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Structural Trends in Group 4 Metal Tetraaza Macrocycle Complexes. Molecular Structures of $(Me_4taen)Zr(O^tBu)_2$ and $(Me_4taen)Hf(NMe_2)_2$

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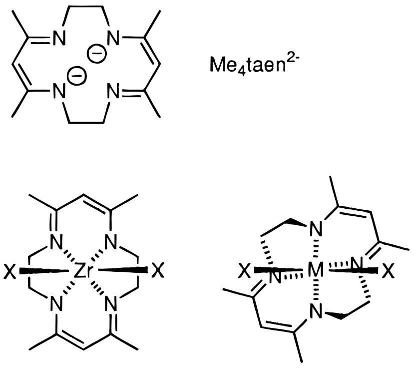
The tetraaza macrocycle complexes $(Me_4taen)Zr(O^tBu)_2$ (**4**) and $(Me_4taen)Hf(NMe_2)_2$ (**5**) have been prepared and characterized by X-ray crystallography. Both species adopt cis structures with distorted octahedral metal geometries. These structures are similar to that observed earlier for $(Me_4taen)Zr(NMe_2)_2$ (**3**) but quite different from the trigonal prismatic structures observed for $(Me_4taen)ZrCl_2$ (**1**) and $(Me_4taen)Zr(CH_2Ph)_2$ (**2**). The structures of these d^0 $(Me_4taen)MX_2$ species are rationalized on electronic grounds. The conformational properties of the Me_4taen^{2-} macrocycle and the covalent character of and absence of a strong π-component in the M−X bonds favor trigonal prismatic structures for **1** and **2**, whereas M−X π-bonding in **3**−**5** promotes distortion toward octahedral structures. Compound **4**, $C_{22}H_{40}N_4O_2Zr$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.6080(8)$ Å, $b = 9.7407(8)$ Å, $c = 14.5916(12)$ Å, $\alpha = 92.714(1)°$, $\beta = 107.808(1)°$ $\gamma = 99.810(1)°$, and $Z = 2$. Compound **5**, $C_{18}H_{34}N_6Hf{\cdot}0.5(C_7H_8)$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.102(3)$ Å, $b = 11.242(4)$ Å, $c = 13.478(5)$ Å, $\alpha = 108.672(5)°$, $\beta = 96.310(5)°$, $\gamma = 106.266(6)°$, and $Z = 2$.

Introduction

We recently described the synthesis and characterization of a series of $(Me_4taen)ZrX_2$ complexes (X = alkyl, Cl, NMe_2) containing the tetraaza macrocyclic ligand Me_4taen^{2-}(Chart 1).[1−3] The large Zr(IV) ion (ionic radius 0.84 Å in a six-coordinate environment) does not fit in the N_4-macrocycle pocket and thus lies out of the N_4 plane, which forces a *cis* orientation of the X groups. However, the precise conformations adopted by these complexes are very sensitive to the identity of the X groups. Specifically, for X = Cl (**1**) and CH_2Ph (**2**), the structures are moderately distorted trigonal prisms, while for X = NMe_2 (**3**), the structure is a distorted octahedron with a severe twist in the ligand framework. In **1** and **2** the Zr−X vectors bisect the N−Zr−N angles, while in **3** the Zr−X groups eclipse the Zr−N groups. Due to the presence of two long Zr−$N_{macrocycle}$ bonds (those *trans* to the NMe_2 groups), the average Zr−$N_{macrocycle}$ bond distance in **3** (2.24 Å) is significantly longer than that in **1** (2.16 Å).

Chart 1



1, X = Cl
2, X = CH_2Ph

3, X =NMe_2, M = Zr
4, X = O^tBu, M = Zr
5, X = NMe_2, M = Hf

VSEPR theory predicts that octahedral geometries are most stable for d^0 ML_6 complexes. This geometry minimizes repulsion between the M−L bonding electrons, and also minimizes interligand steric interactions.[4] However, in recent years it has become clear that d^0 ML_6 compounds can distort from octahedral to trigonal prismatic or other lower symmetry structures. In particular, X-ray crystallographic analyses show

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(1) $(Me_4taen)H_2$ (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene) is also referred to as $H_2(MeHMe(en)_2)$ in the literature.

(2) (a) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493. (b) Black, D. G.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 3539.

