si(4)–N(2)–K(1)	119.51(13)	K(2)–N(2)–K(1)	83.53(7)
C(1)–K(1)–C(2)	25.77(9)	N(1)–K(2)–N(2)	96.47(8)	C(2)–C(1)–Si(1)	131.2(3)	C(2)–C(1)–K(1)	77.5(2)
N(1)–K(2)–M(2)	142.02(10)	N(2)–K(2)–M(2)	97.53(10)	Si(1)–C(1)–K(1)	135.1(2)	N(1)–C(2)–C(1)	125.8(3)
N(1)–K(2)–C(27)	119.00(10)	N(2)–K(2)–C(27)	55.42(9)	N(1)–C(2)–C(3)	117.8(3)	C(1)–C(2)–C(3)	116.3(3)
M(2)–K(2)–C(27)	97.90(9)	N(1)–K(2)–C(12)	54.60(9)	N(1)–C(2)–K(1)	64.0(2)	C(1)–C(2)–K(1)	76.7(2)
N(2)–K(2)–C(12)	113.55(10)	M(2)–K(2)–C(12)	87.47(7)	C(3)–C(2)–K(1)	135.9(2)	Si(1)–C(10)–K(2)[b]	150.2(2)
C(27)–K(2)–C(12)	168.16(11)	N(1)–K(2)–C(10)[a]	82.16(10)	Si(2)–C(12)–K(2)	85.8(2)	C(16)–C(15)–Si(3)	132.0(3)
N(2)–K(2)–C(10)[a]	158.07(10)	M(2)–K(2)–C(10)[a]	96.77(8)	C(16)–C(15)–K(1)	76.7(2)	Si(3)–C(15)–K(1)	123.8(2)
C(27)–K(2)–C(10)[a]	106.09(11)	C(12)–K(2)–C(10)[a]	83.60(11)	N(2)–C(16)–C(15)	124.0(3)	N(2)–C(16)–C(17)	117.9(3)
N(1)–K(2)–C(2)	21.08(7)	N(2)–K(2)–C(2)	95.54(8)	C(15)–C(16)–C(17)	118.0(3)	N(2)–C(16)–K(1)	67.7(2)
M(2)–K(2)–C(2)	160.71(6)	C(27)–K(2)–C(2)	101.19(10)	Si(4)–C(27)–K(2)	87.7(2)	C(17)–C(16)–K(1)	129.2(2)

M(1) and (M2) are the centroids of the C(35) to C(40), and C(29) to C(34) rings, respectively. Symmetry transformations to generate equivalent atoms: [a] $-x + 3/2, y + 1/2, -z - 1/2$. [b] $-x + 3/2, y - 1/2, -z - 1/2$.

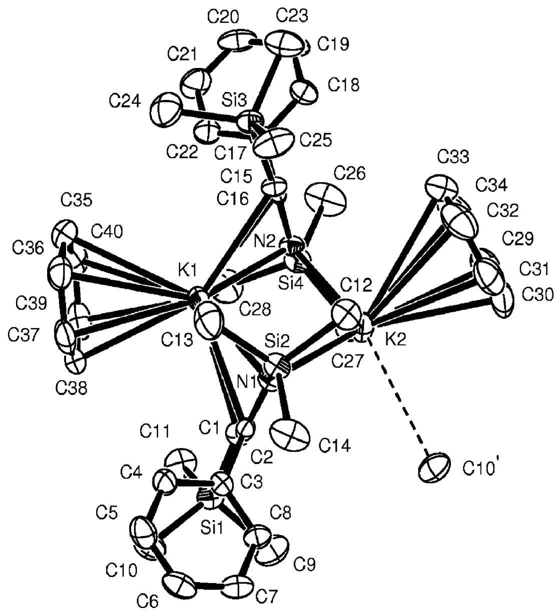


Fig. 6 The X-ray structure of **8** (50% ellipsoids).

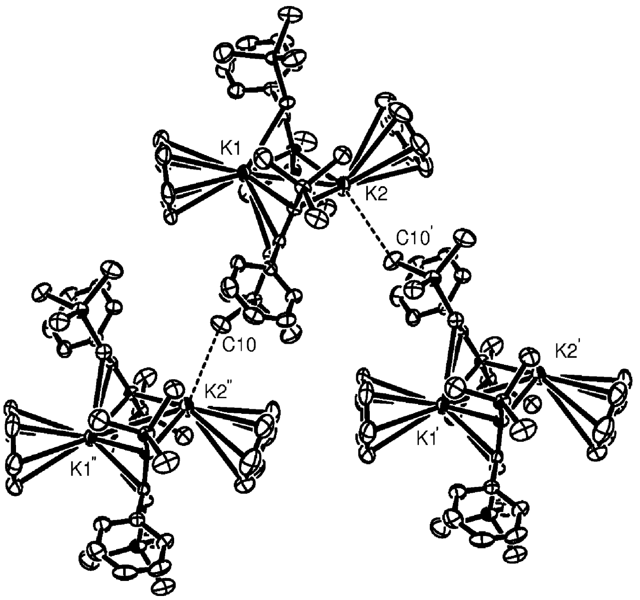


Fig. 7 A section of the polymeric chain, formed by aggregation of units of **8**.

