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Reduction of Tetravalent Group 4 Metal Complexes Supported by an Extremely Bulky, Unsymmetrically Substituted *β*-Diketiminato Ligand Leading to the Regioselective C═N Bond Cleavage Giving Ring-Contracted Metal-Imido Complexes

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Reductions of tetravalent group 4 metal *β*-diketiminates, $[M^{IV}Cl_3(nacnac)(thf)_n]$ (**2a**, M = Ti; **3b**, M = Zr; **3c**, M = Hf; nacnac = $\{N(Tbt)C(Me)CHC(Me)N(Mes)\}^-$, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = 2,4,6-trimethylphenyl, $n = 0, 1$), with 2 equiv of KC_8 in the presence of LiCl and tmeda afforded the metal-imido complexes $[M{=}NTbt\{C(Me)CHC(Me)N(Mes)\}(\mu\text{-}Cl)_2Li(tmeda)]$ (**4a**, M = Ti; **4b**, M = Zr; **4c**, M = Hf; tmeda = $Me_2NCH_2CH_2NMe_2$). The formation of imido complexes **4a**−**c** can be explained in terms of the generation of the corresponding divalent complexes $[M^{II}Cl(nacnac)(L)_n]$ (**6a**, M = Ti; **6b**, M = Zr; **6c**, M = Hf; L = thf or Li(tmeda), etc.), followed by the reductive, regioselective cleavage of the C═N bond tethered to the Tbt group. The intermediacy of the divalent titanium complex **6a** was supported by the alternative formation of **4a** in the reaction of [Li(nacnac)] (**1**) with $[Ti^{II}Cl_2(tmeda)_2]$. Interestingly, **4a**−**c** reacted with H_2O to give the free ligand nacnacH (**8**).

Introduction

Interest in the chemistry of divalent group 4 metal complexes, especially in that of titanium complexes, has been stimulated by the very diverse aspects of their chemical reactivities, including activation of small molecules (N_2,[1] CO,[2] CO_2,[3] H_2,[4] etc.), reductive coupling of olefins[4] and acetylenes,[5] and the role played in Ziegler−Natta catalysis.[6] However, apart from the bicyclopentadienyl system,[7] divalent titanium complexes have been poorly known and only a few examples of highly coordinated complexes have been reported.[8]

The chemistry of *β*-diketiminato complexes is of much current interest.[9] *β*-Diketiminato ligands play important roles as monoanionic spectator ligands by the virtue of their strong binding ability to metals, their tunable steric and electronic demands, and their diversity of bonding modes. They often stabilize metal complexes in low oxidation states[10] and/or coordination numbers[11] and complexes containing a coligand that is multiply bonded to the metal.[12]

β-Diketiminato complexes of trivalent titanium and tetravalent group 4 metals have already been reported by Lappert,[13] Theopold,[14] Budzelaar,[15] Smith,[16] Mindiola,[17] and so forth. The robust nature of *β*-diketiminato ligands with early-transition

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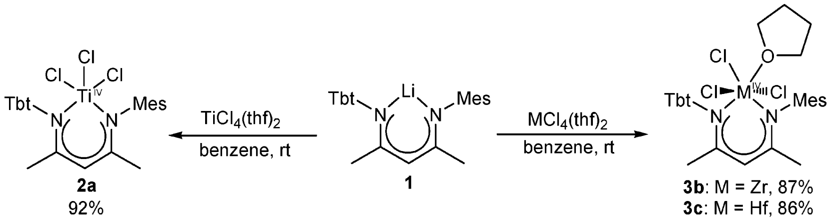
Scheme 1. Synthesis of β-Diketiminato Complexes of Group 4 Metals



metal systems has enabled them to be used as catalysts in olefin polymerization reactions.[15] However, divalent β-diketiminato complexes of group 4 metals have not been reported so far. Recently, Mindiola et al. have reported that two-electron reduction of tetravalent zirconium β-diketiminates bearing 2,6-diisopropylphenyl (Dip) substituents gave the corresponding terminal zirconium-imido complexes via transformation of the β-diketiminato ligand.[18]

Meanwhile, we have already succeeded in the synthesis of a variety of low-coordinate, reactive species (e.g., *heavy ketones*,[19] *heavy aromatics*,[20] and *heavy azo compounds*[21]) containing heavier main group elements by taking advantage of an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt).[22] We recently reported the synthesis and structure of a lithium β-diketiminate [Li(nacnac)] (**1**, nacnac = {N(Tbt)C(Me)CHC(Me)N(Mes)}$^-$, Mes = 2,4,6-trimethylphenyl) bearing a Tbt substituent, which was regarded as a ligand source for the synthesis of transition metal complexes.[23] The X-ray structural analysis of **1** showed that it has a monomeric structure and an essentially two-coordinated lithium center without solvent coordination and interaction with the neighboring molecules in the solid state.

Here, we report the synthesis of tetravalent group 4 metal complexes bearing a novel, extremely bulky β-diketiminato ligand together with their reduction reactions giving the corresponding terminal imido complexes of group 4 metals instead of the expected divalent complexes.

Results and Discussion

Reduction of Tetravalent β-Diketiminato Complexes of Group 4 Metals. Tetravalent titanium, zirconium, and hafnium complexes (**2a**, M = Ti, $n = 0$; **3b**, M = Zr, $n = 1$; **3c**, M = Hf, $n = 1$) were prepared by the reactions of [Li(nacnac)] (**1**) with MCl$_4$(thf)$_2$ (M = Ti, Zr, Hf), respectively (Scheme 1). The titanium complex **2a** was not coordinated by THF molecules, whereas the zirconium and hafnium complexes **3b** and **3c** were coordinated by a THF molecule probably due to their longer M−N bond lengths compared with that in **2a**.

The X-ray study showed that the structures of **3b** and **3c** adopt a distorted, octahedral geometry at the metal center and a meridional arrangement of three chorine atoms (Figure 2). Since hafnium complex **3c** is isomorphous, the ORTEP drawing of zirconium complex **3b** is depicted in Figure 2 as a representative. Selected structural parameters and the crystallographic data are summarized in Tables 1 and 5, respectively.

Two independent molecules are found in the unit cell of **3b**, and both molecules have structures that are essentially identical with each other. The five atoms in the backbone of the β-diketiminato ligand, N1−C1−C2−C3−N2, are coplanar, and the two sets of C−N and C−C distances in the ligand skeleton are almost equivalent to each other. The bond lengths of the C−N and C−C bonds are intermediate values between the typical single and double bond lengths. These results strongly suggest the delocalization of the double bonds of the ligand. The central zirconium atoms of the two independent molecules deviate from the N$_2$C$_3$ planes by 0.7544(16) and 0.7863(15) Å, respectively. However, the Zr−C(ligand backbone) distances [3.1319(14) and 3.1142(12) Å (Zr−C1), 3.4046(13) and 3.3904(12) Å (Zr−C2), 3.1455(12) and 3.1376(12) Å (Zr−C3)] are too long to form real Zr−C bonds. Therefore, the β-diketiminato ligand in **3b** can be considered to have the η^2-coordinaton mode, which is identical with zirconium complexes reported by Smith,[16] in contrast to 1,2,3,5-η^4- or η^5-coordinated β-diketimi-

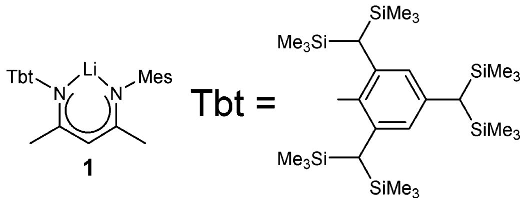


Figure 1. β-Diketiminato ligand bearing a Tbt group.

