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## Titanium and zirconium complexes of the *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-butadiene ligand: syntheses, structures and uses in catalytic hydrosilylation reactions†

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We report here a number of dianionic 1,4-diaza-1,3-butadiene complexes of titanium and zirconium synthesised by a salt metathesis reaction. The reaction of either  $\text{CpTiCl}_3$  or  $\text{Cp}_2\text{TiCl}_2$  with the dilithium salt of *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene [**1**; abbreviated  $(\text{Dipp})_2\text{DADLi}_2$ ] afforded the mono-cyclopentadienyl titanium complex  $[\eta^5\text{-CpTi}((\text{Dipp})_2\text{DAD})\text{Cl}]$  (**2**) bearing a dianionic ene-diamide ligand, while the analogous reaction of zirconocene dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) with the dilithium salt **1** gave the bis-cyclopentadienyl zirconium complex  $[\text{Cp}_2\text{Zr}(\text{Dipp})_2\text{DAD}]$  (**3**). The metal dichloride complexes  $[\text{Ti}((\text{Dipp})_2\text{DAD})\text{Cl}_2]$  (**4**) and  $[(\text{Dipp})_2\text{DADZrCl}(\mu\text{-Cl})_2(\kappa^3\text{-Cl})(\text{Li})(\text{OEt}_2)]$  (**5**) were obtained by the reaction of **1** and anhydrous metal tetrachloride in a 1:1 molar ratio in diethyl ether at room temperature. Meanwhile, the homoleptic titanium complex  $[\text{Ti}((\text{Dipp})_2\text{DAD})_2]$  (**6**) was isolated in good yield by the treatment of **1** with  $\text{TiCl}_4$  in a 1:2 molar ratio in diethyl ether. The complexes **2** and **5** were further reacted with neosilyl lithium to afford mono- and bis-alkyl complexes of titanium  $[\eta^5\text{-CpTi}((\text{Dipp})_2\text{DAD})(\text{CH}_2\text{SiMe}_3)]$  (**7**) and zirconium  $[\text{Zr}((\text{Dipp})_2\text{DAD})(\text{CH}_2\text{SiMe}_3)_2]$  (**8**) respectively. Molecular structures of the complexes **2**, **3**, and **5–8** in the solid states were confirmed by single crystal X-ray diffraction analysis. The solid state structures of all the complexes reveal that the metal ions are chelated through the amido-nitrogen atoms and the olefinic carbons of the  $[(\text{Dipp})_2\text{DAD}]^{2-}$  moiety, satisfying the  $\sigma^2, \pi$  coordination mode. Compound **8** was used as a catalyst for the intermolecular hydrosilylation reaction of a number of olefins, and moderate activity of catalyst **8** was observed.

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## Introduction

Amido metal chemistry of the early transition metals has achieved significant momentum in the last 25 years with the design of novel amido ligands.<sup>1</sup> It was observed that, in the early stages of this field of study, most researchers focused on cyclopentadienyl-analogous amido ligands for comparison with, and for further investigation of, the well-known cyclopentadienyl moiety.<sup>2</sup> Amido–metal bonds are thermodynamically stable and less labile compared to metal–carbon bonds. However, nowadays the stable amido–metal bond is utilized in amido–metal chemistry to produce well-defined reaction centers in transition metal complexes. In this way, the reactivity of the resulting early transition metal compounds can be

specifically tailored to allow applications in areas such as the activation of small, poorly reactive molecules, homogeneous catalysis, or organic synthesis.<sup>3</sup> Recently the use of diamide ligands has gained more importance in early transition metal chemistry for the stabilization of group 4 and 5 metal complexes, due to their ability to chelate metal centers with higher oxidation numbers through the formation of dianionic forms.<sup>4</sup> Metal complexes with these bis (amido) ligands exhibit a closer relationship to the metallocenes and particularly to the constrained-geometry half-sandwich amido–metal complexes, which have been studied as potential catalysts for homogeneous Ziegler–Natta polymerization.<sup>5</sup> The chelating diamide complexes of titanium and zirconium serve as precursors for the highly active and living polymerization of olefins.<sup>6</sup> The potential advantage of the bis (amido) metal system relative to the metallocene or the half-sandwich amido–metal complexes is their lower formal electron count which results in a more electrophilic and therefore potentially more active catalyst fragment.<sup>7</sup> Since the  $\alpha$ -diimine ligand, 1,4-disubstituted diazabutadiene (DAD), was synthesized and utilized in the early 1960s,<sup>8</sup> various substituted DAD ligands have been synthesized by a number of research groups, even today, as it can be reduced to

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† Electronic supplementary information (ESI) available: X-ray crystallographic files for **2**, **3** and **5–8** in CIF format and Table S1. CCDC 1011649–1011654. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt02013h



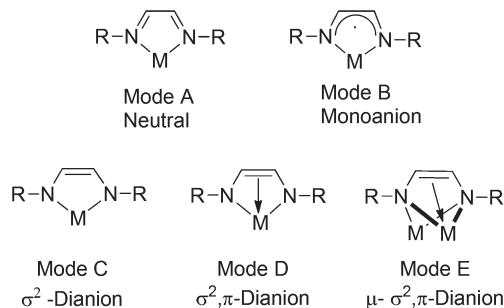


Chart 1 Different coordination modes of the DAD ligand.

generate a diamido ligand.<sup>9</sup> The diversity in coordination and redox properties of this ligand has resulted in a high level of interest in these compounds, which have already proved to have wide-ranging uses in the areas of both fundamental and applied research.<sup>10</sup> The neutral DAD molecule includes two lone electron pairs of nitrogen atoms and  $\pi$ -electrons of the multiple imine (N-C) bonds, and this molecule can act as both a  $\sigma$ - and  $\pi$ -donor, and coordinate to the metal atom as a neutral ligand.<sup>11</sup> Although the dianionic DAD ligands preferentially coordinate to early transition metals and alkaline metals in  $\sigma^2$ - and  $\sigma^2,\pi$ -coordination modes,<sup>12–14</sup> in many cases the DAD ligands coordinate to group 3 metal atoms as a  $\sigma^2$ -monoanion,<sup>15</sup> and, in addition, both monoanionic and dianionic coordination modes were observed for alkaline-earth metals, group 12, and group 13 metal complexes.<sup>16,17</sup> The possible flexible coordination modes depending on the types and redox properties of the central metal are shown in Chart 1.

The DAD ligand is widely utilized not only for early transition metals,<sup>18,19</sup> f-block metals,<sup>20</sup> and late transition metals,<sup>21</sup> but also for s-block and p-block main-group elements.<sup>22–24</sup> In the majority of these complexes, the DAD ligands are coordinated in their dianionic form as chelating enediamides to the metal (mode D) and therefore are reminiscent of diamide ligands.

To get more insight into the structure-reactivity relationships of early transition metal DAD complexes, and to explore their applications in organic transformations, we have studied this chemistry further. In this context, we present the synthesis of a number of dianionic 1,4-diaza-1,3-butadiene complexes with the molecular compositions  $[\eta^5\text{-CpTi}((\text{Dipp})_2\text{DAD})\text{Cl}]$  (2),  $[\text{Cp}_2\text{Zr}((\text{Dipp})_2\text{DAD})]$  (3),  $[\text{Ti}((\text{Dipp})_2\text{DAD})\text{Cl}_2]$  (4),  $[(\text{Dipp})_2\text{DADZrCl}(\mu\text{-Cl})_2(\kappa^3\text{-Cl})(\text{Li})(\text{OEt}_2)]$  (5),  $[\text{Ti}((\text{Dipp})_2\text{DAD})_2]$  (6),  $[\eta^5\text{-CpTi}((\text{Dipp})_2\text{DAD})(\text{CH}_2\text{SiMe}_3)]$  (7),  $[\text{Zr}((\text{Dipp})_2\text{DAD})\text{-}(\text{CH}_2\text{SiMe}_3)_2]$  (8). The solid state structures of complexes 2–3 and 5–8 are also reported. The catalytic hydrosilylation of various alkenes using complex 8 as a catalyst is also presented.