(3) For the synthesis and chemistry of Me_4taen^{2-} and related ligands see: (a) Truex, T. J.; Holm, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 4529. (b) Tokumitsu, T.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2348. (c) Kim, J.-H.; Everett, G. W., Jr. *Inorg. Chem.* **1979**, *18*, 3145. (d) Brawner, S. A.; Lin, I. J. B.; Kim, J.-H.; Everett, G. W., Jr. *Inorg. Chem.* **1978**, *17*, 1304. (e) Tang, S. C.; Koch, S.; Weinstein, G. N.; Lane, R. W.; Holm, R. H. *Inorg. Chem.* **1973**, *12*, 2589. (f) Fujiwara, M.; Nakajima, Y.; Matsushita, T.; Shono, T. *Polyhedron* **1985**, *4*, 1589. (g) Fujiwara, M.; Matsushita, T.; Shono, T. *Polyhedron* **1984**, *3*, 1357. (h) Sakata, K.; Hashimoto, M.; Tagami, N.; Murakami, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2262. (i) Owston, P. G.; Peters, R.; Ramsammy, E.; Tasker, P. A.; Trotter, J. *J. Chem. Soc., Chem. Commun.* **1980**, 1218. (j) Bamfield, P. *J. Chem. Soc. A* **1969**, 2021. (k) Jäger, E.-G. *Z. Chem.* **1968**, *8*, 30. (l) Jäger, E.-G. *Z. Chem.* **1968**, *8*, 490. (m) Fujiwara, M.; Wakita, H.; Matsushita, T.; Shono, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3443. (n) Sakata, K.; Taziri, H.; Yamaura, F.; Hashoto, M. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 757. (o) Green, M.; Tasker, P. A. *Inorg. Chim. Acta* **1971**, *5*, 65. (p) Nishida, Y.; Osha, H.; Kida, S. *Inorg. Chim. Acta* **1978**, *29*, L191. (q) Kim, J.-H.; Everett, G. W., Jr. *Inorg. Chem.* **1981**, *20*, 853. (r) Park, C. H.; Lee, B.; Everett, G. W., Jr. *Inorg. Chem.* **1982**, *21*, 1681.

(4) (a) Gillespie, R. J.; Nyholm, R. S. Q. Rev. *Chem. Soc.* **1957**, *11*, 339. (b) Gillespie, R. J. *Molecular Geometry*; van Nostrand-Reinhold: London, 1972. (c) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991.

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Table 1. Summary of Crystallographic Data

	$(Me_4taen)Zr(O^tBu)_2$ (**4**)	$(Me_4taen)Hf(NMe_2)_2 \cdot 0.5(C_6H_5Me)$ (**5**)
empirical formula	$C_{22}H_{40}N_4O_2Zr$	$C_{18}H_{34}N_6Hf \cdot 0.5(C_7H_8)$
fw	483.80	559.07
temp, K	293(2) K	294(2)K
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens		
a, Å	9.6080(8)	9.102(3)
b, Å	9.7407(8)	11.242(4)
c, Å	14.5916(12)	13.478(5)
α, deg	92.714(1)	108.672(5)
β, deg	107.808(1)	96.310(5)
γ, deg	99.810(1)	106.266(6)
V, Å^3	1273.9(2)	1223.7(8)
Z	2	2
d (calcd), Mg/m^3	1.261	1.517
abs coeff, mm^{-1}	0.454	4.280
radiation/wavelength, Å	Mo Kα, graphite monochrom/0.710 73	Mo Kα, graphite monochrom/0.710 73
R indices $[I>2\sigma(I)]^a$	R1 = 0.0280, wR2 = 0.0710	R1 = 0.0327, wR2 = 0.0887
R indices (all data)	R1 = 0.0300, wR2 = 0.0751	R1 = 0.0346, wR2 = 0.0947

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

that $ZrMe_6^{2-}$ has a slightly distorted trigonal prismatic structure,[5] and WMe_6 has a C_{3v} symmetry structure derived from a trigonal prism by flattening of one WMe_3 unit.[6] These deviations from octahedral structures have been rationalized on electronic grounds.[7] The empty t_{2g} d orbitals (LUMO) and filled t_{1u} M−X σ bonding orbitals (HOMO) split into e′ and a_1' sets and a_2'' and e′ sets, respectively, as the symmetry is lowered from O_h to D_{3h}. This allows mixing of the metal d and M−X σ bonding orbitals, which lowers the HOMO energy and provides a driving force for the distortion (second-order Jahn−Teller distortion). The distortion to the trigonal prismatic or lower symmetry structure increases the participation of the d orbitals in the M−X bonding and thus strengthens the M−X bonds. Factors which increase the $t_{2g}-t_{1u}$ energy gap in the octahedral limit, e.g. ligand to metal π-donation or highly ionic bonding, weaken the mixing and favor an octahedral geometry. These effects are nicely illustrated by the WX_6 series: as mentioned above, WMe_6 has a C_{3v} structure, while $W(NMe_2)_6$,[8] $W(OMe)_6$,[9] and WF_6[10] have octahedral structures due to the M−L π-bonding and relatively polar bonds.

