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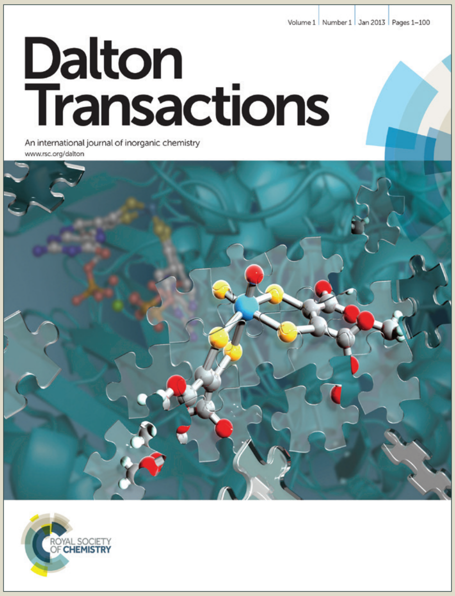

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ARTICLE TYPE

Titanium and Zirconium Complexes of *N*,*N*'-Bis(2,6-diisopropylphenyl)-1,4-diaza-butadiene Ligand: Syntheses, Structures and Their use in Catalytic Hydrosilylation Reactions

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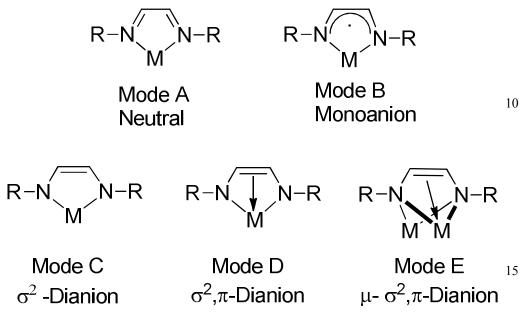
We report here a number of dianionic 1,4-diaza-1,3-butadiene complexes of titanium and zirconium by salt metathesis reaction. The reaction of either $CpTiCl_3$ or Cp_2TiCl_2 with dilithium salt of *N*,*N*'-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene [**1**; abbreviated $(Dipp)_2DADLi_2$] afforded the mono-cyclopentadienyl titanium complex [η^5-$CpTi((Dipp)_2DAD)Cl$] (**2**) bearing a dianionic ene-diamide ligand, while the analogous reaction of zirconocene dichloride (Cp_2ZrCl_2) with the dilithium salt **1** gave the bis-cyclopentadienyl zirconium complex [$Cp_2Zr\{(Dipp)_2DAD\}$] (**3**). The metal dichloride complexes [$Ti((Dipp)_2DAD)Cl_2$] (**4**) and [$Zr\{(Dipp)_2DAD\}$-$Cl_2(LiCl)$] (**5**) were obtained by the reaction of **1** and anhydrous metal tetrachloride in 1:1 molar ratio in diethyl ether at room temperature. However, the homoleptic titanium complex [$Ti\{((Dipp)_2DAD)\}_2$] (**6**) was isolated in good yield by the treatment of **1** with $TiCl_4$ in 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 [η^5-$CpTi\{(Dipp)_2DAD\}(CH_2SiMe_3)$] (**7**) and zirconium [$Zr\{(Dipp)_2DAD\}(CH_2SiMe_3)_2$] (**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 $[(Dipp)_2DAD]^{2-}$ moiety satisfying σ^2,π coordination mode. Compound **8** was used as catalyst for intermolecular hydrosilylation reaction of a number of olefins, and a moderate activity of catalyst **8** was observed.

Introduction

Amido metal chemistry of the early transition metals has been received significant momentum in the last 25 years by designing novel amido ligands.[1] It was observed that, in the early stages of this area most of the researchers focused on cyclopentadienyl-analogous amido ligands for comparison with and for further investigations of the well-known cyclopentadienyl moiety.[2] Amido-metal bonds are thermodynamically stable and less labile compare to metal-carbon bonds. However, today 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.[3] Recently the use of diamide ligands are getting more importance into the early transition metal chemistry to stabilize group 4 and 5 metal complexes due to their ability to chelate metal centers having higher oxidation numbers though the formation of dianionic form.[4] Metal complexes having 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.[5] The chelating diamide complexes of titanium and zirconium serve as precursors for the highly active and living polymerization of olefins.[6] 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.[7] Even the α-diimine ligand 1,4-disubstituted diazabutadienes (DAD) were synthesized and utilized in early 1960s,[8] various substituted DAD ligands were synthesized by a number of research goups even today as it can be reduced to generate diamido ligand.[9] The diversity in coordination and redox properties of this ligand places high level of interest to these compounds, have already proved wide use in the areas of both fundamental and applied research.[10] The neutral DAD molecule includes two lone electron pairs of the nitrogen atoms and π-electrons of the multiple imine (N-C) bonds and this molecule can act as both σ- and π-donor and coordinate to the metal atom as a neutral ligand.[11] Although the dianionic DAD ligands preferentially coordinate to early transition metals and alkaline metals in σ^2- and σ^2,π-coordination modes,[12-14] in many cases the DAD ligands coordinate to group 3 metal atoms as a σ^2-monoanion,[15] and, in addition, both monoanionic and dianionic coordination modes were observed for alkaline-earth metal, group 12, and group 13 metal complexes.[16,17] The possible flexible coordination modes depending on the type and redox properties of the central metal are shown in chart 1.

Chart 1. Different coordination modes of DAD ligand



The DAD ligand is widely utilized not only for early transition metals,[18,19] f-block metals,[20] and late transition metals,[21] but also for s-block and p-block main-group elements.[22–24] In the majority of these complexes the DAD 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 application in organic transformations, we have studied further about this chemistry. In this context, we present the syntheses of a number of dianionic 1,4-diaza-1,3-butadiene complexes having molecular compositions [η^5-CpTi((Dipp)$_2$DAD)Cl] (**2**), [Cp$_2$Zr((Dipp)$_2$DAD)] (**3**), [Ti((Dipp)$_2$DAD)Cl$_2$] (**4**), [Zr((Dipp)$_2$DAD)Cl$_2$(LiCl)] (**5**), [Ti{((Dipp)$_2$DAD)}$_2$] (**6**), [η^5-CpTi((Dipp)$_2$DAD)(CH$_2$SiMe$_3$)] (7), [Zr{(Dipp)$_2$DAD)}-(CH$_2$SiMe$_3$)$_2$] (**8**). The solid state structures of complexes **2**-**3** and **5**-**8** are also reported. Catalytic hydrosilylation of various alkenes by using complex **8** as catalyst are also presented.