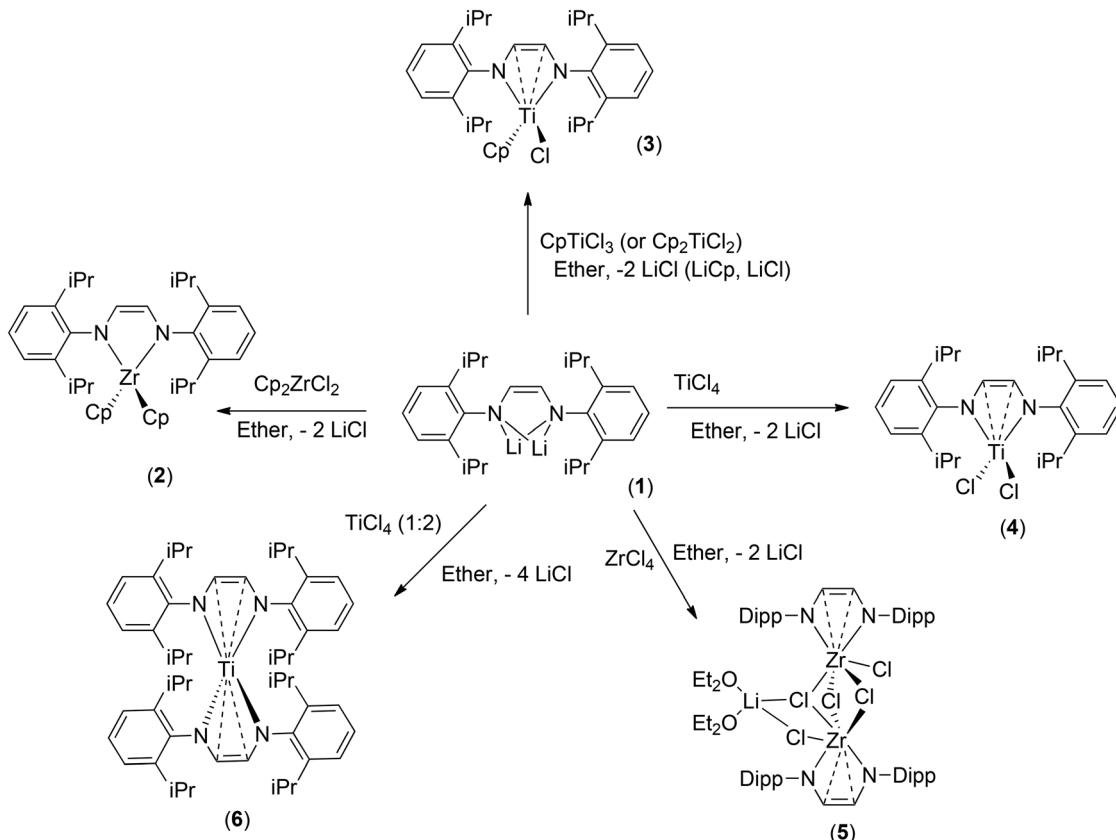
## Results and discussion

### Cyclopentadienyl metal complexes

The cyclopentadienyl titanium complex  $[\eta^5\text{-CpTi}((\text{Dipp})_2\text{DAD})\text{Cl}]$  (2) was isolated in good yield from the reaction of  $(\text{Dipp})_2\text{DADLi}_2$  (1) and  $\text{CpTiCl}_3$  in a 1:1 molar ratio in diethyl ether at room temperature, followed by re-crystallisation from ether at  $-35^\circ\text{C}$  (see Scheme 1). The titanium complex 2 could also be obtained by the reaction of 1 and titanocene dichloride ( $\text{Cp}_2\text{TiCl}_2$ ) under similar reaction conditions. Thus under the reaction conditions, one cyclopentadienyl moiety underwent elimination from  $\text{Cp}_2\text{TiCl}_2$  to  $\text{LiCp}$  along with one equivalent  $\text{LiCl}$ . Such phenomenon was recently observed by Sun *et al.* while treating triscyclopentadienyl yttrium with a lithium amidinate ligand.<sup>25</sup> In contrast, the reaction of zirconocene dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) with dianionic lithium salt 1 afforded the corresponding bis-cyclopentadienyl zirconium complex  $[\text{Cp}_2\text{Zr}((\text{Dipp})_2\text{DAD})]$  (3) in good yield by elimination of two equivalents of lithium chloride (see Scheme 1). Both the titanium and zirconium complexes were characterized by spectroscopic techniques and the solid states of the complexes 2 and 3 were established by X-ray diffraction analysis. In  $^1\text{H}$  NMR spectra measured in  $\text{C}_6\text{D}_6$ , the resonances of the Cp protons in 2 appear at 6.17 ppm as a sharp singlet. The signals for the analogous Cp protons in complex 3 are observed at 5.62 and 5.56 ppm, indicating two different chemical environments for the two cyclopentadienyl rings. The sharp singlets at 6.16 ppm for 2 and 5.35 ppm for 3 are assigned to the olefinic protons of the respective DAD ligand backbone. Therefore the resonances for the olefinic protons in 2 are significantly low field shifted compared to those of bis-cyclopentadienyl complex 3. Two septets for each complex (3.51 and 2.33 ppm for 2 and 3.71 and 2.92 ppm for 3) are observed for the isopropyl groups of the 2,6-diisopropylphenyl moiety present in the DAD ligand. The presence of two distinct septets in each complex can be explained by the asymmetric attachment of the DAD ligand in each case. The isopropyl methyl protons show four doublet resonances with a coupling constant of 6.8 Hz in 2, due to the restricted rotation around the respective carbon nitrogen bond of the DAD ligand moiety; this indicates the presence of non-equivalent 2,6-diisopropylphenyl groups. However, in 3, we observed two doublets for one set of diastereotopic isopropyl  $\text{CH}_3$  groups, indicating the presence of equivalent 2,6-diisopropylphenyl groups. In proton decoupled  $^{13}\text{C}$  NMR spectra for 2, the resonances at 114.6 ppm and 108.3 ppm represent the  $\text{C}_5$  of the Cp moiety and the olefinic carbons of the DAD ligand. For zirconium compound 3, the  $^{13}\text{C}\{^1\text{H}\}$  NMR signals are 114.3 and 110.1 ppm for the two Cp rings and 106.7 ppm for the olefinic carbon atoms. All of the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR signals are in agreement with the values reported in the literature.<sup>14</sup>

The molecular structure of the air- and moisture-sensitive complexes 2–3 were established by single crystal X-ray diffraction analysis. The complex 2 crystallizes in the monoclinic space group  $P2_1/c$  and has four independent molecules in the unit cell (Fig. 1). The zirconium complex 3 crystallizes in the triclinic space group  $P\bar{1}$  and has two independent molecules along with one molecule of diethyl ether in the unit cell as a solvate (Fig. 2). The details of the structural and refinement parameters of the crystal structures of 2–3 are given in Table TS1 in the ESI.<sup>†</sup> Complex 2 is monomeric and the

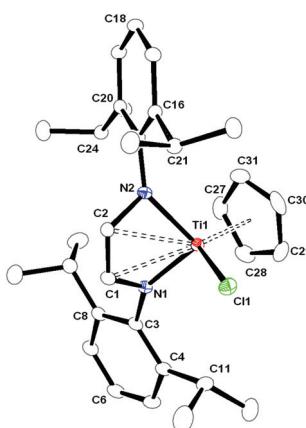




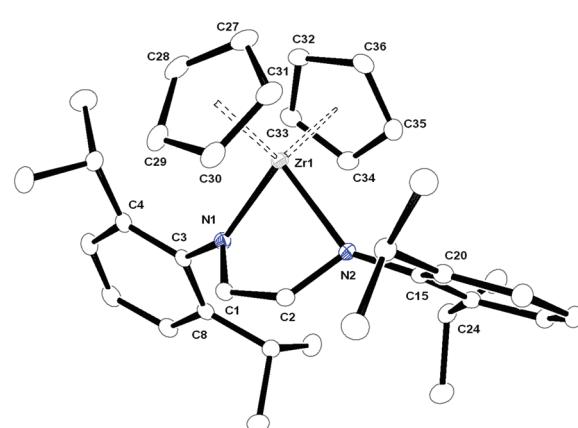
**Scheme 1** Syntheses of titanium and zirconium complexes **2–6** from **1**.

coordination polyhedron is formed by the chelation of two amido nitrogen atoms of the dianionic DAD ligand,  $\eta^5$ -coordination of one cyclopentadienyl moiety, and one chloride atom.

The geometry around the titanium ion can be best described as pseudo tetrahedral, considering the  $\eta^5$ -Cp ring as a pseudo-monodentate ligand. The Ti–N distances [1.928(2) and 1.922(2) Å]



**Fig. 1** ORTEP drawing of **2** showing the atom labelling scheme; ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [°]: Ti1–N1 1.928(2), Ti1–N2 1.922(2), Ti1–Cl1 2.3283(8), Ti1–C27 2.331(3), Ti1–C31 2.338(3), Ti1–C28 2.342(3), Ti1–C30 2.352(3), Ti1–C29 2.358(3), Ti1–C1 2.427(3), Ti1–C2 2.433(3), N1–C1 1.389(3), N1–C3 1.429(3), N2–C2 1.383(3), N2–C15 1.437(3), C1–C2 1.382(4), N2–Ti1–N1 89.90(9), N2–Ti1–C1 109.42(7), N1–Ti1–C1 109.33(7), N2–Ti1–C1 64.88(8), N1–Ti1–C1 34.86(9), Cl1–Ti1–C1 94.15(6), C27–Ti1–C1 117.84(10), C2–N2–Ti1 34.57(8), N1–Ti1–C2 65.43(9), Cl1–Ti1–C2 93.91(6), C27–Ti1–C2 118.68(10), C1–Ti1–C2 33.05(8), C1–N1–Ti1 92.60(15).