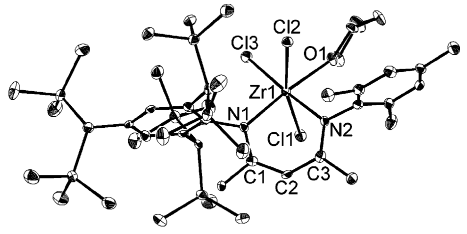


Figure 2. Molecular structure of the zirconium complex **3b** with thermal ellipsoids at the 50% probability level. H atoms and solvent molecules are omitted for clarity. One of the two independent molecules in the unit cell is depicted. The hafnium analogue **3c** is isomorphous. See Table 1 for selected bond distances and angles.

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Table 1. Selected Bond Lengths (Å) and Angles (deg)

	3b		3c		7
M−N1	2.187(3)	2.168(3)	2.1785(18)	2.1619(18)	2.000(3)
M−N2	2.226(3)	2.238(3)	2.2088(18)	2.2185(18)	1.981(3)
C1−C2	1.396(6)	1.388(6)	1.398(3)	1.394(3)	1.396(5)
C2−C3	1.397(6)	1.394(6)	1.392(2)	1.402(3)	1.391(5)
C1−N1	1.367(5)	1.372(5)	1.355(3)	1.355(3)	1.351(4)
C3−N2	1.343(5)	1.326(5)	1.343(3)	1.332(3)	1.345(4)
M−Cl1	2.4197(11)	2.4351(11)	2.4070(5)	2.4117(5)	2.2587(12)
M−Cl2	2.4381(11)	2.4256(11)	2.4219(5)	2.4184(6)	2.2829(11)
M−Cl3	2.4266(11)	2.4178(11)	2.4130(6)	2.4087(6)	
M−O1	2.297(3)	2.302(3)	2.2771(15)	2.2758(15)	
M···C1	3.1319(14)	3.1142(12)	3.106(2)	3.087(2)	2.981(3)
M···C2	3.4046(13)	3.3904(12)	3.389(2)	3.376(2)	3.004(3)
M···C3	3.1455(12)	3.1376(12)	3.120(2)	3.123(2)	3.310(3)
N1−M−N2	86.34(12)	86.12(12)	87.12(7)	86.92(7)	88.59(11)

Scheme 2. Reduction of β-Diketiminato Complexes of Group 4 Metals

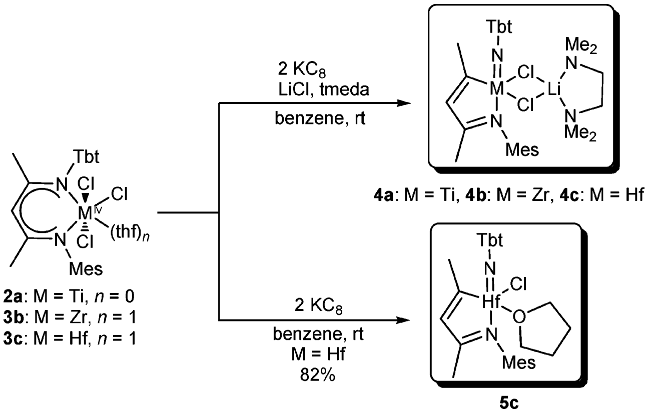

Table 2. Reduction of 2a, 3b, or 3c

entry	S. M.	LiCl, tmeda	yield/%
1	**2a**	+	87 (**4a**)
2	**2a**	−	*a*
3	**3b**	+	80 (**4b**)
4	**3b**	−	*a*
5	**3c**	+	81 (**4c**)
6	**3c**	−	82 (**5c**)

[a] The reaction mixtures showed complicated ^{1}H NMR spectra.

nato ligands of zirconium complexes claimed by Mindiola[18] and Lappert,[13a] respectively.

The X-ray crystallography of the hafnium complex **3c** also showed two independent molecules in the unit cell, and both molecules have structures essentially identical with each other. The two sets of C−N and C−C distances in the ligand skeleton are almost equivalent to each other. The M−N1, M−N2, M−O1, M−Cl1, M−Cl2, and M−Cl3 distances of **3c** are close to those of **3b** probably due to the lanthanoid contraction. The central hafnium atoms of the two independent molecules deviate from the N_2C_3 planes by 0.7409(27) and 0.7744(27) Å, respectively. The β-diketiminato ligand in **3c** can also be considered to have the η^2-coordinaton mode, which is identical with some of the hafnium complexes reported by Lappert.[13b] These characteristics of **3c** are similar to those of **3b**.

Two-electron reduction of **2a**, **3b**, and **3c** to the corresponding divalent complexes was examined by the use of KC$_8$ (Scheme 2 and Table 2).

In the reactions of β-diketiminato complexes of group 4 metals **2c**, **3b**, and **3c** with KC$_8$ in the presence of LiCl and $Me_2NCH_2CH_2NMe_2$ (tmeda), imido complexes [M=NTbt-{C(Me)CHC(Me)N(Mes)}(μ-Cl)$_2$Li(tmeda)] (**4a**, M = Ti; **4b**, M = Zr; **4c**, M = Hf) were quantitatively formed as yellowish-red, red, and violet crystals, respectively, instead of the expected divalent complexes [M^{II}Cl(nacnac)(L)$_n$] (**6a**, M = Ti; **6b**, M = Zr; **6c**, M = Hf; L = thf or LiCl(tmeda), etc.) (Table 2, entries 1, 3, and 5). The formation of **4a**−**c** was confirmed by the combination of ^{1}H, ^{13}C, and ^{7}Li NMR spectra and X-ray diffraction studies.

When the reduction of the titanium and zirconium complexes **2a** and **3b** was performed in the absence of tmeda, the reaction mixtures showed complicated ^{1}H NMR spectra (Table 2, entries 2 and 4). Addition of LiCl and tmeda to a benzene solution of these reaction mixtures resulted in the formation of titanium- and zirconium-imido ate complexes **4a** and **4b**, respectively. In the hafnium case, complex **5c** was formed by the reaction of **3c** with 2 equiv of KC$_8$ (Scheme 2, Table 2, entry 6). Similar types of zirconium-imido complexes have been reported by Mindiola et al., quite recently.[18] Addition of LiCl and tmeda to a benzene solution of **5c** resulted in the formation of hafnium-imido ate complex **4c**.

When a mixture of [Li(nacnac)] (**1**) and an equimolar amount of $TiCl_3(thf)_3$ was stirred in benzene for 3 h, a dark green solution was formed (Scheme 3). Recrystallization of the mixture from toluene gave the corresponding trivalent titanium complex [Ti^{III}Cl$_2$(nacnac)] (**7**). The EPR spectrum of **7** ($g_{\parallel} = 1.931$, $g_{\perp} = 1.949$) at room temperature and the magnetic moment of **7** ($\mu_{\mathrm{eff}} = 1.60\ \mu_{\mathrm{B}}$, determined by Evans method[24]) are consistent with those of d^1 paramagnetic species. For example, Mindiola et al. recently reported the EPR spectrum ($g_{\mathrm{iso}} = 1.97$) and the magnetic moment ($\mu_{\mathrm{eff}} = 2.17\ \mu_{\mathrm{B}}$) of [Ti{CH$_2$(*t*-Bu)$_2$}$_2$[{N-(Dip)C(Me)}$_2$CH]].[17d]

The X-ray study of **7** showed a distorted, tetrahedral geometry at the titanium center (Figure 3). Selected structural parameters and the crystallographic data are summarized in Tables 1 and 5, respectively.

