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FULL PAPER

Synthesis and structural characterisation of new *ansa*-bis(propene)s and {*ansa*-bis(allyl)}alkali metal and {*ansa*-bis(allyl)}transition metal complexes

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The new *ansa*-bis(propene)s, $R_2Si(CH_2CH{=}CHSiR'_3)_2$ (R = R′ = Me **1**; R = Ph, R′ = Me **2**; R = R′ = Ph **3**; R = Me, R′ = Ph **4**; R = Me, R′ = Me_2Bu^t **5**) have been prepared by lithiation of the appropriate 3-silylpropene and quenching with $SiCl_2R_2$ (R = Me or Ph). The η^3-*ansa*-bis(allyllithium) compounds $[\{Li(tmen)\}_2\{3\text{-}(\eta^3\text{-}C_3H_3SiR'_3\text{-}1)_2\}SiR_2]$ (R = R′ = Me **6**; R = Ph, R′ = Me **7**; R = R′ = Ph **8**; R = Me, R′ = Ph **9**; R = Me, R′ = Me_2Bu^t **10**) complexes were obtained from of the appropriate *ansa*-bis(propene) and $LiBu^n$. The lithium complex **6** was transformed into the potassium complex $[K_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}]$ **11** and into $[Hf\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}_2]$ **13** by reaction with $KOBu^t$ or $HfCl_4$, respectively. From **11** and $ZrCl_4$ $[Zr\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}_2]$ **12** was obtained. Single crystal X-ray structures of complexes **4**, **6** and **12** are presented. Complex **12**, in presence of methylaluminoxane (MAO), was an active catalyst for the polymerisation of ethylene.

Introduction

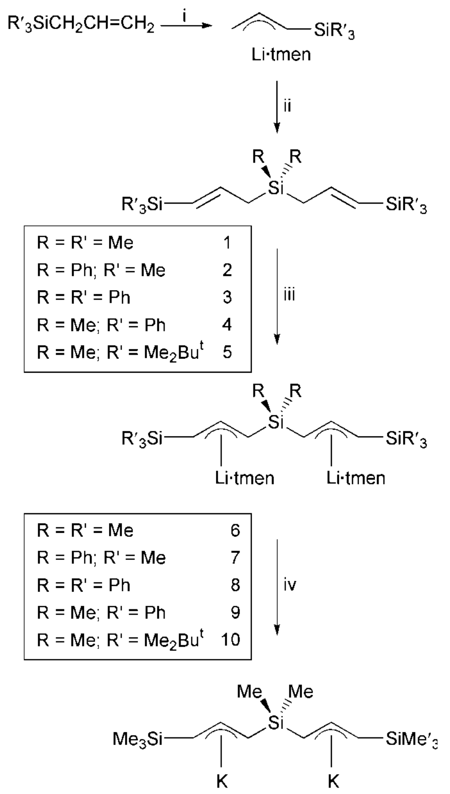
Alkali metal allyls and substituted-allyls have been the subject of extensive investigations of their chemistry,[1–6] molecular structures by X-ray crystallography,[7–13] solution structures by NMR spectroscopy[14–18] and MO calculations.[19–24]

In continuation of our researches on metal allyls and related compounds,[25] we now report the synthesis, structures and some reactions of lithium or potassium derivatives of some new *ansa*-bis(allyl)s, which we believe may prove to be of general interest in organometallic chemistry. These *ansa*-bis(allyl) ligands are $[3\text{-}(\eta^3\text{-}C_3H_3SiR'_3\text{-}1)_2SiR_2]^{2-}$ (R = Me or Ph and R′ = Me or Ph or $R'_3 = Me_2Bu^t$); an example is known, the X-ray-authenticated dimethylsilyl-*ansa*-bis(cyclohexenyl)dipotassium complex $[\{K_2[(\eta^3\text{-}C_6H_4SiMe_3\text{-}6)_2SiMe_2](thf)_3\}_\infty]$.[26b]

Results and discussion

Treatment of the appropriate 3-(trialkylsilyl)propene with $LiBu^n$ and tmen in equimolar amounts in hexane yielded the known compounds $[Li(\eta^3\text{-}C_3H_4SiR_3\text{-}1)(tmen)]$ (R = Me,[11] Ph[26] or $R_3 = Me_2Bu^t$[25]) ((i) in Scheme 1). From each (2 equivalents) and the appropriate dialkyldichlorosilane in hexane the *ansa*-bis(propene)s $R'_2Si(CH_2CH{=}CHSiR_3)_2$ **1**–**5** were obtained ((ii) in Scheme 1). Compounds **1**, **2** and **5** were purified by chromatography (Al_2O_3) and subsequent distillation under vacuum. Compounds **4** and **3** were crystallised from hexane and were stable in air.

The *ansa*-bis(propene)s **1**–**5** were characterised by ^1H and $^{13}C\{^1H\}$-NMR spectroscopy (Tables 1 and 2), mass spectrometry and elemental analysis. The ^1H and $^{13}C\{^1H\}$-NMR spectra showed the appropriate silyl and propenyl signals. The values of the coupling constants between the terminal (H-1) and the central (H-2) proton, in the range 12.3–23.7 Hz, indicate a *trans* arrangement about the C=C bond, as observed in the X-ray crystal structure of **4**. The molecular structure of crystalline $Me_2Si[CH_2CH{=}C(H)SiPh_3]_2$ **4**, Fig. 1, shows that each Si atom is in a tetrahedral environment. The C(2)–C(3) [1.310(5) Å] and C(5)–C(6) [1.313(5) Å] distances are within the range expected for a double bond and the C(1)–C(2) [1.506(5) Å] and C(4)–C(5) [1.461(5) Å] distances are surprisingly different but within the C_{sp2}–C_{sp3} range. Skeletal bond lengths (Å) and



Scheme 1 Reagents and conditions: (i) and (iii) $LiBu^n$, tmen, hexane, −78 °C to room temperature, 18 h; (ii) $SiCl_2R_2'$ *in situ*, 0 °C to room temperature, 18 h; (iv) **6**, $KOBu^t$, hexane, room temperature, 12 h.

