Mono(η-cyclopentadienyl)benzamidinato Alkyl Compounds of Titanium and Zirconium†

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The compounds $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}_2Cl]$, $[\{Zr(\eta\text{-}C_5H_5)[CPh(NSiMe_3)_2]Cl\}_2\{\mu\text{-}CPh(NSiMe_3)_2\}]$ $[\{Zr(\eta\text{-}C_5H_5)[CPh(NSiMe_3)_2]Cl\}_2(\mu\text{-}O)]$, $[Zr(\eta\text{-}C_5R_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)Cl]$ (R = H or Me), $[Zr(\eta\text{-}C_5R_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)_2]$ (R = H or Me) and $[M(\eta\text{-}C_5R_5)\{CPh(NSiMe_3)_2\}Me_2]$ (M = Zr, R = H or Me; M = Ti, R = H have been synthesized and the crystal structures of three of them) determined.

We have recently described the benzamidinato-chloro compounds $[M(\eta\text{-}C_5R_5)\{CPh(NSiMe_3)_2\}Cl_2]$ (R = H, M = Ti, Zr or Hf; R = Me, M = Ti or Zr).[1] Here we describe the synthesis of new η-cyclopentadienyl-alkyl and related derivatives of these benzamidinato compounds. A preliminary account of part of this work has been published.[2]

Results and Discussion

Treatment of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (dme = 1,2-dimethoxyethane) in diethyl ether with 2 equivalents of $Li[CPh(NSiMe_3)_2]$ **1** gave a mixture of white crystals of $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}_2Cl]$ **4** and pale yellow crystals of $[\{Zr(\eta\text{-}C_5H_5)[CPh(NSiMe_3)_2]Cl\}_2\{\mu\text{-}CPh(NSiMe_3)_2\}_2]$ **5**. Alternatively, treatment of a solution of $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **2** in diethyl ether with 1 equivalent of $Li[CPh(NSiMe_3)_2]$ also gave a mixture of **4** and **5** (*ca.* 2:1). The separation of **4** and **5** was achieved by recrystallization from diethyl ether or light petroleum, respectively. The analytical and spectroscopic data which characterize these and all the other new compounds described below are given in Table 1. The ^1H and ^{13}C NMR spectra of compounds **4** and **5** contain four upfield resonances corresponding to four different $SiMe_3$ groups surrounding the zirconium atom. Compound **4** also exhibits two sets of downfield bands assigned to two different benzamidinato ligands. In contrast **5** shows three sets of resonances which can be attributed to three different pseudoallylic fragments (see Table 1). These data are consistent with an octahedral geometry around the metal centre similar to that found in the analogous acetylacetonate (acac) derivative $[Zr(\eta\text{-}C_5H_5)(acac)_2Cl]$.[3] On the basis of the analytical and spectroscopic data we propose a monomer structure for **4** with two different chelating benzamidinato ligands. For **5** we suggest a dimeric structure with two equivalent benzamidinato ligands and also two different benzamidinato bridges: the proposed structures are shown in Scheme 1.

Treatment of $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **3** with $Li[CPh(NSiMe_3)_2]$ gave no reaction. However, treatment of $[Zr(\eta\text{-}C_5Me_5)Cl_3]\cdot 2$thf (thf = tetrahydrofuran) with 2 equivalents of $Li[CPh(NSiMe_3)_2]$ gave a mixture of compounds **3** and **1**.

When a solution of the mixture of **4** and **5** in light petroleum was treated with a small quantity of water, pale yellow crystals of the oxo-bridged dimer $[\{Zr(\eta\text{-}C_5H_5)[CPh(NSiMe_3)_2]Cl\}_2(\mu\text{-}O)]$ **6** were formed in good yield. The crystal structure of **6** is described below.

When a solution of $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **2** in diethyl ether at −30 °C was treated with 1 equivalent of $Mg(CH_2Ph)Cl$ the monobenzyl derivative $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)Cl]$ **7** was formed as a brown oil. However, when compound **2** was treated with a suspension of 2 equivalents of benzylpotassium in benzene the bis(benzyl) compound $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)_2]$ **9** was isolated as a brown-yellow solid. Alternatively, treatment of $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)Cl]$ **7** in diethyl ether with $Mg(CH_2Ph)Cl$ also gave **9**.

Treatment of the previously reported[1] $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **3** in diethyl ether at −30 °C with 1 equivalent of $Mg(CH_2Ph)Cl$ gave the mono(benzyl) compound $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)Cl]$ **8** as a brown solid. In a manner similar for compound **9**, treatment of $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **3** with 2 equivalents of benzylpotassium gave $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)_2]$ **10**, as a brown-yellow solid. Compound **10** could also be prepared from $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}(CH_2Ph)Cl]$ **8** and 1 equivalent of benzylpotassium in benzene.

Compound $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **2** in diethyl ether at −30 °C was treated with 2 equivalents of MgMeBr giving brown-yellow crystals of the dimethyl derivative $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Me_2]$ **11**. The crystal structure of **11** is described below. Likewise, treatment of $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **3** in diethyl ether at −30 °C with 2 equivalents of MgMeBr gave white crystals of $[Zr(\eta\text{-}C_5Me_5)\{CPh(NSiMe_3)_2\}Me_2]$ **12**.

A striking feature of the NMR data for compounds **7**–**12** is the chemical shifts of the methylene and methyl groups. These are shifted downfield compared to the analogues $[Zr(\eta\text{-}C_5Me_5)_2Me_2]$[4] or $[Zr(\eta\text{-}C_5Me_5)Me_3]$[5] and are in the range found for the salt-like compounds $[(\eta\text{-}C_5R_5)_2MeZr(\mu\text{-}Me)\{B(C_6F_5)_3\}]$[6] (R = H or Me) and in the cations of $[ZrMe(\eta\text{-}C_5H_5)_2(thf)][B(C_6H_4F)_4]$.[7] This implies that the hard basic benzamidinato ligand can act as a strong electron-withdrawing group inducing a high electrophilicity on the metal centre.

In contrast to the synthesis of compound **11** described above, treatment of $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **2** with 2 equivalents of LiMe in diethyl ether at −30 °C gave a brown-orange solid which the physical data show to be a 1:1 mixture of $[Zr\{CPh(NSiMe_3)_2\}_2Me_2]$[8] and $[Zr(\eta\text{-}C_5H_5)_2Me_2]$.[4] We

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data[a]

