New dianionic ligands η^5-$\bar{C}_5H_4Si(Me)_2\bar{C}(H)SiMe_3$ and η^5-$\bar{C}_5H_4SiMe_2\{NC(Bu^t)C(H)SiMe_3\}^-$; syntheses, structures and reactivity of their lithium and zirconium derivatives†

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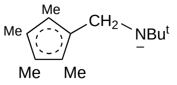
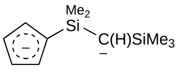
Lithium and zirconium complexes $[Li_2(\mathbf{B})(tmen)]_2$ 4, $[Li_4(\mathbf{C})_2(tmen)]$ 5, $[Zr(\mathbf{B})_2]$ 7 and $[Zr(\mathbf{C})_2]$ of the new ligands η^5-$\bar{C}_5H_4Si(Me)_2\bar{C}(H)SiMe_3$ (≡$[\mathbf{B}]^{2-}$) and η^5-$\bar{C}_5H_4Si(Me)_2\{NC(Bu^t)C(H)SiMe_3\}^-$ (≡$[\mathbf{C}]^{2-}$) are reported, as well as the X-ray structures of the centrosymmetric dimer 4 and of 5 (having each of the four Li atoms in a different environment) and the catalytic activity of 7 for α-alkene polymerisation.

Examples of cyclopentadienyl ligands bearing a neutral Lewis base substitutent include those containing an amine,[1a] ether,[1b] pyridyl,[1c] phosphine,[1d] or vinyl[1e] side chain. Analogues having an anionic substituent are rare. The earliest examples are the 'tucked-in' metal complexes, such as $[W(\eta^5\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)H_2]$,[2] but the cyclopentadienyl amide $[\mathbf{A}]^{2-}$ is noteworthy,[3] because its derived Ti^{IV} complex $[Ti(\mathbf{A})Cl_2]$ is the Dow catalyst for the production of ethylene–styrene copolymer.[4] A cyclopentadienyl(iminoacyl) ligand has been found in a number of Ti^{IV} and Zr^{IV} complexes.[5]

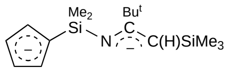
We now draw attention to two new dianionic cyclopentadienyl ligands $[\mathbf{B}]^{2-}$ and $[\mathbf{C}]^{2-}$, having an alkyl and a 1-azaallylsilyl side-chain, respectively, which may well find a useful role in organometallic chemistry.