Results and Discussion

Cyclopentadienyl Metal complexes: Cyclopentadienyl titanium complex [η^5-CpTi((Dipp)$_2$DAD)Cl] (**2**) was isolated in good yield from the reaction of (Dipp)$_2$DADLi$_2$) (**1**) and CpTiCl$_3$ in a 1:1 molar ratio in diethyl ether at room temperature followed by re-crystallisation from ether at -35° C (see Scheme 1). The titanium complex **2** could also be obtained by the reaction of **1** and titanocene dichloride (Cp$_2$TiCl$_2$) under similar reaction condition. Thus during the reaction condition, one cyclopentadienyl moiety was undergone elimination from Cp$_2$TiCl$_2$ occurred as LiCp along with one equivalent LiCl. Such phenomenon is recently observed by Sun et al. while treating with triscyclopemtadienyl yttrium with lithium amidinate ligand.[25] In contrast, the reaction of zirconocene dichloride (Cp$_2$ZrCl$_2$) with dianionic lithium salt **1** afforded corresponding bis-cyclopentadienyl zirconium complex [Cp$_2$Zr{(Dipp)$_2$DAD}] (**3**) in good yield by elimination of two equivalents of lithium chlorides (see scheme 1). Both the titanium and zirconium complexes were characterized by spectroscopic techniques and solid state of the complexes **2** and **3** were established by X-ray diffraction analysis. In ^{1}H NMR spectra measured in C$_6$D$_6$, the resonances of the Cp protons in **2** appear at 6.17 ppm as a sharp singlet. The signals for analogous Cp protons in complex **3** are observed at 5.62 and 5.56 ppm indicating two different chemical environments for 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 back bone. Therefore the resonances for olefinic protons for **2** are significantly low field shifted compared to that 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 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 due to 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 restricted rotation around respective carbon nitrogen bond of the DAD ligand moiety indicating the presence of non-equivalent 2,6-diisopropylphenyl groups. However in **3**, we observed two doublets for one set of diastereotopic isopropyl CH$_3$ groups, indicating the presence of equivalent 2,6-diisopropylphenyl groups. In proton decoupled ^{13}C NMR spectra of **2**, the resonances at 114.6 ppm and 108.3 ppm represent the C$_5$ of Cp moiety and the olefinic carbons of the DAD ligand. For zirconium compound **3**, ^{13}C{^{1}H} NMR signals are 114.3 and 110.1 ppm for two Cp rings and 106.7 ppm for olefinic carbon atoms. All the ^{1}H and ^{13}C-{^{1}H} NMR signals are in agreement with the values reported in literature.[14]

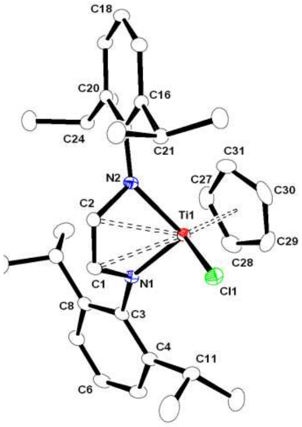


Figure 1. ORTEP drawing of **2** showing atom labelling scheme, ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [°]: Ti1-N1 1.928(2), Ti1-N2 1.922(2), Ti1-Cl1 2.3283(8), Ti1-C27 2.331(3), Ti1-C31 2.338(3), Ti1-C28 2.342(3), Ti1-C30 2.352(3), Ti1-C29 2.358(3), Ti1-C1 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-Cl1 109.42(7), N1-Ti1-Cl1 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).

The molecular structure of air and moisture sensitive complexes **2-3** are established by single crystal X-ray diffraction analysis. The complex **2** crystallizes in the monoclinic space group *P*2$_1$/c and has four independent molecules in the unit cell (Figure 1). The zirconium complex **3** crystallizes in the triclinic space group *P*-1 and has two independent molecules along with one molecule of diethyl ether in the unit cell as solvate (Fig 2). The details of the structural and refinement parameters of the crystal structure of **2-3** are given in table TS1 in supporting information (SI). Complex **2** is monomeric and the coordination polyhedron is formed by chelation of two amido nitrogen atoms of dianionic DAD ligand, η^5-coordination of one cyclopentadienyl moiety, and one chloride atom. The geometry around the titanium ion can be best described as pseudo tetrahedral considering η^5-Cp ring as pseudo-monodentate ligand. The Ti-N distances [1.928(2) and 1.922(2) Å] is close to that of 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 η^5-Cp moiety and one DAD ligand. The geometry around the zirconium ion is pseudo tetrahedral considering the η^5-Cp ring as pseudo-monodentate ligand. The Zr-N distances [2.105(1) and 2.141(1) Å] are slightly longer than that of Ti-N distances due to larger ion radius of Zr(IV) ion, however within the Zr-N covalent bond reported in literature. The Zr-C(Cp) distances [2.52(2) to 2.590(2) Å] are also slightly longer than that of Ti-C(Cp) distances, but in the range of Zr-C(Cp) distances reported for other zirconocene complexes.[26] Notably the coordination of dianionic DAD ligand in complex **2** and **3** are similar and both the complexes form a five membered diazametallacyclopentene structure (Ti1-N1-C1-C2-N2 for **2** and Zr1-N1-C1-C2-N2 for **3**). Both the metallacycles are folded and the dihedral angle between the N1-M-N2 and N1-C1-C2-N2 planes are 50.62º (for **2**) and 50.30º (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 π bonding to display σ^2,π-enediamide mode of DAD ligand. However no such π interactions between zirconium ion and olefinic carbon atoms are observed in the molecular structure. Thus for complex **3**, DAD ligand displayed only σ^2-diamide mode (C in Chart 1). Nevertheless, the DAD ligation can be described as elongation of C-N bond [1.389(3) and 1.383(3) Å for **2**; 1.392(2) and 1.389(2) Å for **3**] and shortening of C-C bond [1.382(4) Å for **2**; 1.377(2) Å for **3**] i.e a long-short-long sequence compared to neutral DAD ligand. Similar coordination behavior also observed for recently reported DAD lanthanide complexes.[14]

