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Synthesis and Structure of Group 4 and 5 Metal Complexes with an Ancillary Sterically Demanding Diamido Ligand

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Reaction of tetrachlorides of group 4 and 5 transition metals with the chelating diamide $[Me_2C(CH_2N(Li)(SiBu^tPh_2))_2]$ (LLi_2) leads to $LMCl_2$ (M = Ti, Zr, Hf, V) complexes, which were characterized by X-ray diffraction. The reactivity of $LMCl_2$ toward ethylene polymerization was tested with MAO as cocatalyst.

In recent years, there has been extensive research in the field of organometallic chemistry of early transition metals related to the polymerization of α-olefins. So far, most of the catalysts prepared for this purpose were supported by two cyclopentadienyl rings,[1] but there is a growing interest in the use of new ancillary noncyclopentadienyl ligands, such as chelating dialkoxide,[2] bisamidinate,[3] or diamido[4−5] ligands. Indeed, a few d^0 dialkyl−Ti or −Zr complexes based on chelating diamido frameworks have proven to be active catalysts in the living polymerization of 1-hexene and ethylene.[5,6] According to a recent theoretical study,[7] one way to improve such systems would be to increase the steric bulk on the α-carbons of the diamido bridge and on the nitrogen substituents. In this respect, we describe herein our contribution to the synthesis of new d^0 group 4 (Ti, Zr, Hf) and unprecedented vanadium (IV) dichloro complexes with the bulky chelating $[Me_2C(CH_2N(H)(SiBu^tPh_2))_2]$ (LH_2) ligand, which possesses two sterically demanding protecting silyl groups on the nitrogen atoms and should also lower the electron density on the metal center, in comparison to the aryl substituents used by McConville.[5a,b] The advantage of a vanadium(IV) catalyst is the possibility of copolymerizing ethylene with various other olefins.[8]

The diamine LH_2 is readily prepared by silylating the 2,2-dimethyl-1,3-propanediamine with Bu^tPh_2SiCl (Scheme 1). The yield of LH_2, a colorless oil, is typically 92% on a 10 g scale. Addition of 2 equiv of butyllithium to LH_2 in pentane at −78 °C caused the precipitation of LLi_2 as a white powder in 66% yield.

The heterogeneous reaction between LLi_2 and MCl_4 (M = Zr, Hf) in pentane at room temperature gives $LZrCl_2$ (**1**) in 59% yield and $LHfCl_2$ (**2**) in 43% yield after 3−5 days (Scheme 2). Starting from $TiCl_4(THF)_2$, more vigorous conditions are needed (toluene, 18 h reflux) to obtain the analogous titanium complex $LTiCl_2$ (**3**). **3** was purified in modest yield as yellow crystals by recrystallization from a toluene−pentane solution. Similarly, addition of LLi_2 to VCl_4·(DME) in toluene at room temperature yields the green $LVCl_2$ complex (**4**), which was recrystallized in toluene−pentane at −30 °C (yield 9%).

Suitable crystals for X-ray analysis of **1**−**4** have been obtained by cooling a toluene−pentane solution to −30 °C, and the crystal structures of the four compounds were determined by X-ray diffraction. Owing to the larger size of Zr and Hf ions compared to Ti and V ions, **1** and **2** are isostructural, but differ from the isostructural **3** and **4** complexes. The molecular structure of **1** and **4** and selected bond distances and angles are shown in Figures 1 and 2, respectively. Overall, the four structures are tetrahedral with a boat conformation for the diamido−metal ring, similar to what is observed in McConville complexes.[6] The average M−N bond distances (see Table 1) of 2.000(4) Å in **1**, 1.991(3) Å in **2**, 1.854(3) Å in **3**, and 1.813(3) Å in **4** are in agreement