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Table 1 ^{1}H-NMR spectral chemical shifts (δ) and coupling constants (J, Hz) in C_6D_6 (unless otherwise stated) at 298 K with assignments for **1**–**11**

Complex	SiR′$_3$	SiR$_2$	Allyl	tmen
1	0.10 (s, 18H)	−0.02 (s, 6H)	1.62 (d, 4H, J = 7.86) 5.53 (d, 2H, J = 21.0) 6.05 (dt, 2H)	
2^a	0.48 (s, 18H)	7.35–7.56 (m, 10H)	2.26 (d, 4H, J = 4.46) 5.55 (d, 2H, J = 12.30) 6.06 (dt, 2H)	
3	7.05–7.2 (m) 7.5–7.6 (m)		2.28 (d, 4H, J = 7.84) 4.86 (d, J = 16.87) 5.85 (dt, 2H)	
4^a	7.11–7.25 (m) 7.35–7.70 (m)	−0.10 (s, 6H)	1.66(d, 4H, J = 7.86) 5.53 (d, 2H, J = 21.00) 6.05 (dt, 2H)	
5	0.06 (s, 12H, SiMe$_2$) 0.94 (s, 18H, SiBu^t)	−0.01 (s, 6H)	1.65 (d, 4H, J = 6.67) 5.53 (d, 2H, J = 18.4) 6.08 (dt, 2H)	
6	0.38 (s, 18H)	0.44 (s, 6H)	2.74 (d, 2H, J = 15.54) 3.21 (d, 2H, J = 15.84) 7.11 (t, 2H, J = 15.84)	1.71 (s, 8H) 1.97 (s, 24H)
7	0.41 (s, 18H)	7.19–7.23 (m, H$_m$, H$_p$) 7.92–7.97 (d, H$_o$)	3.07 (d, 2H, J = 10.44) 3.25 (d, 2H, J = 10.50) 7.40 (t, 2H, J = 10.0)	1.66 (s, 8H) 1.90 (s, 24H)
8	7.10–7.25 (m) 7.94 (br)		2.76 (d, 2H, J = 15.9) 3.57 (d, 2H, J = 15.0) 7.07 (t, 2H, J = 15.01)	1.63 (s, 8H) 1.71 (s, 24H)
9	7.15–72.6 (m, 15H) 7.75–7.83 (m, 15H)	0.30 (s, 6H)	2.76 (d, 2H, J = 15.90) 3.59 (d, 2H, J = 16.30) 6.55 (m, 2H)	1.65 (s, 8H) 1.81 (s, 24H)
10	0.26 (s, 12H, SiMe$_2$) 1.20 (s, 18H, SiBu^t)	0.16 (s, 12H)	2.79 (d, 2H, J = 16.48) 2.87 (d, 2H, J = 16.56) 7.14 (t, 2H, J = 16.20)	1.65 (s, 8H) 1.84 (s, 24H)
11^b	0.10 (s, 18H)	−0.12 (s, 6H)	2.56 (m, 2H) 3.00 (d, 1H, J = 15.90) 3.05 (d, 1H, J = 15.90) 6.55 (m, 2H)	

^{a} In $CDCl_3$. ^{b} In thf-d_8.

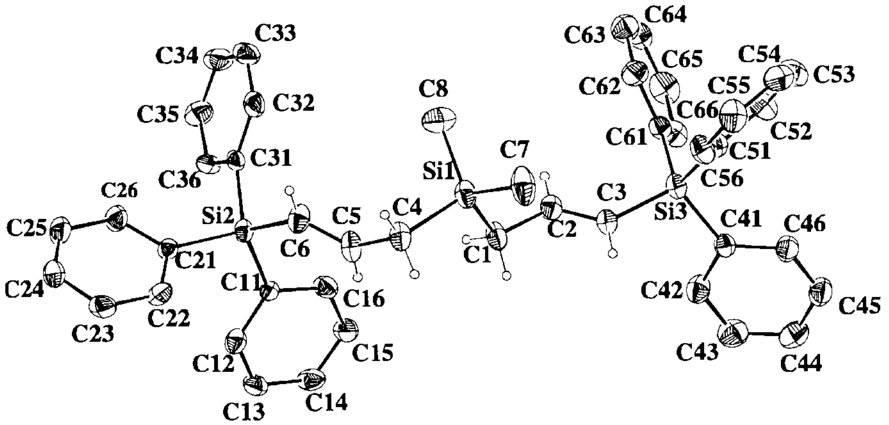
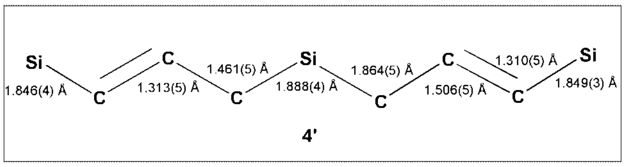


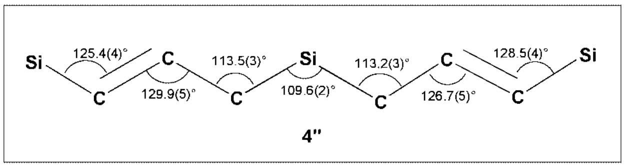
Fig. 1 Molecular structure and atom-labelling scheme for $Me_2Si[CH_2CH{=}C(H)SiPh_3]_2$ (**4**).

angles (°) are illustrated in **4′** and **4″**, respectively. Further bond lengths and angles are listed in Table 3.

