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# Synthesis and characterisation of chlorobis(dialkylamido) and alkylbis(dialkylamido) derivatives of $[(\eta^5\text{-}C_5Me_5)MCl_3](M = Ti,Zr)$

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## Abstract

Reactions of $[Cp^*ZrCl_3](Cp^* = \eta^5\text{-}C_5Me_5)$ with lithium dialkyl(aryl)amides in 1:1, 1:2 or 1:3 molar ratios afford the dialkyl(aryl)amido complexes $[Cp^*ZrCl_{3-n}(NR_2)_n][n = 1$, R = Et (**1**), Me (**2**), $Pr^i$(**3**); $n = 2$, R = Et (**4**), Me (**5**), Ph (**6**), $Pr^i$(**7**), $n = 3$, R = Et (**8**), Me (**9**)]. Treatment of $[Cp^*MCl(NMe_2)_2]$ and $[Cp^*MCl(NPh_2)_2]$ (M = Ti or Zr) with various alkyl- or aryl-lithium reagents generates the corresponding alkyl(aryl)bis[dialkyl(aryl)amide] derivatives $[Cp^*MR'(NMe_2)_2]$ in high yield [M = Ti, $R' = CH_2SiMe_3$(**10**), Me (**12**), Ph (**14**); M = Zr, $R' = CH_2SiMe_3$ (**11**), Me (**13**), R′ = Ph (**15**)] and $[Cp^*MMe(NPh_2)_2]$ [M = Ti (**16**), Zr (**17**)].

*Keywords:* Titanium; Zirconium; Dialkylamido complexes

## 1. Introduction

The chemistry of the Group 4d metals in their higher oxidation states is dominated by the predilection to form extremely strong bonds with "hard" donor atoms such as O, N and Cl. These strong metal–heteroatom interactions are often used to stabilise electronically and coordinatively unsaturated organotitanium/zirconium/hafnium compounds [1].

We have previously studied and reported a series of halo-, oxo- and amido-organotitanium complexes [2,3,4]. We have continued our work on the chemistry of amido-titanium compounds and extended these investigations to monocyclopentadienylzirconium complexes, of which only few examples with amido ligands are known [5]. In this paper we describe the synthesis and characterisation of the new dialkyl(aryl)amidozirconium derivatives, conveniently prepared from $[Cp^*ZrCl_3]$ and the corresponding amidolithium reagents. We also report the preparation and spectroscopic properties of alkyl(aryl)bisamidotitanium and zirconium compounds obtained by alkylation of the monohalidebisamidocomplexes with alkyl(aryl)lithium reagents.

## 2. Results and discussion

Although trichloro(pentamethylcyclopentadienyl)zirconium(IV) is dimeric [6], it is sufficiently soluble in a variety of solvents to react cleanly with stoichiometric amounts of lithium dialkyl(aryl)amides according to Eq. 1.

$$[Cp^*ZrCl_3] + nLiNR_2 \rightarrow$$

$$[Cp^*ZrCl_{3-n}(NR_2)_n] + nLiCl \qquad (1)$$

$n = 1 \quad R = Et(\mathbf{1});\ Me(\mathbf{2});\ {}^{i}\text{-}Pr(\mathbf{3})$

$n = 2 \quad R = Et(\mathbf{4});\ Me(\mathbf{5});\ Ph(\mathbf{6});\ {}^{i}\text{-}Pr(\mathbf{7})$

$n = 3 \quad R = Et(\mathbf{8});\ Me(\mathbf{9})$

Attempts to isolate the monosubstituted $[Cp^*ZrCl_2(NPh_2)]$ and the trisubstituted $[Cp^*Zr(NR_2)_3]$ (R = Ph or $Pr^i$ under various experimental conditions were unsuccessful and we could obtain only mixtures of different substitution products.

The complexes $[Cp^*MCl(NR_2)_2](M = Ti$ or Zr) are very useful as starting materials for the synthesis of a number of mono(alkyl/aryl) complexes. They react cleanly with 1 equivalent of LiR′ ($R' = CH_2SiMe_3$, Me or Ph) to form the monoalkyl(aryl) derivatives $[Cp^*MR'(NR_2)_2]$ in good yield according to Eq. 2.