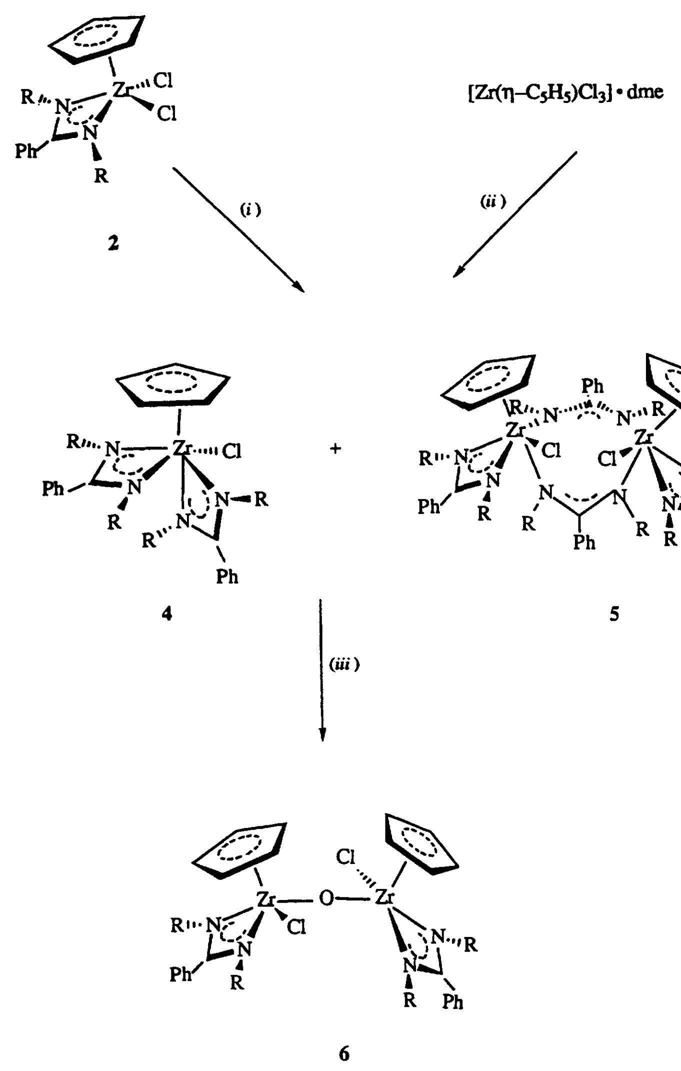
Compound	NMR[b] data
4 White C: 52.1 (51.8) H: 7.3 (7.1) N: 8.4 (7.8) Cl: 4.8 (4.9)	^{1}H: 7.40–6.94 (10 H, m, C$_6$H$_5$), 6.72 (5 H, s, C$_5$H$_5$), 0.19 (2 × 9 H, s, SiMe$_3$), 0.10 (9 H, s, SiMe$_3$), 0.00 (9 H, s, SiMe$_3$) ^{1}H:[c] 7.34 (10 H, m, C$_6$H$_5$), 6.57 (5 H, s, C$_5$H$_5$), 0.00 (9 H, s, SiMe$_3$), −0.01 (9 H, s, SiMe$_3$), −0.09 (9 H, s, SiMe$_3$) −0.11 (9 H, s, SiMe$_3$) ^{13}C:[c] 181.8 [*C*Ph(NSiMe$_3$)$_2$], 177.2 [*C*Ph(NSiMe$_3$)$_2$], 141.3 (C$_{ipso}$, C$_6$H$_5$), 140.5 (C$_{ipso}$, C$_6$H$_5$), 129.0 (*p*-C$_6$H$_5$), 128.8 (*p*-C$_6$H$_5$), 128.1, 127.7, 126.9 (C$_6$H$_5$),[d] 115.0 (C$_5$H$_5$), 4.0 (SiMe$_3$), 3.7 (SiMe$_3$), 3.2 (SiMe$_3$), 2.6 (SiMe$_3$)
5 Pale yellow C: 53.7 (51.8) H: 7.2 (7.1) N: 8.4 (7.8) Cl: 5.0 (4.9)	^{1}H: 7.44–6.94 (20 H, m, C$_6$H$_5$), 6.63 (10 H, s, C$_5$H$_5$), 0.25 (18 H, s, SiMe$_3$), 0.21 (18 H, s, SiMe$_3$), 0.18 (18 H, s, SiMe$_3$), 0.16 (18 H, s, SiMe$_3$) ^{1}H:[c] 7.40, 7.15 (20 H, m, C$_6$H$_5$), 6.41 (10 H, s, C$_5$H$_5$), 0.01 (18 H, s, SiMe$_3$), −0.01 (18 H, s, SiMe$_3$), −0.03 (36 H, s, SiMe$_3$) ^{13}C:[c] 178.2 [*C*Ph(NSiMe$_3$)$_2$], 176.8 [*C*Ph(NSiMe$_3$)$_2$], 165.3 [*C*Ph(NSiMe$_3$)$_2$], 142.6 (C$_{ipso}$, C$_6$H$_5$), 140.7 (C$_{ipso}$, C$_6$H$_5$), 139.0 (C$_{ipso}$, C$_6$H$_5$), 128.9, 128.7, 128.4, 128.2, 127.6, 127.0, 126.8, 126.5 (C$_6$H$_5$),[d] 115.0 (C$_5$H$_5$), 3.3 (SiMe$_3$), 3.0 (SiMe$_3$), 2.2 (SiMe$_3$), 1.0 (SiMe$_3$)
6 Pale yellow C: 46.6 (46.7) H: 6.0 (6.05) N: 6.00 (6.05) Cl: 7.5 (7.7)	^{1}H:[c] 7.37–7.15 (10 H, m, C$_6$H$_5$), 6.52 (10 H, s, C$_5$H$_5$), −0.14 (36 H, s, SiMe$_3$)
7 Yellow-brown C: 55.05 (55.0) H: 6.7 (6.4) N: 5.5 (5.1) Cl: 6.2 (6.5)	^{1}H: 7.42 (2 H, d, J_{HH} 7.8, *o*-CH$_2$C$_6$*H*$_5$), 7.25 (2 H, t, J_{HH} 7.6, *m*-CH$_2$C$_6$*H*$_5$), 6.95–6.73 (6 H, m, C$_6$H$_5$), 6.32 (5 H, s, C$_5$H$_5$), 2.49 (1 H, d, J_{HH} 11.1, CH$_2$), 2.31 (1 H, d, J_{HH} 11.1, CH$_2$), −0.08 (2 × 9 H, s, SiMe$_3$) ^{1}H:[c] 7.41–7.00 (10 H, m, C$_6$H$_5$), 6.52 (5 H, s, C$_5$H$_5$), 2.29 (1 H, d, J_{HH} 11.0, CH$_2$), 2.14 (1 H, d, J_{HH} 11.1, CH$_2$), −0.12 (2 × 9 H, s, SiMe$_3$) ^{13}C: 182.2 [*C*Ph(NSiMe$_3$)$_2$], 146.3 (C$_{ipso}$, CH$_2$*C*$_6$H$_5$), 139.0 (C$_{ipso}$, C$_6$H$_5$), 129.4 (*o*-CH$_2$*C*$_6$H$_5$), 129.1 (C$_6$H$_5$), 128.4 (C$_6$H$_5$), 128.1 (C$_6$H$_5$), 126.4 (*m*-CH$_2$*C*$_6$H$_5$), 121.9 (*p*-CH$_2$*C*$_6$H$_5$), 114.7 (C$_5$H$_5$), 72.1 (CH$_2$), 2.6 (SiMe$_3$)
8 Orange-brown C: 58.2 (58.5) H: 6.9 (7.3) N: 4.4 (4.5) Cl: 5.9 (5.8)	^{13}C:[e] 183.8 [*C*Ph(NSiMe$_3$)$_2$], 148.1 (C$_{ipso}$, CH$_2$*C*$_6$H$_5$), 139.1 (C$_{ipso}$, C$_6$H$_5$), 129.1 (CH$_2$*C*$_6$H$_5$),[d] 129.0 (C$_6$H$_5$),[d] 123.9 (*C*$_5$Me$_5$) 122.0 (*p*-CH$_2$*C*$_6$H$_5$), 74.9 (CH$_2$), 12.3 (C$_5$*Me*$_5$), 4.4 (SiMe$_3$), 2.9 (SiMe$_3$)
9 Yellow-brown C: 63.4 (63.9) H: 6.9 (7.0) N: 4.6 (4.65)	^{1}H:[c,e] 7.20 (4 H, t, J_{HH} 7.6, *m*-CH$_2$C$_6$*H*$_5$), 7.39–7.13 (5 H, m, C$_6$H$_5$), 7.02 (4 H, d, J_{HH} 7.2, *o*-CH$_2$C$_6$*H*$_5$), 6.88 (2 H, t, J_{HH} 7.3, *p*-CH$_2$C$_6$*H*$_5$), 6.18 (5 H, s, C$_5$H$_5$), 2.14 (2 H, d, J_{HH} 11.1, CH$_2$), 1.98 (2 H, d, J_{HH} 11.1, CH$_2$), −0.02 (9 H, s, SiMe$_3$), −0.14 (2 × 9 H, s, SiMe$_3$) ^{13}C: 183.5 [*C*Ph(NSiMe$_3$)$_2$], 149.8 (C$_{ipso}$, CH$_2$*C*$_6$H$_5$), 140.2 (C$_{ipso}$, C$_6$H$_5$), 129.0 (C$_6$H$_5$), 128.8 (*o*-CH$_2$*C*$_6$H$_5$), 126.7 (*m*-CH$_2$*C*$_6$H$_5$), 126.4 (C$_6$H$_5$),[d] 121.6 (*p*-CH$_2$*C*$_6$H$_5$), 114.5 (C$_5$H$_5$), 72.8 (CH$_2$), 2.9 (SiMe$_3$)
10 Orange C: 66.3 (66.15) H: 7.8 (7.7) N: 4.2 (4.2)	^{13}C:[e] 184.5 [*C*Ph(NSiMe$_3$)$_2$], 150.7 (C$_{ipso}$, CH$_2$*C*$_6$H$_5$), 139.4 (C$_{ipso}$, C$_6$H$_5$), 129.0 (C$_6$H$_5$),[d] 122.1 (*C*$_5$Me$_5$) 121.9 (*p*-CH$_2$-*C*$_6$H$_5$),[d] 77.8 (CH$_2$), 12.3 (C$_5$*Me*$_5$), 3.7 (SiMe$_3$)
11 Pale yellow C: 53.3 (53.4) H: 7.5 (7.6) N: 6.4 (6.2)	^{1}H: 6.97–6.94 (5 H, m, C$_6$H$_5$), 6.36 (5 H, s, C$_5$H$_5$), 0.59 (6 H, s, CH$_3$), −0.10 (2 × 9 H, s, SiMe$_3$) ^{1}H:[c] 7.39–7.30 (5 H, m, C$_6$H$_5$), 6.47 (5 H, s, C$_5$H$_5$), 0.09 (6 H, s, CH$_3$), −0.19 (2 × 9 H, s, SiMe$_3$) ^{13}C: 181.9 [*C*Ph(NSiMe$_3$)$_2$], 139.9 (C$_{ipso}$, C$_6$H$_5$), 128.7 (C$_6$H$_5$), 126.6 (C$_6$H$_5$),[d] 112.4 (C$_5$H$_5$), 45.7 (CH$_3$), 2.5 (SiMe$_3$) ^{13}C:[c] 181.8 [*C*Ph(NSiMe$_3$)$_2$], 139.9 (C$_{ipso}$, C$_6$H$_5$), 128.8 (C$_6$H$_5$), 126.7 (C$_6$H$_5$),[d] 112.3 (C$_5$H$_5$), 44.3 (CH$_3$), 2.1 (SiMe$_3$)
12 White C: 57.7 (57.8) H: 8.6 (8.5) N: 5.2 (5.4)	^{1}H: 7.20–6.90 (5 H, m, C$_6$H$_5$), 2.09 (15 H, s, C$_5$Me$_5$), 0.49 (6 H, s, CH$_3$), −0.06 (2 × 9 H, s, SiMe$_3$) ^{13}C: 184.0 [*C*Ph(NSiMe$_3$)$_2$], 139.9 (C$_{ipso}$, C$_6$H$_5$), 129.0 (C$_6$H$_5$), 128.6 (C$_6$H$_5$),[d] 120.5 (*C*$_5$Me$_5$), 47.6 (CH$_3$), 12.2 (C$_5$*Me*$_5$), 3.3 (SiMe$_3$)
14 Orange C: 59.6 (59.1) H: 8.6 (8.4) Ti: 11.65 (11.8)	^{1}H: 7.24–7.10 (5 H, m, C$_6$H$_5$), 6.45 (5 H, s, C$_5$H$_5$), 1.20 (6 H, s, CH$_3$), −0.03 (2 × 9 H, s, SiMe$_3$) ^{13}C: 178.7 [*C*Ph(NSiMe$_3$)$_2$], 139.4 (s, C$_{ipso}$, C$_6$H$_5$), 128.6 (d, C$_6$H$_5$, $^{1}J_{CH}$ 161.0), 128.0 (d, C$_6$H$_5$, $^{1}J_{CH}$ 161.0), 126.9 (d, C$_6$H$_5$, $^{1}J_{CH}$ 161.5), 115.3 (dt, C$_5$H$_5$, $^{1}J_{CH}$ 174.0, $^{2}J_{CH}$ 6.5), 2.6 (q, SiMe$_3$, $^{1}J_{CH}$ 118.5)