**Fig. 2** ORTEP drawing of **3** showing the atom labelling scheme; ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [°]: Zr1–N1 2.1050(14), Zr1–N2 2.1406(14), Zr1–C1 2.5928(17), Zr1–C2 2.5977(16), Zr1–C36 2.5223(19), Zr1–C33 2.5303(18), Zr1–C33 2.5344(18), Zr1–C34 2.5398(19), Zr1–C35 2.5310(18), Zr1–C28 2.5898(19), Zr1–C29 2.5943(19), Zr1–C31 2.5985(18), N1–C1 1.392(2), N1–C3 1.436(2), N2–C2 1.389(2), N2–C15 1.434(2), C1–C2 1.377(2), N1–Zr1–N2 84.08(5), N1–Zr1–C1 32.41(5), N2–Zr1–C1 60.62(5), N1–Zr1–C2 60.77(5), C1–N1–Zr1 93.46(10), C3–N1–Zr1 148.42(11), C2–N2–Zr1 92.28(10), C15–N2–Zr1 145.87(11).



are close to that of the Ti–N covalent bond. The Ti–C(Cp) distances, ranging from 2.331(3) to 2.358(3) Å, are within the agreement of reported Ti–C(Cp) values. The zirconium complex **3** is also monomeric, bearing two  $\eta^5$ -Cp moiety and one DAD ligand. The geometry around the zirconium ion is pseudo tetrahedral, considering the  $\eta^5$ -Cp ring as a pseudo-monodentate ligand. The Zr–N distances [2.105(1) and 2.141(1) Å] are slightly longer than the Ti–N distances, due to the larger ion radius of Zr(IV) ion, however they are in agreement with the Zr–N covalent bonds reported in the literature. The Zr–C(Cp) distances [2.52(2) to 2.590(2) Å] are also slightly longer than the Ti–C(Cp) distances, but are in the range of the Zr–C(Cp) distances reported for other zirconocene complexes.<sup>26</sup> Notably, the coordination of the dianionic DAD ligands in complex **2** and **3** are similar, and both complexes form a five-membered diazametallacyclopentene structure (Ti1–N1–C1–C2–N2 for **2** and Zr1–N1–C1–C2–N2 for **3**). Both metallacycles are folded and the dihedral angles between the N1–M–N2 and N1–C1–C2–N2 planes are 50.62° (for **2**) and 50.30° (for **3**). In complex **2**, the distances between the titanium ion and C1=C2 are short enough [2.427(3) and 2.433(3) Å] for  $\pi$  bonding to display the  $\sigma^2, \pi$ -enediamide mode of the DAD ligand. However, no such  $\pi$  interactions between the zirconium ion and the olefinic carbon atoms are observed in the molecular structure. Thus for complex **3**, the DAD ligand displayed only a  $\sigma^2$ -diamide mode (C in Chart 1). Nevertheless, DAD ligation can be described as the elongation of the C–N bond [1.389(3) and 1.383(3) Å for **2**; 1.392(2) and 1.389(2) Å for **3**] and the shortening of the C–C bond [1.382(4) Å for **2**; 1.377(2) Å for **3**] *i.e.* a long–short–long sequence compared to the neutral DAD ligand. Similar coordination behavior has also been observed in recently reported DAD lanthanide complexes.<sup>14</sup>

### Metal dichloride complexes

Upon treating **1** with  $\text{MCl}_4$  ( $\text{M} = \text{Ti}$  and  $\text{Zr}$ ) either in toluene (in the case of Ti) at  $-78^\circ\text{C}$  or in diethyl ether (in the case of Zr) at room temperature, a DAD titanium dichloride complex  $[\text{Ti}(\text{Dipp})_2\text{DAD}]\text{Cl}_2$  (**4**) and an ‘ate’ complex for zirconium  $[\{(\text{Dipp})_2\text{DAD}\}\text{ZrCl}(\mu\text{-Cl})_2(\text{Li})(\text{OEt}_2)_2]$  (**5**) were obtained respectively in good yields. Both the complexes **4** and **5** were characterized by spectroscopic and combustion analyses. The solid state structure of complex **5** was established by single crystal X-ray diffraction analysis. In the  $^1\text{H}$  NMR spectrum of **5** in  $\text{C}_6\text{D}_6$ , a sharp singlet was observed at  $\delta$  5.81 ppm (6.18 ppm for **4**), which was assigned to the olefinic protons of the DAD ligand backbone; a broad signal was observed at  $\delta$  3.31 ppm (2.98 ppm for **4**); and two doublet resonances of a constant 5.6 Hz appeared at  $\delta$  1.20 and 1.01 ppm (1.14 ppm for **4**), respectively, due to the CH hydrogen and isopropyl methyl hydrogen atoms of the ligand. The above values are quite similar to the corresponding values of compounds **2** and **3** (see above).

The lithium chloride incorporated compound  $[\{(\text{Dipp})_2\text{DAD}\}\text{ZrCl}(\mu\text{-Cl})_2(\text{Li})(\text{OEt}_2)_2]$  was re-crystallized from diethyl ether; this crystallizes in the monoclinic space group  $P2_1/c$  along

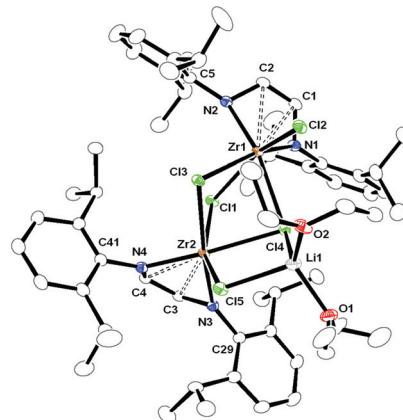


Fig. 3 ORTEP drawing of **5** showing the atom labelling scheme; ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [°]: Zr2–N3 2.044(3), Zr2–N4 2.050(3), Zr2–C4 2.472(4), Zr2–C3 2.472(4), Zr2–Cl5 2.4951(10), Zr2–Cl1 2.5687(9), Zr2–Cl3 2.6569(9), Zr2–Cl4 2.7194(10), Zr1–N1 2.044(3), Zr1–N2 2.045(3), Zr1–Cl2 2.4215(10), Zr1–C1 2.481(4), Zr1–C2 2.485(4), Zr1–Cl3 2.6377(10), Zr1–Cl1 2.7047(9), Zr1–Cl4 2.7079(10), Cl4–Li1 2.4468, Cl5–Li1 2.382(9), C41–N4 1.430(5), C5–N2 1.437(5), C4–N4 1.402(5), N1–C17 1.435(5), C2–N2 1.401(5), N3–C3 1.398(5), N3–Zr2–N4 87.82(13), N3–Zr2–C4 63.83(13), C4–Zr2–C3 32.18(13), N3–Zr2–Cl5 92.82(10), N4–Zr2–Cl5 95.04(9), C4–Zr2–Cl5 118.76(9), C3–Zr2–Cl5 117.80(9), N3–Zr2–C11 100.66(10), N4–Zr2–Cl1 105.87(9), C4–Zr2–Cl1 85.76(9), C3–Zr2–C11 83.66(9), Cl5–Zr2–Cl1 155.39(3), N3–Zr2–Cl3 175.09(10), N4–Zr2–C13 96.97(9), C4–Zr2–Cl3 119.96(9), C3–Zr2–Cl3 148.01(9), Cl5–Zr2–C13 87.86(3), Cl1–Zr2–Cl3 77.02(3), N3–Zr2–Cl4 97.74(10), N4–Zr2–C14 173.77(9), C4–Zr2–Cl4 151.35(10), C3–Zr2–Cl4 122.22(10), Cl5–Zr2–Cl4 81.94(3), Cl1–Zr2–Cl4 75.95(3), Cl3–Zr2–Cl4 77.53(3), N1–Zr1–N2 88.01(14), N1–Zr1–C12 105.15(11), N2–Zr1–Cl2 104.96(10), Cl2–Zr1–C2 87.92(11), N2–Zr1–Cl3 96.64(10), Cl2–Zr1–Cl3 90.97(3), C1–Zr1–Cl3 159.12(11), C2–Zr1–Cl3 127.24(10), N1–Zr1–Cl1 86.96(10), N2–Zr1–Cl1 91.85(10), Cl2–Zr1–Cl1 159.40(3), Cl1–Zr1–Cl1 110.24(11), C2–Zr1–Cl1 112.56(10), Cl3–Zr1–Cl1 75.05(3).