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Table 1
$^1$H and $^{13}$C{$^1$H} NMR data of the derivatives $[\mathrm{Cp^*ZrCl_{3-\mathit{n}}(NR_2)_\mathit{n}}]$ [a]

| Compound | $^1$H NMR | $^{13}$C{$^1$H} NMR |
|---|---|---|
| $n$ = 1, R = Et (**1**) | 1.91 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 3.46 [q, 4H, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{Me)_2}$]; 0.82 [t, 6H, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, $\mathrm{N(CH_2}\mathit{Me}\mathrm{)_2}$] | 123.7 ($\mathit{C}_5\mathrm{Me_5}$); 11.4 ($\mathrm{C_5}\mathit{Me}_5$); 41.4 [$\mathrm{N(}\mathit{CH}_2\mathrm{Me)_2}$]; 12.6 [$\mathrm{N(CH_2}\mathit{Me}\mathrm{)_2}$] |
| $n$ = 1, R = Me (**2**) | 1.87 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.85 (s, 6H, $\mathrm{N}\mathit{Me}_2$) | 123.7 ($\mathit{C}_5\mathrm{Me_5}$); 11.6 ($\mathrm{C_5}\mathit{Me}_5$); 42.5 ($\mathrm{N}\mathit{Me}_2$) |
| $n$ = 1, R = $^i$Pr (**3**) | 1.93 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 3.23 [sept, 2H, $^3J_{\mathrm{H-H}}$ = 6.3 Hz, $\mathrm{N(C}\mathit{H}\mathrm{Me_2)_2}$] 1.14 [d, 12H, $^3J_{\mathrm{H-H}}$ = 6.3 Hz, $\mathrm{N(CH}\mathit{Me}_2\mathrm{)_2}$] | 124.3 ($\mathit{C}_5\mathrm{Me_5}$); 12.0 ($\mathrm{C_5}\mathit{Me}_5$); 45.7 [$\mathrm{N(}\mathit{CH}\mathrm{Me_2)_2}$]; 24.8 [$\mathrm{N(CH}\mathit{Me}_2\mathrm{)_2}$] |
| $n$ = 2, R = Et (**4**) | 1.96 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 3.42, 3.14, 0.95 ($\mathrm{ABK_3}$ spin system, 20 H, $J_{\mathrm{AB}}$ = 13.8 Hz, $J_{\mathrm{AK}} = J_{\mathrm{BK}}$ = 6.9 Hz; $\mathrm{N}\mathit{Et}_2$) | 120.1 ($\mathit{C}_5\mathrm{Me_5}$); 11.4 ($\mathrm{C_5}\mathit{Me}_5$); 42.3 [$\mathrm{N(}\mathit{CH}_2\mathrm{Me)_2}$]; 14.4 [$\mathrm{N(CH_2}\mathit{Me}\mathrm{)_2}$] |
| $n$ = 2, R = Me (**5**) | 1.92 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.84 (s, 12H, $\mathrm{N}\mathit{Me}_2$) | 119.9 ($\mathit{C}_5\mathrm{Me_5}$); 11.0 ($\mathrm{C_5}\mathit{Me}_5$); 42.5 ($\mathrm{N}\mathit{Me}_2$) |
| $n$ = 2, R = Ph (**6**) | 1.81 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 7.07–6.83 (m, 20H, $\mathrm{N}\mathit{Ph}_2$) | 124.6 ($\mathit{C}_5\mathrm{Me_5}$); 12.1 ($\mathrm{C_5}\mathit{Me}_5$); 150.1 ($i$-$\mathrm{N}\mathit{Ph}_2$); 126.2 ($o$-$\mathrm{N}\mathit{Ph}_2$); 129.2 ($m$-$\mathrm{N}\mathit{Ph}_2$); 124.1 ($p$-$\mathrm{N}\mathit{Ph}_2$) |
| $n$ = 2, R = $^i$Pr (**7**) | 2.00 (s, 15H, $\mathrm{C_5Me_5}$); 4.11 [sept, 4H, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, $\mathrm{N(C}\mathit{H}\mathrm{Me_2)_2}$]; 1.28 [d, 12H, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, $\mathrm{N(CH}\mathit{Me}_2\mathrm{)_2}$]; 1.26 (d, 12H, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, $\mathrm{N(CH}\mathit{Me}_2\mathrm{)_2}$] | 120.8 ($\mathit{C}_5\mathrm{Me_5}$); 12.0 ($\mathrm{C_5}\mathit{Me}_5$); 49.2 [$\mathrm{N(}\mathit{CH}\mathrm{Me_2)_2}$]; 26.3 [$\mathrm{N(CH}\mathit{Me}_2\mathrm{)_2}$]; 26.4 [$\mathrm{N(CH}\mathit{Me}_2\mathrm{)_2}$] |
| $n$ = 3, R = Et (**8**) | 2.03 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 3.38 [q, 12H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{Me)_2}$] 1.06 [t, 18H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, $\mathrm{N(CH_2}\mathit{Me}\mathrm{)_2}$] | 117.9 ($\mathit{C}_5\mathrm{Me_5}$); 11.6 ($\mathrm{C_5}\mathit{Me}_5$) 43.4 [$\mathrm{N(}\mathit{CH}_2\mathrm{Me)_2}$]; 15.3 [$\mathrm{N(CH_2}\mathit{Me}\mathrm{)_2}$] |
| $n$ = 3, R = Me (**9**) | 1.97 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.92 (s, 18H, $\mathrm{N}\mathit{Me}_2$) | 117.6 ($\mathit{C}_5\mathrm{Me_5}$); 10.9 ($\mathrm{C_5}\mathit{Me}_5$); 43.5 ($\mathrm{N}\mathit{Me}_2$) |

