Neutral and Cationic Group 4 Metal Compounds Containing Octamethyldibenzotetraazaannulene (Me_8taa^{2-}) Ligands. Synthesis and Reactivity of $(Me_8taa)MX_2$ and $(Me_8taa)MX^+$ Complexes (M = Zr, Hf; X = Cl, Hydrocarbyl, NR_2, OR)

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The synthesis and reactivity of out-of-plane $(Me_8taa)MX_2$ and $(Me_8taa)MX^+$ complexes (M= Zr, Hf; X= Cl, hydrocarbyl, NR_2, OR) containing the dianionic tetraaza-macrocycle ligand octamethyldibenzotetraazaannulene (Me_8taa^{2-}) are described. The reaction of $[Li(Et_2O)]_2[Me_8taa]$ (**1**) with $MCl_4(THF)_2$ yields $(Me_8taa)MCl_2$ complexes (**2a**, M = Zr; **2b**, M = Hf). Alkylation of **2a**,**b** with $LiCH_2SiMe_3$ or LiMe in hydrocarbon solvents yields $(Me_8taa)M(CH_2SiMe_3)_2$ (**3a**, M = Zr; **4a**, M = Hf) or $(Me_8taa)MMe_2$ (**3b**, M = Zr; **4b**, M = Hf) complexes. Compound **3b** rearranges by migration of a Me group from Zr to a Me_8taa imine carbon in coordinating solvents. The reaction of $(Me_8taa)H_2$ with the appropriate ZrR_4 compound yields $(Me_8taa)Zr(CH_2Ph)_2$ (**3c**) and $(Me_8taa)Zr(CH_2CMe_3)_2$ (**3d**). The reaction of $(Me_8taa)H_2$ and $Zr(NR_2)_4$ yields $(Me_8taa)Zr(NR_2)_2$ (**6a**, R = Me; **6b**, R = Et). Spectroscopic data for $(Me_8taa)MX_2$ compounds **2**, **3**, **4**, and **6** are consistent with *cis*, C_{2v}-symmetric structures. Dialkyl complexes **3** and **4** and bis(amide) complexes **6** react with chlorinated solvents (1,1,2,2-tetrachloroethane, CH_2Cl_2) to yield **2**. Compound **6a** reacts with $AlMe_3$ to afford the heterobimetallic μ-amido complex $[(Me_8taa)Zr(\mu\text{-}NMe_2)_2AlMe_2][AlMe_4]$ (**8**), which does not undergo further reaction to yield **3b**. The reaction of dialkyl complexes **3** and **4a** with HNR_3^+ reagents yields cationic $[(Me_8taa)MR][B(C_6F_5)_4]$ compounds (**10a**, M = Zr, R = η^2-CH_2Ph; **10b**, M = Zr, R = CH_2SiMe_3; **10c**, M = Zr, R = CH_2CMe_3; **10d**, M = Hf, R = Me). These species form labile adducts with PMe_2Ph and THF. Cation **10a** polymerizes ethylene to a linear polymer with low activity, while **10d** is unreactive with ethylene. **10a** reacts with $HOCMe_2CH_2CH_2CH{=}CH_2$ to yield the mononuclear alkoxide complex $(Me_8taa)Zr(OCMe_2CH_2CH_2CH{=}CH_2)^+$ (**13**), in which the pendant alkene is not coordinated. **10a** also reacts with water or ethanol to yield binuclear complexes $[\{(Me_8taa)Zr(\mu\text{-}OR)\}_2]^{2+}$ (**14a**, R = H; **14b**, R = Et). An X-ray structural analysis of **14a** reveals that one of the $(Me_8taa)Zr$ units has an unusual inverted conformation, and NMR data suggest that **14a**,**b** adopt similar structures in solution. **10d** reacts with 2-butyne to yield the double insertion product $[(Me_8taa)Hf(CMe{=}CMeCMe{=}CMe_2)]^+$ (**15**) and with $MeC{\equiv}CSiMe_3$ to afford $[(Me_8taa)Hf(C(SiMe_3){=}CMe_2)]^+$ (**16**), while **10a** and **10b** are unreactive with these alkynes. **10a** and **10c** react with terminal alkynes by protonolysis to afford binuclear $[\{(Me_8taa)Zr(\mu\text{-}C{\equiv}CR)\}_2]^{2+}$ complexes (**17a**, R = Ph; **17b**, R = Pr). Complex **17a** reacts reversibly with PMe_3 to yield the mononuclear cation $(Me_8taa)Zr(C{\equiv}CPh)(PMe_3)^+$ (**18a**). $(Me_8taa)MR^+$ species are less reactive for alkene and alkyne insertion than are Cp_2MR^+ species.

Introduction

Group 4 metal $(taa)MX_2$ complexes containing dibenzotetraazaannulene ligands (taa^{2-}, **A**, Chart 1) invariably adopt *cis*, trigonal prismatic structures (**B**) in which the metal is displaced out of the N_4-plane. In these species, the taa^{2-} ligand adopts a saddle-shape conformation and the benzo groups project toward the X ligands.[1−4] The small bonding pocket associated with the 14-membered macrocycle precludes *trans*, in-plane $(taa)MX_2$ structures with the large group 4 metal ions, and steric interactions between the diiminato methyl groups and the benzo rings enforce the saddle conformation of the taa^{2-} ligand.[5] The molecular shape of $(taa)MX_2$ compounds is grossly similar to that of Cp_2MX_2 bent metallocenes (**C**).[6] However, important dif-

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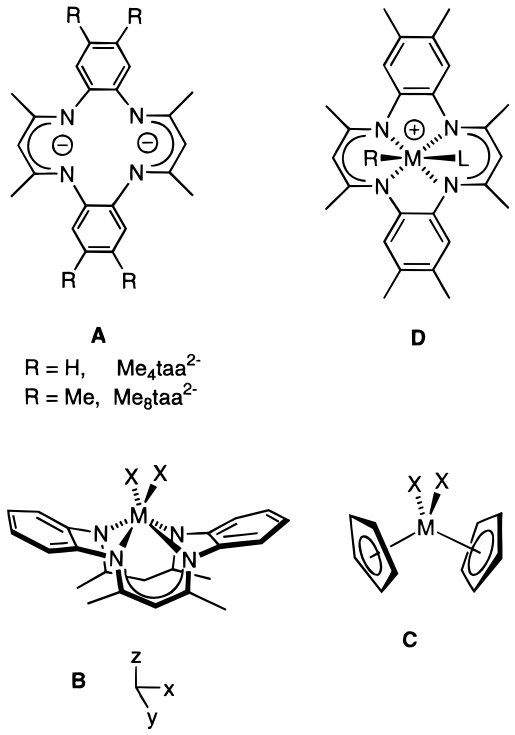
Chart 1



ferences between these classes of compounds exist, which may be summarized as follows. (i) The X−M−X angles in $(taa)MX_2$ compounds (80−87°) are ca. 10° smaller than those in Cp_2MX_2 species;[6a] however, the taa^{2-} conformation can adjust somewhat to the steric/electronic demands of the metal ion. (ii) The d^0 $(taa)M^{2+}$ fragment has four low-lying empty metal *d* orbitals (z^2, *xz*, *yz*, $x^2 - y^2$; see coordinate system in Chart 1) and two low-lying empty orbitals localized on the taa imine carbons, while the Cp_2M^{2+} ion has three empty metal-based frontier orbitals which are localized in the equatorial plane between the Cp ligands.[6b] (iii) The $(taa)M^{2+}$ ion can coordinate four additional ligands, as demonstrated by the formation of $(taa)_2M$ sandwich complexes,[2b] while Cp_2M^{2+} can accommodate only three additional ligands. (iv) On the basis of computed metal charges and electrophilicity indices, the metal center in $(taa)M^{2+}$ is less electrophilic than that in Cp_2M^{2+};[2e] however, the N_4-ligation should make the $(taa)M^{2+}$ ion a harder Lewis acid than Cp_2M^{2+}.

The strong tendency for $(taa)MX_2$ complexes to adopt *cis* structures implies that five-coordinate $(taa)MR^+$ alkyl complexes should form *cis* adducts (**D**) with Lewis bases and organic substrates (L) and raises the possibility that such cations might display insertion and σ-bond metathesis reactivity similar to that observed for Cp_2MR^+ metallocene analogs.[7] As part of a program aimed at the development of non-metallocene electrophilic metal alkyl compounds, we initiated studies of the chemistry of $(taa)M(R)^+$ cations to determine how the structural and electronic differences between the $(taa)M^{2+}$ and Cp_2M^{2+} cores influence the comparative reactivity of the corresponding cationic alkyls.[8,9] In this paper, we describe the synthesis and reactivity of a series of neutral $(Me_8taa)MX_2$ and cationic $(Me_8taa)MX^+$ and $(Me_8taa)MX(L)^+$ complexes (X = chloride, hydrocarbyl, amide, alkoxide; L = neutral Lewis base) containing the octamethyltetraazaannulene ligand Me_8taa^{2-}. The parent macrocycle $(Me_8taa)H_2$ is easily prepared by Ni-templated condensation of 2,4-pentanedione and 4,5-dimethyl-1,2-phenylenediamine, and the enhanced solubility imparted by the aryl methyl substituents facilitates the study of cationic complexes.[10−12]

Results and Discussion

Synthesis of $(Me_8taa)MR_2$ Complexes by Anion Metathesis. As illustrated in Scheme 1, double deprotonation of $(Me_8taa)H_2$ with 2 equiv of MeLi in ether yields the dilithium salt $[Li(Et_2O)]_2[Me_8taa]$ (**1**), which

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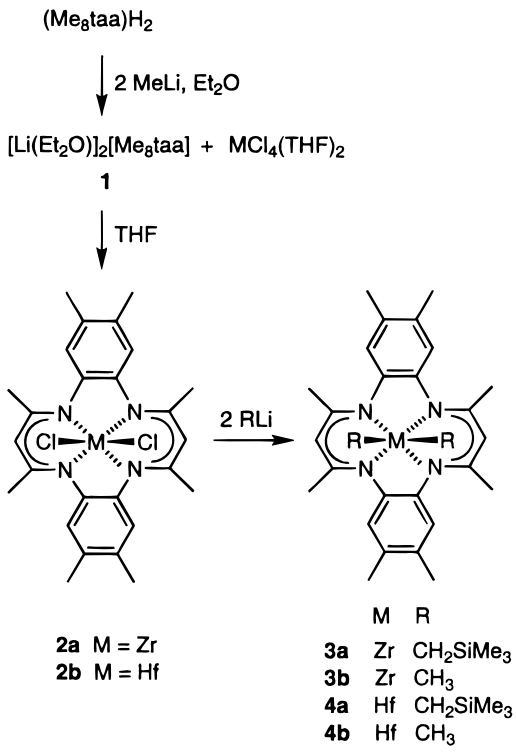
Scheme 1

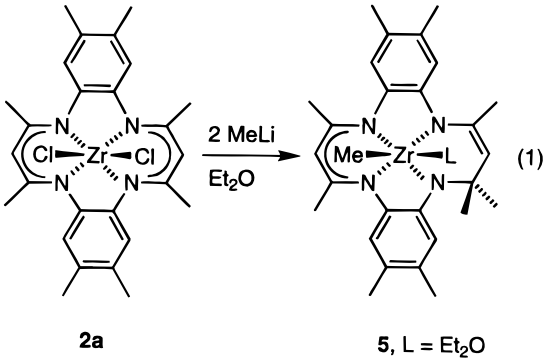


can be isolated as a purple solid. The reaction of **1** with $MCl_4(THF)_2$ (M = Zr, Hf) in THF at 23 °C yields the dichloride complexes $(Me_8taa)MCl_2$ (**2a**, M = Zr; **2b**, M = Hf). These complexes can be isolated as yellow solids and are soluble in chlorinated solvents, but only sparingly soluble in benzene or toluene. The ^1H and ^{13}C NMR spectra of **2a**,**b** are consistent with *cis* C_{2v}-symmetric structures analogous to those observed for $(Me_4taa)MX_2$ compounds (**B**).[2a,e]

The reaction of **2a** with 2 equiv of $LiCH_2SiMe_3$ in pentane/toluene at 23 °C affords $(Me_8taa)Zr(CH_2SiMe_3)_2$ (**3a**), which is isolated in good yield as a toluene solvate (Scheme 1). The reaction of **2a** with solid MeLi in toluene at low temperature affords $(Me_8taa)ZrMe_2$ (**3b**), which is isolated in low (15%) yield. Attempts to improve the yield of **3b** or isolate other reaction products by varying the reaction conditions were unsuccessful. Attempts to prepare **3b** using other methylating agents were also unsuccessful.[13] The poor yield of **3b** most likely results from facile migration of the methyl group to an electrophilic Me_8taa imine carbon. This process is promoted by Lewis bases, and thus, the synthesis of **3b** is successful only in noncoordinating media. For example, the reaction of **2a** with MeLi in Et_2O at low temperature yields the ligand-alkylation product $(Me_9taa)ZrMe(OEt_2)$ (**5**, eq 1). Isolated **3b** reacts with THF to yield a similar product. Metal-to-ligand alkyl migrations in $(Me_4taa)ZrR_2$ compounds have been studied in detail by Floriani,[2a,e] and similar reactions have been noted for $(Me_4taen)ZrR_2$ compounds.[12]

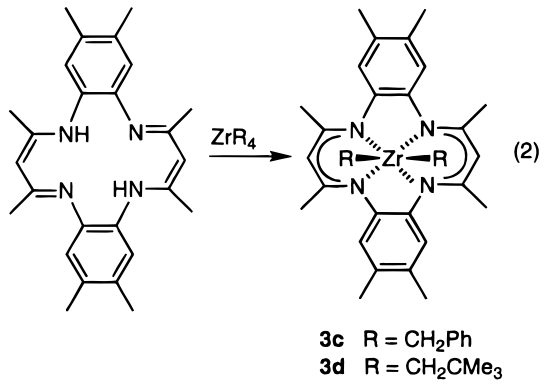
The reaction of **2b** with $LiCH_2SiMe_3$ or MeLi in benzene or toluene (23 °C) affords $(Me_8taa)HfR_2$ complexes **4a** (R = CH_2SiMe_3) and **4b** (R = CH_3) in 60–

(13) $(Me_8taa)ZrCl_2$ forms an adduct with $AlMe_3$, reacts with $MgMe_2$ to yield uncharacterized products, and does not react with $SnMe_4$ or $HgMe_2$.



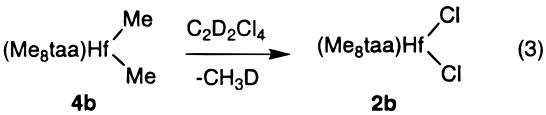
80% isolated yield (Scheme 1). Metal-to-ligand methyl migration is not observed for **4b** at ambient temperature.

Synthesis of $(Me_8taa)MR_2$ Complexes by Alkane Elimination. The reaction of a slurry of $(Me_8taa)H_2$ and $Zr(CH_2Ph)_4$ in pentane at 23 °C affords dibenzyl complex **3c**, which is insoluble in pentane and can be isolated in 95% yield by simple filtration (eq 2). The



reaction of $(Me_8taa)H_2$ and $Zr(CH_2CMe_3)_4$ requires more vigorous conditions (toluene, 50 °C, 5 days) due to the increased steric requirements of the neopentyl ligand but affords bis(neopentyl) complex **3d** in 43% isolated yield. Complex **3d** can also be prepared by alkylation of **2a** with $LiCH_2CMe_3$, but in lower yield (21%).

Chemical Properties of $(Me_8taa)MR_2$ Compounds. The (trimethylsilyl)methyl and neopentyl complexes **3a**, **3d**, and **4a** are soluble in benzene and toluene, but the methyl and benzyl complexes **3b**, **3c**, and **4b** are only sparingly soluble in these solvents. All of these complexes are soluble in chlorinated solvents, in which they slowly decompose to the parent dichlorides **2a** and **2b**. For example, **4b** reacts with 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) within 12 h at 23 °C to yield **2b** and methane-d_1 as the only NMR-detectable products (eq 3). Compound **3a** reacts with $C_2D_2Cl_4$ more slowly, but



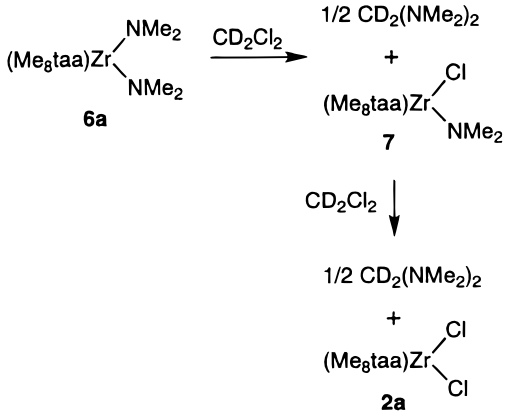
after 8 days at 23 °C it is converted to a 2:1 mixture of **2a** and $(Me_8taa)Zr(CH_2SiMe_3)Cl$; $SiMe_4$-d_1 is also detected.