The addition of LiBu^n to a stirred solution of each *ansa*-bis(propene) **1**–**5** in the presence of tmen in hexane yielded the appropriate complex $[\{Li(tmen)\}_2\{3\text{-}(\eta^3\text{-}C_3H_3SiR'_3\text{-}1)_2SiR_2\}]$ **6**–**10** ((iii) in Scheme 1).These *ansa*-bis(allyllithium) complexes were characterised by ^{1}H, ^{13}C{^{1}H} (Tables 1 and 2), ^{7}Li{^{1}H} NMR and mass spectra. Each ^{1}H-NMR spectrum showed the expected signals for the allylic protons: a doublet assigned to each terminal allyl proton (H-1 and H-1′) and a multiplet due to the central allylic proton (H-2 and H-2′). The coupling constant between a terminal and a central proton was in the range 12.3–23.7 Hz, indicating a *trans*-arrangement, as observed in the X-ray crystal structure of **6**. The NMR spectral data were consistent with the X-ray structure of **6**.



4′



4″

The molecular structure of crystalline $[\{Li(tmen)\}_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}]$ **6** is shown in Fig. 2 and selected bond lengths and angles are listed in Table 4. Crystalline **6** is a

Table 2 $^{13}C\{^1H\}$ and $^7Li\{^1H\}$ NMR spectral shifts (δ) in C_6D_6 (unless otherwise stated) at 298 K with assignments for **1**–**10**

		$^{13}C\{^1H\}$			
Complex	$^7Li\{^1H\}$	SiR'_3	SiR_2	Allyl	tmem
1		−0.66	−3.76	26.80 CH_2 128.92 CH 143.26 CH	
2[a]		−1.81 −1.08	127.69 C-*m*, 129.17 C-*p* 135.12 C-*o*, 141.84 C-*ipso*	25.43 CH_2 122.38 CH 149.56 CH	
3		128.18 C-*m*, 129.80 C-*p*, 136.15 C-*o*		21.53 CH_2 121.92 CH 135.01 CH	
4		127.70 C-*m* 129.30 C-*p* 135.86 C-*o* 149.71 C-*ipso*	−3.74	27.17 CH_2 121.92 CH 135.74 CH	
5		−5.65 $SiMe_2$ 26.77 $SiBu^t$	−3.76	26.99 CH_2 125.89 CH 144.75 CH	
6	−2.02	2.97	2.40	63.51 C-1 76.01 C-3 153.00 C-2	46.41 NMe_2 56.80 CH_2
7	−2.16		126.55 135.44 149.36	66.02 C-1 68.24 C-3 155.31 C-2	45.91 NMe_2 56.32 CH_2
8	0.57	127.68 C-*m*, 129.69 C-*p* 136.14 C-*o*, 149.48 C-*ipso*		46.42 C-1 70.55 C-3 142.41 C-2	45.88 NMe_2 55.81 CH_2
9		127.68 C-*m* 129.46 C-*p* 136.42 C-*o* 142.17 C-*ipso*	2.93	54.33 C-1 80.95 C-3 154.88 C-2	46.16 NMe_2 56.62 CH_2
10		−2.88 $SiMe_2$ 18.60 $SiBu^t$	−3.52	63.78 C-1 67.62 C-3 155.54 C-2	46.30 NMe_2 56.69 CH_2

[a] In $CDCl_3$.

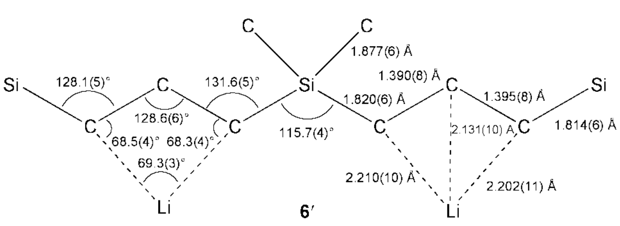
Table 3 Selected bond lengths [Å] and angles [°] for **4**

Si(1)–C(8)	1.850(5)	Si(1)–C(1)	1.864(5)
Si(1)–C(7)	1.866(4)	Si(1)–C(4)	1.888(4)
C(1)–C(2)	1.506(5)	C(2)–C(3)	1.310(5)
C(4)–C(5)	1.461(5)	C(5)–C(6)	1.313(5)
C(3)–S(2)–C(1)	126.7(5)	C(6)–C(5)–C(4)	129.9(5)
C(8)–Si(1)–C(1)	109.2(2)	C(2)–C(1)–Si(1)	113.2(3)
C(8)–Si(1)–C(7)	111.2(3)	C(1)–Si(1)–C(7)	109.5(2)
C(8)–Si(1)–C(4)	109.2(2)	C(1)–Si(1)–C(4)	109.6(2)
C(7)–Si(1)–C(4)	108.0(2)	C(6)–Si(2)–C(21)	110.0(2)