[a] Spectra recorded in benzene-$d_6$ at 20°C. $\delta$ (ppm) measured with respect to residual proton or to carbon of solvent.

$$[\mathrm{Cp^*MCl(NR_2)_2}] + \mathrm{LiR'} \rightarrow [\mathrm{Cp^*ZrR'(NR_2)_2}] + \mathrm{LiCl} \qquad (2)$$

$\mathrm{R = Me,\ R' = CH_2SiMe_3}$ $\quad$ M = Ti(**10**); Zr(**11**)
R = R′ = Me $\quad$ M = Ti(**12**); Zr(**13**)
R = Me, R′ = Ph $\quad$ M = Ti(**14**); Zr(**15**)
R = Ph, R′ = Me $\quad$ M = Ti(**16**); Zr(**17**)

All the isolated complexes are air-sensitive but quite stable at room temperature under argon. They are also very soluble in common hydrocarbon solvents, with the exception that the bis(diphenylamido) complex **6** is only slightly soluble in pentane or hexane. The products were characterised by IR, MS, $^1$H and $^{13}$C{$^1$H} NMR spectroscopy and C, H, N elemental analysis. Selected data are given in Section 3 and Tables 1 and 2.

IR data for all the new products show the presence of $\eta^5$-$\mathrm{C_5Me_5}$ [7], and the spectra show bands in the range 590–500 cm$^{-1}$ which are assigned to M–N (M = Ti or Zr) stretching vibrations, consistent with the reported values for other titanium or zirconium di(alkyl/aryl)amido complexes [8]. The electron impact mass spectra of **2**, **4–6**, **8**, **9** and **12–15**, indicate that they are monomers in the gas phase. The titanium complexes **10**, **12**, **14** and **16** may keep the monomeric structure in the solid state, as we have previously found by

Table 2
$^1$H and $^{13}$C-{$^1$H} NMR data of the new derivatives $[\mathrm{Cp^*MR'(NR_2)_2}]$ [a]

