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Tetraaza Macrocycles as Ancillary Ligands in Early Metal Alkyl Chemistry. Synthesis and Characterization of Out-of-Plane (Me$_4$taen)ZrX$_2$ (X = Alkyl, Benzyl, NMe$_2$, Cl) and (Me$_4$taen)ZrX$_2$(NHMe$_2$) (X = Cl, CCPh) Complexes

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The synthesis, properties, and structures of a series of out-of-plane (N$_4$-macrocycle)ZrX$_2$ complexes incorporating the tetraaza macrocycle Me$_4$taen^{2-} are described ((Me$_4$taen)H$_2$ = 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene). Alkane elimination reactions of (Me$_4$taen)H$_2$ (**1**) with ZrR$_4$ yield (Me$_4$taen)ZrR$_2$ (**2**, R = CH$_2$Ph; **3**, R = CH$_2$SiMe$_3$). The amine elimination reaction of **1** with Zr(NMe$_2$)$_4$ yields (Me$_4$taen)Zr(NMe$_2$)$_2$ (**4**). Protonolysis of **4** with [HNHMe$_2$]Cl yields the seven-coordinate amine adduct (Me$_4$taen)ZrCl$_2$(NHMe$_2$) (**5**), which loses amine under vacuum (120 °C, 10 h) to afford base-free (Me$_4$taen)ZrCl$_2$ (**6**). The reaction of **4** with phenylacetylene yields the seven-coordinate bisacetylide complex (Me$_4$taen)Zr(CCPh)$_2$(NHMe$_2$) (**7**). The reaction of **6** with RLi reagents in toluene yields (Me$_4$taen)ZrR$_2$ (**8**, R = CH$_2$CMe$_3$; **9**, R = CH$_3$). Halide displacement does not provide facile access to **6**. Deprotonation of **1** yields [Li(THF)]$_2$[Me$_4$taen] (**10**), which readily loses THF to yield Li$_2$[Me$_4$taen] (**11**); however, the reaction of **11** with ZrCl$_4$(THF)$_2$ yields mixtures of **6** and (Me$_4$taen)$_2$Zr (**12**). Bismacrocycle complex **12** is formed in good yield via reaction of Zr(NMe$_2$)$_4$ with 2 equiv of **1**. Dialkyls **2** and **9** rearrange thermally by migration of an alkyl group from Zr to a macrocycle imine carbon. The solid state structures of **1**, **2**, **4**−**6**, and **10** have been determined. Compounds **1** and **10** exhibit rather planar Me$_4$taen conformations. Dichloride **6** adopts a trigonal prismatic structure in which the chlorides occupy adjacent edge sites, and the Me$_4$taen^{2-} conformation is similar to that in **1** and **10**. Dibenzyl complex **2** adopts a similar but more twisted trigonal prismatic structure. Bisamide complex **4** adopts a distorted octahedral structure in which the Me$_4$taen^{2-} ligand is significantly folded. These structural differences are rationalized in terms of the conformational preference of the Me$_4$taen^{2-} ligand, as deduced from the structures of **1** and **10**, and the π-donating ability of the X group. Seven-coordinate complex **5** adopts a side-capped trigonal prismatic structure with a tripodal arrangement of chloride and amine ligands. The structures and properties of these new compounds are compared to those of Cp$_2$MX$_2$ and other early metal analogues.

Introduction

Zirconium(IV) and hafnium(IV) complexes of 14- or 16-membered tetraaza macrocyclic ligands (N$_4$-macrocycle)MX$_2$ adopt "out-of-plane" cis structures because the large metal ions cannot fit in the macrocycle N$_4$-plane (**A**, Chart 1).$^{1-11}$ Complexes of this type can coordinate one or two additional ligands cis to the X groups giving seven- or eight-coordinate adducts (**B**, **C**); coordination of ligands trans to the X groups is precluded by the out-of-plane structure. The potential availability of coordination sites cis to the X ligands

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(9) Me$_4$taa^{2-} is also referred to as taa^{2-} in the literature.

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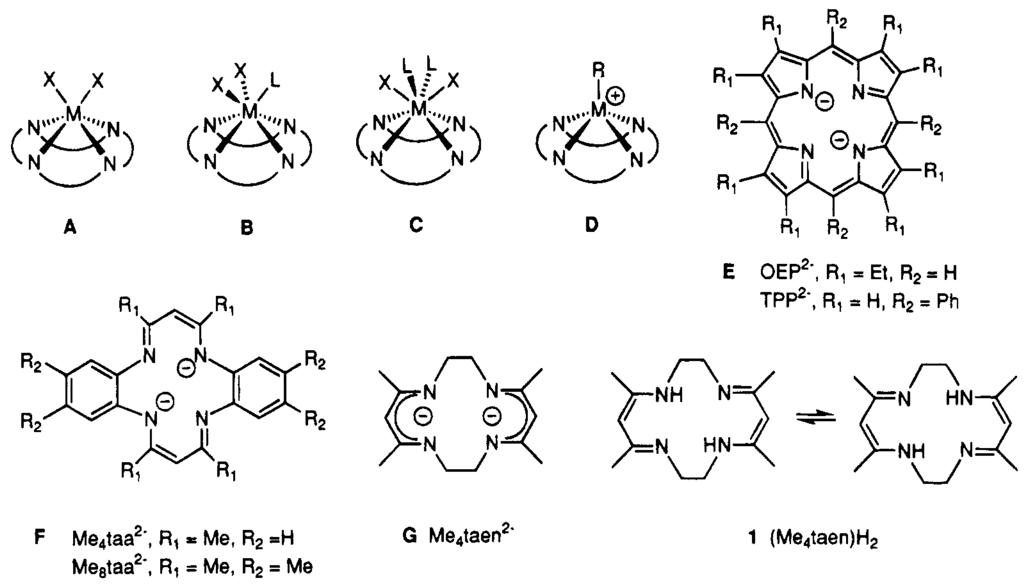
Chart 1



makes organometallic derivatives of these systems of interest for synthetic and catalytic applications. Our own long-term goal in this area is to develop *cationic* (N$_4$-macrocycle)M(R)$^+$ alkyl complexes (**D**) which, given the cis structures of (N$_4$-macrocycle)MX$_2$ species, should form cis (N$_4$-macrocycle)M(R)(substrate)$^+$ adducts, possibly leading to insertion and σ-bond metathesis chemistry.[1]

To date, group 4 metal macrocycle chemistry has focused on porphyrin and tetraazaannulene (taa) ligands (**E** and **F**, Chart 1). Arnold has prepared an extensive series of out-of-plane cis (OEP)ZrR$_2$ dialkyls and investigated their reactivity.[2-7] These complexes undergo rapid Zr$-$C protonolysis, yielding new (OEP)ZrX$_2$ (X$^-$ = TfO$^-$, R′CO$_2$$^-$, R′O$^-$, Cl$^-$) and (OEP)Zr(R)$^+$ derivatives, and also cleanly insert CO$_2$ and acetone, yielding carboxylate and alkoxide complexes. Hydrogenolysis of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ yields hydride species which can be trapped by olefins yielding (OEP)Zr(CH$_2$SiMe$_3$)(CH$_2$CH$_2$R) and (OEP)Zr(CH$_2$CH$_2$R)$_2$ (R = H, Me). This system catalytically hydrogenates ethylene, presumably via an insertion/Zr$-$C hydrogenolysis process. Recently, Inoue reported that (TPP)ZrX$_2$ complexes (X$^-$ = RCO$_2$$^-$, Cl$^-$)^2 catalyze the carboalumination of terminal alkynes.[8]

Goedken and Floriani have investigated (Me$_4$taa)MCl$_2$ (M = Ti, Zr, Hf) and several derivatives containing the 14-membered macrocycle Me$_4$taa^{2-}.[9,10] These complexes invariably exhibit out-of-plane cis structures in which the ligand adopts a relatively rigid saddle conformation dut to steric interactions between the methyl and benzo groups.[10f,g] However, the organometallic chemistry of this system is less well developed. Floriani showed that (Me$_4$taa)ZrCl$_2$ can be alkylated by PhCH$_2$MgCl to yield cis (Me$_4$taa)Zr(CH$_2$Ph)$_2$; however reaction with MeMgX results in methylation at a Me$_4$taa imine carbon, yielding (Me$_5$taa)Zr(Me)(THF).[11] Recently, we prepared a series of (Me$_8$taa)MR$_2$ alkyls (M = Zr, Hf; R = Me, CH$_2$Ph, CH$_2$SiMe$_3$) via salt metathesis or direct alkane elimination routes.[1] Protonolysis of these species with ammonium reagents yields (Me$_8$taa)M(R)$^+$ cations which insert alkynes and polymerize ethylene. The potential utility of out-of-plane (Me$_x$taa)MX$_n$ compounds in organic synthesis is further demonstrated by Geoffroy's earlier discovery that (Me$_4$taa)Ti(=O) undergoes facile cycloaddition reactions with metal carbonyls, electrophilic ketones, epoxides, and other substances.[12]

In the present contribution we describe the synthesis and characterization of a series of neutral Zr(IV) complexes of the 12-π-electron, 14-membered macrocyclic ligand Me$_4$taen^{2-} (**G**), the dianion of (Me$_4$taen)H$_2$ (**1**).[13] This ligand was chosen for study for several reasons. Macrocycle **1** is easily available in good yield by non-template ketoenamine/diamine condensation routes developed by Holm and Tokumitsu or by a Au^{III}-templated β-diketone/diamine condensation route developed by Everett.[14-16] Analogues of **1** with different substituents on the diiminato or $-$CH$_2$CH$_2$$-$ fragments, or an increased level of unsaturation, may be prepared by derivatization of **1** or by direct synthesis.[17] The Me$_4$taen^{2-} ligand is more flexible than Me$_x$taa^{2-} or porphyrin^{2-} ligands, which may allow for greater M$-$N

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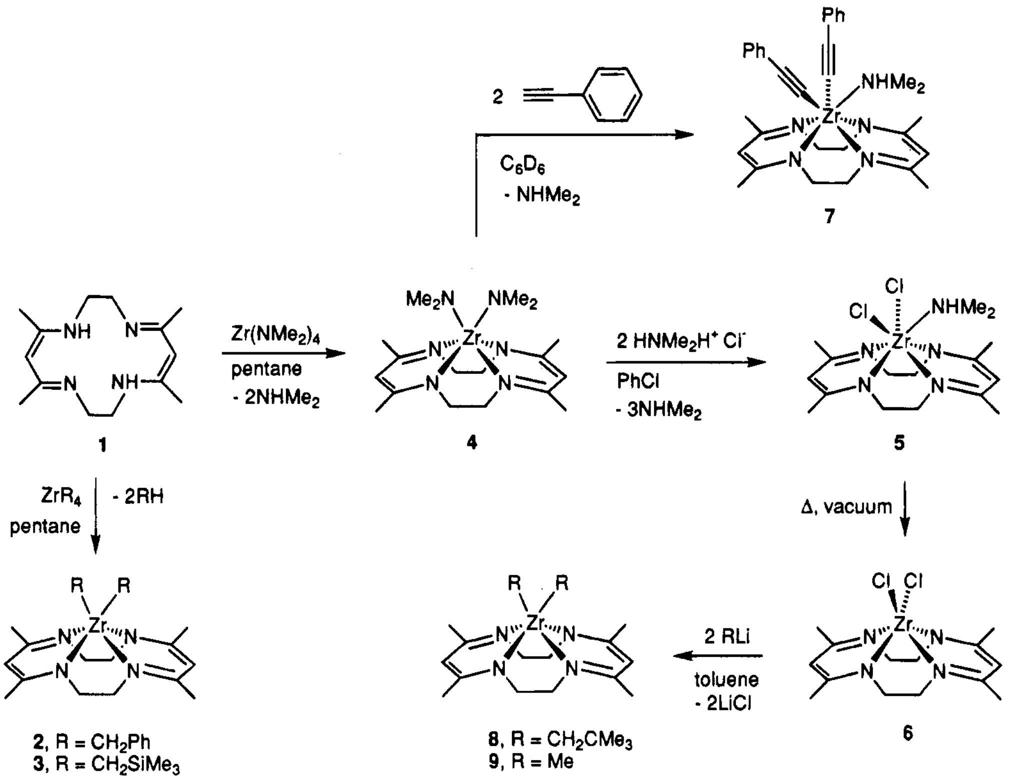
Scheme 1



π-bonding and concomitant greater stabilization of electron-deficient (N_4-macrocycle)M(R)$^+$ species. The steric properties of Me$_4$taen^{2-} (i.e., macrocycle pocket size, degree of steric crowding above or below the N_4-plane) are intermediate relative to those of Me$_x$taa^{2-} and porphyrin^{2-} ligands.