with four independent molecules in the unit cell. The incorporation of lithium chloride into the coordination sphere of metal complexes is commonly reported in the literature, due to the smaller size of lithium.<sup>27</sup> Lithium chloride incorporated complexes  $[(\text{Me}_3\text{SiNPPPh}_2)_2\text{CH}]\text{Yb}(\mu\text{-Cl})_2\text{LiCl}(\text{THF})_2$ ,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$ <sup>28</sup> and  $[(\text{Me}_3\text{SiNPPPh}_2)_2\text{CH}]\text{Yb}(\mu\text{-Cl})_2\text{LiCl}(\text{THF})_2$  have been reported by us and others.<sup>29</sup> The solid state structure of complex **5** is given in Fig. 3 and the details of the structural parameters are given in Table TS1 in the ESI.† Zirconium complex **5** has a dimeric structure bearing the DAD ligand and four bridging chloride atoms. One terminal chloride atom Cl2 is attached with the second zirconium atom to make both the zirconium centers non symmetric. However, the geometry of each metal ion can be best described as distorted octahedral. In this complex, the lighter alkali metal lithium coordinates to one zirconium through two  $\mu$ -chlorine atoms, along with two solvent diethyl ether molecules coordinating to the lithium atom. The geometry around the lithium can be considered as distorted tetrahedral. Three four-membered metallacycles, Li1–Cl5–Zr2–Cl4, Zr1–Cl1–Zr2–Cl3 and Zr1–Cl3–Zr2–Cl4, are formed by the  $\mu$ -bridging of three chlorine atoms (Cl1, Cl3, Cl5) and one  $\kappa^3$  chlorine (Cl4) toward



the lithium and zirconium atoms, with a distance of 3.665(1) Å, and between two zirconium atoms, with a distance of 3.737(1) Å, respectively. One chloride atom is terminally bonded with the zirconium atom Zr1, making the two metal ions asymmetric in nature. The terminal Zr–Cl2 bond length (2.422(2) Å) is significantly shorter than the bridging Zr–Cl distances (2.495(3) to 2.719 (2) Å). The Zr–N distances [Zr1–N1 2.044(3), Zr1–N2 2.045(3), Zr2–N3 2.044(3), Zr2–N4 2.050(3) Å] are slightly shorter, due to the presence of electron-withdrawing chloride ions, than that for complex 3, where electron-donating cyclopentadienyl moieties are present. Two zirconium metallacycles present in the dimeric structure of 5 are folded and the DAD ligands satisfy the  $\sigma^2,\pi$ -enediamide mode of coordination to the zirconium ion, with a long–short–long sequence within the ligand fragments [N1–C1 1.394(5), N2–C2 1.401(5), C3–N3 1.398(5), C4–N4 1.402(5), C1–C2 1.364(6), C3–C4 1.370(6) Å].

### Homoleptic complex

The bis-DAD titanium complex  $[\text{Ti}\{(\text{Dipp})_2\text{DAD}\}_2]$  (6) was isolated by the treatment of 1 with  $\text{TiCl}_4$  in a 1:2 molar ratio, by the elimination of  $\text{LiCl}$ . The corresponding complex of zirconium was also recently synthesized by the reaction reduction of the neutral DAD ligand followed by a reaction with zirconium tetrachloride.<sup>30</sup> The complex 6 was characterized by  $^1\text{H}$ ,  $^{13}\text{C}\{\text{H}\}$  NMR spectroscopy and combustion analysis, and its molecular structure was established by single crystal X-ray diffraction analysis. The  $^1\text{H}$  NMR spectra of the complex 6 show two sets of signals for each DAD ligand. Four doublets at  $\delta$  1.24, 1.21, 1.17 and 1.15 ppm in a 12:12:12:12 ratio, and a coupling constant of 4.8 Hz in each case can be assigned to the resonances of 48 methyl protons distributed in four diisopropylphenyl moieties. The magnetically asymmetric protons indicate that the orientations of the two DAD ligands must be in different planes. The resonances for the olefinic protons of the two DAD ligands' backbones are observed at  $\delta$  6.18 and 6.05 ppm as doublets, indicating a clear distinction between the two ligands' magnetic environments. However two multiplets at  $\delta$  3.12 and 2.95 ppm are obtained for the eight isopropyl protons, due to the overlapping of two closely associated septets for each DAD ligand. In proton decoupled  $^{13}\text{C}$  NMR spectra, we observed that the characteristic peaks for the two DAD ligands match with complexes 2 and 4 (see the Experimental section).<sup>30</sup>

The X-ray quality crystal of titanium complex 6 was re-crystallized from diethyl ether at  $-35^\circ\text{C}$  as a red crystal. Compound 6 crystallizes in the monoclinic space group  $P2_1/c$  with four independent molecules in the unit cell. The solid state structure of complex 6 is given in Fig. 4 and details of the structural parameters are given in Table TS1 in the ESI.† All the hydrogen atoms were located in the Fourier difference map and were subsequently refined. The coordination polyhedron is formed by four amido nitrogen atoms from the two DAD ligands. The geometry around the titanium ion is best described as distorted tetrahedral. The Ti–N distances [Ti1–N1 1.968(14), Ti1–N2 1.920(14), Ti1–N3 1.928(14) and Ti–N4

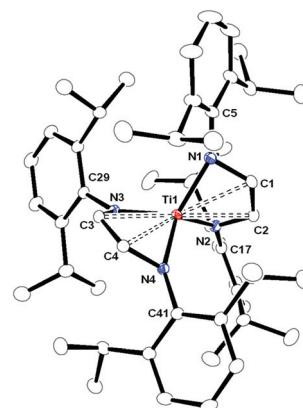


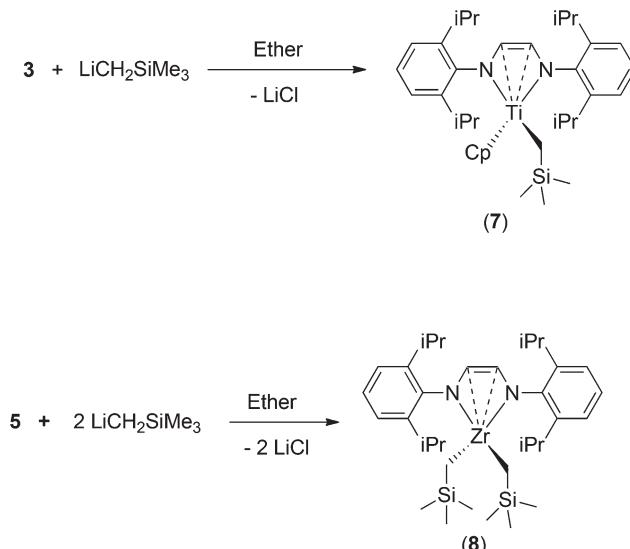
Fig. 4 ORTEP drawing of 6 showing the atom labelling scheme; ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [°]: Ti1–N1 1.9675(14), Ti1–N2 1.9196(14), Ti1–N3 1.9282(14), Ti1–N4 1.9566(13), Ti1–C1 2.3941(17), Ti1–C2 2.3841(18), Ti1–C3 2.3722(17), Ti1–C4 2.3942(17), N1–C1 1.390(2), N1–C5 1.431(2), N2–C2 1.399(2), N2–C17 1.431(2), N3–C3 1.391(2), N3–C29 1.4333(19), N4–C4 1.392(2), N4–C41 1.4292, C1–C2 1.366(3), C3–C4 1.377(2), N2–Ti1–N3 112.80(6), N2–Ti1–N4 116.40(6), N3–Ti1–N4 91.26(6), N2–Ti1–N1 90.85(6), N3–Ti1–N1 118.87(6), N4–Ti1–N1 128.30(6), N2–Ti1–C3 146.47(6), N3–Ti1–C3 35.91(5), N1–Ti1–C3 113.88(6), N3–Ti1–C2 147.10(6), N4–Ti1–C2 111.07(6), C3–Ti1–C2 176.90(6), N3–Ti1–C1 150.94(6), N4–Ti1–C1 115.68(6), C3–Ti1–C1 145.59(6), C2–Ti1–C1 33.21(6), N2–Ti1–C4 148.58(6), N1–Ti1–C4 117.62(6).

1.957(13) Å] are similar to those of complex 2 and can be considered as covalent bonds. The Ti–C distances [Ti1–C1 2.394(17), Ti1–C2 2.384(18), Ti1–C3 2.372(17), 2.394(17) Å] are sufficiently shorter, considering the  $\sigma$  bonds between the metal ion and the C=C backbone of the ligands. Two folded metallacycles Ti1–N1–C1–C2–N2 and Ti1–N3–C3–C4–N4 are formed by the ligation of two dianionic DAD ligands which satisfy the  $\sigma^2,\pi$ -enediamide mode of coordination to the zirconium ion, with a long–short–long sequence within the ligand fragments [N1–C1 1.390(3), C1–C2 1.366(3) N2–C2 1.399(2); C3–N3 1.391(2), C3–C4 1.377(2), C4–N4 1.392(2) Å]. A dihedral angle of 59.2° was observed between the two planes containing N1, C1, C2, N2 atoms and N3, C3, C4, N4 atoms present in the two ligands. The center metal titanium ion is 1.104 and 1.101 Å, respectively, away from the above-mentioned two planes.