| Compound | $^1$H NMR | $^{13}$C{$^1$H} NMR |
|---|---|---|
| $\mathrm{Cp^*Ti(CH_2SiMe_3)(NMe_2)_2}$ (**10**) | 1.83 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.98 (s, 12H, $\mathrm{N}\mathit{Me}_2$) 0.49 (s, 2H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); 0.20 (s, 9H, $\mathrm{CH_2Si}\mathit{Me}_3$) | 118.9 ($\mathit{C}_5\mathrm{Me_5}$); 11.5 ($\mathrm{C_5}\mathit{Me}_5$); 46.5 ($\mathrm{N}\mathit{Me}_2$) 48.8 ($\mathit{CH}_2\mathrm{SiMe_3}$); 4.6 ($\mathrm{CH_2Si}\mathit{Me}_3$) |
| $\mathrm{Cp^*Zr(CH_2SiMe_3)(NMe_2)_2}$ (**11**) | 1.88 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.80 (s, 12H, $\mathrm{N}\mathit{Me}_2$) −0.20 (s, 2H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); 0.24 (s, 9H, $\mathrm{CH_2Si}\mathit{Me}_3$) | 117.6 ($\mathit{C}_5\mathrm{Me_5}$); 11.1 ($\mathrm{C_5}\mathit{Me}_5$); 42.2 ($\mathrm{N}\mathit{Me}_2$) 35.6 ($\mathit{CH}_2\mathrm{SiMe_3}$); 4.0 ($\mathrm{CH_2Si}\mathit{Me}_3$) |
| $\mathrm{Cp^*TiMe(NMe_2)_2}$ (**12**) | 1.85 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 3.02 (s, 12H, $\mathrm{N}\mathit{Me}_2$); 0.38 (s, 3H, $\mathrm{Ti}\mathit{Me}$) | 117.9 ($\mathit{C}_5\mathrm{Me_5}$); 10.6 ($\mathrm{C_5}\mathit{Me}_5$); 45.2 ($\mathrm{N}\mathit{Me}_2$) 39.2 ($\mathrm{Ti}\mathit{Me}$) |
| $\mathrm{Cp^*ZrMe(NMe_2)_2}$ (**13**) | 1.91 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.83 (s, 12H, $\mathrm{N}\mathit{Me}_2$); 0.05 (s, 3H, $\mathrm{Zr}\mathit{Me}$) | 117.3 ($\mathit{C}_5\mathrm{Me_5}$); 10.9 ($\mathrm{C_5}\mathit{Me}_5$); 41.5 ($\mathrm{N}\mathit{Me}_2$); 26.7 ($\mathrm{Zr}\mathit{Me}$) |
| $\mathrm{Cp^*TiPh(NMe_2)_2}$ (**14**) | 1.77 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 3.02 (s, 12H, $\mathrm{N}\mathit{Me}_2$); 7.32–7.16 (m, 5H, $\mathrm{Ti}\mathit{Ph}$) | 120.1 ($\mathit{C}_5\mathrm{Me_5}$); 11.7 ($\mathrm{C_5}\mathit{Me}_5$); 46.5 ($\mathrm{N}\mathit{Me}_2$); 193.0 (*i-Ph*); 127.0 (*o-Ph*); 133.9 (*m-Ph*); 125.1 (*p-Ph*) |
| $\mathrm{Cp^*ZrPh(NMe_2)_2}$ (**15**) | 1.84 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.86 (s, 12H, $\mathrm{N}\mathit{Me}_2$); 7.50–7.20 (m, 5H, $\mathrm{Zr}\mathit{Ph}$) | 118.5 ($\mathit{C}_5\mathrm{Me_5}$); 11.1 ($\mathrm{C_5}\mathit{Me}_5$); 42.1 ($\mathrm{N}\mathit{Me}_2$); 185.9 (*i-Ph*); 127.2 (*o-Ph*); 135.7 (*m-Ph*); 126.3 (*p-Ph*) |
| $\mathrm{Cp^*TiMe(NPh_2)_2}$ (**16**) | 1.69 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 0.88 (s, 3H, $\mathrm{Ti}\mathit{Me}$) 7.10–6.85 (m, 20H, $\mathrm{N}\mathit{Ph}_2$) | 129.5 ($\mathit{C}_5\mathrm{Me_5}$); 12.2 ($\mathrm{C_5}\mathit{Me}_5$); 64.0 ($\mathrm{Ti}\mathit{Me}$); 154.4 ($i$-$\mathrm{N}\mathit{Ph}_2$) 125.5 ($o$-$\mathrm{N}\mathit{Ph}_2$); 128.8 ($m$-$\mathrm{N}\mathit{Ph}_2$); 123.7 ($p$-$\mathrm{N}\mathit{Ph}_2$) |
| $\mathrm{Cp^*ZrMe(NPh_2)_2}$ (**17**) | 1.83 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 0.15 (s, 3H, $\mathrm{Zr}\mathit{Me}$); 7.13–6.78 (m, 20H, $\mathrm{N}\mathit{Ph}_2$) | 121.4 ($\mathit{C}_5\mathrm{Me_5}$); 11.8 ($\mathrm{C_5}\mathit{Me}_5$); 44.8 ($\mathrm{Zr}\mathit{Me}$); 149.2 ($i$-$\mathrm{N}\mathit{Ph}_2$) 125.8 ($o$-$\mathrm{N}\mathit{Ph}_2$); 129.4 ($m$-$\mathrm{N}\mathit{Ph}_2$); 123.3 ($p$-$\mathrm{N}\mathit{Ph}_2$) |

[a] Spectra recorded in benzene-$d_6$ at 20°C. $\delta$ (ppm) measured with respect to residual protons or to carbon of solvent.

X-ray crystallography for the similar compound [Cp* Ti(NMe$_2$)$_3$] [3], but definitive molecular-weight studies have not been undertaken.

