

Transformation of the Bis(trimethylsilyl)methyl into Aza-allyl and β -Diketimato Ligands; the X-Ray Structures of $[\text{Li}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CH}(\text{R})\}]_2$ and $[\text{Zr}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CHC}(\text{Ph})\text{N}(\text{R})\}\text{Cl}_3]$ ($\text{R} = \text{SiMe}_3$)†

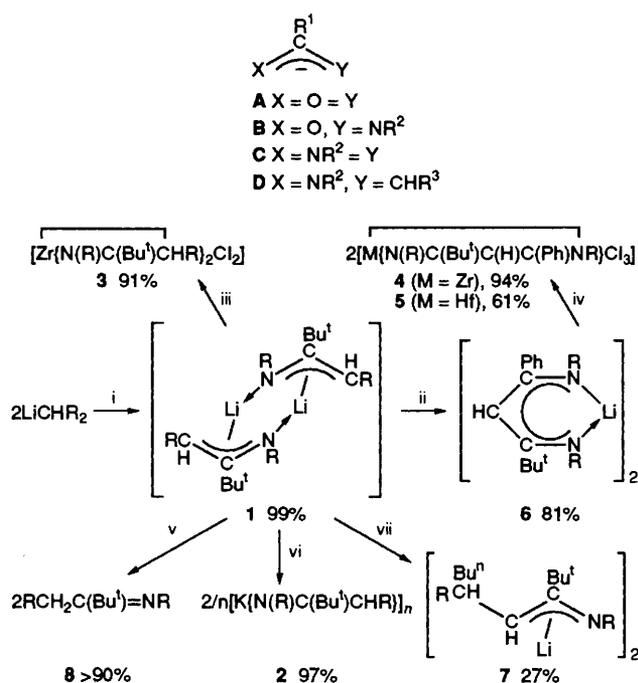
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The reaction of LiCHR_2 with Bu^tCN gives the η^3 -aza-allyl $[\text{Li}(\overline{\text{LL}}')]_2$ **1**, which in turn affords (i) the aza-allyls $[\{\text{K}(\overline{\text{LL}}')\}_n]$ (with KOBU^t), *rac*- $[\text{Zr}(\overline{\text{LL}}')_2\text{Cl}_2]$ (with ZrCl_4) and $[\text{Li}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{CH}(\text{R})\text{Bu}^n\}]_2$ (with successively CH_2Br_2 and LiBu^n), (ii) the β -diketimates $[\text{M}(\overline{\text{L}}^n\overline{\text{L}}^m)\text{Cl}_3]$ ($\text{M} = \text{Zr}$ or Hf , via MCl_4) and $[\text{Li}(\overline{\text{L}}^n\overline{\text{L}}^m)]_2$ (with 2PhCN), and (iii) the imine $\text{RCH}_2\text{C}(\text{Bu}^t)=\text{NR}$ (with H_2O); X-ray data are provided for **1** and **4** [$\overline{\text{LL}}' = \text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CHR}$, $\overline{\text{L}}^n\overline{\text{L}}^m = \text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$; $\text{R} = \text{SiMe}_3$].

The carboxylato ligand **A** and its isoelectronic relatives the amidates **B** and amidinates **C** have an important role in coordination chemistry, partly because of the variety of bonding modes which they display: η^1 or η^3 , terminal, chelating or bridging. Related 1-aza-allyls, *e.g.* **D**, have received scant attention, although their potential should be considerable, not least because the groups R^1 , R^2 and R^3 in **D** may be varied.