[a] Unless otherwise stated analytical data given as: found (calc.) %. ^{1}H NMR at 300 MHz, ^{13}C at 75 MHz. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), relative intensity, coupling constant (in Hz) and assignment. [b] At 25 °C in [^{2}H$_6$]benzene. [c] In [^{2}H$_2$]dichloromethane. [d] Rest of the signals overlapping. [e] For ^{1}H data in C$_6$D$_6$ see ref. 2.

believe that this intermolecular ligand-exchange reaction is catalysed by traces of excess of LiMe. In support of this proposal we found that when LiMe was used in an exact 1:2 ratio only **11** was formed. Further, treatment of **2** with an excess of the weaker nucleophile MgMeCl gave **11** in very high yield and only traces of the ligand-exchange reaction occurred.

The crystal structures of complexes **6** and **11** have been determined. The structure determination shows that in the solid state both compounds are composed of discrete molecules with no intermolecular contacts closer than the sum of the appropriate van der Waals radii. Perspective views of complexes **6** and **11** with the atom numbering scheme are shown in Figs. 1 and 2, respectively. Selected intramolecular distances and angles are listed in Tables 2 and 3 respectively and fractional atomic coordinates in Tables 4 and 5.

The main geometrical features of complexes **6** and **11** are very similar to those for **2**.[1] The most noticeable differences are an increase in the Zr–Cp (cyclopentadienyl centroid) distance from 2.186 Å in **2** to 2.225 and 2.216 Å in **6** and **11** and an elongation of the Zr–Cl bond from 2.4212(9) Å in **2** to 2.4662(6) Å in **6**. In both **6** and **11** the four-membered ZrN$_2$C rings are slightly puckered: the dihedral angle between the planes N(1)ZrN(2) and N(1)C(1)N(2) are 6.6 and 17.1° respectively. The C(2)–C(7) phenyl rings lie orthogonal to the



Scheme 1 R = $SiMe_3$. Reagents and conditions: (*i*) Li[CPh($NSiMe_3$)$_2$] (1 equivalent), diethyl ether, room temperature (r.t.), 12 h; (*ii*) Li[CPh($NSiMe_3$)$_2$] (2 equivalents), diethyl ether, r.t., 12 h; (*iii*) H_2O, light petroleum (b.p. 40–60 °C), r.t.

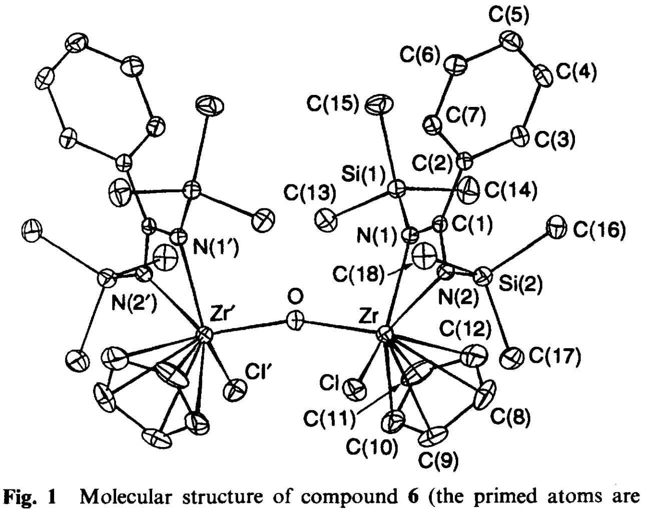


Fig. 1 Molecular structure of compound **6** (the primed atoms are generated from the asymmetric unit using the two-fold axis). Hydrogen atoms are omitted for clarity

four-membered ring, forming dihedral angles of 83.6 and 88.5° for **6** and **11**, respectively.

The Zr–O bond length 1.9466(3) Å in the symmetrical Zr–O–Zr linkage of **6** is close to the values of 1.948(1) Å for [{Zr(η-C_5H_5)$_2$Me}$_2$(μ-O)],[9] 1.945(10) Å for [{Zr(η-C_5H_5)$_2$Cl}$_2$(μ-O)][10] and 1.966(3) Å for [{Zr(η-C_5H_5)$_2$(SC_6H_5)}$_2$(μ-O)].[11] The Zr–O–Zr' bond angle of 163.1(1)° in **6** is comparable with the corresponding values of 174.1(3), 168.9(8) and 165.5(8)° respectively in the compounds given above.