Spectroscopic Properties of $(Me_8taa)MR_2$ Compounds. The ^1H and ^{13}C NMR spectra of **3a**–**d** and **4a**,**b** are consistent with *cis* C_{2v}-symmetric structures

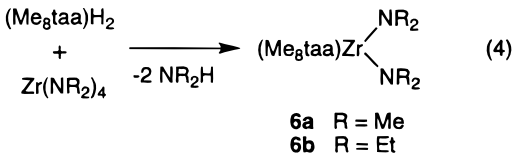
analogous to those observed for $(Me_4taa)Zr(CH_2Ph)_2$.[2a] In each case, one benzo-Me, one benzo-H, one diiminato-Me, and one diiminato-CH resonance are observed for the Me_8taa^{2-} ligand, and a single set of hydrocarbyl resonances is observed. The MCH_2R J_{CH} values are quite low, ranging from 100 Hz for $(Me_8taa)Hf(CH_2SiMe_3)_2$ (**4a**) to 119 Hz for $(Me_8taa)Zr(CH_2Ph)_2$ (**3c**), which is characteristic of hydrocarbyl groups bound to electropositive metal centers.[14] The Zr−CH_3 J_{CH} value for **3b** (111 Hz) is smaller than that for Cp_2ZrMe_2 (118 Hz), which implies that the $(Me_8taa)Zr$ fragment is effectively more electropositive than the Cp_2Zr fragment, or in other words, the Zr−C bonding in the former compound is more ionic than that in the latter.[15,16] This is consistent with the rapid solvolysis noted above for the $(Me_8taa)MR_2$ compounds in chlorinated solvents. Note that there is no evidence for agostic interactions in Cp_2ZrMe_2 from X-ray crystallographic studies or NMR studies of the partially deuterated derivative $Cp_2Zr(CH_2D)_2$,[17] and X-ray structural and NMR data for $(Me_4taa)Zr(CH_2Ph)_2$ and $(Me_4taen)Zr(CH_2Ph)_2$ reveal normal undistorted benzyl ligands,[2a,12a] which suggests that agostic interactions are unlikely to be present in $(Me_8taa)ZrMe_2$. Therefore, the difference in the J_{CH} values of Cp_2ZrMe_2 and $(Me_8taa)ZrMe_2$ is probably not influenced by agostic interactions.[18] The ZrCH_2Ph J_{CH} value for **3c** (119 Hz) is consistent with normal η^1-benzyl bonding.[19]

Synthesis and Properties of $(Me_8taa)Zr(NR_2)_2$ Complexes. Group 4 metal amide complexes are readily prepared by amine-elimination reactions of $M(NR_2)_4$ compounds and sufficiently acidic ligand reagents and are useful intermediates in the synthesis of other derivatives.[20] For example, the reaction of $Zr(NMe_2)_4$ and 1,2-bis(indenyl)ethane ((EBI)H_2) or Me_2(indenyl)$_2$Si ((SBI)H_2) yields the metallocene complexes *rac*-(EBI)$Zr(NMe_2)_2$ and *rac*-(SBI)$Zr(NMe_2)_2$, which are converted to the corresponding dimethyl complexes and $\{AlMe_2(\mu\text{-}NMe_2)\}_2$ by reaction with 4 equiv of $AlMe_3$.[21] We investigated the synthesis of $(Me_8taa)Zr(NR_2)_2$ complexes and their utility as possible precursors to **3b**, which, as noted above, is difficult to prepare by salt elimination.

Scheme 2



The reaction of $(Me_8taa)H_2$ and $Zr(NMe_2)_4$ in toluene (1 h, 23 °C) affords $(Me_8taa)Zr(NMe_2)_2$ (**6a**), which is isolated as a red powder in 90% yield by crystallization from toluene/pentane at −40 °C (eq 4). Bis(diethylamido) analog **6b** is prepared in a similar fashion by the reaction of $(Me_8taa)H_2$ and $Zr(NEt_2)_4$, but in this case more vigorous reaction conditions are required (toluene, 48 h, 60 °C) due to the increased steric crowding in the starting metal amide compound. NMR data for **6a**,**b** are consistent with *cis* C_{2v}-symmetric structures.



Complexes **6a**,**b** are soluble in benzene but insoluble in aliphatic solvents, and react with CH_2Cl_2 ultimately yielding **2a**. The reaction of **6a** with CD_2Cl_2 was monitored by ^{1}H NMR spectroscopy (Scheme 2). Complex **6a** is cleanly (>90%) converted to $(Me_8taa)Zr(Cl)(NMe_2)$ (**7**) and 0.5 equiv of $CD_2(NMe_2)_2$ within 5 h at 23 °C in CD_2Cl_2 solution. After an additional 14 h, **7** is completely transformed into **2a**, and a second 0.5 equiv of $CD_2(NMe_2)_2$ is formed. In a parallel experiment, **6a** was reacted with CH_2Cl_2 under the same conditions. The volatiles were removed by vacuum distillation (and trapped) to afford **2a** in 93% isolated yield. ^{1}H and ^{13}C NMR spectra and mass spectral analysis of the volatiles established the presence of $CH_2(NMe_2)_2$ as the sole NMe_2-containing product.

While the mechanistic details of the reaction of **6a** with CH_2Cl_2 are unknown, this reaction clearly involves nucleophilic displacement of chloride from CH_2Cl_2 by the metal amide, which may occur by formation of an intermediate solvent adduct. The expected initial or-

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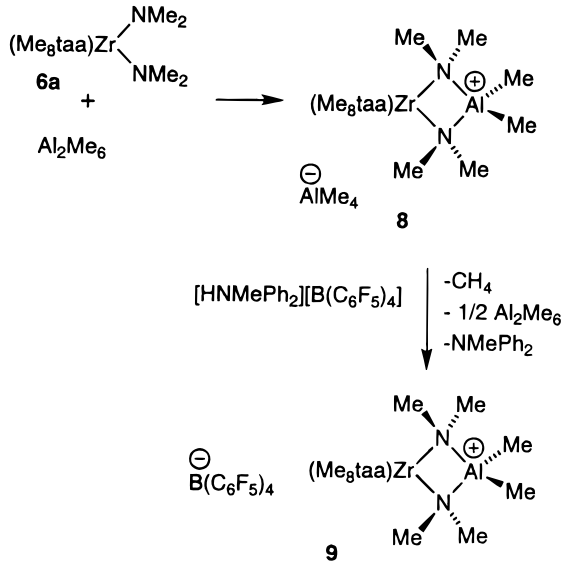
Scheme 3



ganic product, $CH_2(NMe_2)Cl$, must be more reactive than CH_2Cl_2 toward **6a**, since it was not observed as an intermediate. The high reactivity of **6a** with CH_2Cl_2 contrasts with the stability of $Cp_2M(NR_2)_2$ compounds in this solvent and indicates that the amide ligands in $(Me_8taa)Zr(NR_2)_2$ compounds are highly nucleophilic.[22] This is consistent with the suggestion made above that the $(Me_8taa)MX_2$ systems are more ionic than the analogous metallocene complexes.

Reaction of $(Me_8taa)Zr(NMe_2)_2$ and $AlMe_3$. Complex **6a** reacts with 1 equiv of Al_2Me_6 in benzene at 23 °C to yield the unusual hetero-dinuclear μ-amido salt $[(Me_8taa)Zr(\mu\text{-}NMe_2)_2AlMe_2][AlMe_4]$ (**8**), which precipitates as a yellow solid and is isolated by filtration (Scheme 3). Compound **8** does not react further with excess Al_2Me_6, even at 65 °C in benzene, and is soluble and stable in CH_2Cl_2 and Et_2O.

The structural assignment for **8** is based on NMR spectral data, elemental analysis, and reactivity data. The NMR spectra establish the presence of a C_{2v}-symmetric $(Me_8taa)Zr$ unit, two symmetric NMe_2 groups (^{13}C NMR δ 44.1, qq, $J_{CH} = 134$, 6 Hz), and a symmetric $AlMe_2$ unit (^1H NMR δ −1.72 , s, 6H; ^{13}C NMR δ −14.6, br q, $J_{CH} = 111$ Hz) in the cation of **8**. These data do not conclusively allow differentiation between the μ-NMe_2 or μ-Me structures, but the proposed structure is the most reasonable given the general preference for amide groups rather than alkyl groups to occupy bridging positions in $[AlR_2(NR'_2)]_2$ compounds.[23] The NMR spectra of **8** also contain characteristic resonances for the free $AlMe_4^-$ anion; *i.e.*, a 1:1:1:1:1:1 sextet (δ −1.22, $J_{Al-H} = 6.3$ Hz) which integrates for 12 H is observed in the ^1H NMR spectrum, and an 18 line pattern (δ −5.2, $J_{Al-C} = 71.2$ Hz, $J_{C-H} = 106.5$ Hz) is observed in the ^{13}C NMR spectrum.[24] The presence of the $AlMe_4^-$ anion was confirmed by the reaction of **8** with 1 equiv of the noncoordinating acid $[HNMePh_2][B(C_6F_5)_4]$ (CD_2Cl_2, 23 °C, NMR scale), which yields the ion-exchange product **9**, methane, Al_2Me_6, and $NMePh_2$. The ^1H NMR spectrum of **9** is identical to that of **8**, with the exception of the anion resonances.

The formation of **8** from the reaction of $AlMe_3$ and **6a** is reminiscent of reactions of AlX_3 compounds (X = halide, alkyl, etc.) with Lewis bases, which in many cases yield $[L_mAlX_2][AlX_4]$ ($m = 2-5$) salts.[25] Thus, **6a** may be viewed as a bidentate Lewis base in Scheme 3, a description which underscores the high nucleophilicity of the amide groups noted above. The retention of the Zr−N bonds in the formation of **8** contrasts with the complete amide/methyl exchange observed in reactions of $Cp_2Zr(NMe_2)_2$ compounds with $AlMe_3$[21,22] and suggests that the $(Me_8taa)Zr^{2+}$ unit is a harder Lewis acid than the Cp_2Zr^{2+}unit.

Synthesis of Lewis-Base-Free $[(Me_8taa)MR][B(C_6F_5)_4]$ Complexes. Cationic complexes **10** are formed by protonolysis of **3** and **4**, using either $[HNMe_2Ph][B(C_6F_5)_4]$ or $[HNMePh_2][B(C_6F_5)_4]$ (eq 5).[26] These reactions are complete within minutes at 23 °C in chlorinated or aromatic solvents and afford **10a**−**d** in 80−100% NMR yield. Compounds **10a**−**d** are soluble in chlorinated solvents but separate as oils from aromatic solvents. Compounds **10a** and **10c** were isolated from the reaction mixtures as solid benzene or toluene solvates by removal of the volatiles under vacuum, washing with benzene or toluene to remove the amine coproduct, and vacuum drying. Complexes **10b** and **10d** were generated *in situ* and characterized by NMR.

The ^1H and ^{13}C NMR spectra of **10a** (CD_2Cl_2) are unchanged between 23 and −90 °C and establish that this species has effective C_{2v} symmetry. The ^1H and ^{13}C NMR data also establish that the benzyl ligand is coordinated in an η^2-fashion, as observed for other coordinatively unsaturated early metal benzyl species.[9c,d]

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(24) (a) For the ^1H NMR spectrum of $AlMe_4^-$, see: Oliver, J. P.; Wilkie, C. A. *J. Am. Chem. Soc.* **1967**, *89*, 104. (b) A 24-line pattern is expected for the ^{13}C NMR spectrum of $AlMe_4^-$, but several resonances overlap. The observed spectrum closely matched a simulated spectrum generated using the J_{Al-C} and J_{C-H} values quoted in the text, which are in agreement with those reported in Yamamoto, O. *Chem. Lett.* **1975**, 511.

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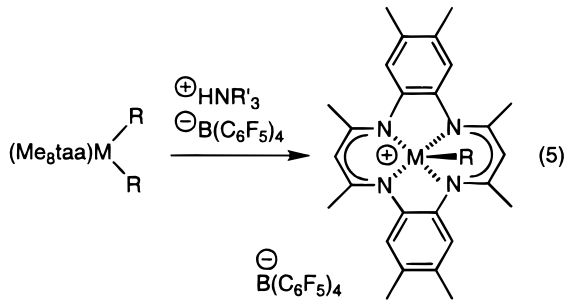
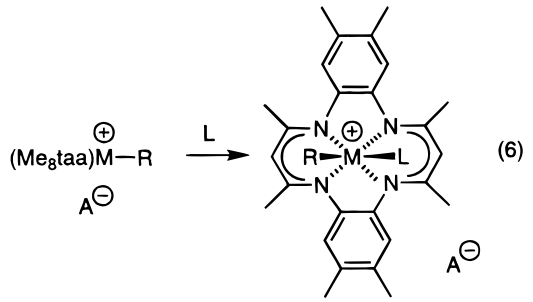


	M	R
10a	Zr	CH_2Ph
10b	Zr	CH_2SiMe_3
10c	Zr	CH_2CMe_3
10d	Hf	CH_3



	M	R	L	A⁻
11a	Zr	CH_2SiMe_3	PMe_2Ph	BPh_4^-
11b	Zr	CH_2SiMe_3	THF	BPh_4^-
11c	Zr	CH_2Ph	THF	$B(C_6F_5)_4^-$
11d	Hf	CH_3	THF	$B(C_6F_5)_4^-$

The *ortho*-Ph ^{1}H NMR resonance appears at high field (δ 5.01), and the ZrCH_2Ph J_{CH} value (136 Hz) is large, characteristic of an acute Zr−C−Ph angle. The benzyl ligand is probably less distorted than that in $Cp_2Zr(\eta^2$-$CH_2Ph)(NCMe)^+$, for which a larger J_{CH} value (145 Hz) was observed.[27] The ^{19}F NMR spectrum of **10a** contains resonances for free $B(C_6F_5)_4^-$ and is unchanged down to −90 °C, and there is no evidence for solvent coordination from low-temperature ^{13}C NMR experiments.[28] Collectively, the NMR data for **10a** are consistent with a base-free η^2-benzyl structure and rapid rotation around the Zr−C bond (even at low temperature).

The NMR spectra of **10b**−**d** imply that these species also have C_{2v} symmetry on the NMR time scale at ambient temperature and, for **10c**, −90 °C. The hydrocarbyl ligands probably project out along the C_2 axis of the (Me8taa)Zr unit (cf. (Me4taa)Ti=O);[3a] however, the NMR data are also consistent with fluxional C_s-symmetric structures in which the hydrocarbyl ligands exchange rapidly between the two lateral coordination sites. The MCH_2R ^{1}H NMR resonances are shifted to higher field and the MCH_2R ^{13}C NMR resonances are shifted to lower field versus the corresponding resonances for the neutral precursors. The ZrCH_2R J_{CH} value for **10b**,**c** (107 Hz) is similar to the values observed for the corresponding neutral dialkyls. While detailed studies of the solution structures of these cations were not pursued, the available data indicate that agostic interactions and solvent or anion interactions are weak at best.

Generation of Lewis-Base-Stabilized (Me8taa)M(R)(L)$^+$ Species. Base-free (Me8taa)M(R)$^+$ cations form isolable Lewis-base adducts (eq 6). The reaction of **3a** with [$HNBu_3$][BPh_4] and 1 equiv of PMe_2Ph ($C_2H_4Cl_2$, 23 °C) affords [(Me8taa)Zr(CH_2SiMe_3)(PMe_2Ph)][BPh_4] (**11a**), which can be isolated as a yellow solid in 77% yield. The ^{1}H and ^{13}C NMR spectra (CD_2Cl_2, 23 °C) of **11a** establish that this species has effective C_{2v} symmetry and do not contain the expected J_{PH} or J_{PC} couplings between the phosphine and alkyl ligands, indicating that PMe_2Ph exchange is rapid on the NMR time scale. The labile THF adduct **11b** is generated by protonolysis of **3a** in the presence of THF.