We now report (Scheme 1) (a) the synthesis of the lithium, potassium and zirconium(IV) η^3 -1-aza-allyls $[\text{Li}(\overline{\text{LL}}')]_2$ **1**, $[\{\text{K}(\overline{\text{LL}}')\}_n]$ **2** and $[\text{Zr}(\overline{\text{LL}}')_2\text{Cl}_2]$ **3**; and the conversion of **1** into (b) the Zr^{IV} , Hf^{IV} or Li β -diketimates $[\text{Zr}(\overline{\text{L}}^n\overline{\text{L}}^m)\text{Cl}_3]$ **4**, $[\text{Hf}(\overline{\text{L}}^n\overline{\text{L}}^m)\text{Cl}_3]$ **5** and $[\text{Li}(\overline{\text{L}}^n\overline{\text{L}}^m)]_2$ **6**, (c) the η^3 -1-aza-allyl-lithium compound $[\text{Li}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{CH}(\text{R})\text{Bu}^n\}]_2$ **7** and (d) the ketimine $\overline{\text{LL}}'\text{H}$ **8** [$\overline{\text{LL}}' = \text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CHR}$, $\overline{\text{L}}^n\overline{\text{L}}^m = \text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$; $\text{R} = \text{SiMe}_3$]. Each of **1–8** gave satisfactory C, H and N microanalytical results, as well as NMR spectroscopic and X-ray diffraction (not **2**, **5**, **6**, or **8**) data; the latter are reported here only for **1** (Fig. 1) and **4** (Fig. 2).‡



Scheme 1 Synthesis of **Li 1** and **7**, **K 2**, and Zr^{IV} **3** 1-aza-allyls; **Li 6**, Zr^{IV} **4** and Hf^{IV} **5** β -diketimates; and the ketimine **8** ($\text{R} = \text{SiMe}_3$). **Reagents and conditions:** i, $2\text{Bu}^t\text{CN}$ or $4\text{Bu}^t\text{CN}$, Et_2O , 12 h, 0–25 °C; ii, 2PhCN , Et_2O , 12 h, 25 °C; iii, ZrCl_4 or 2ZrCl_4 , Et_2O , 12 h, 25 °C; iv, ZrCl_4 or HfCl_4 , Et_2O , 12 h, 25 °C; v, $2\text{H}_2\text{O}$, hexane, 1 h, 25 °C; vi, 2KOBU^t , hexane, 24 h, 25 °C; vii, (a) CH_2Br_2 , hexane, 6 h, 60 °C, (b) LiBu^n , hexane, 12 h, 25 °C. The yields have not been optimised and refer to recrystallised samples.

In contrast to the reaction between ArCN and the alkali metal bis(trimethylsilyl)methyl MCHR_2 ,¹ which gave the 2 : 1 adduct the β -diketiminate $[\text{M}\{\text{N}(\text{R})\text{C}(\text{Ar})\text{C}(\text{H})\text{C}(\text{Ar})\text{NR}\}]_2 \equiv [\text{M}(\overline{\text{LL}}')]_2$,² Bu^tCN with LiCHR_2 reacted together in a 1 : 1 stoichiometry (i in Scheme 1) to yield **1** irrespective of whether or not an excess of Bu^tCN was used ($\text{Ar} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me-4}$, $\text{M} = \text{Li}$ or K). The proposed reaction pathway involves initial formation of $\text{Li}[\text{N}=\text{C}(\text{CHR}_2)\text{Bu}^t]$ **1'** followed by a 1,3-silico-tropic rearrangement to yield the isolated isomer **1**. Compounds related to **1'** and **1** (Ar in place of Bu^t) were postulated to be intermediates in the pathway to $[\text{M}(\overline{\text{LL}}')]_2$ from $2\text{ArCN}/\text{MCHR}_2$.² This proposal gains further support from the demonstration (Scheme 1) that **1** + 2 PhCN yielded the β -diketiminate $[\text{Li}(\overline{\text{L}}^n\overline{\text{L}}^m)]_2$ **6**.

The 1-aza-allyl ligand $[\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CHR}]^- \equiv [\overline{\text{LL}}']^-$ when η^3 -bonded to a metal is chiral; it is noteworthy that crystalline *rac*- $[\text{Zr}(\overline{\text{LL}}')_2\text{Cl}_2]$ **3** was formed (Scheme 1) diastereospecifically.