An extensive series of mid and late transition metal (Me$_4$taen)M^{n+} complexes (n = 0, M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}; n = 1, M = Au^{III}) and analogues containing differently substituted taen^{2-} ligands has been prepared.[18] The electronic, spectroscopic, and magnetic properties of these compounds are in accord with square planar structures. An X-ray diffraction study of [(Me$_4$taen)Au]Cl·H_2O established that the (Me$_4$taen)Au$^+$ cation adopts a nearly planar structure with square planar Au^{3+} coordination geometry.[19] However, due to disorder problems, the conformation of the $-CH_2CH_2-$ fragments of the Me$_4$taen^{2-} ligand was not well determined.

The objectives of the present work were to develop efficient routes to (Me$_4$taen)ZrR$_2$ compounds and a general understanding of their structures and properties. The chemistry of cationic derivatives will be discussed in a subsequent paper.[1]

Results and Discussion

Synthesis of (Me$_4$taen)ZrR$_2$ Complexes via Alkane Elimination. Alkane elimination reactions have been utilized to prepare a wide variety of group 4 metal complexes containing alkoxide, Schiff base, carborane, and other ligands.[20] Alkane elimination reactions of the neutral macrocycle (Me$_4$taen)H$_2$ (**1**) and homoleptic ZrR$_4$ compounds provide the most efficient approach to (Me$_4$taen)ZrR$_2$ complexes. Compound **1** reacts readily with ZrR$_4$ (R = CH_2Ph, CH_2SiMe_3) in pentane at 23 °C affording (Me$_4$taen)Zr(CH_2Ph)$_2$ (**2**) and (Me$_4$taen)Zr(CH_2SiMe_3)$_2$ (**3**) in high yield (Scheme 1). Complexes **2** and **3** are isolated as orange solids after recrystallization and have been characterized by ^1H and ^{13}C NMR and analysis. Complex **2** is sparingly soluble, **3** is quite soluble in benzene, and both are soluble and stable in THF and CH_2Cl_2.

The ^1H NMR spectra of **2** and **3** contain singlets for the Me$_4$taen methyl and methine hydrogens, and two multiplets for the $-CH_2CH_2-$ hydrogens. These data are consistent with cis C_{2v}-symmetric structures, in which the "upper" and "lower" $-CH_2CH_2-$ hydrogens are inequivalent. The ZrCH_2 J_{CH} values for **2** (106 Hz) and **3** (105 Hz) are at the low end of the normal range observed for alkyl complexes of electropositive metals, and indicate that the hydrocarbyl ligands are not significantly distorted by non-classical η^2-benzyl or α-agostic interactions.[21,22]

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Synthesis of $(Me_4taen)Zr(NMe_2)_2$. The alkane elimination approach to $(Me_4taen)ZrR_2$ complexes is limited by the small pool of easily accessible homoleptic ZrR_4 compounds. It has been shown previously that group 4 metal amido complexes containing Cp, linked Cp_2, Cp–amido, carborane, and other ligands (L) may be prepared by amine elimination reactions of weakly acidic L–H species and $M(NR_2)_4$ complexes, and are useful precursors to other derivatives.[23] This approach also works well in the $(Me_4taen)ZrX_2$ system. The reaction of **1** with $Zr(NMe_2)_4$ proceeds readily in hydrocarbon solvents to afford $(Me_4taen)Zr(NMe_2)_2$ (**4**) in high yield (Scheme 1). Complex **4** is isolated as a yellow solid which is extremely soluble in aromatic solvents and moderately soluble in hot hexane, from which it may be recrystallized. The NMR data for **4** are similar to data for **2** and **3**, and confirm the expected cis structure. Complex **4** does not coordinate $HNMe_2$, which is a coproduct of its synthesis.

Synthesis of $(Me_4taen)ZrCl_2(NHMe_2)$ and $(Me_4taen)ZrCl_2$. The reaction of **4** with 2 equiv of $[HNHMe_2]Cl$ (chlorobenzene, 0–23 °C) results in selective protonolysis of the $Zr-NMe_2$ bonds and quantitative formation of the seven-coordinate complex $(Me_4taen)ZrCl_2(NHMe_2)$ (**5**, Scheme 1). Complex **5** is isolated as a yellow solid which is soluble in chlorinated solvents and slightly soluble in aromatic solvents. The ^1H and ^{13}C NMR spectra of **5** ($CDCl_2CDCl_2$) contain amine resonances which are significantly shifted from those of free $NHMe_2$, indicating that the amine remains coordinated in solution. These spectra also indicate that **5** has effective C_{2v} symmetry on the NMR time scale, which may result from stereochemical nonrigidity (as expected for a seven-coordinate complex) or from rapid amine exchange. Complex **5** undergoes rapid (NMR time scale) exchange with free $NHMe_2$ at 23 °C.

Complex **5** retains the $NHMe_2$ ligand upon recrystallization from chlorobenzene/pentane and upon vacuum drying at 80 °C. However, thermolysis of solid **5** at 120 °C (10 h) under vacuum yields the base-free dichloride complex $(Me_4taen)ZrCl_2$ (**6**, Scheme 1) as an analytically pure yellow solid.[24] Complex **6** is moderately soluble in chlorinated solvents but only sparingly soluble in hydrocarbons.

Interestingly, **5** is formed directly by the reaction of **1** and $Zr(NMe_2)_4$ in CD_2Cl_2 (5 h, 0 °C; then 4 h, 23 °C). This reaction provides a convenient synthesis of **5**, although the yield (73%) is less than that described above. Control experiments show that $Zr(NMe_2)_4$ is stable in CH_2Cl_2 under these conditions but that **4** is converted to **5**, via an intermediate monoamido species $(Me_4taen)Zr(NMe_2)Cl$.[25] This reaction was not investigated in detail.

Generation of $(Me_4taen)Zr(C\equiv CPh)_2(NHMe_2)$. The reaction of **4** with 2 equiv of $PhC\equiv CH$ yields the bisalkynyl complex $(Me_4taen)Zr(C\equiv CPh)_2(NHMe_2)$ (**7**), which was characterized spectroscopically (Scheme 1). The ^{13}C NMR spectrum of **7** contains resonances at δ 148.5 and 103.8, which are assigned to α and β alkynyl carbons, respectively, on the basis of comparisons to other acetylide complexes of electropositive metals.[23b,26] The ^1H and ^{13}C NMR data indicate that **7** has effective C_{2v} symmetry on the NMR time scale, as a result of amine exchange or stereochemical nonrigidity. Interestingly, the ^1H NMR resonances for the diastereotopic $-CH_2CH_2-$ hydrogens in **7** are much more widely separated ($\Delta\delta = 1.1$) than for other $(Me_4taen)ZrX_2L_n$ species (**2**–**6**, **8**, and **9**, *vide infra*; $\Delta\delta < 0.5$). This suggests that the predominant conformation of **7** in solution is that in which the alkynyl ligands point over the $-CH_2CH_2-$ fragments of the Me_4taen ligand. This conformation is analogous to that observed in the solid state for **5** (*vide infra*), and places the "upper" $-CH_2CH_2-$ hydrogens within the anisotropic shielding environment of the $C\equiv C$ triple bonds.

Complex **7** is stable in benzene solution at 23 °C in the presence of excess $NHMe_2$. Exchange of free and coordinated $NHMe_2$ is rapid on the NMR time scale under these conditions. However, in the absence of added $NHMe_2$, **7** rapidly decomposes to insoluble product(s). Presumably $NHMe_2$ dissociation yields base-free $(Me_4taen)Zr(CCPh)_2$, which is unstable.

Alkylation of $(Me_4taen)ZrCl_2$. Dichloride complex **6** is a useful precursor to $(Me_4taen)ZrR_2$ complexes (Scheme 1). The reaction of **6** with $LiCH_2CMe_3$ in toluene at 23 °C affords $(Me_4taen)Zr(CH_2CMe_3)_2$ (**8**) in high yield as an orange solid. Similarly, the reaction of **6** with solid LiMe (generated by removal of solvent from a Et_2O solution) in toluene yields $(Me_4taen)ZrMe_2$ (**9**) as a yellow solid. These alkylations are highly selective; there is no evidence for alkylation at the Me_4taen imine carbons as observed in alkylations of related systems, e.g., $(Me_4taa)ZrCl_2$, $(salen)MCl_2$, and $(acen)MCl_2$ (M = Ti, Zr).[11,20f,27] Bisneopentyl complex **8** is highly soluble in aromatic solvents, while dimethyl complex **9** is only sparingly so.

Attempted Synthesis of $(Me_4taen)ZrCl_2$ via Salt Elimination. The successful alkylations of **6** prompted us to explore more direct routes to this compound. However, simple salt elimination routes to **6** are problematic. The Me_4taen^{2-} reagent $[Li(THF)]_2[Me_4taen]$ (**10**) is easily prepared as a red crystalline solid via double deprotonation of **1** with $Li[N(SiMe_3)_2]$ in THF (eq 1). Solid **10** loses THF upon standing or under vacuum, yielding the base-free reagent $Li_2[Me_4taen]$ (**11**, eq 1) as a tan powder. However, the reaction of $ZrCl_4(THF)_2$ with 1 equiv of **11** in THF or dimethoxyethane under a variety of conditions yields mixtures of **6** and

$$\begin{array}{c} (Me_4taen)H_2 \\ \mathbf{1} \\ + \\ 2\ Li[N(TMS)_2] \end{array} \xrightarrow{THF} \begin{array}{c} [Li(THF)]_2[Me_4taen] \\ \mathbf{10} \\ \big\downarrow \ -2THF \\ Li_2[Me_4taen] \\ \mathbf{11} \end{array} \qquad (1)$$

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[23] (a) Chandra, G.; Lappert, M. F. *J. Chem. Soc. A* **1968**, 1940. (b) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (c) Herrmann, W. A.; Morawietz, M. J. A.; Priermeier, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1946. (d) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. (e) Bowen, D. E.; Jordan, R. F.; Rogers, R. D.; submitted. (f) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.

[24] In some experiments **6** was contaminated by small amounts ($\leq$5%) of a C_{2v}-symmetric $(Me_4taen)Zr$ hydrolysis product (^1H NMR: δ 5.12 (s, 2H), 4.00 (m, partially obscured), 3.60 (m, 4H), 1.97 (s, 12H)). This same species is formed by addition of H_2O to **6**; however, this issue was not studied further.

[25] ^1H NMR: δ 5.04 (s, 2 H), 3.90, (m, 4 H), 3.64 (m, 4 H), 2.72 (s, 6 H), 2.01 (s, 12 H). $^{13}C\{^1H\}$ NMR: δ 164.6 (C=N), 102.7 (CH), 50.5 (CH_2), 42.7 (NMe_2), 22.8 (CH_3).