We have also synthesized the analogous dimethyl titanium derivative of **11**. Treatment of a toluene solution of [Ti(η-C_5H_5){CPh($NSiMe_3$)$_2$}Cl_2] **13** with 2 equivalents of LiMe at −80 °C, followed by warming to room temperature affords the corresponding dimethyl complex [Ti(η-C_5H_5){CPh($NSiMe_3$)$_2$}Me_2] **14** (Scheme 2). Recrystallization from pentane yielded pure **14** as thermally sensitive orange crystals. The thermolysis of **14** in benzene was studied by ^1H NMR spectroscopy (75 °C) and showed the formation of methane while in the ^1H NMR spectrum broad resonances appear, apparently due to the formation of paramagnetic products. Similar products are found in the thermal decomposition of analogous dimethyl titanocene complexes.[12]

Crystals of complex **14** suitable for X-ray diffraction study were grown by the slow cooling of a saturated pentane solution at −30 °C. As can be seen from Fig. 3 complex **14** consists of a distorted tetrahedral titanium atom formed by the η-cyclopentadienyl, benzamidinato and two methyl ligands [Cp–Ti–C(6) 129.23(7), Cp–Ti–C(13) 108.67(7), Cp–Ti–C(14) 112.68(7), C(6)–Ti–C(13) 107.98(5), C(6)–Ti–C(14) 104.72(7),

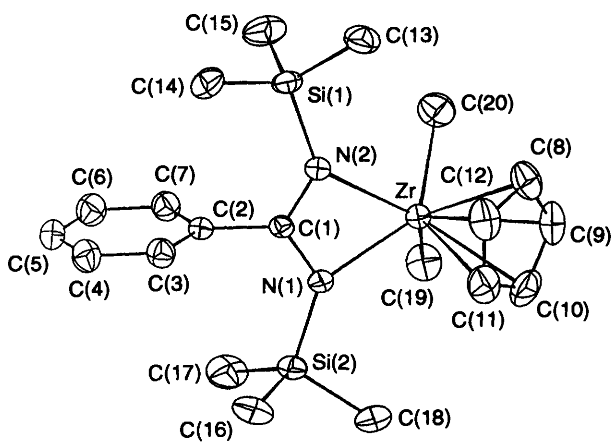


Fig. 2 Molecular structure of the compound **11**. Hydrogen atoms are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Zr(\eta\text{-}C_5H_5)[CPh(NSiMe_3)_2]Cl\}_2(\mu\text{-}O)]$ **6**

Zr–Cl	2.4662(6)	Zr–C(12)	2.527(3)
Zr–O	1.9466(3)	Zr–Cp	2.225
Zr–N(1)	2.263(2)	Si(1)–N(1)	1.747(2)
Zr–N(2)	2.263(2)	Si(2)–N(2)	1.758(2)
Zr–C(8)	2.531(3)	N(1)–C(1)	1.327(2)
Zr–C(9)	2.504(3)	N(2)–C(1)	1.327(2)
Zr–C(10)	2.487(3)	C(1)–C(2)	1.497(3)
Zr–C(11)	2.496(3)	Zr ··· C(1)	2.665(2)
Cl–Zr–O	92.24(3)	Zr–O–Zr′	163.1(1)
Cl–Zr–N(1)	137.97(4)	Zr–N(1)–Si(1)	136.61(9)
O–Zr–N(1)	91.06(7)	Zr–N(1)–C(1)	92.1(1)
Cl–Zr–N(2)	85.59(4)	Si(1)–N(1)–C(1)	131.3(1)
O–Zr–N(2)	126.66(6)	Zr–N(2)–Si(2)	138.09(9)
N(1)–Zr–N(2)	59.62(6)	Zr–N(2)–C(1)	92.1(1)
Cl–Zr–Cp	109.7	Si(2)–N(2)–C(1)	129.6(1)
O–Zr–Cp	115.6	N(1)–C(1)–N(2)	115.9(2)
N(1)–Zr–Cp	106.4	N(1)–C(1)–C(2)	122.4(2)
N(2)–Zr–Cp	115.1	N(2)–C(1)–C(2)	121.7(2)

Cp denotes the centroid of the cyclopentadienyl ring C(8)–C(12).

Table 3 Selected bond lengths (Å) and angles (°) for $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Me_2]$ **11**

Zr–N(1)	2.282(2)	Zr–C(20)	2.265(3)
Zr–N(2)	2.265(2)	Zr–Cp	2.216
Zr–C(8)	2.512(3)	Si(1)–N(2)	1.750(2)
Zr–C(9)	2.523(3)	Si(2)–N(1)	1.751(2)
Zr–C(10)	2.521(4)	N(1)–C(1)	1.332(3)
Zr–C(11)	2.500(3)	N(2)–C(1)	1.328(3)
Zr–C(12)	2.500(3)	C(1)–C(2)	1.495(3)
Zr–C(19)	2.247(3)	Zr ··· C(1)	2.651(2)
N(1)–Zr–N(2)	59.45(7)	Zr–N(1)–Si(2)	136.7(1)
N(1)–Zr–C(19)	90.0(1)	Zr–N(1)–C(1)	90.4(1)
N(2)–Zr–C(19)	123.7(1)	Si(2)–N(1)–C(1)	128.9(2)
N(1)–Zr–C(20)	135.5(1)	Zr–N(2)–Si(1)	137.5(1)
N(2)–Zr–C(20)	85.6(1)	Zr–N(2)–C(1)	91.3(1)
C(19)–Zr–C(20)	87.7(2)	Si(1)–N(2)–C(1)	129.9(2)
N(1)–Zr–Cp	114.3	N(1)–C(1)–N(2)	115.9(2)
N(2)–Zr–Cp	123.1	N(1)–C(1)–C(2)	121.7(2)
C(19)–Zr–Cp	112.1	N(2)–C(1)–C(2)	122.3(2)
C(20)–Zr–Cp	107.6		

Cp denotes the centroid of the cyclopentadienyl ring C(8)–C(12).

C(13)–Ti–C(14) 84.41(7)°]. Selected bond lengths and angles are shown in Table 6 and atomic coordinates in Table 7.

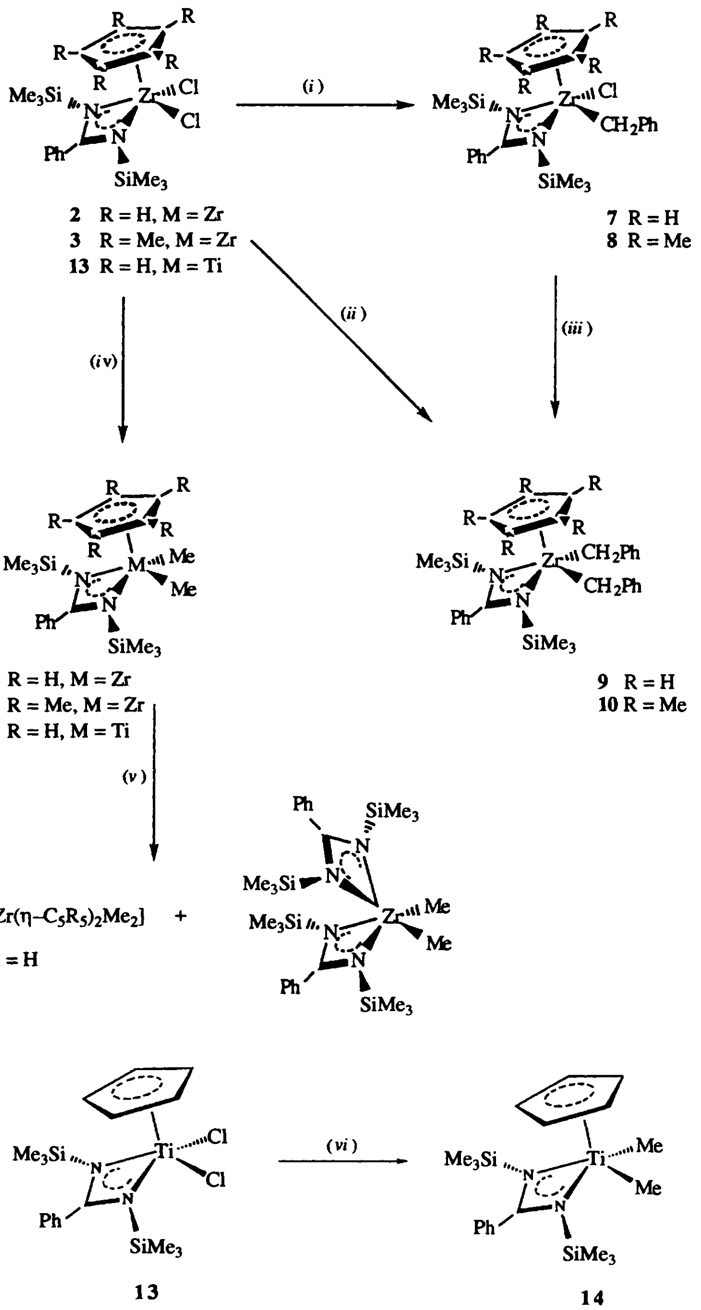
Table 4 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of $[\{Zr(\eta\text{-}C_5H_5)[CPh(NSiMe_3)_2]Cl\}_2(\mu\text{-}O)]$ **6**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr	0.425 816(7)	0.424 11(2)	0.681 24(1)
Cl	0.414 70(3)	0.536 14(7)	0.804 93(4)
Si(1)	0.449 38(2)	0.131 27(6)	0.577 94(4)
Si(2)	0.306 43(2)	0.311 11(6)	0.714 72(4)
O	0.500 0	0.397 4(2)	0.750 0
N(1)	0.417 01(6)	0.226 7(2)	0.627 1(1)
N(2)	0.359 22(6)	0.301 5(2)	0.680 8(1)
C(1)	0.376 49(7)	0.204 6(2)	0.649 2(1)
C(2)	0.352 27(7)	0.077 6(2)	0.640 9(1)
C(3)	0.321 00(9)	0.029 1(2)	0.558 6(2)
C(4)	0.297 8(1)	−0.087 5(3)	0.552 6(2)
C(5)	0.305 5(1)	−0.155 5(2)	0.628 2(2)
C(6)	0.337 1(1)	−0.109 7(3)	0.709 5(2)
C(7)	0.360 47(9)	0.007 0(2)	0.716 3(1)
C(8)	0.362 2(1)	0.548 8(4)	0.553 1(3)
C(9)	0.399 7(2)	0.632 4(3)	0.607 0(2)
C(10)	0.445 9(1)	0.601 4(3)	0.600 9(3)
C(11)	0.438 1(2)	0.503 5(4)	0.546 7(3)
C(12)	0.386 7(2)	0.469 4(3)	0.516 4(2)
C(13)	0.516 2(1)	0.194 9(3)	0.608 4(2)
C(14)	0.414 5(1)	0.136 0(4)	0.454 8(2)
C(15)	0.455 5(1)	−0.033 4(3)	0.615 0(2)
C(16)	0.249 89(9)	0.211 5(3)	0.645 7(2)
C(17)	0.281 3(1)	0.474 2(3)	0.696 0(2)
C(18)	0.327 9(1)	0.268 6(3)	0.834 1(2)