The structures of **1**−**3** were rationalized in terms of these electronic arguments. The conformation of the Me_4taen^{2-} ligand in **1** and **2** is very similar to that observed in $[Li(THF)]_2[Me_4taen]$ and $(Me_4taen)H_2$.[2b] The trigonal prismatic structures for **1** and **2** are thus favored by the conformational preference of the macrocycle and by the covalent character and small π-component in the Zr−Cl and Zr−CH_2Ph bonds. For **3**, however, the strong π-donor ability of the NMe_2 ligand favors an octahedral structure, and the Me_4taen^{2-} ligand distorts accordingly.[11] To test this proposal, we have synthesized two new examples with strong π-donor X groups, $(Me_4taen)Zr(O^tBu)_2$ (**4**) and $(Me_4taen)Hf(NMe_2)_2$ (**5**), and determined their structures. We have also carried out extended Hückel molecular orbital calculations for several model complexes to probe how the bonding capabilities of the (Me_4taen)M unit are influenced by structural changes.

Experimental Section

$(Me_4taen)Zr(O^tBu)_2$ (4). A slurry of $(Me_4taen)ZrCl_2$ (0.535 g, 1.31 mmol) and KO^tBu (0.294 g, 2.62 mmol) in toluene (15 mL) was stirred for 4.5 h at 23 °C. The reaction mixture turned from yellow to brown. The slurry was filtered, the filter cake was washed with toluene (5 mL), and the filtrate and washes were combined and concentrated to 7 mL under vacuum. Pentane (5 mL) was gently layered over the mother liquor, and the flask was stored at −40 °C for 6 h. A few yellow crystals were collected and used in the X-ray diffraction study. The mother liquor was decanted and the solvent removed under high vacuum, yielding a cream-colored solid. Yield: 0.39 g, 61.5%. ^1H NMR (C_6D_6): δ 4.84 (s, 2H, CH), 3.54 (m, 4H, CH_2), 3.10 (m, 4H, CH_2), 1.74 (s, 12H, ligand Me), 1.39 (s, 18H, O^tBu). $^{13}C\{gated\text{-}^1H\}$ NMR (C_6D_6): δ 162.0 (s, C═N), 100.5 (d, J = 156, CH), 74.3 (s, O*C*Me), 50.5 (t, J = 135, CH_2), 33.7 (q, J = 124, OC*C*H_3), 22.4 (qd, J = 125, 4.3, ligand CH_3). Anal. Calcd for $C_{22}H_{40}N_4O_2Zr$: C, 54.62; H, 8.33; N, 11.58. Found: C, 54.84; H, 8.32; N, 11.42.

$(Me_4taen)Hf(NMe_2)_2$ (5). A solution of $Hf(NMe_2)_4$ (0.310 g, 0.873 mmol) and $(Me_4taen)H_2$ (0.217 g, 0.873 mmol) in toluene (12 mL) was stirred for 18 h at 23 °C. The solution was concentrated to 5 mL under vacuum, pentane (5 mL) was gently layered on, and the flask was stored at −40 °C for 2 d. The yellow solid was collected by filtration, washed with 2 × 5 mL of cold hexanes, and dried under vacuum for 14 h (0.110 g). The filtrate and washes were combined, concentrated to 3 mL and cooled to −40 °C for 4 d. The yellow solid was collected on a frit, washed with 2 × 5 mL of cold hexanes, and dried under vacuum for 27 h (0.086 g). Combined yield: 0.196 g, 93.3%. ^1H NMR analysis established that this material contains 0.21 equiv of toluene. Crystals for the X-ray crystallographic analysis were grown from toluene/hexanes at −40 °C. ^1H NMR (C_6D_6): δ 4.91 (s, 2H, CH), 3.54 (m, 4H, CH_2), 3.25 (s, 12H, NMe_2), 3.15 (m, 4H, CH_2), 1.69 (s, 12H, ligand Me). $^{13}C\{gated\text{-}^1H\}$ NMR (C_6D_6): δ 163.1 (s, C═N), 101.4 (d, J = 157, CH), 50.5 (t, J = 135, CH_2), 44.9 (qq, J =

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(5) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114.

