# New monocyclopentadienyl complexes of Group 4 and 5 metals with chelating nitrogen ligands. Crystal and molecular structures of [Zr(η³-C₃H₅)(η⁴-Ph₂N₂C₂Me₂-2,3)Cp″] and [TaCl₂{η⁴-C₆H₄(NSiMe₃-1,2)₂}Cp″] [Cp″ = C₅H₃(SiMe₃)₂-1,3] †

**Gerardo Jiménez Pindado, Mark Thornton-Pett and Manfred Bochmann ***

*School of Chemistry, University of Leeds, Leeds, UK LS2 9JT*

Reduction of [MCl₃Cp″] [M = Zr or Hf; Cp″ = C₅H₃(SiMe₃)₂-1,3] with magnesium in the presence of 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene (DAD) gave the diazadiene complexes [MCl(DAD)Cp″] in high yield. Alkylation with RMgCl affords the alkyls [MR(DAD)Cp″] (R = CH₃ or CH₂Ph) and the more stable allyl complexes [M(η³-C₃H₅)(DAD)Cp″] as yellow to light brown solids. The reaction of Li₂[C₆H₄(NSiMe₃)₂-1,2] with [MCl₃Cp″] leads to the bis(amido) complexes [MCl{C₆H₄(NSiMe₃)₂-1,2}Cp″], while the analogous reaction with [MCl₄Cp″] (M = Nb or Ta) generates the red to red-brown niobium and tantalum half-sandwich compounds [MCl₂{C₆H₄(NSiMe₃)₂-1,2}Cp″]. The crystal structures of two representative examples, [Zr(η³-C₃H₅)(DAD)Cp″] and [TaCl₂{C₆H₄(NSiMe₃)₂-1,2}Cp″], are reported.

Mono- and bis-cyclopentadienyl complexes of early transition metals are now well established as important classes of olefin polymerisation catalysts.[1] However, although many systems are highly active and widely studied, the precise reasons why certain ligands and ligand combinations should be particularly appropriate for the design of effective catalysts remain obscure. Ligands incorporating nitrogen donors are attracting increasing interest in this context, such as the well known 'constrained geometry' complexes of the type {Me₂Si(Cp)(NR)}MX₂.[2] Mono- and poly-dentate amido complexes without Cp ligands have also been reported to lead to catalytically active species.[3] As part of our interest in structure–reactivity relationships in soluble polymerisation catalysts we have recently reported the synthesis of a series of butadiene complexes [M(allyl)(L)Cp] (L = 1,3-diene) which act as sources for catalytically active 14-electron [M(allyl)₂Cp]⁺ cations.[4] We report here the synthesis of related complexes with L = dianionic nitrogen chelates and the extension of this chemistry to some Group 5 complexes.

## Results and Discussion

The treatment of [MCl₃Cp″] with 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene (DAD) in diethyl ether in the presence of magnesium turnings leads to the formation of the corresponding half-sandwich complexes [MCl(DAD)Cp″] **1a** (M = Zr) and **1b** (M = Hf), respectively, both of which are pale yellow solids in high yields (Scheme 1).[5] Throughout this study the C₅H₃(SiMe₃)₂-1,3 (Cp″) ligand was employed which is comparable in bulk and electronic characteristics to C₅Me₅ (Cp*) but more flexible in the rotational conformers it is able to adopt and often imparts subtly different reactivity patterns.[4a,6]

Alkylation of **1a** and **1b** with Grignard reagents affords the alkyl derivatives [MR(DAD)Cp″] (**2**, R = Me; **3**, R = CH₂Ph; **a**, M = Zr; **b**, M = Hf) as pale yellow to light brown solids. These compounds are thermally significantly more stable than the related 14-electron 1,3-diene complexes [MR(diene)Cp″][4a,6] and can be stored at room temperature without noticeable decomposition. The η³-allyl complexes [M(η³-C₃H₅)(DAD)Cp″] **4a** (M = Zr) and **4b** (M = Hf) are similarly prepared using allylmagnesium chloride. All these compounds are highly soluble in common hydrocarbon solvents.

† Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.
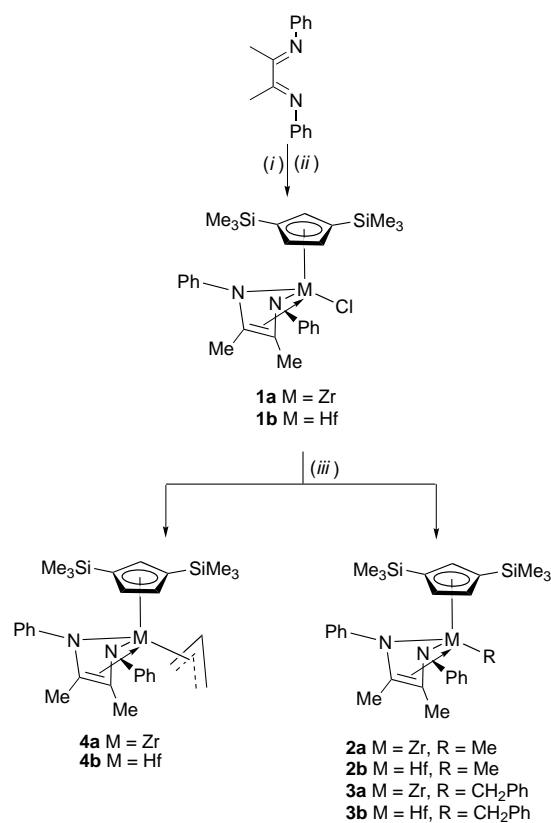


**Scheme 1** (*i*) [MCl₃Cp″]; (*ii*) 2 Mg, Et₂O, −78 °C to room temperature; (*iii*) RMgCl, Et₂O

Phenylenediamide complexes were obtained by the dropwise addition of Li₂[C₆H₄(NSiMe₃)₂-1,2] to solutions of [MCl₃Cp″] in diethyl ether (Scheme 2). The reaction proceeds through a very dark green intermediate to give finally orange solutions of the bis(amido) complexes [MCl{C₆H₄(NSiMe₃)₂}Cp″] **5a** (M = Zr) and **5b** (M = Hf) which are isolated as a green solid and a dark orange oil, respectively. In a similar manner Group 5 compounds were prepared from Li₂[C₆H₄(NSiMe₃)₂-1,2] and [MCl₄Cp″] to give the complexes [MCl₂{C₆H₄(NSiMe₃)₂}Cp″] **6a** (M = Nb) and **6b** (M = Ta) as red to red-brown crystalline