The $^1$H and $^{13}$C{$^1$H} NMR spectra (Tables 1 and 2) show the presence of only one Cp* group and the signals corresponding to the NR$_2$ (R = Et, Me, Ph or Pr$^i$) and R′ (CH$_2$SiMe$_3$, Me, or Ph) ligands. In the $^{13}$C {$^1$H} NMR spectra of the alkyl derivatives [Cp* MR′(NMe$_2$)$_2$] (**10**, **11**, **12**) the $\alpha$-carbon resonances are found at considerably higher field (49–26 ppm) than those reported for the trialkyl compounds [Cp* MR′$_3$] (85–61 ppm) (M = Ti or Zr) [4], and these differences are larger for the zirconium than for the titanium complexes. Also, in the series [Cp*ZrCl$_{3-n}$(NEt$_2$)$_n$] (**1**, **4**, **8**) and [Cp*ZrCl$_{3-n}$(NMe$_2$)$_n$] (**2**, **5**, **9**) the signal corresponding to the Cp* ring carbon atoms is shifted progressively upfield with the higher degree of halide replacement. All these data are consistent with the increase of the electronic density on the metal centre caused by the strong donor dialkylamido groups. The methylene protons Zr–N(C*H*$_2$Me)$_2$ in **4** and methyl groups Zr–N(CH*Me*$_2$)$_2$ of **7** are diastereotopic as shown by their NMR spectra.

The ease of the syntheses in the Eqs. 1 and 2, combined with the intrinsic solubility and stability of compounds containing the pentamethylcyclopentadienyl ring [9], suggests that the chemistry associated with these amido complexes is promising, and further explorations are certainly warranted.

## 3. Experimental section

All reactions were carried out under argon by Schlenk techniques. Hexane and pentane were refluxed over Na/K amalgam, toluene over sodium, diethylether over Na/benzophenone and all distilled under argon. Lithium amides were prepared from the corresponding freshly distilled amines and n-butyllithium (Aldrich, 1.6 M in hexane), except LiNMe$_2$ (95%) which was purchased from Aldrich and used without further purification. LiMe was purchased from Aldrich as a 1.6 M solution in diethyl ether, LiCH$_2$SiMe$_3$ was synthesised according to literature procedures [10] and LiPh was prepared in hexane, as solvent-free solid, from PhI and n-butyllithium. [Cp*TiCl(NMe$_2$)$_2$], [Cp*TiCl(NPh$_2$)$_2$], and [Cp*ZrCl$_3$] were prepared by published procedures [3,11]. IR spectra were measured on a Perkin-Elmer 883 spectrophotometer using KBr pellets or Nujol mulls between CsI discs. $^1$H and $^{13}$C {$^1$H} NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. Electron impact mass spectra were obtained at 70 eV with a Hewletts Packard 5988 spectrometer. C, H and N analysis were carried out with a Heraeus CHN-O-Rapid microanalyzer.

### 3.1. [Cp*ZrCl$_2$(NEt$_2$)] (1)

A suspension of 0.80 g (2.40 mmol) of [Cp*ZrCl$_3$] and 0.19 g (2.40 mmol) of LiNEt$_2$ was stirred in hexane (80 ml) for 1 d at room temperature. The yellow solution was filtered and the solvent removed under vacuum to give an oily yellow residue which was extracted with 20 ml of cool pentane, filtered and then dried under vacuum. 0.73 g (83% yield) of pure **1** was obtained. Anal. Found: C, 45.21; H, 6.65; N, 3.03. C$_{14}$H$_{25}$Cl$_2$NZr Calc.: C, 45.51; H, 6.82; N, 3.79%. IR (Nujol/CsI, cm$^{-1}$): 1186 w, 1146 w, 1024 w, 1000 w, 588 s, 470 s, 358 s, 330 s.

### 3.2. [Cp*ZrCl$_2$(NMe$_2$)] (2)

A suspension of 0.50 g (1.50 mmol) of [Cp*ZrCl$_3$] and 0.08 g (1.60 mmol) of LiNMe$_2$ (95%) was stirred in hexane (80 ml) for 1 d at room temperature. The resulting pale yellow solution was filtered and the solvent removed under vacuum to yield 0.43 g (85%) of **2** as yellow crystals. Anal. Found: C, 42.27; H, 6.01; N, 3.98. C$_{12}$H$_{21}$Cl$_2$NZr Calc.: C, 42.48; H, 6.24; N, 4.13%. IR (Nujol/CsI, cm$^{-1}$): 1252 m, 1144 m, 1056 w, 1024 w, 900 s, 552 m, 392 s, 354 s. MS: *m/e* [assignment, rel. int. (%)] 339 [M$^+$, 13], 295 [M$^+$–NMe$_2$, 23].