Table 5 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Me_2]$ **11**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zr	0.997 50(3)	0.406 21(3)	0.774 94(2)
Si(1)	1.130 43(8)	0.061 73(8)	0.699 91(7)
Si(2)	0.613 92(8)	0.520 40(8)	0.746 73(7)
N(1)	0.797 8(2)	0.417 4(2)	0.730 2(2)
N(2)	1.005 3(2)	0.228 0(2)	0.718 1(2)
C(1)	0.863 6(2)	0.281 7(2)	0.725 6(2)
C(2)	0.781 4(3)	0.193 1(3)	0.735 4(2)
C(3)	0.723 8(3)	0.211 3(3)	0.645 4(2)
C(4)	0.644 9(4)	0.129 9(4)	0.657 9(3)
C(5)	0.623 3(4)	0.032 2(4)	0.759 5(4)
C(6)	0.680 5(4)	0.012 4(4)	0.849 2(3)
C(7)	0.760 8(3)	0.092 4(3)	0.837 4(3)
C(8)	1.197 2(4)	0.494 4(5)	0.661 0(3)
C(9)	1.122 1(5)	0.576 8(5)	0.737 0(3)
C(10)	0.985 4(5)	0.663 1(4)	0.707 7(5)
C(11)	0.979 4(5)	0.632 0(5)	0.614 7(4)
C(12)	1.108 2(5)	0.529 7(5)	0.586 8(3)
C(13)	1.299 1(3)	0.093 7(4)	0.622 9(3)
C(14)	1.079 1(4)	−0.004 4(4)	0.611 2(4)
C(15)	1.159 5(4)	−0.078 8(4)	0.837 7(3)
C(16)	0.537 4(4)	0.576 8(4)	0.616 5(3)
C(17)	0.509 6(4)	0.426 6(5)	0.868 3(4)
C(18)	0.592 4(4)	0.689 7(4)	0.768 5(5)
C(19)	0.870 2(4)	0.452 6(5)	0.938 6(3)
C(20)	1.173 5(4)	0.232 4(4)	0.873 9(3)

The structure contains pseudo bilateral (C_s) symmetry where the two methyl groups are mirror images with respect to the plane of symmetry bisecting the Me–Ti–Me angle. The benzamidinato ligand forms an almost coplanar four-membered ring with the titanium atom [torsion angle N(2)–Ti–N(1)–C(6) −7.85(8)°]. The Ti–N(1) [2.1257(12) Å] and Ti–N(2) [2.1536(12) Å] distances are within the range of values observed for other crystallographically characterized bis(benzamidinato) titanium complexes, *e.g.* $[TiCl_2\{CPh(NSiMe_3)_2\}_2]$ [2.006(5)–2.106(5) Å][13] and $[Ti\{CPh(NSiMe_3)_2\}_2X]$ [X = $(\mu\text{-}Cl)_2Li{\cdot}Me_2NCH_2CH_2NMe_2$, BH_4 or $\eta^3\text{-}C_3H_5$] [2.059(3)–2.198(2) Å],[14] but are longer than found in $[\{TiCl_3[CPh(NSiMe_3)_2]_2\}]$ [2.072(2) and 1.986(2) Å].[15] The Cp–Ti distance of 2.055(1) Å is normal and compares well with values observed in Ti^{IV} η-cyclopentadienyl complexes.[16,17] The



Scheme 2 Reagents and conditions: (*i*) $Mg(CH_2Ph)Cl$ (1 equivalent) in Et_2O at −30 °C, stirring at r.t. for 12 h, yield 55–60%; (*ii*) $K(CH_2Ph)$ (2 equivalents), benzene, r.t., 12 h, yield 75–85%; (*iii*) **7**, $Mg(CH_2Ph)Cl$ (1 equivalent) in Et_2O at −30 °C, stirring at r.t. for 12 h, yield 79%; **8**, $K(CH_2Ph)$ (1 equivalent), benzene, r.t., 12 h, yield 79%; (*iv*) MgMeCl (2 equivalents) in Et_2O at −30 °C, stirring at r.t. for 12 h, yield 70–85%; (*v*) LiMe (slight excess) in Et_2O at −30 °C, stirring at r.t. for 12 h; (*vi*) LiMe in toluene at −80 °C, stirring at r.t. for 1 h, extraction in pentane, yield 62%

considerable steric bulk of the benzamidinato ligand is reflected in the rather small angle between the two methyl groups [84.41(7)°].[16,17] On the other hand the Ti–Me bond lengths [Ti–C(13) 2.1385(17), Ti–C(14) 2.131(2) Å] lie in the range of 2.00(1)–2.21(2) Å found for other Ti^{IV}–Me bonds.[17]

In conclusion, the new reactions and the structures proposed are shown in Schemes 1 and 2. All these results show that the *N*,*N*′-bis(trimethylsilyl)benzamidinato group acts as an inert spectator ligand which in combination with the η-C_5H_5 ligand provides a stable co-ordination environment to the metal, which is kinetically inert with respect to redistribution of the η-C_5H_5 and benzamidinato ligands.

Experimental

All manipulations of air- and moisture-sensitive materials were performed using either standard Schlenk-line techniques under an atmosphere of argon, which had been purified by passage over BASF catalyst and 4 Å molecular sieves, or in an inert-atmosphere dry-box containing dinitrogen, unless stated otherwise. Solvents were pre-dried by standing over 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from phosphorus pentaoxide (dichloromethane), sodium (toluene, benzene), potassium–benzophenone (thf) or sodium–potassium alloy (1:3 w/w) [light petroleum (b.p. 40–60 °C throughout), diethyl ether, pentane]. Deuteriated solvents for NMR studies were stored in Young's ampoules under an atmosphere of dinitrogen over sodium–potassium alloy ([$^2H_6$]benzene) or molecular sieves ([$^2H_2$]dichloromethane).