The reaction of base-free benzyl complex **10a** with THF (CD_2Cl_2, 23 °C), results in clean formation of the THF adduct [(Me8taa)Zr(CH_2Ph)(THF)][$B(C_6F_5)_4$] (**11c**). The low-temperature (−80 °C) ^{1}H NMR spectrum of **11c** contains two benzo-H, two diiminato-CH, four methyl resonances, one set of benzyl resonances, and signals for coordinated THF. This spectrum is consistent with a C_s-symmetric structure in which the THF and benzyl ligands are oriented over the diiminato sectors of the Me8taa ligand, i.e., a trigonal-prismatic structure analogous to those observed for (Me4taa)ZrX_2 compounds.[2a,e] The chemical shift of the benzyl ortho hydrogens (δ 6.07) is similar to that of (Me8taa)Zr(CH_2Ph)$_2$ (δ 6.39) and far downfield from that of (Me8taa)Zr(η^2-CH_2Ph)$^+$ (**10a**, δ 5.01), which indicates that the benzyl ligand is not significantly distorted.[9c,d] Complex **11c** undergoes rapid intermolecular THF exchange at ambient temperature; however, addition of excess THF does not shift the resonances for **11c**, which indicates that a bis(THF) adduct is not formed. The labile THF adduct (Me8taa)Hf(Me)(THF)$^+$ (**11d**) is generated by addition of THF to **10d**.

Reactivity of (Me8taa)M(R)$^+$ Complexes with Ethylene. Isolated salt **10a** is a low-activity ethylene polymerization catalyst. At 50 °C (toluene, 1.3 atm of ethylene), **10a** produces linear polyethylene of moderate molecular weight (M_w = 99 300) and narrow molecular weight distribution (M_w/M_n = 2.6), with a minimum activity of 300 (g of PE)(mol of cat.)$^{-1}$ atm^{-1} h^{-1}; the activity was slightly higher in the presence of Al(^{i}Bu)$_3$ added as a scavenger (550 (g of PE)(mol of cat.)$^{-1}$ atm^{-1} h^{-1}). The activity of **10a** is ca. 100 times lower than that measured for Cp_2ZrMe_2/[$HNMePh_2$][$B(C_6F_5)_4$]/Al(^{i}Bu)$_3$ under the same conditions (≥48 000 (g of PE)(mol of cat.)$^{-1}$ atm^{-1} h^{-1}). The reaction of **10a** with ethylene (1 atm) at 90 °C in chlorobenzene with Al(^{i}Bu)$_3$ added as scavenger produced very low molecular weight linear polyethylene (M_w = 1,410, M_w/M_n = 1.8). NMR analysis of this polymer established that the ratio of saturated end groups/vinyl end groups is 13/1, suggesting that chain transfer to aluminum is the predominant chain-transfer process under these conditions. Benzyl end groups were not detected in any of the polyethylene

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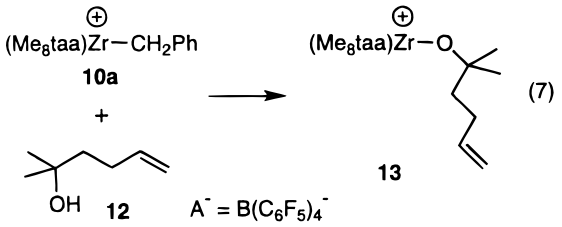
(28) The possibility of solvent coordination was probed by low-temperature ^{13}C NMR studies of a solution of **10a** in a 1:1 mixture of CH_2Cl_2 and CD_2Cl_2. No resonances attributable to coordinated CH_2Cl_2 were observed at −80 °C, which indicates that solvent is either not coordinated, or that exchange of coordinated and free solvent is rapid at this temperature. See: (a) Fernández, J.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (b) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398. (c) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89 and references therein.

samples produced by **10a**. NMR monitoring of ethylene polymerization by **10a** revealed the disappearance of **10a** and formation of polyethylene, but intermediate $(Me_8taa)Zr(R)^+$ species (R = growing chain) were not detected. The cationic hafnium methyl complex **10d** does not polymerize ethylene under conditions similar to those discussed above for **10a**.

Synthesis and Structure of $(Me_8taa)Zr(\eta^1$-OC$Me_2CH_2CH_2CH{=}CH_2)^+$. One possible reason for the low reactivity of $(Me_8taa)M(R)^+$ species with ethylene is that these cations are insufficiently electrophilic to efficiently coordinate and activate olefins. To probe this possibility, we investigated the reaction of **10a** with the alcohol $HOCMe_2CH_2CH_2CH{=}CH_2$ (**12**), which contains a pendant olefin group. We previously showed that $(C_5R_5)_2Zr(\eta^2$-O,C^1-$OCMe_2CH_2CH_2CH{=}CH_2)^+$ complexes ($(C_5R_5)_2$ = Cp$_2$, *rac*-EBI), which contain the alkoxide ligand derived from **12**, coordinate the pendant olefin in preference to CD_2Cl_2, $MeB(C_6F_5)_3^-$, or $B(C_6F_5)_4^-$.[29] Benzyl cation **10a** reacts rapidly with **12** at 23 °C in CH_2Cl_2 or benzene to yield the cationic alkoxide complex $(Me_8taa)Zr(\eta^1$-$OCMe_2CH_2CH_2CH{=}CH_2)^+$ (**13**), which is isolated as a yellow solid (eq 7). The ^{1}H and ^{13}C NMR



data for the olefin group of **13** are unchanged from data for **12**, indicating that the pendant olefin is not coordinated in this species. In contrast, large coordination shifts are observed for the olefinic resonances in $(C_5R_5)_2Zr(\eta^2$-O,C^1-$OCMe_2CH_2CH_2CH{=}CH_2)^+$ species. The ^{1}H and ^{13}C NMR data also establish that **13** has effective C_{2v} symmetry, and the ^{19}F NMR spectrum indicates that the $B(C_6F_5)_4^-$ anion is not coordinated. Additionally, the ^{1}H, ^{13}C, and ^{19}F NMR spectra of **13** are unchanged down to −80 °C, which suggests that neither solvent coordination nor anion coordination is important for this species. Interestingly, the alkoxide methyl resonance appears at high field in the ^{1}H NMR spectrum (δ 0.37), which presumably is due to anisotropic shielding from the Me_8taa^{2-} benzo groups. On the basis of these observations and data for other $(Me_8taa)Zr(OR)^+$ complexes (*vide infra*), we conclude that **13** has a mononuclear, five-coordinate structure and contains a terminal alkoxide ligand.

Synthesis and Structures of $[\{Me_8taa)Zr(\mu$-OR$)\}_2][B(C_6F_5)_4]_2$ (R = H, Et). One possible reason for the lack of olefin coordination in **13** is that this species forms a dimeric μ-alkoxide species. To probe this possibility, we investigated the reactions of **10a** with less hindered hydroxy compounds which are more likely to result in dimeric species. The reaction of **10a** with 1 equiv of water or ethanol in CH_2Cl_2 at 23 °C yields dinuclear

(29) The Zr−olefin bonding in $(C_5R_5)_2Zr(\eta^2$-O,C^1-$OCMe_2CH_2CH_2$-$CH{=}CH_2)^+$ complexes is very unsymmetrical; the Zr−C^1 distance is significantly shorter than the Zr−C2 distance. See: (a) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867. (b) Strömberg, S.; Christopher, J. C.; Lee, C. W.; Swenson, D. C.; Jordan, R. F. Manuscript in preparation.

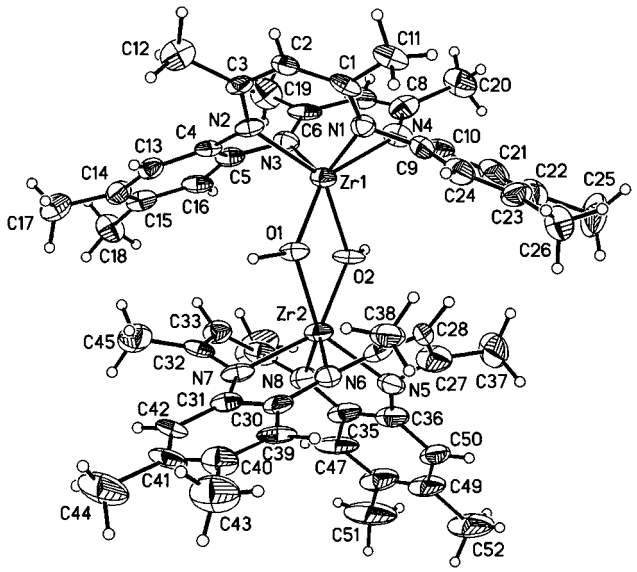
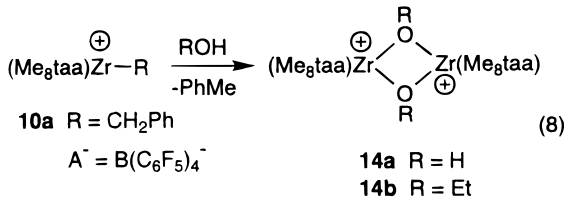


Figure 1. Structure of the $\{(Me_8taa)Zr(\mu$-OH$)\}_2^{2+}$ Cation of **14a**.

hydroxy and ethoxy complexes **14a** and **14b**, which are isolated as yellow solids after crystallization from CH_2Cl_2/pentane (eq 8).



The structure of **14a**·pentane was determined by a single-crystal X-ray diffraction analysis of the pentane solvate (Table 1). Compound **14a**·pentane crystallizes as discrete $\{(Me_8taa)Zr(\mu$-OH$)\}_2^{2+}$ and $B(C_6F_5)_4^-$ ions. The structure of the cation is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The cation structure consists of two $(Me_8taa)Zr$ units linked by two symmetrical hydroxide bridges. One $(Me_8$-taa)Zr unit (Zr1) adopts the normal saddle conformation with trigonal-bipyramidal geometry around Zr (see **B** in Chart 1). The Zr(1)−N bond distances (average = 2.16(3) Å) and the Zr(1)−N_4 plane displacement (1.034(5) Å) are similar to those observed for $(Me_4taa)ZrCl_2$ (average Zr−N = 2.166(5) Å; Zr−N_4 = 1.071(2) Å) and $(Me_4taa)Zr(CH_2Ph)_2$ (average Zr−N = 2.190(8) Å; Zr−N_4 = 1.019(2) Å).[2a,b,e] The angle between the benzo planes (50.8(3)°) and the angle between the diiminato planes (73.5(4)°), which define the shape of the saddle are also quite normal. In contrast, the second (Me_8taa)-Zr unit of **14a** (Zr2) adopts an unusual inverted conformation, in which the benzo groups project away from and the diiminato units project toward the Zr center; i.e., the Zr binds to the backside of the macrocycle. Despite this difference in $(Me_8taa)Zr$ conformation, the Zr(2)−N bond distances (average = 2.141(9) Å) and Zr-(2)−N_4 plane displacement (1.064(5) Å) are very similar to the corresponding values for the normal $(Me_8taa)Zr$ unit. Interestingly, the angle between the benzo planes (74.3(3)°) is larger and the angle between the diiminato planes (60.7(4)°) is smaller in the inverted macrocycle than in the normal macrocycle, which allows proper

Table 1. Crystal Data and Structure Refinement for [{(Me_8taa)Zr(μ-OH)}$_2$][B(C_6F_5)$_4$]$_2$·C_5H_{12} (14a·pentane)

compound	**14a**·pentane
color/shape	yellow/fragment
empirical formula	$C_{105}H_{74}B_2F_{40}N_8O_2Zr_2$
fw	2443.78
temp	173(2) K
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens (8192 reflections in full θ range)	a = 16.6305(2) Å b = 26.3707(5) Å c = 24.1933(5) Å β = 106.799(1)°
volume	10 157.4(3) Å^3
Z	4
density (calcd)	1.598 Mg/m^3
abs coeff	0.334 mm^{-1}
diffractometer/scan	Siemens SMART/CCD area detector
radiation/wavelength	Mo Kα (graphite monochromator)/0.710 73 Å
F(000)	4904
cryst size	0.10 × 0.40 × 0.40 mm
θ range for data collection	1.17−20.84°
index ranges	$-16 \le h \le 15$, $-26 \le k \le 21$, $-24 \le l \le 24$
no. of reflns collected	28 506
no. of indep/obsd reflns	10 516 (R_{int} = 0.0852)/7456 ([$I > 2\sigma(I)$])
abs corr	semiempirical
range of relat. transm. factors	0.9965 and 0.8925
refinement method	full-matrix-block least-squares on F^2
computing	SHELXTL, Ver. 5[a]
data/restraints/params	10 508/0/1440
goodness-of-fit on F^2	1.227
SHELX-93 weight parameters	0.0210, 106.9067
final R indices [$I > 2\sigma(I)$][b]	R1 = 0.1030, wR2 = 0.1799
R indices (all data)	R1 = 0.1486, wR2 = 0.2131
ext coeff	0.00030(5)
largest diff. peak and hole	0.674 and −0.407 e Å^{-3}

[a] *SHELXTL*, PC Version 5; Siemens Analytical X-ray Instruments, Inc.: Madison, WI. [b] R1 = $\Sigma(|F_o| - |F_c|)/\Sigma F_o$; wR2 = $\{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [{(Me_8taa)Zr(μ-OH)}$_2$][B(C_6F_5)$_4$]$_2$ (14a)

Zr(1)−N(3)	2.122(10)	Zr(1)−O(1)	2.141(7)
Zr(1)−N(1)	2.143(10)	Zr(1)−N(2)	2.159(9)
Zr(1)−N(4)	2.198(10)	Zr(1)−O(2)	2.222(7)
Zr(2)−N(5)	2.130(10)	Zr(2)−N(7)	2.136(10)
Zr(2)−N(8)	2.147(10)	Zr(2)−N(6)	2.152(10)
Zr(2)−O(1)	2.196(7)	Zr(2)−O(2)	2.220(8)
N(3)−Zr(1)−O(1)	129.3(3)	N(3)−Zr(1)−N(1)	123.7(3)
O(1)−Zr(1)−N(1)	98.2(3)	N(3)−Zr(1)−N(2)	75.2(3)
O(1)−Zr(1)−N(2)	89.0(3)	N(1)−Zr(1)−N(2)	77.6(4)
N(3)−Zr(1)−N(4)	79.2(4)	O(1)−Zr(1)−N(4)	144.8(3)
N(1)−Zr(1)−N(4)	74.7(3)	N(2)−Zr(1)−N(4)	121.6(3)
N(3)−Zr(1)−O(2)	94.7(3)	O(1)−Zr(1)−O(2)	70.9(3)
N(1)−Zr(1)−O(2)	132.8(3)	N(2)−Zr(1)−O(2)	144.5(3)
N(4)−Zr(1)−O(2)	88.5(3)	N(5)−Zr(2)−N(7)	119.2(4)
N(5)−Zr(2)−N(8)	70.0(4)	N(7)−Zr(2)−N(8)	81.2(4)
N(5)−Zr(2)−N(6)	81.1(4)	N(7)−Zr(2)−N(6)	70.3(4)
N(8)−Zr(2)−N(6)	121.6(4)	N(5)−Zr(2)−O(1)	141.1(4)
N(7)−Zr(2)−O(1)	91.2(3)	N(8)−Zr(2)−O(1)	143.5(4)
N(6)−Zr(2)−O(1)	88.1(3)	N(5)−Zr(2)−O(2)	95.9(3)
N(7)−Zr(2)−O(2)	138.9(3)	N(8)−Zr(2)−O(2)	92.6(3)
N(6)−Zr(2)−O(2)	141.1(3)	O(1)−Zr(2)−O(2)	70.0(3)
Zr(1)−O(1)−Zr(2)	111.5(3)	Zr(2)−O(2)−Zr(1)	107.6(3)

orientation of the N σ-donor orbitals for bonding with Zr2. Thus, the bonding capability of the macrocycle ligand is similar in both conformations. The hydroxide bridges are symmetrical, and the Zr_2O_2 unit is planar. The two O−Zr−O angles are quite acute (Zr1, 70.9(3)°; Zr2, 70.0(3)°) due to the constraints of the four-membered ring structure. For comparison, the X−Zr−X angles in (Me_4taa)ZrX_2 complexes are 10−15° larger (*e.g.*, X = CH_2Ph, 80.1(4)°; X = Cl, 85.6(1)°).[2a,b,e]

The unusual dinuclear structure of **14a**, with one normal and one inverted (Me_8taa)Zr unit, allows both (Me_8taa)Zr units to achieve the favored trigonal-prismatic structure and minimizes interligand steric interactions. Steric crowding between the hydroxide groups and the C30−C42 and C35−C50 benzo groups would be increased if the inverted (Me_8taa)Zr unit (Zr2) adopted a normal conformation. A similar inverted (Me_4taa)M conformation was found earlier for the main-group compound (Me_4taa)Ge=Te.[30] In contrast, singly-bridged dinuclear compounds such as {(Me_4taa)Ti}$_2$(μ-O) and {(Me_4taa)Fe}$_2$(μ-O),[3a,31] nonbridged metal−metal bonded compounds such as {(Me_4taa)Mo}$_2$ and {(Me_4taa)Cr}$_2$,[32−34] and the bis(ligand) sandwich compound (Me_4taa)$_2$Zr[2b] all exhibit normal (Me_4taa)M conformations.