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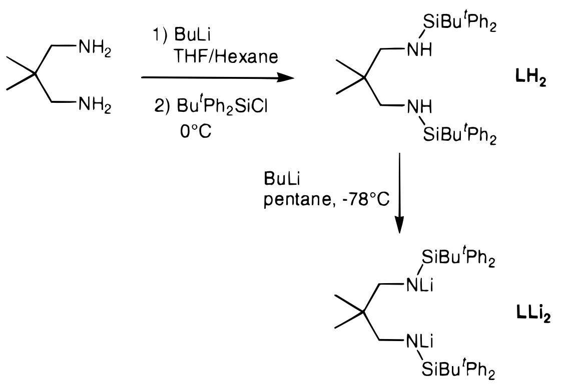
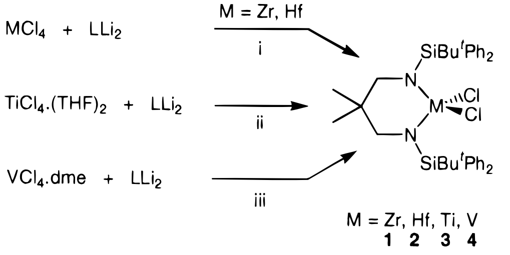
Scheme 1. Synthesis of LH_2 and LLi_2



Scheme 2. Synthesis of $LMCl_2$ Complexes 1−4[a]



[a] *Conditions*: i, room temperature in pentane; ii, toluene, reflux; iii, toluene, room temperature.

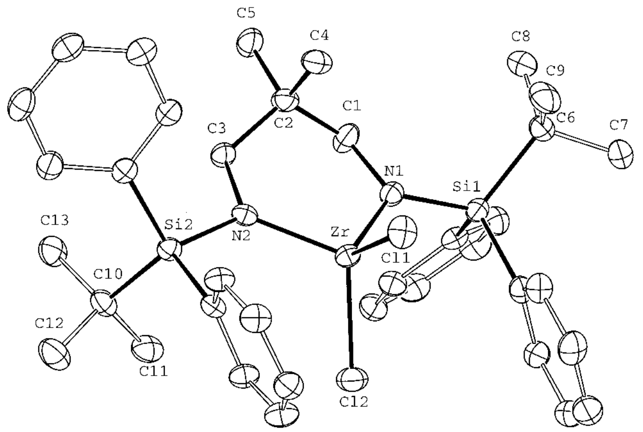


Figure 1. Molecular structure of **1** with selected bond distances (Å) and angles (deg): Zr−N1 2.001(4), Zr−N2 1.999(4), Zr−Cl1 2.3946(16), Zr−Cl2 2.3934(16), N1−C1 1.506(6), N2−C3 1.511(6), N1−Si1 1.762(4), N2−Si2 1.767(4), N1−Zr−N2 97.69(16), N1−Zr−Cl1 112.23(14), N1−Zr−Cl2 106.31(14), N2−Zr−Cl1 109.55(14), N2−Zr−Cl2 111.91(13), Si1−N1−Zr 125.2(2), Si2−N2−Zr 124.3(2), Cl1−Zr−Cl2 117.38(6) Zr−N1−C1 121.7(3), Zr−N2−C3 121.9(3), Si1−N1−C1 111.6(3), Si2−N2−C3 113.6(3).