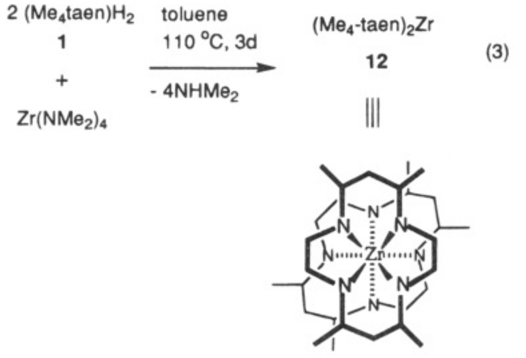
[26] (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911. (b) Sebald, A.; Fritz, P.; Wrackmeyer, B. *Spectrochim. Acta* **1985**, *41A*, 1405.

[27] Solari, E.; Floriani, C.,; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1992**, 367.

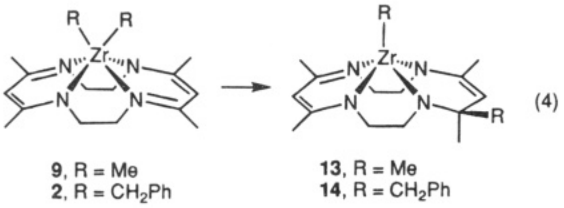
the bis-ligand sandwich compound $(Me_4taen)_2Zr$ (**12**, eq 2). Separation of these mixtures was not pursued because undesired compound **12** was generally the major component.

$$\underset{\mathbf{11}}{Li_2[Me_4taen]} + ZrCl_4(THF)_2 \longrightarrow \underset{\mathbf{6}}{(Me_4taen)ZrCl_2} + \underset{\mathbf{12}}{(Me_4tean)_2Zr} \qquad (2)$$

Synthesis of $(Me_4taen)_2Zr$ (12). Compound **12** was prepared in pure form via the amine elimination reaction of $Zr(NMe_2)_4$ and 2 equiv of **1** (eq 3). The ^1H NMR spectrum of **12** contains two Me resonances but only a single methine resonance, and the ^{13}C NMR spectrum contains two Me and imine carbon resonances but only a single methine resonance. These patterns establish that **12** adopts a square antiprismatic structure in which the Me_4taen^{2-} ligands are rotated 45° with respect to each other. Complex **12** is an analogue of $Zr(OEP)_2$, $Zr(TPP)_2$, $Ta(OEP)_2^+$, and related bisporphyrin complexes, and is structurally similar to $(por)Zr(acac)_2$ and $(por)Zr(OAc)_2$ species.[28]



Thermal Rearrangement of $(Me_4taen)ZrR_2$ Complexes. Dimethyl complex **9** undergoes facile rearrangement to a new species **13** (23 °C, 24 h, toluene), which results from net migration of a methyl group from Zr to a Me_4taen imine carbon (eq 4). The NMR spectra



of **13** are complicated but consistent with the proposed highly unsymmetrical structure. The ^{13}C spectrum contains resonances at δ 163.8, 163.5, and 100.4 which are in the range observed for the imino and methine carbons of $(Me_4taen)ZrX_2$ and $(Me_4taen)ZrX_2L$ complexes, resonances at δ 147.5 and 91.7 which are assignable to the eneamide sp^2 carbons, five resonances in the range δ 57.4−50.3 for the sp^3 carbons bonded to nitrogen, and six methyl resonances in the range 31.7−20.3. The ^1H NMR spectrum of **13** contains six methyl and two methine resonances, and a complicated pattern for the $-CH_2CH_2-$ hydrogens.[29]

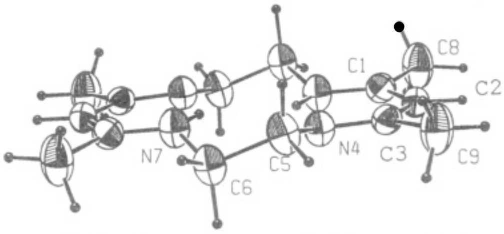


Figure 1. Molecular structure of $(Me_4taen)H_2$ (**1**).

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for $(Me_4taen)H_2$ (1)

atom[a]	*x/a*	*v/b*	*z/c*	occ	*B* (Å^2)[b]
N4	0.8969(1)	0.4055(2)	0.7865(2)	1.0	4.33(3)
N7	1.1658(1)	0.4218(2)	0.9743(2)	1.0	4.77(3)
C1	0.7125(1)	0.5759(2)	0.9170(2)	1.0	4.31(3)
C2	0.6812(1)	0.4951(2)	0.7622(2)	1.0	4.22(3)
C3	0.7711(1)	0.4177(2)	0.6966(2)	1.0	4.00(3)
C5	0.9951(3)	0.3553(3)	0.7043(3)	0.591	4.59(6)
C5′	0.9944(4)	0.3067(5)	0.7518(5)	0.409	5.23(8)
C6	1.1192(3)	0.3032(3)	0.8450(3)	0.591	4.30(5)
C6′	1.1245(4)	0.3752(6)	0.7912(5)	0.409	5.9(1)
C8	0.6046(2)	0.6652(3)	0.9570(3)	1.0	7.16(5)
C9	0.7185(2)	0.3493(3)	0.5189(2)	1.0	6.74(5)

[a] C5′ and C6′ correspond to the disordered methylene carbons. [b] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Dibenzyl complex **2** undergoes a similar but much slower rearrangement process to **14** (110 °C, 3 days, eq 4). The NMR parameters of **14** are similar to those of **13** and are consistent with a highly unsymmetrical structure. The ^1H NMR spectrum of **14** contains an AB pattern with a small geminal J_{HH} value (8.9 Hz) for the diastereotopic $Zr-CH_2$ methylene hydrogens and a high field doublet for the $ZrCH_2Ph$ ortho hydrogens (δ 6.51), which together indicate that the Zr benzyl group adopts a η^2 or η^n bonding mode.[21]

Structural Trends in $(Me_4taen)ZrX_n$ Complexes. X-ray diffraction studies have been carried out on the parent macrocycle **1**, the Me_4taen^{2-} salt **10**, and several representative $(Me_4taen)ZrX_n$ complexes to investigate how deprotonation and metal complexation influence the structure and conformation of the macrocycle and to probe metal geometries.

The structure of the free macrocycle $(Me_4taen)H_2$ (**1**) resides around a center of inversion and is disordered between two orientations, one of which is shown in Figure 1; atomic coordinates and metrical parameters are listed in Tables 1 and 2. The orientations differ in the position of the imine hydrogen atoms (on N7 vs N4) and in the conformation of the $-CH_2CH_2-$ sectors, and correspond to two of the several possible tautomeric forms of **1** (Chart 1). The eight N4, C5, C6, and N7 atoms adopt a chair-like conformation (N4−C5−C6−N7 dihedral angle 54.1°), and the four nitrogens are coplanar. The two diiminato sectors are planar and are

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(28) (a) Kim, K.; Lee, W. S.; Kim, H.; Cho, S.; Girolami, G. S.; Gorlin, P. A.; Suslick, K. S. *Inorg. Chem.* **1991**, *30*, 2652. (b) Buchler, J. W.; De Cian, A.; Fischer, J.; Hammerschmitt, P.; Weiss, R. *Chem. Ber.* **1991**, *124*, 1051. (c) Kim, H. J.; Whang, D.; Kim, J.; Kim, K. *Inorg. Chem.* **1992**, *31*, 3882. (d) Buchler, J. W.; De Cian, A.; Elschner, S.; Fischer, J.; Hammerschmitt, P.; Weiss, R. *Chem. Ber.* **1992**, *125*, 107. (e) Dawson, D. Y.; Brand, H.; Arnold, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 9797.

(29) The rate of the rearrangement of **9** to **13** in toluene is unaffected by the addition of small amounts of THF (1 equiv) and **13** does not coordinate THF. Thus the methyl migration appears not to be ligand induced. The decomposition of bisalkynyl complex **7** may involve a similar rearrangement.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(Me_4taen)H_2$ (1)

N4–C3	1.315(2)	C1–C8	1.510(3)
N4–C5	1.464(7)	C2–C3	1.405(7)
N7–C1[a]	1.322(2)	C3–C9	1.505(3)
N7–C6	1.471(4)	C5–C6	1.53(1)
C1–C2	1.396(2)		
C3–N4–C5	121.0(3)	N4–C3–C9	120.9(2)
C2–C1–C8	118.6(2)	N4–C5–C6	109.1(4)
C1–C2–C3	126.2(2)	N7–C6–C5	109.5(4)
N4–C3–C2	121.4(1)	C2–C3–C4	117.7(2)
C6–N7–C1[a]	122.2(3)	C8–C1–N7[a]	119.9(2)
C2–C1–N7[a]	121.5(1)		

[a] Symmetry code = $2 - x, 1 - y, 2 - z$.

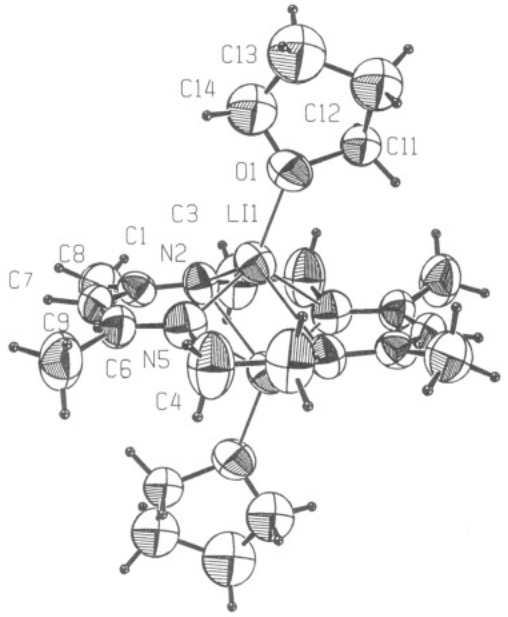

Figure 2. Molecular structure of $[Li(THF)]_2[Me_4taen]$ (**10**).

tipped by ca. 10° in opposite directions relative to the N_4 plane. An analysis of key dihedral angles indicates that the N–H bond and the nitrogen σ-lone pair in one diiminato unit point ca. 5° out of the N_4-plane, while those on the other diiminato unit point ca. 5° out of the N_4-plane in the opposite direction. The nitrogen-to-center distance (1.95 Å), which defines the size of the binding pocket, is intermediate relative to those of $(Me_4taa)H_2$ (1.90 Å) and porphyrin ligands (2.04 Å).[10f]

The molecular structure of $[Li(THF)]_2[Me_4taen]$ (**10**, Figure 2, Tables 3 and 4) consists of a Me_4taen^{2-} dianion capped on both faces by $Li(THF)^+$ cations. Compound **10** resides around a center of inversion. The conformation of the macrocycle is similar to that in **1**. The large thermal parameters for C3 and C4 suggest that the CH_2-CH_2 units are disordered as in **1**; however this disorder was not resolved. The bond distances and angles within the macrocycle are essentially unchanged from the corresponding parameters in **1**. The geometry of the Li^+ cations may be described as distorted square pyramidal; each Li^+ cation coordinates one THF and interacts strongly with the nitrogens of one diiminato unit (average Li–N, 2.01 Å) and weakly with the nitrogens of the other (average Li–N, 2.42 Å). Similar though more symmetric square pyramidal structures have been observed in Li^+ crown ether complexes.[30] The structure of **10** contrasts with that of the $Li_2(THF)_4(OEP)$, which crystallizes as discrete $Li(THF)_4^+$ and $Li(OEP)^-$ ions.[31]