Metal dichloride complexes: Upon treating **1** with MCl_4 (M = Ti and Zr) either in toluene (in case of Ti) at -78º C or in diethyl ether (in case of Zr) at room temperature, DAD titanium dichloride complex [Ti((Dipp)$_2$DAD)Cl$_2$] (**4**) and an 'ate' complex for zirconium [Zr((Dipp)$_2$DAD)Cl$_2$(LiCl)] (**5**) were obtained respectively in good yield. 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 ^{1}H NMR spectrum of **5** in C_6D_6, a sharp singlet was observed at δ 5.81 ppm (for **4** 6.18 ppm), assignable to olefinic protons of the DAD ligand back bone, a broad signal at δ 3.31 ppm (for **4** 2.98 ppm) and two doublet resonances having a constant 5.6 Hz appeared at δ□ 1.20 and 1.01 ppm (for **4** 1.14 ppm), 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).

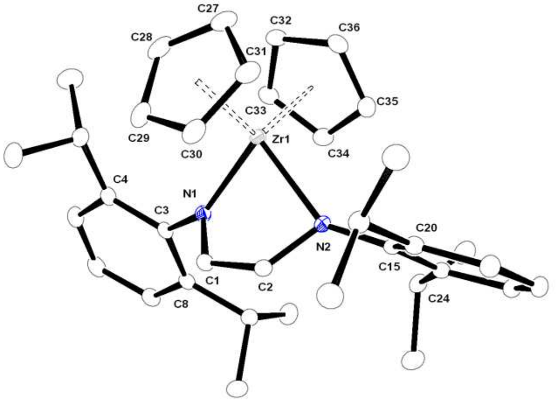


Figure 2. ORTEP drawing of **3** showing atom labelling scheme, ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [º]: Zr1-N1 2.1050(14), Zr1-N2 2.1406(14), Zr1-C1 2.5928(17), Zr1-C2 2.5977(16), Zr1-C36 2.5223(19), Zr1-C32 2.5303(18), Zr1-C33 2.5344(18), Zr1-C34 2.5398(19), 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).

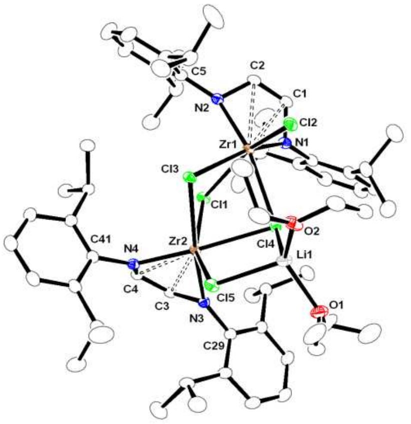
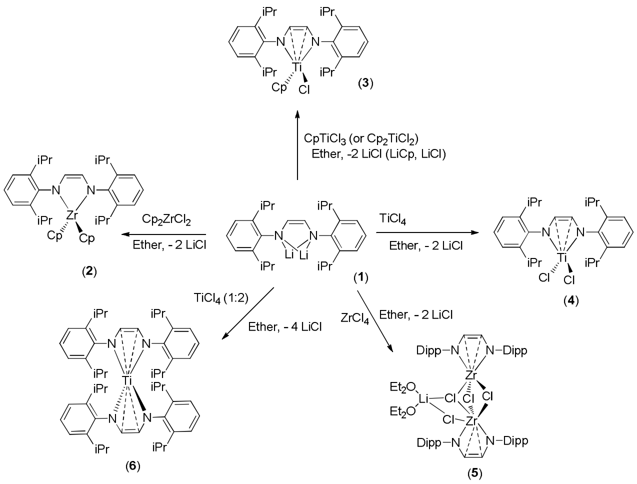


Figure 3. ORTEP drawing of **5** showing atom labelling scheme, ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [º]: Zr2-N3 2.044(3), Zr2-N4 2.050(3), Zr2-C4 2.472(4), Zr2-C3 2.472(4), Zr2-Cl5 2.4951(10), Zr2-Cl1 2.5687(9), Zr2-Cl3 2.6569(9), Zr2-Cl4 2.7194(10), 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-Cl1 100.66(10), N4-Zr2-Cl1 105.87(9), C4-Zr2-Cl1 85.76(9), C3-Zr2-Cl1 83.66(9), Cl5-Zr2-Cl1 155.39(3), N3-Zr2-Cl3 175.09(10), N4-Zr2-Cl3 96.97(9), C4-Zr2-Cl3 119.96(9), C3-Zr2-Cl3 148.01(9), Cl5-Zr2-Cl3 87.86(3), Cl1-Zr2-Cl3 77.02(3), N3-Zr2-Cl4 97.74(10), N4-Zr2-Cl4 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-Cl2 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), C1-Zr1-Cl1 110.24(11), C2-Zr1-Cl1 112.56(10), Cl3-Zr1-Cl(1) 75.05(3).



Scheme 1. Synthesis of titanium and zirconium complexes **2-6** from **1**.