The central titanium atom deviates from the N_2C_3 planes by 0.5474(36) Å. However, the Ti−C (ligand backbone) distances [2.981(3) Å (Ti−C1), 3.004(3) Å (Ti−C2), and 3.310(3) Å (Ti−C3)] are too long to form real Ti−C bonds. Therefore, the β-diketiminato ligand in **7** can be considered to have the η^2-coordinaton mode, which is identical with those of titanium(III) complexes reported by Budzelaar[15] and Mindiola.[17d] Hence, **7** is best described as a nine-electron, electron-deficient complex.

Next, the reduction of trivalent titanium β-diketiminate **7** to the corresponding divalent titanium complex was examined by using several reductants (Scheme 3 and Table 3).

The reactions of **7** with Na, K, LiC$_{10}$H$_8$ (lithium naphthalenide), and KC$_8$ in the presence of LiCl and tmeda afforded

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Scheme 3. Reduction of Trivalent Titanium *β*-Diketiminates

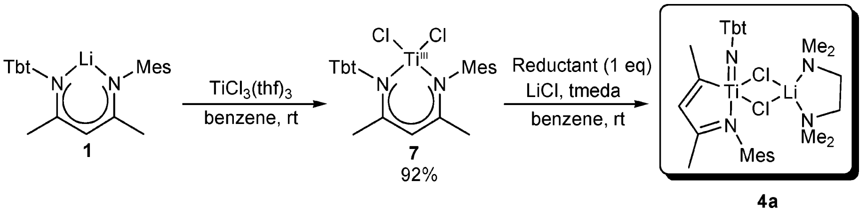


Table 3. Reduction of 7

entry	reductant	results[a]
1	Li	complicated mixture
2	Na	**4a** (quant)
3	K	**4a** (quant)
4	$LiC_{10}H_8$/THF	**4a** (97%) + **1**·(thf) (3%)
5	KC_8	**4a** (quant)

[a] Judged by the ^{1}H NMR spectrum.

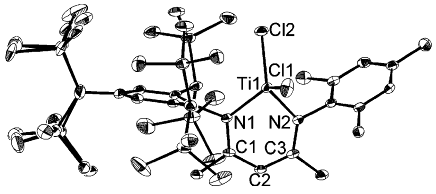
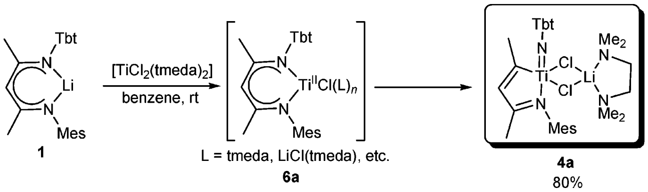


Figure 3. Molecular structure of the trivalent titanium complex **7** with thermal ellipsoids at the 50% probability level. H atoms and solvent molecules are omitted for clarity. See Table 1 for selected bond distances and angles.

Scheme 4. Reaction of Lithium *β*-Diketiminate with Divalent [$TiCl_2(tmeda)_2$]



the titanium-imido ate complex **4a** almost quantitatively (Table 3, entries 2−5), while the reduction of **7** using Li resulted in the formation of a complicated mixture (Table 3, entry 1). In addition, the reaction of **1** with a divalent titanium complex, [$TiCl_2(tmeda)_2$], also resulted in the formation of **4a** (Scheme 4).

Taking these results into consideration, we propose that imido complexes **4a**−**c** and **5c** are formed via the regioselective, reductive cleavage of the C−N bond connecting to the bulkier Tbt group of the intermediary divalent complexes [$M^{II}Cl(nacnac)(L)_n$] (**6a**−**c**, Scheme 5).

Table 4. Selected Bond Lengths (Å) and Angles (deg)

	4a	**4b**	**4c**	**5c**
M−N1	1.717(4)	1.8534(16)	1.8427(17)	1.799(9)
M−N2	2.202(4)	2.3233(17)	2.2884(18)	2.301(10)
M−C1	2.192(5)	2.322(2)	2.288(2)	2.293(13)
C1−C2	1.339(7)	1.347(3)	1.347(3)	1.358(16)
C2−C3	1.448(7)	1.454(3)	1.455(3)	1.453(18)
C3−N2	1.296(6)	1.301(3)	1.301(3)	1.289(15)
M−Cl1	2.4185(17)	2.5429(8)	2.5078(6)	2.429(3)
M−Cl2	2.4223(17)	2.5481(8)	2.5112(6)	
M−O1				2.222(9)
M−N1−C6	175.1(3)	172.44(13)	173.29(15)	166.7(7)
C1−M−N2	75.50(16)	72.53(7)	73.59(7)	72.6(4)

This unique regioselectivity may be explained in terms of the more servere repulsion of the Tbt group with the methyl group at the 5-position in the exited state or the product in path B compared with that in path A (Scheme 5), although it is unclear whether this reaction is controlled thermodynamically or kinetically.

Structures of Imido Complexes. A characteristic feature of **4a**−**c** and **5c** is the ^{13}C NMR chemical shifts for the vinylic carbons connecting to the metal atoms, which resonated at 237.2, 237.2, 242.6, and 236.3 ppm, respectively. These values are consistent with those of the reported group 4 metal complexes bearing a vinyl group.[18]

The molecular structures of imido complexes **4a**−**c** and **5c** were determined by X-ray diffraction. Since all three metal-imido ate complexes **4a**−**c** are isomorphous, the ORTEP drawing of hafnium complex **4c** is depicted in Figure 4 as the representative (Figure 4a) together with that of THF-coordinated hafnium **5c** (Figure 4b). The selected bond lengths and angles and crystallographic data are summarized in Tables 4 and 5, respectively.

The M−N1 distances of **4a**−**c** and **5c** [**4a**, 1.717(4) Å; **4b**, 1.8534(16) Å; **4c**, 1.8427(17) Å; **5c**, 1.799(9) Å] are close to

Scheme 5. Possible Mechanism for the Formation of Metal-Imido Complexes 4a−**c and 5c via Divalent Complexes 6a**−**c**