Preparation and structure of the bis(1,3-diazaallyl)nickel(II) complex 11

The lithium 1,3-diazaallyllithium compound **III′** proved to be an effective ligand transfer reagent in its reaction with a nickel(II) bromide complex. Thus, the crystalline, deep purple, diamagnetic, monomeric purple nickel(II) complex **11** was obtained in 63% yield, eqn (2). It was characterised by microanalysis (C, H, N), ^{1}H and ^{13}C{^{1}H} NMR spectra in solution, and its EI-mass spectrum which showed its parent molecular ion. The molecular structure (Fig. 8) was established by a single-crystal X-ray diffraction study; selected geometrical parameters are in Table 3.

$$[\mathrm{Li}\{\mu-\mathrm{N(R)C(Ph)}\overset{|}{\mathrm{N}}\mathrm{C(PH){=}C(H)R}\}]_2 + [\mathrm{NiBr_2(dme)}]$$

$$\xrightarrow{\mathrm{thf}} [\overline{\mathrm{Ni}\{\mu\text{-}\mathrm{N(R)C(Ph}})\mathrm{C(Ph){=}C(H)R}\}]_2 \mathbf{11} + 2\mathrm{LiBr} \qquad (2)$$

The nickel atom of the molecule **11** is at the spiro junction of two η^3-1,3-diazaallyl ligands and is in a distorted square planar environment. The dihedral angle between the NiN(1)C(1)N(2) and

Table 3 Selected bond lengths (Å) and angles (°) of **11**

Ni–N(1)	1.949(7)	Ni–N(2)	1.885(7)
Ni–N(3)	1.934(7)	Ni–N(4)	1.898(7)
Si(1)–N(1)	1.741(8)	Si(2)–C(9)	1.848(10)
Si(3)–N(3)	1.737(8)	Si(4)–C(30)	1.779(9)
N(1)–C(1)	1.337(11)	N(2)–C(1)	1.312(11)
N(2)–C(2)	1.415(11)	N(3)–C(22)	1.335(10)
N(4)–C(22)	1.321(10)	N(4)–C(23)	1.437(11)
C(1)–C(10)	1.472(12)	C(2)–C(9)	1.349(13)
C(2)–C(3)	1.492(13)	C(10)–C(15)	1.395(12)
C(22)–C(31)	1.473(12)	C(23)–C(24)	1.492(13)
C(23)–C(30)	1.364(12)		
N(2)–Ni–N(4)	111.4(3)	N(2)–Ni–N(3)	174.1(3)
N(4)–Ni–N(3)	68.9(3)	N(2)–Ni–N(1)	68.9(3)
N(4)–Ni–N(1)	174.0(3)	N(3)–Ni–N(1)	111.4(3)
C(1)–N(1)–Si(1)	126.7(6)	C(1)–N(1)–Ni	88.8(5)
Si(1)–N(1)–Ni	127.6(4))	C(1)–N(2)–C(2)	127.9(7)
C(1)–N(2)–Ni	92.4(6)	C(2)–N(2)–Ni	139.7(6)
C(22)–N(3)–Si(3)	129.7(6)	C(22)–N(3)–Ni	89.7(5)
Si(3)–N(3)–Ni	130.8(4)	C(22)–N(4)–C(23)	127.8(7)
C(22)–N(4)–Ni	91.7(5)	C(23)–N(4)–Ni	137.5(6)
N(2)–C(1)–N(1)	109.9(7)	N(2)–C(1)–C(10)	126.7(8)
N(1)–C(1)–C(10)	123.3(8)	C(9)–C(2)–N(2)	122.6(9)
C(9)–C(2)–C(3)	125.3(9)	N(2)–C(2)–C(3)	112.1(9)
C(4)–C(3)–C(2)	123.1(11)	C(8)–C(3)–C(2)	120.3(9)
C(3)–C(4)–C(5)	120.9(14)	C(2)–C(9)–Si(2)	129.4(7)
C(15)–C(10)–C(1)	122.7(8)	C(11)–C(10)–C(1)	119.4(8)
N(4)–C(22)–N(3)	109.5(7)	N(4)–C(22)–C(31)	125.8(8)
N(3)–C(22)–C(31)	124.7(8)	C(30)–C(23)–N(4)	125.1(8)
C(30)–C(23)–C(24)	122.4(8)	N(4)–C(23)–C(24)	112.5(8)
C(25)–C(24)–C(23)	120.8(9)	C(29)–C(24)–C(23)	121.3(8)
C(27)–C(26)–C(25)	118.9(11)	C(27)–C(28)–C(29)	120.4(12)
C(23)–C(30)–Si(4)	135.2(8)	C(32)–C(31)–C(22)	119.5(8)
C(36)–C(31)–C(22)	122.4(8)		