The lithium chloride incorporated compound [Zr{(Dipp)$_2$-DAD}Cl$_2$(LiCl)] was re-crystallized from diethyl ether and it crystallizes in monoclinic space group $P2_1/c$ along with four independent molecules in the unit cell. The incorporation of lithium chloride into the coordination sphere of metal complexes is common in the literature due to smaller size of lithium.[27] Lithium chloride incorporated complexes [{(Me$_3$SiNPPh$_2$)$_2$CH}-Yb(μ-Cl)$_2$LiCl(THF)$_2$], [(η^5-C$_5$Me$_5$)$_2$Nd(μ-Cl)$_2$Li(THF)$_2$][28] and [{(Me3SiNPPh$_2$)$_2$CH}Yb(μ-Cl)$_2$LiCl-(THF)$_2$] have been reported by others and us.[29] The solid state structure of complex **5** is given in Figure 3 and the details of the structural parameters are given in table TS1 in the supporting information. Zirconium complex **5** has dimeric structure bearing the DAD ligand, four bridging chloride atoms. One terminal chloride atom Cl2 is attached with second zirconium atom to make both the zirconium center 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 μ-chlorine atoms along with two solvent diethyl ether molecules 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, Zr1-Cl3-Zr2-Cl4 are formed by μ-bridging of three chlorine atoms (Cl1, Cl3, Cl5) and one κ^3 chlorine (Cl4) toward lithium and zirconium atoms having 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 zirconium atom Zr1 making two metal ions asymmetric in nature. The terminal Zr-Cl2 bond length (2.422(2) Å) is significantly shorter than 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 DAD ligands satisfy the σ^2,π-enediamide mode of coordination to the zirconium ion having the 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 [Ti-{(Dipp)$_2$DAD}$_2$] (**6**) was isolated by the treatment of **1** with TiCl$_4$ in 1:2 molar ratio by elimination of LiCl. The corresponding complex of zirconium also recently synthesized by the reaction reduction of neutral DAD ligand followed by reaction with zirconium tetrachloride.[30] The complex **6** was characterized by ^{1}H, ^{13}C{^{1}H} NMR spectroscopy, combustion analysis and the molecular structure of complex **6** was established by single crystal X-ray diffraction analysis. The ^{1}H NMR spectra of the complex **6** show two sets of signals for each DAD ligand. Four doublets at δ 1.24, 1.21, 1.17 and 1.15 ppm in 12:12:12:12 ratio and coupling constant of 4.8 Hz in each case can be assigned to the resonances 48 methyl protons distributed in four diisopropylphenyl moieties. The magnetically asymmetric protons indicate the orientation of the two DAD ligands must be in different planes. The resonances for olefinic protons of the two DAD ligands back bone are observed at δ 6.18 and 6.05 ppm as doublets indicating a clear distinction between two ligand's magnetic environments. However two multiplets at δ 3.12 and 2.95 ppm are obtained for the eight isopropyl protons due to overlapping of two closely associated septets for each DAD ligand. In proton decoupled ^{13}C NMR spectra, we observed the characteristic peaks for two DAD ligands matches with complexes **2** and **4** (see experimental section).[30]

The X-ray quality crystal of titanium complex **6** was re-crystallized from diethyl ether at -35° C as red crystal. Compound **6** crystallizes in the monoclinic space group $P2_1/c$ having four independent molecules in the unit cell. The solid state structure of complex **6** is given in Figure 4 and the details of the structural parameters are given in table TS1 in the supporting information. 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 two DAD ligands. The geometry around the titanium ion is best described as distorted tetrahedral. Ti-N distances [Ti1-N1 1.968(14), Ti1-N2 1.920(14), Ti1-N3 1.928(14) and Ti-N4 1.957(13) Å] are similar with that of complex **2** and can be consider 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] sufficiently shorter to consider σ bonds between the metal ion and C=C back bone 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 σ^2,π-enediamide mode of coordination to the zirconium ion having the 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 59.2º was observed between the two planes containing N1, C1, C2, N2 atoms and N3, C3, C4, N4 atoms present in two ligands. The center metal titanium ion is 1.104 and 1.101 Å away from the above mentioned two planes respectively.

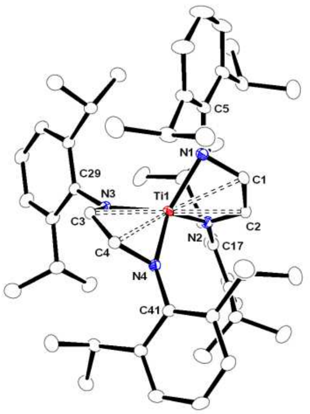
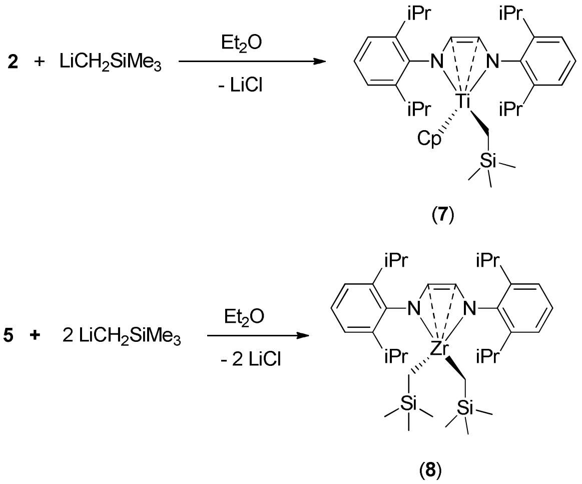


Figure 4. ORTEP drawing of **6** showing atom labelling scheme, ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [º]: Ti1-N1 1.9675(14), Ti1-N2 1.9196(14), Ti1-N3 1.9282(14), Ti1-N4 1.9566(13), Ti1-C1 2.3941(17), Ti1-C2 2.3841(18), Ti1-C3 2.3722(17), Ti1-C4 2.3942(17), 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).

Metal mono- and bis-alkyl complexes: To learn more about the reactivity of complexes metal halide complexes **2** and **5**, we were interested in synthesizing their alkyl derivatives. Metal alkyl complexes are important precursors as catalyst for a number of organic transformations.[31] To explore the reactivity of titanium and zirconium halide complexes in hand **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 solvent to afford corresponding mono-alkyl [η^5-CpTi((Dipp)$_2$DAD)(CH$_2$SiMe$_3$)] (**7**) and bis-alkyl [Zr-{(Dipp)$_2$DAD}(CH$_2$SiMe$_3$)$_2$] **(8)** complexes respectively in good yield after re-crystallisation from hexane at -35º C (Scheme 2). Compounds **7** and **8** are soluble in THF, toluene and hydrocarbon solvents like pentane and hexane. Both the 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.