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($Å^2$) for $[Li(THF)]_2[Me_4taen]$ (10)

atom[a]	*x/a*	*y/b*	*z/c*	occ	*B* ($Å^2$)[b,c]
O1	0.1820(7)	0.6945(5)	0.9919(6)	1.0	8.9(2)
N2	−0.1466(8)	0.5715(6)	1.0895(6)	1.0	6.8(2)
N5	0.1318(8)	0.4599(6)	1.1441(6)	1.0	7.3(2)
C1	−0.1612(9)	0.5565(6)	1.2014(7)	1.0	6.2(2)
C3	−0.282(1)	0.6025(9)	1.0082(9)	1.0	10.3(3)
C4	0.251(1)	0.387(1)	1.1124(9)	1.0	11.3(4)
C6	0.087(1)	0.4565(7)	1.2515(7)	1.0	7.1(2)
C7	−0.046(1)	0.5087(7)	1.2800(7)	1.0	6.7(2)
C8	−0.310(1)	0.5829(8)	1.2544(9)	1.0	9.4(3)
C9	0.175(1)	0.3875(9)	1.3464(9)	1.0	11.2(4)
C11	0.162(3)	0.747(2)	0.871(2)	0.4	6.8(5)*
C12	0.323(2)	0.803(1)	0.879(1)	0.8	10.7(4)*
C13	0.338(2)	0.834(1)	1.015(11)	0.8	13.5(5)*
C14	0.213(3)	0.775(2)	1.066(2)	0.4	10.4(8)*
C15	0.248(3)	0.709(2)	0.878(2)	0.4	7.6(6)*
C18	0.304(3)	0.753(2)	1.073(2)	0.4	6.9(5)*
C19	0.324(6)	0.688(5)	0.962(4)	0.2	10(1)*
C20	0.392(4)	0.806(3)	0.951(3)	0.2	3.5(7)*
C21	0.288(4)	0.864(3)	0.955(3)	0.2	6(1)*
C22	0.133(7)	0.796(5)	0.974(5)	0.2	11(2)*
LI1	0.065(2)	0.572(1)	1.026(1)	1.0	7.0(4)

[a] C11–C22 correspond to the disordered THF; see Experimental Section. [b] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [c] Starred values denote atoms refined isotropically.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Li(THF)]_2[Me_4taen]$ (10)

O1–Li1	1.92(2)	N5–Li1	2.00(2)
N2–Li1	2.02(2)	N5–Li1[a]	2.43(2)
N2–Li1[a]	2.41(2)		
O1–Li1–N2	126(1)	N2–Li1–N5	88(1)
O1–Li1–N2[a]	109(1)	N2–Li1–N2[a]	121(1)
O1–Li1–N5	127(1)	N2–Li1–N5[a]	73(1)
O1–Li1–N5[a]	108(1)	N5–Li1–N5[a]	121(1)

[a] Symmetry code = $-x, 1 - y, 2 - z$.

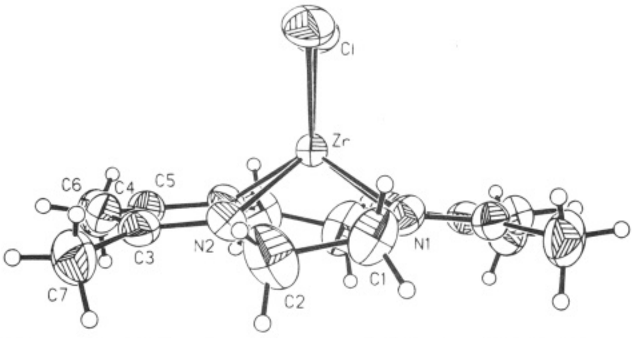

Figure 3. Molecular structure of $(Me_4taen)ZrCl_2$ (**6**).

The dichloride complex $(Me_4taen)ZrCl_2$ (**6**, Figure 3, Tables 5 and 6) adopts a trigonal prismatic structure in which the chloride ligands occupy adjacent edge sites. The eight N1, C1, C2, and N2 atoms of the macrocycle adopt a twist-boat-like conformation which orients the four nitrogen σ lone pairs toward the same side of the macrocycle, as required for out-of-plane Zr coordination. The bond distances and angles within the macrocycle are very similar to those in **1** and **10**; however, the ligand is somewhat flattened as assessed by the N1–C1–C2–N2 dihedral angle (19.9°). The structure is

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[30] For reviews see (a) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (b) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1992**, *37*, 47.

[31] (a) Arnold, J.; Dawson, D. Y.; Hoffman, C. G. *J. Am. Chem. Soc.* **1993**, *115*, 2707. (b) Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $(Me_4taen)ZrCl_2$ (6)

atom	*x/a*	*y/b*	*z/c*	$U(eq)^a$
Zr	5000	7082(1)	2500	30(1)
Cl	6465(1)	8441(1)	2012(1)	58(1)
N1	5450(3)	6409(2)	992(2)	38(1)
N2	6882(3)	6333(2)	2998(2)	37(1)
C1	6899(4)	6256(4)	960(3)	55(1)
C2	7607(5)	6035(4)	2072(4)	69(1)
C3	7476(4)	6246(3)	4024(3)	41(1)
C4	6778(4)	6349(3)	4938(3)	45(1)
C5	5386(4)	6345(3)	4935(3)	42(1)
C6	4868(5)	6224(4)	6036(3)	61(1)
C7	8949(4)	6008(4)	4252(4)	61(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $(Me_4taen)ZrCl_2$ (6)

Zr−N1	2.156(3)	Zr−Cl	2.503(1)
Zr−N2	2.171(3)		
$N1-Zr-N1^a$	128.7(2)	$N1-Zr-N2^a$	79.61(11)
N1−Zr−Cl	86.24(9)	N1−Zr−N2	76.45(12)
$Cl-Zr-Cl^a$	82.34(6)	$N2-Zr-N2^a$	122.8(2)
$Cl-Zr-N1^a$	135.85(9)	$N2-Zr-Cl^a$	143.84(8)
N2−Zr−Cl	85.03(8)		

[a] Symmetry code = $1 - x, y, 0.5 - z$.

Table 7. Zr−Cl Distances and Cl−Zr−Cl Angles in Representative Zr(IV) Dichloride Complexes

compd	Zr−Cl (Å)	Cl−Zr−Cl (deg)	ref
$Cp\{N(SiMe_3)_2\}ZrCl_2$	2.380(1), 2.398(1)	97.53(5)	33c
$Cp^*(\eta^3\text{-allyl})ZrCl_2$	2.429(2)	96.12(9)	33e
$(msal)_2ZrCl_2{}^a$	2.435(2), 2.440(3)	97.9(1)	33b
Cp_2ZrCl_2	2.436(5), 2.446(5)	97.1(2)	33a
$(OEP)ZrCl_2$	2.459(1), 2.473(1)	81.70(3)	3c
$(acen)ZrCl_2$	2.465(1), 2.482(1)	87.2(1)	33b
$(Me_4taa)ZrCl_2$	2.490(2), 2.493(2)	85.6(1)	10d
$(COT)ZrCl_2(THF)$	2.496(1)	87.2(1)	33d
$(Me_4taen)ZrCl_2$ (**6**)	2.503(1)	82.34(6)	this work

[a] msal = *N*-methylsalicylideneaminate.

distorted from an ideal trigonal prism by a slight twist ($\Theta = 6°$),[32] which is also reflected in a slight relative twisting of the two diiminato units (N−N−N−N dihedral angle, 4.4°). The structure of **6** is similar to that of $(Me_4taa)ZrCl_2$.[10d] The Zr−N distances in **6** (2.164 Å, average) and $(Me_4taa)ZrCl_2$ (2.166 Å, average) are nearly identical, while the Zr to N_4-plane distance in **6** (0.987 Å) is slightly shorter than that in $(Me_4taa)ZrCl_2$ (1.070 Å) due to the larger pocket size of Me_4taen^{2-} vs Me_4taa^{2-}. For comparison, in $(OEP)ZrCl_2$ the Zr−N distance is longer (average 2.221 Å) and the Zr to N_4-plane distance is shorter (0.93 Å), as a result of the larger pocket size (16- vs 14-membered macrocycle).[3c] The Zr−Cl distances in **6** are at the extreme long end of the range observed for other cis $L_nZr^{IV}\,Cl_2$ complexes (Table 7).[33] This suggests that net electron donor ability of Me_4taen^{2-} is comparable to or greater than that of other ancillary ligand sets such as OEP^{2-}, $Cp_2{}^{2-}$, $Cp(amido)^{2-}$, and $N_2O_2{}^{2-}$ Schiff bases.

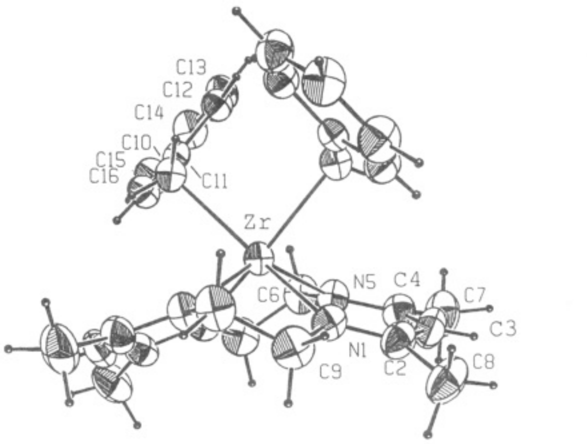

Figure 4. Molecular structure of $(Me_4taen)Zr(CH_2Ph)_2$ (**2**).

Table 8. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(Me_4taen)Zr(CH_2Ph)_2$ (2)

$atom^a$	*x/z*	*y/b*	*z/c*	$B\ (Å^2)^b$
Zr	1.000	0.23679(2)	0.250	3.516(5)
N1	0.9050(1)	0.3269(1)	0.2992(1)	4.42(4)
N5	0.9546(1)	0.3005(2)	0.1076(1)	4.61(4)
C2	0.8418(1)	0.3569(2)	0.2420(2)	5.07(5)
C3	0.8294(1)	0.3475(2)	0.1393(2)	5.73(6)
C4	0.8824(1)	0.3265(2)	0.0747(2)	5.19(6)
C6	1.0152(2)	0.2953(2)	0.0435(2)	5.54(6)
C7	0.8558(2)	0.3361(3)	−0.0347(2)	7.38(8)
C8	0.7788(2)	0.4083(2)	0.2886(3)	7.33(8)
C9	0.9161(2)	0.3523(2)	0.4050(2)	5.73(6)
C10	1.0933(1)	0.1127(2)	0.2810(2)	4.19(5)
C11	1.1193(1)	0.0814(2)	0.1879(2)	3.79(4)
C12	1.0820(1)	0.0078(2)	0.1275(2)	4.48(5)
C13	1.1050(2)	−0.0185(2)	0.0383(2)	5.36(6)
C14	1.1656(2)	0.0292(2)	0.0056(2)	5.87(6)
C15	1.2037(1)	0.1010(2)	0.0631(2)	5.80(6)
C16	1.1816(1)	0.1272(2)	0.1526(2)	4.81(5)
C31	0.5386(3)	0.2159(6)	0.2724(5)	7.9(2)
C32	0.4733(4)	0.2557(4)	0.2341(6)	7.7(2)
C33	0.3988(3)	0.1976(5)	0.1854(5)	7.0(2)
C34	0.4063(3)	0.1056(5)	0.1873(5)	7.5(2)
C35	0.4783(4)	0.0629(4)	0.2313(6)	8.1(2)
C36	0.5408(4)	0.1174(5)	0.2732(5)	8.3(2)
C37	0.5940(6)	0.2812(7)	0.3054(7)	11.1(3)

[a] C31−C37 correspond to the toluene solvent molecule. [b] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table 9. Selected Bond Distances (Å) and Angles (deg) for $(Me_4taen)Zr(CH_2Ph)_2$ (2)

Zr−N1	2.244(2)	C11−C16	1.400(3)
Zr−N5	2.178(2)	C12−C13	1.387(4)
Zr−C10	2.338(3)	C13−C14	1.371(4)
C10−C11	1.478(3)	C14−C15	1.363(4)
C11−C12	1.395(4)	C15−C16	1.384(4)
N1−Zr−N5	82.13(8)	Zr−C10−C11	110.0(2)
N1−Zr−C10	149.82(8)	$C10-Zr-C10^a$	88.4(1)
N5−Zr−C10	127.09(8)	$N1-Zr-N1^a$	114.27(8)
$N5-Zr-N5^a$	133.46(8)		

[a] Symmetry code = $2 - x, y, 0.5 - z$.