Proton and ^{13}C NMR spectra were recorded on a Brüker AM 300 (^1H 300 MHz, ^{13}C 75.5 MHz), Varian Gemini 200 (^1H

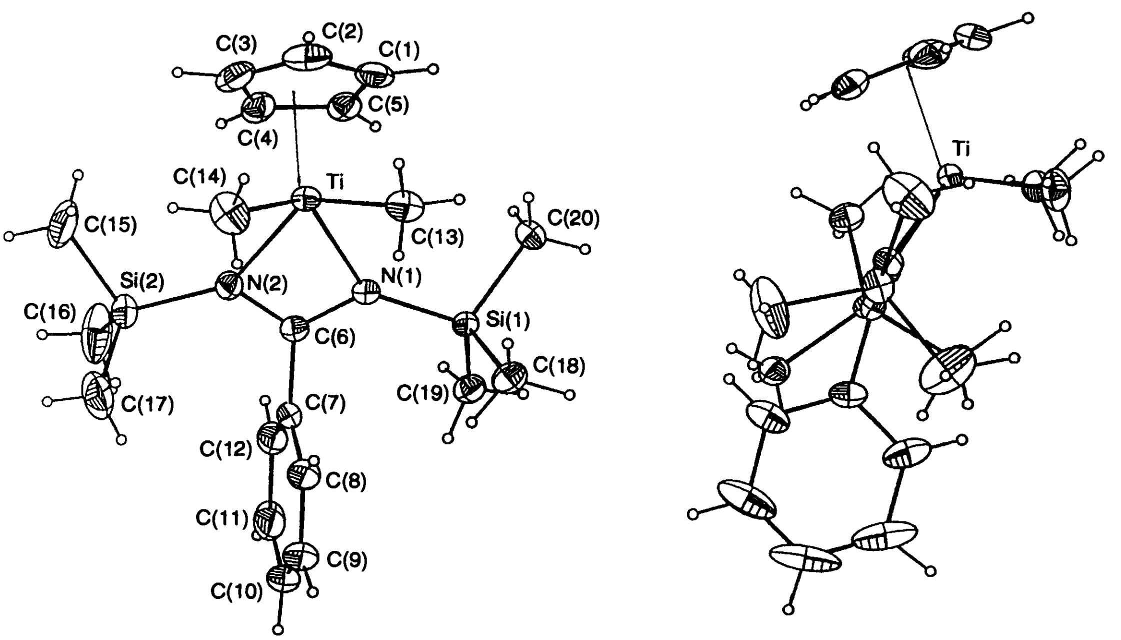


Fig. 3 ORTEP drawings of compound **14** with 50% probability ellipsoids

Table 6 Selected bond lengths (Å) and angles (°) for [Ti(η-C_5H_5){CPh($NSiMe_3$)$_2$}Me_2] **14**

Ti–N(1)	2.1257(12)	Ti–C(13)	2.1385(17)
Ti–N(2)	2.1536(12)	Ti–C(14)	2.131(2)
Ti–C(1)	2.3872(16)	Si(1)–N(1)	1.7526(12)
Ti–C(2)	2.3965(16)	Si(1)–N(2)	1.7496(13)
Ti–C(3)	2.3857(18)	N(1)–C(6)	1.3291(17)
Ti–C(4)	2.3577(18)	N(2)–C(6)	1.3285(18)
Ti–C(5)	2.3561(15)	C(6)–C(7)	1.5037(18)
Ti–C(6)	2.5129(14)	Cp–Ti	2.055(1)
N(1)–Ti–N(2)	63.36(4)	Si(1)–N(1)–C(6)	129.94(9)
N(1)–Ti–C(13)	84.70(5)	Ti–N(2)–Si(2)	139.71(7)
N(1)–Ti–C(14)	124.84(7)	Ti–N(2)–C(6)	89.12(8)
N(2)–Ti–C(13)	133.55(6)	Si(2)–N(2)–C(6)	129.57(10)
N(2)–Ti–C(14)	87.40(7)	N(1)–C(6)–N(2)	115.49(12)
C(1)–Ti–C(6)	133.79(6)	N(1)–C(6)–C(7)	121.55(11)
C(6)–Ti–C(13)	107.98(5)	N(2)–C(6)–C(7)	122.86(12)
C(6)–Ti–C(14)	104.72(7)	Cp–Ti–C(6)	129.23(7)
C(13)–Ti–C(14)	84.41(7)	Cp–Ti–C(13)	108.67(7)
Ti–N(1)–Si(1)	139.22(6)	Cp–Ti–C(14)	112.68(7)
Ti–N(1)–C(6)	90.31(8)		

Cp denotes the centroid of the cyclopentadienyl ring C(1)–C(5).

200 MHz) or Varian VXR 300 (^1H 300 MHz, ^{13}C 75.5 MHz) spectrometer, referenced internally using the residual protio solvent (^1H) or solvent (^{13}C) resonances relative to tetramethylsilane (δ = 0). Low-resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data handling system supplied by Mass Spectra Services. Elemental analyses were performed by the analytical departments of the Oxford and Groningen laboratories. The compounds Li[CPh($NSiMe_3$)$_2$] **1** [Zr(η-C_5H_5){CPh($NSiMe_3$)$_2$}Cl_2] **2** and [Zr(η-C_5Me_5){CPh($NSiMe_3$)$_2$}Cl_2] **3** and [Ti(η-C_5H_5){CPh($NSiMe_3$)$_2$}Cl_2] **13** were prepared as described previously.[1,2]

Preparation of [Zr(η-C_5H_5){CPh($NSiMe_3$)$_2$}$_2$Cl] **4** *and* [{Zr(η-C_5H_5)[CPh($NSiMe_3$)$_2$]Cl}$_2${μ-CPh($NSiMe_3$)$_2$}$_2$] **5**.—*Method* (*i*). A solution of [Zr(η-C_5H_5)Cl_3]·dme (0.4 g, 1.13 mmol) in diethyl ether (50 cm^3) was treated with Li[CPh($NSiMe_3$)$_2$] (0.67 g, 2.48 mmol) in diethyl ether (20 cm^3) and the mixture stirred for 12 h at room temperature. The volatiles were removed under reduced pressure and the residues extracted with light petroleum (60 cm^3). Subsequent filtration and removal of volatiles gave a *ca.* 2 : 1 (by NMR spectroscopy) mixture of **4** and **5** (yield: 0.65 g). Recrystallization from diethyl ether (15 cm^3) afforded **4** as white crystals (yield: 0.15 g, *ca.* 35% based on mixture). Recrystallization of the mixture from light petroleum (20 cm^3) gave **5** as pale yellow crystals (yield: 0.16 g, *ca.* 75% based on mixture).

Method (*ii*). A solution of [Zr(η-C_5H_5){CPh($NSiMe_3$)$_2$}Cl_2] **2** (0.35 g, 0.71 mmol) in diethyl ether (50 cm^3) was treated with one equivalent of Li[CPh($NSiMe_3$)$_2$] (0.21 g, 0.78 mmol) in diethyl ether (10 cm^3) and the mixture stirred for 12 h at room temperature. Subsequent work-up of the reaction gave the same mixture of **4** and **5** (*ca.* 2 : 1).

Preparation of [{Zr(η-C_5H_5)[CPh($NSiMe_3$)$_2$]Cl}$_2$(μ-O)] **6**.—A solution of a mixture of **4** and **5** in light petroleum was treated with a drop of water without stirring. This resulted in the slow precipitation of **6** as pale yellow crystals, which were suitable for an X-ray determination. Yield: 43%.

Preparation of [Zr(η-C_5H_5){CPh($NSiMe_3$)$_2$}(CH_2Ph)Cl] **7**.—A solution of [Zr(η-C_5H_5){CPh($NSiMe_3$)$_2$}Cl_2] **2** (0.5 g, 1.02 mmol) in diethyl ether (50 cm^3) at −30 °C was treated with Mg(CH_2Ph)Cl (0.85 cm^3, 1.2 mol dm^{-3} in diethyl ether, 1.02 mmol). The solution was allowed to warm slowly to room temperature and was stirred for 12 h. Volatiles were removed under reduced pressure and the resulting brown solid was extracted with light petroleum (80 cm^3). The solution was filtered and the solvent removed from the filtrate under reduced pressure to give **7** as a brown oil. The oily product was cooled *in vacuo* and allowed to warm to room temperature, affording **7** as a brown solid. Yield: 0.31 g, 56%. Recrystallization from light petroleum at −80 °C gave an analytically pure sample.