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

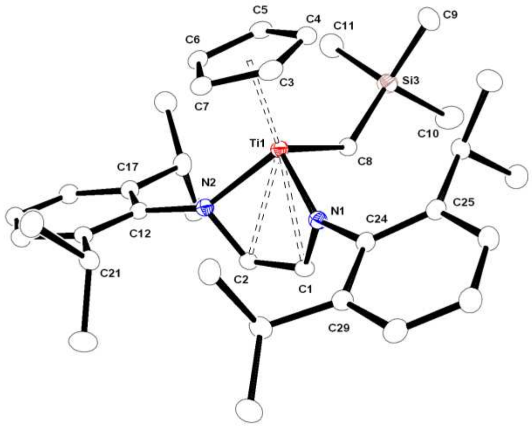


Figure 5. ORTEP drawing of **7** showing atom labelling scheme, ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [º]: Ti1-N1 1.945(2), Ti1-N2 1.928(2), Ti1-C(3) 2.367(3), Ti1-C4 2.382(3), Ti1-C5 2.383(3), Ti1-C6 2.361(3), Ti1-C7 2.347(3), Ti1-C8 2.174(3), Ti1-C1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

The ^{1}H NMR spectrum of **7** in C$_6$D$_6$ is very similar to the spectra recorded for complex **2** exhibits four characteristic doublet resonances in a 6:6:6:6 ratio for four different types of isopropyl methyl groups present in the DAD ligand along with two high field septet resonance at 3.25 and 2.42 ppm for the isopropyl -CH hydrogen atoms. Thus it is evident that the chemical and magnetic environment of isopropyl methyl and -CH protons are different due to the presence of alkyl group attached to the titanium ion. Between two sharp singlets, the signal at δ 6.19 ppm can be assigned to the five protons present in cyclopentadienyl ring where as signal at δ 5.95 ppm was confirmed for the olefinic protons (C=C) of the DAD ligand. For the neosilyl (CH$_2$SiMe$_3$) group in **7**, one singlet at δ 0.18 ppm (SiMe$_3$) and one singlet at δ -0.46 ppm is observed at high field, which can be assigned to methylene (CH_2) hydrogen atoms. In ^{1}H NMR spectra, zirconium bis-alkyl complex **8** exhibits two doublets at δ 5.97 and 5.91 ppm, assignable to olefinic protons of the DAD ligand back bone, two septets at δ 3.54 and 3.17 ppm for two chemically different isopropyl -CH proton along with four doublet resonances having a coupling constant 6.8 Hz appeared at δ 1.33, 1.22, 1.10 and 0.92 ppm in 6:6:6:6 ration for methyl protons of the ligand. In addition two singlets at δ 0.10 and 0.03 ppm were observed for the two neosilyl (CH_2SiMe_3) groups present in **8**. Similar chemical shift values for neosilyl groups (δ 0.13 and 0.04 ppm) were reported for $Cp''_2Zr(CH_2SiMe_3)_2$ (Cp” = $CH_2{=}CHCH_2C_5H_4$) by Piers et al.[32]

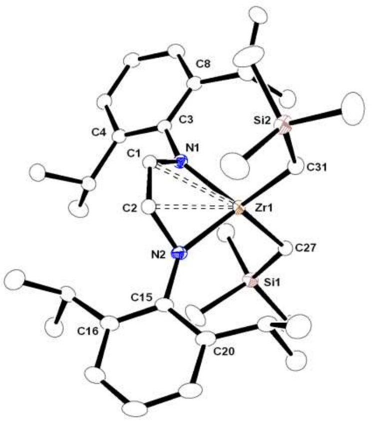
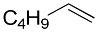
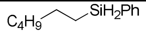
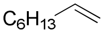
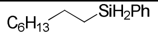
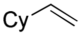
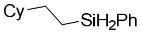
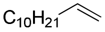
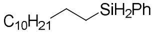
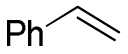
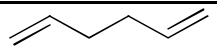
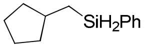
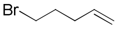
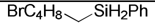
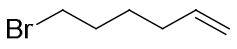
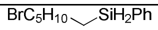


Figure 6. ORTEP drawing of **8** showing atom labelling scheme, ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] or angles [°]: Zr1-N1 2.048(2), Zr1-N2 2.055(2), Zr1-C31 2.236(3), Zr1-C27 2.240(3), Zr1-C2 2.529(3), Zr1-C1 2.521(3), C2-C1 1.361(4), N1-C1 1.411(4), N1-C3 1.436(3), 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).

Although there has been ongoing interest in alkyl complexes of group 4 organometallics and particularly in the cyclopentadienyl chemistry of these elements, complexes **7-8** represent, to the best of our knowledge, the first titanium and zirconium alkyl complexes containing dianionic 1,4-diaza-1,3-butadiene ligand and neosilyl group attached to it.[18c] 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 $P\ 2_1/c$ and have four molecules of either **7** or **8** in the respective unit cell. The details of the structural parameters are given in table TS1 in the supporting information. The solid state structures of complexes **7** and **8** are shown in Figure 5 and Figure 6, respectively. The coordination polyhedron of half sandwich titanium alkyl complex **7** is formed by η^5 coordination of cyclopentadienyl ring with an average Ti-C(Cp) distance of 2.368 Å which is similar with the corresponding value in compound **2** (2.344 Å) and other titanocene complexes in literature.[33] Beside the Cp ring, DAD ligand is chelated in a dianionic ene-diamide canonical form to the titanium ion through two amido- nitrogen atoms and one neosilyl (Me_3SiCH_2) group is ligated to the center metal through carbon atom. The DAD ligand is folded to have titanium olefin interaction which is observed in all the DAD metal complexes reported in this work. In contrast, the zirconium coordination sphere in **8** is constructed by folded DAD ligand moiety similar with compound **7** and two neosilyl groups. The Ti-C(C=C) distances in **7** [2.377(3) and 2.375(2) Å] are slightly shorter than those in complex **2** [2.427(3) and 2.433(3) Å]. In contrast, the Zr-C(C=C) distances in **8** [2.521(3) and 2.529(3) Å] are slightly longer than starting material **5** [2.471-2.485 Å]. Nevertheless, in both the complexes we can consider as M-C π bonds between the titanium (for **7**) and zirconium (for **8**) and olefinic carbon atoms of DAD ligand. Thus in both the complexes **7** and **8**, DAD ligand maintained its σ^2,π-enediamide mode of coordination to the metal ion having the long-short-long sequence within the ligand fragments [N1-C1 1.386(3), C1-C2 1.375(3), C2-N2 1.381(3) Å for **7** and N1-C1 1.411(4), C1-C2 1.361(4), C2-N2 1.405(3) for **8** Å]. 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 DAD ligand to the metal ion. The titanium ion is 1.108 Å away from the plane containing 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 Cp^- as pseudo-monodentate ligand. The fourth coordination site of the titanium atom in **7** (third and fourth for zirconium complex **8**) is occupied by neosilyl group and the Ti-C bond distance of 2.174(3) Å is within the range of Ti-C distances reported for titanium alkyl complexes.[34] The Zr-C distances of 2.236(3) and 2.240(3) Å are also in the accepted range for reported organo-zirconium complexes.[35]