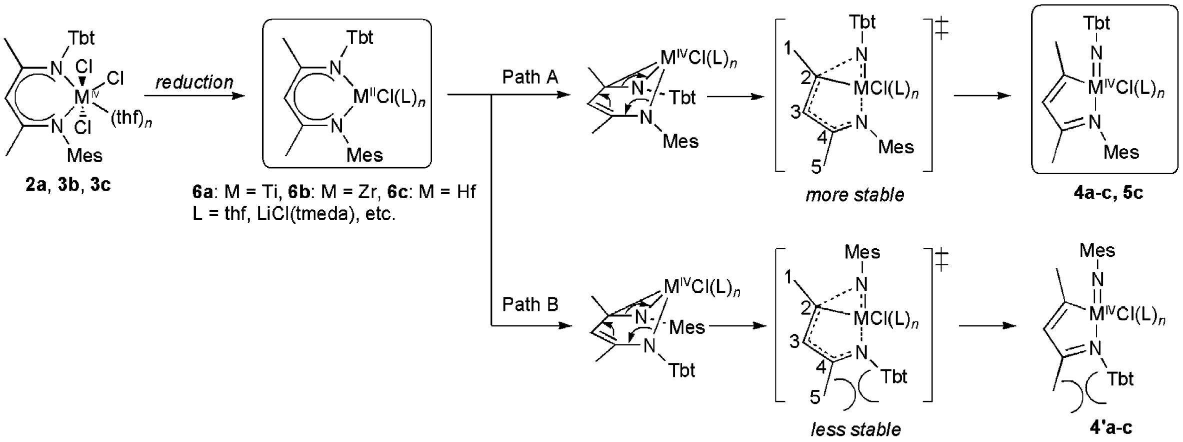


Table 5. Crystal Data and Structure Refinement Details for 3b,c, 4a−c, 5c, and 7

	3b·$0.25C_6H_{14}$	**3c**·$0.25C_6H_{14}$	**4a**	**4b**·C_6H_{14}
empirical formula	$C_{45}H_{85}Cl_3N_2OSi_6Zr\cdot 0.25C_6H_{14}$	$C_{45}H_{85}Cl_3HfN_2OSi_6\cdot 0.25C_6H_{14}$	$C_{47}H_{93}Cl_2LiN_4Si_6Ti$	$C_{47}H_{93}Cl_2LiN_4Si_6Zr\cdot C_6H_{14}$
fw	1057.80	1145.07	1008.53	1138.03
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a (Å)	11.6646(2)	11.65970(10)	12.724(5)	12.718(3)
b (Å)	18.3088(2)	18.3005(2)	12.781(6)	15.788(4)
c (Å)	28.9532(7)	28.9162(3)	19.884(8)	19.011(5)
α (deg)	74.582(5)	74.6796(8)	85.729(15)	99.7567(19)
β (deg)	82.573(6)	82.5888(4)	72.206(12)	108.1972(17)
γ (deg)	77.117(6)	77.1249(5)	87.540(15)	102.239(2)
V (Å^3)	5794.67(18)	5785.06(10)	3070(2)	3427.8(15)
Z	4	4	2	2
D_{calc} (g cm^{-3})	1.213	1.315	1.091	1.103
cryst dimens	0.50 × 0.20 × 0.02	0.30 × 0.30 × 0.30	0.50 × 0.30 × 0.20	0.60 × 0.20 × 0.20
θ range (deg)	2.63−25.0	1.18−25.0	2.29−25.0	2.33−25.0
abs coeff (mm^{-1})	0.485	2.099	0.375	0.376
no. of reflcns collcd	48 307	48 984	25 376	28 098
no. of unique reflcns	20 236	20 242	10 719	11 929
no. of params	1118	1119	550	686
R_1, wR_2 (for $I > 2\sigma(I)$)[a]	0.0607, 0.1246	0.0204, 0.0477	0.0848, 0.1558	0.0330, 0.0795
goodness-of-fit	1.121	1.069	1.181	1.062
largest peak, hole (e/Å^{-3})	0.819, −0.398	0.657, −0.454	0.461, −0.543	0.701, −0.275

	4c·C_6H_{14}	**5c**·C_6H_{14}	**7**
empirical formula	$C_{47}H_{93}Cl_2HfLiN_4Si_6\cdot C_6H_{14}$	$C_{45}H_{85}ClHfN_2OSi_6\cdot C_6H_{14}$	$C_{41}H_{77}Cl_2N_2Si_6Ti$
fw	1250.30	1052.63	885.39
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$C2/c$ (#15)
a (Å)	12.6966(17)	9.5578(18)	47.617(3)
b (Å)	15.754(2)	12.345(2)	9.5808(5
c (Å)	19.249(3)	25.424(6)	23.4963(16)
α (deg)	72.090(5)	87.842(10)	
β (deg)	69.348(4)	82.127(12)	101.676(3)
γ (deg)	77.721(6)	71.02(2)	
V (Å^3)	3404.6(8)	2809.9(10)	10497.3(11)
Z	2	2	8
D_{calc} (g cm^{-3})	1.195	1.244	1.120
cryst dimens	0.30 × 0.20 × 0.10	0.50 × 0.30 × 0.10	0.60 × 0.20 × 0.15
θ range (deg)	2.74−25.0	2.96−25.0	2.31−25.00
abs coeff (mm^{-1})	1.749	2.063	0.429
no. of reflcns collcd	29 459	16 469	42 496
no. of unique reflcns	12 554	8329	9188
no. of params	686	528	545
R_1, wR_2 (for $I > 2\sigma(I)$)[a]	0.0225, 0.0487	0.0786, 0.1337	0.0688, 0.1669
goodness-of-fit	1.062	1.097	1.104
largest peak, hole (e/Å^{-3})	0.742, −0.449	2.564, −1.669	0.960, −0.623

[a] $R_1 = \sum||F_o| - |F_c||/|F_o|$; $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2 + (aP)^2 + bP]$, $P = (F_o{}^2 + 2F_c{}^2)/3$, and a and b are constants given in the Supporting Information.

those of the reported imido complexes of group 4 metals (Ti=N, 1.67−1.73 Å;[12a,17,25] Zr=N, 1.83−1.93 Å;[18,26] and Hf=N, 1.82−1.86 Å[26b,27]) and much shorter than the M−N2 distances [**4a**, 2.202(4) Å; **4b**, 2.3233(17) Å; **4c**, 2.2884(18) Å; **5c**, 2.301(10) Å]. The M−N1 distance of **4c** is close to that of **4b** probably due to the lanthanoid contraction and longer than that of **5c**. Complexes **4a−c** and **5c** have a nearly linear M=N−C6 alignment. These characteristics of **4a−c** and **5c** are similar to those for the reported imido complexes.[12a,17,18,25−27] In addition, the ring M−C1−C2−C3−N2 is almost planar.

Hydrolysis of Imido Complexes. The reactions of the group 4 metal-imido complexes **4a−c** and **5c** with H_2O resulted in the quantitative formation of the free ligand nacnacH (**8**) via the reconstruction of the β-diketiminato ligand (Scheme 6). The regeneration of the β-diketiminato ligand is a fascinating process, although the mechanism for the hydrolysis is unclear at present.

Conclusion

We presented here the systematic studies on the synthesis of the imido complexes of group 4 metals [M=NTbt{C(Me)CHC-

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(25) (a) Wilson, P. J.; Blake, A. J.; Mountford, P.; Schröder, M. *J. Organomet. Chem.* **2000**, *600*, 71−83. (b) Adams, N.; Arts, H. J.; Bolton, P. D.; Cowell, D.; Dubberley, S. R.; Friederichs, N.; Grant, C. M.; Kranenburg, M.; Sealey, A. J.; Wang, B.; Wilson., P. J.; Cowley, A. R.; Mountford, P.; Schröder, M. *Chem. Commun.* **2004**, 434−435. (c) Stewrat, P. J.; Blake, A. J.; Mountford, P. *Organometallics* **1998**, *17*, 3271−3281.