**Table 1** Spectroscopic data for diazadiene and di(amide) complexes *

| | $^1$H NMR | | $^{13}$C NMR | |
|---|---|---|---|---|
| | δ | Assignment | δ | Assignment |
| **1a** [ZrCl(DAD)Cp″] | 0.06 (s, 18 H) | SiMe$_3$ | −0.22 (q, $J = 119.3$) | SiMe$_3$ |
| | 1.87 (s, 6 H) | =C$Me$ | 15.92 (q, $J = 128.0$) | =C$Me$ |
| | 6.96 (t, 1 H, $J = 7.3$) | $p$-PhN | 116.25 (m) | =CMe |
| | 7.05 (d, 2 H, $J = 7.3$) | $m$-PhN | 121.92 (d, $J = 169.3$) | C$^2$ of C$_5$H$_3$ |
| | 7.09 (d, 2 H, $J = 1.9$) | C$^{4,5}$ of C$_5$H$_3$ | 122.01 (d, $J = 169$) | C$^{4,5}$ of C$_5$H$_3$ |
| | 7.22 (t, 2 H, $J = 7.3$) | $o$-PhN | 123.83 (d, $J = 156.5$) | $p$-PhN |
| | 7.35 (t, 1 H, $J = 1.9$) | C$^2$ of C$_5$H$_3$ | 124.45 (d, $J = 158.3$) | $m$-PhN |
| | | | 129.25 (d, $J = 159$) | $o$-PhN |
| | | | 130.84 (m) | C$^{1,3}$ of C$_5$H$_3$ |
| | | | 150.84 (m) | $ipso$-PhN |
| **1b** [HfCl(DAD)Cp″] | 0.06 (s, 18 H) | SiMe$_3$ | −0.24 (q, $J = 119.4$) | SiMe$_3$ |
| | 1.86 (s, 6 H) | =C$Me$ | 15.66 (q, $J = 127.7$) | =C$Me$ |
| | 6.96 (t, 1 H, $J = 7.2$) | $p$-PhN | 115.63 (m) | =CMe |
| | 7.0 (d, 2 H, $J = 1.9$) | C$^{4,5}$ of C$_5$H$_3$ | 121.1 (d, $J = 170$) | C$^{4,5}$ of C$_5$H$_3$ |
| | 7.05 (d, 2 H, $J = 7.2$) | $m$-PhN | 121.16 (d, $J = 168.9$) | C$^2$ of C$_5$H$_3$ |
| | 7.25 (t, 2 H, $J = 7.2$) | $o$-PhN | 123.43 (d, $J = 157.9$) | $p$-PhN |
| | 7.32 (t, 1 H, $J = 1.9$) | C$^2$ of C$_5$H$_3$ | 124.53 (d, $J = 158.2$) | $m$-PhN |
| | | | 128.98 (d, $J = 158.1$) | $o$-PhN |
| | | | 129.51 (m) | C$^{1,3}$ of C$_5$H$_3$ |
| | | | 150.74 (m) | $ipso$-PhN |
| **2a** [ZrMe(DAD)Cp″] | −0.56 (s, 3 H) | Zr−Me | −0.12 (q, $J = 119.2$) | SiMe$_3$ |
| | 0.04 (s, 18 H) | SiMe$_3$ | 16.30 (q, $J = 127.7$) | =C$Me$ |
| | 1.87 (s, 6 H) | =CMe | 22.71 (q, $J = 113.9$) | Zr−Me |
| | 6.95 (t, 2 H, $J = 7.2$) | $p$-PhN | 116.02 (m) | =CMe |
| | 7.00 (d, 2 H, $J = 1.9$) | C$^{4,5}$ of C$_5$H$_3$ | 120.16 (d, $J = 167.3$) | C$^2$ of C$_5$H$_3$ |
| | 7.05 (d, 4 H, $J = 7.3$) | $o$-PhN | 120.23 (d, $J = 168.9$) | C$^{4,5}$ of C$_5$H$_3$ |
| | 7.08 (t, 1 H, $J = 1.9$) | C$^2$ of C$_5$H$_3$ | 122.72 (d, $J = 161.2$) | $p$-PhN |
| | 7.25 (t, 4 H, $J = 8.0$) | $m$-PhN | 123.30 (d, $J = 158.9$) | $m$-PhN |
| | | | 129.04 (d, $J = 157.6$) | $o$-PhN |
| | | | 129.49 (m) | C$^{1,3}$ of C$_5$H$_3$ |
| | | | 150.83 (m) | $ipso$-PhN |
| **2b** [HfMe(DAD)Cp″] | −0.61 (s, 3 H) | Hf−Me | −0.12 (q, $J = 119.4$) | SiMe$_3$ |
| | 0.04 (s, 18 H) | SiMe$_3$ | 15.93 (q, $J = 127.2$) | =C$Me$ |
| | 1.87 (s, 6 H) | =CMe | 28.48 (q, $J = 112.7$) | Hf−Me |
| | 6.90 (t, 2 H, $J = 1.8$) | C$^{4,5}$ of C$_5$H$_3$ | 115.09 (m) | =CMe |
| | 6.95 (d, 2 H, $J = 7.3$) | $p$-PhN | 119.94 (d, $J = 169.0$) | C$^{4,5}$ of C$_5$H$_3$ |
| | 7.04 (d, 4 H, $J = 7.5$) | $o$-PhN | 120.11 (d, $J = 167.6$) | C$^2$ of C$_5$H$_3$ |
| | 7.26 (t, 4 H, $J = 7.5$) | $m$-PhN | 122.65 (d, $J = 157.7$) | $p$-PhN |
| | (C$^2$ of C$_5$H$_3$ overlaps | | 123.67 (d, $J = 157.0$) | $m$-PhN |
| | with $o$-Ph) | | 128.83 (m) | C$^{1,3}$ of C$_5$H$_3$ |
| | | | 128.98 (d, $J = 160.0$) | $o$-Ph |
| | | | 151.09 (m) | $ipso$-Ph |
| **3a** [Zr(CH$_2$Ph)(DAD)Cp″] | 0.03 (s, 18 H) | SiMe$_3$ | 0.01 (q, $J = 119.4$) | SiMe$_3$ |
| | 1.60 (s, 2 H) | C$H_2$Ph | 16.42 (q, $J = 127.7$) | =C$Me$ |
| | 1.73 (s, 6 H) | =CMe | 51.07 (t, $J = 120.0$) | $CH_2$Ph |
| | 6.80 (d, 2 H, $J = 1.9$) | C$^{4,5}$ of C$_5$H$_3$ | 115.38 (m) | =CMe |
| | 6.84–7.27 (m, 16 H) | C$^2$ of C$_5$H$_3$, Ph, | 121.10 (d, $J = 170.5$) | C$^{4,5}$ of C$_5$H$_3$ |
| | | CH$_2$Ph | 121.21 (d, $J = 168.3$) | C$^2$ of C$_5$H$_3$ |
| | | | 122.02, 122.89 (d, $J = 156.0, 156.9$) | $p$-$Ph$CH$_2$, $p$-PhN |
| | | | 123.7, 126.32 (d, $J = 159.2, 152.4$) | $m$-$Ph$CH$_2$, $m$-PhN |
| | | | 128.63, 128.91 (d, $J = 158.0, 158.2$) | $o$-$Ph$CH$_2$, $o$-PhN |
| | | | 130.1 (m) | C$^{1,3}$ of C$_5$H$_3$ |
| | | | 148.02 (m) | $ipso$-$Ph$CH$_2$ |
| | | | 150.83 (m) | $ipso$-PhN |
| **3b** [Hf(CH$_2$Ph)(DAD)Cp″] | 0.04 (s, 18 H) | SiMe$_3$ | 0.05 (q, $J = 119.3$) | SiMe$_3$ |
| | 1.42 (s, 2 H) | C$H_2$Ph | 16.14 (q, $J = 127.6$) | =C$Me$ |
| | 1.72 (s, 6 H) | =CMe | 55.97 (t, $J = 116.9$) | $CH_2$Ph |
| | 6.74 (d, 2 H, $J = 1.9$) | C$^{4,5}$ of C$_5$H$_3$ | 114.77 (m) | =CMe |
| | 6.84–7.30 (m, 16 H) | C$^2$ of C$_5$H$_3$, Ph, | 120.74 (d, $J = 168.8$) | C$^{4,5}$ of C$_5$H$_3$ |
| | | CH$_2$Ph | 121.44, 122.85 (d, $J = 156.9, 157.7$) | $p$-PhCH$_2$, $p$-PhN |
| | | | 122.12 (d, $J = 169.0$) | C$^2$ of C$_5$H$_3$ |
| | | | 123.97, 127.03 (d, $J = 159.2, 151.0$) | $m$-PhCH$_2$, $m$-PhN |
| | | | 128.50, 128.86 (d, $J = 158.9, 158.1$) | $o$-PhCH$_2$, $o$-PhN |
| | | | 129.57 (m) | C$^{1,3}$ of C$_5$H$_3$ |
| | | | 148.69 (m) | $ipso$-$Ph$CH$_2$ |
| | | | 150.93 (m) | $ipso$-PhN |