The NMR data for **14a** provide strong evidence that the dimeric hydroxide-bridged structure is maintained in solution. The ^{1}H NMR spectrum contains two benzo-H, two diiminato-CH, and four methyl resonances, consistent with the presence of two inequivalent C_{2v}-symmetric (Me_8taa)Zr units. Significantly, one of the diiminato-CH resonances (δ 5.60) appears in the normal range observed for the (Me_8taa)Zr(X)$^+$ species discussed above (δ 5.6−5.7), while the other is shifted 1.5 ppm upfield to δ 4.14. The high-field diiminato CH resonance is assigned to the methine hydrogens of the inverted Me_8taa ligand (Zr2), which are anisotropically

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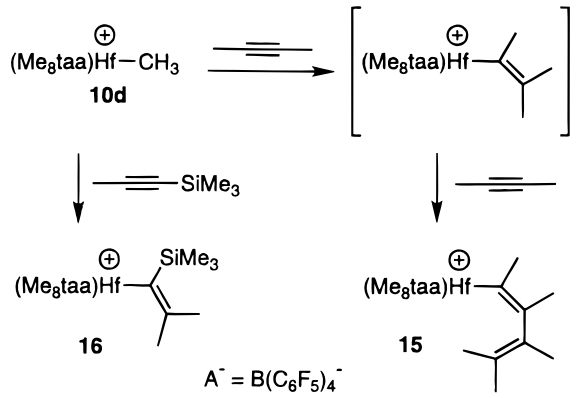
Scheme 4



shielded due to their proximity to the benzo groups of the normal Me_8taa ligand in the dinuclear structure. The ^{13}C NMR spectrum of **14a** also contains two sets of Me_8taa resonances, including one normal methine resonance (δ 107.3; cf. δ 106−108 for other $(Me_8taa)Zr(X)^+$ species) and one high-field methine resonance (δ 90.2). The NMR data for the ethoxide complex **14b** are similar to those for **14a**; in particular high-field methine resonances for the inverted Me_8taa ligand are observed in the ^1H and ^{13}C NMR spectra. The spectra for **14b** also contain a single set of ethyl resonances, which is consistent with the equivalence of the two ethoxide ligands in the proposed dinuclear structure.

The NMR spectra of **13** contain resonances for a single C_{2v}-symmetric $(Me_8taa)Zr$ unit and lack the high-field methine resonances which are characteristic of the dinuclear structures of **14a**,**b**, thus implying that **13** does not have a similar dinuclear structure. Presumably, the steric bulk of the alkoxide ligand in **13** disfavors alkoxide bridging. Inspection of the structure of **14a** suggests that steric crowding would disfavor a dinuclear structure with two normal $(Me_8taa)Zr$ units for **13**.

Comparative Olefin Binding Affinity of $(Me_8taa)MR^+$ and $(C_5R_5)_2MR^+$. The results described in the last two sections show that $(Me_8taa)Zr(OR)^+$ species have a lower affinity for olefin binding than do $(C_5R_5)_2Zr(OR)^+$ species, at least in the intramolecular case studied, and suggest that the corresponding cationic alkyl species, $(Me_8taa)MR^+$ and $(C_5R_5)_2MR^+$, would show a similar difference in olefin binding affinity. However, it should be noted that extrapolation from alkoxide compounds to alkyl compounds may be complicated by the differences in the frontier-orbital properties of the $(Me_8taa)M^{2+}$ and Cp_2M^{2+} fragments noted in the introduction. Oxygen−M π-donation to both the d_{xz} and the d_{yz} orbitals is possible in a five-coordinate $(Me_8taa)M(OR)^+$ cation, while only a single O−M π bond can form in a $Cp_2M(OR)^+$ cation. The selective enhancement of O−M π-donation in $(Me_8taa)M(OR)^+$ may disfavor olefin coordination. Studies of this issue are continuing.

Reactions of $(Me_8taa)M(R)^+$ Complexes with Internal Alkynes. Cationic Hf methyl complex **10d** reacts with excess 2-butyne (CH_2Cl_2, 23 °C, 12 h) to yield the double-insertion product $[(Me_8taa)Hf(CMe{=}CMe\text{-}CMe{=}CMe_2)][B(C_6F_5)_4]$ (**15**, Scheme 4), which is isolated as a golden brown solid (78%). The ^{13}C NMR spectrum of **15** contains four alkenyl carbon resonances (δ 214.0 (Hf−*C*), 147.1, 141.6, and 139.1) for the butadienyl ligand. NMR data indicate that **15** has effective C_{2v} symmetry at ambient temperature, so the pendant olefin coordinates only weakly to Hf if at all. Cationic $(C_5R_5)_2Zr(CH_3)(NMe_2Ph)^+$ species ($C_5R_5 = C_5H_5$, $C_5H_4SiMe_3$, $C_5H_4CMe_3$, *rac*-EBI) undergo similar double insertion of internal alkynes, but in these systems a subsequent 1,5-H shift (intramolecular C−H activation) results in the formation of $(C_5R_5)_2ZrCH_2CR{=}CR\text{-}CR{=}CRH)^+$ pentadienyl species.[35]

Cation **10d** inserts 1-(trimethylsilyl)-1-propyne (<1 h, 23 °C) more rapidly to yield $[(Me_8taa)Hf(C(SiMe_3){=}CMe_2)][B(C_6F_5)_4]$ (**16**), which was isolated (80%) as an orange solid (Scheme 4). The alkenyl regiochemistry is assigned on the basis of hydrolysis experiments, which gave 2-methyl-1-(trimethylsilyl)-propene. The ^1H NMR spectrum of **16** at −20 °C contains two benzo-H, two diiminato-CH, and four methyl resonances for the Me_8taa ligand, which establishes that this species adopts a C_s-symmetric structure. However, at 23 °C, the two benzo-H resonances are collapsed to one resonance and the remaining Me_8taa resonances are broadened, consistent with the existence of a dynamic process which renders the sides of the Me_8taa ligand equivalent. Similarly, the low-temperature (−20 °C) ^{13}C NMR spectrum of **16** is consistent with a C_s-symmetric structure, but the Me_8taa resonances are broadened at room temperature. These observations suggest that a weak Hf- - -Me_3Si agostic interaction which hinders rotation around the Hf−C bond is present in **16**; however, this issue was not probed further. Complex **16** does not insert a second equivalent of $(Me_3Si)C{\equiv}CMe$. Similar 2,1-insertions of silylalkynes are observed for Cp_2MR^+ species (M = Ti, Zr).[36,37] Agostic coordination of a Si−Me group was observed in $[Cp_2Zr(C(SiMe_3){=}CMe_2)][B(C_6F_5)_4]$,[36a] and the acute Ti−C−Si angle (88.9°) in $[Cp_2Ti(C(SiMe_3){=}CMePh)][AlCl_4]$ suggests that a similar interaction may be present in this species as well.[37]

In contrast, neither **10a** nor **10b** react with these alkynes under similar conditions. Steric factors are expected to strongly influence the reactivity of $(Me_8taa)MR^+$ species with alkynes. Additionally, the Zr−Ph interaction in **10a** may inhibit alkyne coordination as well as migratory insertion,[38] and electronic interactions may stabilize **10b** toward migratory insertion (σ hyperconjugation; Si α to nucleophilic Zr−*C* and β to Zr).[39] The base-stabilized $(Me_8taa)Zr(R)(L)^+$ species **11** are also unreactive with these alkynes.

Reactions of $(Me_8taa)M(R)^+$ Species with Terminal Alkynes. Complexes **10a** and **10c** react with phenylacetylene and 1-pentyne (CH_2Cl_2, 23 °C, <30 min, excess alkyne) to yield the dinuclear μ-alkynyl complexes **17** and toluene or neopentane, respectively

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Scheme 5

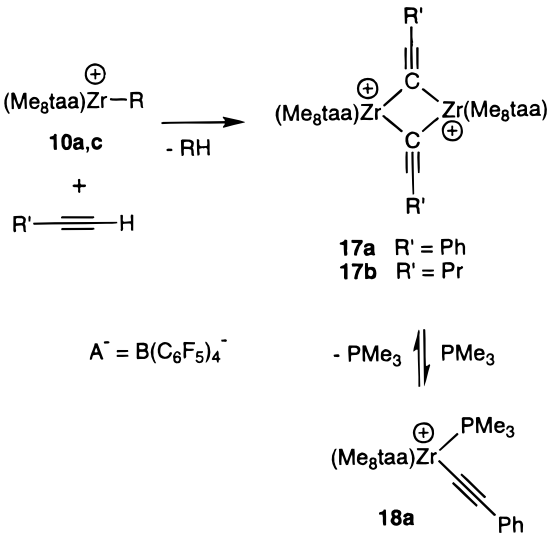
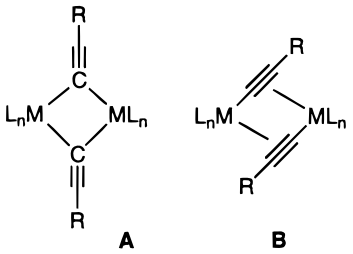


Chart 2



(Scheme 5). Complexes **17a** and **17b** were isolated as yellow solids in 76% and 92% yield, respectively. These reactions proceed by protonolysis of the Zr−C bond by the acidic alkyne hydrogen and subsequent dimerization to stabilize the unsaturated metal center.

The ^{1}H and ^{13}C NMR spectra of **17a**,**b** (23 °C) are similar to those observed for μ-OR complexes **14** and establish that these cations adopt similar dinuclear structures. The ^{1}H NMR spectrum of **17a** contains one set of phenyl resonances for the two equivalent −CCPh ligands and two benzo-H, two diiminato-CH, and four methyl resonances for the two inequivalent C_{2v}-symmetric (Me$_8$taa)Zr units. One Me$_8$taa−methine resonance (δ 4.09) is shifted upfield from the normal range observed for mononuclear (Me$_8$taa)Zr(X)$^+$ species (δ 5.6−5.7) and is assigned to the methine hydrogen of the inverted (Me$_8$taa)Zr unit of the dinuclear cation. The other methine signal (δ 5.25) appears close to the normal range and is assigned to the methine hydrogen of the normal (Me$_8$taa)Zr unit. The ca. 0.4 ppm upfield shifting of this resonance is due to anisotropic shielding by the alkynyl group. The ^{1}H NMR data for **17b** are similar to those for **17a**, and the ^{13}C NMR spectra of both cations contain one normal and one high-field methine resonance.

Bridging alkynyl complexes, L$_n$M(μ-CCR)ML$_n$, exhibit a variety of bonding modes (Chart 2), ranging from μ-η^1:η^1 (or μ-σ:σ; **A**) structures to highly unsymmetric μ-η^1:η^2 (or μ-σ:π; **B**) structures in which the alkynyl ligand is σ-bonded to one metal and forms a π-complex with the second.[40] Binuclear L$_n$M(μ-CCR)ML$_n$ complexes in which the metals have d^0 electron configurations normally exhibit μ-η^1:η^1 alkynyl bridges, as in {Cp$_2$Er(μ-C≡C^{t}Bu)}$_2$ and {Cp$_2$Zr}$_2$(μ-C≡CMe)(μ-MeC=CMe)$^+$.[41,42] This alkynyl bonding mode is characterized by IR ν_{CC} values (2000−2050 cm^{-1}) and ^{13}C NMR chemical shifts (δ 100−130) which are similar to those for terminal alkynyl compounds and reflect the retention of the C≡C triple bond. In contrast, d^n,d^n systems ($n \geq 1$) typically adopt μ-η^1:η^2 structures, as in {(C$_5$H$_4$Me)$_2$Zr(μ-CCPh)}$_2$ and Cp$_2$Zr(μ-CCSiMe$_3$)$_2$Ni(PPh$_3$).[43] In these cases, reduced ν_{CC} values (1750−1900 cm^{-1}), reflecting the reduced CC bond order, and low-field ^{13}C chemical shifts for the M−*C*CR carbon (δ > 200) are observed. The spectroscopic data for **17a**,**b** are consistent with the expected μ-η^1:η^1-bonding mode. The ^{13}C NMR resonances for the alkynyl carbons appear at δ 121.0 and 119.0 for **17a** and at δ 125.5 and 115.0 for **17b**. The IR spectrum of **17a** displays a ν_{CC} band at 2034 cm^{-1}.

Complexes **17a**,**b** do not react further with excess alkyne and do not catalyze alkyne oligomerization under mild conditions. Heating a CD$_2$ClCD$_2$Cl solution of **17a** (65 °C, 24 h) with excess phenylacetylene resulted in a complex mixture of products with no apparent reaction of the phenylacetylene, and **17b** does not react with excess 1-pentyne at 65 °C (24 h). This lack of reactivity contrasts with the catalytic oligomerization of terminal alkynes observed for Cp*$_2$ZrR$^+$ and many other d^0 metal alkynyl complexes, which proceeds by sequential insertion/σ-bond metathesis steps.[44−47]

One likely reason for the lack of reactivity of **17a**,**b** with alkynes is that the dinuclear structures are too robust to allow alkyne coordination. To probe this issue, the reaction of **17a** with the stronger Lewis base PMe$_3$ was investigated by NMR spectroscopy. Complex **17a** reacts cleanly with excess PMe$_3$ (3 equiv, 23 °C, CH$_2$Cl$_2$, 1 h) to afford the PMe$_3$ adduct (Me$_8$taa)Zr(C≡CPh)(PMe$_3$)$^+$ (**18a**, >90% NMR, Scheme 5). The low-

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temperature (<−80 °C) ^{1}H NMR spectrum of **18a** shows that this species has a C_s-symmetric structure and contains one coordinated PMe_3 ligand. Complex **18a** undergoes rapid (NMR time scale) exchange with free PMe_3 above ca. −80 °C. Attempts to isolate complex **18a** by crystallization from CH_2Cl_2/hydrocarbon solvents followed by drying under vacuum yielded **17a**. Thus, **17a** only reversibly coordinates PMe_3. Therefore, it is reasonable that cleavage of the dinuclear structure of **17a** by coordination of alkynes, which are expected to be much weaker Lewis bases for the d^0 cation, is disfavored.

Conclusions

Salt-elimination, alkane-elimination, and amine-elimination reactions provide access to a wide variety of $(Me_8taa)MX_2$ chloride, alkyl, and amide complexes. NMR data for these complexes and the cationic species derived from them are in accord with *cis*, out-of-plane structures similar to those established previously for the $(Me_4taa)MX_2$ analogues.[1−4] $(Me_8taa)ZrMe_2$ undergoes metal-to-ligand methyl migration in the presence of Lewis bases, but the bulkier Zr analogues and the Hf alkyls are resistant to this process.

$(Me_8taa)MR_2$ alkyls react under mild conditions with $CHCl_2CHCl_2$ and CH_2Cl_2 to yield RH and $(Me_8taa)MCl_2$. $(Me_8taa)Zr(NMe_2)_2$ reacts with CH_2Cl_2 via nucleophilic chloride displacement to yield $CH_2(NMe_2)_2$ and $(Me_8taa)ZrCl_2$ and with $AlMe_3$ by nucleophilic substitution to yield $[(Me_8taa)Zr(\mu\text{-}NMe_2)_2AlMe_2][AlMe_4]$. These reactions indicate that the alkyl and amide ligands in these systems are very nucleophilic and imply that the M−R and M−NR_2 bonds are highly polarized. This property appears to be enhanced relative to Cp_2MR_2 systems, which may reflect the harder character of the Me_8taa^{2-} versus the Cp_2^{2-} ancillary ligands.