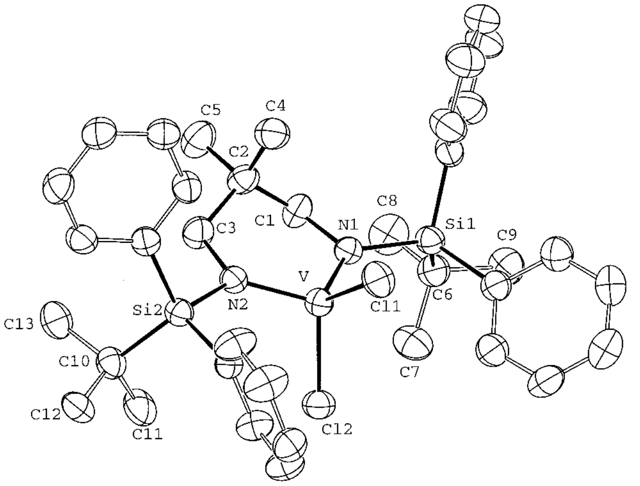


Figure 2. Molecular structure of **4** with selected bond distances (Å) and angles (deg): V−N1 1.814(3), V−N2 1.807(3), V−Cl1 2.2083(13), V−Cl2 2.2296(13), N1−C1 1.503(5), N2−C3 1.517(5), N1−Si1 1.787(3), N2−Si2 1.792(3), N1−V−N2 106.77(14), N1−V−Cl1 108.06(10), N1−V−Cl2 105.87(11), N2−V−Cl1 108.41(11), N2−V−Cl2 107.30(11), Si1−N1−V 130.42(18), Si2−N2−V 127.14(18), Cl1−V−Cl2 119.76(5) V−N1−C1 117.6(2), V−N2−C3 119.8(2), Si1−N1−C1 111.9(2), Si2−N2−C3 112.8(2).

Table 1. Comparison of Average Interatomic Distances (Å) and Angles (deg) of $LMCl_2$ (M = Ti, Zr, Hf, V)

	M = Zr (**1**)	M = Hf (**2**)	M = Ti (**3**)	M = V (**4**)
M−N	2.000(4)	1.991(3)	1.854(3)	1.813(3)
M-Cl	2.394(2)	2.364(2)	2.251(2)	2.219(2)
N−C	1.499(5)	1.500(5)	1.494(5)	1.497(4)
N−Si	1.765(4)	1.764(3)	1.783(3)	1.790(3)
N1−M−N2	97.64(14)	98.37(12)	105.02(13)	106.64(13)
Cl1−M−Cl2	117.39(5)	116.57(5)	114.21(5)	119.79(5)

with those previously found in zirconium,[4a,e,5b] hafnium,[9] titanium,[6] or vanadium[10−12] compounds with mono- and bidentate amido ligands. The larger size of zirconium and hafnium compare to titanium and vanadium accounts for the longer metal−ligand bonds (M−N and M−Cl). Each nitrogen amide donor in **1**−**4** is sp^2-hybridized, as evidenced by the sum of the angles about each nitrogen (N1 358.5° and N2 359.8° in **1**, N1 358.9° and N2 359.8° in **2**, N1 359.7° and N2 359.5° in **3**, and N1 359.9° and N2 359.7° in **4**). The positions of the two *tert*-butyl groups on the silyl substituents are, however, different in **1**/**2** and **3**/**4**: these two *tert*-butyl groups are anti in complexes **1** and **2**, in comparison with the plane of the diamido−metal ring, whereas they are syn in **3** and **4**.

Methyl groups on the diamido bridge and *tert*-butyl groups are shown to be unequivalent in the crystal structure of **1** (C_s symmetry about zirconium in the solid state), but in solution a rapid equilibrium between bridge conformations and between variants of the silyl substituents occurs, resulting in the equivalence of the protons in the ^1H NMR spectrum of **1**, even at −80 °C. Similar behavior is observed in the ^1H NMR of **2** and **3**.

The reaction between **1** and MAO in a Al/Zr ratio of 10−50 in C_6D_6 at room temperature did not lead to the observation of methylated product. Reaction of **1** with 2 equiv of $AlMe_3$ at room temperature and at 60 °C failed to give an alkylated product, nor did we observe the transmetalation product. LH_2 was reacted with 1 equiv of $AlMe_3$ to determine whether an aluminum complex can be prepared. No change in the ^1H NMR spectrum was observed at room temperature and up to 60 °C. Altogether these results explain the difficulty of alkylating **1**, presumably due to the enhanced steric hindrance of the bulky substituents on the nitrogen

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atoms (vide infra), as already observed with $SiPr^i_3$ protecting groups in another diamido−Zr complex.[4g]