(6) (a) Pfennig, V.; Seppelt, K. *Science* **1996**, *271*, 626. (b) Haaland, A.; Hammel, A.; Rypdal, K.; Volden, H. V. *J. Am. Chem. Soc.* **1990**, *112*, 4547.

(7) (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. (d) Kang, S. K.; Tang, H.; Albright, T. A. *J. Am. Chem. Soc.* **1993**, *115*, 1971. (e) Kaupp, M. *J. Am. Chem. Soc.* **1996**, *118*, 3018. (f) Shen, M.; Schaefer, H. F.; Partridge, H. *J. Chem. Phys.* **1993**, *98*, 508. (g) Jonas, V.; Frenking, G.; Gauss, J. *Chem. Phys. Lett.* **1992**, *194*, 109.

(8) Hagen, K. L.; Holwill, C. J.; Rice, D. A.; Runnacles, J. D. *Acta Chem. Scand.* **1988**, *A42*, 578.

(9) Haaland, A.; Rypdal, K.; Volden, H. V.; Jacob, E.; Weidlein, J. *Acta Chem. Scand.* **1989**, *43*, 911.

(10) Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1966**, *20*, 2698.

(11) Extensive structural, spectroscopic and reactivity data establish that Cl^- is a weaker π-donor ligand than R_2N^- or RO^-. See for example: (a) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190. (b) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organometallic Chem.* **1980**, *201*, 389. (c) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(Me_4taen)Zr(O^tBu)_2$ (**4**)

Zr−O(1)	1.945(2)	Zr−O(2)	1.948(2)
Zr−N(2)	2.178(2)	Zr−N(4)	2.189(2)
Zr−N(3)	2.315(2)	Zr−N(1)	2.317(3)

O(1)−Zr−O(2)	94.69(7)	O(1)−Zr−N(1)	173.88(7)
O(2)−Zr−N(2)	101.63(8)	N(2)−Zr−N(1)	78.95(8)
O(2)−Zr−N(4)	109.18(8)	N(3)−Zr−N(1)	100.53(7)
O(1)−Zr−N(3)	82.55(7)	N(4)−Zr−N(1)	72.59(8)
N(2)−Zr−N(3)	72.47(8)	N(4)−Zr−N(3)	78.52(7)
O(1)−Zr−N(2)	107.09(8)	O(2)−Zr−N(1)	82.91(7)
O(1)−Zr−N(4)	103.07(8)	C(19)−O(2)−Zr	169.5(2)
N(2)−Zr−N(4)	134.39(8)	C(15)−O(1)−Zr	179.4(4)
O(2)−Zr−N(3)	172.26(7)		

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $(Me_4taen)Zr(OtBu)_2$ (**4**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Zr	103(1)	2977(1)	2211(1)	40(1)
O(1)	−1147(2)	1354(2)	2476(1)	52(1)
O(2)	1961(2)	2576(2)	3054(1)	55(1)
N(1)	1695(2)	4742(2)	1816(2)	52(1)
N(2)	−145(2)	4802(2)	3026(2)	55(1)
N(3)	−2180(2)	3519(2)	1399(2)	47(1)
N(4)	−59(2)	2463(2)	701(2)	49(1)
C(1)	2552(3)	5785(2)	2445(2)	60(1)
C(2)	2242(3)	6225(3)	3282(2)	67(1)
C(3)	936(3)	5886(3)	3503(2)	61(1)
C(4)	−1697(3)	4724(3)	2991(2)	68(1)
C(5)	−2641(3)	4566(3)	1932(2)	66(1)
C(6)	−3126(3)	2748(3)	628(2)	51(1)
C(7)	−2696(3)	1842(3)	27(2)	54(1)
C(8)	−1279(3)	1839(3)	−13(2)	52(1)
C(9)	1388(3)	2883(3)	553(2)	67(1)
C(10)	1949(3)	4431(3)	894(2)	66(1)
C(11)	3940(4)	6603(4)	2294(3)	86(1)
C(12)	733(5)	6792(4)	4308(2)	90(1)
C(13)	−4767(3)	2824(4)	307(3)	79(1)
C(14)	−1150(4)	1157(4)	−930(2)	78(1)
C(15)	−2053(3)	179(3)	2656(2)	54(1)
C(16)	−1832(5)	−1116(3)	2165(3)	93(1)
C(17)	−1630(6)	114(4)	3721(3)	119(2)
C(18)	−3670(4)	326(4)	2223(4)	100(1)
C(19)	3204(3)	2360(3)	3800(2)	61(1)
C(20)	3192(5)	806(4)	3794(3)	110(1)
C(21)	3085(5)	2962(5)	4744(3)	104(1)
C(22)	4597(4)	3154(5)	3638(3)	103(1)

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

129, 6.6, $N(Me_2)_2$), 22.2 (qd, $J = 126$, 4.1, CH_3). Anal. Calcd for $C_{18}H_{34}N_6Hf\cdot(0.21\ C_7H_8)$: C, 43.41; H, 6.68; N, 15.59. Found: C, 43.86; H, 6.68; N, 15.64.