### Metal mono- and bis-alkyl complexes

To learn more about the reactivity of metal halide complexes 2 and 5, we were interested in synthesizing their alkyl derivatives. Metal alkyl complexes are important precursors to catalysts for a number of organic transformations.<sup>31</sup> To explore the reactivity of titanium and zirconium halide complexes 2 and 5, we decided to isolate the corresponding metal alkyl complexes. Both the complexes 2 and 5 were reacted with trimethylsilylmethyl lithium in diethyl ether as a solvent to afford the corresponding mono-alkyl [ $\eta^5\text{-CpTi}((\text{Dipp})_2\text{DAD})(\text{CH}_2\text{SiMe}_3)$ ] (7) and bis-alkyl [ $\text{Zr}\{(\text{Dipp})_2\text{DAD}\}(\text{CH}_2\text{SiMe}_3)_2$ ] (8) complexes, respectively, in good yields after re-crystallisation from hexane at  $-35^\circ\text{C}$  (Scheme 2). Compounds 7 and 8 are soluble in THF,





Scheme 2 Syntheses of titanium and zirconium alkyl complexes 7–8.

toluene and hydrocarbon solvents like pentane and hexane. Both air- and moisture-sensitive complexes were characterized by spectroscopic analysis and the solid state structures of the complexes 7–8 were established by single crystal X-ray diffraction analysis.

The  $^1\text{H}$  NMR spectrum of 7 in  $\text{C}_6\text{D}_6$  is very similar to the spectrum recorded for complex 2, exhibiting four characteristic doublet resonances in a 6:6:6:6 ratio for the four different types of isopropyl methyl groups present in the DAD ligand, along with two high field septet resonances at 3.25 and 2.42 ppm for the isopropyl –CH hydrogen atoms. Thus it is evident that the chemical and magnetic environments of isopropyl methyl and –CH protons are different due to the presence of the alkyl group attached to the titanium ion. Between two sharp singlets, the signal at  $\delta$  6.19 ppm can be assigned to the five protons present in the cyclopentadienyl ring, whereas the signal at  $\delta$  5.95 ppm was confirmed for the olefinic protons ( $\text{C}=\text{C}$ ) of the DAD ligand. For the neosilyl ( $\text{CH}_2\text{SiMe}_3$ ) group in 7, one singlet at  $\delta$  0.18 ppm ( $\text{SiMe}_3$ ) and one singlet at  $\delta$  –0.46 ppm is observed at high field, which can be assigned to methylene ( $\text{CH}_2$ ) hydrogen atoms. In the  $^1\text{H}$  NMR spectrum, zirconium bis-alkyl complex 8 exhibits two doublets at  $\delta$  5.97 and 5.91 ppm, assignable to the olefinic protons of the DAD ligand backbone and two septets at  $\delta$  3.54 and 3.17 ppm for two chemically different isopropyl –CH protons, while four doublet resonances with a coupling constant of 6.8 Hz appeared at  $\delta$  1.33, 1.22, 1.10 and 0.92 ppm in a 6:6:6:6 ratio for the methyl protons of the ligand. In addition, two singlets at  $\delta$  0.10 and 0.03 ppm were observed for the two neosilyl ( $\text{CH}_2\text{SiMe}_3$ ) groups present in 8. Similar chemical shift values for the neosilyl groups ( $\delta$  0.13 and 0.04 ppm) were reported for  $\text{Cp}''_2\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$  ( $\text{Cp}'' = \text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4$ ) by Piers *et al.*<sup>32</sup>

Although there has been ongoing interest in the alkyl complexes of group 4 organometallics, and particularly in the

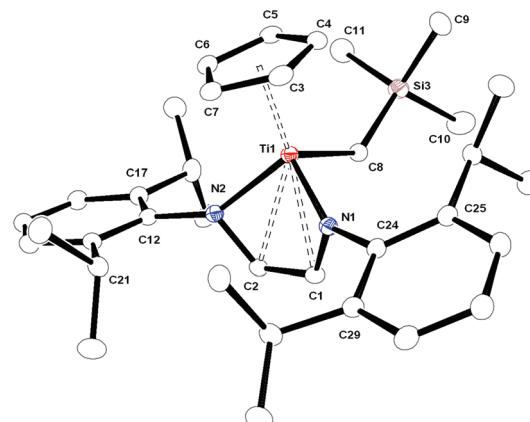
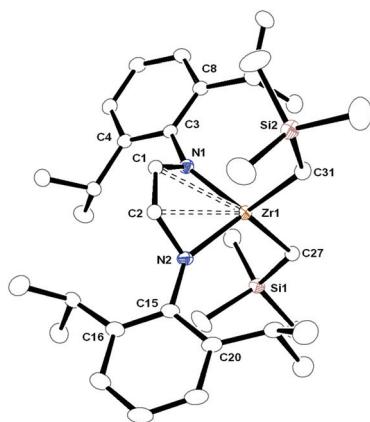


Fig. 5 ORTEP drawing of 7 showing the atom labelling scheme; ellipsoids are drawn to encompass 30% probability. Selected bond lengths [ $\text{\AA}$ ] or angles [ $^\circ$ ]:  $\text{Ti1}-\text{N1}$  1.945(2),  $\text{Ti1}-\text{N2}$  1.928(2),  $\text{Ti1}-\text{C3}$  2.367(3),  $\text{Ti1}-\text{C4}$  2.382(3),  $\text{Ti1}-\text{C5}$  2.383(3),  $\text{Ti1}-\text{C6}$  2.361(3),  $\text{Ti1}-\text{C7}$  2.347(3),  $\text{Ti1}-\text{C8}$  2.174(3),  $\text{Ti1}-\text{C1}$  2.377(3),  $\text{Ti1}-\text{C2}$  2.375(2),  $\text{Si3}-\text{C8}$  1.851(3),  $\text{N1}-\text{C1}$  1.386(3),  $\text{N1}-\text{C24}$  1.438(3),  $\text{N2}-\text{C2}$  1.381(3),  $\text{N2}-\text{C12}$  1.440(3),  $\text{C1}-\text{C2}$  1.375(3),  $\text{N2}-\text{Ti1}-\text{N1}$  90.77(9),  $\text{N2}-\text{Ti1}-\text{C8}$  109.56(10),  $\text{N1}-\text{Ti1}-\text{C8}$  104.87(9),  $\text{N2}-\text{Ti1}-\text{C1}$  66.27(9),  $\text{N1}-\text{Ti1}-\text{C1}$  35.67(8),  $\text{N2}-\text{Ti1}-\text{C2}$  35.54(8),  $\text{N1}-\text{Ti1}-\text{C2}$  66.42(9),  $\text{C24}-\text{N1}-\text{Ti1}$  150.38(17),  $\text{C12}-\text{N2}-\text{Ti1}$  146.16(17).

cyclopentadienyl chemistry of these elements, to the best of our knowledge complexes 7–8 represent the first titanium and zirconium alkyl complexes containing a dianionic 1,4-diaza-1,3-butadiene ligand and a neosilyl group attached to it.<sup>18c</sup> Therefore, their molecular structures in the solid state were determined by X-ray diffraction analysis. Both the titanium and zirconium complexes 7 and 8 crystallize in the monoclinic space group  $P2_1/c$  and have four molecules of either 7 or 8 in the respective unit cells. The details of the structural parameters are given in Table TS1 in the ESI.† The solid state structures of complexes 7 and 8 are shown in Fig. 5 and 6, respectively. The coordination polyhedron of half sandwich titanium alkyl complex 7 is formed by  $\eta^5$  coordination of the cyclopentadienyl ring with an average  $\text{Ti}-\text{C}(\text{Cp})$  distance of 2.368  $\text{\AA}$ , which is similar to the corresponding value in compound 2 (2.344  $\text{\AA}$ ) and other titanocene complexes in the literature.<sup>33</sup> Beside the Cp ring, the DAD ligand is chelated in a dianionic ene-diamide canonical form to the titanium ion through two amido-nitrogen atoms, and one neosilyl ( $\text{Me}_3\text{SiCH}_2$ ) group is ligated to the center metal through a carbon atom. The DAD ligand is folded to have a titanium olefin interaction, which is observed in all of the DAD metal complexes reported in this work. In contrast, the zirconium coordination sphere in 8 is constructed by a folded DAD ligand moiety similar to compound 7, and two neosilyl groups. The  $\text{Ti}-\text{C}(\text{C}=\text{C})$  distances in 7 [2.377(3) and 2.375(2)  $\text{\AA}$ ] are slightly shorter than those in complex 2 [2.427(3) and 2.433(3)  $\text{\AA}$ ]. In contrast, the  $\text{Zr}-\text{C}(\text{C}=\text{C})$  distances in 8 [2.521(3) and 2.529(3)  $\text{\AA}$ ] are slightly longer than in the starting material 5 [2.471–2.485  $\text{\AA}$ ]. Nevertheless, in both complexes they can be considered as  $\text{M}-\text{C}$   $\pi$  bonds between the titanium (for 7) and zirconium (for 8), and the olefinic carbon atoms of the DAD