Although we have not yet prepared dialkyl derivatives of the type LMR_2 in order to isolate cationic complexes, we have already conducted preliminary catalytic ethylene polymerization tests on **1**−**4**, using MAO (methylaluminoxane) as cocatalyst (Al/M 500/1) in toluene or pentane at 20 °C (1 atm of ethylene). Deceptively, activities were relatively low in toluene, respectively 2.1×10^4 (**1**), 3.3×10^2 (**2**), 7.0×10^3 (**3**), and 7.0×10^2 (**4**) (in g of PE/(mol of catalyst·h)), compared to an activity of 3.7×10^5 with Cp_2ZrCl_2 under the same conditions. Activities are slightly increased when using pentane as solvent (6.6×10^4 (**1**) and 1.9×10^3 (**4**)). The lower activity observed in toluene may be due to deactivation of the cationic species by coordination of a toluene molecule as previously suggested.[6,13] Polyethylenes obtained from **1** have very broad polydispersities: 78.2 for the polymerization conducted in toluene ($M_w = 9.197 \times 10^5$ g/mol, $M_n = 1.176 \times 10^4$ g/mol) and 39.2 for the polymerization in pentane ($M_w = 2.398 \times 10^6$ g/mol, $M_n = 6.121 \times 10^4$ g/mol).

Although the use of silicon protecting groups should lower the electron density on the metal center, activities of our complexes in preliminary ethylene polymerization tests are low; the steric hindrance of the bulky ligand may protect the metal too much from access or insertion by the monomer and may explain the low activities observed. This point is supported by the difficulty in observing the formation of methylated species from **1** and MAO or $AlMe_3$. Another explanation might be the cleavage of the N−Si bond of the ligand in our complexes by the large excess of MAO cocatalyst, as already observed on silylamido−zirconium[14] or vanadium[15] complexes; such a decomposition would explain why **1** does not behave in a living manner for ethylene polymerization.

In summary, a series of diamido−dichloro $LMCl_2$ complexes of group 4 metals and for the first time of V(IV) have been prepared. Preliminary ethylene polymerization tests conducted with these metal−chloride catalysts show only low activities with high polydispersities, a fact that is probably related to the low accessibility of the metal centers due to the steric hindrance of the silyl-protecting groups and to some adverse reactions involving the trialkylsilyl substituents $SiBu^tPh_2$ on the amido nitrogen atoms in the presence of a large excess of MAO.

Experimental Section

General Comments. All experiments were performed under an inert atmosphere of argon using standard Schlenk and glovebox techniques. Solvents were dried and distilled over Na/K alloy (pentane, THF) or Na (toluene) under argon before use. $ZrCl_4$ (Strem), $HfCl_4$ (Strem), MAO (Aldrich), BuLi (Aldrich), $AlMe_3$ (Aldrich), 2,2-dimethyl-1,3-propanediamine (Aldrich), and *tert*-butylchlorodiphenylsilane (Aldrich) were used as received. $TiCl_4(THF)_2$ was synthesized following known procedures.[16] NMR spectra were run on Brüker AC200, AM250, or DPX300 spectrometers. EPR spectra were recorded on a Brüker ESP300E. Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) (C,H,N) or by the Service Central de Microanalyses du CNRS at Vernaison (France). GPC measurements were carried out in *o*-dichlorobenzene at 140 °C by Bayer (Leverkusen, Germany).