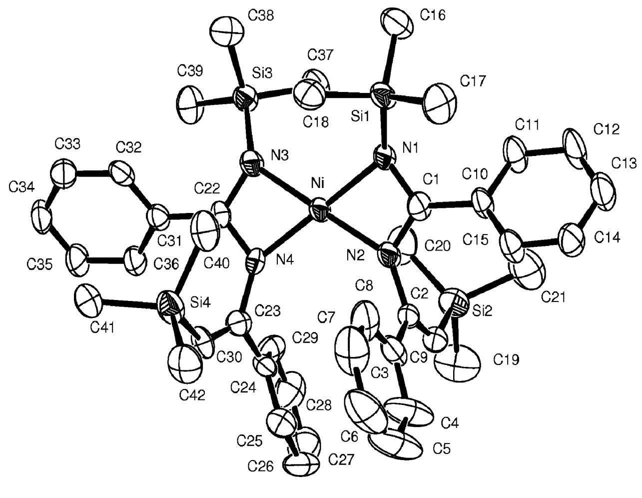


Fig. 8 The X-ray structure of **11** (50% ellipsoids).

the NiN(3)N(4) planes is 10.8(4)°. The *ipso*-carbon C(31) attached to C(22) of the [η^3-N(3)(SiMe$_3$)C(22)(Ph)N(4)] fragment is *ca.* 0.12 Å out of the NiN(3)N(4) plane, whereas the corresponding *ipso*-carbon C(10) of the other ligand is more nearly (0.06 Å) within its NiN(1)C(1)N(2) plane. The Me$_3$Si substituents at the terminal nitrogen atoms of each ligand are arranged in a *gauche* fashion. The Ni–N(SiMe$_3$) bonds are slightly longer than the Ni–N{C(Ph)}, as are the (Me$_3$Si)N–C(Ph) bonds compared with the {Ph(C)}N–C(Ph). The endocyclic bond angles in each NiNCN′ moiety are close to 90° at the nitrogen atoms, and somewhat narrower at each (Me$_3$Si)N than the N′ atom, while that at C(1) or C(22) is 109.7 ± 0.3°.

A number of mononuclear 1,3-diazaallylnickel(II) complexes have been previously published. The[N(R)C(Ph)-NC(Ph) = C(H)R]$^-$ (LL′$^-$) has featured in the six-coordinate Ni(II) complex [Ni(LL′)(acac)(tmeda)].[3] Two other C_1-symmetric ligands [η^3-N(SiMe$_3$)C(Ph)NR*]$^-$ (LL*$^-$) (R* = myrtanyl) and [η^3-N(SiMe$_3$)C(Ph)N(C$_6$H$_3$Pr$^i_2$-2,6)]$^-$ (LL″$^-$) were present in the diamagnetic [Ni(LL*)$_2$], [Ni(LL*)Me(py)] and *trans*-[Ni(LL*)$_2$(py)$_2$][12] and [Ni(LL″)$_2$].[13] Homoleptic mononuclear nickel(II) C_2-symmetric 1,3-diazaallyls characterised earlier include the tetrahedral, paramagnetic ($\mu_{\text{eff}} = 3.1\ \mu_B$) [Ni{$\eta^3$-N(R)-C(Ph)NR}$_2$],[14] and the square planar, diamagnetic [Ni{η^3-N(Pr^i)-C(Me)NPr^i}$_2$][15] and [Ni{η^3-N(C$_6$H$_3$Pr$^i_2$-2,6)C(Ph)NC$_6$H$_3$Pr^i-2,6}$_2$].[16] It has long been established that steric effects in an N,N′-chelating anionic ligand can control the geometry of homoleptic late transition metal(II) complexes.[17] Thus, in the β-diketiminates [M{N(R^1)C(R^2)C(H)C(R^2)N(R^1)}$_2$] those with M = Ni and R^2 = Me were diamagnetic for R^1 = Ph but paramagnetic for R^1 = C$_6$H$_4$Me-2,[18] and the cobalt complex with R^2 = Ph was tetrahedral for R^1 = SiMe$_3$ but square planar for R^1 = H.[19]