(26) (a) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, *19*, 4795−4809. (b) Thorman, J. L.; Guzei, I. A.; Young, V. G., Jr.; Woo, L. K. *Inorg. Chem.* **1999**, *38*, 3814−3824. (c) Krska, S. W.; Zuckeman, R. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 11828−11829. (d) Profilet, R. D.; Zambrano, C. H.; Fanwick, P. E.; Nash, J. J.; Rothwell, I. P. *Inorg. Chem.* **1990**, *29*, 4362−4364. (e) Fryzuk, M. D.; Love, J. B.; Rettig, S. J. *Organometallics* **1998**, *17*, 846−853. (f) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1−3. (g) Blake, A. J.; Collier, P. E.; Gade, L. H.; Mountford, P.; Lloyd, J.; Pugh, S. M.; Schubart, M.; Skinner, M. E. G.; Trösch, D. J. M. *Inorg. Chem.* **2001**, *40*, 870−877. (h) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729−8731. (i) Arney, D. J.; Bruck. M. A.; Huber, S. R.; Wigley, D. E. *Inorg. Chem.* **1992**, *31*, 3749−3755. (j) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914−11921.

(27) (a) Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689−708. (b) Castillo, I.; Tilley T. D. *J. Organomet. Chem.* **2002**, *643−644*, 431−440.

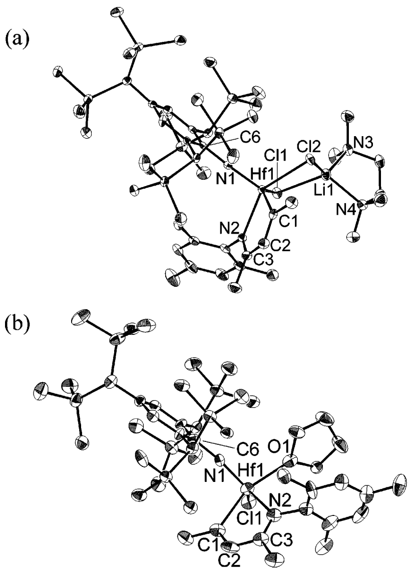
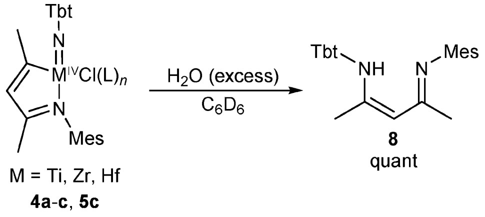


Figure 4. Molecular structures of the hafnium-imido complexes **4c** (a) and **5c** (b) with thermal ellipsoids at the 50% and 30% probability levels, respectively. H atoms and solvent molecules are omitted for clarity. The titanium and zirconium analogues (**4a** and **4b**) are isomorphous. See Table 5 for selected bond distances and angles of **4a**−**c** and **5c**.

Scheme 6. Reaction of Metal-Imido Complexes with H_2O



(Me)N(Mes)}(μ-Cl)$_2$Li(tmeda)] (M = Ti, Zr, Hf, **4a**−**c**) by the reduction of the tetravalent or trivalent group 4 metal β-diketiminates [$M^{IV}Cl_3$(nacnac)(thf)$_n$] (M = Ti, Zr, Hf, **2a**, **3b**, and **3c**) or [$Ti^{III}Cl_2$(nacnac)] (**7**) in the presence of LiCl and tmeda. As another hafnium complex, THF-coordinated complex [Hf═NTbt{C(Me)CHC(Me)N(Mes)}Cl(thf)] (**5c**) was also formed by the reaction of **3c** with 2 equiv of KC_8. In addition, the reaction of [Li(nacnac)] (**1**) with a divalent titanium complex, [$TiCl_2(tmeda)_2$], resulted in the formation of **4a**. The formation of the imido complexes **4a**−**c** is most likely explained in terms of the initial generation of the corresponding divalent complexes [M^{II}Cl(nacnac)(L)$_n$] (M = Ti, Zr, Hf; L = thf or Li(tmeda), etc., **6a**−**c**) followed by the regioselective, reductive cleavage of the C═N bond tethered to the Tbt group. Interestingly, the reactions of **4a**−**c** with H_2O resulted in the quantitative formation of the free ligand, nacnacH (**8**), via the reconstruction of the β-diketiminato ligand.

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in an MBRAUN Labmaster glovebox under an atmosphere of purified argon. Celite was activated at 200 °C under vacuum for 1 day. [Li(nacnac)] (**1**),[23] [$MCl_4(thf)_2$] (M = Ti, Zr, Hf),[28] [$TiCl_2(tmeda)_2$],[8a] $LiC_{10}H_8$,[29] and KC_8[30] were prepared according to the methods in the literatures. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{7}Li NMR (116 MHz) spectra were recorded on a JEOL JNM AL-300 spectrometer. The ^{1}H NMR chemical shifts were reported with reference to the internal residual $CHCl_3$ (7.25 ppm) or C_6D_5H (7.15 ppm). The ^{13}C NMR chemical shifts were reported with reference to the carbon-13 signal of C_6D_6 (128.0 ppm). Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT techniques. The ^{7}Li NMR chemical shifts were reported with reference to the external standards, LiCl (0 ppm). The X-band EPR spectrum was recorded on a Bruker EMX spectrometer. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Multiple attempts to obtain a satisfactory elemental analysis of complexes **2a** and **3b** were unsuccessful due to their extremely high moisture sensitivity. EI- and FAB-mass spectra (matrix: 3-nitrobenzyl alcohol or 2-nitrophenyl octyl ether) of all complexes indicated that the highest mass fragment was observed at *m/z* 766 (nacnacH, **8**) or 767 ([**8** + H]$^+$), suggesting hydrolysis during the measurements. The purity of all complexes was confirmed by the ^{1}H NMR spectra. The ^{1}H NMR spectra of all complexes are depicted in Figures S1−S7 in the Supporting Information.

Synthesis of [$TiCl_3$(nacnac)] (2a). A solution of [Li(nacnac)] (**1**, 80.3 mg, 103 μmol) in benzene (1 mL) was added to a slurry of $TiCl_4(thf)_2$ (34.5 mg, 103 μmol) in benzene (1 mL), causing the development of a dark red color. The reaction mixture was stirred for 3 h, and the solvent was removed under reduced pressure. Toluene was added to the red residue, and the filtration through Celite gave a dark red solution. The filtrate was dried under vacuum, and the product was recrystallized from toluene at −40 °C, yielding the almost pure product as dark red crystals. [$TiCl_3$(nacnac)] (**2a**, 86.3 mg, 92%): mp 184−187 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ 0.17 (s, 18 H, Si*Me*$_3$), 0.22 (s, 18H, Si*Me*$_3$), 0.37 (s, 18H, Si*Me*$_3$), 1.31 (s, 3H, *Me*), 1.49 (s, 1H, Tbt *p*-benzyl), 1.73 (s, 3H, *Me*), 2.03 (s, 3H, *Me*), 2.27 (s, 6H, Mes *o-Me*), 2.61 (s, 1H, Tbt *o*-benzyl), 2.81 (s, 1H, Tbt *o*-benzyl), 5.79 (s, 1H, 3-C*H*), 6.56 (br s, 1H, Tbt *m-H*), 6.68 (s, 2H, Mes *m-H*), 6.70 (br s, 1H, Tbt *m-H*). ^{13}C NMR (75 MHz, C_6D_6): δ 1.2 (q, Si*Me*$_3$), 2.6 (q, Si*Me*$_3$), 2.8 (q, Si*Me*$_3$), 20.5 (q, *Me*), 20.9 (q, Mes *o-Me*), 22.6 (d, Tbt *o*-benzyl), 23.2 (d, Tbt *o*-benzyl), 23.6 (q, *Me*), 29.8 (q, *Me*), 30.3 (d, Tbt *p*-benzyl), 110.1 (d, 3-*C*H), 124.4 (d, Tbt C_m), 128.3 (d, Mes C_m), 129.1 (d, Tbt C_m), 129.2 (s), 131.2 (s), 138.8 (s), 139.5 (s), 141.7 (s, Mes C_o), 146.2 (s), 147.8 (s), 166.6 (s, *C*(N)), 176.6 (s, *C*(N)).