**Fig. 6** ORTEP drawing of **8** showing the atom labelling scheme; ellipsoids are drawn to encompass 30% probability. Selected bond lengths [ $\text{\AA}$ ] or angles [ $^\circ$ ]: Zr1–N1 2.048(2), Zr1–N2 2.055(2), Zr1–C31 2.236(3), Zr1–C27 2.240(3), Zr1–C2 2.529(3), Zr1–C1 2.521(3), C2–C1 1.361(4), N1–C1 1.411(4), N1–C3 1.436(3), N2–C2 1.405(3), N2–C15 1.431(3), Si1–C(27) 1.860(3), Si2–C31 1.858(3), N1–Zr1–N2 87.93(9), N1–Zr1–C31 115.33(10), N2–Zr1–C31 114.07(11), N1–Zr1–C27 114.69(10), N2–Zr1–C27 115.79(10), C31–Zr1–C27 108.18(11), N1–Zr1–C2 63.00(9), N2–Zr1–C2 33.73(9), C31–Zr1–C2 102.88(10), C27–Zr1–C2 145.20(10), N1–Zr1–C1 34.03(9), N2–Zr1–C1 62.75(9), C31–Zr1–C1 103.27(10), C27–Zr1–C1 144.72(10), C2–Zr1–C1 31.27(9), C3–N1–Zr1 149.68(19), C1–N1–Zr1 91.68(16), C2–N2–Zr1 91.96(16), C15–N2–Zr1 146.9(2).

ligand. Thus in both complexes **7** and **8**, the DAD ligand maintained its  $\sigma^2, \pi$ -enediamide mode of coordination to the metal ion with a long–short–long sequence within the ligand fragments [N1–C1 1.386(3), C1–C2 1.375(3), C2–N2 1.381(3)  $\text{\AA}$  for **7** and N1–C1 1.411(4), C1–C2 1.361(4), C2–N2 1.405(3)  $\text{\AA}$  for **8**]. One four-membered metallacycle in each complex (Ti1–N1–C1–C2 for **7** and Zr1–N1–C1–C2 for **8**) is formed by the coordination of the DAD ligand to the metal ion. The titanium ion is 1.108  $\text{\AA}$  away from the plane containing the N1–C1–C2 and N2

atoms, and this plane is orthogonal to the cyclopentadienyl plane. The center metal titanium possesses distorted pseudo-tetrahedral geometry if we consider  $\text{Cp}^-$  as a pseudo-monodentate ligand. The fourth coordination site of the titanium atom in **7** (third and fourth for zirconium complex **8**) is occupied by a neosilyl group and the Ti–C bond distance of 2.174(3)  $\text{\AA}$  is within the range of Ti–C distances reported for titanium alkyl complexes.<sup>34</sup> The Zr–C distances of 2.236(3) and 2.240(3)  $\text{\AA}$  are also in the accepted range for reported organozirconium complexes.<sup>35</sup>

### Catalytic hydrosilylation of alkenes

The catalytic addition of an organic silane Si–H bond to alkenes or alkynes (hydrosilylation) to give silicon-containing molecules is of great interest.<sup>36</sup> Currently, most organosilanes are made using multistep syntheses that produce significant amounts of waste. Therefore, hydrosilylation offers an attractive alternative route to obtain silicon-containing molecules that are important for the preparation of fine chemicals and pharmaceuticals. It has been demonstrated that group 3 metal complexes with  $\text{Cp}$ <sup>37,38</sup> and non- $\text{Cp}$ <sup>39,40</sup> ligands are efficient catalysts or precatalysts for the hydrosilylation of olefins, and the mechanism is generally believed to involve the insertion of the olefin into the M–Si or M–H bond of a metal-silyl or metal-hydride species, followed by  $\sigma$ -bond metathesis.<sup>40,41</sup> In our study, the mono and bis(neosilyl) complexes **7** and **8** proved to be highly efficient pre-catalysts for the intermolecular hydrosilylation of hexene and octene, using a small excess (10%) of phenylsilane ( $\text{PhSiH}_3$ ) and 5 mol% catalyst loadings. However it was observed that complex **7** is poorly active for intermolecular hydrosilylation and thus the screening was tested using only zirconium complex **8**.

Selected data obtained from the catalytic hydrosilylation reaction of various alkenes with respect to complex **8** are given in Table 1. In entries 1–3 and 6–7, the substrates (1-hexene,

**Table 1** Catalytic hydrosilylation reactions

| Entry | Alkene   | Product  | Time (h)        | Olefin conversion (%) | Product selectivity ( <i>n</i> and iso) |      |
|-------|--|--|-----------------|-----------------------|---|------|
|       |  |  |                 |                       | <i>n</i> -                              | Iso- |
| 1     | $\text{C}_4\text{H}_9\text{ } \text{\texttt{C=C}}$       | $\text{C}_4\text{H}_9\text{ } \text{\texttt{CH}_2\text{SiH}_2\text{Ph}}$       | 2               | 100                   | 99                                      | 1    |
| 2     | $\text{C}_6\text{H}_{13}\text{ } \text{\texttt{C=C}}$    | $\text{C}_6\text{H}_{13}\text{ } \text{\texttt{CH}_2\text{SiH}_2\text{Ph}}$    | 2               | 100                   | 99                                      | 1    |
| 3     | $\text{Cy}\text{ } \text{\texttt{C=C}}$                  | $\text{Cy}\text{ } \text{\texttt{CH}_2\text{SiH}_2\text{Ph}}$                  | 2               | 100                   | 99                                      | 1    |
| 4     | $\text{C}_{10}\text{H}_{21}\text{ } \text{\texttt{C=C}}$ | $\text{C}_{10}\text{H}_{21}\text{ } \text{\texttt{CH}_2\text{SiH}_2\text{Ph}}$ | 24 <sup>a</sup> | 26                    | 99                                      | 1    |
| 5     | $\text{Ph}\text{ } \text{\texttt{C=C}}$                  | <i>n</i> + iso   | 24 <sup>a</sup> | 99                    | 27                                      | 73   |
| 6     | $\text{\texttt{C=C=C=C}}$                                | $\text{\texttt{Cyclo-C}_2\text{SiH}_2\text{Ph}}$                               | 2               | 100                   | 99                                      | 1    |
| 7     | $\text{Br}\text{ } \text{\texttt{C=C=C=C}}$              | $\text{BrC}_4\text{H}_8\text{ } \text{\texttt{CH}_2\text{SiH}_2\text{Ph}}$     | 2               | 100                   | 99                                      | 1    |
| 8     | $\text{Br}\text{ } \text{\texttt{C=C=C=C}}$              | $\text{BrC}_5\text{H}_{10}\text{ } \text{\texttt{CH}_2\text{SiH}_2\text{Ph}}$  | 24              | 86                    | 99                                      | 1    |

The reaction was done in  $\text{C}_6\text{D}_6$  at r.t. The conversion and product selectivity was calculated from  $^1\text{H}$  NMR.<sup>a</sup> 60 °C.



1-octene, vinyl cyclohexane, 1,5-hexadiene and 1-bromopen-tene) essentially show complete conversion to the corresponding organosilanes in 2 hours at ambient temperature, as judged by  $^1\text{H}$  NMR spectroscopy. Full selectivity for the *n*-products and no side reactions were observed (for example iso-products, hydrogenation, alkene dimerization, and/or dehydrogenative coupling of organosilanes). In the case of using dodecene as the substrate, only 26% conversion was observed after 24 hours even at an elevated temperature (entry 4). The lower activity of dodecene in contrast to those of 1-hexene and 1-octene is not surprising. It seems that the presence of a longer alkyl chain in dodecene causes its sluggish reactivity in catalytic hydrosilylation. When we tried the hydrosilylation reaction using **8** in combination with  $\text{B}(\text{C}_6\text{F}_5)_3$ , the reactivity slightly improved in entry 4; however, it still remains lower than those of 1-hexene and 1-octene. Styrene gave a complete conversion to a mixture of products (27% *n*-product and 73% iso-product) after 24 hours at room temperature (entry 5). We also screened the alkenes with a halo functionality as substrates, and observed that even 1-bromopentene can be completely converted to the corresponding *n*-product in 2 hours at room temperature (entry 7), while 1-bromohexene shows 86% conversion even after 24 hours at the same temperature (entry 8). The lower reactivity for 1-bromohexene can be explained by the deactivation of the catalyst due to the presence of the bromine atom, followed by a sluggish reactivity towards hydrosilylation. Thus a sluggish reactivity in the hydrosilylation of the olefins is observed in the zirconium bis-alkyl complex **8** compared to catalysts known in the literature.<sup>40</sup>

## Experimental

### General consideration

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced with a high vacuum ( $10^{-4}$  torr) line, or in an argon-filled M. Braun glovebox. Diethyl ether was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene, hexane and *n*-pentane) were distilled under nitrogen from  $\text{LiAlH}_4$  and stored in the glovebox.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz), spectra were recorded on a BRUKER AVANCE III-400 spectrometer. A BRUKER ALPHA FT-IR was used for the FT-IR measurements. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology, Hyderabad. The  $(\text{Li}_2\text{DippDAD})^{42}$  and  $[\text{LiCH}_2\text{SiMe}_3]^{43}$  were prepared according to the literature procedures.  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{CpTiCl}_3$ ,  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{Cp}_2\text{ZrCl}_2$  and the NMR solvents  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  were purchased from Sigma Aldrich.