X-ray Crystallographic Analysis of $(Me_4taen)Zr(O^tBu)_2$ (4). A yellow single crystal was mounted in a thin-walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric *P*1. The subsequent solution and successful refinement of the structure was carried out in the centric space group $P\bar{1}$. Data collection parameters are given in Table 1. The geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2U_{eq}(C)$. Refinement of non-hydrogen atoms was carried out with anisotropic temperature factors. Positional parameters are listed in Table 3.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $(Me_4taen)Hf(NMe_2)_2$ (**5**)

Hf−N(5)	2.091(5)	Hf−N(6)	2.093(5)
Hf−N(1)	2.175(5)	Hf−N(2)	2.283(6)
Hf−N(4)	2.272(5)	Hf−N(3)	2.176(5)

N(5)−Hf−N(6)	87.7(2)	N(5)−Hf−N(1)	99.8(2)
N(6)−Hf−N(1)	113.3(2)	N(5)−Hf−N(3)	112.6(2)
N(6)−Hf−N(3)	99.8(2)	N(1)−Hf−N(3)	134.3(2)
N(5)−Hf−N(4)	82.1(2)	N(6)−Hf−N(4)	168.3(2)
N(1)−Hf−N(4)	74.3(2)	N(3)−Hf−N(4)	79.1(2)
N(5)−Hf−N(2)	170.3(2)	N(6)−Hf−N(2)	83.8(2)
N(1)−Hf−N(2)	79.4(2)	N(3)−Hf−N(2)	73.6(2)
N(4)−Hf−N(2)	106.9(2)	C(15)−N(5)−C(16)	108.8(6)
C(15)−N(5)−Hf	128.0(4)	C(16)−N(5)−Hf	122.9(5)
C(18)−N(6)−C(17)	109.7(6)	C(18)−N(6)−Hf	124.7(5)
C(17)−N(6)−Hf	125.9(5)		

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $(Me_4taen)Hf(NMe_2)_2\cdot0.5(C_6H_5Me)$ (**5**·0.5C6H5Me)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Hf	3376(1)	8964(1)	6878(1)	39(1)
N(1)	5909(6)	9494(6)	7084(4)	54(1)
N(2)	3692(7)	7020(5)	6877(4)	53(1)
N(3)	1688(6)	8168(5)	7724(4)	51(1)
N(4)	4396(6)	10482(5)	8577(4)	48(1)
N(5)	3075(6)	10616(5)	6600(4)	51(1)
N(6)	2160(7)	7810(6)	5291(5)	57(1)
C(1)	6862(8)	8776(9)	6928(6)	63(2)
C(2)	6335(10)	7413(9)	6664(6)	73(2)
C(3)	4877(10)	6586(7)	6716(6)	66(2)
C(4)	2294(10)	6133(7)	7050(6)	73(2)
C(5)	1010(8)	6739(7)	7103(6)	68(2)
C(6)	1370(8)	8694(7)	8680(5)	56(2)
C(7)	2249(9)	9946(7)	9410(5)	61(2)
C(8)	3736(9)	10754(6)	9397(5)	55(2)
C(9)	6021(8)	11320(7)	8691(6)	66(2)
C(10)	6544(8)	10952(7)	7634(7)	66(2)
C(11)	8607(9)	9471(13)	7089(8)	92(3)
C(12)	4755(15)	5181(9)	6619(9)	108(4)
C(13)	34(10)	7893(10)	9019(8)	85(2)
C(14)	4581(12)	11939(8)	10425(6)	83(2)
C(15)	2749(10)	11720(8)	7325(6)	73(2)
C(16)	3359(11)	10891(9)	5634(7)	80(2)
C(17)	2480(12)	6680(9)	4575(6)	84(3)
C(18)	764(9)	7948(9)	4780(6)	77(2)
C(19)[b]	−739(33)	4462(21)	9008(19)	84(5)[c]
C(20)[b]	−1235(46)	5163(34)	9995(32)	144(10)[c]
C(21)[b]	−2181(38)	5578(30)	10303(27)	127(8)[c]
C(22)[d]	−125(65)	5810(46)	11261(38)	99(12)[c]
C(23)[b]	−1718(55)	4619(41)	8998(34)	167(12)[c]
C(24)[b]	−5(37)	4554(25)	9395(23)	102(7)[c]
C(25)[d]	−2571(65)	5143(56)	9515(49)	113(14)[c]
C(26)[b]	−1067(46)	5776(32)	10865(29)	134(9)[c]