The dibenzyl complex $(Me_4taen)Zr(CH_2Ph)_2$ (**2**, Figure 4, Tables 8 and 9), which crystallizes as a toluene solvate, adopts an out-of-plane cis structure with normal (undistorted) benzyl ligands (Zr−C−Ph angle, 110.0(2)°). The Zr coordination geometry is best described as a distorted trigonal prism (twist angle $\Theta = 17°$) in which the benzyl ligands occupy adjacent edge sites. The larger twist angle (vs **6**) results in a more pronounced relative twisting of the two diiminato units (N−N−N−N

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(32) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, NY, 1993; p 488−490.

(33) (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290. (b) Corazza, F.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1335. (c) Coalter, J. N.; Pupi, R. M.; Petersen, J. L. unpublished results. (d) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1975**, *14*, 3053. (e) Vance, P. J.; Prins, T. J.; Hauger, B. E.; Silver, M. E.; Wemple, M. E.; Pederson, L. M.; Kort, D. A.; Kannisto, M. R.; Geerligs, S. J.; Kelly, R. S.; McCandless, J. J.; Huffman, J. C.; Peters, D. G. *Organometallics* **1991**, *10*, 917.

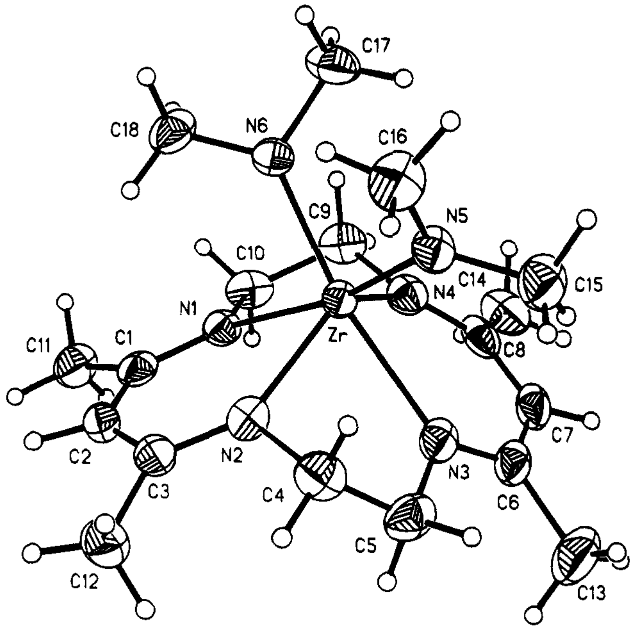

Figure 5. Molecular structure of $(Me_4taen)Zr(NMe_2)_2$ (**4**).

Table 10. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters ($Å^2$ × 10^3) for $(Me_4taen)Zr(NMe_2)_2$ (4)

atom[a]	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[b]
Zr	6619(1)	6019(1)	8137(1)	25(1)
N(1)	5633(3)	4512(2)	6412(2)	30(1)
N(2)	8334(3)	6854(2)	7256(2)	31(1)
N(3)	6249(3)	7962(3)	8142(2)	33(1)
N(4)	4018(3)	5461(3)	7895(2)	34(1)
N(5)	7896(3)	7193(3)	9738(2)	35(1)
N(6)	6881(3)	4349(3)	8429(2)	31(1)
C(1)	6322(4)	4263(3)	5568(2)	34(1)
C(2)	7817(4)	5099(3)	5549(3)	35(1)
C(3)	8683(4)	6353(3)	6288(3)	33(1)
C(4)	9009(4)	8286(3)	7889(3)	39(1)
C(5)	7658(4)	8862(3)	7962(3)	43(1)
C(6)	5018(4)	8371(3)	8294(3)	37(1)
C(7)	3534(4)	7529(4)	8331(3)	41(1)
C(8)	3023(4)	6167(4)	8053(3)	38(1)
C(9)	3407(4)	4011(3)	7352(3)	39(1)
C(10)	3990(4)	3647(3)	6286(3)	37(1)
C(11)	5489(5)	3079(3)	4545(3)	45(1)
C(12)	10019(4)	7178(4)	5935(3)	46(1)
C(13)	5106(5)	9755(4)	8397(3)	60(1)
C(14)	1246(4)	5455(4)	7882(3)	51(1)
C(15)	7670(5)	8370(4)	10449(3)	50(1)
C(16)	9297(4)	7027(4)	10248(3)	46(1)
C(17)	6587(4)	4099(4)	9424(3)	45(1)
C(18)	7130(4)	3197(3)	7685(3)	43(1)
C(19)	9475(22)	9420(7)	4063(8)	120(4)
C(20)	8199(41)	9684(27)	4021(27)	171(13)
C(21)	7596(67)	10296(36)	5062(45)	130(16)
C(22)	9196(33)	10846(14)	6006(19)	99(5)
C(23)	10853(47)	9853(11)	4853(19)	144(11)
C(24)	11998(68)	9381(37)	4592(36)	115(12)

[a] C19–C24 correspond to the disordered toluene molecule. C19 is present at full occupancy, and C20–C24 are present at half occupancy. [b] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 11. Selected Bond Distances (Å) and Angles (deg) for $(Me_4taen)Zr(NMe_2)_2$ (4)

Zr–N6	2.108(3)	Zr–N5	2.117(3)
Zr–N4	2.193(3)	Zr–N2	2.197(3)
Zr–N1	2.285(3)	Zr–N3	2.306(3)
N6–Zr–N5	88.22(10)	N6–Zr–N4	98.87(10)
N5–Zr–N4	115.93(10)	N6–Zr–N2	114.90(10)
N5–Zr–N2	98.73(10)	N4–Zr–N2	132.16(10)
N6–Zr–N1	81.97(10)	N5–Zr–N1	167.42(9)
N4–Zr–N1	73.62(9)	N2–Zr–N1	78.52(9)
N6–Zr–N3	169.32(9)	N5–Zr–N3	83.67(10)
N4–Zr–N3	78.60(10)	N2–Zr–N3	73.36(10)
N1–Zr–N3	106.97(9)	C16–N5–Zr	124.1(2)
C15–N5–Zr	126.7(2)	C18–N6–Zr	128.5(2)
C17–N6–Zr	122.5(2)		

dihedral angle, 14.8°), greater puckering of the NCH_2CH_2N units (N1–C9–C6′–N5′ dihedral angle, 42.8°), and unequal Zr–N bond distances (2.244(2) and 2.178(2) Å). The average Zr–N distance (2.21 Å) and the Zr–(N_4-plane) distance (1.038 Å) in **2** are somewhat longer than in **6**, consistent with replacement of the chloride ligands by the stronger σ-donor benzyl ligands. The Zr–C distance (2.338(3) Å) is slightly shorter than that in $(Me_4taa)Zr(CH_2Ph)_2$ (2.37(1) Å),[11] and, consistent with the trend in Zr–Cl distances noted above, is at the long end of the range spanned by other Zr^{IV} η^1-benzyl complexes (ca. 2.25–2.37 Å).[34] However, detailed comparisons of M–benzyl bond distances are complicated by steric factors and the possibility of Zr–η^n-benzyl interactions.

The molecular structure of $(Me_4taen)Zr(NMe_2)_2$ (**4**, Figure 5, Tables 10 and 11), which crystallizes as a toluene hemisolvate, is quite different from those of **6** and **2**. Complex **4** adopts an out-of-plane cis structure, but the Me_4taen^{2-} ligand is significantly folded such that the angle between the diiminato planes is 53.0°. The zirconium coordination geometry is best described as distorted octahedral; two trans angles are nearly 180° (N6–Zr–N3, 169.32(9)°; N5–Zr–N1, 167.42(9)°) while the third is significantly contracted (N2–Zr–N4, 132.2(1)°). There is clear evidence for π-donation from the $-NMe_2$ ligands in **4**. The amide nitrogens are flat (sum of angles around N, 359.5°), and the $Zr-NMe_2$ distances (2.11 Å, average) are in the range observed for other unsaturated Zr(IV) amide complexes in which N–Zr π-donation is present (ca. 2.04–2.17 Å).[35] The $Zr-N_{macrocycle}$ bonds trans to the $-NMe_2$ ligands are significantly longer (average, 2.30 Å) than the cis $Zr-N_{macrocycle}$ bonds (average 2.20 Å). This unsymmetrical bonding reflects a balancing of the trans influence of the $-NMe_2$ ligands and the structural constraints of the macrocycle.

The structural differences between **4** (distorted octahedral) and **2** and **6** (distorted trigonal prismatic) may be traced to electronic factors.[36] Recent work has shown that trigonal prismatic structures are favored over octahedral structures for some d^0 ML_6 species (e.g., $ZrMe_6^{2-}$ and WMe_6).[37] Mixing of empty d (e′) orbitals

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(34) Representative examples of $Zr^{IV}-(\eta^1$-benzyl) complexes and average Zr–C distances. (a) $(OAr)_2Zr(CH_2Ph)_2$, 2.258(8) Å: Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P. *Organometallics* **1985**, *4*, 902. (b) $Cp_2ZrBr(CH_2Ph)$, 2.29(1) Å: Randall, C. R.; Silver, M. E.; Ibers, J. A. *Inorg. Chim. Acta* **1987**, *128*, 39. (c) (4,7-F_2-indenyl)$_2$-$Zr(CH_2Ph)_2$, 2.294(2) Å: Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098. (d) $Cp\{\eta^6-PhCH_2B^{(-)}(C_6F_5)_3\}Zr^{(+)}(CH_2Ph)_2$, 2.29(2) Å: Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (e) $(EBTHI)Zr(CH_2Ph)_2$, 2.314(4) Å: Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539. (f) (dmpe)(η^2-$CH_2Ph)Zr(CH_2Ph)_3$, 2.346 Å: Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2789.

(35) Representative Zr(IV) amide complexes and average Zr–N distances. (a) $Zr(NMe_2)_4$, 2.07 Å: Hagen, K.; Holwill, C. J.; Rice, D. A.; Runnacles, J. D. *Inorg. Chem.* **1988**, *27*, 2032. (b) $(Me_2N)_2Zr(\mu-N^tBu)_2Zr(NMe_2)_2$, 2.06 Å: Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030. (c) *rac*-$(EBI)Zr(NMe_2)_2$, 2.06 Å: Diamond, G. M.; Petersen, J. L.; Jordan, R. F. unpublished results. (d) $Cp_2Zr(NC_4H_4)_2$, 2.17 Å: Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368.

(36) Inspection of space-filling computer models of **2**, **4**, and **6** indicates that these compounds are not highly crowded. In particular, in **4** there are no interligand H–H contacts <2.5 Å (closest contacts H16B–H17A, 2.67 Å, and H9B–H17C, 2.54 Å).