**Preparation of  $[\eta^5\text{CpTi}\{(\text{Dipp})_2\text{DAD}\}\text{Cl}]$  (2).** In a pre-dried Schlenk flask, 0.117 g (0.531 mmol) of  $\text{CpTiCl}_3$  in 3 mL of diethylether was placed and to this, freshly prepared diethyl ether (10 mL) solution of dilithium complex  $[\text{Li}_2(\text{Dip})_2\text{DAD}]$  (1) (200 mg, 0.531 mmol) was added dropwise with stirring at

room temperature. The reaction mixture was then stirred for another 12 h. A white precipitate was formed and was filtered through a G4-frit and dried *in vacuo*. Red crystals were obtained after re-crystallization from diethyl ether at  $-35^\circ\text{C}$ . Yield was 0.223 g (80%). Compound **2** was soluble in THF and toluene.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.18–7.14 (m, 4H, ArH), 7.07–7.04 (m, 2H, ArH), 6.17 (s, 5H, Cp-H), 6.16 (s, 2H, CH), 3.51 (sept, 2H, CH ( $\text{CH}_3$ )<sub>2</sub>), 2.33 (sept, 2H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.28 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.21 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.13 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.08 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  149.1 (ArC), 143.7 (ArC), 124.5 (ArC), 123.5.9 (ArC), 114.6 (Cp-C), 108.3 (C=C), 27.7, 27.6, 26.0, 25.4, 24.0, 23.9 (CH,  $\text{CH}_3$ ) ppm. FT-IR (selected frequencies):  $\tilde{\nu} = 2960$  (ArC-H), 2861 (C-H), 1622(C=C), 1459, 1258, 798, 753  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $\text{C}_{31}\text{H}_{41}\text{ClN}_2\text{Ti}$  (524.98): C 70.92, H 7.87, N 5.34; found C 70.38, H 7.29, N 4.93.

**Preparation of  $[\eta^5\text{Cp}_2\text{Zr}\{(\text{Dipp})_2\text{DAD}\}]$  (3).** In a 25 mL Schlenk flask, a suspension of 154 mg  $\text{Cp}_2\text{ZrCl}_2$  (0.531 mmol) in 3 mL diethyl ether was added dropwise to the freshly prepared diethyl ether (10 mL) solution of dilithium complex  $[\text{Li}_2(\text{Dip})_2\text{DAD}]$  (1) (200 mg, 0.531 mmol) at room temperature. The reaction mixture was then stirred for another 12 h. The white precipitate of LiCl was filtered through a G4-frit and dried *in vacuo*. Red crystals were obtained after re-crystallization from diethyl ether at  $-35^\circ\text{C}$ . Yield was 203 mg (82%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.02–6.90 (m, 6H, ArH), 5.62 (s, 5H, Cp-H), 5.56 (s, 5H, Cp-H), 5.35 (s, 2H, CH), 3.71 (sept, 2H, CH ( $\text{CH}_3$ )<sub>2</sub>), 2.92 (sept, 2H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.14 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.11 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.08 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>), 1.01 (d,  $J = 6.8$  Hz, 6H, CH ( $\text{CH}_3$ )<sub>2</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  148.9 (ArC), 145.7 (ArC), 142.7 (ArC), 125.6 (ArC), 124.7 (ArC), 123.6 (ArC), 114.3 (Cp-C), 110.1 (Cp-C) 106.7 (C=C), 27.8 (CH), 27.1, 27.0, 25.5, 24.9, 24.2 (CH<sub>3</sub>) ppm. FT-IR (selected frequencies):  $\tilde{\nu} = 2960$  (ArC-H), 2863 (C-H), 16257 (C=C), 1434, 1255, 795, 778  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $\text{C}_{40}\text{H}_{56}\text{N}_2\text{OZr}$  (3-THF 672.09): C 71.48, H 8.40, N 4.17; found: C 70.89, H 7.93, N 3.88.

**Preparation of  $[\text{Ti}\{(\text{Dipp})_2\text{DAD}\}\text{Cl}_2]$  (4).** To a solution of freshly prepared dilithium complex  $[\text{Li}_2(\text{Dip})_2\text{DAD}]$  (1) (200 mg, 0.531 mmol) in toluene (10 mL) was added slowly a solution of  $\text{TiCl}_4$  (1 M in toluene, 0.53 mL, 0.26 mmol) at  $-78^\circ\text{C}$ . The mixture was slowly allowed to warm to room temperature and was stirred for another 12 h. A white precipitate was formed and was filtered through a G4-frit and dried *in vacuo*, resulting in a dark brown solid which was washed with hexane and dried under vacuum. Yield was 178 mg (68%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.08–7.00 (m, 6H, Ph) 6.18 (s, 2H, CH), 2.98 (br, 4H, CH( $\text{CH}_3$ )<sub>2</sub>), 1.14 (d,  $J = 6.2$  Hz, 24H, CH( $\text{CH}_3$ )<sub>2</sub>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  148.1 (*ipso*-C), 142.9 (*o*-C), 128.5 (Ph) 123.9 (Ph), 123.9 (Ph), 105.2 (C=C), 28.3 (CH), 24.6 (CH<sub>3</sub>). FT-IR (selected frequencies):  $\tilde{\nu} = 2961$ , 2865, 1622, 1459, 1258, 798, 753  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $\text{C}_{26}\text{H}_{36}\text{Cl}_2\text{N}_2\text{Ti}$  (495.35): C 63.04, H 7.33, N 5.66; found: C 62.84, H 7.01, N 5.41.



**Preparation of  $[(Dipp)_2DADZrCl(\mu-Cl)\}_2(\kappa^3-Cl)(Li)(OEt_2)_2$  (5).** In a Schlenk flask, a suspension of 124 mg  $ZrCl_4$  (0.531 mmol) in 3 mL diethyl ether was added dropwise to the freshly prepared diethyl ether (10 mL) solution of dilithium complex  $[Li_2(Dipp)_2DAD]$  (1) (200 mg, 0.531 mmol) at room temperature. The reaction mixture was then stirred for another 12 h. The white precipitate of  $LiCl$  was filtered through a G4-frit and dried *in vacuo*. Yellow crystals were obtained after re-crystallization from diethyl ether at  $-35\text{ }^\circ\text{C}$ . Yield was 270 mg (85%).  $^1\text{H}$  NMR (400 MHz,  $C_6D_6$ , 25  $^\circ\text{C}$ ):  $\delta$  7.15 (m, 6H, ArH), 5.81 (s, 2H, CH), 3.31 (br, 4H, CH ( $CH_3)_2$ ), 1.20 (d,  $J$  = 5.6 Hz, 12H, CH ( $CH_3)_2$ ), 1.01 (d,  $J$  = 5.6 Hz, 12H, CH ( $CH_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $C_6D_6$ , 25  $^\circ\text{C}$ ):  $\delta$  147.7 (*ipso*-ArC), 144.1 (*o*-ArC), 143.3 (*o*-ArC) 126.8 (*m*-ArC), 124.1 (*m*-ArC), 105.8 (C=C), 28.1 (CH), 26.4, 24.3 ( $CH_3$ ) ppm. FT-IR (selected frequencies):  $\tilde{\nu}$  = 2961 (ArC-H), 2928 (ArC-H), 2866 (C-H), 1622 (C=C), 1439, 1212, 796, 754  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $C_{60}H_{92}Cl_5LiN_4O_2Zr_2$  (1268.05): C 56.83, H 7.31, N 4.42; found: C 56.29, H 6.88, N 4.02.