Cationic $(Me_8taa)MR^+$ species are formed by protonolysis of $(Me_8taa)MR_2$ complexes by noncoordinating ammonium reagents and are thermally stable as the $B(C_6F_5)_4^-$ salts. NMR data are in accord with five-coordinate square-pyramidal structures. While $(Me_8taa)Zr(\eta^2\text{-}CH_2Ph)^+$ exhibits a weak Zr- - -Ph interaction, agostic M- - -H−C interactions are weak at best in $(Me_8taa)M(CH_2R)^+$ alkyls, and no evidence for strong solvent coordination or site-specific ion-pairing is observed for these species in CH_2Cl_2 solution. While $(Me_8taa)Zr(\eta^2\text{-}CH_2Ph)^+$ polymerizes ethylene and $(Me_8taa)HfMe^+$ inserts internal alkynes, in general $(Me_8taa)MR^+$ species are significantly less reactive toward alkene and alkyne insertion than are Cp_2MR^+ cations.[7,44] As $(Me_8taa)MR^+$ cations are not sterically crowded and the M−R bonds are highly polarized, the lack of insertion reactivity probably reflects a low tendency for these cations to form π complexes with (and hence activate) alkenes and alkynes. The observation that $(Me_8taa)Zr(OCMe_2CH_2CH_2CH{=}CH_2)^+$ does not coordinate the pendant alkene while $(C_5R_5)_2Zr(\eta^2\text{-}O,C^1\text{-}OCMe_2CH_2CH_2CH{=}CH_2)^+$ species adopt chelated structures supports the supposition that $(Me_8taa)MR^+$ cations have a lower affinity for unsaturated hydrocarbons than do Cp_2MR^+ cations. However, as noted above, differences in the frontier-orbital properties of the $(Me_8taa)M^{2+}$ and Cp_2M^{2+} fragments may complicate this comparison. The reluctance of $(Me_8taa)MR^+$ to coordinate unsaturated hydrocarbons may reflect both the lower Lewis acidity and the harder character of these metal cations as compared to Cp_2MR^+. More highly unsaturated three- and four-coordinate cationic group 4 metal alkyls containing nitrogen- and oxygen-based ligands, such as $\{(2,6\text{-}^iPr_2\text{-}C_6H_3)N(CH_2)_3N(2,6\text{-}^iPr_2\text{-}C_6H_3)\}TiR^+$ and $[\{(^tBu\text{-}d_6)N\text{-}o\text{-}C_6H_4\}_2O]ZrR^+$, are more reactive with olefins than are $(Me_8taa)MR^+$ species.[48] Benzamidinate-stabilized yttrium alkyls $\{PhC(NSiMe_3)_2\}_2YR$ are less reactive for alkene and alkyne insertion than are $(C_5R_5)_2YR$ metallocenes, which was ascribed to the higher ionic character of the former systems which disfavors π-complex formation with unsaturated hydrocarbons.[49]

The formation of dinuclear mono- and dications, *e.g.*, $(Me_8taa)Zr(\mu\text{-}NMe_2)_2AlMe_2^+$, $\{(Me_8taa)Zr(\mu\text{-}OR)\}_2^{2+}$, and $\{(Me_8taa)Zr(\mu\text{-}CCR)\}_2^{2+}$, is a general feature of group 4 Me_8taa^{2-} chemistry. The sterically open out-of-plane structures, the conformational flexibility of the $(Me_8taa)Zr$ fragment, the delocalization of the positive charge onto the Me_8taa^{2-} ligands, and the nucleophilic character of the X^- ligands in $(Me_8taa)MX_2$ and $(Me_8taa)MX^+$ species favor the formation of bridged dinuclear complexes.

Experimental Section

General Procedures. All manipulations were performed on a high-vacuum line or in a glovebox under a purified N_2 atmosphere. Solvents were distilled from Na/benzophenone, except for the chlorinated solvents which were distilled from activated molecular sieves (3 Å) or P_2O_5. $(Me_8taa)H_2$,[10] $Zr(CH_2CMe_3)_4$,[50] $Zr(CH_2Ph)_4$,[51] $MCl_4(THF)_2$ (M = Zr, Hf),[52] and $Zr(NR_2)_4$ (R = Me, Et)[21,22] were prepared by literature procedures. Solid MeLi was obtained by evaporating a commercial Et_2O solution of MeLi under vacuum and drying the resulting white solid under high vacuum for 0.5 h at 110 °C. $Li[B(C_6F_5)_4]$ was prepared from BCl_3 and 4 equiv of $Li[C_6F_5]$ (generated *in situ*) in Et_2O at −78 °C.[53] $[HNMe_2Ph][B(C_6F_5)_4]$ and $[HNMePh_2][B(C_6F_5)_4]$ were prepared by metathesis of $Li[B(C_6F_5)_4]$ with $[NMe_2PhH]Cl$ and $[NMePh_2H]Cl$, respectively, in degassed H_2O.

NMR spectra were recorded on a Bruker AMX 360 or AC 300 (^{19}F) spectrometer in sealed or Teflon-valved tubes at ambient-probe temperature unless otherwise indicated. ^{1}H and ^{13}C NMR chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. Coupling constants are reported in hertz. The spectra of the cationic complexes contained resonances for free $B(C_6F_5)_4^-$ or BPh_4^- anions.[54,55] The spectra of the cationic complexes generated *in situ* also contained resonances for free

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(54) $B(C_6F_5)_4^-$: ^{13}C NMR ($C_2D_2Cl_4$) δ 146.6 (dm, $^1J_{CF}$ = 245), 136.6 (dm, $^1J_{CF}$ = 245), 134.6 (dm, $^1J_{CF}$ = 244), 122.6 (br m, BC).

(55) BPh_4^-: ^{1}H NMR (CD_2Cl_2) δ 7.37 (m, 8 H), 7.04 (t, J = 7, 8 H), 6.89 (t, J = 7, 4 H); $\{^1H\}^{13}$C NMR (CD_2Cl_2) δ 164.3 (q, J_{BC} = 49, *ipso*), 136.2, 126.0, 122.2.

NMe_2Ph or NBu_3.[56,57] Elemental analyses were performed by E & R Microanalytical Laboratory, Inc.

In some cases, the neutral dialkyl and dichloro complexes were initially isolated containing traces of very fine, insoluble material (*e.g.*, LiCl in **2a**,**b**, **3a**,**b**, and **4a,b**) which could not be removed by filtration or which would clog fritted glass filters. These impurities could best be removed by centrifugation. Once this was done, further purification was usually unnecessary; however, most of the neutral complexes could be recrystallized if desired.

[Li(Et2O)]2[Me8taa] (1). A solution of MeLi in Et_2O (1.4 M, 18 mL, 25 mmol) was added over 15 min to a rapidly stirred slurry of $(Me_8taa)H_2$ (5.0 g, 12 mmol) in Et_2O (200 mL). The evolution of CH_4 diminished with addition of the last aliquot. The deep purple mixture was stirred for 3 h and concentrated under vacuum to 40 mL. Pentane (10 mL) was added, and the mixture was filtered to give a purple solid, which was broken up with a spatula and dried under high vacuum for 3 h (6.2 g, 92%). ^{1}H NMR (THF-d_8): δ 6.54 (s, 4 H), 4.42 (s, 2 H, NC═C*H*—CN), 3.39 (q, J = 7, 8 H, Et_2O), 2.11 (s, 12 H), 2.08 (s, 12 H), 1.12 (t, J = 7, 12 H, Et_2O). {^{1}H}^{13}C NMR (THF-d_8): δ 160.3 (N═*C*), 145.0 (benzo-*C*N), 127.7 (benzo-*C*Me), 123.1 (benzo-*C*H), 98.8 (NC═*C*H—CN), 66.3 (Et_2O), 22.8, 19.7, 15.7 (Et_2O). Anal. Calcd for $C_{34}H_{50}Li_2N_4O_2$: C, 72.83; H, 8.99; N, 9.99. Found: C, 72.81; H, 8.78; N, 10.24.

(Me8taa)ZrCl2 (2a). A slurry of **1** (2.8 g, 5.0 mmol) and $ZrCl_4(THF)_2$ (1.9 g, 5.0 mmol) in THF (40 mL) was stirred for 19 h, concentrated under vacuum to 25 mL, and filtered. The yellow solid was washed with THF (3 × 5 mL) and dried under high vacuum for 10 min at 70 °C to remove residual solvent. Methylene chloride (25 mL) was added, and the mixture was centrifuged. The resulting homogeneous yellow supernatant was decanted and cooled to −35 °C overnight. Yellow crystals were isolated by filtration and dried under high vacuum for 6 h at 80 °C. The mother liquor was concentrated under vacuum to 10 mL. Pentane was layered onto the slurry, and the mixture was placed in a −35 °C freezer overnight. A second crop of a yellow solid was isolated by filtration and dried as described above (2.20 g total, 78%). ^{1}H NMR (CD_2Cl_2): δ 7.40 (s, 4 H), 5.65 (s, 2 H, NC═C*H*—CN), 2.49 (s, 12 H), 2.42 (s, 12 H). {^{1}H}^{13}C NMR (CD_2Cl_2): δ 158.4 (N═*C*), 139.2 (benzo-*C*N), 127.0 (benzo-*C*Me), 126.2 (benzo-*C*H), 105.3 (NC═*C*H—CN), 23.0, 20.4. In a similar experiment, the yellow solid isolated from the original THF slurry was dried under high vacuum at 23 °C to give a THF solvate of **2a** (0.75 equiv by ^{1}H NMR), which was submitted for analysis. Anal. Calcd for $C_{29}H_{36}Cl_2N_4O_{0.75}Zr$: C, 56.66; H, 5.90; N, 9.11; Cl, 11.53. Found: C, 56.82; H, 5.91; N, 8.85; Cl, 10.66.

(Me8taa)HfCl2 (2b). A slurry of **1** (1.52 g, 2.71 mmol) and $HfCl_4(THF)_2$ (1.26 g, 2.71 mmol) in THF (50 mL) was stirred for 2 h at 23 °C, refluxed for 15 min, concentrated under vacuum to 10 mL, and filtered to yield a yellow solid. This solid was washed with THF (2 × 2 mL) and dried under high vacuum overnight at 90 °C. The solid was taken up in CH_2Cl_2 (15 mL), and the slurry was centrifuged. The supernatant was evaporated under vacuum, and the resulting yellow solid was washed with hexane and dried under high vacuum overnight at 70 °C. The original THF mother liquor and the THF washes were combined and evaporated under vacuum. The residue was slurried in benzene (25 mL) and centrifuged. The supernatant was decanted off, and this process was repeated 7 times. The combined supernatants were evaporated under vacuum, and the residue was recrystallized from CH_2Cl_2/hexane to give a second crop of yellow solid, which was dried as above (1.25 g total, 71%). ^{1}H NMR (CD_2Cl_2): δ 7.24 (s, 4 H), 5.57 (s, 2 H, NC═C*H*—CN), 2.47 (s, 12 H), 2.39 (s, 12 H). Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 159.6 (m, *C*═N), 138.4 (benzo-*C*N), 127.0 (d, J = 6, benzo-*C*Me), 126.5 (dm, J = 160, benzo-*C*H), 105.3 (dm, J = 160, NC═*C*H—CN), 23.3 (qd, J = 128, 4), 20.4 (qd, J = 127, 5). Anal. Calcd for $C_{26}H_{30}Cl_2HfN_4$: C, 48.20; H, 4.67; N, 8.65; Cl, 10.94. Found: C, 48.08; H, 4.61; N, 8.49; Cl, 10.70.

(Me8taa)Zr(CH2SiMe3)2 (3a). A pentane solution of $LiCH_2SiMe_3$ (1.0 M, 6.6 mL, 6.6 mmol) was added to a rapidly stirred slurry of **2a** (1.5 g, 2.7 mmol) in toluene (100 mL). Additional toluene (25 mL) was added to facilitate stirring. The mixture was stirred for 1 h and filtered. The filter cake was washed with toluene (5 × 15 mL), and the combined filtrates were evaporated under vacuum. The residue was slurried in toluene (25 mL) and centrifuged. The homogeneous orange supernatant was decanted off, and this process was repeated 4 times. The supernatants were combined and concentrated under vacuum to 20 mL, giving a slurry. Pentane (20 mL) was added, and the slurry was filtered to give an orange solid, which was washed with pentane (2 × 5 mL) and dried under high vacuum overnight. The mother liquor was evaporated under vacuum, and the residue was recrystallized from toluene/pentane to give a second crop of orange solid, which was dried as above (1.29 g total, 72%). ^{1}H NMR analysis indicated the presence of *ca*. 0.5 equiv of toluene. ^{1}H NMR (C_6D_6): δ 7.22 (s, 4 H), 5.04 (s, 2 H, NC═C*H*—CN), 2.07 (s, 24 H, the two sets of 4 Me's are coincident), 0.08 (s, 18 H), 0.06 (s, 4 H, Zr*C*H_2). Gated-{^{1}H}−^{13}C NMR (C_6D_6): δ 158.6 (m, N═*C*), 135.2 (m, benzo-*C*N), 131.6 (d, J = 7, benzo-*C*Me), 126.4 (dm, J = 158, benzo-*C*H), 103.6 (dm, J = 157, NC═*C*H—CN), 43.8 (t, J = 104, Zr*C*H_2), 23.1 (qd, J = 128, 4, Me), 20.0 (qd, J = 126, 5, Me), 3.9 (q, J = 117, $SiMe_3$). A solvent-free sample of **3a** was prepared by dissolving the above toluene solvate of **3a** (220 mg) in CH_2Cl_2 (5 mL), evaporating the solvent under vacuum, and drying the residue under high vacuum for 1 day. This sample was spectroscopically pure, but duplicate analysis gave low C values, possibly due to SiC formation during analysis. Anal. Calcd for $C_{34}H_{52}N_4Si_2Zr$: C, 61.48; H, 7.89; N, 8.44. Found: C, 59.81 and 59.68; H, 7.56; N, 8.52.

(Me8taa)ZrMe2 (3b). A slurry of **2a** (1.1 g, 2.0 mmol) and solid MeLi (86 mg, 3.9 mmol) in toluene (40 mL) was stirred at −78 °C for 1 day and at 0 °C for 2 days and filtered. The solvent was evaporated under vacuum, and the orange solid residue was dried under high vacuum for 3 h (150 mg, 15%). ^{1}H NMR (C_6D_6): δ 7.12 (s, 4 H), 5.10 (s, 2 H, NC═C*H*—CN), 2.11 (s, 12 H), 1.98 (s, 12 H), 0.14 (s, 6 H, ZrCH_3). Gated-{^{1}H}−^{13}C NMR (C_6D_6): δ 158.4 (*C*═N), 135.2 (benzo-*C*N), 131.3 (benzo-*C*Me), 126.0 (dd, J = 153, 5, benzo-*C*H), 103.2 (d, J = 157, NC═*C*H—CN), 30.4 (q, J = 111, Zr*C*H_3), 22.9 (qd, J = 118, 4), 19.9 (qd, J = 122, 5). Anal. Calcd for $C_{28}H_{36}N_4Zr$: C, 64.69; H, 6.98; N, 10.78; Zr, 17.55. Found: C, 64.36; H, 6.85; N, 10.50; Zr, 17.98. Attempts to scale up this reaction, recrystallize the product, or isolate additional product were unsuccessful.

(Me8taa)Zr(CH2Ph)2 (3c). A slurry of $(Me_8taa)H_2$ (1.8 g, 4.4 mmol) and $Zr(CH_2Ph)_4$ (2.0 g, 4.4 mmol) in pentane (75 mL) was stirred for 14 h at 23 °C. An orange solid was isolated by filtration, washed with pentane (2 × 10 mL), and dried under high vacuum for 1 h (2.8 g, 95%). This complex is only sparingly soluble in C_6H_6. ^{1}H NMR (CD_2Cl_2): δ 7.12 (s, 4 H), 6.91 (t, J = 8, 4 H, *meta*-benzyl), 6.57 (t, J = 7, 2 H, *para*-benzyl), 6.39 (d, J = 8, 4 H, *ortho*-benzyl), 5.08 (s, 2 H, NC═C*H*—CN), 2.39 (s, 12 H), 2.23 (s, 12 H), 1.20 (s, 4 H, Zr*C*H_2). {^{1}H}^{13}C NMR (CD_2Cl_2): δ 158.6 (*C*═N), 153.9 (*ipso*-Ph), 136.6 (benzo-*C*N), 128.8, 127.1, 126.4, 124.6, 117.7, 103.6 (NC═*C*H—CN), 59.6 (Zr*C*H_2, J_{CH} = 119 from gated-{^{1}H} spectrum), 23.1, 20.3. Anal. Calcd for $C_{40}H_{44}N_4Zr$: C, 71.49; H, 6.60; N, 8.34; Zr, 13.57. Found: C, 71.73; H, 6.71; N, 8.21; Zr, 13.62.