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.[36] Currently, most organosilanes are made in multistep syntheses that produce significant amounts of waste. Therefore, hydrosilylation offers an attractive alternative route to silicon-containing molecules that are important for the preparation of fine chemicals and pharmaceuticals. It could be demonstrated that group 3 metal complexes with Cp[37,38] and non-Cp[39,40] 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 σ-bond metathesis.[40,41] In our hands, 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 ($PhSiH_3$) and 5 mol% catalyst loadings. However it was observed that complex **7** in poorly active for intermolecular hydrosilylation and thus the screening was tested by using only zirconium complex **8**.

Table 1. Catalytic Hydrosilation Reactions.

Entry	Alkene	Product	Time (h)	Olefin conversion %	Product selectivity (*n* and *iso*)	
					n-	*iso-*
1			2	100	99	1
2			2	100	99	1
3			2	100	99	1
4			24[a]	26	99	1
5		***n + iso***	24[a]	99	27	73
6			2	100	99	1
7			2	100	99	1
8			24	86	99	1

The reaction was done in C_6D_6 at r.t. The conversion and product selectivity was calculated from ^{1}H NMR; [a] 60^0C

Selected data obtained from the catalytic hydrosilylation reaction of various alkenes with respect to complex **8** are given in Table 1. In entry 1-3 and 6-7, the substrates (1-hexene, 1-octene, vinyl cyclohexane, 1,5-hexadiene, 1-bromopentene) are essentially showed complete conversion to the corresponding organo-silanes in 2 hours at ambient temperature as judged by ^{1}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 case of do-decene as substrate, only 26% conversion was observed after 24 hours even at elevated temperature (entry 4). The lower activity of do-decene is not surprising in contrast to those of 1-hexene and 1-octene. It seems that the presence of longer alkyl chain in dodecene makes the sluggish reactivity in catalytic hydrosilylation. We have tried the hydrosilylation reaction by **8** in combination of $B(C_6F_5)_3$, the reactivity slightly improved in entry 4, however still remains lower than that of 1-hexene and 1-octene. Styrene gave a complete conversion to mixture of products (27% *n*-product and 73% *iso*-product) after 24 hours at room temperature (entry 5). We also have screened the alkenes having a halo functionality as substrates and observed that even the 1-bromopentene can be completely converted to corresponding *n*-product in 2 hours at room temperature (entry 7), 1-bromo hexene shows 86% conversion even after 24 hours at same temperature (entry 8). The lower reactivity for 1-bromo hexene can be explained as the deactivation of catalyst by the presence of bromine atom followed by sluggish reactivity towards hydrosilylation. Thus a sluggish reactivity for the hydrosilylation of the olefins are observed by the zirconium bis-alkyl complex **8** compared to catalysts known in literature.[40]

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 glove box. 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 $LiAlH_4$ and stored in the glove box. ^{1}H NMR (400 MHz), ^{13}C{^{1}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 (Li_2DippDAD),[42] [$LiCH_2SiMe_3$],[43] were prepared according to the literature procedures. $TiCl_4$, $ZrCl_4$, $CpTiCl_3$, Cp_2TiCl_2, Cp_2ZrCl_2 and the NMR solvents $CDCl_3$ and C_6D_6 were purchased from Sigma Aldrich.

Preparation of [η^5CpTi{(Dipp)$_2$DAD}Cl] (2)

In a pre-dried Schlenk flask 0.117 g (0.531 mmol) of $CpTiCl_3$ in 3 mL of diethylether was placed and to this, freshly prepared diethyl ether (10 mL) solution of dilithium complex of [Li_2(Dip)$_2$DAD] (**1**) (200 mg, 0.531 mmol) was added drop wise 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^{o}C (Yield: 0.223 g, 80%). Compound **2** was soluble in THF and toluene. ^{1}H NMR (400 MHz, C_6D_6, 25º C): δ 7.18-7.14 (m, 4H, ArH), 7.07-7.04 (m, 2H, ArH), 6.17 (s, 5H, Cp-*H*), 6.16 (s, 2H, C*H*), 3.51 (sept, 2H, C*H* (CH_3)$_2$), 2.33 (sept, 2H, C*H* (CH_3)$_2$), 1.28 (d, *J* = 6.8 Hz, 6H, CH (C*H*$_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 6H, CH (C*H*$_3$)$_2$), 1.13 (d, *J* = 6.8 Hz, 6H, CH (C*H*$_3$)$_2$), 1.08 (d, *J* = 6.8 Hz, 6H, CH (C*H*$_3$)$_2$)ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25º C): δ 149.1 (Ar*C*), 143.7 (Ar*C*), 124.5 (Ar*C*), 123.5.9 (Ar*C*), 114.6 (*Cp*-C), 108.3 (*C*=*C*), 27.7, 27.6, 26.0, 25.4, 24.0, 23.9 (*C*H, *C*H$_3$) ppm. FT-IR (selected frequencies): ν˜ = 2960 (ArC-H), 2861(C-H), 1622(C=C), 1459, 1258, 798, 753 cm^{-1}. Elemental analysis calculated (%) for $C_{31}H_{41}ClN_2Ti$ (524.98): C 70.92, H 7.87, N 5.34; found C 70.38, H 7.29, N 4.93.