$[\mathbf{A}]^{2-}$



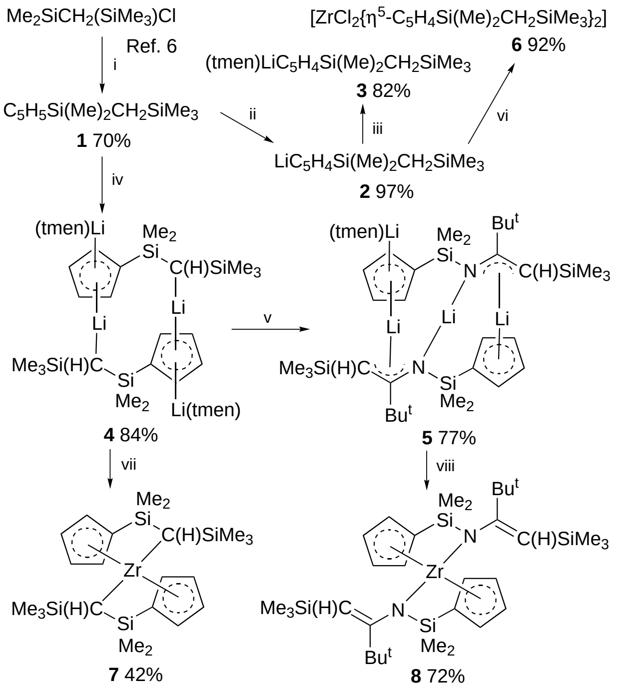
$[\mathbf{B}]^{2-}$



$[\mathbf{C}]^{2-}$

Treatment of Cl_2SiMe_2 with $LiCH_2SiMe_3$ gave $ClSi(Me)_2CH_2SiMe_3$,[6] which with NaC_5H_5 gave **1** (Scheme 1, step i). From **1** and LiBu^n (even when used in excess) in tetrahydrofuran (thf), only the monodeprotonated complex $LiC_5H_4Si(Me)_2C(H)_2SiMe_3$ **2** was obtained (step ii), derivatised (step iii) as the 1 : 1tmen adduct **3** [tmen = $(Me_2NCH_2)_2$]. However, from **1**, 2 LiBu^n and 2 tmen, the dimeric complex $[Li_2(\mathbf{B})(tmen)]_2$ **4** was isolated (step iv). Reacting **4** with Bu^{t}CN led (step v) to the tetranuclear complex $[Li_4(\mathbf{C})_2(tmen)]$ **5**. The reaction between $ZrCl_4$ and each of the lithium compounds **2**, **4** and **5** gave (steps vi–viii, respectively) **6**–**8**, respectively. Complexes **6** and **7** (but not **8**) with methylaluminoxane (MAO) were shown to be effective catalysts for the polymerisation of C_2H_4, and **7** also for $MeCH{=}CH_2$ and $PhCH{=}CH_2$.

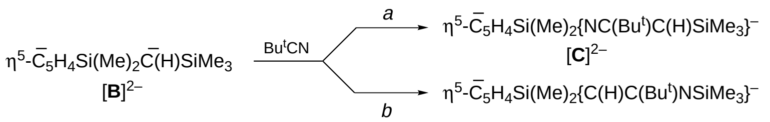
Since treatment of $Li\{CH(SiMe_3)_2\}$ with Bu^{t}CN readily gave the 1-azaallyllithium compound $[Li\{N(SiMe_3)C(Bu^t)C(H)SiMe_3\}]_2$,[7] in which a 1,3-SiMe$_3$ migration from C → N had taken place, there appeared to be two possible pathways upon reacting **4** with Bu^{t}CN, *a* and *b* in eqn. (1). In the event, Scheme 1, step v, as ultimately the X-ray structure of **5** revealed (*vide infra*) migration of the η^5-$C_5H_4SiMe_2$ group (pathway *a*) was preferred over SiMe$_3$.



Scheme 1 *Reagents and conditions*: i, NaCp, thf, 24 h, 0 °C; ii, LiBu^n, C_6H_{14}, 24 h, 0 °C; iii, tmen, C_6H_{14}, 3 h, 25 °C; iv, 2 tmen, 2 LiBu^n, C_6H_{14}, 24 h, 0 °C; v, Bu^{t}CN, Et_2O, 24 h, 25 °C; vi, 1/2 $ZrCl_4$, C_6H_{14}, 48 h, 25 °C; vii, or viii, $ZrCl_4$, C_6H_{14}, 48 h, 25 °C

Each of the compounds **1** and **3**–**8** gave satisfactory microanalysis, as well as multinuclear NMR spectra. For **1** [bp 93–98 °C (13 mmHg)], GCMS confirmed its purity and EI mass spectra showed the parent molecular ion to be the highest *m/z* peak for each of the zirconium compounds **6**–**8**. Compounds **3**–**8** were isolated as crystals and X-ray diffraction data‡ on **4** (Fig. 1) and **5** (Fig. 2) established their molecular structures; such data for **6** and **8** will be presented in a full paper.