(56) NMe_2Ph: ^{1}H NMR ($C_2D_2Cl_4$) 7.22 (t, 2 H, Ph), 6.70 (m, 3 H, Ph), 2.91 (s, 6 H, Me). In certain cases, minor shifts (<0.05 ppm) are observed due to trace excesses of $[HNMe_2Ph][B(C_6F_5)_4]$, differences in ionic strength, or other factors. Gated-{^{1}H}−^{13}C NMR ($C_2D_2Cl_4$): 149.0 (m, *ipso*), 127.6 (dd, J = 158, 8, *m*), 115.2 (d, J = 160, *p*), 111.2 (d, J = 156, *o*), 39.1 (q, J = 137, N*Me*$_2$Ph).

(57) NBu_3: ^{1}H NMR (CD_2Cl_2) δ 2.32 (m, 6 H), 1.30 (m, 12 H), 0.91 (t, J = 7, 9 H).

The ^{1}H NMR spectrum of **3c** in THF-d_8 exhibits a complicated pattern of resonances, most likely as a result of THF-induced migration of a benzyl group to a Me_8taa imine carbon.

(Me_8taa)Zr(CH_2CMe_3)$_2$ (3d). A slurry of (Me_8taa)H_2 (1.14 g, 2.84 mmol), and Zr(CH_2CMe_3)$_4$ (1.07g, 2.84 mmol) was stirred in toluene (40 mL) at 50 °C for 5 days. The red solution was cooled to 23 °C, which resulted in crystallization of a red solid, which was collected by filtration, washed with pentane (2 × 10 mL), and dried under high vacuum overnight. The mother liquor was concentrated to dryness, slurried in hexane, and filtered to obtain a second crop of orange solid. This solid was recrystallized from a mixture of toluene (10 mL) and pentane (5 mL) at −40 °C overnight, isolated by filtration, washed with pentane (2 × 5 mL), and dried under high vacuum overnight. Total yield: 0.774 g (43.1%). ^{1}H NMR (C_6D_6) δ: 7.25 (s, 4 H), 5.04 (s, 2 H, NC═C*H*—CN), 2.07 (s, 12 H), 2.00 (s, 12 H), 1.19 (s, 18 H, CH_2CMe_3), 0.84 (s, 4 H, CH_2-CMe_3). Gated-{^{1}H}−^{13}C NMR (C_6D_6) δ: 158.6 (M, *C*═N), 135.4 (m, benzo-*C*N), 133.1 (d, J = 4, benzo-CMe), 125.4 (dm, J = 151, benzo-*C*H), 103.0 (dm, J = 157, NC═*C*H—CN), 77.2 (tm, J = 108, ZrCH_2), 35.5 (m, CH_2CMe_3 and qm, J = 122, C(CH_3)$_3$), 22.8 (qd, J = 127, 4, Me), 19.8 (qd, J = 125, 5, Me). Anal. Calcd for $C_{36}H_{52}N_4Zr$: C, 68.41; H, 8.29; N, 8.86. Found: C, 68.28; H, 8.11; N, 8.64.

(Me_8taa)Hf(CH_2SiMe_3)$_2$ (4a). A slurry of **2b** (320 mg, 0.49 mmol) and solid LiCH_2SiMe_3 (obtained from evaporation of a pentane solution of LiCH_2SiMe_3, 92 mg, 0.98 mmol) in C_6H_6 (50 mL) was stirred for 1 h. The mixture was filtered, and the solvent was evaporated under vacuum to give an orange-red solid (220 mg, 60%). ^{1}H NMR (C_6D_6): δ 7.18 (s, 4 H), 5.00 (s, 2 H, NC═C*H*—CN), 2.07 (s, 24 H), 0.09 (s, 18 H), −0.36 (s, 4 H, HfCH_2). Gated-{^{1}H}−^{13}C NMR (C_6D_6) δ: 159.5 (m, *C*═N), 134.8 (m, benzo-*C*N), 131.8 (d, J = 7, benzo-CMe), 126.3 (dd, J = 157, 5, benzo-CH), 103.9 (dm, J = 157, CN—*C*H═CN), 47.9 (t, J = 100, *C*H_2), 23.4 (t, J = 100, *C*H_3), 19.9 (qd, J = 126, 5, *C*H_3), 4.1 (qm, J = 116, SiMe).

(Me_8taa)HfMe_2 (4b). A solution of MeLi in Et_2O (1.4 M, 1.2 mL, 1.7 mmol) was added over 15 min to a slurry of **2b** (543 mg, 0.838 mmol) in toluene (60 mL). The mixture was stirred for 1.5 h and centrifuged. The supernatant was decanted off and evaporated under vacuum. The resulting orange solid was slurried in toluene (25 mL) and centrifuged. The supernatant was decanted off, and this process was repeated 7 times. The combined supernatants were evaporated under vacuum, and the resulting orange solid was washed with pentane (3 × 5 mL) and dried under high vacuum for 1 h (385 mg, 76%). This complex is only sparingly soluble in C_6D_6 and slowly decomposes to **2b** in chlorinated solvents. ^{1}H NMR (C_6D_6): δ 7.08 (s, 4 H), 5.06 (s, 2 H, NC═C*H*—CN), 2.10 (s, 12 H), 1.97 (s, 12 H), −0.03 (br s, 6 H, HfCH_3). ^{1}H NMR ($C_2D_2Cl_4$): δ 7.11 (s, 4 H), 5.24 (s, 2 H, NC═C*H*—CN), 2.38 (s, 12 H), 2.29 (s, 12 H), −1.24 (s, 6 H, HfCH_3). {^{1}H}^{13}C NMR ($C_2D_2Cl_4$): δ 157.5 (*C*═N), 133.6 (benzo-*C*N), 128.2 (benzo-*C*Me), 123.8 (benzo-*C*H), 101.1 (NC═*C*H—CN), 33.3 (Hf*C*H_3), 22.0, 18.8. This NMR sample reacted overnight to give **2b** as the sole product. Anal. Calcd for $C_{28}H_{36}HfN_4$: C, 55.39; H, 5.98; N, 9.23. Found: C, 55.61; H, 6.02; N, 8.99.

(Me_9taa)Zr(Me)(Et_2O) (5). A solution of MeLi (1.4 M, 0.70 mL, 0.98 mmol) in Et_2O was added to a slurry of **2a** (0.28 g, 0.50 mmol) in Et_2O at −100 °C. The slurry was warmed to 23 °C and stirred overnight. The solvent was evaporated under vacuum, and the residue was extracted with pentane (3 × 25 mL). The combined extracts were evaporated under vacuum, giving an orange solid (0.26 g, 87%). ^{1}H NMR (C_6D_6): δ 6.62 (s, 2 H, benzo-C*H*), 6.61 (s, 2 H, benzo-C*H*), 4.72 (s, 2 H, NC═C*H*—CN), 2.92 (m, 4 H, Et_2O), 2.24 (br s, 6 H, 2 Me), 2.22 (s, 3 H, Me), 1.90 (s, 6 H, 2 Me), 1.85 (s, 6 H, 2 Me), 1.53 (s, 6 H, 2 Me), 0.14 (s, 3 H, ZrMe); the remaining Et_2O resonance is obscured by resonances for excess pentane. The reaction of isolated **3b** with THF yields a product with a similar NMR spectrum.

(Me_8taa)Zr(NMe_2)$_2$ (6a). A slurry of Zr(NMe_2)$_4$ (1.00 g, 3.74 mmol) and (Me_8taa)H_2 (1.50 g, 3.74 mmol) in toluene (50 mL) was stirred at 23 °C for 1 h. The volatiles were removed under vacuum, yielding a red solid which was dried under high vacuum overnight. This solid was dissolved in toluene (10 mL), and pentane (10 mL) was layered on carefully and allowed to slowly diffuse at −40 °C for 24 h, which resulted in the formation of a red precipitate. This product was collected by filtration, washed with pentane (5 × 10 mL), and dried under high vacuum for 12 h (1.94 g, 90%). ^{1}H NMR (C_6D_6): δ 7.18 (s, 4 H), 5.07 (s, 2 H, NC═C*H*—CN), 2.86 (s, 12 H) NMe, 2.11 (s, 12 H, Me), 2.05 (s, 12 H, Me). Gated-{^{1}H}−^{13}C NMR (C_6D_6): δ 158.6 (m, *C*═N), 135.4 (m, benzo-*C*N), 133.1 (m, benzo-*C*Me), 125.4 (dm, J = 157, benzo-*C*H), 103.0 (dm, J = 151, NC═*C*H—CN), 45.5 (qq, J = 129, 6, N*C*H_3), 22.8 (qd, J = 127, 5, *C*H_3), 19.8 (qd, J = 125, 5, *C*H_3). Anal. Calcd for $C_{30}H_{42}N_6Zr$: C, 62.35; H, 7.32; N, 14.54. Found: C, 62.15; H, 7.10; N, 14.34.

(Me_8taa)Zr(NEt_2)$_2$ (6b). A solution of Zr(NEt_2)$_4$ (1.00 g, 2.63 mmol) in toluene (10 mL) was transferred by cannula to a solution of (Me_8taa)H_2 (1.05 g, 2.63 mmol) in toluene (25 mL). The mixture was stirred at 60 °C for 48 h under N_2. The solvent was evaporated under vacuum to yield a red solid, which was slurried in toluene (10 mL) and filtered. The filtrate was cooled to −40 °C for 12 h to afford red crystals, which were collected by filtration and washed with pentane (5 mL). The combined mother liquor and washes were cooled to −40 °C to give a second crop of red crystals. Both solids were dried under vacuum overnight. Total yield: 0.973 g (58.3%). ^{1}H NMR (C_6D_6): δ 7.11 (s, 4 H), 5.02 (s, 2H, NC═C*H*—CN), 3.22 (q, J = 6.9, 8 H, N*C*H_2CH$_3$), 2.10 (s, 12 H, Me), 2.09 (s, 12 H, Me), 0.87 (t, J = 6.9, 12 H, NCH$_2$C*H*$_3$). Gated-{^{1}H}−^{13}C NMR (C_6D_6): δ 158.6 (m, *C*═N), 136.4 (m, benzo-*C*N), 133.2 (m, benzo-*C*Me), 125.8 (dm, J = 166, benzo-*C*H), 102.7 (dm, J = 156, NC═*C*H—CN), 45.2 (tm, J = 130, N*C*H_2CH$_3$), 23.0 (qd, J = 126, 4, Me), 19.9 (qd, J = 125, 5, Me), 16.0 (qm, J = 123, NCH$_2$*C*H$_3$). Anal. Calcd for $C_{34}H_{50}N_6$-Zr: C, 64.41; H, 7.95; N, 13.25. Found C, 64.64; H, 7.92; N, 13.01.

Reaction of (Me_8taa)Zr(NMe_2)$_2$ with CH_2Cl_2. A solution of **6a** (0.020 g, 0.035 mmol) in CD_2Cl_2 (0.5 mL) was maintained at 23 °C and monitored by ^{1}H NMR. (Me_8taa)Zr(Cl)(NMe_2) (**7**) was cleanly formed (>90%) in *ca.* 5 h. ^{1}H NMR (CD_2Cl_2): δ 7.25 (s, 4 H, benzo-C-*H*), 5.43 (s, 2 H, NC═C*H*—CN), 2.38 (s, 12 H, Me), 2.35 (s, 12 H, Me), 2.20 (s, 6 H, NMe). A singlet at δ 2.18 (6 H) for the organic byproduct $CD_2(NMe_2)_2$ was also observed. ^{1}H NMR (CD_2Cl_2, −90 °C): δ 7.23 (s, 4H, benzo-C*H*), 5.47 (br s, $\nu_{1/2}$ = 30 Hz, 2H, NC═C*H*—CN), 2.36 (s, 12 H, Me), 2.29 (s, 12 H, Me), 2.08 (s, 12 H, NMe and $CD_2(NMe_2)_2$). {^{1}H}^{13}C NMR (CD_2Cl_2): δ 158.6 (*C*═N), 136.5 (benzo-CN), 129.9 (benzo-CMe), 126.0 (benzo-CH), 103.8 (NC═*C*H—CN), 45.6 (NMe), 20.4 (Me). A signal at δ 43.3 for $CD_2(NMe_2)_2$ was also observed. After 14 h, **7** was completely transformed into **2a**. At this point, the signal at δ 2.18 integrated for 12 H.

In a parallel reaction, a solution of (Me_8taa)Zr(NMe_2)$_2$ (**6a**, 0.276 g, 0.477 mmol) in CH_2Cl_2 (10 mL) was stirred at 23 °C for 24 h. The volatiles were vacuum-transferred to another flask, and the remaining solid was dried overnight (**2a**, 0.250 g, 93.5% yield). The NMR spectra of the volatiles contained resonances for $CH_2(NMe_2)_2$, which were identical to those of an authentic sample (Aldrich). ^{1}H NMR (CD_2Cl_2): δ 2.17 (s, 12 H), 2.64 (s, 2 H). Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 83.8 (tm, J = 137), 43.3 (qm, J = 132). Resonances for CH_2Cl_2 were also observed.

[(Me_8taa)Zr(μ-NMe_2)$_2$AlMe_2][AlMe_4] (8). A solution of Al_2Me_6 (66.5 μL, 0.346 mmol) in benzene (1 mL) was added to a rapidly stirred solution of **6a** (0.200 g, 0.346 mmol) in benzene (2 mL). The color changed instantaneously from red to yellow, and a yellow precipitate formed. Pentane (3 mL) was added to the mixture, and the solid was isolated by filtration (122 mg, 48.8%). ^{1}H NMR (CD_2Cl_2): δ 7.46 (s, 4 H,

benzo-C*H*), 5.78 (s, 2 H, CN═C*H*—CN), 2.57 (s, 12 H, *Me*), 2.48 (s, 12 H, *Me*), 1.83 (s, 12 H, *Me*), −1.22 (1:1:1:1:1:1 sextet, J = 6.3 Hz, 12 H, $AlMe_4^-$), −1.72 (s, 6 H, Al*Me*$_2$). Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 161.0 (m, *C*═N), 140.4 (m, benzo-CN), 127.9 (d, J = 7, benzo-CMe), 127.6 (dq, J = 159, 5, benzo-CH), 107.1 (d of septet, J = 161, 4, NC═*C*H—CN), 44.1 (qq, J = 134, 6, NMe), 24.0 (qd, J = 128, 4, Me), 20.5 (qd, J = 127, 5, Me), −5.2 (m, J_{C-Al} = 72, J_{C-H} = 106, $AlMe_4^-$), −14.6 (q, J = 111, $AlMe_2$). Anal. Calcd for $C_{36}H_{60}Al_2N_6Zr$: C, 59.88; H, 8.38; N, 11.64. Found C, 59.78; H, 8.11; N, 11.44.

[(Me8taa)Zr(μ-NMe2)2AlMe2][B(C6F5)4] (9). This complex was generated in NMR-scale reactions. An NMR tube was charged with **8** (0.015 g, 0.021 mmol) and $[HNMePh_2][B(C_6F_5)_4]$ (0.018 g, 0.021 mmol). CD_2Cl_2 (0.5 mL) was added by vacuum transfer at −78 °C. Gas evolution was observed. The tube was warmed to 23 °C, and a ^{1}H NMR spectrum was obtained. ^{1}H NMR (23 °C): Signals for **9** δ 7.44 (s, 4 H), 5.74 (s, 2 H), 2.54 (s, 12 H), 2.47 (s, 12 H), 1.82 (s, 12 H), −1.72 (s, 6 H); Signals for $NMePh_2$ δ 7.29 (t, J = 7.9, 4 H), 7.08 (d, J = 7.9, 4 H), 7.02 (t, J = 7.9, 2 H), 3.30 (s, 3 H); Signal for Al_2Me_6 δ −0.48 (s). The solvent was removed under vacuum to afford a foamy solid, which was washed with benzene and pentane and dried under vacuum overnight. Fresh CD_2Cl_2 (0.5 mL) was added to the tube at −78 °C. The ^{1}H NMR spectrum of this sample contained only resonances for **9**.