Preparation of [η^5-Cp_2Zr{(Dipp)$_2$DAD}] (3)

In a 25 mL Schlenk flask a suspension of 154 mg Cp_2ZrCl_2 (0.531 mmol) in 3 mL diethyl ether was added drop wise to the freshly prepared diethyl ether (10 mL) solution of dilithium complex of [Li_2(Dip)$_2$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^{o}C. Yield 203 mg (82%). ^{1}H NMR (400 MHz, C_6D_6, 25º C): δ 7.02-6.90 (m, 6H, ArH), 5.62 (s, 5H, Cp-*H*), 5.56 (s, 5H, Cp-*H*), 5.35 (s, 2H, C*H*), 3.71 (sept, 2H, C*H* (CH_3)$_2$), 2.92 (sept, 2H, C*H* (CH_3)$_2$), 1.14 (d, *J* = 6.8 Hz, 6H, CH (C*H*$_3$)$_2$), 1.11 (d, *J* = 6.8Hz, 6H, CH (C*H*$_3$)$_2$), 1.08 (d, *J* = 6.8 Hz, 6H, CH (C*H*$_3$)$_2$), 1.01 (d, *J* = 6.8 Hz, 6H, CH (C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H}NMR (100 MHz, C_6D_6, 25º C): δ 148.9 (Ar*C*), 145.7 (Ar*C*), 142.7 (Ar*C*), 125.6 (Ar*C*), 124.7 (Ar*C*), 123.6 (Ar*C*), 114.3 (*Cp*-C), 110.1 (*Cp*-C) 106.7 (*C*=*C*), 27.8 (*C*H), 27.1, 27.0, 25.5, 24.9, 24.2 (*C*H$_3$). ppm .FT-IR (selected frequencies): ν˜= 2960 (ArC-H), 2863 (C-H), 16257 (C=C), 1434, 1255, 795, 778 cm^{-1}. Elemental analysis calculated (%) for $C_{40}H_{56}N_2OZr$ (**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 [Ti{(Dipp)$_2$DAD}Cl$_2$] (4)

To a solution of freshly prepared dilithium complex of [Li_2(Dip)$_2$DAD] (**1**) (200 mg, 0.531 mmol) in toluene (10 mL) was added slowly a solution of $TiCl_4$ (1M in toluene, 0.53 mL, 0.26 mmol) at -78º C. The mixture was slowly allowed to warm to come at room temperature and stirring for another 12 h. A white precipitate was formed and was filtered through a G4-frit and dried *in vacuo* resulting dark brown solid which washed with hexane and dried under vacuum. Yield (178mg, 68%). ^{1}HNMR (400 MHz, C_6D_6, 25º C): δ 7.08 -7.00 (m, 6H, Ph) 6.18 (s, 2H, CH), 2.98 (br, 4H, CH(CH_3)$_2$), 1.14 (d, *J* = 6.2 Hz, 24H, CH(CH_3)$_2$). ^{13}CNMR (100MHz, C_6D_6, 25º C): δ 148.1(*ipso*-C), 142.9 (o-C), 128.5 (Ph) 123.9 (Ph), 123.9 (Ph), 105.2 (C=C), 28.3 (*C*H), 24.6 (*C*H$_3$). FT-IR (selected frequencies): ν˜ = 2961, 2865, 1622, 1459, 1258, 798, 753 cm^{-1}. Elemental analysis calculated (%) for $C_{26}H_{36}Cl_2N_2Ti$ (495.35): C 63.04, H 7.33, N 5.66; found: C 62.84, H 7.01, N 5.41.

Preparation of [Zr{(Dipp)$_2$DAD}Cl$_2$(LiCl)] (5)

In a Schlenk flask a suspension of 124 mg $ZrCl_4$ (0.531 mmol) in 3 mL diethyl ether was added drop wise to the freshly prepared diethyl ether (10 mL) solution of dilithium complex of [Li$_2$(Dipp)$_2$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* Yellow crystals were obtained after re-crystallization from diethyl ether at -35ºC. Yield (270 mg 85%). ^{1}H NMR (400 MHz, C_6D_6, 25º C): δ 7.15 (m, 6H, Ar*H*), 5.81 (s, 2H, C*H*), 3.31 (br, 4H, C*H* (CH$_3$)$_2$), 1.20 (d, *J* = 5.6 Hz, 12H, CH (C*H$_3$*)$_2$), 1.01 (d, *J* = 5.6 Hz, 12H, CH (C*H$_3$*)$_2$) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25º C): δ 147.7 (*ipso*-Ar*C*), 144.1 (*o*-Ar*C*), 143.3 (*o*-ArC) 126.8 (*m*-Ar*C*), 124.1 (*m*-Ar*C*), 105.8 (*C*=*C*), 28.1 (*C*H), 26.4, 24.3 (*C*H$_3$) ppm. FT-IR (selected frequencies): ν˜ = 2961 (ArC-H), 2928 (ArC-H), 2866 (C-H), 1622 (C=C), 1439, 1212, 796, 754 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)$_2$DAD}$_2$] (6)