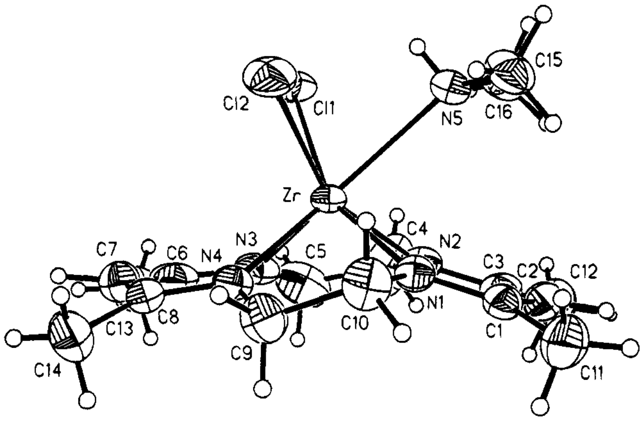

Figure 6. Molecular structure of (Me$_4$taen)ZrCl$_2$(NHMe$_2$) (**5**).

with filled M−L σ-bonding (e′) orbitals is possible in the trigonal prismatic geometry and results in net stabilization versus an octahedral structure (second-order Jahn−Teller distortion).[38] However, factors which increase the energy gap between the empty d and filled M−L σ-bonding orbitals (ligand to metal π-donation or strong σ-donation) weaken the mixing and favor octahedral geometry.[39] The distorted trigonal prismatic structures of **6** and **2** are favored by the conformational preference of the Me$_4$taen^{2-} ligand and the weak π-donor ability of the chloride and benzyl ligands.[40,41] In **4**, destabilization of the metal d orbitals by strong π-donation from the amide ligands favors an octahedral structure, and the Me$_4$taen^{2-} ligand distorts accordingly. Synthetic and theoretical studies to probe the electronic structures of these compounds in more detail are in progress.[42]

The seven-coordinate amine adduct (Me$_4$taen)ZrCl$_2$(NHMe$_2$) (**5**, Figure 6, Tables 12 and 13) adopts an out-of-plane structure with a tripodal arrangement of chloride and amine ligands and a side-capped trigonal prismatic geometry around Zr. As a result of the higher coordination number, the Zr−N$_{\text{macrocycle}}$ (average, 2.21 Å), Zr−(N$_4$-plane) (1.104 Å), and Zr−Cl (2.565(1) Å) distances are slightly longer in **5** than in base-free analogue **6**. Complex **5** is structurally related to (TPP)ZrCl$_2$(THF), Hf(OEP)Cl$_2$(H$_2$O), [NBu$_4$][Hf(OEP)(P$_3$O$_9$)],[4] {(TPP)Zr}$_2$(μ-OH)$_2$(μ-O),[43] and U(TPP)Cl$_2$(THF),[44] all of which are out-of-plane porphyrin complexes with three ligands on the top face. The structures of these (N$_4$-macrocycle)MX$_3$ species differ significantly from the structures of Cp$_2$ML$_3$ species, in which the L ligands are invariably arranged in a meridional manner.[45]

Table 12. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for (Me$_4$taen)ZrCl$_2$(NHMe$_2$) (5)

atom	x/a	y/b	z/c	B(eq)[a]
Zr	0.24646(4)	0.04235(4)	0.25596(3)	2.11
Cl1	0.2554(1)	−0.1120(1)	0.4220(1)	3.93
Cl2	0.4884(1)	−0.0536(2)	0.2297(1)	4.32
N1	0.3064(4)	0.2416(4)	0.1586(3)	2.46
N2	0.1137(4)	0.1983(4)	0.3155(3)	2.94
N3	0.0065(4)	−0.0891(4)	0.2436(3)	3.11
N4	0.1905(4)	−0.0461(4)	0.0866(3)	2.72
N5	0.4576(4)	0.2013(5)	0.3910(3)	3.02
C1	0.3089(5)	0.3890(5)	0.1797(3)	2.74
C2	0.2421(5)	0.4414(5)	0.2612(4)	3.23
C3	0.1423(5)	0.3515(5)	0.3199(3)	3.20
C4	−0.0088(8)	0.1170(7)	0.3698(5)	6.37
C5	−0.0867(6)	−0.0328(7)	0.3156(5)	4.96
C6	−0.0465(5)	−0.2280(6)	0.1952(4)	3.79
C7	0.0138(6)	−0.2792(5)	0.1108(4)	4.12
C8	0.1123(6)	−0.1867(5)	0.0512(4)	3.51
C9	0.2654(6)	0.0501(5)	0.0104(4)	3.74
C10	0.3686(6)	0.1972(5)	0.0650(4)	3.69
C11	0.3830(6)	0.5102(6)	0.1117(4)	4.17
C12	0.0640(7)	0.4363(7)	0.3918(5)	5.42
C13	−0.1852(7)	−0.3347(7)	0.2279(6)	5.90
C14	0.1188(7)	−0.2490(7)	−0.0594(4)	4.97
C15	0.5848(6)	0.3115(6)	0.3548(4)	4.26
C16	0.4174(6)	0.2667(6)	0.4886(4)	4.46

[a] $B(\text{eq}) = (8\pi^2/3)[a^2U_{11}(a^*)^2 + b^2U_{22}(b^*)^2 + c^2U_{33}(c^*)^2 + ab(\cos\gamma)U_{12}a^*b^* + ac(\cos\beta)U_{13}a^*c^* + bc(\cos\alpha)U_{23}b^*c^*]$.

Table 13. Selected Bond Distances (Å) and Angles (deg) for (Me$_4$taen)ZrCl$_2$(NHMe$_2$) (5)

Zr−Cl1	2.565(1)	Zr−Cl2	2.565(1)
Zr−N1	2.222(3)	Zr−N2	2.207(3)
Zr−N3	2.193(3)	Zr−N4	2.212(3)
Zr−N5	2.497(4)	N5−C15	1.475(6)
N5−C16	1.477(6)		
Cl1−Zr−Cl2	83.68(4)	Cl1−Zr−N1	157.16(9)
Cl2−Zr−N1	93.17(9)	Cl1−Zr−N2	95.4(1)
Cl2−Zr−N2	156.6(1)	N1−Zr−N2	78.6(1)
Cl1−Zr−N3	77.3(1)	Cl2−Zr−N3	128.7(1)
N1−Zr−N3	120.8(1)	N2−Zr−N3	73.2(1)
Cl1−Zr−N4	127.9(1)	Cl2−Zr−N4	77.96(9)
N1−Zr−N4	72.9(1)	N2−Zr−N4	119.2(1)
N3−Zr−N4	77.4(1)	Cl1−Zr−N5	74.4(1)
Cl2−Zr−N5	75.5(1)	N1−Zr−N5	82.9(1)
N2−Zr−N5	81.7(1)	N3−Zr−N5	139.8(1)
N4−Zr−N5	142.8(1)	Zr−N5−C15	119.4(3)
Zr−N5−C16	119.1(3)		

Conclusions

Alkane and amine elimination reactions of (Me$_4$taen)H$_2$ (**1**) and ZrR$_4$ or Zr(NMe$_2$)$_4$ provide convenient access to (Me$_4$taen)ZrX$_2$ complexes (X = alkyl, benzyl, NMe$_2$). Additionally, (Me$_4$taen)ZrCl$_2$ is formed by protonolysis of (Me$_4$taen)Zr(NMe$_2$)$_2$ with [HNHMe$_2$]Cl followed by vacuum thermolysis and can be alkylated to yield (Me$_4$taen)ZrR$_2$ complexes.

(Me$_4$taen)ZrX$_2$ complexes adopt out-of-plane, cis structures because the Me$_4$taen^{2-} pocket size is too small to accommodate a Zr(IV) center in the N$_4$-plane. The flexibility of the Me$_4$taen^{2-} ligand allows a variety of metal geometries in these complexes. The solid state structures of (Me$_4$taen)ZrX$_2$ complexes range from nearly ideal trigonal prismatic for (Me$_4$taen)ZrCl$_2$ (**6**) to distorted octahedral for (Me$_4$taen)Zr(NMe$_2$)$_2$ (**4**).

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(37) (a) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114. (b) Haaland, A.; Hammel, A.; Rypdal, K.; Volden, H. V. *J. Am. Chem. Soc.* **1990**, *112*, 4547.

(38) (a) Kang, S. K.; Albright, T. A.; Eisenstein, O. *Inorg. Chem.* **1989**, *28*, 1611. (b) Demolliens, A.; Jean, Y.; Eisenstein, O. *Organometallics* **1986**, *5*, 1457. (c) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.

(39) Or, put in an alternative way, distortion of a trigonal prismatic structure toward an octahedral structure lowers the energies of the empty e′ (d) orbitals, favoring π-donation.[38a]

(40) (a) Zhu, L.; Kostic, N. M. *J. Organomet. Chem.* **1987**, *335*, 395. (b) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389. (c) Chisholm, M. H.; Clark, D. L. *Comments Inorg. Chem.* **1987**, *6*, 23. (d) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190. (e) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

(41) The greater distortion from trigonal prismatic toward octahedral geometry of **2** versus **6** may be due to the greater σ-donor ability of the benzyl versus the chloride ligands.

(42) In particular, the π-donor ability of Me$_4$taen^{2-} needs to be probed.

(43) Kim, H.-J.; Whang, D.; Do, Y.; Kim, K. *Chem. Lett.* **1993**, 807.

(44) Girolami, G. S.; Milam, S. N.; Suslick, K. S. *Inorg. Chem.* **1987**, *26*, 343.

(45) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and Organo-Hafnium Compounds*; John Wiley: New York, 1986.

Comparison of the ligand conformations in **1**, $[Li(THF)]_2$-$[Me_4taen]$ (**10**), and $(Me_4taen)ZrX_2$ complexes suggests that the trigonal prismatic extreme is favored by the Me_4taen^{2-} ligand, but that π-bonding from the X ligands can override this preference and distort the structure toward octahedral.

The long Zr–Cl bond distances observed in **6** suggest that the Me_4taen^{2-} is a stronger net electron donor than Cp_2^{2-} and other ancillary ligand sets commonly used in early metal chemistry. However, the formation of the seven-coordination amine adducts $(Me_4taen)ZrX_2(NHMe_2)$ (X = Cl, CCPh) indicate that $(Me_4taen)ZrX_2$ species are effectively more Lewis acidic than Cp_2ZrX_2 species, which do not form such amine adducts. The relatively open structure of the $(Me_4taen)ZrX_2$ complexes favors coordination of an additional ligand.

Dialkyl species **2** and **9** rearrange via alkyl migration to a Me_4taen imine carbon. This reaction is favored by the electrophilic character of the Me_4taen imine carbons, and represents a potential obstacle to general application of the Me_4taen^{2-} ligand in early metal chemistry. Efforts to modify the ligand to disfavor this process are in progress.

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 ketyl, except for chlorinated solvents, which were distilled from activated molecular sieves (3 Å) or P_2O_5. $(Me_4taen)H_2$ (**1**),[14] $Zr(CH_2Ph)_4$,[46] $Zr(CH_2SiMe_3)_4$,[47] $ZrCl_4(THF)_2$,[48] and $Zr(NMe_2)_4$[23d,49] were prepared by literature procedures. NMR spectra were recorded on a Bruker AC-300 or an AMX 360 spectrometer in sealed or Teflon-valved tubes at ambient probe temperature unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. Coupling constants *J* are in hertz. Elemental analyses were performed by E & R Microanalytical Laboratory, Inc.