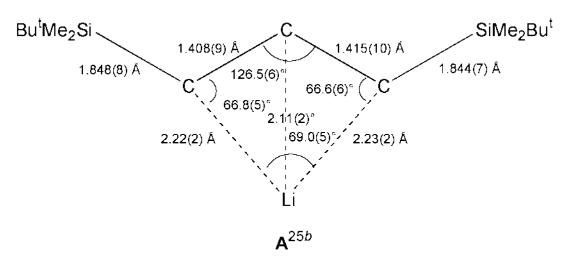
dinuclear complex with the η³-coordination mode of ligand to metal and an *exo*, *exo* orientation of the $SiMe_3$ groups. The molecule lies on a crystallographic 2-fold rotation axis. The two lithium atoms and their coordinated tmen ligands lie *anti* to one another; this maybe due to the greater steric hindrance between the two ligands in the alternative *syn*-configuration. The skeletal bond lengths (Å) and angles (°) are illustrated schematically in **6′** and are similar to those in $[\{Li(tmen)\}\{\eta^3\text{-}CH(CHSiMe_2Bu^t)_2\}]$ (**A**);[25] comparison with $[Li(tmen)\{\eta^3\text{-}CH(CHSiMe_3)_2\}]$[11] is less useful because of its less symmetrical structure. The dihedral angle in **6** between the planes LiC1C3/C1C2C3 is 66.3°, which compares with the ZrC1C3/C1C2C3 of 65.7° and ZrC4C6/C4C5C6 of 59.4° in **12**.

Treatment of $[\{Li(tmen)\}_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}]$ **6** with an equivalent amount of $KOBu^t$ in hexane at room temperature afforded a precipitate of the tmen-free *ansa*-bis(allyl)-dipotassium complex **11** ((iv) in Scheme 1). It was a white solid, insoluble in hexane or pentane and air-sensitive and was characterised by ¹H and $^{13}C\{^1H\}$ NMR and mass spectra.

When MCl_4 (M = Zr or Hf) was reacted with two equivalents of **6** or **11** in toluene at room temperature, followed by removal of the solvent and extraction with hexane,



6′



A[25b]

the crystalline compounds $[M\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}_2]$ (M = Zr **12** or Hf **13**) were obtained in good yield, eqns. (1) and (2).

$$\underset{\mathbf{11}}{2[K_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}]} + ZrCl_4 \longrightarrow \underset{\mathbf{12}}{[Zr\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}_2]} + 4KCl \quad (1)$$

$$\underset{\mathbf{6}}{2[\{Li(tmen)\}_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}]} + HfCl_4 \longrightarrow \underset{\mathbf{13}}{[Hf\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}_2]} + 4LiCl \quad (2)$$

Table 4 Selected bond lengths (Å) and angles (°) for **6**

Li–N(1)	2.093(10)	Li–N(2)	2.079(10)
Li–C(1)	2.210(10)	Li–C(2)	2.131(10)
Li–C(3)	2.202(11)	Si(1)–C(1)	1.820(6)
Si(1)–C(4)	1.877(6)	Si(2)–C(3)	1.814(8)
Si(2)–C(6)	1.837(9)	Si(2)–C(5)	1.844(8)
Si(2)–C(7)	1.870(8)	N(1)–C(8)	1.456(8)
N(1)–C(11)	1.463(8)	N(1)–C(10)	1.465(8)
N(2)–C(13)	1.428(9)	N(2)–C(12)	1.452(10)
N(2)–C(9)	1.458(9)	C(1)–C(2)	1.390(8)
C(2)–C(3)	1.395(8)	C(8)–C(9)	1.410(10)
N(2)–Li–N(1)	87.7(4)	N(2)–Li–C(2)	127.6(5)
N(1)–Li–C(2)	144.6(5)	N(2)–Li–C(3)	133.3(5)
N(1)–Li–C(3)	120.3(5)	C(2)–Li–C(3)	37.5(3)
N(2)–Li–C(1)	128.5(5)	N(1)–Li–C(1)	123.0(5)
C(2)–Li–C(1)	37.3(2)	C(3)–Li–C(1)	69.3(3)
C(1)–Si(1)–C(1)′	115.7(4)	C(1)–Si(1)–C(4)	112.6(3)
C(1)–Si(1)–C(4)′	106.7(3)	C(4)–Si(1)–C(4)′	101.7(4)
C(2)–C(1)–Si(1)	131.6(5)	C(2)–C(1)–Li	68.3(4)
Si(1)–C(1)–Li	127.5(4)	C(1)–C(2)–C(3)	128.3(6)
C(1)–C(2)–Li	74.4(4)	C(3)–C(2)–Li	74.0(4)
C(2)–C(3)–Si(2)	128.1(5)	C(2)–C(3)–Li	68.5(4)
Si(2)–C(3)–Li	128.9(4)		

Symmetry transformations used to generate equivalent atoms: $-x$, y, $-z + 1/2$.

Table 5 ^{1}H-NMR and [^{13}C{^{1}H}] spectral chemical shifts (δ) and coupling constants (J, Hz) in C_6D_6 with assignments for **12** and **13**

Complex	$SiMe_3$	$SiMe_2$	Allyl
12	0.28 (s, 36H) [0.97]	0.00 (s, 12H) [−5.22]	3.86 (d, 4H, J = 17.17) [76.41, C-1] 4.63 (d, 4H, J–11.43) [96.10, C-3] 6.88 (dd, 4H) [160.43, C-2]
13	0.29 (s, 36H) [1.34]	0.03 (s, 12H) [−5.12]	3.85 (d, 4H, J = 17.22) [71.85, C-1] 4.59 (d, 4H, J = 11.60) [95.43, C-3] 7.02 (dd, 4H) [164.09, C-2]