Conclusions

We have prepared a number of sodium or potassium 1-azaallyls [M{N(R)C(Ph)C(H)R}]$^-$ [≡ M(L)], 1,3-diazaallylsM[N(R)C(Ph)NC(Ph) = C(H)R] [≡ M(LL′)], and the isomeric β-diketiminates M[{N(R)C(Ph)}]$_2$CH] [≡ M(LL)] from the appropriate metal alkyl M[C(H)R$_2$] (M = Na or K, R = SiMe$_3$) and PhCN in Et$_2$O. It is noteworthy that the metal 1-azaallyl Na(L) (**6**) and [K(μ-L)(η^6-C$_6$H$_6$)]$_2$ (**8**) were accessible from Na[C(H)R$_2$] or the K analogue and an equivalent portion of PhCN; this is a contrast with the Li[C(H)R$_2$]–PhCN system which in Et$_2$O gave Li(LL). The formation of M(L) from M[C(H)R$_2$] is believed to implicate as an intermediate the donor–acceptor adduct$R_2(H)C\overset{-}{M}-\overset{+}{N}CPh$, which by a Brook 1,3-SiMe$_3$ migration from C → N yields in solution an equilibrium mixture of the enamide and ketimide: M–N(R)C(Ph)=C(H)R ⇄ M–C(R)(H)C(Ph)=NR; crystallisation from the appropriate solvent yielded **6** or **8**. The isolation of the crystalline metal 1,3-diazaallyl or β-diketiminate is further proposed to implicate the solution reaction between the metal enamide or ketimide M(L), respectively, involving a further 1,3-SiMe$_3$ migration for M(LL). A particular structural feature of an unprecedented nature is the ability of the 1,3-diazaallyl ligand LL′$^-$ to function in [Na(μ-LL′)]$_8$ (**7**) not only as an N,N′-centered moiety but also as a chelating species in which it binds to a sodium ion both through a nitrogen-centre but also *via* an η^2-C=C close contact. Such binding participation of an alkene moiety is not found in other 1,3-diazaallyl metal complexes of the LL′$^-$ ligand: [K(thf)$_2$(μ-LL)]$_\infty$ (**10**),[8] [Ni(LL′)$_2$] (**11**), [Ni(LL′)(acac)(tmeda)],[3] [Li(LL′)(thf)],[1] or [{UCl(LL)(=NR)}$_2$][UCl$_2$(LL)(LL′)]$_2$.[19] The preparation of the β-diketimine H(L) (**2**) from Li(L) and CpH in C$_5$H$_{12}$ is noteworthy.

Experimental

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were pre-dried over sodium wire, distilled from drying agents and stored over molecular sieves (4 Å). Deuteriated solvents were likewise stored over such molecular sieves and degassed prior to use. The NMR spectra were recorded in C_6D_6, $C_6D_5CD_3$ or C_5D_5N at 298 K using a DPX 300 (^1H, 300.1; ^{13}C 75.5 MHz) Bruker instrument and referenced to residual solvent resonances (data in δ). All ^{13}C NMR spectra 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. Elemental analyses (calculated data are for empirical formulae) were determined by Medac Ltd., Brunel University. The compounds $Hg[C(H)R_2]_2$,[20] $Li[C(H)R_2]$,[21] $K[C(H)R_2]$,[4a] $[NiBr_2(dme)]$,[22] $[Li\{N(R)C(Ph)\}_2CH]$,[1] and$[Li-\{\mu\text{-}N(R)C(Ph)\overset{|}{N}C(Ph){=}C(H)R\}(thf)]_2$[3] were synthesised according to published procedures ($R = SiMe_3$).

Preparations

$[NaC(H)R_2]_\infty$ (1). A solution of $Hg[C(H)R_2]_2$ (4.5 g, 8.66 mmol) in hexane (20 mL) was added to a 40/60 Na/Hg amalgam (6.8 g) already covered with hexane (50 mL) at *ca.* 23 °C. The reaction mixture was stirred for *ca.* 12 h. The pale yellow mother-liquor was filtered from a Na/Hg black residue and the volatiles were removed from the filtrate *in vacuo*, affording the pale brown solid **1** (2.5 g, 78%), which was used without further purification. ^1H NMR (C_6D_6): δ −2.19 (s, CH, 1 H) and 0.19 (s, $SiMe_3$, 18 H); this was identical to that published.[4b]

$H[N(R)C(Ph)C(H)C(Ph)NR]$ (2). Cyclopentadiene (2.2 mL, 32.6 mmol) was added to a suspension of $[Li\{N(R)C(Ph)\}_2CH]$ (9.14 g, 24.53 mmol) in pentane (75 mL) at ambient temperature. The mixture was stirred for *ca.* 12 h, then filtered. The yellow filtrate was dried *in vacuo* affording the yellow solid **2** (8.52 g, 95%) which was used without further purification. ^1H NMR ($C_6D_5CD_3$): δ 0.11 (s, $SiMe_3$, 18 H), 5.51 (s, CH, 1 H), 7.02 (m, Ph, 6 H), 7.30 (m, Ph, 4 H) and 12.52 (s, NH, 1 H); this was identical to the published spectrum.[1]

$Na[\{N(R)C(Ph)\}_2CH]$ (3) and $[Na\{N(R)C(Ph))_2CH\}(thf)_2]$ (4).