Synthesis of [$ZrCl_3$(nacnac)(thf)] (3b). A solution of [Li(nacnac)] (**1**, 79.8 mg, 103 μmol) in benzene (1 mL) was added to a slurry of $ZrCl_4(thf)_2$ (39.0 mg, 103 μmol) in benzene (1 mL), causing the development of a yellow color. The procedure similar to that in the preparation of **2a** afforded the almost pure product as yellow crystals. [$ZrCl_3$(nacnac)(thf)] (**3b**, 92.9 mg, 87%): mp 189−192 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ 0.22 (s, 9H, Si*Me*$_3$), 0.30 (s, 9H, Si*Me*$_3$), 0.33 (s, 9H, Si*Me*$_3$), 0.49 (s, 9H, Si*Me*$_3$), 0.53 (s, 9H, Si*Me*$_3$), 0.57 (s, 9H, Si*Me*$_3$), 1.14 (br, 4H, thf β-H), 1.37 (s, 3H, *Me*), 1.47 (s, 3H, *Me*), 1.55 (s, 1H, Tbt *p*-benzyl), 2.09 (s, 3H, *Me*), 2.25 (s, 3H, *Me*), 2.34 (s, 3H, *Me*), 2.86 (s, 1H, Tbt *o*-benzyl), 3.26 (s, 1H, Tbt *o*-benzyl), 3.82 (br, 4H, thf β-H), 5.49 (s, 1H, 3-C*H*), 6.64 (br s, 1H, Tbt *m-H*), 6.72 (br, 2H, Mes *m-H*), 6.86 (br s, 1H, Tbt *m-H*). ^{13}C NMR (75 MHz, C_6D_6): δ 1.3 (q, Si*Me*$_3$), 1.4 (q, Si*Me*$_3$), 2.8 (q, Si*Me*$_3$), 3.0 (q, Si*Me*$_3$), 3.58 (q, Si*Me*$_3$), 3.63 (q, Si*Me*$_3$), 20.1 (q, *Me*), 20.6 (q, *Me*), 20.9 (q, *Me*), 22.2 (d, Tbt *o*-benzyl), 23.2 (d, Tbt *o*-benzyl), 24.6 (q, *Me*), 25.0 (t, thf C_β), 30.5 (q, *Me*), 30.6 (d, Tbt *p*-benzyl), 76.1 (t, thf C_α), 107.1 (d, 3-*C*H), 125.1 (d, Tbt C_m), 129.1 (d, Tbt C_m), 129.8 (d, Mes C_m), 130.1 (d, Mes C_m), 134.0 (s), 135.5 (s), 139.2 (s), 140.3 (s), 140.8 (s), 141.9 (s), 142.7 (s), 145.3 (s), 170.3 (s, *C*(N)), 171.7 (s, *C*(N)).

Synthesis of [$HfCl_3$(nacnac)(thf)] (3c). A solution of [Li(nacnac)] (**1**, 80.1 mg, 103 μmol) in benzene (1 mL) was added to

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[28] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135−140.

[29] Suga, K.; Watanabe, S.; Kamma, K. *Can. J. Chem.* **1967**, *45*, 933−937.

[30] Schwindt, M.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814−2819.

a slurry of $HfCl_4(thf)_2$ (48.0 mg, 103 μmol) in benzene (1 mL), causing the development of a pale yellow color. The procedure similar to that in the preparation of **2a** afforded the almost pure product as yellow crystals. [$HfCl_3$(nacnac)(thf)] (**3c**, 99.5 mg, 86%): mp 196−199 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ 0.23 (s, 9H, Si*Me*$_3$), 0.30 (s, 9H, Si*Me*$_3$), 0.34 (s, 9H, Si*Me*$_3$), 0.50 (s, 9H, Si*Me*$_3$), 0.534 (s, 9H, Si*Me*$_3$), 0.58 (s, 9H, Si*Me*$_3$), 1.07 (br, 4H, thf β-H), 1.33 (s, 3H, *Me*), 1.45 (s, 3H, *Me*), 1.55 (s, 1H, Tbt *p*-benzyl), 2.09 (s, 3H, *Me*), 2.26 (s, 3H, *Me*), 2.35 (s, 3H, *Me*), 2.94 (s, 1H, Tbt *o*-benzyl), 3.31 (s, 1H, Tbt *o*-benzyl), 3.82 (br, 4H, thf β-H), 5.37 (s, 1H, 3-C*H*), 6.63 (br s, 1H, Tbt *m-H*), 6.72 (br, 2H, Mes *m-H*), 6.86 (br s, 1H, Tbt *m-H*). ^{13}C NMR (75 MHz, C_6D_6): δ 1.0 (q, Si*Me*$_3$), 1.3 (q, Si*Me*$_3$), 2.8 (q, Si*Me*$_3$), 3.0 (q, Si*Me*$_3$), 3.6 (q, Si*Me*$_3$), 3.7 (q, Si*Me*$_3$), 20.1 (q, *Me*), 20.5 (q, *Me*), 20.7 (q, *Me*), 22.1 (d, Tbt *o*-benzyl), 23.0 (d, Tbt *o*-benzyl), 24.8 (q, *Me*), 25.0 (t, thf C_β), 30.4 (d, Tbt *p*-benzyl), 30.9 (q, *Me*), 77.2 (t, thf C_α), 106.8 (d, 3-*C*H), 125.1 (d, Tbt C_m), 129.1 (d, Tbt C_m), 129.8 (d, Mes C_m), 130.1 (d, Mes C_m), 134.5 (s), 135.4 (s), 139.2 (s), 140.2 (s), 141.2 (s), 142.4 (s), 142.6 (s), 144.9 (s), 170.9 (s, *C*(N)), 173.1 (s, *C*(N)). Anal. Calcd for $C_{45}H_{85}N_2OSi_6Cl_3Hf$: C, 48.11; H, 7.63; N, 2.49. Found: C, 48.33; H, 7.86; N, 2.36.