**Table 1** (*Contd.*)

| | $^1$H NMR | | $^{13}$C NMR | |
|---|---|---|---|---|
| | δ | Assignment | δ | Assignment |
| **4a** [Zr(C$_3$H$_5$)(DAD)Cp″] | 0.36 (s, 18 H) | SiMe$_3$ | −0.08 (q, $J$ = 119.2) | SiMe$_3$ |
| | 1.54 (s, 6 H) | =CMe | 15.55 (q, $J$ = 127.0) | =C*Me* |
| | 2.54 (br d, 4 H, $J$ = 12.2) | CH$_2$ of C$_3$H$_5$ | 62.77 (t, $J$ = 151.8) | CH$_2$ of C$_3$H$_5$ |
| | 5.40 (q, 1 H, $J$ = 12.2) | CH of C$_3$H$_5$ | 112.17 (m) | =C*Me* |
| | 6.63 (m, 2 H) | C$^{4,5}$ of C$_5$H$_3$ | 117.51 (d, $J$ = 168.3) | C$^{4,5}$ of C$_5$H$_3$ |
| | 6.94 (m, 7 H) | o-PhN, p-PhN, C$^2$ of C$_5$H$_3$ | 119.45 (d, $J$ = 168.3) | C$^2$ of C$_5$H$_3$ |
| | 7.30 (t, 4 H, $J$ = 7.2) | m-PhN | 122.18 (d, $J$ = 157.7) | p-PhN |
| | | | 125.05 (d, $J$ = 157.7) | m-PhN |
| | | | 128.67 (d, $J$ = 157.7) | o-PhN |
| | | | 137.71 (d, $J$ = 147.2) | CH of C$_3$H$_5$ |
| | | | 152.34 (m) | ipso-PhN |
| **4b** [Hf(C$_3$H$_5$)(DAD)Cp″] | 0.04 (s, 18 H) | SiMe$_3$ | −0.11 (q, $J$ = 119.2) | SiMe$_3$ |
| | 1.55 (s, 6 H) | =CMe | 15.30 (q, $J$ = 127.2) | =C*Me* |
| | 2.58 (br d, 4 H, $J$ = 12.6) | CH$_2$ of C$_3$H$_5$ | 61.91 (t, $J$ = 151.5) | CH$_2$ of C$_3$H$_5$ |
| | 5.34 (q, 1 H, $J$ = 12.6) | CH of C$_3$H$_5$ | 110.95 (m) | =C*Me* |
| | 6.61 (m, 2 H) | C$^{4,5}$ of C$_5$H$_3$ | 117.31 (d, $J$ = 169.2) | C$^{4,5}$ of C$_5$H$_3$ |
| | 6.95 (m, 1 H) | C$^2$ of C$_5$H$_3$ | 118.63 (d, $J$ = 169.2) | C$^2$ of C$_5$H$_3$ |
| | 6.99 (t, 2 H, $J$ = 7.3) | p-PhN | 122.02 (d, $J$ = 158.1) | p-PhN |
| | 7.06 (d, 4 H, $J$ = 7.2) | o-PhN | 125.40 (d, $J$ = 159.8) | m-PhN |
| | 7.31 (t, 4 H, $J$ = 7.3) | m-PhN | 128.63 (d, $J$ = 158.1) | o-PhN |
| | | | 138.0 (d, $J$ = 147.6) | CH of C$_3$H$_5$ |
| | | | 152.33 (m) | ipso-PhN |
| **5a** [ZrCl{C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}Cp″] | 0.30, 0.33 (s, 18 H each) | SiMe$_3$ | 0.15, 1.95 (q, $J$ = 119.4, 118.6) | SiMe$_3$ |
| | 5.37 (d, 2 H, $J$ = 1.8) | C$^{4,5}$ of C$_5$H$_3$ | 119.77 (d, $J$ = 169.8) | C$^{4,5}$ of C$_5$H$_3$ |
| | 6.96 (t, 1 H, $J$ = 1.8) | C$^2$ of C$_5$H$_3$ | 126.41, 128.83 (d, $J$ = 161.5, 157) | o-C$_6$H$_4$, m-C$_6$H$_4$ |
| | 7.12, 7.23 (m, 2 H each) | C$_6$H$_4$ | 127.15, 129.24 (m) | C$^{1,3}$ of C$_5$H$_3$, ipso-C$_6$H$_4$ |
| | | | 127.88 (d, $J$ = 168.3) | C$^2$ of C$_5$H$_3$ |
| **5b** [HfCl{C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}Cp″] | 0.31, 0.32 (s, 18 H each) | SiMe$_3$ | 0.08, 2.07 (q, $J$ = 119.3, 118.6) | SiMe$_3$ |
| | 5.64 (d, 2 H, $J$ = 2) | C$^{4,5}$ of C$_5$H$_3$ | 119.68 (d, $J$ = 169.8) | C$^{4,5}$ of C$_5$H$_3$ |
| | 6.84 (t, 1 H, $J$ = 2) | C$^2$ of C$_5$H$_3$ | 125.12, 126.7 (d, $J$ = 160.7, 159) | o-C$_6$H$_4$, m-C$_6$H$_4$ |
| | 7.09, 7.21 (m, 2 H each) | C$_6$H$_4$ | 126.46 (d, $J$ = 169) | C$^2$ of C$_5$H$_3$ |
| | | | 129.02, 129.26 (m) | C$^{1,3}$ of C$_5$H$_3$, ipso-C$_6$H$_4$ |
| **6a** [NbCl$_2${C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}Cp″] | 0.35, 0.40 (s, 18 H each) | SiMe$_3$ | 0.01, 3.55 (q, $J$ = 119.7, 119.4) | SiMe$_3$ |
| | 4.22 (br s, 2 H) | C$^{4,5}$ of C$_5$H$_3$ | 113.72 (d, $J$ = 173.6) | C$^{4,5}$ of C$_5$H$_3$ |
| | 6.90 (m, 1 H) | C$^2$ of C$_5$H$_3$ | 121.65, 129.19 (m) | C$^{1,3}$ of C$_5$H$_3$, ipso-C$_6$H$_4$ |
| | 6.85, 7.07 (m, 2 H each) | C$_6$H$_4$ | 130.4, 130.99 (d, $J$ = 165.3, 163.7) | o-C$_6$H$_4$, m-C$_6$H$_4$ |
| | | | 134.2 (d, $J$ = 175.8) | C$^2$ of C$_5$H$_3$ |
| **6b** [TaCl$_2${C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}Cp″] | 0.32, 0.36 (s, 18 H each) | SiMe$_3$ | −0.05, 3.92 (q, $J$ = 119.8, 119.2) | SiMe$_3$ |
| | 4.83 (d, 2 H, $J$ = 2.0) | C$^{4,5}$ of C$_5$H$_3$ | 113.10 (d, $J$ = 174.3) | C$^{4,5}$ of C$_5$H$_3$ |
| | 6.89 (t, 1 H, $J$ = 2.0) | C$^2$ of C$_5$H$_3$ | 125.11, 127.85 (m) | C$^{1,3}$ of C$_5$H$_3$, ipso-C$_6$H$_4$ |
| | 6.80, 6.96 (m, 2 H each) | C$_6$H$_4$ | 128.77, 128.9 (d, $J$ = 162.2) | o-C$_6$H$_4$, m-C$_6$H$_4$ |
| | | | 132.65 (d, $J$ = 172) | C$^2$ of C$_5$H$_3$ |