Method 1. Addition of $Na[N(SiMe_3)_2]$ (4.05 g, 22.09 mmol) to a solution of **2** (6.85 g, 18.68 mmol) in toluene (100 mL) at *ca.* 25 °C rapidly gave a yellow precipitate. After stirring for 20 h, the solid **3** (6.84 g, 94%) was separated by decantation, filtration and washing with toluene (20 mL); it was used without further purification.

Method 2. $NaNH_2$ (0.10 g, 2.56 mmol) was added to a solution of **2** (0.47 g, 1.28 mmol) in Et_2O (50 mL) at *ca.* 25 °C. The mixture was vigorously stirred for 12 h. Unreacted $NaNH_2$ was then separated by filtration and the volatiles were removed from the filtrate *in vacuo.* The yellow residue was washed with hexane (2 × 20 mL) and **3** (0.23 g, 46%) was recovered as a yellow solid after drying.

Method 3. Benzonitrile (2.4 mL, 23.52 mmol) was added slowly to a solution of **1** (2.11 g, 11.57 mmol) in Et_2O (30 mL) at 0 °C. After 4 h, the yellow mixture was allowed to warm to room temperature. The volatiles were removed *in vacuo* and stripped off twice with hexane. The residue was then washed with hexane to give the yellow solid **3** (3.37 g, 75%). ^1H NMR (C_5D_5N): δ −0.04 (s, $SiMe_3$, 18 H), 5.23 (s, CH, 1 H), 7.18–7.24 (m, Ph, 6 H), 7.44–7.47 (m, Ph, 4 H). Crystals of $[Na\{(N(R)C(Ph))_2CH\}(thf)_2]$ (**4**), suitable for X-ray analysis,[3] were obtained from thf.

$Na[N(R)C(Ph)C(H)R]$ (6). A solution of benzonitrile (0.8 mL, 7.84 mmol) in Et_2O (30 mL) was added dropwise to a solution of $Na[C(H)R_2]$ (1.46 g, 8 mmol) in Et_2O (30 mL) at *ca.* −78 °C. The initially colourless solution immediately became yellow. After stirring for 2 h the volatiles were removed *in vacuo* at ambient temperature. Recrystallisation from hexane at *ca.* −30 °C afforded orange crystals of compound **6** (1.89 g, 83%), mp 111–112 °C (change in colour at 56–57 °C). MS: *m/z* (%, assignment, L = ligand): 263 (32, $[LH]^+$), 248 (7, $[LH - Me]^+$), 190 (3, $[LH - SiMe_3]^+$), 186 (11, $[LH - Ph]^+$), 176 (42, $[LH - NSiMe_3 - Me]^+$), 146 (100). ^1H NMR (C_6D_6): δ (s, $SiMe_3$, 9 H), 0.05 (s, $NSiMe_3$, 9 H), 3.63 (s br, CH, 1 H), 7.12–7.30 (m, Ph, 10 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.4 (s, $SiMe_3$), 4.0 (s, $NSiMe_3$), 87.5 (s, CH), 125.6., 126.9–128.3 (s, aromatic carbons), 148.6 (s, *ipso*-C) and 177.1 (s, CN).