Reduction of [$TiCl_3$(nacnac)] (2a). A reductant [$LiC_{10}H_8$/THF solution (1.0 M, 52 μL, 52 μmol) or KC_8 (7.0 mg, 52 μmol)] was added to a benzene suspension (1 mL) of [Li(nacnac)] (**1**, 40.0 mg, 51.7 μmol) and $TiCl_4(thf)_2$ (17.2 mg, 51.7 μmol) in the presence of tmeda (100 μL, 100 μmol), causing the development of a dark red color. The reaction mixture was stirred for 1 day, and the solvent was removed under reduced pressure. Toluene was added to the dark red residue, and filtration through Celite gave a dark red solution. The filtrate was dried under vacuum, and the product was recrystallized from hexane at 0 °C, yielding yellowish-red crystals of **4a**. [Ti═NTbt{C(Me)CHC(Me)N(Mes)}(μ-Cl)$_2$Li(tmeda)] (**4a**, 45.4 mg, 87%): mp 164−166 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ 0.24 (s, 18H, Si*Me*$_3$), 0.41 (s, 36H, Si*Me*$_3$), 1.45 (s, 1H, Tbt *p*-benzyl), 1.48 (s, 3H, *Me*), 1.67 (br s, 4H, tmeda C*H$_2$*), 1.90 (br s, 12H, tmeda *Me*), 2.20 (s, 3H, *Me*), 2.20−2.40 (br s, 6H, Mes *o-Me*), 3.02 (d, $^4J_{HH}$ = 1.4 Hz, 3H, *Me*), 3.94 (s, 2H, Tbt *o*-benzyl), 6.45 (br s, 2H, Tbt *m-H*), 6.59 (q, $^4J_{HH}$ = 1.4 Hz, 1H, vinyl-*H*), 6.84 (s, 2H, Mes *m-H*). ^{13}C NMR (75 MHz, C_6D_6): δ 1.2 (q, Si*Me*$_3$), 1.9 (q, Si*Me*$_3$), 19.7 (q, *Me*), 20.1 (q, Mes *o-Me*), 20.7 (q, *Me*), 20.9 (d, Tbt *o*-benzyl), 30.2 (d, Tbt *p*-benzyl), 33.9 (q, *Me*), 45.7 (q, tmeda *Me*), 56.4 (t, tmeda *C*H$_2$), 128.3 (d, Tbt C_m), 128.6 (d, Mes C_m), 130.5 (s), 132.6 (d, vinyl *C*), 134.2 (s), 134.5 (s), 139.7 (s), 145.5 (s), 160.5 (s, Tbt C_{ipso}), 180.8 (*C*(N)), 237.2 (Ti-*C*). ^{7}Li NMR (116 MHz, C_6D_6): δ 0.81. Anal. Calcd for $C_{47}H_{93}LiN_4Si_6Cl_2Ti$: C, 55.97; H, 9.29; N, 5.56. Found: C, 55.72; H, 9.52; N, 5.80.

Reduction of [$ZrCl_3$(nacnac)(thf)] (3b). A reductant [$LiC_{10}H_8$/THF solution (1.0 M, 210 μL, 210 μmol) or KC_8 (35.9 mg, 266 μmol)] was added to a benzene suspension (1 mL) of [Li(nacnac)] (**1**, 79.8 mg, 103 μmol) and $ZrCl_4(thf)_2$ (39.1 mg, 103 μmol) in the presence of tmeda (200 μL, 200 μmol), causing the development of a dark red color. The procedure similar to that in the preparation of **4a** afforded the almost pure product **4b** as red crystals. [Zr═NTbt{C(Me)CHC(Me)N(Mes)}(μ-Cl)$_2$Li(tmeda)] (**4b**, 86.7 mg, 80%): mp 207−210 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ 0.28 (s, 18H, Si*Me*$_3$), 0.41 (s, 36H, Si*Me*$_3$), 1.48 (br, 4H, Tbt *p*-benzyl + *Me*), 1.85 (br s, 4H, tmeda C*H$_2$*), 1.95 (br s, 12 H, tmeda *Me*), 2.17 (s, 3H, *Me*), 2.22−2.35 (br s, 6H, Mes *o-Me*), 2.97 (d, $^4J_{HH}$ = 1.5 Hz, 3H, *Me*), 3.76 (s, 2H, Tbt *o*-benzyl), 6.57 (br s, 2H, Tbt *m-H*), 6.78 (q, $^4J_{HH}$ = 1.5 Hz, 1H, vinyl-*H*), 6.83 (s, 2H, Mes *m-H*). ^{13}C NMR (75 MHz, C_6D_6): δ 1.2 (q, Si*Me*$_3$), 1.8 (q, Si*Me*$_3$), 20.1 (q, *Me*), 20.3 (q, Mes *o-Me*), 20.9 (q, *Me*), 21.4 (d, Tbt *o*-benzyl), 29.7 (d, Tbt *p*-benzyl), 32.7 (q, *Me*), 45.6 (q, tmeda *Me*), 56.5 (t, tmeda *C*H$_2$), 128.3 (d, Tbt C_m), 128.5 (d, Mes C_m), 129.7 (s), 131.1 (s), 135.0 (s), 135.7 (d, vinyl *C*), 137.0 (s), 143.0 (s), 153.8 (s, Tbt C_{ipso}), 183.2 (*C*(N)), 237.2 (Zr-*C*). ^{7}Li NMR (116 MHz, C_6D_6): δ 0.68. Anal. Calcd for $C_{47}H_{93}LiN_4Si_6Cl_2Zr$: C, 53.67; H, 8.91; N, 5.33. Found: C, 53.42; H, 9.12; N, 5.04.

Reduction of [$HfCl_3$(nacnac)(thf)] (3c). A reductant [$LiC_{10}H_8$/THF solution (1.0 M, 210 μL, 210 μmol) or KC_8 (36.0 mg, 266 μmol)] was added to a benzene suspension (1 mL) of [Li(nacnac)] (**1**, 79.8 mg, 103 μmol) and $HfCl_4(thf)_2$ (48.3 mg, 103 μmol) in the presence of tmeda (200 μL, 200 μmol), causing the development of a violet color. The procedure similar to that in the preparation of **4a** afforded the almost pure product **4c** as violet crystals. [Hf═NTbt{C(Me)CHC(Me)N(Mes)}(μ-Cl)$_2$Li(tmeda)] (**4c**, 95.0 mg, 81%): mp 173−176 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ 0.31 (s, 18H, Si*Me*$_3$), 0.42 (s, 36H, Si*Me*$_3$), 1.48 (s, 3H, *Me*), 1.49 (s, 1H, Tbt *p*-benzyl), 1.90 (br s, 4H, tmeda C*H$_2$*), 1.96 (br s, 12H, tmeda *Me*), 2.16 (s, 3H, *Me*), 2.25−2.45 (br s, 6H, Mes *o-Me*), 3.01 (d, $^4J_{HH}$ = 1.5 Hz, 3H, *Me*), 3.75 (s, 2H, Tbt *o*-benzyl), 6.63 (br s, 2H, Tbt *m-H*), 6.83 (s, 2H, Mes *m-H*), 6.86 (q, $^4J_{HH}$ = 1.5 Hz, 1H, vinyl-*H*). ^{13}C NMR (300 MHz, C_6D_6): δ 1.3 (q, Si*Me*$_3$), 1.8 (q, Si*Me*$_3$), 20.2 (q, *Me*), 20.8 (d, Tbt *o*-benzyl), 20.9 (q, Mes *o-Me*), 21.4 (q, *Me*), 29.4 (d, Tbt *p*-benzyl), 32.9 (q, *Me*), 45.7 (q, tmeda *Me*), 56.8 (t, tmeda *C*H$_2$), 128.3 (d, Tbt C_m), 129.1 (d, Mes C_m), 129.9 (s), 132.3 (s), 135.1 (s), 135.3 (d, vinyl *C*), 137.5 (s), 143.1 (s), 154.0 (s, Tbt C_{ipso}), 182.6 (*C*(N)), 242.6 (Hf-*C*). ^{7}Li NMR (rt, 116 MHz, C_6D_6): δ 0.57. Anal. Calcd for $C_{47}H_{93}LiN_4Si_6Cl_2Hf$: C, 49.56; H, 8.23; N, 4.92. Found: C, 49.59; H, 8.49; N, 4.53.