[(Me8taa)Zr(η2-CH2Ph)][B(C6F5)4] (10a). A flask was charged with **3c** (0.100 g, 0.149 mmol) and $[HNMePh_2][B(C_6F_5)_4]$ (0.131 g, 0.151 mmol), and CH_2Cl_2 (5 mL) was added by vacuum transfer at −78 °C. The mixture was allowed to warm to 23 °C and was stirred for 10 min. The volatiles were evaporated under vacuum, yielding a yellow-orange solid. Toluene (5 mL) was added, resulting in an orange-red oil. The mixture was stirred for 1 min, and the supernatant was decanted off. This procedure was repeated 3 times and then once with pentane. The oil was dried under vacuum overnight, yielding $[(Me_8taa)ZrCH_2Ph][B(C_6F_5)_4]\cdot$2toluene as an orange solid (0.180 g, 83.6%). ^{1}H NMR (CD_2Cl_2): δ 7.34 (s, 4 H, benzo-C*H*), 6.90 (t, J = 7.7, 2H, *m*-Ph), 6.82 (t, J = 7.2, 1 H, *p*-Ph), 5.64 (s, 2 H, NC═C*H*—CN), 5.01 (d, J = 7.1, 2 H, *o*-Ph), 2.50 (s, 12 H, Me), 2.49 (s, 12 H, Me), 0.94 (s, 2 H, CH_2Ph). Resonances for toluene (2 equiv) were also observed. Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 161.1 (m, *C*═N), 141.2 (m, *ipso*-CH_2Ph), 139.1 (m, benzo-*C*N), 132.3 (d, J = 158.7, *o*-CH_2Ph), 128.7 (dm, J = 158, benzo-*C*H), 125.9 (d, J = 6, benzo-*C*Me), 124.1 (overlapping dm, *p*- and *m*-CH_2Ph), 106.8 (d of septets, J = 161, 4, NC═*C*H—NC), 60.6 (tt, J = 136, 3, *C*H_2Ph), 23.2 (qd, J = 128, 4, Me), 20.5 (qd, J = 127, 5, Me). Resonances for toluene were also observed. Anal. Calcd for $C_{57}H_{37}BF_{20}N_4Zr\cdot 2C_7H_8$: C, 59.05; H, 3.70; N, 3.88. Found: C, 59.33, H, 3.47; N, 3.81.

[(Me8taa)ZrCH2SiMe3][B(C6F5)4] (10b). This complex was generated *in situ* by the following procedure. Attempts to isolate **10b** in larger-scale reactions were unsuccessful. An NMR tube was charged with **3a** (31.7 mg, 47.7 μmol) and $[HNMe_2Ph][B(C_6F_5)_4]$ (38.3 mg, 44.4 μmol), and $C_2D_2Cl_4$ (0.5 mL) was added by vacuum transfer at −78 °C. The tube was sealed and warmed to 23 °C. A slightly turbid orange solution formed. The NMR yield of **9** was 80%. ^{1}H NMR ($C_2D_2Cl_4$): δ 7.51 (s, 4 H), 5.72 (s, 2 H, NC═C*H*—CN), 2.55 (s, 12 H), 2.48 (s, 12 H), −0.67 (s, 9 H), −0.87 (s, 2 H, ZrCH_2); resonances for free NMe_2Ph and $SiMe_4$ were also observed. Gated-{^{1}H}−^{13}C NMR ($C_2D_2Cl_4$): δ 159.8 (m, *C*═N), 139.9 (d, J = 5, benzo-*C*N), 126.4 (dd, J = 161, 5, benzo-*C*H), 124.4 (d, J = 6, benzo-*C*Me), 106.4 (d, J = 162, NC═*C*H—CN), 53.0 (t, J = 107, Zr*C*H_2), 21.4 (q, J = 123), 18.8 (q, J = 129), −1.4 (q, J = 118); resonances for free NMe_2Ph and $SiMe_4$ were also observed.

[(Me8taa)ZrCH2CMe3][B(C6F5)4] (10c). A mixture of **3d** (0.300 g, 0.475 mmol) and $[HNMePh_2][B(C_6F_5)_4]$ (0.410 g, 0.475 mmol) in benzene (10 mL) was stirred for 15 min at 23 °C. A red oil separated. The supernatant was decanted off, and the oil was washed with benzene (2 × 10 mL) and dried under high vacuum overnight to afford **10c** as a golden solid, which contained 1.9 equiv of benzene (0.408 g, 61.8%). ^{1}H NMR (CD_2ClCD_2Cl): δ 7.56 (s, 4 H, benzo-*H*), 5.72 (s, 2 H, NC═C*H*—CN), 2.54 (s, 12 H, CH_3), 2.47 (s, 12 H, CH_3), 0.14 (s, 9 H, $CH_2C(CH_3)_3$), −0.51 (s, 2 H, ZrCH_2). The resonance of benzene was also observed. Gated-{^{1}H}−^{13}C NMR (CD_2Cl-CD_2Cl): δ 161.7 (m, *C*═N), 141.5 (m, benzo-*C*N), 128.6 (dm, J = 161, benzo-*C*H), 126.6 (d, J = 7, benzo-*C*Me), 107.5 (dm, J = 161, NC═*C*H—CN), 79.1 (tm, J = 107, ZrCH_2), 33.5 (m, CH_2CMe_3), 33.4 (qm, J = 123, CH_2CMe_3), 22.9 (qd, J = 122, 4, *C*H_3), 20.2 (q, J = 128,*C*H_3).

[(Me8taa)HfMe][B(C6F5)4] (10d). This complex was generated *in situ* by the following procedure. An NMR tube was charged with **4b** (24.4 mg, 40.2 μmol) and $[HNMe_2Ph]$-$[B(C_6F_5)_4]$ (32.1 mg, 37.2 μmol), and CD_2Cl_2 (0.5 mL) was added by vacuum transfer at −78 °C. The tube was sealed and warmed to 23 °C, and a homogeneous orange solution formed. The NMR yield of **11c** was 87%. ^{1}H NMR (CD_2Cl_2): δ 7.51 (s, 4 H), 5.77 (s, 2 H, NC═C*H*—CN), 2.59 (s, 12 H), 2.48 (s, 12 H), −1.11 (s, 3 H, HfCH_3); resonances for free NMe_2Ph and CH_4 were also observed. {^{1}H}^{13}C NMR (CD_2Cl_2): δ 163.0 (*C*═N), 141.1 (benzo-*C*N), 129.5, 126.1, 108.3 (NC═*C*H—CN), 46.6 (Hf*C*H_3), 23.3, 20.4; resonances for free NMe_2Ph were also observed.

[(Me8taa)Zr(CH2SiMe3)(PMe2Ph)][BPh4] (11a). Solid $[HNBu_3][BPh_4]$ (118 mg, 0.233 mmol) was added to a solution of **3a** (159 mg, 0.239 mmol) and PMe_2Ph (36 μL, 0.25 mmol) in 1,2-dichloroethane (10 mL). The mixture was stirred for 15 min and concentrated under vacuum to 2 mL. Pentane (10 mL) was added, and the mixture was stirred until a yellow solid formed. The solid was isolated by filtration and dried under high vacuum overnight (192 mg, 77%). ^{1}H NMR (CD_2-Cl_2): δ 7.44 (t, J = 7, 1 H, *p*-Ph), 7.28 (s, ca. 4 H), 6.97 (t, J = 7, 2 H, *m*-Ph), 5.60 (s, 2 H, NC═C*H*—CN), 2.44 (s, 12 H), 2.43 (s, 12 H), 1.16 (br s, 6 H), −0.46 (s, 9 H), −1.00 (s, 2 H, ZrCH_2); the *o*-Ph resonance of PMe_2Ph was obscured by the BPh_4^- resonances. {^{1}H}^{13}C NMR (CD_2Cl_2): δ 161.2 (*C*═N), 140.3 (benzo-*C*N), 130.5 (d, J_{CP} = 12, PMe_2Ph), 130.1 (br, PMe_2Ph), 129.0 (d, J_{CP} = 8, PMe_2Ph), 127.4 (benzo-*C*H), 126.8 (benzo-*C*Me), 106.2 (NC═*C*H—CN), 49.6 (Zr*C*H_2), 23.2, 20.5, 12.9 (br d, J_{CP} = 3, P*Me*$_2$Ph), 2.5; the *ipso*-C of PMe_2Ph was not observed. Anal. Calcd for $C_{62}H_{72}BN_4PSiZr$: C, 71.99; H, 7.02; N, 5.42. Found: C, 71.80; H, 6.78; N, 5.61.

[(Me8taa)Zr(CH2SiMe3)(THF)n][BPh4] (11b). This complex was generated *in situ* in 76% NMR yield by the following procedure. An NMR tube was charged with **3a**·0.5toluene (9.0 mg, 14 μmol) and $[HNBu_3][BPh_4]$ (7.1 mg, 14 μmol), and CD_2-Cl_2 (ca. 0.5 mL) was added by vacuum transfer at −78 °C. The tube was immediately cooled to −196 °C, and THF (1.6 equiv) was condensed in. The tube was sealed and warmed to 23 °C, and a homogeneous orange solution formed. ^{1}H NMR (CD_2Cl_2): δ 7.42 (s, 4 H), 5.62 (s, 2 H, NC═C*H*—CN), 3.39 (br m, THF), 2.46 (s, 24 H, both sets of 4 Me's are coincident), 1.75 (m, THF), −0.54 (s, 9 H), −1.02 (s, 2 H, ZrCH_2); resonances for $SiMe_4$ and free NBu_3 were also observed.

[(Me8taa)Zr(CH2Ph)(THF)][B(C6F5)4] (11c). This species was generated *in situ* and characterized by ^{1}H NMR. THF (0.75 equiv) was added to a solution of $[(Me_8taa)Zr(CH_2Ph)]$-$[B(C_6F_5)_4]$ (0.15 mmol) in CD_2Cl_2 (0.5 mL), and the ^{1}H NMR spectrum was recorded at −80 °C. Separate resonances for $(Me_8taa)Zr(CH_2Ph)(THF)^+$ and $(Me_8taa)Zr(CH_2Ph)^+$ were observed. A single set of resonances was observed at ambient temperature, indicating that THF exchange is fast on the NMR time scale under these conditions. Addition of excess THF (4.9 equiv total) did not change the spectrum of $(Me_8taa)Zr(CH_2$-$Ph)(THF)^+$. ^{1}H NMR (CD_2Cl_2, −80 °C): δ 7.28 (s, 2 H, benzo-H), 6.95 (t, J = 7.4, 2 H, *meta*-benzyl), 6.93 (s, 2 H, benzo-H), 6.68 (t, J = 7.4, 1 H, *para*-benzyl), 6.07 (d, J = 7.8, 2 H, *ortho*-benzyl), 5.70 (s, 1 H, NC═C*H*—CN), 5.46 (s, 1 H, NC═C*H*—CN), 3.17 (br m, 4 H, THF), 2.39 (s, 6 H, Me), 2.36 (s, 6 H, Me),

2.34 (s, 6 H, Me), 2.33 (s, 6 H, Me), 1.67 (br m, 4 H, THF), 0.66 (s, 2 H, $ZrCH_2$).

[(Me$_8$taa)Hf(CH$_3$)(THF)][B(C$_6$F$_5$)$_4$] (11d). Excess THF (4.9 equiv) was added to a solution of **10d** in CD_2Cl_2, and ^{1}H NMR spectra were recorded. ^{1}H NMR (CD_2Cl_2, −90 °C, fast exchange of free and coordinated THF): δ 7.21 (s, 4 H), 5.51 (s, 2 H), 3.53 (br, THF), 2.41 (s, 12 H), 2.31 (s, 12 H), 1.73 (br, THF), −1.36 (s, 3 H).

Olefin Polymerization with 10a. (i) Method 1: A Fisher−Porter bottle was charged with toluene (400 mL), Al(^{i}Bu)$_3$ (150 μL, 0.58 mmol) if desired, and **10a**·1.8C_6H_6 (0.040 g, 0.029 mmol). The bottle was thermostatted at 50 °C, charged with ethylene (1.3 atm), and vigorously stirred. After 17−24 h, EtOH (1 L) was added and the polymer was isolated by filtration, washed with EtOH and H_2O, and dried under vacuum. Without Al(^{i}Bu)$_3$: yield 0.27 g, activity = 300 (g of PE)(mol of cat.)$^{-1}$ atm^{-1} h^{-1}; M_w = 99 300, M_n = 38 500, M_w/M_n = 2.6; linear by NMR, benzyl end groups not detected. With Al(^{i}Bu)$_3$: yield 0.35 g, activity = 550 (g of PE) (mol of cat.)$^{-1}$ atm^{-1} h^{-1}. (ii) Method 2: A flask was charged with chlorobenzene (5 mL), Al(^{i}Bu)$_3$ (150 μL, 0.58 mmol), and **10a**·1.8C_6H_6 (0.040 g, 0.029 mmol) in the drybox and then attached to a high-vacuum line. The flask was degassed by freeze−pump−thaw cycles, exposed to 1 atm of ethylene, and heated to 90 °C. After 17 h, the reaction was quenched with EtOH/HCl and the polymer was isolated as described above. Yield 0.20 g, activity = 400 (g of PE) (mol of cat.)$^{-1}$ atm^{-1} h^{-1}; M_w = 1,410, M_n = 800, M_w/M_n = 1.8; ^{1}H NMR ratio of saturated end groups/vinyl end groups = 13/1, M_n = 786; ^{13}C NMR saturated end groups detected, no branching detected. (iii) Control experiment: Using conditions and procedures similar to those outlined in method 1, an activity of 48 000 (g of PE)(mol of cat.)$^{-1}$ atm^{-1} h^{-1} was measured for Cp_2ZrMe_2/[HNMePh$_2$][B(C$_6$F$_5$)$_4$]/Al(iBu)$_3$.

[(Me$_8$taa)Zr(OCMe$_2$CH$_2$CH$_2$CH=CH$_2$)][B(C$_6$F$_5$)$_4$] (13). The alcohol $HOCMe_2CH_2CH_2CH{=}CH_2$ (26.4 μL, 0.220 mmol) was added in 3 portions to a slurry of **10a**·1.3C_6H_6 (0.300 g, 0.194 mmol) in benzene (5 mL). A pale orange oil separated. The supernatant was decanted off, and the oil was washed with benzene (5 mL). Hexane (20 mL) was added, and the mixture was stirred, which resulted in the formation of a yellow solid. The solid was collected by filtration, washed with hexane (2 × 10 mL), and dried under vacuum (0.220 g, 88%). ^{1}H NMR (CD_2Cl_2): δ 7.45 (s, 4 H, benzo-C*H*), 5.69 (s, 2 H, CN−CH=CN), 5.40 (ddt, J = 17.0, 10.3, 10.1, 1 H, $-H_2C{=}CH$), 4.76 (dm, J = 10.2, 1 H, *cis*-*H*HC=CH), 4.69 (dq, J = 17.0, 1.8, 1 H, *trans*-H*H*C=CH), 2.53 (s, 12 H, Me), 2.45 (s, 12 H, Me), 1.18 (m, 2 H, CH_2), 0.75 (m, 2 H, CH_2), 0.38 (s, 6H, Me). Resonances for toluene were also observed. Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 162 (m, *C*=N), 140.5 (m, benzo-*C*N), 139.7 (d, overlapped with $B(C_6F_5)_4^-$ resonance, *C*H=CH_2), 127.8 (m, benzo-*C*Me), 127.1 (dm, J = 159, benzo-*C*H), 113.7 (tm, J = 154, CH=*C*H$_2$), 107.1 (d, J = 160, NC=*C*H−CN), 80.5 (m, *C*−O), 42.4 (tm, J = 122, *C*H$_2$), 30.0 (qm, J = 125, Me), 28.5 (tm, J = 124, *C*H$_2$), 22.8 (qd, J = 128, 4, Me), 20.3 (qd, J = 127, 5, Me). ^{19}F NMR (CD_2Cl_2) δ −132.8 (br s, 8 F), −163.6 (t, J_{FF} = 20.3, 4F), −167.4 (br t, 8 F).