Crystalline **4** is a centrosymmetric dimer. Each cyclopentadienyl group bridges two Li one of which Li(2)/Li(2′) has its coordination environment completed by a chelating tmen ligand, while the other Li(1)/Li(1′) has the carbanionic carbon C(1)/C(1′). Atoms Li(1)/Li(1′) are arranged in an almost linear fashion with respect to C(1)/C(1′) and the centroid M(1′)/M(1) of the cyclopentadienyl ring, C(1)–Li(1)–M(1′) 178.5. The Li(1)–C(1) bond of 2.075(8) Å is longer than the Li(1)–M(1′) distance of 1.93 Å. The former may be compared with the Li–C



(1)

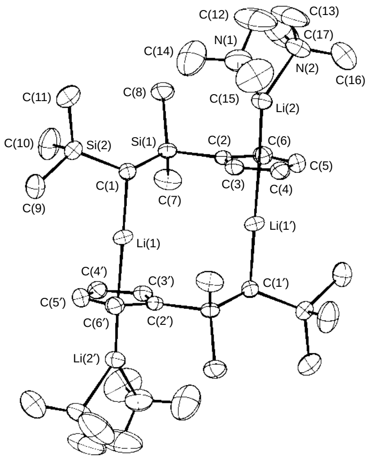


Fig. 1 The molecular structure of **4**. Selected bond lengths (Å) and angles (°) (also see text): Li(2)–M(1) 1.96, Li(2)–N(2) 2.092(8), Li(2)–N(1) 2.108(9); M(1) is the centroid of the C(2)–C(6) ring.

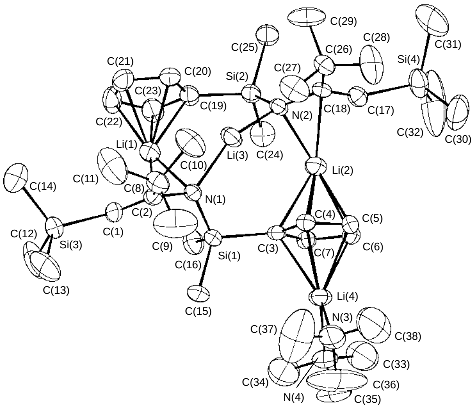
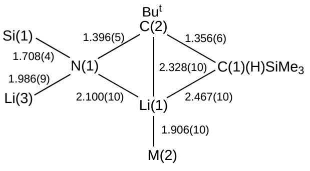


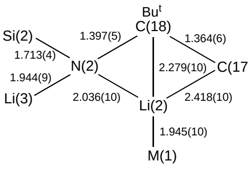
Fig. 2 The molecular structure of **5**. Selected bond lengths (Å) and angles (°) (see also **5a** and **5b**, and text): Li(4)–M(1) 2.004, Li(4)–N(3) 2.104(10), Li(4)–N(4) 2.093(10); M(1) is the centroid of the C(3)–C(7) ring, M(2) of the C(19)–C(23) ring.

bond lengths in $[\text{Li}\{\text{CH(SiMe}_3)_2\}]_\infty$ [av. 2.19(5) Å][8] and $\text{Li}\{\text{CH(SiMe}_3)_2\}\{\text{N(Me)(CH}_2\text{CH}_2\text{NMe}_2)_2\}$, 2.13(5) Å.[9] The Li(1)–M(1′) distance is similar to that in Li(η^5-$C_5H_4SiMe_3$)(tmen), 1.928 Å;[10] the latter has average Li–N bond lengths of 2.13(1) Å, compared with 2.100(9) Å in **4**.

Crystalline **5** is a tetranuclear complex in which each of the four Li atoms is in a different environment. Li(1) and Li(2) are somewhat similar (see **5a** and **5b**), except that the cyclopentadienyl having the centroid M(1) bridges Li(2) and Li(4), whereas the cyclopentadienyl having the centroid M(2) acts as a terminal ligand with respect to Li(1). The coordination environment around Li(4) is completed by a chelating tmen. The situation regarding Li(3) is the most unusual: it is two-coordinate, being the bridge between N(1) and N(2) of the two 1-azaallyl moieties, N(1) and N(2) being four-coordinate and N(1)–Li(3)–N(2) 145.2(5)°. The azaallyl–lithium environment around L(1) and Li(2) is similar to that in $[\overline{\text{Li}\{\text{N(SiMe}_3)\text{C(Bu}^t)\text{C}}\text{(H)SiMe}_3\}]_2$.[7]