Preparation of [Zr(η-C_5Me_5){CPh($NSiMe_3$)$_2$}(CH_2Ph)Cl] **8**.—A solution of [Zr(η-C_5Me_5){CPh($NSiMe_3$)$_2$}Cl_2] **3** (0.5 g, 0.89 mmol) in diethyl ether (50 cm^3) at −30 °C was treated with Mg(CH_2Ph)Cl (0.74 cm^3, 1.2 mol dm^{-3} in diethyl ether, 0.89 mmol). The solution was allowed to warm slowly to room temperature and stirred for 12 h. Removal of volatile components, extraction into light petroleum (50 cm^3) and filtration gave an orange solution. The solvent was removed under reduced pressure to afford a brown oil which after cooling

Table 7 Fractional atomic coordinates (× 10^4) for [Ti(η-C_5H_5){CPh($NSiMe_3)_2$}Me_2] **14**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ti	0.145 96(3)	0.400 75(2)	0.265 84(2)
Si(1)	0.356 45(6)	0.221 31(3)	0.443 85(2)
Si(2)	0.318 37(6)	0.231 79(4)	0.061 99(3)
N(1)	0.305 09(17)	0.265 88(9)	0.332 10(8)
N(2)	0.296 31(18)	0.271 85(10)	0.177 75(8)
C(1)	0.204 9(3)	0.579 51(12)	0.329 48(12)
C(2)	0.082 5(3)	0.604 34(13)	0.259 08(15)
C(3)	0.186 2(3)	0.572 98(14)	0.174 43(13)
C(4)	0.373 8(3)	0.527 62(13)	0.191 95(11)
C(5)	0.385 5(2)	0.531 61(13)	0.288 10(11)
C(6)	0.337 1(2)	0.210 90(11)	0.252 88(9)
C(7)	0.403 2(2)	0.086 09(11)	0.250 46(9)
C(8)	0.266 8(3)	0.004 80(14)	0.279 30(12)
C(9)	0.326 5(5)	−0.111 32(15)	0.278 55(14)
C(10)	0.517 7(5)	−0.145 42(16)	0.250 35(13)
C(11)	0.652 9(4)	−0.065 63(17)	0.222 59(12)
C(12)	0.596 5(3)	0.050 93(14)	0.222 12(11)
C(13)	−0.056 9(2)	0.394 12(14)	0.388 70(12)
C(14)	−0.108 3(3)	0.380 02(19)	0.196 09(14)
C(15)	0.238 6(4)	0.357 7(2)	−0.009 55(13)
C(16)	0.578 2(3)	0.196 8(3)	0.017 52(14)
C(17)	0.157 7(5)	0.112 7(2)	0.047 17(15)
C(18)	0.145 7(2)	0.148 23(14)	0.508 97(11)
C(19)	0.585 8(2)	0.126 64(13)	0.440 91(11)
C(20)	0.403 1(3)	0.351 17(13)	0.506 79(11)
H(1)	0.177(3)	0.590 1(16)	0.396 2(13)
H(2)	−0.048(4)	0.633(2)	0.266 7(17)
H(3)	0.143(4)	0.578(2)	0.112 0(16)
H(4)	0.464(3)	0.502 6(17)	0.146 6(14)
H(5)	0.488(3)	0.502 7(17)	0.318 9(13)
H(8)	0.136(4)	0.026(2)	0.296 7(16)
H(9)	0.219(4)	−0.160(2)	0.301 1(15)
H(10)	0.561(4)	−0.220(2)	0.245 7(16)
H(11)	0.783(4)	−0.088(2)	0.202 7(19)
H(12)	0.687(3)	0.103 5(16)	0.205 8(13)
H(13)	0.009(3)	0.404 9(16)	0.445 4(14)
H(13′)	−0.108(3)	0.322 9(18)	0.388 7(14)
H(13″)	−0.165(3)	0.455 6(17)	0.384 7(13)
H(14)	−0.141(3)	0.307(2)	0.210 0(15)
H(14′)	−0.089(4)	0.386 7(18)	0.130 9(17)
H(14″)	−0.211(4)	0.431(2)	0.215 1(15)
H(15)	0.267(4)	0.339(2)	−0.071 5(18)
H(15′)	0.319(7)	0.427(4)	−0.002(3)
H(15″)	0.095(5)	0.378(2)	0.006 8(19)
H(16)	0.623(5)	0.116(3)	0.036(2)
H(16′)	0.650(5)	0.244(3)	0.037(2)
H(16″)	0.589(4)	0.193(2)	−0.045(2)
H(17)	0.161(5)	0.103(3)	−0.010(2)
H(17′)	0.221(5)	0.050(3)	0.074(2)
H(17″)	−0.001(5)	0.133(3)	0.075(2)
H(18)	0.029(4)	0.198 2(18)	0.510 4(14)
H(18′)	0.123(4)	0.084(2)	0.471 5(17)
H(18″)	0.175(4)	0.125 1(19)	0.575 9(16)
H(19)	0.564(3)	0.055 3(16)	0.421 9(12)
H(19′)	0.686(4)	0.156 3(19)	0.404 6(15)
H(19″)	0.629(3)	0.120 0(17)	0.499 0(15)
H(20)	0.425(3)	0.331 4(18)	0.567 9(15)
H(20′)	0.522(4)	0.384 7(18)	0.479 1(15)
H(20″)	0.297(3)	0.406 8(16)	0.506 7(12)

in vacuo gave the product **8** as a brown solid. Yield: 0.32 g, 58%. Recrystallization of the compound from light petroleum at − 80 °C produced an analytically pure sample.

Preparation of [Zr(η-C_5H_5){CPh($NSiMe_3)_2$}($CH_2Ph)_2$] **9**.—*Method* (*i*). A mixture of [Zr(η-C_5H_5){CPh($NSiMe_3)_2$}Cl_2] **2** (0.5 g, 1.02 mmol) and K(CH_2Ph) (0.28 g, 2.15 mmol) in benzene (50 cm^3) was stirred for 12 h at room temperature. Volatiles were removed under reduced pressure and the resulting red solid was extracted with light petroleum (60 cm^3). The solution was filtered and the solvent removed under reduced pressure to give **9** as a brown-yellow oil which turned to a solid after 2–3 d *in vacuo*. Yield: 0.52 g, 84%. Recrystallization of the compound from light petroleum at −80 °C gave an analytically pure sample.

Method (*ii*). A solution of [Zr(η-C_5H_5){CPh($NSiMe_3)_2$}(CH_2Ph)Cl] **7** (0.5 g, 0.91 mmol) in diethyl ether (50 cm^3) at −30 °C was treated with Mg(CH_2Ph)Cl (0.76 cm^3, 1.2 mol dm^{-3} in diethyl ether, 0.91 mmol). The solution was allowed to warm slowly to room temperature and stirred for 12 h. Volatiles were removed under reduced pressure and the resulting brown solid was extracted with light petroleum (80 cm^3). The solution was filtered and the solvent removed under reduced pressure to give **9** as a brown oil. The oily product was cooled *in vacuo* to give **9** as an orange-brown solid. Yield: 0.44 g, 79%. The product always contained small quantities of residual solvent.

Preparation of [Zr(η-C_5Me_5){CPh($NSiMe_3)_2$}($CH_2Ph)_2$] **10**.—*Method* (*i*). A mixture of [Zr(η-C_5Me_5){CPh($NSiMe_3)_2$}Cl_2] **3** (0.5 g, 0.89 mmol) and K(CH_2Ph) (0.24 g, 1.87 mmol) in benzene (50 cm^3) was stirred for 12 h at room temperature. Volatiles were removed under reduced pressure and the resulting red solid was extracted with light petroleum (60 cm^3). The extract was filtered and the solvent removed from the filtrate under reduced pressure to give **10** as a brown-yellow oil which became a solid after 2–3 d *in vacuo*. Yield: 0.45 g, 76%. Recrystallization from light petroleum at −80 °C gave an analytically pure sample.

Method (*ii*). A mixture of [Zr(η-C_5Me_5){CPh($NSiMe_3)_2$}(CH_2Ph)Cl] **8** (0.5 g, 0.81 mmol) and K(CH_2Ph) (0.10 g, 0.81 mmol) in benzene (50 cm^3) was stirred for 12 h at room temperature. Volatiles were removed under reduced pressure and the resulting red solid was extracted with light petroleum (60 cm^3). The solution was filtered and the solvent removed under reduced pressure to give a brown-yellow oil which on cooling *in vacuo* gave the product **10** as an orange-brown solid. Yield: 0.43 g, 79%. The product always contained small quantities of residual solvent.

Preparation of [Zr(η-C_5H_5){CPh($NSiMe_3)_2$}Me_2] **11**.—A solution of [Zr(η-C_5H_5){CPh($NSiMe_3)_2$}Cl_2] **2** (1 g, 2.04 mmol) in diethyl ether (70 cm^3) at −30 °C was treated with MgMeBr (1.36 cm^3, 3 mol dm^{-3} in diethyl ether, 4.08 mmol). The solution was allowed to warm slowly to room temperature and stirred for 12 h. Volatiles were removed under reduced pressure and the resulting brown solid was extracted with light petroleum (80 cm^3). The solution was filtered and the filtrate reduced in volume to *ca.* 15 cm^3 and placed at −80 °C to afford brown-yellow crystals of **11**. Yield: 0.79 g, 86%.