[{(Me$_8$taa)Zr(μ-OH)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (14a). Water (1.2 μL, 0.066 mmol) was added by syringe to a solution of **10a**·1.8C_6H_6 (0.105 g, 0.066 mmol) in CH_2Cl_2 (1 mL). The solution was stirred for 2 min and cooled to −78 °C. Pentane (2 mL) was added, and an orange oil separated. The supernatant was removed by cannula, and the oil was dried under vacuum, affording a yellow solid (0.058 g, 74%). The solid was recrystallized from CH_2Cl_2/pentane and dried under vacuum. ^{1}H NMR (CD_2Cl_2): δ 7.39 (s, 4 H, benzo-C*H*), 6.88 (s, 4 H, benzo-C*H*), 5.60 (s, 2 H, CN−C*H*=CN), 4.14 (s, 2 H, CN−C*H*=CN), 3.09 (s, 2 H, O*H*), 2.70 (s, 12 H, Me, 2.46 (s, 12 H, Me), 2.40 (s, 12 H, Me), 2.20 (s, 12 H, Me). Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 161.5 (m, *C*=N), 157.8 (m, *C*=N), 140.2 (m, benzo-*C*N), 138.3 (m, benzo-*C*N), 136.2 (m, benzo-*C*Me), 127.6 (m, benzo-*C*Me), 126.7 (dm, J = 154, benzo-*C*H), 120.8 (dm, J = 157, benzo-*C*H), 107.3 (d, J = 161, NC=*C*H−CN), 90.2 (d, J = 161, NC=*C*H−CN), 23.1 (qd, J = 129, 4, Me), 22.4 (qd, J = 129, 3, Me), 20.8 (qd, J = 127, 5, Me), 19.9 (qd, J = 126, 5, Me). Anal. Calcd for $C_{50}H_{31}BF_{20}N_4OZr$: C, 50.64; H, 2.63; N, 4.72. Found: C, 50.39; H, 2.62; N, 4.47.

[{(Me$_8$taa)Zr(μ-OEt)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (14b). Ethanol (5.7 μL, 0.095 mmol) was added by syringe to a solution of **10a**·C_6H_6 (0.144 g, 0.095 mmol) in CH_2Cl_2 (5 mL). The color of the solution changed from orange to yellow in a few seconds. The reaction mixture was stirred at 23 °C for 30 min. The volatiles were removed under vacuum to afford a yellow solid, which was dried under vacuum for 12 h. The solid was recrystallized from CH_2Cl_2/pentane (0.083 g, 72%). ^{1}H NMR (CD_2Cl_2): δ 7.41 (s, 4 H, benzo-C*H*), 6.87 (s, 4 H, benzo-C*H*), 5.69 (s, 2 H, CN−C*H*=CN), 4.31 (s, 2 H, CN−C*H*=CN), 2.77 (q, J = 7.0, 4 H, OC*H*$_2$), 2.72 (s, 12 H, Me), 2.55 (s, 12 H, Me), 2.39 (s, 12 H, Me), 2.18 (s, 12 H, Me), 0.47 (t, J = 7.0, 6 H, CH_2CH_3). Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 161.8 (m, *C*=N), 157.5 (m, *C*=N), 140.5 (m, benzo-*C*N), 137.7 (m, benzo-*C*Me), 136.3 (m, benzo-*C*N), 127.3 (m, benzo-*C*Me), 126.6 (dd, J = 158, 4, benzo-*C*H), 121.0 (dd, J = 163, 4, benzo-*C*H), 107.3 (dm, J = 162, NC=*C*H−CN), 90.8 (dm, J = 160, NC=*C*H−CN), 66.0 (tm, J = 143, O*C*H$_2$), 23.4 (qd, J = 129, 4, Me), 23.0 (qd, J = 128, 4, Me), 20.9 (qd, J = 127, 5, Me), 20.0 (qd, J = 126, 5, Me), 17.7 (q, J = 125, CH_2CH_3). Anal. Calcd for $C_{52}H_{35}BF_{20}N_4OZr$: C, 51.45; H, 2.91; N, 4.62. Found: C, 50.51; H, 2.64; N, 4.44.

[(Me$_8$taa)HfCMe=CMeCMe=CMe$_2$][B(C$_6$F$_5$)$_4$] (15). A solution of **4b** (106 mg, 0.175 mmol), [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (139 mg, 0.161 mmol), and 2-butyne (1.1 mmol) in CH_2Cl_2 (4 mL) was stirred for 1 day at 23 °C, and the volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2 (3 mL), and the solution was filtered and concentrated under vacuum to 1 mL. Pentane was added, and a brown, oily solid was isolated by filtration and dried under high vacuum for 1 day (172 mg, 78%). ^{1}H NMR (CD_2Cl_2): δ 7.40 (s, 4 H), 5.64 (s, 2 H, NC=C*H*−CN), 2.52 (s, 12 H), 2.44 (s, 12 H), 1.60 (s, 3 H), 1.51 (s, 3 H), 1.13 (s, 3 H), 1.10 (s, 3 H), 0.90 (s, 3H). {^{1}H}^{13}C NMR (CD_2Cl_2): δ 214.0 (Hf*C*), 163.1 (*C*=N), 147.1, 141.6, 139.1 (benzo-*C*N), 135.5, 128.7 (benzo-*C*Me), 127.0 (benzo-*C*H), 107.4 (NC=*C*H−CN), 23.9 (4 Me), 23.7, 22.1, 20.9, 20.2 (4 Me), 17.5, 14.5. Anal. Calcd for $C_{59}H_{45}BF_{20}HfN_4$: C, 51.38; H, 3.29; N, 4.06. Found: C, 51.11, H, 3.49; N, 4.06.

[(Me$_8$taa)Hf(C(SiMe$_3$)=CMe$_2$)][B(C$_6$F$_5$)$_4$] (16). A frozen CH_2Cl_2 solution (5 mL) of **4b** (99.9 mg, 0.165 mmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (131 mg, 0.152 mmol) was exposed to 1-Me$_3$Si-1-propyne (0.9 mmol) at −196 °C and warmed to 23 °C. The orange solution was stirred for 1.5 h and concentrated under vacuum to 3 mL. Pentane was added, resulting in the formation of a red oil. The supernatant was decanted off, and the oil was briefly dried under vacuum to give an orange solid, which was washed with pentane and dried under high vacuum for 2 days. ^{1}H NMR analysis indicated the presence of pentane (0.72 equiv). Yield: 175 mg, 80%. Low-temperature NMR spectra establish that **16** adopts a C_s-symmetric structure. However, at 23 °C, the ^{1}H and ^{13}C NMR spectra of **16** exhibit broadened and/or coalesced resonances, indicative of a dynamic process which results in effective C_{2v} symmetry. ^{1}H NMR (CD_2Cl_2, −20 °C): δ 7.42 (s, 2 H), 7.41 (s, 2 H), 5.81 (s, 1 H, NC=C*H*−CN), 5.73 (s, 1 H, NC=C*H*−CN), 2.57 (s, 6 H), 2.56 (s, 6 H), 2.43 (2 s, 2 × 6 H), 1.36 (s, 3 H), 1.33 (s, 3 H), −0.52 (s, 9 H). {^{1}H}^{13}C NMR (CD_2Cl_2, −20 °C): δ 202.3 (Hf*C*), 166.5 (=*C*Me$_2$), 162.6 (*C*=N), 162.5 (*C*=N), 140.4 (benzo-*C*N), 140.2 (benzo-*C*N), 127.3 (benzo-*C*H), 126.9 (benzo-*C*H), 126.1 (benzo-*C*Me), 125.8 (benzo-*C*Me), 108.1 (NC=*C*H−CN), 107.7 (NC=*C*H−CN), 29.2 (1 Me), 26.9 (1 Me), 23.2 (4 Me), 20.3 (2 Me), 20.1 (2 Me), −0.1 (SiMe$_3$). Anal. Calcd for $C_{57}H_{45}BF_{20}HfN_4Si$: C, 49.49; H, 3.28; N, 4.05. Found: C, 48.98; H, 3.73; N, 3.81. Duplicate analysis also gave a low C value (48.89).

[{(Me$_8$taa)Zr(μ-CCPh)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (17a). Phenylacetylene (3.2 μL, 0.29 mmol) was added by syringe to a solution of **10a**·2toluene (0.208 g, 0.145 mmol) in CH_2Cl_2 (5 mL). The solution was stirred at 23 °C for 1 h, and the color changed from orange to red. The volatiles were removed under vacuum to yield a brown solid. The solid was taken up in benzene (10 mL), and the resulting slurry was filtered, affording a yellow powder which was washed with hexane (2 × 10 mL) and dried under vacuum overnight (0.140 g, 76.1%). The product was further purified by recrystallization from CH_2Cl_2/pentane at 23 °C and CH_2Cl_2 at −40 °C. ^{1}H NMR (CD_2Cl_2): δ 7.53 (s, 4 H, benzo-C*H*), 7.44 (t, J = 7.9, 2 H, *p*-Ph), 7.28 (t, J = 7.9, 4 H, *m*-Ph), 6.84 (s, 4 H, benzo-C*H*), 6.75 (d, J = 8.4, 4 H, *o*-Ph), 5.25 (s, 2 H, NC═C*H*—CN), 4.09 (s, 2H, NC═C*H*—CN), 2.77-(s, 12 H, Me), 2.38 (s, 12 H, Me), 2.28 (s, 12 H, Me), 2.17 (s, 12 H, Me). Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 160.2 (m, *C*═N), 157.2 (m, *C*═N), 141.2 (m, *C*CPh), 139.5 (d, J = 7, benzo-*C*Me), 136.3 (m, benzo-*C*N), 135.4 (benzo-*C*N, overlapped with anion resonance), 132.5 (dt, J = 159, 6, *o*-Ph), 132.1 (dt, J = 164, 7, *p*-Ph), 129.2 (dd, J = 163, 8, benzo-*C*H), 127.0 (dm, J = 159, benzo-*C*H), 125.6 (d, J = 7, benzo-*C*Me), 121.8 (s, *i*-Ph), 121.0 (dm, J = 158, *m*-Ph), 119.0 (t, J = 8, C*C*Ph), 107.4 (dm, J = 162, NC═*C*H—CN), 83.0 (dm, J = 162, NC═*C*H—CN), 23.3 (qd, J = 128, 4, Me), 22.1 (qd, J = 129, 3, Me), 21.1 (qd, J = 127, 5, Me), 20.0 (qd, J = 126, 5, Me). ^{19}F NMR (CD_2Cl_2): δ −132.8 (8 F), −163.5 (t, J_{FF} = 20.4, 4 F), 167.3 (br t, 8F). Anal. Calcd for $C_{58}H_{35}BF_{20}N_4Zr$: C, 54.86; H, 2.78; N, 4.41. Found: C, 54.93; H, 2.65; N, 4.33.

[{(Me$_8$taa)Zr(μ-CCPr)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (17b). 1-Pentyne (163 mm, 50 mL, 23 °C; 0.44 mmol) was vacuum transferred into a flask containing a frozen solution of **10a**·1.2C_6H_6 (0.198 g, 0.146 mmol) in CH_2Cl_2 (5 mL) at −196 °C. The reaction mixture was warmed to 23 °C and stirred for 21 h. The volatiles were evaporated under vacuum to afford a yellow solid, which was slurried in benzene (5 mL), filtered, and washed with benzene (10 mL) and pentane (40 mL). The solid was dried under vacuum for 12 h (0.167 g, 92%). ^{1}H NMR (CD_2Cl_2): δ 7.36 (s, 2 H, benzo-C*H*), 6.89 (s, 2 H, benzo-C*H*), 5.70 (s, 1 H, CN—C*H*═CN), 4.13 (s, 1 H, CN—C*H*═CN), 2.70 (s, 6 H, Me), 2.43 (s, 6 H, Me), 2.35 (s, 6 H, Me), 2.19 (s, 6 H, Me), 1.53 (t, J = 7.2, 2H, CCC*H*$_2$), 0.94 (sextet, J = 7.2, $CH_2CH_2CH_3$), 0.61 (t, J = 7.2, 3H, $CH_2CH_2CH_3$). Gated-{^{1}H}−^{13}C NMR (CD_2Cl_2): δ 160.2 (m, *C*═N), 156.9 (m, *C*═N), 141.6 (m, *C*CPr), 140.8 (m, benzo-*C*N), 139.2 (d, J = 8 Hz, benzo-*C*Me), 136.2 (m, benzo-*C*N), 126.8 (dd, J = 160, 5, benzo-*C*H), 125.5 (d, J = 6, benzo-*C*Me), 120.9 (dd, J = 157, 4, benzo-*C*H), 115.0 (m, C*C*Pr), 107.1 (dm, J = 161, NC═*C*H—CN), 83.6 (dm, J = 162, NC═*C*H—CN), 23.2 (qd, J = 125, 4, Me), 22.9 (tm, J = 130, *C*H$_2$), 22.6 (overlapped, *C*H$_2$), 21.9 (qd, J = 125, 3, Me), 21.0 (qd, J = 127, 5, Me), 20.0 (qd, J = 126, 5, Me), 13.6 (qm, J = 125, CH_2CH_3).

[(Me$_8$taa)Zr(CCPh)(PMe$_3$)][B(C$_6$F$_5$)$_4$] (18a). This complex was generated *in situ* by the following procedure. An NMR tube was charged with **17a** (0.0237 g, 0.0093 mmol), and CD_2Cl_2 (0.5 mL) was added by vacuum transfer at −78 °C. The mixture was cooled to −196 °C, and PMe_3 (0.028 mmol) was added. The tube was sealed and warmed to 23 °C. The ^{1}H NMR spectrum indicated that **18a** was formed in ca. 85% NMR yield after 1 h. ^{1}H NMR (CD_2Cl_2, rapid PMe_3 exchange): δ 7.46 (s, 4 H, benzo-CH), 7.13 (m, 3 H), 6.84 (m, 2 H), 5.74 (s, 2 H, NC═C*H*—CN), 2.55 (s, 12 H, Me), 2.46 (s, 12H, Me), 0.70 (br, 27 H, PMe_3). ^{1}H NMR (CD_2Cl_2, −93 °C, slow PMe_3 exchange): δ 7.33−7.32 (m, 3 H, benzo-C*H* and *p*-Ph), 7.05−7.13 (m, 4 H, benzo-C*H* and *m*-Ph), 6.73 (d, J = 6.9, 2 H, *o*-Ph), 5.65 (s, 2 H, NC═C*H*—CN), 2.47 (s, 6 H, Me), 2.44 (s, 6 H, Me), 2.32 (s, 6 H, Me), 1.94 (s, 6 H, Me), 0.97 (d, J = 5, free PMe_3), 0.91 (s, 9 H, coordinated PMe_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 160.4, 140.8, 131.2, 128.5, 127.7, 126.9 (overlapped signals), 126.5, 125.3, 106.4, 23.1, 20.4, 14.5.

X-ray Data Collection, Structure Determination, and Refinement for [{(Me$_8$taa)Zr(μ-OH)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (14a). A yellow single crystal was mounted on a fiber and transferred to the goniometer. The crystal was cooled to −100 °C during data collection by using a stream of cold nitrogen gas. The space group was determined to be the centric $P2_1/n$ from the systematic absences. A summary of the data collection parameters is given in Table 1.

One molecule of pentane per formula unit was found to be disordered within the lattice. The refinement of these atoms was poor, although at least two orientations of the molecule were resolved. C101 was refined at full occupancy, C102 and C103 at 75% occupancy, C104−C107 at 50% occupancy, and C108 and C109 at 25% occupancy for a total of 5 C atom positions. These atoms were refined isotropically only, and no H atoms were included for these positions. Refinement of non-hydrogen atoms (except for the disordered solvent molecule) was carried out with anisotropic temperature factors. The geometrically constrained hydrogen atoms (except for the disordered solvent molecule) were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2U_{eqv}$(*C*). The methyl H atoms (except for the disordered solvent molecule) were included as a rigid group with rotational freedom at the bonded carbon atom ($B = 1.2U_{eqv}$(*C*)). The remaining H atoms were not included in the final refinement. The lack of resolution in the disordered solvent resulted in R values which are higher than normal; however, the geometrical parameters associated with **14a** (Table 2) are quite good.

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Supporting Information Available: Tables of data collection parameters, atomic coordinates, bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for **14a**·pentane (20 pages). Ordering information is given on any current masthead page.

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