\* In C$_6$D$_6$, 25 °C, $J$ in Hz.
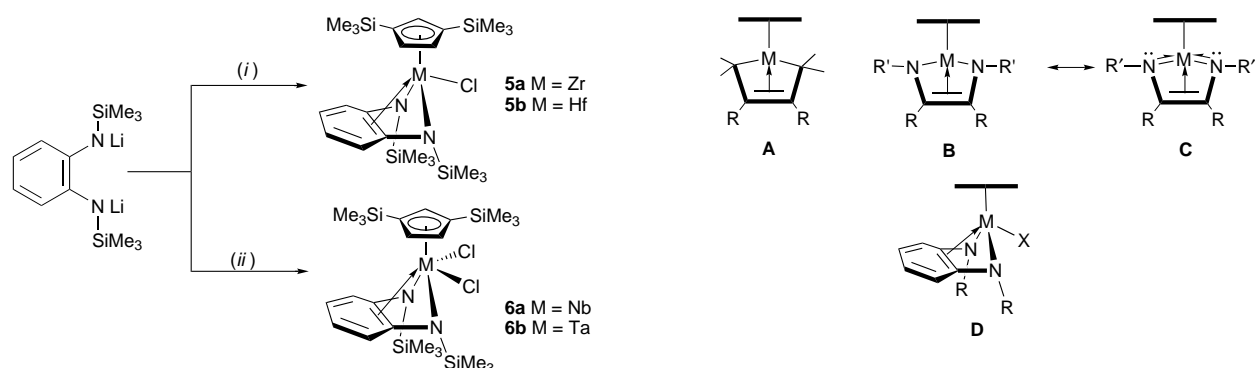


**Scheme 2** (*i*) [MCl$_3$Cp″], Et$_2$O, −78 °C to room temperature; (*ii*) [MCl$_4$Cp″], Et$_2$O, −78 °C to room temperature

solids in high yields. Spectroscopic data for all new compounds are given in Table 1.

The most significant feature of these complexes are the different co-ordination modes and conformations that can be adopted by these nitrogen ligands in comparison with the 1,3-diene ligands in [MX(η$^4$-C$_4$H$_4$R$_2$)Cp″] (R = H or Me) complexes reported earlier.[4a] For complexes of dimethylbutadiene and related dienes the 'folded envelope' geometry is well established,[7] the bonding of which is best described by a σ$^2$-π structure, with extensive dianionic character of the diene which acts as a four-electron donor, as shown in structure **A**. In the