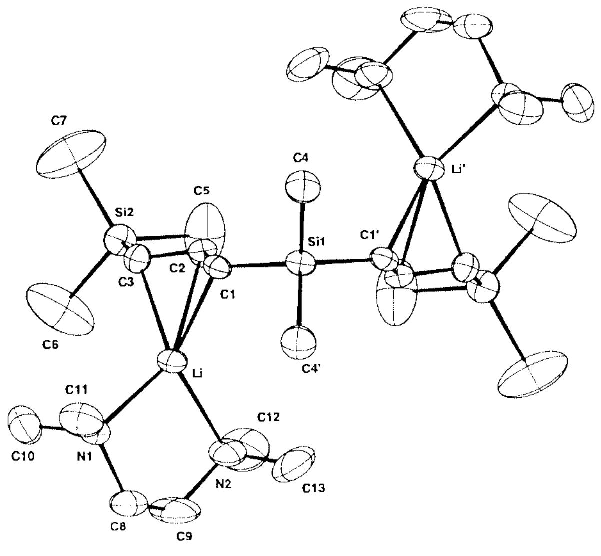


Fig. 2 Molecular structure and atom-labelling scheme for [{Li(tmen)}$_2${3-(η^3-$C_3H_3SiMe_3$-1)$_2SiMe_2$}] (**6**).

Complexes **12** and **13** were air-sensitive, yellow-brown, crystalline solids and were characterised by ^{1}H and ^{13}C{^{1}H} NMR (Table 5) and MS spectra (which showed the parent molecular ion as the highest m/z peak). The NMR spectra of **12** and **13** were very similar and showed η^3-allylic coordination to the metal centre, as verified in the X-ray crystal structure of **12**.

Table 6 Selected bond lengths [Å] and angles [°] for **12**

Zr–C(1)	2.594(5)	Zr–C(2)	2.516(5)
Zr–C(3)	2.462(5)	Zr–C(4)	2.488(5)
Zr–C(5)	2.525(5)	Zr–C(6)	2.462(5)
Si(1)–C(7)	1.846(6)	Si(1)–C(1)	1.846(5)
Si(1)–C(9)	1.854(6)	Si(2)–C(5)	1.859(6)
Si(2)–C(3)	1.822(6)	Si(2)–C(4)	1.844(6)
Si(2)–C(10)	1.868(6)	Si(2)–C11)	1.870(6)
C(1)–C(2)	1.381(7)	C(2)–C(3)	1.381(7)
C(4)–C(5)	1.355(7)	C(5)–C(6)	1.382(7)
C(1)–Zr–C(1)′	120.9(2)	C(2)–Zr–C(2)′	74.1(2)
C(3)–Zr–C(3)′	99.9(3)	C(4)–Zr–C(4)′	120.3(3)
C(5)–Zr–C(5)′	78.1(3)	C(6)–Zr–C(6)′	106.7(3)
C(6)–Zr–C(2)	123.6(2)	C(4)–Zr–C(2)	86.1(2)
C(3)–Zr–C(2)′	79.6(2)	C(6)–Zr–C(2)′	113.5(2)
C(3)–Zr–C(2)	32.2(2)	C(3)–Zr–C(6)′	137.1(2)
C(2)–Zr–C(5)	115.9(2)	C(2)–Zr–C(1)	31.3(2)
C(4)–C(5)–C(6)	126.2(6)	C(3)–C(2)–C(1)	127.7(5)
C(3)–C(2)–Zr	71.8(3)	C(1)–C(2)–Zr	77.5(3)
C(2)–C(3)–Si(2)	118.7(4)	C(5)–C(4)–Si(2)	121.7(5)
C(5)–C(6)–Si(3)	122.8(4)	Si(3)–C(6)–Zr	137.3(3)

Symmetry transformations used to generate equivalent atoms: $-x$, y, $-z + 1/2$.

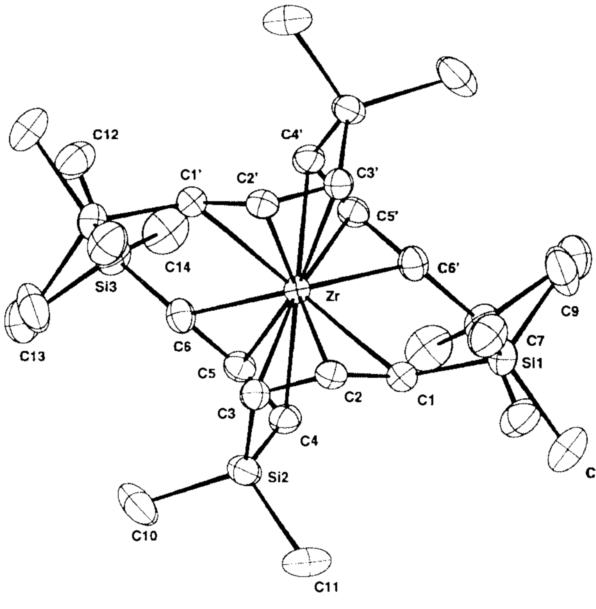
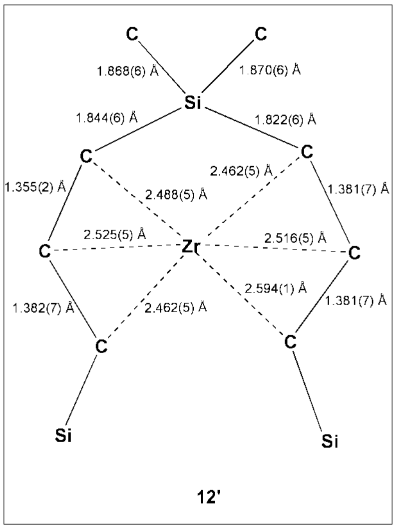