### 3.3. [Cp*ZrCl$_2$(NPr$^i_2$)] (3)

A suspension of 0.80 g (2.40 mmol) of [Cp*ZrCl$_3$] and 0.26 g (2.40 mmol) of LiNPr$^i_2$ was stirred in hexane (80 ml) for 1 d at room temperature. The orange solution obtained was filtered and the solvent removed under vacuum to give **3** as an orange solid in 80% yield (0.76 g). Anal. Found: C, 48.31; H, 7.28; N, 3.21. C$_{16}$H$_{29}$Cl$_2$NZr Calc.: C, 48.34; H, 7.35; N, 3.52%. IR (Nujol/CsI, cm$^{-1}$): 1188 m, 1165 s, 1124 m, 1097 m, 1024 m, 998 m, 917 m, 856 m, 804 m, 592 w, 539 w, 486 w, 444 w, 348 s.

### 3.4. [Cp*ZrCl(NEt$_2$)$_2$] (4)

A suspension of 0.80 g (2.40 mmol) of [Cp*ZrCl$_3$] and 0.38 g (4.80 mmol) of LiNEt$_2$ was stirred in hexane (80 ml) for 1 d at room temperature. The pale yellow solution was filtered and the solvent removed under vacuum to afford a yellow solid of **4** in 80% yield (0.78 g). Anal. Found: C, 52.96; H, 8.35; N, 6.67. C$_{18}$H$_{35}$ClN$_2$Zr Calc.: C, 53.23; H, 8.69; N, 6.90%. IR (Nujol/CsI, cm$^{-1}$): 1186 s, 1144 s, 996 s, 876 s, 860 s, 788 s, 570 m, 360 s. MS: *m/e* [assignment, rel. int. (%)]: 404 [M$^+$, 9], 332 [M$^+$–NEt$_2$, 77], 260 [M$^+$–2 NEt$_2$, 39].

### 3.5. *[Cp*ZrCl(NMe$_2$)$_2$] (5)*

Prepared similarly to **2** from 0.50 g (1.50 mmol) of [Cp*ZrCl$_3$] and 0.10 g (3.15 mmol) of LiNMe$_2$ (95%), **5** was obtained in 90% yield (0.47 g). Anal. Found: C, 48.15; H, 7.61; N, 7.75. $C_{14}H_{27}ClN_2Zr$ Calc.: C, 48.26; H, 7.82; N, 8.05%. IR (Nujol/CsI, cm$^{-1}$): 1248 m, 1142 m, 1058 w, 944 s, 914 m, 540 m, 366 s. MS: *m/e* [assignment, rel. int. (%)] 348 [M$^+$, 3]; 304 [M$^+$–NMe$_2$, 4], 260 [M$^+$–2 NMe$_2$, 19].

### 3.6. *[Cp*ZrCl(NPh$_2$)$_2$] (6)*

A suspension of 0.60 g (1.80 mmol) of [Cp*ZrCl$_3$] and 0.63 g (3.60 mmol) of LiNPh$_2$ was stirred in toluene (80 ml) for 2 d at room temperature. The yellow solution was filtered and the solvent removed under vacuum to give **6** as yellow solid in 93% yield (1.00 g). Anal. Found: C, 68.02; H, 5.81; N, 4.59. $C_{34}H_{35}ClN_2Zr$ Calc.: C, 68.25; H, 5.90; N, 4.68%. IR (Nujol/CsI, cm$^{-1}$): 1590 s, 1308 m, 1245 s, 1179 s, 1079 w, 1066 w, 1025 m, 995 w, 921 s, 861 s, 754 s, 730 m, 696 s, 500 s, 442 w, 369 m, 335 m. MS: *m/e* [assignment, rel. int. (%)]: 596 [M$^+$, 1], 428 [M$^+$–NPh$_2$, 14], 260 [M$^+$–2 NPh$_2$, 3].

### 3.7. *[Cp*ZrCl(NPr$^i_2$)$_2$] (7)*

A solution of 0.52 g (4.80 mmol) of LiN$^i$Pr$_2$ in diethyl ether (60 ml) was added to a suspension of 0.80 g (2.40 mmol) of [Cp*ZrCl$_3$] in 60 ml of the same solvent at 0°C. The mixture was stirred maintaining the same temperature for 2 d. The brown solution was filtered and the solvent removed under vacuum to give **7** as a brown solid in 85% yield (0.94 g). Anal. Found: C, 56.95; H, 9.16; N, 5.98. $C_{22}H_{43}ClN_2Zr$ Calc.: C, 57.16; H, 9.38; N, 6.06%. IR (Nujol/CsI, cm$^{-1}$): 1185 m, 1107 m, 1061 w, 989 w, 919 w, 800 w, 781 w, 538 w, 435 w, 347 m.