That both the 1-aza-allyl $[\overline{\text{LL}}']^-$ and the β -diketimato $[\overline{\text{L}}^n\overline{\text{L}}^m]^-$ ligands are sterically demanding is evident from the fact that compounds **3–5** are mononuclear. In contrast, $[\{\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\mu\text{-Cl})_2\}_\infty]$ is polymeric.³

Reaction of $[\text{Li}(\overline{\text{LL}}')]_2$ **1** with successively CH_2Br_2 and LiBu^n surprisingly gave (vii in Scheme 1) the higher homologue $[\text{Li}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{CH}(\text{R})\text{Bu}^n\}]_2$ **7**, rather than the isomer $[\text{Li}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{R})\text{CH}_2\text{Bu}^n\}]_2$. This apparent 1,2-H/R ($\text{R} = \text{SiMe}_3$) exchange is an example of dyotropy.⁴

Reactions v and vi of Scheme 1 demonstrate that **1** may behave as a C-centred nucleophile, whereas in reactions ii, iii, and vii both the C- and N-centres are implicated.

Crystalline **1** has a central $\overline{\text{LiNLiN}}$ rhombus, Li–N–Li 73.0(4) and 74.2(4), N–Li–N 104.9(4) and 107.5(5)°, Fig. 1; the coordination environment for each Li atom is completed by the η^3 -1-aza-allyl ligand as well as an agostic $\text{Li}\cdots\text{CH}_3$ - $(\text{SiMe}_2\text{CH-})$ contact. The Li atom is 1.44 Å out of the NCC aza-allyl plane.

In crystalline $[\text{Zr}(\overline{\text{L}}^n\overline{\text{L}}^m)\text{Cl}_3]$ **4**, the five coordinate Zr environment may be regarded as being distorted trigonal bipyramidal with $\text{Cl}(2)$ and $\text{N}(2)$ axial [$\text{Cl}(2)\text{–Zr–N}(2)$ 166.3(2)°] and $\text{Cl}(1)\text{ZrCl}(3)\text{N}(1)$ coplanar: $\text{Cl}(1)\text{–Zr–Cl}(3)$ 101.5(1), $\text{Cl}(1)\text{–Zr–N}(1)$ 131.8(2) and $\text{Cl}(3)\text{–Zr–N}(1)$

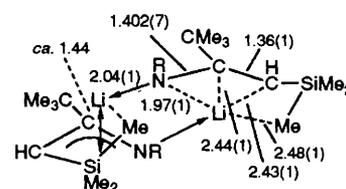


Fig. 1 A simplified bonding pattern for complex $[\text{Li}(\overline{\text{LL}}')]_2$ **1** with bond distances (Å)

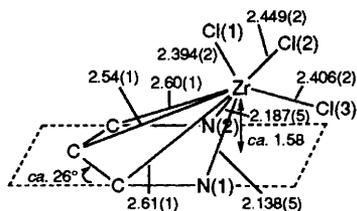


Fig. 2 A simplified bonding pattern for complex $[Zr(L''L''')Cl_3]$ **4** with selected bond distances (Å) and angles ($^\circ$)

$126.7(2)^\circ$ (Σ Zr 359°), Fig. 2. The $[L''L''']^-$ ligand in **4** may have some η^5 -character, cf. Fig. 2. These general features resemble those of $SnCl(Me)_2(LL)$, in which Cl and N are quasi-axial $[LL = N(R)C(Ph)C(H)C(Ph)NR]$.²