$(Me_4taen)Zr(CH_2Ph)_2$ (2). A slurry of **1** (0.58 g, 2.3 mmol) and $Zr(CH_2Ph)_4$ (1.1 g, 2.3 mmol) in pentane (50 mL) was stirred for 3 h at 23 °C. The slurry was filtered to yield an orange solid, which was dried under high vacuum overnight (0.87 g, 87%). The product may be recrystallized from toluene/pentane. This compound strongly retains toluene from the recrystallization solvent and, even when toluene is not used for recrystallization, from the toluene byproduct of the synthesis. ^1H NMR (C_6D_6): δ 7.26–6.88 (m, Ph), 4.89 (s, 2 H, NC=C*H*–CN), 2.95 (m, 4H, NCH_2), 2.86 (m, 4H, NCH_2), 2.70 (s, 4H, $ZrCH_2$), 1.54 (s, 12H). ^1H NMR (THF-d_8): δ 6.99 (t, 4H), 6.89 (d, 4H), 6.55 (t, 2H), 5.04 (s, 2H), 3.42 (m, 4H, NCH_2), 3.19 (m, 4H, NCH_2), 2.11 (s, 4H, $ZrCH_2$), 1.94 (s, 12H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 165.4 (C=N), 150.4 (*i*-Ph), 128.0 (*o*- or *m*-Ph), 127.1 (*m*- or *o*-Ph), 119.0 (*p*-Ph), 102.0 (NC=*C*H–CN), 65 ($ZrCH_2$), 50.4 (NCH_2), 22.7. Anal. Calcd for $C_{28}H_{36}N_4Zr$: C, 64.69; H, 6.98; N, 10.78. Found: C, 63.20; H, 6.70; N, 11.66.[50]

$(Me_4taen)Zr(CH_2SiMe_3)_2$ (3). A slurry of **1** (1.5 g, 6.2 mmol) and $Zr(CH_2SiMe_3)_4$ (2.9 g, 6.6 mmol) in pentane (50 mL) was stirred for 3 h at 23 °C. The solvent was removed under vacuum, and the resulting brown solid was slurried in 25 mL of benzene and centrifuged. The supernate was decanted, and this process was repeated. The supernates were combined and evaporated under vacuum. The resulting brown solid was washed with cold pentane and dried under high vacuum for 20 min (2.4 g, 76%). The product may be recrystallized from toluene/pentane. ^1H NMR (C_6D_6): δ 4.94 (s, 2H, NC=C*H*–CN), 3.5 (m, 4H, NCH_2), 3.0 (m, 4H, NCH_2), 1.64 (s, 12H), 0.70 (s, 4H, $ZrCH_2$), 0.36 (s, 18H). $^{13}C\{gated\text{-}^1H\}$ NMR (C_6D_6): δ 164.7 (m, *C*=N), 102.0 (dm, *J* = 157, NC=*C*H–CN), 50.4 (t, *J* = 105, $ZrCH_2$), 49.3 (t, *J* = 136, NCH_2), 22.6, 4.2. Anal. Calcd for $C_{22}H_{44}N_4Si_2Zr$: C, 51.61; H, 8.66; N, 10.94. Found: C, 51.44; H, 8.40; N, 11.05.

$(Me_4taen)Zr(NMe_2)_2$ (4). A slurry of **1** (1.12 g, 4.51 mmol) and $Zr(NMe_2)_4$ (1.19 g, 4.51 mmol) in pentane (25 mL) was stirred for 6 h at 23 °C. The volatiles were removed under vacuum, yielding analytically pure **4** (100%) as a yellow solid. This product was recrystallized from the hot hexane (57.3%). ^1H NMR (C_6D_6): δ 4.95 (s, 2H), 3.55 (m, 4H), 3.20 (s, 12H), 3.15 (m, 4H), 1.71 (s, 12H). $^{13}C\{gated\text{-}^1H\}$ NMR (C_6D_6): δ 162.4 (s, N=C), 100.9 (d, *J* = 157, CH), 50.7 (t, *J* = 128, CH_2), 45.0 (qq, *J* = 130, 6, NCH_3), 22.1 (q, *J* = 126, CH_3). Anal. Calcd for $C_{18}H_{34}N_6Zr$: C, 50.78; H, 8.05; N, 19.73. Found: C, 50.56; H, 7.96; N, 19.92.

$(Me_4taen)ZrCl_2(NHMe_2)$ (5). Method 1: A yellow slurry of $(Me_4taen)Zr(NMe_2)_2$ (**4**, 1.90 g, 4.46 mmol) and $[Me_2NH_2]Cl$ (0.728 g, 8.92 mmol) in chlorobenzene (20 mL) was stirred at 0 °C for 4 h and at 23 °C for 3 h. The volatiles were removed under vacuum, yielding a yellow solid which was washed with cold chlorobenzene/pentane (2/1) and dried under vacuum, yielding analytically pure **5** (74.5%). Method 2: A yellow solution of **1** (1.00 g, 4.04 mmol) and $Zr(NMe_2)_4$ (1.06 g, 4.04 mmol) in CH_2Cl_2 (25 mL) was stirred for 5 h at 0 °C and for 4 h at 23 °C. The solution darkened during the last 2 h. The solvent was removed under vacuum, yielding an orange/brown solid which was recrystallized from chlorobenzene/pentane (10/2), washed with pentane (2 × 5 mL) and dried under vacuum (1.34 g, 73.2%). ^1H NMR ($CDCl_2CDCl_2$): δ 5.12 (s, 2H), 4.9 (br s, 1H), 4.23 (m, 4H), 3.76 (m, 4H), 2.40 (s, 6H), 1.98 (s, 12H). $^{13}C\{gated\text{-}^1H\}$ NMR ($CDCl_2CDCl_2$): δ 162.3 (s, N=C), 102.4 (d, *J* = 158, CH), 49.0 (t, *J* = 138, CH_2), 36.1 (q, *J* = 139, NCH_3), 21.8 (qd, *J* = 127, 4, CH_3). IR (KBr ν_{NH} 3251 cm^{-1}. Anal. Calcd for $C_{16}H_{29}Cl_2N_5Zr$: C, 42.37; H, 6.44; N, 15.28; Cl, 15.63. Found: C, 42.22; H, 6.28, N, 15.44; Cl, 15.79.

$(Me_4taen)ZrCl_2$ (6). $(Me_4taen)ZrCl_2(NHMe_2)$ was heated at 120 °C for 10 h under vacuum ^1H NMR ($CDCl_2CDCl_2$): δ 5.24 (s, 2H), 4.04 (m, 4H), 3.75 (m, 4H), 2.02 (s, 12H). $^{13}C\{gated\text{-}^1H\}$ NMR ($CDCl_2CDCl_2$): δ 163.2 (s, N=C), 102.9 (d, *J* = 160, CH), 48.47 (t, *J* = 138, NCH_2), 21.3 (qd, *J* = 127, 3.9, CH_3). Anal. Calcd for $C_{14}H_{22}Cl_2N_4Zr$: C, 41.17; H, 5.40; N, 13.71; Cl, 17.36. Found: C, 41.15; H, 5.43, N, 13.58; Cl, 17.41.

$(Me_4taen)Zr(CCPh)_2(NHMe_2)$ (7). This compound was generated on an NMR scale only. An NMR tube was charged with $(Me_4taen)Zr(NMe_2)_2$ (0.053 g, 1.2 mmol) and phenylacetylene (27 μL, 2.5 mmol) was added to the tube via microsyringe. Benzene-d_6 (0.3 mL) was added via vacuum transfer, and the tube was sealed and warmed to 23 °C. A brown solution formed. NMR spectra were recorded after 30 min and indicated complete conversion to **7**. ^1H NMR (C_6D_6): δ 7.58 (d, *J* = 7.7, 4H), 7.06 (t, *J* = 7.3, 4H), 6.95 (t, *J* = 7.5, 2H), 4.86 (s, 2H), 4.42 (m, 4H), 3.30 (m, 4H), 2.6 (broad singlet, 2H, free and coordinated *H*NMe_2), 2.35 (d, *J* = 6.2, 12H, free and coordinated *H*NMe_2), 2.35 (d, *J* = 6.2, 12H, free and coordinated HN*Me*$_2$), 1.70 (s, 12H). $^{13}C\{gated\text{-}^1H\}$ NMR (C_6D_6): δ 162.2 (s, C=N), 148.5 (s, Zr*C*), 131.9 (dt, *J* = 158, 7, Ph), 128.3 (dt, *J* = 157, 7, Ph), 125.7 (dt, *J* = 159, 8, Ph), 103.8 (s, ZrC*C*), 103.0 (d, *J* = 152, CH), 51.4 (t, *J* = 135, CH_2), 39.8 (q, *J* = 133, HN*Me*$_2$), 22.4 (qd, *J* = 124, 4, *Me*$_4$aen). The Ph ipso carbon signal was observed at δ 128.5 in the $\{^1H\}$ ^{13}C spectrum. The volatiles were removed under vacuum, and the residue was redissolved in benzene-d_6, yielding a black solution. The ^1H NMR spectrum was identical to that listed above

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(50) Poor C and N analyses were consistently obtained for spectroscopically pure samples of 2.

Table 14. Summary of Crystallographic Data

compd	$(Me_4taen)H_2$ (**1**)	$[Li(THF)]_2[Me_4taen]$ (**10**)	$(Me_4taen)ZrCl_2$ (**6**)	$(Me_4taen)Zr(CH_2Ph)_2\cdot PhMe$ (**2**)	$(Me_4taen)Zr(NMe_2)_2(0.5\cdot PhMe$ (**4**)	$(Me_4taen)ZrCl_2(NHMe_2)$ (**5**)
empirical formula	$C_{14}H_{22}N_4$	$C_{22}H_{38}Li_2N_4O_2$	$C_{14}H_{22}Cl_2N_4Zr$	$C_{28}H_{36}N_4Zr\cdot C_7H_8$	$C_{18}H_{34}N_6Zr\cdot 0.5C_7H_8$	$C_{16}H_{29}Cl_2N_5Zr$
fw	248.37	404.46	408.48	612.87	471.80	453.57
cryst size (mm^3)	0.26 × 0.31 × 0.35	0.14 × 0.18 × 0.32	0.40 × 0.20 × 0.15	0.32 × 0.45 × 0.50	0.20 × 0.10 × 0.09	0.15 × 0.15 × 0.45
color/shape	colorless/ parallelepiped	yellow/parallelepiped	yellow/fragment	orange/fragment	yellow/fragment	colorless/parallelepiped
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.587(3)	8.554(3)	10.008(2)	17.529(3)	8.946(3)	8.965(3)
b (Å)	9.005(2)	12.836(3)	13.862(5)	13.508(3)	11.277(4)	8.970(2)
c (Å)	8.069(2)	11.273(3)	12.174(4)	13.711(3)	13.288(5)	12.699(6)
α (deg)	90	90	90	90	108.415(5)	92.06(3)
β (deg)	107.54(2)	96.67(2)	97.03(2)	98.21(1)	95.453(6)	98.43(3)
γ (deg)	90	90	90	90	106.565(5)	102.80(3)
V ($Å^3$)	733.5(6)	1229(1)	1676.2(9)	3213(1)	1193.6(8)	982.6(1)
Z	2	2	4	4	2	2
T (K)	293	291	290	295	173	295
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Siemens SMART/CCD area detector	Enraf-Nonius CAD-4
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
2θ range (deg)	$4 < 2\theta < 60$	$4 < 2\theta < 40$	$5 < 2\theta < 50$	$4 < 2\theta < 60$	$3 < 2\theta < 46$	$2 < 2\theta < 50$
data collected: h; k; l	±14; −11, 12; −11, 5	±8; −12, 10; ±10	+11; +16; ±14	−1, 6; −14, 17; ±22	±9; ±12; −14, 10	+10; ±10; ±15
no. of reflns	6104	4333	1558	8803	4686	3474
no. of unique reflns	2106	1141	1476	4650	3314	3216
R_{int}	0.008	0.028	0.0192	0.025	0.0296	
no. of obsd reflns	$I > 2\sigma(I)$, 1110	$I > 2\sigma(I)$, 671		$I > 2\sigma(I)$, 3014		$I > 2.5\sigma(I)$, 2862
μ (cm^{-1})	0.65	0.65	9.73	11.84	4.79	8.29
transmissn range (%)				97−100		92−100
structure soln	direct methods[a]	direct methods[a]	direct methods[c]	direct methods[a]	direct methods[c]	direct methods[b]
refinement	all non-H anisotropic; H refined, isotropic	non-H anisotropic; THF carbons isotropic; H isotropic, fixed	all non-H anisotropic; H isotropic, fixed	all non-H anisotropic; H isotropic, fixed	all non-H anisotropic; H isotropic, fixed	all non-H anisotropic; amine H isotropic; other H isotropic, fixed
GOF			1.063		1.025	0.97
R	0.047	0.093	0.0485 (R, all data)	0.036	0.0417 (R, all data)	0.039
R_w	0.066	0.102	0.0899 (wR, all data)	0.041	0.0858 (wR, all data)	0.050
max resid density (e/$Å^3$)	0.037	0.19	0.679	0.66	0.36	0.8

[a] *MOLEN*; *An* (Interactive *System for Crystal Structure Analysis*; Fair, C. K. Enraf Nonius: Delft, The Netherlands, 1990. [b] *SHELX-86* and *SHELXS-93*. [c] *SHELXTL*, PC Version 5; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI.

except that (i) the amine resonances were shifted to δ 3.57 (NH) and 2.41 (NMe_2) and reduced to an intensity corresponding to 1 equiv vs Zr and (ii) ca. 5% decomposition was evident. Attempts to isolate this compound on a preparatory scale were unsuccessful due to thermal decomposition.