### 3.8. *[Cp*Zr(NEt$_2$)$_3$] (8)*

Prepared as **4**, from 1.00 g (3.00 mmol) of [Cp*ZrCl$_3$] and 0.71 g (9.00 mmol) of LiNEt$_2$. A 92% yield (1.22 g) of brown **8** was obtained. Anal. Found: C, 59.35; H, 10.05; N, 9.31. $C_{22}H_{45}N_3Zr$ Calc.: C, 59.67; H, 10.24; N, 9.49%. IR (Nujol/CsI, cm$^{-1}$): 1180 s, 1146 s, 1000 s, 868 m, 794 m, 576 m, 340 m. MS: *m/e* [assignment, rel. int. (%)]: 441 [M$^+$, 5], 369 [M$^+$–NEt$_2$, 46], 297 [M$^+$–2 NEt$_2$, 21], 225 [M$^+$–3 NEt$_2$, 42].

### 3.9. *[Cp*Zr(NMe$_2$)$_3$] (9)*

Prepared as **2**, from 2.54 g (7.62 mmol) of [Cp*ZrCl$_3$] and 1.25 g (24.06 mmol) of LiNMe$_2$ (95%), **9** was obtained in 90% yield (2.46 g). Anal. Found: C, 53.10; H, 9.15; N, 11.01. $C_{16}H_{33}N_3Zr$ Calc.: C, 53.58; H, 9.27; N, 11.72%. IR (Nujol/CsI, cm$^{-1}$): 1240 vs, 1142 vs, 1058 s, 934 vs, 530 s, 350 s. MS: *m/e* [assignment, rel. int. (%)]: 357 [M$^+$, 23], 313 [M$^+$–NMe$_2$, 28], 269[M$^+$–2 NMe$_2$, 23], 225 [M$^+$–3 NMe$_2$, 35].

### 3.10. *[Cp*Ti(CH$_2$SiMe$_3$)(NMe$_2$)$_2$] (10)*

[Cp*TiCl(NMe$_2$)$_2$] (0.50 g, 1.63 mmol) was suspended in 50 ml of hexane and treated with 0.17 g (1.79 mmol) of LiCH$_2$SiMe$_3$. The orange mixture was stirred at room temperature overnight, then filtered and the solution obtained concentrated to *ca.* 10 ml. After cooling the solution at −40°C for 24 h, a red solid of **10** was isolated in 74% yield (0.43 g). Anal. Found: C, 59.98; H, 10.47; N, 7.75. $C_{18}H_{38}N_2SiTi$ Calc.: C, 60.35; H, 10.62; N, 7.82%. IR (Nujol/CsI, cm$^{-1}$): 1375 m, 1239 m, 1135 m, 1049 w, 1020 w, 950 m, 922 m, 848 m, 789 m, 728 vs, 569 m, 447 w.

### 3.11. *[Cp*Zr(CH$_2$SiMe$_3$)(NMe$_2$)$_2$] (11)*

**5** (0.50 g, 1.43 mmol) and 0.15 g (1.57 mmol) of LiCH$_2$SiMe$_3$ were stirred in 60 ml of hexane for 1 d at room temperature. The pale yellow solution was filtered and the solvent removed under vacuum to give a yellow solid of **11** in 78% yield (0.45 g). Anal. Found: C, 53.64; H, 9.39; N, 6.88. $C_{18}H_{38}N_2SiZr$ Calc.: C, 53.83; H, 9.47; N, 6.98%. IR (Nujol/CsI, cm$^{-1}$): 1378 m, 1243 vs, 1142 s, 1058 m, 1024 m, 942 vs, 924 vs, 893 s, 851 vs, 820 s, 742 m, 536 m, 352 m.

### 3.12. *[Cp*TiMe(NMe$_2$)$_2$] (12)*

0.50 g (1.63 mmol) of [Cp*TiCl(NMe$_2$)$_2$] were dissolved in 60 ml of pentane, the solution was cooled to 0°C and treated with 1.20 ml of LiMe (1.92 mmol). After stirring for 2 h the resulting orange suspension was filtered and the volatiles were removed in vacuo to yield 0.40 g (86%) of **12**. Anal. Found: C, 62.76; H, 10.38; N, 9.59. $C_{15}H_{30}N_2Ti$ Calc.: C, 62.96; H, 10.49; N, 9.79%. IR (KBr, cm$^{-1}$): 1444 s, 1375 m, 1240 s, 1135 m, 1049 m, 1023 m, 949 s, 920 s, 785 vs, 582 m, 557 m, 491 s, 411 m, 387 s. MS: *m/e* [assignment, rel. int. (%)]: 286 [M$^+$, 14].