**Table 2** Selected bond distances (Å) and angles (°) for [Zr(C₃H₅)-(DAD)Cp″] **4a** with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| Zr(1)–C(1) | 2.517(5) | Zr(1)–C(10) | 2.490(5) |
| Zr(1)–C(2) | 2.505(4) | N(6)–C(61) | 1.403(6) |
| Zr(1)–C(3) | 2.551(5) | N(6)–C(6) | 1.409(6) |
| Zr(1)–C(4) | 2.541(5) | C(6)–C(7) | 1.384(7) |
| Zr(1)–C(5) | 2.516(5) | C(6)–C(67) | 1.519(6) |
| Zr(1)–C(6) | 2.597(5) | C(7)–N(7) | 1.406(6) |
| Zr(1)–C(7) | 2.591(5) | N(7)–C(71) | 1.400(6) |
| Zr(1)–N(6) | 2.100(4) | C(7)–C(77) | 1.514(7) |
| Zr(1)–N(7) | 2.105(4) | C(8)–C(9) | 1.366(8) |
| Zr(1)–C(8) | 2.480(5) | C(9)–C(10) | 1.388(8) |
| Zr(1)–C(9) | 2.518(5) | | |
| | | | |
| N(6)–Zr(1)–N(7) | 81.5(2) | N(7)–Zr(1)–C(8) | 91.3(2) |
| C(8)–Zr(1)–C(10) | 59.1(2) | N(6)–Zr(1)–C(10) | 85.8(2) |
| C(61)–N(6)–C(6) | 119.4(4) | C(71)–N(7)–C(7) | 118.8(4) |
| C(61)–N(6)–Zr(1) | 146.3(3) | C(71)–N(7)–Zr(1) | 147.9(3) |
| C(6)–N(6)–Zr(1) | 93.4(3) | N(7)–C(7)–Zr(1) | 54.2(2) |
| C(7)–C(6)–N(6) | 118.9(4) | C(6)–C(7)–N(7) | 118.9(4) |
| C(7)–C(6)–C(67) | 121.8(4) | C(6)–C(7)–C(77) | 121.6(4) |
| N(6)–C(6)–C(67) | 118.7(4) | N(7)–C(7)–C(77) | 119.1(4) |
| C(7)–C(6)–Zr(1) | 74.3(3) | C(6)–C(7)–Zr(1) | 74.8(3) |
| N(6)–C(6)–Zr(1) | 53.8(2) | C(7)–N(7)–Zr(1) | 92.9(3) |
| C(8)–C(9)–C(10) | 125.8(6) | | |
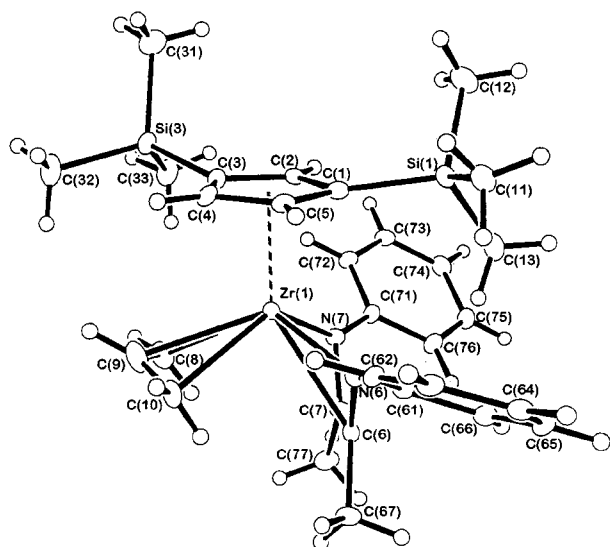


**Fig. 1** Crystal structure of [Zr(η³-C₃H₅)(DAD)Cp″] **4a** showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability

compounds [MX(diene)Cp″] and most related complexes the diene ligand adopts a supine conformation[7,8] which minimises steric interactions with the Cp ring.

The diazadiene complexes **1**–**4** also prefer a supine conformation, for similar steric reasons. This is evident from the spectroscopic data. In the ¹³C NMR spectra of **1**–**4** the signals of imine C atoms are observed between δ 110 and 116. By contrast, the corresponding resonances of the unco-ordinated DAD ligand are found at *ca.* δ 160, and for diazadienes co-ordinated in σ²-N,N′-4e fashion, *i.e. via* the nitrogen donor atoms only, the diene ¹³C resonances occur at even lower field, *e.g.* for [ZrCl₄{RN=C(Ph)C(Ph)=NR}] at δ 177.3 (R = C₆H₄-Me-4).[9] The data are in agreement with an s-*cis* configurated η⁴-bound DAD ligand[5] with significant dianionic (enediamido) character. The MN₂C₂ core in **1**–**4** is best described as a σ²-π-1,3-diazametallacyclopent-2-ene moiety with a 'folded envelope' geometry, as confirmed crystallographically in the case of **4a**.

Whereas diene complexes of the type [MX(diene)Cp] are clearly 14-electron compounds, bonding of a diazadiene involves the nitrogen lone pairs in addition to the π electrons of

the C=C double bonds, and such a ligand is therefore capable of effectively donating (up to) eight electrons, as indicated in structures **B** and **C**, leading to electronically comparatively saturated complexes. The π donation from the nitrogen lone pairs makes the alkyl compounds **2** and **3** thermally more robust than the related 14-electron butadiene complexes.[4a,6] Further evidence for the reduced electron deficiency of the metal centre comes from a comparison of the spectroscopic data with the analogous diene complexes. The M–CH₃ ligands in **2** show ¹³C chemical shifts of δ 22.7 (**2a**) and 28.5 (**2b**); *i.e.* they are high-field shifted by Δδ = 22.4 and 24.8 ppm, respectively, compared to the M–CH₃ signals of the corresponding 1,3-dimethylbutadiene complexes (δ 45.1 and 53.3).[4a] In the benzyl complexes **3** the resonances due to the *ipso*-carbons of the phenyl rings, at δ 148, and the ¹J$_{C–H}$ coupling constants (**3a**: 120 Hz; **3b**: 116.9 Hz) of the benzylic methylene groups are clear evidence for η¹-bound benzyl ligands, whereas in the related buta-1,3-diene they are η²-co-ordinated.[10] More significantly, at room temperature the ¹H NMR spectra of **4** exhibit only two signals in a 1 : 4 ratio for the central and terminal protons, respectively, of the allyl ligands, indicative of rapid exchange between the *syn* and *anti* protons. Such an exchange involves the rapid equilibration between η³- and η¹-allyl co-ordination modes, not observed in the case of 1,3-diene allyl complexes. The slow exchange limit for this process is reached at 268 K (M = Zr) and 203 K (M = Hf). The estimated activation barriers at the coalescence temperatures for the allylic rearrangements, ΔG‡ = 50.2 and 38.8 kJ mol⁻¹ for **4a** and **4b**, respectively, are very low and close to those values reported for complexes in which the η³-bound allyl ligand is significantly distorted toward an η¹-bonded configuration.[11]

Apart from these allylic rearrangements there are also other fluxional processes. On lowering the temperature, for all of these compounds, the resonances for the SiMe₃ groups and methyl substituents of the DAD ligands split into two peaks. This behaviour can be explained in terms of the hindered rotation of Cp″ about the Cp–M vector, most likely due to the interaction with the N-phenyl substituents of the DAD ligands. This leads to rotational activation barriers (**2a**, 37.6; **2b**, 38.3; **3a**, 40.9; **3b**, 41; **4a**, 43.1; **4b**, 42.4 kJ mol⁻¹) close to those observed in metallocene complexes.[12] The inequivalence of the two C₅H₃–SiMe₃ groups suggests a ground-state conformation where one of them is trapped between the two phenyl groups of the DAD ligand; this conformation is indeed found in the solid-state structure of **4a** (see below). Finally, for **4a** is observed a third rearrangement process which leads to two sets of NMR resonances belonging to two different isomers in which the allyl ligands adopt supine and prone conformations.

The same disposition towards η⁴-co-ordination as discussed above for DAD ligands has to be considered for the phenylenediamide complexes **5** and **6**, which in this case would involve donation of electron density from the C₆H₄ ring to the metal.[13] An indication of the conformation adopted by the phenylene ring is provided by the ¹H NMR resonance of the hydrogen atoms in 4- and 5-position of the Cp″ ligand which show a significant upfield shift. Such a shift would be expected if a prone (*endo*) conformation **D** was adopted, so that the Cp protons are positioned close enough to the phenylene ring to experience the influence of its magnetic anisotropy. This prone conformation of the diamido ligand is sterically favoured since it allows the bulky SiMe₃ substituents to point away from the Cp″ ligand and was confirmed crystallographically for the tantalum complex **6b** (see below).