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] 50% occupancy. [c] Isotropic refinement. [d] 25% occupancy.

X-ray Crystallographic Analysis of $(Me_4taen)Hf(NMe_2)_2$ (5). A yellow single crystal was mounted in a thin-walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric *P*1. The subsequent solution and successful refinement of the structure was carried out in the centric space group $P\bar{1}$. Data collection parameters are given in Table 1. After the ready location of the positions of the $(Me_4taen)Hf(NMe_2)_2$ Hf, C, and N atoms, several diffuse peaks around a crystallographic center of inversion were observed. These peaks were determined to correspond to a disordered half formula unit (per Hf) of toluene. The disorder was modeled with eight carbon positions, six with 0.5 occupancy (C(19), C(20), C(21), C(23), C(24), C(26)) and two with 0.25 occupancy (C(22), C(25)). The solvent C atoms were refined isotropically only, and solvent hydrogen atoms were not included in any of the refinements. The geometrically constrained hydrogen atoms in the Me_4taen and NMe_2 ligands were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2U_{eq}(C)$. The methyl hydrogens were included as a rigid group with rotational freedom at the bonded carbon atom ($B = 1.2U_{eq}(C)$). Refinement of all ordered nonhydrogen atoms was carried out with anisotropic temperature factors. Positional parameters are listed in Table 5.

Results and Discussion

Synthesis of $(Me_4taen)Zr(O^tBu)_2$ (4). We showed previously that chloride substitution reactions of **1** provide access to a variety of $(Me_4taen)ZrX_2$ complexes.[2] The reaction of **1** and

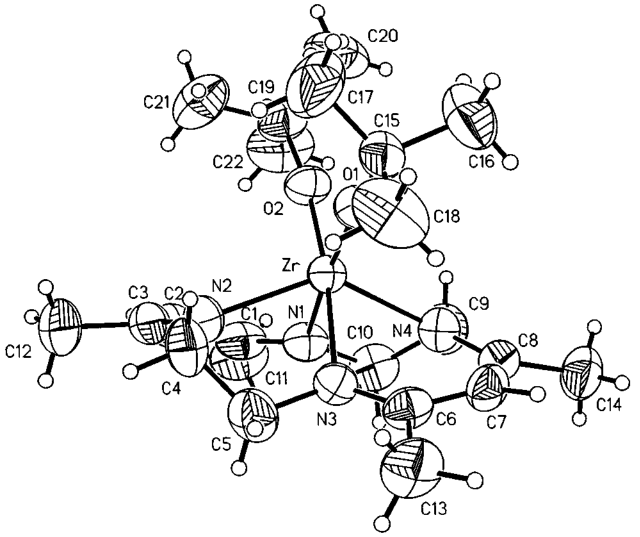
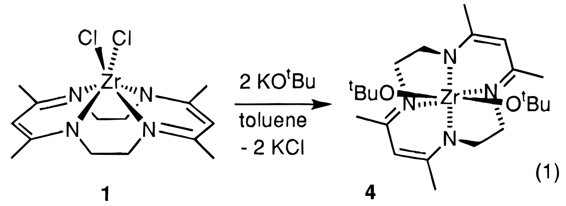
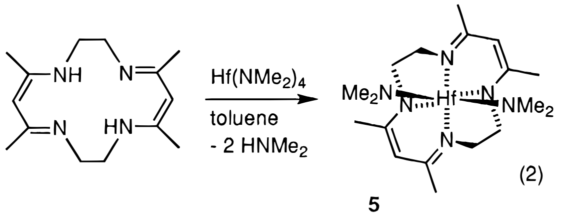


Figure 1. Molecular structure of $(Me_4taen)Zr(O^tBu)_2$ (**4**).