$[Na\{N(R)C(Ph)\overset{|}{N}C(Ph){=}C(H)R\}]_8$(7). Benzonitrile (2.3 mL, 22.4 mmol) was added at *ca.* 23 °C to a solution of $Na[C(H)R_2]$ (2.3 g, 10.9 mmol) in Et_2O (30 mL). The volatiles were removed *in vacuo* at 50 °C and the orange/brown residue was treated with pentane (30 mL). Filtration and concentration of the pale brown filtrate gave upon cooling yellow crystals of **7** (1.1 g, 26%) (Found: C, 64.3; H, 7.50; N, 7.12. $C_{21}H_{29}NaN_2Si_2$ requires C, 64.9; H, 7.52; N, 7.21%), mp 84–86 °C. MS: *m/z* (%, assignment, L = ligand): 365 (37, $[L]^+$), 351 (7, $[LH - Me]^+$), 293 (46, $[LH - SiMe_3]^+$), 277 (22, $[L - SiMe_3 - Me]^+$), 263 (10, $[L - NSiMe_3 - Me]^+$), 220 (88, $[LH - 2SiMe_3]^+$), 176 (52, $[N(SiMe_3)C(Ph)]^+$), 147 (78), 103 (100) and 73 (76, $[SiMe_3]^+$). ^1H NMR (C_5D_5N): δ −0.15 (s, $SiMe_3$, 9 H), 0.01 (s, $NSiMe_3$, 9 H), 4.56 (s br, CH, 1 H), 7.15–7.63 (m, Ph, 10 H). $^{13}C\{^1H\}$ NMR (C_5D_5N): δ 1.6 (s, $SiMe_3$), 3.7 (s, $NSiMe_3$), 107.1 (s, CH), 125.6, 126.6, 127.2, 127.8, 129.2 and 129.5 (s, Ph *o*-, *m*- and *p*-CH), 132.4 and 133.9 (s, Ph *ipso*-C), 166.8 and 172.4 (s, CN).

$[K\{\mu\text{-}N(R)C(Ph){=}C(H)R\}(\eta^6\text{-}C_6H_6)]_2$ (8). Addition of benzonitrile (0.21 mL, 2.06 mmol) to a solution of $K[C(H)R_2]$ (0.40 g, 2.02 mmol) in Et_2O (30 mL) at −78 °C immediately gave a yellow solution. After stirring for 1 h, the volatiles were removed *in vacuo* and stripped off with hexane (5 mL); the resulting yellow solid was washed with hexane yielding **8** (0.48 g, 79%) (Found: C, 55.35; H, 7.95; N, 4.62. $C_{14}H_{24}KNSi_2$ requires C, 55.75; H, 8.02; N, 4.64%). Crystals suitable for X-ray analysis were obtained from benzene; mp 131–133 °C (change in colour at 56–57 °C). MS: *m/z* (%, assignment): 263 (69, $[LH]^+$), 248 (18, $[LH - Me]^+$), 190 (9, $[LH - SiMe_3]^+$), 186 (22, $[LH - Ph]^+$), 176 (74, $[LH - NSiMe_3 - Me]^+$), 146 (100). ^1H NMR ($C_6D_5CD_3$): δ −0.11 (s, $SiMe_3$, 9 H), 0.23 (s, $NSiMe_3$, 9 H), 3.18 (s, CH, 1 H), 7.05–7.15 (m, Ph, 10 H). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$): δ 2.9 (s, $SiMe_3$), 3.6 (s, $NSiMe_3$), 84.7 (s, CH), 126.4, 127.8, 128.2 (s, aromatic carbons), 149.6 (s, *ipso*-C) and 176.3 (s, CN).

$[K\{N(R)C(Ph)\overset{|}{N}C(Ph){=}C(H)R\}(thf)_2]$(9). Benzonitrile (0.38 mL, 3.73 mmol) was added to a solution of $K[C(H)R_2]$ (0.74 g, 3.73 mmol) in Et_2O at −78 °C. The mixture was stirred for 45 min and the solvent was removed *in vacuo.* The resulting yellow sticky solid was dissolved and refluxed in thf (20 mL). Benzonitrile (0.40 mL, 3.92 mmol) was added dropwise and the yellow–brown solution was stirred for 2 min. The solvent was removed *in vacuo.* Addition of hexane (30 mL) afforded the yellow–brown solid of thf-free **9** (0.61 g, 40%) (Found: C, 61.57; H, 6.97; N, 7.04.

Table 4 Crystal and refinement details for **7**, **8** and **11**

Compound	**7**	**8**	**11**
Formula	$C_{168}H_{232}N_{16}Na_8Si_{16}\cdot 4C_5H_{12}$	$C_{40}H_{60}K_2N_2Si_4$	$C_{42}H_{58}N_4NiSi_4$
M	3397.64	759.5	790.0
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group (no.)	$P4/n$ (85)	$P2_1/n$ (14)	$P2_1/c$ (14)
a/Å	32.690(7)	18.754(3)	11.439(6)
b/Å	32.690(7)	13.053(2)	12.9546)
c/Å	9.819(2)	18.970(4)	30.37(3)
β/°	90	105.88(2)	97.85(6)
U/Å^3	10,493(4)	4,467(1)	4,458(6)
Z	2	4	4
μ/mm^{-1}	0.16	0.347	0.58
Unique reflections, R_{int}	6,404, 0.112	5,447, 0.027	6,217, 0.065
Reflection with $I > 2\sigma(I)$	3063	3972	3732
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.092$, $wR2 = 0.209$	$R1 = 0.042$, $wR2 = 0.086$	$R1 = 0.080$, $wR2 = 0.168$
R Indices (all data)	$R1 = 0.198$, $wR2 = 0.273$	$R1 = 0.069$, $wR2 = 0.096$	$R1 = 0.149$, $wR2 = 0.227$