**Structural studies**

The structures of complexes **4a** and **6b** were determined by X-ray diffraction. The structure of **4a** is shown in Fig. 1, selected bond lengths and angles are given in Table 2. The ligand environment about the Zr atom is approximately square-pyramidal, with the DAD ligand in a supine conformation. The

Table 3 Selected bond distances (Å) and angles (°) for [TaCl$_2${C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}Cp″] 6b with e.s.d.s in parentheses
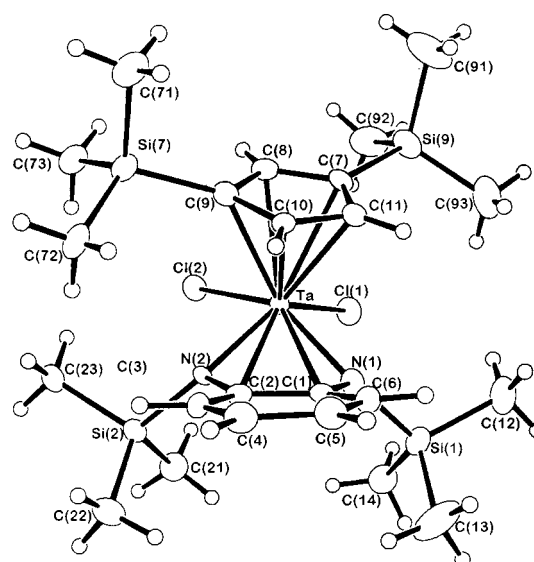
| | Molecule 1 | Molecule 2 | | Molecule 1 | Molecule 2 |
|---|---|---|---|---|---|
| Ta(1)–Cl(1) | 2.4450(10) | 2.4369(10) | N(1)–C(1) | 1.414(5) | 1.406(5) |
| Ta(1)–Cl(2) | 2.3995(11) | 2.4041(10) | N(1)–Si(1) | 1.758(3) | 1.775(3) |
| Ta(1)–N(1) | 2.014(3) | 2.025(3) | C(1)–C(2) | 1.403(6) | 1.419(5) |
| Ta(1)–N(2) | 2.023(3) | 2.033(3) | C(1)–C(6) | 1.417(6) | 1.406(5) |
| Ta(1)–C(1) | 2.557(4) | 2.581(4) | N(2)–C(2) | 1.416(5) | 1.392(5) |
| Ta(1)–C(2) | 2.532(4) | 2.544(4) | N(2)–Si(2) | 1.762(4) | 1.767(3) |
| Ta(1)–C(7) | 2.445(4) | 2.458(4) | C(2)–C(3) | 1.421(5) | 1.421(5) |
| Ta(1)–C(8) | 2.463(4) | 2.513(4) | C(3)–C(4) | 1.351(6) | 1.355(6) |
| Ta(1)–C(9) | 2.554(4) | 2.544(4) | C(4)–C(5) | 1.387(6) | 1.412(6) |
| Ta(1)–C(10) | 2.433(4) | 2.424(4) | C(5)–C(6) | 1.376(6) | 1.366(5) |
| Ta(1)–C(11) | 2.401(4) | 2.387(4) | | | |
| | | | | | |
| N(1)–Ta(1)–N(2) | 82.91(13) | 83.42(13) | Si(1)–N(1)–Ta(1) | 138.5(2) | 136.4(2) |
| N(1)–Ta(1)–Cl(1) | 81.42(9) | 83.48(8) | C(1)–C(2)–N(2) | 116.8(3) | 117.3(3) |
| N(1)–Ta(1)–Cl(2) | 130.00(10) | 130.87(10) | N(2)–C(2)–C(3) | 123.9(4) | 124.2(4) |
| N(2)–Ta(1)–Cl(2) | 81.66(9) | 81.22(9) | C(1)–C(2)–Ta(1) | 75.0(2) | 75.4(2) |
| Cl(1)–Ta(1)–Cl(2) | 79.58(4) | 79.06(4) | N(2)–C(2)–Ta(1) | 52.9(2) | 52.9(2) |
| C(2)–C(1)–N(1) | 116.4(3) | 117.0(3) | C(3)–C(2)–Ta(1) | 141.9(3) | 143.3(3) |
| C(2)–C(1)–C(6) | 119.5(4) | 119.3(3) | C(2)–N(2)–Si(2) | 121.0(3) | 122.0(3) |
| N(1)–C(1)–C(6) | 123.8(4) | 123.3(4) | C(2)–N(2)–Ta(1) | 93.2(2) | 94.1(2) |
| C(2)–C(1)–Ta(1) | 73.0(2) | 72.5(2) | Si(2)–N(2)–Ta(1) | 145.1(2) | 142.8(2) |
| N(1)–C(1)–Ta(1) | 51.7(2) | 51.3(2) | C(4)–C(3)–C(2) | 119.8(4) | 120.7(4) |
| C(6)–C(1)–Ta(1) | 145.8(3) | 147.0(3) | C(3)–C(4)–C(5) | 121.6(4) | 120.6(4) |
| C(1)–N(1)–Si(1) | 122.3(3) | 123.8(3) | C(6)–C(5)–C(4) | 120.4(4) | 120.0(4) |
| C(1)–N(1)–Ta(1) | 94.8(2) | 95.9(2) | C(5)–C(6)–C(1) | 119.5(4) | 120.8(4) |

five-membered ZrN$_2$C$_2$ ring is folded along the N(7)···N(6) vector, as seen in other structures reported for Group 4 enediamido complexes.[5,14] The allyl ligand is η$^3$-co-ordinated, with a prone (endo) conformation; it contrasts in this respect with the allyl ligands in a number of 1,3-diene complexes [M(η$^3$-C$_3$H$_5$)(η$^4$-diene)Cp][4a,15] which show supine conformation. The Cp ligand is oriented such that one of the SiMe$_3$ groups is in the plane bisecting the N–Zr–N angle, and both N-phenyl groups are twisted to minimise steric repulsion.