2 equiv of $K[O^tBu]$ in toluene yields $(Me_4taen)Zr(O^tBu)_2$ (**4**), which is isolated in 62% yield as a cream-colored solid (eq 1). The ^1H NMR spectrum of **4** contains singlets for the O^tBu and Me_4taen methyl groups, a singlet for the methine hydrogens, and two multiplets for the $-CH_2CH_2-$ hydrogens. The latter feature is characteristic of *cis*-$(Me_4taen)MX_2$ complexes in which the endo and exo $-CH_2CH_2-$ hydrogens are inequivalent. Complex **4** is highly soluble in benzene and toluene and moderately soluble in aliphatic hydrocarbons.



Synthesis of $(Me_4taen)Hf(NMe_2)_2$ (5). The amine elimination reaction of $Hf(NMe_2)_4$ and $(Me_4taen)H_2$ in toluene yields $(Me_4taen)Hf(NMe_2)_2$ (**5**), which is isolated as a yellow solid in 93% yield (eq 2). This reaction is considerably slower than the corresponding reaction of $Zr(NMe_2)_4$ with $(Me_4taen)H_2$ which yields **3** (18 h vs 6 h at 23 °C), presumably due to the differences in $Zr-NMe_2$ and $Hf-NMe_2$ bond strengths (83.6 kcal/mol vs 88.4 kcal/mol).[12] The spectroscopic properties of **5** are very similar to those of the zirconium analogue **3**, and are consistent with a *cis* structure. The ^1H NMR spectrum contains singlets for the NMe_2 and Me_4taen methyl groups, a singlet for the methine hydrogens, and two multiplets for the $-CH_2CH_2-$ hydrogens.



X-ray Structural Analysis of 4. The molecular structure of **4** is shown in Figure 1. Crystallographic details, key bond distances and angles, and atom coordinates are listed in Tables 1−3. Complex **4** adopts a *cis* structure in which the metal geometry is best described as distorted octahedral. Two *trans* angles approach 180° (O(1)−Zr−N(1), 173.88(7)°; O(2)−Zr−N(3), 172.26(7)°) while the third is markedly contracted (N(2)−Zr−N(4), 134.39(8)°). The *cis* N−Zr−N angles associated with the $-NCH_2CH_2N-$ ligand sectors are highly acute (N(2)−Zr−N(3), 72.47(8)°; N(4)−Zr−N(1), 72.59(8)°), but the remaining *cis* angles around Zr are in the range 82−110°. The (Me_4taen)-Zr fragment in **4** adopts a "basket-like" conformation; the C(1)−N(1)−C(10) and C(5)−N(3)−C(6) units comprise the base of the basket and the N(2)−Zr−N(4) unit comprises the handle. The structure is characterized by a fold angle of 145° between the N(1)−N(2)−N(3) and N(1)−N(3)−N(4) planes. The diiminato units of the ligand are twisted relative to one another such that the N(1)−N(2)−N(3)−N(4) dihedral angle is 25.2°. The average Zr−N distance (2.25(7) Å) in **4** is much larger than in **1** (2.16 Å). The Zr−N bond distances for the nitrogens which are *cis* to the alkoxide groups (Zr−N(2), 2.178(2) Å; Zr−N(4), 2.189(2) Å) are significantly shorter than those for the nitrogens which are *trans* to the alkoxide groups (Zr−N(1), 2.317(2) Å; Zr−N(3), 2.315(2) Å). This difference reflects the strong *trans* influence of the alkoxide ligands. Overall, the structure is very similar to the structure of **3**.

The Zr−O bond distances in **4** (Zr−O(1), 1.945(2) Å; Zr−O(2), 1.948(2) Å) are in the long end of the range (ca. 1.89−1.95 Å) observed for other Zr(IV) *tert*-butoxide complexes with formal valence electron counts of 14−16 (neglecting Zr−O π interactions).[13,14] In particular, the Zr−O distances in **4** are essentially equal to those in $(octaethylporphyrin)Zr(O^tBu)_2$.[13f] These distances are shorter than the sum of the Zr and O covalent radii (ca. 2.14−2.21 Å),[15] which likely reflects a combination of ionic shortening and O−Zr π-donation.[16] Complex **4** is formally a 16 electron species (considering the Me_4taen^{2-} ligand as a 12-electron $\sigma^8\pi^4$ donor), so the two *tert*-butoxide groups share one Zr−O π−bond. The Zr−O−C bond angles of **4** approach 180° (C15−O1−Zr, 179.4(2)°; C19−O2−Zr, 169.5(2)°).