Group 1 and 2 metal enamines and analogues are valuable synthons, undergoing various C–C bond-forming reactions with electrophiles.⁵ Such complexes are not isolated but used *in situ*, and little is known about their structures, although it is often assumed that they are *N*-metallo-enamines (*i.e.*, isomers of 1-aza-allyls); there is NMR spectral evidence in the cases of (i) $[M\{N(H)C(Bu^i)CHPr^n\}\{OP(NMe_2)_3\}_x]_n$ ($M = Li$, $x = 1$; or $M = Na$, $x = 2$), obtained from $MBu^n + Bu^iCN$ with or without $OP(NMe_2)_3$,⁶ and (ii) $[Li\{N(Ph)C:CH(CH_2)_3CH_2\}(THF)_x]_n$ ($x = 0$; or $x = 1$ and $n = 1$).⁷ X-Ray structural data are available on various metal complexes derived from the 2-pyridylalkyl ligand $NC_5H_4CR_2$ ($R = SiMe_3$), including $[LiNC_5H_4C(R)_2LiNC_5H_4CR_2]$,⁸ and analogues of Mg, Cu^I, Ag^I, Co^{II}, Zn, Cd, Hg^{II}, Al, Ga, As^{III}, Sb^{III}, Bi, Si, Sn^{II}, and Sn^{IV}.⁹ The complex $[Hf(\eta-C_5H_5)_2(Cl)\{N(Ar)CH:CH(C_5H_3N-2-Me-6)\}]$ was obtained by thermolysing the isomeric imino-acyl.¹⁰ Other *d*-block aza-allyls, which have been of η^3 -type, are restricted to $[Mo(\eta-C_5H_5)(CO)_2\{N-(Me)C(Ph)CH_2\}]$ or close analogues, obtained from $[Mo(\eta-C_5H_5)(CO)_2]_2$ and $N(C(Ph)CH_2)$,¹¹ thermal isomerisation of an η^2 -iminoacyl,¹² R^1NC insertion into a $Mo^{II}-R^2$ bond ($R^2 = Me$ or Et),¹³ or from $Mo^{II}-CH_2C(O)R^1$ and R^2NH_2 .¹⁴

The results here presented provide further illustration of the versatility of the $\bar{C}H(SiMe_3)_2$ ligand. Its conversion into the 1-aza-allyl $[LL']^-$ and the β -diketiminato $[LL]^{-2}$ or $[L''L''']^-$ ligands provides promise of a useful contribution to coordination chemistry.

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Footnotes

† No reprints available.

‡ *Crystal data for 1*: $C_{24}H_{56}Li_2N_2Si_4$, $M = 499$, monoclinic, space group $P2_1/n$ (non-standard No. 14), $a = 12.279(4)$, $b = 16.370(2)$, $c = 17.198(6)$ Å, $\beta = 101.74(2)^\circ$, $U = 3384.5$ Å³, $F(000) 1104$; $Z = 4$, $D_c = 0.98$ g cm⁻³, $\mu(Mo-K\alpha) = 1.8$ cm⁻¹, specimen $0.2 \times 0.2 \times 0.15$ mm³, 4308 unique reflections for $2 < \theta < 25^\circ$, 1675 reflections with $[|F^2| > 3\sigma(F^2)]$ used in the refinement; $R = 0.047$, $R_w = 0.051$, $S = 1.3$. For **4**: $C_{19}H_{33}Cl_3N_2Si_2Zr$, $M = 543.2$, monoclinic, space group $P2_1/n$ (non-standard No. 14), $a = 10.898(4)$, $b = 20.706(7)$, $c = 11.701(3)$ Å, $\beta = 100.27(2)^\circ$, $U = 2598$ Å³, $F(000) 1120$; $Z = 4$, $D_c = 1.39$ g cm⁻³, $\mu(Mo-K\alpha) = 8.3$ cm⁻¹, specimen $0.15 \times 0.15 \times 0.1$ mm³, 3720 unique reflections for $2 < \theta < 25^\circ$, 2456 reflections with $[|F^2| > 2\sigma(F^2)]$ used in the refinement; $R = 0.051$, $R_w = 0.052$, $S = 1.1$.

$[T = 295$ K, Enraf-Nonius CAD-4 diffractometer, $\lambda(Mo-K\alpha) 0.71069$ Å, no absorption corrections, full-matrix least-squares refinement with non-hydrogen atoms anisotropic, $w = 1/\sigma^2(F)$]; direct method for **1**, and heavy atom method for **4**.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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