The nitrogen atoms maintain a trigonal-planar environment and are sp$^2$ hybridised, as seen by the angle sums at the N atoms (359.1 and 359.9°). The average Zr–N distances of 2.103(4) Å are comparatively short, in agreement with a significant p$_\pi$–d$_\pi$ interaction. We have shown earlier that Zr–N σ-bond lengths can be quite variable, depending on the degree of electronic unsaturation of the metal centre, and can range from ca. 2.05 to 2.2 Å, the latter value being indicative of little or no π-bonding contribution.[3j]

The structural parameters within the diazadiene are in agreement with an enediamido dianion, as discussed above, i.e. the C–N distances are significantly longer than in the unco-ordinated ligand,[16] and the C(6)–C(7) distance of 1.384(7) Å indicates a C=C double bond. As a result of the folding of the ZrN$_2$C$_2$ ring the distances between Zr and C(6) and C(7) [2.597(5) and 2.591(5) Å] fall well within the range expected for π co-ordination to the C=C bond. However, this is weaker than in the butadiene complex [Zr(η$^3$-C$_3$H$_5$)(η$^4$-C$_4$H$_4$Me$_2$)Cp] where the bonds to C(6) and C(7) are on average 0.09 Å shorter.

Crystals of the tantalum complex 6b contain two crystallographically independent molecules. The structure of molecule 2 is shown in Fig. 2. Selected bond lengths and angles are collected in Table 3. The compound strongly resembles the recently reported, sterically slightly bulkier SiPr$^i_3$ derivative [TaCl$_2$-{C$_6$H$_4$(NSiPr$^i_3$)$_2$}Cp*] 7.[13b] Both C$_5$H$_3$–SiMe$_3$ groups point away from the phenylenediamide ligand; in contrast to the Cp″ orientation in the diazadiene complex 4a. Complex 6b shows rather short Ta–N bond distances [average 2.020 Å for molecule 1 and 2.029 Å for molecule 2] compared to 7 (2.037 Å). The N(1)–M–N(2) angles for both compounds are similar (4a: 81.5°; 6b: 83°). The Ta–Cl distances and the Cl(1)–Ta–Cl(2) angles are comparable to those in 7. The nitrogen atoms are essentially trigonal planar, although in both independent molecules one nitrogen tends slightly more towards pyramidality than the



Fig. 2 Crystal structure of [TaCl$_2${C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}Cp″] 6b (molecule 2), showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability

other, with angle sums of 355.7 and 359.3° for molecule 1 and 356.1 and 358.8° for molecule 2. As expected on the basis of the NMR spectra, the amido ligand is co-ordinated in a prone conformation. The metal centre interacts closely with the C(1)–C(2) bond of the phenylene ring. The TaN$_2$C$_2$ ring is folded, with a dihedral angle between the TaN$_2$ and C(1)C(2)N$_2$ least squares planes of 56.8(2)° for molecule 1 and 53.8(2)° for molecule 2. The N(1)–C(1) and N(2)–C(2) distances are identical within experimental error to the corresponding bond lengths in the diazadiene complex 4a above, within the range expected for partial N–C double-bond character of an η$^4$-bound ligand. Similar geometric parameters have recently been observed in [Zr{C$_6$H$_4$(NSiPr$^i_3$)$_2$-1,2}$_2$], [TiCl$_2${C$_6$H$_4$(NSiPr$^i_3$)$_2$-1,2}] and [W(NPh)Cl$_2${C$_6$H$_4$(NSiMe$_3$)$_2$-1,2}].[13]

## Conclusion

Monocyclopentadienyl complexes of Group 4 and 5 metals readily form compounds with chelating nitrogen ligands in

**Table 4** Analytical data of complexes **1**–**6**

| Complex | Colour | Yield (%) | Analysis * (%) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | N | Cl |
| **1a** [ZrCl(DAD)Cp″] | Pale yellow | 76 | 55.9 (56.6) | 6.7 (6.5) | 5.0 (4.8) | |
| **1b** [HfCl(DAD)Cp″] | Pale yellow | 78 | 48.6 (49.2) | 6.1 (5.7) | 4.1 (4.2) | |
| **2a** [ZrMe(DAD)Cp″] | Yellow-green | 85 | 60.9 (60.9) | 7.6 (6.7) | 5.0 (5.1) | |
| **2b** [HfMe(DAD)Cp″] | Light brown | 82 | 51 (52.6) | 5.8 (5.8) | 4.3 (4.4) | |
| **3a** [Zr(CH₂Ph)(DAD)Cp″] | Yellow | 93 | 64.3 (65.0) | 7.2 (7.1) | 4.3 (4.5) | |
| **3b** [Hf(CH₂Ph)(DAD)Cp″] | Orange-brown | 90 | 56.3 (57.1) | 6.7 (6.2) | 3.1 (3.9) | |
| **4a** [Zr(C₃H₅)(DAD)Cp″] | Pale yellow | 88 | 59.0 (58.2) | 7.5 (7.3) | 4.7 (4.8) | |
| **4b** [Hf(C₃H₅)(DAD)Cp″] | Pale yellow | 87 | 51.3 (50.5) | 6.5 (6.4) | 3.6 (4.2) | |
| **5a** [ZrCl{C₆H₄(NSiMe₃)₂}Cp″] | Green | 92 | 47.3 (47.1) | 7.5 (7.4) | 4.7 (4.8) | 6.0 (6.0) |
| **6a** [NbCl₂{C₆H₄(NSiMe₃)₂}Cp″] | Red | 88 | 44.1 (44.3) | 7.1 (7.0) | 4.5 (4.5) | 11.1 (11.4) |
| **6b** [TaCl₂{C₆H₄(NSiMe₃)₂}Cp″] | Red-brown | 90 | 39.1 (38.8) | 6.2 (6.1) | 3.8 (3.9) | 9.6 (10.0) |

* Required values given in parentheses.

which $\sigma^2$-π co-ordination is adopted. The compounds are thermally more stable than the related 1,3-diene complexes and show different ground-state conformations. The increased electronic saturation through π interactions with the nitrogen atoms leads to pronounced fluxionality of the allyl derivatives. The influence of these changes on the activity of these complexes as precursors for olefin polymerisation catalysts will be reported separately.

## Experimental

### General procedures

All manipulations were performed under dried nitrogen using Schlenk techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium–benzophenone (diethyl ether, thf), sodium–potassium alloy (light petroleum, b.p. 40–60 °C) or CaH₂ (CH₂Cl₂). Deuteriated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. The compounds [MCl₃Cp″] (M = Zr or Hf),[17] [MCl₄Cp″] (M = Nb or Ta),[18] 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene (DAD)[19] and C₆H₄(NHSiMe₃)₂-1,2[20] were prepared according to published procedures. The NMR spectra were recorded on a Bruker DPX300 spectrometer and referenced to the residual solvent protons. Analytical data are collected in Table 4.

### Preparation of [ZrCl(DAD)Cp″] 1a

A solution of [ZrCl₃Cp″] (4.6 g, 11.3 mmol) in Et₂O (60 cm³) at −78 °C was added to a mixture of activated Mg turnings (5.5 g, 226 mmol) and DAD (2.7 g, 11.4 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The Et₂O was removed and the residue extracted with toluene (2 × 50 cm³). The filtrate was taken to dryness and washed with light petroleum (20 cm³). On drying under vacuum **1a** was obtained as a pale yellow solid (4.9 g, 8.5 mmol, 76%).