Reduction of [$HfCl_3$(nacnac)(thf)] (3c) in the Absence of tmeda. KC_8 (35.9 mg, 266 μmol) was added to a benzene suspension (1 mL) of [Li(nacnac)] (**1**, 80.2 mg, 51.7 μmol) and $HfCl_4(thf)_2$ (48.1 mg, 103 μmol), causing the development of a dark violet color. The procedure similar to that in the preparation of **4a** afforded the almost pure product **5c** as violet crystals. [Hf═NTbt{C(Me)CHC(Me)N(Mes)}Cl(thf)] (**5c**, 87.8 mg, 82%): mp 143−145 °C (dec). ^{1}H NMR (300 MHz, C_6D_6): δ 0.31 (s, 18H, Si*Me*$_3$), 0.42 (s, 36H, Si*Me*$_3$), 1.48 (s, 3H, *Me*), 1.49 (s, 1H, Tbt *p*-benzyl), 1.90 (br s, 4H, tmeda C*H$_2$*), 1.96 (br s, 12H, tmeda *Me*), 2.16 (s, 3H, *Me*), 2.25−2.45 (br s, 6H, Mes *o-Me*), 3.01 (d, $^4J_{HH}$ = 1.3 Hz, 3H, *Me*), 3.75 (s, 2H, Tbt *o*-benzyl), 6.63 (br s, 2H, Tbt *m-H*), 6.83 (s, 2H, Mes *m-H*), 6.86 (q, $^4J_{HH}$ = 1.3 Hz, 1H, vinyl-*H*). ^{13}C NMR (75 MHz, C_6D_6): δ 0.9 (q, Si*Me*$_3$), 1.2 (q, Si*Me*$_3$), 1.8 (q, Si*Me*$_3$), 20.4 (q, *Me*), 20.9 (q, Mes *o-Me*), 21.6 (q, *Me*), 21.9 (d, Tbt *o*-benzyl), 25.0 (t, thf C_β), 29.4 (d, Tbt *p*-benzyl), 30.8 (q, *Me*), 75.0 (t, thf C_α), 129.1 (d, Tbt C_m), 129.8 (d, Mes C_m), 130.5 (s), 130.7 (s), 131.3 (s), 135.5 (s), 136.7 (s), 137.1 (d, vinyl *C*), 153.8 (s, Tbt C_{ipso}), 183.8 (*C*(N)), 236.3 (Hf-*C*). Anal. Calcd for $C_{45}H_{85}N_2OSi_6ClHf$: C, 51.35; H, 8.14; N, 2.66. Found: C, 51.61; H, 8.29; N, 2.72.

Synthesis of [$TiCl_2$(nacnac)] (7). A solution of [Li(nacnac)] (**1**, 80.0 mg, 103 μmol) in benzene (1 mL) was added to a slurry of $TiCl_3(thf)_3$ (38.3 mg, 103 μmol) in benzene (1 mL), causing the development of a dark green color. The procedure similar to that in the preparation of **2a** afforded the product as dark green crystals. [$TiCl_2$(nacnac)] (**7**, 82.1 mg, 90%): mp 268−273 °C (dec). EPR (benzene, rt) $g_{\parallel} = 1.931$, $g_{\perp} = 1.949$. A 10 mM C_6D_6 solution (2.00 mL) of **7** (18.4 mg) was measured by ^{1}H NMR spectroscopy at 26.6 °C. The magnetic moment of **7** was determined by Evans' method ($\mu_{eff} = 1.60\ \mu_B$).[24] Anal. Calcd for $C_{41}H_{77}N_2Si_6Cl_2Ti$: C, 55.62; H, 8.77; N, 3.16. Found: C, 55.33; H, 8.95; N, 2.96.

Reduction of [$TiCl_2$(nacnac)] (7). A reductant [Li (0.4 mg, 50 μmol), Na (1.2 mg, 50 μmol), K (2.0 mg, 52 μmol), $LiC_{10}H_8$/THF solution (1.0 M, 52 μL, 52 μmol), or KC_8 (7.0 mg, 52 μmol)] was added to a benzene suspension (1 mL) of [Li(nacnac)] (**1**, 40.0 mg, 51.7 μmol) and $TiCl_3(thf)_3$ (19.2 mg, 51.7 μmol) in the presence of tmeda (100 μL, 100 μmol), causing the development of a dark red color. The procedure similar to that in the preparation of **2a** afforded the product **4a**. In the reactions of **7** with Na, K, $LiC_{10}H_8$, and KC_8, titanium-imido complex [Ti═NTbt{C(Me)CHC(Me)N-

(Mes)}(μ-Cl)$_2$Li(tmeda)] (**4a**) was quantitatively formed, but the reduction of **7** using Li resulted in the formation of a complicated mixture.

Reaction of [Li(nacnac)] (1) with TiCl$_2$(tmeda). A solution of [Li(nacnac)] (**1**, 40.0 mg, 51.7 μmol) in benzene (1 mL) was added to a slurry of TiCl$_2$(tmeda)$_2$ (15.8 mg, 67.2 μmol) in benzene (1 mL), causing the development of a dark red color. The procedure similar to that in the preparation of **4a** afforded a mixture of **4a** and **1** (8:2). The product ratio was determined by ^{1}H NMR spectroscopy.

Reaction of Metal-Imido Complexes 4a−c or 5c with H$_2$O. A solution of **4a** (40.1 mg, 39.7 μmol), **4b** (40.1 mg, 38.0 μmol), **4c** (40.3 mg, 35.1 μmol), or **5c** (40.0 mg, 38.0 μmol) in C$_6$D$_6$ was exposed to the air to result in the quantitative formation of the free ligand nacnacH (**8**), which was confirmed by the ^{1}H NMR spectrum. **8**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 0.13 (s, 18H, Si*Me*$_3$), 0.16 (s, 18H, Si*Me*$_3$), 0.23 (s, 18H, Si*Me*$_3$), 1.44 (s, 1H, Tbt *p*-benzyl), 1.57 (s, 3H, *Me*), 1.81 (s, 3H, *Me*), 2.15 (s, 3H, *Me*), 2.17 (s, 2H, Tbt *o*-benzyl), 2.26 (s, 6H, Mes *o*-*Me*), 4.84 (s, 1H, 3-C*H*), 6.57 (br s, 2H, Tbt *m*-*H*), 6.83 (s, 2H, Mes *m*-*H*), 11.50 (s, 1H, N*H*).[23a]

X-ray Crystallography. Single crystals of **3b**,**c** were grown by the slow evaporation of the saturated toluene/hexane solution at 40 °C. Single crystals of **4a**−**c**, **5c**, and **7** were grown by the slow evaporation of their saturated hexane solutions at 0 °C. The preparation of all samples consisted of coating the crystal with silicon grease, mounting it on a glass fiber, and placing it under a cold stream of N$_2$ on the diffractometer. The intensity data of **3b**,**c**, **4a**−**c**, **5c**, and **7** were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71071 Å) to $2\theta_{\max} = 50°$ at 93 K. The structures of **3b**,**c**, **4a**−**c**, **5c**, and **7** were solved by direct methods (SIR97).[31] All crystallographic data were refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[32] All the non-hydrogen atoms of **3b**,**c**, **4a**−**c**, **5c**, and **7** were placed using AFIX instruction.

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Supporting Information Available: ^{1}H NMR spectra of **2a**, **3b**,**c**, **4a**−**c**, and **5c**, EPR spectrum of **7**, and crystallographic information files for **3b**,**c**, **4a**−**c**, and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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