Synthesis of LH_2 and LLi_2. A 14.6 mL sample of a 2.5 M solution of BuLi in hexanes (0.0364 mol) was syringed into a solution of 1.86 g of 2,2-dimethyl-1,3-propanediamine (0.0182 mol) in THF (50 mL) at −78 °C with stirring. The solution was allowed to warm to room temperature and stirred for an additional 3 h. To this suspension was added dropwise 10 g of *tert*-butylchlorodiphenylsilane (0.0364 mol) at 0 °C with stirring. Stirring was continued overnight at 20 °C, and then the mixture was refluxed for 3 h. The volatiles were removed under vacuum. Extraction with 3 × 20 mL of pentane and filtration through Celite gave after evaporation to dryness 9.75 g of LH_2 as a colorless oil (yield: 92%). ^1H NMR (C_6D_6): δ 7.76 (m, 8, H_{aryl}), 7.23 (m, 12, H_{aryl}), 2.63 (d, 4, CH_2), 1.09 (s, 18, *t*-Bu), 0.68 (s, 6, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ [136.8, 136.1, 129.9, 128.3] (C_{aryl}) 51.8 (CH_2N), 37.7 ($\mathit{C}Me_2$), 28.3 ($C\mathit{Me_3}$), 23.8 ($C\mathit{Me_2}$), 19.3 ($\mathit{C}Me_3$). LH_2 was redissolved in 50 mL of pentane, and 14.6 mL of BuLi (2.5 M in hexanes) was slowly added at −78 °C and stirred for 24 h at room temperature. Filtration of the suspension, washing the solid with pentane (6 × 20 mL), and drying in vacuo afforded 5.75 g of LLi_2 as a white solid (yield: 54% based on 2,2-dimethyl-1,3-propanediamine). Anal. Calcd for $C_{37}H_{48}N_2Si_2Li_2$: C 75.21, H 8.19, N 4.74. Found: C 74.85, H 8.31, N 4.63. ^1H NMR (C_6D_6): δ 7.65 (m, 8, H_{aryl}), 7.25 (m, 12, H_{aryl}), 3.16 (s, 4, CH_2), 1.06 (s, 18, *t*-Bu), 0.73 (s, 6, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ [142.2, 136.4, 128.9, 128.3] (C_{aryl}), 62.7 (CH_2N), 39.3 ($\mathit{C}Me_2$), 29.8 ($C\mathit{Me_3}$), 26.9 ($C\mathit{Me_2}$), 20.5 ($\mathit{C}Me_3$).

Synthesis of $LZrCl_2$ (1). A suspension of 276 mg of $ZrCl_4$ (1.185 mM) and 700 mg of LLi_2 (1.185 mM) in 20 mL of pentane was stirred at room temperature for 3 days under argon. Filtration of the suspension gave a cream solid, from which **1** was extracted with toluene (5 × 3 mL). Removal of the volatiles gave 520 mg of **1** as a white solid (59%). Cooling a satured toluene−pentane solution of **1** to −20 °C gave colorless crystals suitable for X-ray analysis. Anal. Calcd for $C_{37}H_{48}Cl_2N_2Si_2Zr$: C 60.13, H 6.55, N 3.79, Cl 9.59. Found: C 60.11, H 6.23, N 3.61, Cl 9.45. ^1H NMR (C_6D_6): δ 8.04 (d, 8, H_{aryl}), 7.24−7.12 (m, 12, H_{aryl}), 3.62 (s, 4, CH_2), 1.30 (s, 18, *t*-Bu), 0.98 (s, 6, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ [137.7, 133.3, 131.4, 129.1] (C_{aryl}), 67.4 (CH_2N), 43.7 ($\mathit{C}Me_2$), 29.9 ($C\mathit{Me_3}$), 25.5 ($C\mathit{Me_2}$), 21.5 ($\mathit{C}Me_3$).

Synthesis of $LHfCl_2$ (2). A 600 mg sample of LLi_2 (1.016 mM) was added to 276 mg of $HfCl_4$ (1.016 mM) in 8 mL of pentane. The suspension was stirred at room temperature for 5 days and was filtered through Celite. The solid was washed with pentane (2 × 2 mL) and extracted with toluene (3 × 4 mL + 2 × 2 mL). The toluene was removed under vacuum, giving a slightly sticky cream solid, washed again with 1 mL of pentane, and dried under vacuum (yield 365 mg, 43%). Anal. Calcd for $C_{37}H_{48}Cl_2N_2Si_2Hf$: C 53.78, H 5.85, N 3.39. Found: C 53.28, H 5.86, N 3.22. ^1H NMR (C_6D_6): δ 8.01 (d, 8, H_{aryl}), 7.26−7.12 (m, 12, H_{aryl}), 3.85 (s, 4, CH_2), 1.36 (s, 18, *t*-Bu), 0.99 (s, 6, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ [137.7, 133.6, 131.2, 128.9] (C_{aryl}), 66.9 (CH_2N), 43.1 ($\mathit{C}Me_2$), 29.9 ($C\mathit{Me_3}$), 25.4 ($C\mathit{Me_2}$), 21.5 ($\mathit{C}Me_3$).