Preparation of [Zr(η-C_5Me_5){CPh($NSiMe_3)_2$}Me_2] **12**.—A solution of [Zr(η-C_5Me_5){CPh($NSiMe_3)_2$}Cl_2] **3** (0.7 g, 1.25 mmol) in diethyl ether (60 cm^3) at −30 °C was treated with MgMeBr (0.86 cm^3, 3 mol dm^{-3} in diethyl ether, 2.60 mmol). The solution was allowed to warm slowly to room temperature and stirred for 12 h. Volatiles were removed under reduced pressure and the resulting black solid was extracted with light petroleum (60 cm^3). The solution was filtered and the filtrate reduced in volume (to *ca.* 10 cm^3) and placed at −80 °C to give white crystals of **12**. Yield: 0.47 g, 72%.

Table 8 Crystal data, data collection and processing parameters for compounds **6**, **11** and **14**

	6	**11**	**14**
	$C_{36}H_{56}Cl_2N_4OSi_4Zr_2$	$C_{20}H_{34}N_2Si_2Zr$	$C_{20}H_{34}N_2Si_2Ti$
M	926.55	449.89	406.55
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	27.747(1)	10.508(1)	6.823(1)
b/Å	10.6902(5)	10.7672(6)	11.696(1)
c/Å	16.313(1)	12.9438(8)	14.523(1)
α/°	90.0	67.68(1)	87.989(6)
β/°	112.77(1)	72.58(1)	83.786(5)
γ/°	90.0	64.04(1)	86.750(6)
U/Å^3	4461.6(7)	1202.4(3)	1149.8(2)
Z	4	2	2
D_c/g cm^{-3}	1.38	1.24	1.174
μ/cm^{-1}	7–16	5.52	4.7
F(000)	1912	472	436
ω scan width/°	0.81 + 0.34 tan θ	0.82 + 0.34 tan θ	0.80 + 0.34 tan θ
Lattice segment	$-h, h, -1, k, -1, l$	$-h, h, -k, k, -1, l$	$0, h, -k, k, -l, l$
Crystal size/mm	0.28 × 0.50 × 0.68	0.20 × 0.33 × 0.41	0.30 × 0.45 × 0.45
θ_{max}/°	30	28	27.5
No. of reflections			
Total	7479	6389	5692
Unique	6491	5709	5247
In refinement	4669	4018	4725
R_{merge}	0.026	0.013	0.016
No. of variables	222	226	363
Observations/variables	21.0	17.8	13.0
Weighting coefficient	17.3, −23.6, 14.9, −6.3	9.3, −5.5, 7.0	$1/\sigma(F)$
Max., min. peaks in the final difference maps/e Å^{-3}	0.43, −0.27	0.36, −0.41	−0.33, 0.55
R	0.029	0.033	0.032
R'	0.032	0.037	0.045

$R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o - F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Reaction of $[Zr(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **2** *with* LiMe.—A solution of **2** (0.5 g, 1.02 mmol) in diethyl ether (30 cm^3) at −30 °C was treated with a slight excess of LiMe (1.55 cm^3, 1.36 mol dm^{-3} in hexane, 2.11 mmol). The mixture was allowed to warm slowly to room temperature and stirred for 12 h. Removal of volatile components, extraction into light petroleum (40 cm^3) and filtration produced a brown-orange solution. The solvent was removed under reduced pressure to give a brown-orange solid which ^{1}H NMR spectroscopy showed to be a 1 : 1 mixture of $[Zr\{CPh(NSiMe_3)_2\}_2Me_2]$ and $[Zr(\eta\text{-}C_5H_5)_2Me_2]$.

Preparation of $[Ti(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Me_2]$ **14**.—To a suspension of $[Ti(\eta\text{-}C_5H_5)\{CPh(NSiMe_3)_2\}Cl_2]$ **13** (8.9 g, 19.9 mmol) in toluene (100 cm^3), LiMe (33 cm^3, 1.2 mol dm^{-3} in diethyl ether, 39.8 mmol) was added slowly at −80 °C. After the addition was completed, the mixture was allowed to warm to room temperature. After stirring for a further 1 h the solvent was removed *in vacuo* and the solid extracted with pentane (70 cm^3). After cooling the extract to −30 °C a dark orange crystalline material was isolated and subsequently recrystallized from pentane (100 cm^3). Slow cooling to −30 °C gave **14** as orange crystals. Yield: 5.0 g, 12.3 mmol, 62%.

Crystal-structure Determinations of Compounds **6** *and* **11**.—Crystal data, data collection and processing parameters are given in Table 8. The general procedure was as follows. A crystal was mounted in a Lindeman tube (0.7 mm) under dinitrogen and sealed with a small flame. This was transferred to the goniometer head of an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the setting angles of 24 strong, high-angle carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation control reflections were measured every 200 reflections. The data were collected at room temperature using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and a ω–2θ scan mode (the ratio of the scanning rates ω/θ = 1.2, ω scan speed 1.4–6.7° min^{-1}). Neither significant crystal decay nor movement was noted.

The data were corrected for Lorentz and polarization effects and an empirical absorption correction [18] based on azimuthal scan data was applied. Both structures were solved by direct methods. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures [the refinement used reflections with $I > 3\sigma(I)$]. An empirical absorption correction using the DIFABS [19] program was applied after isotropic convergence. For both structures all hydrogen atoms were located in Fourier difference maps and included in the refinement with fixed positional and thermal parameters. A Chebyshev weighting scheme [20] was applied and the data were corrected for the effects of anomalous dispersion. All crystallographic calculations were performed using the CRYSTALS [21] suite on a MicroVAX 3800 computer. Neutral-atom scattering factors were taken from the usual sources.[22]

Crystal-structure Determination of Compound **14**.—Suitable orange crystals were obtained by recrystallization from pentane. The air-sensitive crystals used for this study were selected and glued on a glass fibre in a dry-box equipped with a locally modified microscope. A block-shape crystal of approximate size 0.30 × 0.45 × 0.45 mm was transferred to the goniostat using inert atmosphere handling techniques and cooled to 130 K by using an on-line liquid-nitrogen cooling system [23] mounted on an Enraf–Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Details of crystal data, data collection and refinement are given in Table 8. Unit-cell parameters and the orientation matrix were determined from least-squares treatment of the setting angles of 22 reflections in the range 14.39 < θ < 17.29° in four alternative settings.[24] The unit cell was identified as triclinic, space group $P\bar{1}$. The $|E|$ distribution statistics indicated a centrosymmetric space group. This choice was confirmed by the solution and the successful refinement of the structure.

Reduced cell calculations did not indicate any higher metric lattice symmetry[25] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[26,27] The intensities of three representative reflections which were measured after every 3 h of X-ray exposure time remained constant throughout the data collection indicating crystal and electronic stability. Intensity data were corrected for Lorentz and polarization effects and scale variation, but not for absorption. Standard deviations $\sigma(I)$ in the intensities were increased according to an analysis of the excess variance of the reference reflections. Variance was calculated based on counting statistics and the term P^2I^2 where P (= 0.032) is the instability constant[28] as derived from the excess variance in the reference reflections. Equivalent reflections were averaged and stated observed if satisfying the $I > 2.5\sigma(I)$ criterion of stability. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS 86).[29] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined with blocked-diagonal least-squares procedures (CRYLSQ)[30] minimizing the function $Q = \Sigma(w\Delta^2)$ (over all *hkl*). A subsequent Fourier difference synthesis provided all the hydrogen atoms, whose coordinates and isotropic displacement parameters were refined. Final refinement on F_o by full-matrix least-squares techniques with anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for the hydrogen atoms converged at $R = 0.032$ ($R' = 0.045$). Weights were introduced in the final refinement cycles. A final Fourier difference map did not show residual peaks outside the range ±0.55 e Å^{-3}. The crystal exhibited some secondary extinction for which the F values were corrected by refinement of an empirical isotropic extinction parameter.[31] Scattering factors were taken from Cromer and Mann.[32] Anomalous dispersion factors taken from Cromer and Liberman[33] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31 computer at the University of Groningen with the program packages XTAL,[34] PLATON[35] (calculation of geometric data) and locally modified versions of the programs PLUTO[36] and ORTEP[37] (preparation and illustration).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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