### Preparation of [HfCl(DAD)Cp″] 1b

The compound was prepared from [HfCl₃Cp″] (5.1 g, 10.3 mmol) following the method given for **1a** and obtained as a pale yellow solid (5.3 g, 8 mmol, 78%).

### Preparation of [Zr(CH₂Ph)(DAD)Cp″] 3a

To a solution of **1a** (1.77 g, 3.1 mmol) in Et₂O (30 cm³) at −40 °C was added by syringe 3.1 cm³ of a 1.0 M solution of PhCH₂MgCl (3.1 mmol) in Et₂O. The mixture was allowed to warm to room temperature and stirred for 3 h. After removal of the solvent the resultant solid was extracted with light petroleum (2 × 20 cm³) to give a bright yellow solution and a white precipitate of magnesium chloride. Concentration and cooling of the filtrate produced **3a** as a yellow solid (1.8 g, 2.9 mmol, 93%).

The other methyl (**2**), benzyl (**3b**) and allyl (**4**) derivatives [M(R)(DAD)Cp″] were prepared similarly in yields of 82–93% which gave satisfactory elemental analyses (Table 4).

### Preparation of [ZrCl{C₆H₄(NSiMe₃)₂-1,2}Cp″] 5a

A solution of C₆H₄(NLiSiMe₃)₂-1,2 (1.27 g, 4.8 mmol) in Et₂O (20 cm³) was added to a solution of [ZrCl₃Cp″] (1.92 g, 4.72 mmol) in Et₂O (30 cm³) at −78 °C. The solution was stirred for 12 h, while slowly being allowed to warm to room temperature. The volatile material was removed under vacuum, and the residue extracted with light petroleum (2 × 30 cm³), The resulting solution was taken to dryness, kept under high vacuum for several days and cooled (−20 °C) for 2 months to afford **5a** as a green solid (2.58 g, 4.32 mmol, 92%).

### Preparation of [HfCl{C₆H₄(NSiMe₃)₂-1,2}Cp″] 5b

This compound was prepared from [HfCl₃Cp″] (2.24 g, 4.53 mmol) following the method given for **5a** and obtained as a dark orange oil in 93% yield.

### Preparation of [NbCl₂{C₆H₄(NSiMe₃)₂-1,2}Cp″] 6a

A solution of C₆H₄(NLiSiMe₃)₂-1,2 (1.50 g, 5.67 mmol) in Et₂O (20 cm³) was added to a suspension of [NbCl₄Cp″] (2.52 g, 5.67 mmol) in Et₂O (50 cm³) at −78 °C. The solution was stirred for 12 h and allowed to warm slowly to room temperature. The volatiles were removed *in vacuo*, and the residue was extracted with light petroleum (2 × 50 cm³). The resulting solution was concentrated and cooled (−20 °C) to afford **6a** as a red crystalline solid (3.11 g, 4.99 mmol, 88%).

### Preparation of [TaCl₂{C₆H₄(NSiMe₃)₂-1,2}Cp″] 6b

The compound was prepared from [TaCl₄Cp″] (2 g, 3.75 mmol) following the method given for **6a** and obtained as a crystalline red-brown solid (2.4 g, 3.38 mmol, 90% yield). Crystals suitable for X-ray diffraction were obtained from toluene.

### X-Ray crystallography

Data for compound **4a** were collected at 160 K on a Stoe STADI4 diffractometer operating in the ω–θ scan mode. Data for **6b** were collected at 150 K on a Delft Instruments FAST TV-area detector diffractometer positioned at the window of a rotating anode generator and following previously described procedures.[21] In both cases Mo-Kα radiation (λ = 0.710 73 Å) was used. Full details of crystal data, data collection and structure refinement are given in Table 5.

The structures of both compounds were solved by standard heavy-atom methods using SHELXS 86.[23] Refinement, by full-matrix least squares on $F^2$ using SHELXL 93,[24] was essentially the same for both compounds. Non-hydrogen atoms were

**Table 5** Crystal data for compounds **4a** and **6b**

| | **4a** | **6b** |
|---|---|---|
| Formula | $C_{30}H_{42}N_2Si_2Zr$ | $C_{23}H_{43}Cl_2N_2Si_4Ta$ |
| $M$ | 578.06 | 711.89 |
| Crystal dimensions/mm | $0.41 \times 0.28 \times 0.19$ | $0.35 \times 0.215 \times 0.215$ |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $a$/Å | 10.0793(8) | 21.803(3) |
| $b$/Å | 17.201(2) | 13.681(2) |
| $c$/Å | 17.707(2) | 23.7284(9) |
| $\beta$/° | 98.890(8) | 114.672(11) |
| $U$/Å$^3$ | 3033.1(5) | 6431.7(13) |
| $Z$ | 4 | 8 |
| $D_c$/g cm$^{-3}$ | 1.27 | 1.47 |
| $\mu$/mm$^{-1}$ | 0.462 | 3.564 |
| $F(000)$ | 1216 | 2864 |
| Absorption correction | $\psi$ scans | DIFABS [22] |
| Maximum, minimum transmission factors | 0.917, 0.529 | 0.616, 0.371 |
| $\theta$ Range/° | $1.66 \leqslant \theta \leqslant 24.99$ | $1.76 \leqslant \theta \leqslant 24.99$ |
| Index range | $-11 \leqslant h \leqslant 11,$ | $-25 \leqslant h \leqslant 21,$ |
| | $0 \leqslant k \leqslant 20,$ | $-15 \leqslant k \leqslant 12,$ |
| | $0 \leqslant l \leqslant 21$ | $-26 \leqslant l \leqslant 24$ |
| Reflections collected | 5962 | 24 855 |
| Unique reflections, $n$ | 5335 ($R_{int} = 0.069$) | 9616 ($R_{int} = 0.046$) |
| Reflections with $F_c^2 > 2.0\sigma(F_c^2)$ | 4201 | 8123 |
| Number of parameters, $p$ | 340 | 601 |
| Goodness of fit on $F^2$, $s^a$ | 1.197 | 0.993 |
| $R1^b$ | 0.0508 | 0.0278 |
| $wR2^c$ | 0.1611 | 0.0647 |
| Weighting parameters $a,b^d$ | 0.0673, 8.242 | 0.0325, 0.0000 |
| Largest difference peak, hole/e Å$^{-3}$ | 0.621, $-0.702$ | 1.955, $-1.025$ |

$^a s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{\frac{1}{2}}$. $^b R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^c wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. $^d w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealised positions using a riding model (with free rotation for methyl groups).

CCDC reference number 186/816.

See http://www.rsc.org/suppdata/dt/1998/393/ for crystallographic files in .cif format.

## Acknowledgements

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