Synthesis of $LTiCl_2$ (3). A solution of 100 mg of $TiCl_4(THF)_2$ (0.294 mM) and 173 mg of LLi_2 (0.294 mM) in 1 mL of toluene was refluxed for 18 h. Filtration through Celite and removal of the volatiles under vacuum gave an oily brown residue, which was washed with pentane (3 + 2 mL) and dried under vacuum. A light yellow solid was obtained (110 mg, 54%). Bright yellow crystals were obtained by recrystallization from a saturated toluene−pentane solution at −30 °C. Anal. Calcd for $C_{37}H_{48}Cl_2N_2Si_2Ti$: C 63.87, H 6.95, N 4.03. Found:

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C 63.86, H 6.99, N 3.94. ^{1}H NMR (C_6D_6): δ 8.01 (d, 8, H_{aryl}), 7.19−7.14 (m, 12, H_{aryl}), 3.89 (s, 4, CH_2), 1.30 (s, 18, *t*-Bu), 0.81 (s, 6, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ [137.9, 133.6, 130.9, 128.5] (C_{aryl}), 73.6 (CH_2N), 47.1 (CMe$_2$), 29.9 (CMe_3), 24.8 (CMe_2), 22.1 (CMe$_3$).

Synthesis of VCl_4·dme. A solution of freshly distilled VCl_4 (6.0 g) in 50 mL of pentane was slowly added at −78 °C under stirring into a pentane solution (25 mL) of 9.34 g of dme. The solution was stirred for 1 h at −60 °C and for 2 h at 20 °C, during which time a dark solid precipitated. The precipitate was collected by filtration, washed thoroughly with pentane, and dried under vacuum, giving 8.30 g (94%) of a dark microcrystaline solid. Anal. Calcd for $C_4H_{10}Cl_4O_2V$: C 16.98, H 3.56. Found: C 17.24, H 3.31.

Synthesis of $LVCl_2$ (4). A solution of 150 mg of VCl_4(dme) (0.530 mM) and 300 mg of LLi_2 (0.530 mM) in 2 mL of toluene was stirred for 11 h at room temperature. Removal of the volatiles under vacuum and extraction with pentane (10 mL) gave a green solution that was filtered through Celite. The pentane was removed under vacuum to give 290 mg of an oily green residue. Recrystallization in 1 mL of cold pentane yielded 40 mg of pure material as green crystals (9%). Anal. Calcd for $C_{37}H_{48}Cl_2N_2Si_2V$: C 63.59, H 6.92, N 4.01. Found: C 63.69, H 6.78, N 3.52. EPR ($PhCH_3$, 20 °C) $g = 1.975$, $a(^{51}V) = 65.1$ G.

Reaction between 1 and MAO. In an NMR tube charged with 20 mg of **1** (0.0271 mM) in C_6D_6 was added 71 mg of solid MAO (1.365 mM) at room temperature and sealed under argon. NMR spectra were recorded to follow the reaction at room temperature.

Reaction between 1 and $AlMe_3$. In an NMR tube charged with 10 mg of **1** (0.0135 mM) in C_6D_6 was slowly added at room temperature 14 μL of a 2.0 M toluene solution of $AlMe_3$ (0.0271 mM), and the tube was sealed under argon. The reaction was followed by ^{1}H NMR spectroscopy at room temperature and 60 °C.

Reaction between LH_2 and $AlMe_3$. In an NMR tube charged with 20 mg of LH_2 (0.0345 mM) in C_6D_6 was slowly added at room temperature 35 μL of a 2.0 M toluene solution of $AlMe_3$ (0.0346 mM), and the tube was sealed under argon. The reaction was followed by ^{1}H NMR spectroscopy at room temperature and 60 °C.