A freshly prepared diethyl ether (10 mL) solution of dilithium complex of [Li$_2$(Dip)$_2$DAD] (**1**) (200 mg, 0.531 mmol) was charged with a ether solution of $TiCl_4$ in toluene (1M, 0.26 mL, 0.26 mmol) at -78º C. The mixture was slowly allowed to warm at room temperature and kept 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° C. Yield 153 mg (73%). ^{1}H NMR (400 MHz, C_6D_6, 25º C): δ 7.12-6.98 (m, 12H, ArH), 6.18 (s, *J* = 3 Hz, 2H, C*H*), 6.06 (d, *J* = 3 Hz, 2H, C*H*), 3.12 (sept, 4H, (C*H*(CH$_3$)$_2$), 2.95 (sept, 4H, (C*H*(CH$_3$)$_2$), 1.24 (d, *J* = 4.8 Hz, 12H, CH (C*H$_3$*)$_2$), 1.21 (d, *J* = 4.8 Hz, 12H, CH (C*H$_3$*)$_2$), 1.17 (d, *J* = 4.8 Hz, 12H, CH (C*H$_3$*)$_2$), 1.15 (d, *J* = 4.8 Hz, 12H, CH (C*H$_3$*)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25º C): δ 148.9 (*ipso*-Ar*C*), 144.1 (*o*-Ar*C*), 143.3 (*o*-Ar*C*), 124.4 (Ar*C*), 123.6 (Ar*C*), 112.3 (*C*=*C*), 28.7 (*C*H), 27.5, 26.7, 25.6, 24,3, 23.1 (*C*H$_3$) ppm. FT-IR (selected frequencies): ν˜ = 2961 (ArC-H), 2865(C-H), 1622(C=C), 1459, 1258, 798, 753 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 [η^5-CpTi{(Dipp)$_2$DAD}(CH$_2$SiMe$_3$)] (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, 0156 mmol) in diethyl ether (3 mL) and the reaction mixture was stirred at ambient temperature for 6 h. LiCl were removed by filtration and the filtrate was evaporated to dryness resulting a light orange solid residue which was re-crystallized form hexane at - 35º Cto give yellow crystals (80 mg, 88% yield). ^{1}H NMR (400 MHz, C_6D_6, 25º C): δ 7.16-7.14 (m, 4H, ArH), 7.08-707 (m, 2H, ArH), 6.19 (s, 5H, Cp-*H*), 5.95 (s, 2H, C*H*), 3.25 (sept, 2H, C*H*(CH$_3$)$_2$), 2.42 (sept, 2H, C*H*(CH$_3$)$_2$), 1.32 (d, *J* = 8 Hz, 6H, CH(C*H$_3$*)$_2$), 1.16 (d, *J* = 8 Hz, 6H, CH(C*H$_3$*)$_2$), 1.11 (d, *J* = 4 Hz, 6H, CH(C*H$_3$*)$_2$), 1.09 (d, *J* = 4 Hz, 6H, CH(C*H$_3$*)$_2$), 0.18 (s, 9H, Si(CH$_3$)$_3$), -0.46 (s, 2H, C*H$_2$*) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 149.3 (*ispo*-Ar*C*),144.5 (*o*-Ar*C*), 142.8 (Ar*C*), 126.5 (Ar*C*), 124.1(Ar*C*), 123.9 (Ar*C*), 112.2 (Cp-*C*), 109.4 (*C*=*C*), 28.0, 27.6, 27.0, 25.3, 24.5, 23.1(*C*H, *C*H$_3$), 3.4 (Ti-*C*H$_2$), 1.4 (Si-*C*H$_3$) ppm. FT-IR (selected frequencies): ν˜= 2961 (ArC-H), 2865(C-H), 1622 (C=C), 1459, 1258, 798, 753 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)$_2$DAD)(CH$_2$SiMe$_3$)$_2$] (8)

To a solution of **5** (80 mg, 0.067 mmol) in diethyl ether (3mL) was added a pre-cooled solution of $LiCH_2SiMe_3$ (29 mg, .0.134 mmol) in diethyl ether (3mL) at ambient temperature for 6 h. LiCl were removed by filtration, after evaporation of solvent resulting red oily compound re-crystallized from pentane at -35ºC to give yellow crystals (65 mg, 65% yield). ^{1}HNMR (C_6D_6, 400MHz): δ 7.26-7.08 (m, 6H, Ph), 5.97(d, J = 3.6 Hz, 1H, C*H*), 5.91(d, *J* = 3.6 Hz, 1H, C*H*), 3.54 (sept, 2H, C*H*(CH$_3$)$_2$), 3.17 (sept, 2H, C*H*(CH$_3$)$_2$), 1.33 (d, *J* = 6.8 Hz, 6H, CH(C*H$_3$*)$_2$), 1.22 (d, *J* = 6.8 Hz, 6H, CH(C*H$_3$*)$_2$), 1.10 (d, *J* = 6.8 Hz, 6H, CH(C*H$_3$*)$_2$), 0.92 (d, *J* = 6.8 Hz, 6H, CH(CH$_3$)$_2$), 0.10 (s, 18H, Si(C*H$_3$*)$_3$), 0.03 (s, 4H, C*H$_2$*) ppm. ^{13}CNMR (C_6D_6, 100MHz): δ 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-*C*H2), 28.7, 28.0, 26.6, 24.9, 24.8, 24.4 (*C*H, *C*H3), 1.3 (Si*Me*3) ppm. FT-IR (selected frequencies): ν˜ = 2958, 2896, 2869, 1624, 1459, 1247, 1045, 858, 830 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 can be conveniently monitored by ^{1}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 –35º C under inert atmosphere. Compounds **7** and **8** were grown either from hexane (for **7**) or pentane (for **8** at –35º C under 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-Kα (1.54184 Å) radiation. Absorption corrections were performed on the basis of multi-scans. Crystal data and structure refinement parameters are summarised in table TS1 in the supporting information. The structures were solved by direct methods (SIR92)[44] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97.[45] 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 all the compounds. The function minimised was $[\Sigma w(Fo^2- Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (Max(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, 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 supplementary publication no. CCDC 1011649-1011654. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Conclusion

With this contribution, we have presented homoleptic and heteroleptic titanium and zirconium complexes having dianioinc 1,4-diaza-1,3-butadiene in the backbone to explore their coordination modes in straight forward 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 display σ^2,π-enediamide mode towards titanium and zirconium centers having the long-short-long sequence within the ligand fragments. The metal alkyl complexes were tested as catalysts for intermolecular hydrosilylation of alkenes, a moderate activity was observed for the zirconium complex **8**.

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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 are included in Supporting Information. These materials are available free of charge see DOI: 10.1039/b000000x/

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Titanium and Zirconium Complexes of *N*,*N*'-Bis(2,6-diisopropyl-phenyl)-1,4-diaza-butadiene Ligand: Syntheses, Structures and Their use in Catalytic Hydrosilylation Reactions

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Table of content

A number homoleptic and heteroleptic titanium and zirconium 1,4-diaza-1,3-butadiene ($(Dipp_2DAD)$)complexes and their alkyl derivatives are synthesized by salt metathesis reactions; catalytic hydrosilylation reactions of different alkenes are reported by using $Dipp_2DAD$ zirconium alkyl complex.