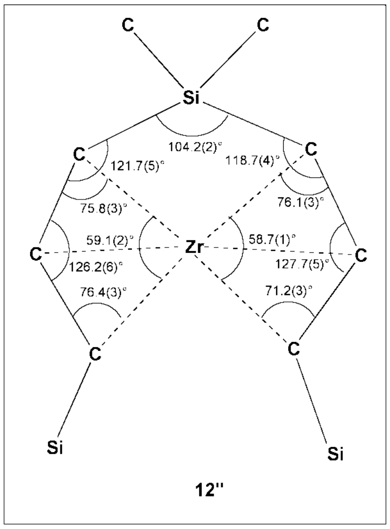
Fig. 3 Molecular structure and atom-labelling scheme for [Zr{3-(η^3-$C_3H_3SiMe_3$-1)$_2SiMe_2$}$_2$] (**12**).

The ^{1}H-NMR spectra in C_6D_6 showed three sets of allylic proton signals: a doublet for each terminal allylic proton (H-1 and H-1′) and a doublet of doublets for the central allylic protons (H-2 and H-2′).

The molecular structure of [Zr{3-(η^3-$C_3H_3SiMe_3$-1)$_2SiMe_2$}$_2$] **12** is shown in Fig. 3 and selected bond lengths and angles are listed in Table 6. Crystalline **12** is a mononuclear complex, the molecule lying on a crystallographic 2-fold rotation axis. Each of the two ligands binds to the metal atom in a bidentate chelating η^3-fashion. The skeletal bond lengths (Å) and angles (°) are illustrated schematically in **12**′ and **12**″, respectively and are available for comparison with similar data for [{Li(tmen)}$_2$-{3-(η^3-$C_3H_3SiMe_3$-1)$_2SiMe_2$}] **6**, shown in **6**′. The average C–C bond lengths in **12** of 1.376 Å are slightly shorter than the 1.393 Å in **6**. The C–C–C angles within the η^3-C_3 framework are similar: 128.6(6)° in **6** and a mean of 127.0° in **12**, but the C–Si(Me)$_2$–C angle in **12** of 104.2(2)° is significantly narrower than the 115.7(4)° in **6**, attributable to the chelating nature of the dianionic ligand in **12**. The Zr–C distances in **12** are unexceptional, with a mean of 2.50 Å for the C_α and C_γ atoms and 2.52 Å for Zr–C_β; these may be compared with correspond-



12'



12''

ing values of 2.46(1) and 2.51(1) Å in [Zr(η^5-C_5Me_5)(η^3-$C_3H_2Me_3$-1,2,3)Br_2].[27] However, unlike in **12**, the central metal–C_β bond distance in **6** is slightly shorter at 2.11 Å than the metal–$C_{\alpha\ \mathrm{or}\ \gamma}$ distance of 2.22 Å (*cf.* **6′**).

The polymerisation of C_2H_4 has been investigated using **12** as a catalyst in the presence of MAO as cocatalyst. At this time, the catalytic activity obtained at 70 °C was 53.16 or 51.48 kg mol^{-1} PE Zr^{-1} h^{-1} for a 500 : 1 or 1000 : 1 Al : Zr mole ratio, respectively. Further experiments are currently in progress and will be reported later, as also experiments on related allyls of tin(IV) and niobium(III).

Experimental

All reactions were performed under argon using standard Schlenk techniques. The thf and diethyl ether solvents were dried using sodium–benzophenone and hexane and pentane by use of potassium alloy. Allyl(trimethyl)silane, allyl(triphenyl)silane, dichloro(dimethyl)silane and dichloro(diphenyl)silane were purchased from Aldrich. The NMR spectra were recorded on Bruker AC-P250 or WM-360 instruments; the residual protio solvent resonances were taken as the internal reference for ^1H or ^{13}C spectra; LiCl (1 mol dm^{-3} aqueous solution) was the external reference for ^7Li NMR spectra. GC-MS data were recorded using an MD800 apparatus: EI 70 eV. Elemental analyses were carried out using a Perkin-Elmer 2400CHN microanalyser.

Preparations

$Me_2Si(CH_2CH{=}CHSiMe_3)_2$ 1. $LiBu^n$ (40 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 64 mmol) was added dropwise to a stirring solution of 3-(trimethylsilyl)propene (7.20 g, 63.2 mmol) and tmen (9.6 cm^3, 63.6 mmol) in hexane (50 cm^3) at −78 °C. The mixture was allowed to warm to room temperature and was stirred overnight. The solution was then treated dropwise with dichloro(dimethyl)silane (4.06 g, 32 mmol) at 0 °C. The mixture was stirred overnight at room temperature yielding a white solid and an orange solution. After filtration, tmen was removed by column chromatography (Al_2O_3) and the hexane eluent was evaporated; the residue was distilled *in vacuo* to produce the colourless compound **1** (8.04 g, 91%) (Found: C, 59.1; H, 12.47. $C_{14}H_{32}Si_3$ requires C, 59.1; H, 11.25%), bp 120–130 °C (0.5 mmHg), MS: $m/z = 284$ (M^+).