Typical Ethylene Polymerization Tests. The catalyst precursor (about 5 mg) and 500 equiv of solid MAO were premixed for 5 min in 10 mL of pentane. Ethylene (1 bar) was introduced under stirring at room temperature. After 15 min, the polymerization was quenched with acidified methanol. The polyethylene was filtered, washed with methanol and then acetone, and dried under vacuum at 80 °C for 24 h.

Crystallographic Data for 1−4. For **1**: $C_{37}H_{48}N_2Cl_2Si_2Zr$; M_w 739.07; triclinic; space group $P\bar{1}$; temperature of data collection $T = 160$ K; unit cell $a = 10.381(2)$ Å, $b = 13.415(2)$ Å, $c = 13.896(2)$ Å, $\alpha = 95.90(2)°$, $\beta = 98.50(2)°$, $\gamma = 104.68(2)°$; $U = 1831.3(5)$ Å^3; $Z = 2$; $\mu = 0.540$ mm^{-1}; $\rho_{calcd} = 1.34$ mg.m^{-3}; $F(000) = 772$; total reflections 10842 (4982 unique); $R = 0.0460$; $R_w = 0.1108$; GOF = 0.938. For **2**: $C_{37}H_{48}N_2Cl_2Si_2Hf$; M_w 826.35; triclinic; space group $P\bar{1}$; temperature of data collection $T = 160$ K; unit cell $a = 10.390(2)$ Å, $b = 13.437(2)$ Å, $c = 13.858(3)$ Å, $\alpha = 96.08(3)°$, $\beta = 98.43(3)°$, $\gamma = 104.76(3)°$; $U = 1829.8(7)$ Å^3; $Z = 2$; $\mu = 0.3.090$ mm^{-1}; $\rho_{calcd} = 1.50$ mg·m^{-3}; $F(000) = 836$; total reflections 13 510 (4977 unique); $R = 0.0250$; $R_w = 0.519$; GOF = 0.9. For **3**: $C_{37}H_{48}N_2Cl_2Si_2Ti$; M_w 695.75; monoclinic; space group $P2_1/n$; temperature of data collection $T = 160$ K; unit cell $a = 13.261(2)$ Å, $b = 15.935(2)$ Å, $c = 18.000(2)$ Å, $\beta = 105.26(2)°$; $U = 3669.6(8)$ Å^3; $Z = 4$; $\mu = 0.472$ mm^{-1}; $\rho_{calcd} = 1.259$ mg·m^{-3}; $F(000) = 1472$; total reflections 26383 (5248 unique); $R = 0.0403$; $R_w = 0.0735$; GOF = 0.848. For **4**: $C_{37}H_{48}N_2Cl_2Si_2V$; M_w 698.79; monoclinic; space group $P2_1/n$; temperature of data collection $T = 160$ K; unit cell $a = 13.239(2)$ Å, $b = 15.958(3)$ Å, $c = 17.967(3)$ Å, $\beta = 105.46(2)°$; $U = 3658.6(9)$ Å^3; $Z = 4$; $\mu = 0.511$ mm^{-1}; $\rho_{calcd} = 1.269$ mg·m^{-3}; F(000) = 1476; total reflections 18 499 (4475 unique); $R = 0.0368$; $R_w = 0.0815$; GOF = 0.903.

Data collection was performed at low temperature ($T = 160$ K) on a STOE imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems Cryostream cooler device and using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å); for each measurement final unit cell parameters were obtained by a least-squares refinement on a set of 5000 reflections equally distributed in reciprocal space; a crystal decay was monitored by measuring two hundred reflections per image. Any fluctuations of the intensity were observed over the course of data collection. The structures were solved by direct methods using (SIR92) and refined by least-squares procedures on F^2. Hydrogen atoms were located on difference Fourier maps and refined by using a riding model with a fixed isotropical thermal parameter at 20% higher than those of the carbon atoms to which they were connected. All non-hydrogen atoms were anisotropically refined. Molecule drawing is performed using the program ZORTEP with 50% probability diplacement ellipsoids for non-hydrogen atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary information. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

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Supporting Information Available: ORTEP drawings, crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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