$(Me_4taen)Zr(CH_2CMe_3)_2$ (8). A slurry of $(Me_4taen)ZrCl_2$ (0.400 g, 0.979 mmol) and neopentyllithium (0.153 g, 1.96 mmol) in toluene (12 mL) was stirred for 3 h at 23 °C and filtered twice through a frit. The orange filtrate was concentrated to 1 mL under vacuum and layered with pentane (5 mL). Filtration yielded an orange solid, which was washed with cold pentane and dried under vacuum (0.270 g). The filtrate was stored at −40 °C for 1 day and, an additional 82 mg was isolated in the same manner (total yield = 0.35 g, 75%), ^1H NMR (C_6D_6): δ 4.95 (s, 2H), 3.44 (m, 4H), 3.03 (m, 4H), 1.63 (s, 12H), 1.39 (s, 18H), 1.27 (s, 4H). $^{13}C\{gated\text{-}^1H\}$ NMR (C_6D_6): δ 164.6 (s, N=C), 101.9 (d, *J* = 157, CH), 79.9 (t, *J* = 106, $ZrCH_2$), 49.1 (t, *J* = 135, NCH_2), 36.4 (s, CMe_3), 36.3 (q, *J* = 122, CMe_3), 22.7 (qd, *J* = 126, 4, CH_3). Anal. Calcd for $C_{24}H_{44}N_4Zr$: C, 60.01; H, 9.24; N, 11.67. Found: C, 59.80; H, 9.27; N, 11.43.

$(Me_4taen)ZrMe_2$ (9). A slurry of solid MeLi (2.45 mmol, prepared by removal of solvent from 1.75 mL of a 1.4 M MeLi/Et_2O solution under vacuum) and $(Me_4taen)ZrCl_2$ (0.500 g, 1.22 mmol) in toluene (12 mL) was stirred for 30 min at 23 °C. The reaction mixture was filtered through a glass fiber filter, yielding a homogeneous, brown solution. The precipitate was washed with toluene (8 mL). The combined filtrate and wash were concentrated to 7 mL under vacuum, layered with pentane, and cooled to −40 °C for 4 h to yield a bright yellow solid which was collected by filtration, washed with pentane (2 × 5 mL), and dried under vacuum (0.239 g, 53.3%). ^1H NMR (CD_2Cl_2): δ 5.00 (s, 2H), 3.98 (m, 4H), 3.67 (m, 4H), 2.00 (s, 12H), −0.17 (s, 6H). $^{13}C\{gated\text{-}^1H\}$ NMR (CD_2Cl_2): δ 164.7 (s, N=C), 101.5 (d, *J* = 157, CH), 49.8 (*J* = 136 Hz, NCH_2), 37.7 (qd, *J* = 110, 4, $ZrCH_3$), 22.5 (*J* = 126, CH_3). Anal. Calcd for $C_{16}H_{28}N_4Zr$: C, 52.28; H 7.68; N, 15.23. Found: C, 51.95; H, 7.48; N, 15.46.

$[Li(THF)]_2[Me_4taen)]$ (10) and $Li_2[Me_4taen]$ (11). A slurry of $(Me_4taen)H_2$ (1.17 g, 4.73 mmol) and $LiN(SiMe_3)_2$ (1.58 g, 9.46 mmol) in THF (25 mL) was refluxed for 3 h. The resulting solution was cooled to ambient temperature and then −40 °C. Filtration yielded a red crystalline solid ($[Li(THF)]_2[Me_4taen]$, **10**), which was washed with pentane (2 × 5 mL) and dried under vacuum overnight, yielding $Li_2[Me_4taen]$ (**11**) as a tan powder (0.489 g). The red filtrate was concentrated to 10 mL, and an additional 0.289 g of **11** was isolated in the same manner (total 0.778 g, 63.2%). ^1H NMR (acetone-d_6): δ 4.29 (s, 2H), 3.65 (s, 8H), 1.82 (s, 12H). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 160.4 (N=C), 95.3 (CH), 47.4 (CH_2), 19.6 (CH_3). Anal. Calcd for $C_{14}H_{22}Li_2N_4$: C, 64.62; H, 8.52; N, 21.52. Found: C, 64.40; H, 8.64; N, 21.51.

$(Me_4taen)_2Zr$ (12). A slurry of **1** (0.208 g, 0.838 mmol) and $Zr(NMe_2)_4$ (0.110 g, 0.419 mmol) in toluene (5 mL) was heated to 110 °C for 3 days and cooled to −40 °C for 6 h. The slurry was filtered, yielding a tan solid which was washed with pentane (2 × 5 mL) and dried under vacuum for 30 min (0.143 g). The filtrate was concentrated to 2 mL, and pentane (3 mL) was added. The resulting slurry was cooled to −40 °C overnight and filtered, yielding an additional 0.061 g of product (total yield 0.204 g, 83.3%). ^1H NMR (CD_2Cl_2): δ 4.73 (s, 2H), 3.61 (m, 2H), 3.3 (m, 6H), 1.93 (s, 6H), 1.77 (s, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 164.5 (N=C), 161.6 (N=C), 101.5 (CH), 52.2 (CH_2), 51.1, (CH_2), 24.4 (CH_3), 23.4 (CH_3). Anal. Calcd for $C_{28}H_{44}N_8Zr$: C, 57.60; H, 7.60; N, 19.18. Found: C, 57.27; H, 7.41; N, 19.32.

Rearrangement of $(Me_4taen)_2ZrMe_2$ to Compound 13. A solution $(Me_4taen)ZrMe_2$ in toluene-d_8 was maintained at 23 °C for 24 h. NMR analysis revealed complete conversion to **13**. Preparative scale: Methyl lithium (0.874 mL of a 1.40 M solution in ether, 1.22 mmol) was added to a frozen mixture of $(Me_4taen)ZrCl_2$ (0.250 g, 0.612 mmol) and toluene (15 mL) at −196 °C. The mixture was allowed to warm to 23 °C and was stirred for 17 h. The resulting yellow slurry was filtered, concentrated to 5 mL under vacuum, layered with pentane (10 mL), and cooled to −40 °C for 1 day. The tan solid was isolated by filtration, washed with pentane (2 × 5 mL), and dried under vacuum (0.166 g, 73.8%). ^1H NMR (chlorobenzene-d_5): δ 4.82 (s, 1H), 4.21 (s, 1H), 3.93 (m, 2H), 3.53 (m, 4H), 3.23 (m, 2H), 1.93 (s, 3H), 1.83 (s, 3H), 1.78 (s, 3H), 1.41 (s, 3H), 1.18 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 163.8, 163.5, 147.5, 100.4, 91.7, 57.4, 54.2, 52.7, 50.8, 50.3, 31.7, 28.6, 22.7, 22.4, 21.8, 20.3. Anal. Calcd for $C_{16}H_{28}N_4Zr$: C, 52.28; H 7.68; N, 15.23. Found: C, 52.03; H, 7.48; N, 15.07.

Rearrangement of $(Me_4taen)Zr(CH_2Ph)_2$ to Compound 14. A slurry of $(Me_4taen)Zr(CH_2Ph)_2$ (50 mg) in benzene-d_6 (0.3 mL) in a sealed NMR tube was heated to 110 °C for 3 days yielding a black solution. ^1H NMR (benzene-d_6): δ 7.33 (m, 3H), 7.20 (m, 2H), 6.65 (t, 1H, *J* = 7.5), 6.51 (d, 2H, *J* = 7.2, ortho $ZrCH_2Ph$), 4.75 (s, 1H), 4.15 (s, 1H), 3.57 (m, 4H), 3.25 (m, 3H), 3.02 (d, *J* = 13.2), 2.98 (m, 1H), 2.73 (d, *J* = 13.1), 1.75 (d, *J* = 8.9, $ZrCH_2$) 1.68 (d, partially obscured, $ZrCH_2$), 1.67 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6): 163.7, 163.0, 149.1, 144.8, 140.0, 138.9, 131.6, 129.0, 127.9, 126.3, 125.8, 119.8, 101.5, 86.8, 58.4, 57.9, 56.6, 52.5, 51.2, 51.0, 47.0, 23.3, 22.3, 22.0, 20.1. Two aryl resonances were not observed.

X-ray Structural Determinations. The structures of **1**, **2**, and **10** were determined at the University of Iowa by D. C. Swenson. The structures of **4**, **5**, and **6** were determined at Northern Illinois University by R. D. Rogers. Data collection, solution, and refinement procedures and parameters are summarized in Table 14. Additional comments specific to each structure follow.

The structure of **1** is disordered. The disorder is manifested in two ways. One is the existence of two orientations for the C5−C6 ethylene groups. The occupancies of the two orientations were refined and constrained to sum to 1.0. The second disorder is a superposition of two tautomeric forms for the diiminato groups which results in two partially occupied eneamine hydrogen positions. The occupancies of the two partially occupied hydrogen atom positions were adjusted to give approximately equal thermal parameters. The resulting occupancies were nearly the same as those for the two orientations of the C5−C6 ethylene group (0.58 and 0.42 for H N7 and H N4 vs 0.59 and 0.41 for C5−C6 and C5′−C6′) and were arbitrarily set to be the same. The enamine hydrogen atoms are involved in intramolecular hydrogen bonds (H7···N4, 2.05(2) Å; N7−H7···N4, 135(1)°; H4···N7, 2.12(2) Å; N4−H4···N7, 135(1)°). Conversion from one tautomer to the other involves moving the hydrogen atom ca. 1.4 Å and shifting of the single and double bonds.

The THF ligand in **10** is disordered between three orientations. The bonding scheme is as follows: orientation 1, O1, C11, C12, C13, C14 (occupancy 0.4); orientation 2, O1, C15, C13, C18 (occupancy 0.4); orientation 3, O1, C19, C20, C21, C22 (occupancy 0.2).

Crystals of **2** contain 1 equiv of toluene. Crystals of **4** contain 0.5 equiv of toluene which is located around a center of inversion and is disordered between two equally occupied orientations. C19 is present at full occupancy while C20−C24 are present at half occupancy.

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Supporting Information Available: Summaries of crystallographic data, tables of bond distances, angles, anisotropic thermal parameters, hydrogen atom coordinates, and least-squares planes, and alternative views for **1**, **2**, **4**−**6**, and **10** (43 pages). Ordering information is given on any current masthead page.

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