$Ph_2Si(C_3H_4SiMe_3$-1$)_2$ 2. $LiBu^n$ (20 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 32 mmol), was added dropwise at −78 °C with stirring to a solution of tmen (4.8 cm^3, 31.8 mmol) and allyl(trimethyl)silane (3.6 g, 31.6 mmol) in hexane (25 cm^3). The mixture was stirred overnight at room temperature, then treated dropwise with dichloro(diphenyl)silane (4.05 g, 16 mmol) at 0 °C and was stirred overnight at room temperature. A white solid and an orange solution were obtained. After filtration, tmen was removed from the filtrate by column chromatography (Al_2O_3) and the hexane eluent was evaporated. The residue was the complex **2** (4.95 g, 79%) (Found: C, 71.1; H, 9.33. $C_{24}H_{36}Si_3$ requires C, 70.6; H, 8.88%), MS: $m/z = 408$ (M^+).

$Ph_2Si(C_3H_4SiPh_3$-1$)_2$ 3. $LiBu^n$ (5 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 8 mmol) was added dropwise at −78 °C with stirring to a solution of tmen (1.2 cm^3, 8 mmol) and allyl(triphenyl)silane (2.40 g, 8 mmol) in hexane (25 cm^3). The mixture was allowed to warm to room temperature and was stirred overnight. A white solid and a yellow solution were formed. Dichloro(diphenyl)silane (1.01 g, 4 mmol) was added and the mixture was stirred for 15 h, yielding a white solid and a yellow solution. After filtration, the solution was concentrated. Crystallisation at −4 °C yielded the white crystalline complex **3** (1.71 g, 55%) (Found: C, 82.9; H, 6.95. $C_{14}H_{32}Si_3$ requires C, 83.1; H, 6.15%), mp 96 °C.

$Me_2Si(C_3H_4SiPh_3$-1$)_2$ 4. $LiBu^n$ (5 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 8 mmol) was added dropwise at −78 °C to a solution of tmen (1.2 cm^3, 8 mmol) and allyl(triphenyl)silane (2.40 g, 8 mmol) in hexane (25 cm^3). The mixture was allowed to warm to room temperature and was stirred for 3 days, then filtered to obtain the white solid [Li(η^3-$C_3H_3SiPh_3$-1)(tmen)] (3.06 g, 91%); a portion (3.0 g, 7.09 mmol) was treated with a solution of dichloro(dimethyl)silane (0.47 g, 3.55 mmol) in thf (25 cm^3) at −78 °C and was stirred overnight at room temperature. After work-up, all volatiles were removed and the residue was treated with hexane. The extract was concentrated to give the white solid **4** (2.16 g, 61%) (Found: C, 79.0; H, 6.99. $C_{44}H_{44}Si_3$ requires C, 80.5; H, 6.70%), mp 119 °C, MS: $m/z = 656$ (M^+).

$Me_2Si(C_3H_4SiMe_2Bu^t$-1$)_2$ 5. $LiBu^n$ (1.19 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 1.91 mmol) was added dropwise at −78 °C with stirring to a solution of tmen (0.28 cm^3, 1.41 mmol) and (*tert*-butyl)(dimethyl)allylsilane (0.30 g, 1.91 mmol) in hexane (25 cm^3). The mixture was allowed to warm to room temperature and was stirred overnight. A white solid and a yellow solution had formed. Dichloro(dimethyl)silane (0.12 g, 0.96 mmol) was added and the mixture was stirred for 15 h. A pale brown solid and a yellow solution were obtained. After filtration, tmen was removed by column chromatography (Al_2O_3) and the hexane eluent was evaporated. The residue was the complex **5** (0.48 g, 99%) (Found: C, 65.2; H, 13.27. $C_{20}H_{44}Si_3$ requires C, 65.2; H, 11.94%).

[{Li(tmen)}$_2${3-(η^3-$C_3H_3SiMe_3$-1$)_2SiMe_2$}] 6. $LiBu^n$ (8.85 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 14.08 mmol) was added dropwise at −78 °C to a stirring solution of **1** (2.00 g, 7.04 mmol) and tmen (2.12 cm^3, 14.08 mmol) in hexane (25 cm^3). The mixture was stirred overnight at room temperature. After filtration, all volatiles were removed from the filtrate *in vacuo*. The resultant orange oil was redissolved in hexane (10 cm^3), concentrated and cooled. Colourless crystals of complex **6** (1.52 g, 41%) were isolated by filtration and dried *in vacuo*.

[{Li(tmen)$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiPh$_2$}] 7. LiBu^n (3.06 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 4.89 mmol) was added dropwise at −78 °C with stirring to a solution of **2** (1 g, 1.28 mmol) and tmen (0.73 cm^3, 4.89 mmol) in hexane (25 cm^3) and was stirred overnight at room temperature. After filtration, all volatiles were removed under reduced pressure. The oily residue was treated with pentane and cooled. The yellow solid complex **7** (0.58 g, 36%) was isolated by filtration and dried *in vacuo*. MS: $m/z = 652$ (M$^+$).

[{Li(tmen)}$_2${3-(η^3-C$_3$H$_3$SiPh$_3$-1)$_2$SiPh$_2$}] 8. LiBu^n (1.6 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 2.56 mmol) was added dropwise at −78 °C with stirring to a solution of complex **3** (1.0 g, 1.28 mmol) and tmen (0.38 cm^3, 2.56 mmol) in hexane (25 cm^3) and was stirred overnight at room temperature. A yellow solid had formed, which was filtered off, washed with additional hexane and dried *in vacuo* to obtain the complex **8** (0.93 g, 71%).

[{Li(tmen)}$_2${3-(η^3-C$_3$H$_3$SiPh$_3$-1)$_2$SiMe$_2$}] 9. LiBu^n (2.02 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 3.24 mmol) was added dropwise at −78 °C with stirring to a solution of complex **4** (1.0 g, 1.62 mmol) and tmen (0.49 cm^3, 3.24 mmol) in hexane (25 cm^3). The mixture was stirred overnight at room temperature. A yellow-white precipitate was obtained from the yellow solution. The solid was filtered off, washed with hexane and dried, yielding the white solid complex **9** (1.35 g, 97%).