**Preparation of  $[Ti\{(Dipp)_2DAD\}_2]$  (6).** A freshly prepared diethyl ether (10 mL) solution of dilithium complex  $[Li_2(Dip)_2DAD]$  (1) (200 mg, 0.531 mmol) was charged with an ether solution of  $TiCl_4$  in toluene (1 M, 0.26 mL, 0.26 mmol) at  $-78\text{ }^\circ\text{C}$ . The mixture was slowly allowed to warm to room temperature and was kept under stirring for another 12 h. The white precipitate of  $LiCl$  was filtered through a G4-frit and dried *in vacuo*. Red crystals were obtained after re-crystallization from diethyl ether at  $-35\text{ }^\circ\text{C}$ . Yield was 153 mg (73%).  $^1\text{H}$  NMR (400 MHz,  $C_6D_6$ , 25  $^\circ\text{C}$ ):  $\delta$  7.12–6.98 (m, 12H, ArH), 6.18 (d,  $J$  = 3 Hz, 2H, CH), 6.06 (d,  $J$  = 3 Hz, 2H, CH), 3.12 (sept, 4H, ( $CH(CH_3)_2$ ), 2.95 (sept, 4H, ( $CH(CH_3)_2$ ), 1.24 (d,  $J$  = 4.8 Hz, 12H, CH ( $CH_3)_2$ ), 1.21 (d,  $J$  = 4.8 Hz, 12H, CH ( $CH_3)_2$ ), 1.17 (d,  $J$  = 4.8 Hz, 12H, CH ( $CH_3)_2$ ), 1.15 (d,  $J$  = 4.8 Hz, 12H, CH ( $CH_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $C_6D_6$ , 25  $^\circ\text{C}$ ):  $\delta$  148.9 (*ipso*-ArC), 144.1 (*o*-ArC), 143.3 (*o*-ArC), 124.4 (ArC), 123.6 (ArC), 112.3 (C=C), 28.7 (CH), 27.5, 26.7, 25.6, 24.3, 23.1 ( $CH_3$ ) ppm. FT-IR (selected frequencies):  $\tilde{\nu}$  = 2961 (ArC-H), 2865(C-H), 1622(C=C), 1459, 1258, 798, 753  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $C_{52}H_{72}N_4Ti$  (801.01): C 77.97, H 9.06, N 6.99; found: C 77.51, H 8.75, N 6.44.

**Preparation of  $[\eta^5-\text{CpTi}\{(Dipp)_2DAD\}(CH_2SiMe_3)]$  (7).** To a solution of 2 (82 mg, 0.156 mmol) in diethyl ether (3 mL) was added a pre-cooled solution of  $LiCH_2SiMe_3$  (15 mg, 0.156 mmol) in diethyl ether (3 mL), and the reaction mixture was stirred at an ambient temperature for 6 h.  $LiCl$  was removed by filtration and the filtrate was evaporated to dryness, resulting in a light orange solid residue which was re-crystallized from hexane at  $-35\text{ }^\circ\text{C}$  to give yellow crystals. Yield was 80 mg (88%).  $^1\text{H}$  NMR (400 MHz,  $C_6D_6$ , 25  $^\circ\text{C}$ ):  $\delta$  7.16–7.14 (m, 4H, ArH), 7.08–7.07 (m, 2H, ArH), 6.19 (s, 5H, Cp-H), 5.95 (s, 2H, CH), 3.25 (sept, 2H,  $CH(CH_3)_2$ ), 2.42 (sept, 2H,  $CH(CH_3)_2$ ), 1.32 (d,  $J$  = 8 Hz, 6H,  $CH(CH_3)_2$ ), 1.16 (d,  $J$  = 8 Hz, 6H,  $CH(CH_3)_2$ ), 1.11 (d,  $J$  = 4 Hz, 6H,  $CH(CH_3)_2$ ), 1.09 (d,  $J$  = 4 Hz, 6H,  $CH(CH_3)_2$ ), 0.18 (s, 9H,  $Si(CH_3)_3$ ), -0.46 (s, 2H, CH<sub>2</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $C_6D_6$ ):  $\delta$  149.3 (*ipso*-ArC), 144.5 (*o*-ArC), 142.8 (ArC), 126.5 (ArC), 124.1 (ArC), 123.9 (ArC), 112.2

(Cp-C), 109.4 (C=C), 28.0, 27.6, 27.0, 25.3, 24.5, 23.1 (CH,  $CH_3$ ), 46.8 (Ti-CH<sub>2</sub>), 1.4 (Si-CH<sub>3</sub>) ppm. FT-IR (selected frequencies):  $\tilde{\nu}$  = 2961 (ArC-H), 2865(C-H), 1622 (C=C), 1459, 1258, 798, 753  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $C_{35}H_{52}N_2SiTi$  (576.75): C 72.89, H 9.09, N 4.86; found C 72.07, H 8.83, N 4.32.

**Preparation of  $[Zr((Dipp)_2DAD)(CH_2SiMe_3)_2]$  (8).** To a solution of 5 (80 mg, 0.067 mmol) in diethyl ether (3 mL) was added a pre-cooled solution of  $LiCH_2SiMe_3$  (29 mg, 0.134 mmol) in diethyl ether (3 mL) at an ambient temperature for 6 h.  $LiCl$  was removed by filtration, after evaporation of the solvent, resulting in a red oily compound which was re-crystallized from pentane at  $-35\text{ }^\circ\text{C}$  to give yellow crystals. Yield was 65 mg (65%).  $^1\text{H}$  NMR ( $C_6D_6$ , 400 MHz):  $\delta$  7.26–7.08 (m, 6H, Ph), 5.97 (d,  $J$  = 3.6 Hz, 1H, CH), 5.91 (d,  $J$  = 3.6 Hz, 1H, CH), 3.54 (sept, 2H,  $CH(CH_3)_2$ ), 3.17 (sept, 2H,  $CH(CH_3)_2$ ), 1.33 (d,  $J$  = 6.8 Hz, 6H,  $CH(CH_3)_2$ ), 1.22 (d,  $J$  = 6.8 Hz, 6H,  $CH(CH_3)_2$ ), 1.10 (d,  $J$  = 6.8 Hz, 6H,  $CH(CH_3)_2$ ), 0.92 (d,  $J$  = 6.8 Hz, 6H,  $CH(CH_3)_2$ ), 0.10 (s, 18H,  $Si(CH_3)_3$ ), 0.03 (s, 4H, CH<sub>2</sub>) ppm.  $^{13}\text{C}$  NMR ( $C_6D_6$ , 100 MHz):  $\delta$  147.4 (*ipso*-C), 143.0 (*o*-C), 125.8 (Ph), 124.9 (Ph), 124.6 (Ph), 123.9 (Ph), 110.2 (C=C), 109.1 (C=C), 34.4 (Zr-CH<sub>2</sub>), 28.7, 28.0, 26.6, 24.9, 24.8, 24.4 (CH, CH<sub>3</sub>), 1.3 (SiMe<sub>3</sub>) ppm. FT-IR (selected frequencies):  $\tilde{\nu}$  = 2958, 2896, 2869, 1624, 1459, 1247, 1045, 858, 830  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $C_{34}H_{58}N_2Si_2Zr$  (642.22): C 63.59, H 9.10, N 4.36; found C 62.98, H 8.79, N 4.02.

### Typical procedure for catalytic hydrosilylation of alkenes

An NMR tube was charged in the glovebox with 8 (0.018 mmol),  $PhSiH_3$  (0.407 mmol), olefin (1-hexene or 1-octene, 0.370 mmol), and  $C_6D_6$  (3 mL). The tube was closed and taken out of the glovebox. The disappearance of the substrates and formation of new organosilanes could be conveniently monitored using  $^1\text{H}$  NMR spectroscopy.

### X-Ray crystallographic studies of 2, 3 and 5–8

Single crystals of compounds 2, 3, 5 and 6 were grown from diethyl ether at  $-35\text{ }^\circ\text{C}$  under an inert atmosphere. Compounds 7 and 8 were grown from either hexane (for 7) or pentane (for 8) at  $-35\text{ }^\circ\text{C}$  under an inert atmosphere. For compounds 2, 3 and 5–8, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil, and placed in a nitrogen stream at 150(2) K. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic  $Cu-K\alpha$  (1.54184  $\text{\AA}$ ) radiation. Absorption corrections were performed on the basis of multi-scans. Crystal data and structure refinement parameters are summarised in Table TS1 in the ESI.† The structures were solved by direct methods (SIR92)<sup>44</sup> and refined on  $F^2$  by the full-matrix least-squares method, using SHELXL-97.<sup>45</sup> Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint has been made for any of the compounds. The function minimised was  $[\sum w(F_o^2 - F_c^2)^2]$  ( $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ), where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. The func-



tions  $R_1$  and  $wR_2$  were  $(\sum ||F_o| - |F_c||)/\sum |F_o|$  and  $[\sum w(F_o^2 - F_c^2)^2/\sum (wF_o^4)]^{1/2}$ , respectively. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication, with the CCDC no. 1011649–1011654.

## Conclusion

In this contribution, we have presented homoleptic and heteroleptic titanium and zirconium complexes with dianionic 1,4-diaza-1,3-butadiene in the backbone, to explore their coordination modes in straightforward synthesis. The titanium and zirconium alkyl complexes were also synthesized from the respective chloride complexes 2 and 5 and trimethylsilylmethyl lithium. In the solid state structures of all the DAD complexes, it was observed that the dianionic 1,4-diaza-1,3-butadiene ligand displayed a  $\sigma^2,\pi$ -enediamide mode towards the titanium and zirconium centers with a long–short–long sequence within the ligand fragments. The metal alkyl complexes were tested as catalysts for the intermolecular hydrosilylation of alkenes, and moderate activity was observed for the zirconium complex 8.

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