$C_{21}H_{29}KN_2Si_2$ requires C, 62.32; H, 7.22; N, 6.92%), which was separated by filtration and dried *in vacuo.* Crystals suitable for X-ray analysis were obtained from thf, mp > 220 °C. MS: m/z (%, assignment, L = ligand): 500 (23, [M − 3SiMe$_3$ − CHSiMe$_3$ − 2thf]$^+$), 404 (4, [1/2M − thf]$^+$), 365 (29, [L]$^+$), 351 (7, [LH − Me]$^+$), 293 (48, [LH − SiMe$_3$]$^+$), 278 (43, [L − NSiMe$_3$]$^+$), 263 (21, [L − NSiMe$_3$ − Me]$^+$), 220 (88, [LH − 2SiMe$_3$]$^+$), 147 (100), 128 (28), 104 (42) and 73 (53, [SiMe$_3$]$^+$). ^{1}H NMR (C_6D_6): δ −0.04 (s, SiMe$_3$, 9 H), 0.01 (s, NSiMe$_3$, 9 H), 1.39 (m, CH$_2$, 4 H), 3.55 (m, OCH$_2$, 4 H), 4.40 (s br, CH, 1 H), 7.07–7.41 (m, Ph, 10 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 1.1 (s, SiMe$_3$), 3.4, (s, NSiMe$_3$), 25.8 (s, CH$_2$), 67.9 (s, OCH$_2$), 109.8 (s, *C*H), 126.8., 127.1, 127.4, 127.8, 127.9 and 128.5 (s, Ph *o*-, *m*- and *p*-CH), 132.4, 133.0, 144.7 and 146.5 (s, Ph *ipso*-C), 166.3 and 171.3 (s, CN).

[Ni{N(R)C(Ph)$\overset{|}{\text{N}}$C(Ph)=C(H)R}$_2$](11). [Li{μ-N(R)C(Ph)N–C(Ph)=C(H)R}(thf)]$_2$ (0.8 g, 0.90 mmol) in thf (20 mL) was added dropwise to a solution of [NiBr$_2$(dme)] (0.26 g, 0.84 mmol) in thf (20 mL) at *ca.* 23 °C. The resulting deep-yellow/brown mixture was stirred for *ca.* 5 min. The solvent was removed *in vacuo*, the residue "stripped" (this procedure refers to adding the solvent and then removing it *in vacuo*) with pentane (3 × 10 mL) and then dissolved in pentane (10 mL). Filtration from a white precipitate followed by concentration of the filtrate to *ca.* 3–4 mL and cooling to −30 °C yielded deep purple crystals (0.41 g, 63%) (Found: C, 62.9; H, 7.48; N, 7.09; $C_{42}H_{58}N_4NiSi_4$ requires C, 63.9; H, 7.40; N, 7.09%), which were dried *in vacuo.* Three compounds of relative intensities 94, 3 and 3 were observed from ^{1}H NMR, the CH= region at δ 4.99, 5.18 and 5.48 ppm; one of the latter two may be due to a geometric isomer of **11** and the other to Ni(1,3-diazaallyl)Br]. The compound **11** had mp: 62–64 °C. MS: m/z (%, assignment, L = ligand): 788 (24, [M]$^+$), 716 (2, [M − SiMe$_3$]$^+$), 612 (4, [M − 2SiMe$_3$ − 2Me]$^+$, 424 (3, [M − L]$^+$), 365 (75, [L]$^+$), 351 (39, [LH − Me]$^+$), 293 (75, [LH − SiMe$_3$]$^+$), 278 (68, [L − NSiMe$_3$]$^+$), 263 (29, [L − NSiMe$_3$ − Me]$^+$), 220 (14, [LH − 2SiMe$_3$]$^+$), 176 (90, [N(SiMe$_3$)C(Ph)]$^+$), 147 (82), 104 (42) and 73 (100, [SiMe$_3$]$^+$). ^{1}H NMR ($C_6D_5CD_3$): δ major) 0.21 (s, SiMe$_3$, 9 H), 0.60 (s, NSiMe$_3$, 9 H), 4.99 (s br, 0.08, C*H*, 1 H), 6.64–8.45 (Ph), 7.56 (s br, Ph, 2 H) and 8.45 (s br, Ph, 1 H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$): δ (major) 1.1 (s, SiMe$_3$), 4.1 (s, NSiMe$_3$), 118.0 (s, CH), 126.7, 127.7, 128.3, 129.2 and 130.6 (s, Ph *o*-, *m*- and *p*-CH), 142.2 (s, Ph *ipso*-C), 154.4 and 168.6 (s, CN).