[{Li(tmen)}$_2${3-(η^3-C$_3$H$_3$SiMe$_2$Bu^t-1)$_2$SiMe$_2$}] 10. LiBu^n (3.18 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 5.08 mmol) was added dropwise at −78 °C with stirring to a solution of complex **5** (1.29 g, 2.54 mmol) and tmen (0.77 cm^3, 5.09 mmol) in hexane (25 cm^3). The mixture was stirred overnight at room temperature. A yellow solution was obtained; solvent was removed to obtain the very labile complex **10** as an orange oil.

[K$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$}] 11. KOBu^t (0.70 g, 5.98 mmol, 95%) was added at room temperature to a stirring hexane (25 cm^3) solution of complex **6** (1.58 g, 2.99 mmol). After several minutes a white precipitate had formed and stirring was continued for 18 h. The mixture was filtered; the precipitate was washed with hexane and dried *in vacuo* to afford the white solid **11** (0.83 g, 77%), MS: $m/z = 360$ (M$^+$).

[Zr{3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$}] 12. ZrCl$_4$ (0.09 g, 0.38 mmol) was added to a solution of [K$_2${3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$-SiMe$_2$}] (0.28 g, 0.77 mmol) in toluene (25 cm^3) at room temperature. The yellow solution became red immediately; the mixture was stirred overnight. Solvent was removed *in vacuo* and the remaining deep red oil was treated with pentane. The crystalline complex **12** (0.10 g, 80%) (Found: C, 51.8; H, 9.21. C$_{28}$H$_{60}$Si$_6$Zr requires C, 51.3; H, 9.14%), was obtained after filtration and was dried *in vacuo*.

[Hf{3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$SiMe$_2$}$_2$] 13. HfCl$_4$ (0.19 g, 0.59 mmol, 98%) was added to a solution of the lithium salt **6** (0.62 g, 1.18 mmol) in toluene (25 cm^3) at room temperature. The yellow solution changed to red immediately; the mixture was stirred overnight. Solvent was removed *in vacuo* and the remaining deep red oil was treated with pentane. The crystalline solid complex **13** (0.34 g, 78%) was obtained after filtration and was dried *in vacuo*.

Table 7 Crystal data and refinement for complexes **4**, **6** and **12**

	4	**6**	**12**
Formula	C$_{44}$H$_{44}$Si$_3$	C$_{26}$H$_{62}$Li$_2$N$_4$Si$_3$	C$_{28}$H$_{60}$Si$_6$Zr
M	657.06	529.0	656.52
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a/Å	17.037(2)	17.496(6)	11.512(2)
b/Å	11.300(7)	13.420(7)	17.267(3)
c/Å	20.304(1)	16.247(6)	19.367(2)
β/°	93.86(1)	99.78(3)	103.39(2)
U/Å	3900(3)	3759(3)	3745.1(1)
Z	4	4	4
μ(Mo-K$_\alpha$)	0.15	0.14	0.50
T/K	293	173(2)	293(2)
Total reflections	9360	3397	4830
Independent reflections	9360	3293	4622
Reflections with $I > 2\sigma(I)$	1963	1591	2835
$R1$ [$I > 2\sigma(I)$]	0.0551	0.090	0.0627
$wR2$ (all data)	0.1222	0.273	0.1661

Polymerisation of ethylene with [Zr{3-(η^3-C$_3$H$_3$SiMe$_3$-1)$_2$-SiMe$_2$}$_2$] 12. A toluene solution (125 cm^3) of **12** (either (i) 6.58 mg (10 µmol) of **12** and 9.97 µmol of Zr, or (ii) 3.29 mg (5 µmol) of **12** and 4.93 µmol of Zr) and a 10% solution of MAO (9.79 g, 10% in toluene,10 µmol, 455 mg Al) (Al/Zr = 500 or 1000 respectively) was pressurised with ethylene at 70 °C for 1 h, whereafter the mixture was quenched by addition of methanolic HCl (10 : 1). The gummy polymer was filtered off, washed successively with 1 M aq. HCl, water and MeOH dried at 60 °C for 2 h and weighed. The activity corresponded to 53.16 kg PE mol^{-1} Zr^{-1} h^{-1} for (i) or 51.48 Kg PE mol^{-1} Zr^{-1} h^{-1} for (ii) (530 mg for each).

Crystal data

X-Ray crystallographic studies. Crystallographic details are given in Table 7. Single crystals of the *ansa*-bis(propene) **4** were obtained from a hexane solution at room temperature. Crystals of the *ansa*-bis(allyl)lithium compound **6** were grown from a pentane solution at 253 K; while those of the zirconium compound **12** were obtained from a mixture of CH$_2$Cl$_2$ and pentane at 253 K. Diffraction data were collected on a Nonius Mach3 (**4**) or Enraf-Nonius CAD4 (**6** and **12**) diffractometer, using monochromatic Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) in the θ–2θ mode. The structures of **4**, **6** and **12** were solved by direct methods (SIR-92[28] for **4** and SHELXS-86[29] for **6** and **12**) and refined by full-matrix, least-squares on all F^2 (SHELXL-93).[30] All non-H-atoms were anisotropic. Hydrogen atoms were included in riding mode, except for the allyl hydrogen atoms which were freely refined.

CCDC reference number 186/1926.

See http://www.rsc.org/suppdata/dt/b0/b000451k/ for crystallographic files in .cif format.

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