### 3.13. *[Cp*ZrMe(NMe$_2$)$_2$] (13)*

A suspension of **5** (0.40 g, 1.14 mmol) in hexane at 0°C was treated with LiMe (0.85 ml, 1.37 mmol) and a white solid was formed immediately. The solution was filtered to remove the LiCl and the filtrate dried under vacuum. The solid was recrystallised from pentane to yield 0.31 g (83%) of **13** as pale yellow microcrystals. Anal. Found: C, 54.12; H, 9.02; N, 8.42. $C_{15}H_{30}N_2Zr$

Calc.: C, 54.67; H, 9.11; N, 8.50%. IR (KBr, $cm^{-1}$): 1452 s, 1377 m, 1245 s, 1144 s, 1059 m, 1024 m, 942 vs, 915 vs, 759 m, 541 m, 455 m, 351 m. MS: *m/e* [assignment, rel. int. (%)]: 329 [$M^+$, 7].

### 3.14. $[Cp^*TiPh(NMe_2)_2]$ (14)

Prepared as **10**, from 0.53 g (1.73 mmol) $[Cp^*TiCl(NMe_2)_2]$ and 0.19 g (2.08 mmol) of LiPh in 50 ml of pentane. The red solid **14** was isolated in 86% yield (0.52 g). Anal. Found: C, 68.74; H, 9.11; N, 7.97. $C_{20}H_{32}N_2Ti$ Calc.: C, 68.99; H, 9.20; N, 8.05%. IR (KBr, $cm^{-1}$): 1481 m, 1444 s, 1414 s, 1375 s, 1239 s, 1132 s, 1050 s, 1025 m, 948 vs, 922 vs, 780 vs, 723 vs, 702 vs, 569 s, 416 m, 391 s. MS: *m/e* [assignment, rel. int. (%)]: 348 [$M^+$, 37].

### 3.15. $[Cp^*ZrPh(NMe_2)_2]$ (15)

Prepared as **11**, from 0.50 g (1.43 mmol) of **5** and LiPh (0.15 g, 1.71 mmol) in 60 ml of hexane, 0.44 g (79% yield) of yellow **15** were obtained. Anal. Found: C, 61.02; H, 8.09; N, 7.11. $C_{20}H_{32}N_2Zr$ Calc.: C, 61.35; H, 8.18; N, 7.16%. IR (Nujol/CsI, $cm^{-1}$): 1377 m, 1242 m, 1143 m, 1058 m, 1025 m, 943 s, 913 s, 752 m, 537 m, 360 m. MS: *m/e* [assignment, rel. int. (%)]: 391 [$M^+$, 2].

### 3.16. $[Cp^*TiMe(NPh_2)_2]$ (16)

$[Cp^*TiCl(NPh_2)_2]$ (0.33 g, 0.59 mmol) was dissolved in 70 ml of hexane and the solution treated with 0.44 ml (0.71 mmol) of LiMe at 0°C. After stirring for 2 h the orange solution was filtered. Concentration to *ca.* 15 ml followed by cooling to −40 °C for 24 h afforded red crystals of **16** in 79% yield (0.25 g). Anal. Found: C, 78.27; H, 6.99; N, 5.02. $C_{35}H_{38}N_2Ti$ Calc.: C, 78.67; H, 7.12; N, 5.24%. IR (KBr, $cm^{-1}$): 1586 vs, 1480 vs, 1377 m, 1215 vs, 1184 vs, 1070 s, 1023 s, 933 s, 869 vs, 746 vs, 699 s, 604 m, 525 s, 503 s, 408 m.

### 3.17. $[Cp^*ZrMe(NPh_2)_2]$ (17)

Compound **6** (0.60 g, 1.00 mmol) was dissolved in 50 ml of toluene and treated with 0.75 ml of LiMe (1.20 mmol) at −78°C. The resulting suspension was stirred for 1 d at room temperature then filtered and the solvent removed under vacuum. The resulting crude yellow solid was recrystallised from pentane to yield 0.43 g (75%) of **17**. Anal. Found: C, 72.34; H, 6.45; N, 4.76. $C_{35}H_{38}N_2Zr$ Calc.: C, 72.76; H, 6.58; N, 4.85%. IR (KBr, $cm^{-1}$): 1587 vs, 1481 vs, 1376 m, 1308 m, 1250 vs, 1180 vs, 1073 m, 1024 m, 919 m, 860, 751 vs, 694 vs, 526 m, 500 s, 452 m, 359 m.

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