Crystal data and refinement details for 7, 8 and 11

Diffraction data for each of **7**, **8** and **11** were collected on an Enraf-Nonius CAD-4 diffractometer using monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å at 173(2) K. Crystals were coated in oil and then mounted directly on the diffractometer under a stream of cold nitrogen gas. The structures were solved on all F^2 using SHELXL-97.[23] Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the riding mode for **7** and **11** for **10**, those H atoms which might have been affected by interactions with K atoms had their positions freely refined (no distortions from normal were found); other H atoms were included in the riding mode. The diffraction data for **7** were very weak at high theta values; the poorly defined pentane solvate was included with isotropic C atoms, N atoms omitted, and 1,2 and 1,3 distance constraints. Further details are in Table 4.

CCDC reference numbers 297453–297455.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601881e

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References

1 P. B. Hitchcock, M. F. Lappert, M. Layh, D.-S. Liu, R. Sablong and S. Tian, *J. Chem. Soc., Dalton Trans.*, 2000, 2301.

2 E. Shaviv, M. Botoshansky and M. S. Eisen, *J. Organomet. Chem.*, 2003, **683**, 165.

3 E. Nelkenbaum, M. Kapon and M. S. Eisen, *J. Organomet. Chem.*, 2005, **690**, 2297.

4 (*a*) P. B. Hitchcock, M. F. Lappert, W.-P. Leung, D.-S. Liu and S. Tian, *J. Chem. Soc., Chem. Commun.*, 1993, 1386; (*b*) W. M. Boesveld, P. B. Hitchcock, M. F. Lappert, D.-S. Liu and S. Tian, *Organometallics*, 2000, **19**, 4030; (*c*) A. J. Hart, D. H. O'Brien and C. R. Russell, *J. Organomet. Chem.*, 1974, **72**, C19.

5 P. B. Hitchcock, M. F. Lappert and S. Tian, *J. Organomet. Chem.*, 1997, **549**, 1.

6 J. W. F. L. Seetz, G. Schat, O. S. Akkerman and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1982, **104**, 6848.

7 Y. Cheng, P. B. Hitchcock, M. F. Lappert and M. Zhou, *Chem. Commun.*, 2005, 752.

8 P. B. Hitchcock, M. F. Lappert, D.-S. Liu and R. Sablong, *Chem. Commun.*, 2002, 1920.

9 (*a*) P. B. Hitchcock, M. F. Lappert and S. Tian, *J. Chem. Soc., Dalton Trans.*, 1997, 1945; (*b*) P. B. Hitchcock, J. Hu, M. F. Lappert and S. Tian, *J. Organomet. Chem.*, 1997, **536–537**, 473.

10 C. Schade and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1987, **27**, 169 (see p. 186).

11 P. B. Hitchcock, M. F. Lappert and D.-S. Liu, *J. Chem. Soc., Chem. Commun.*, 1994, 1699.

12 E. Nelkenbaum, M. Kapon and M. S. Eisen, *J. Organomet. Chem.*, 2005, **690**, 3154.

13 H. K. Lee, T. S. Lam, C.-K. Lam, H.-W. Li and S. M. Fung, *New J. Chem.*, 2003, **27**, 1310.

14 D. Walther, P. Gebhardt, R. Fischer, U. Kreher and H. Görls, *Inorg. Chim. Acta*, 1988, **281**, 181.

15 B. S. Lim, A. Rahtu, J.-S. Park and R. G. Gordon, *Inorg. Chem.*, 2003, **42**, 7951.

16 C. A. Nijhuis, E. Jellema, T. J. J. Sciarone, A. Meetsma, P. H. M. Budzelaar and B. Hessen, *Eur. J. Inorg. Chem.*, 2005, 2089.

17 A. G. Avent, P. B. Hitchcock, M. F. Lappert, R. Sablong and J. R. Severn, *Organometallics*, 2004, **23**, 2591.

18 J. E. Parks and R. H. Holm, *Inorg. Chem.*, 1968, **7**, 1408.

19 P. B. Hitchcock, M. F. Lappert and D.-S. Liu, *J. Organomet. Chem.*, 1995, **500**, 203.

20 S. Al-Hashimi and J. D. Smith, *J. Organomet. Chem.*, 1978, **153**, 253.

21 N. Wiberg and G. Wagner, *Chem. Ber.*, 1986, **119**, 1455.

22 L. G. L. Ward, *Inorg. Synth.*, 1972, **13**, 162.

23 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, 1993.