5a



5b

The catalytic activity of the zirconocene(IV) chloride **6** (with MAO) for polymerisation of ethylene was comparable to that of $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]$.§ While this is not surprising, the activity of **7** (with MAO) for C_2H_4 (mp of polymer: 138 °C by DSC), C_3H_6 (atactic oligomer of low average molecular mass) and PhCH=CH$_2$§ (atactic polymer of high average molecular mass) was unexpected. The high activity combined with the relatively low chain lengths for the latter two suggests that chain transfer is frequent, consistent with the high polydispersity. As far as we are aware, a zirconium(IV) bis(chelate) catalyst has not previously been reported.

Ligands related to $[\mathbf{B}]^{2-}$ and $[\mathbf{C}]^{2-}$, including η^5-$\overline{\text{C}}_5\text{H}_4\text{Si(Me)}_2\overline{\text{C}}\text{(SiMe}_3)_2$ are being explored, as are extensions to their role in titanium chemistry.

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Footnotes and References

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† No reprints available.

‡ *Crystal data*: **4**, $C_{34}H_{72}Li_4N_4Si_4$, M = 677.1, monoclinic, space group $P2_1/n$, a = 10.730(2), b = 10.126(2), c = 22.125(4) Å, β = 103.73(2)°, U = 2335.2(8) Å^3, $F(000)$ = 744, Z = 2, D_c = 0.96 g cm^{-3}, μ(Mo-Kα) = 0.15 mm^{-1}, specimen 0.35 × 0.20 × 0.20 mm, 4088 unique reflections for $2 < \theta < 25°$, R_1 = 0.068 for 2170 reflections with $I > 2\sigma(I)$, wR_2 = 0.191 (all data), S = 1.012, the dimer lies on a crystallographic inversion centre. **5**, $C_{38}H_{74}Li_4N_4Si_4$, M = 727.13, triclinic, space group $P\bar{1}$ (no. 2), a = 13.811(3), b = 13.848(3), c = 14.683(3) Å, α = 88.65(2), β = 89.32(2), γ = 60.51(2)°, U = 2443.7(9) Å^3, $F(000)$ = 796, Z = 2, D_c = 0.99 g cm^{-3}, μ(Mo-Kα) = 0.15 mm^{-1}, specimen 0.5 × 0.3 × 0.1 mm, 8596 unique reflections for $2 < \theta < 25°$, R_1 = 0.080 for 3824 reflections with $I > 2\sigma(I)$, wR_2 = 0.211 (all data), S = 1.018. T = 273 K, Enraf-Nonius CAD-4 diffractometer, λ(Mo-Kα) = 0.710 73 Å, no absorption corrections, solution by direct method, full-matrix least-squares refinement on all F^2. CCDC 182/681.

§ Catalytic properties of **7** for α-alkene polymerisation [25 °C in toluene (*ca.* 200 cm^3)]. C_2H_4: **7** (0.064 mM), MAO (12.7 mM), 1.4 bar; activity, 1.41 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1} (bar)$^{-1}$; $\overline{M}_w$, 7.4 × 10^5 (using polystyrene as calibrant for PE); $\overline{M}_w/M_n$, 4.4; mp 138 °C. C_3H_6: **7** (0.048 mM), MAO (15 mM); activity, 1.86 × 10^5 g PP (mol Zr)$^{-1}$ h^{-1} (bar)$^{-1}$; $\overline{M}_w$, 710; M_w/M_n, 1.4; oil. PhCHCH$_2$: **7** (0.050 mM), MAO (40 mM); activity, 1.16 × 10^6 g PS (mol Zr)$^{-1}$ h^{-1} (bar)$^{-1}$; $\overline{M}_w$, 22.3 × 10^3; M_w/M_n, 3.2.

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