X-ray Structural Analysis of 5. The molecular structure of **5** is shown in Figure 2. Crystallographic details, atom coordinates, and key bond distances and angles are listed in

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(12) (a) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701. (b) Ziegler, T.; Tschinke, V.; Versluis, L.; Baerends, E. V.; Ravenek, W. *Polyhedron* **1988**, *7*, 1625. (c) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830.

(13) (a) $Cp_2Zr(O^tBu)(THF)^+$, 1.899(3) Å; Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092. (b) $Cp_2Zr(O^tBu)Ru(CO)_2Cp$, 1.910(4) Å: Casey, C. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1983**, *105*, 665. (c) $(\eta^8\text{-COT})(\eta^4\text{-allyl})Zr(O^tBu)$, 1.91 Å average: Brauer, D. J.; Krüger, C. *Organometallics* **1982**, *1*, 204. (d) $(Tp)Zr\{C(=N^tBu)Me\}(Me)(O^tBu)$, 1.924(6) Å: Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *2*, 1763. (e) *S,S*-$(EBTHI)Zr(O^tBu)(THF)^+$, 1.929(3) Å: Hong, Y.; Kuntz, B. A.; Collins, S. *Organometallics* **1993**, *12*, 964. (f) $(OEP)Zr(O^tBu)_2$ 1.948 Å average: Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655.

(14) Zr−O distances in more highly electron deficient Zr(IV) alkoxides are expected to be shorter, but may be lengthened by steric crowding. (a) $ZrCl_4(MeOH)(OMe)^-$, 1.847(10) Å: Karia, R.; Willey, G. R.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.*, **1986**, 2493. (b) $Zr\{Si(SiMe_3)_3\}(O^tBu)_3$ 1.89 Å average: Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1989**, *28*, 1768. (c) $(Et_2O)_2Li(\mu\text{-}Cl)_2ZrCl\{OC(^tBu)_3\}_2$, 1.89 Å average: Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics*, **1984**, *3*, 977.

(15) Ranges for the covalent radii sums were estimated from data in the following sources: (a) Covalent radii (Å): Zr, 1.48; Hf, 1.49; O, 0.73; N, 0.75. Porterfield, W. W. *Inorganic Chemistry*, 2nd ed.; Academic Press, Inc.: San Diego, CA, 1993; p 214. (b) Covalent radii (Å): O, 0.66; N, 0.70. Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill, Inc.: New York, 1984; p 52. (c) For a discussion of the O and N covalent radii see ref 15b, p 54.

(16) (a) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900, and references therein. (b) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron*, **1990**, 9, 963. (c) Acho, J. A.; Doerrer, L. H.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 2542. (d) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.

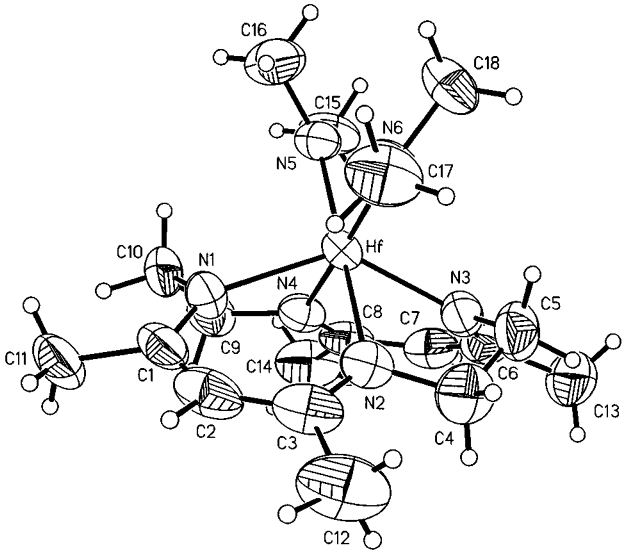

Figure 2. Molecular structure of (Me$_4$taen)Hf(NMe$_2$)$_2$ (**5**).

Tables 1, 4, and 5. Compound **5** adopts a cis structure with a distorted octahedral metal geometry, which is very similar to those of **3** and **4**. Two *trans* angles approach 180° (N(5)−Hf−N(2), 170.3(2)°; N(6)−Hf−N(4), 168.3(2)°) and the third is contracted (N(1)−Hf−N(3), 134.3(2)°). As for **4**, the N−Hf−N angles associated with the −NCH$_2$CH$_2$N− ligand sectors are acute (N(1)−Hf−N(4), 74.3(2)°; N(2)−Hf−N(3), 73.6(2)°) while the remaining *cis* angles range from 79.1(2) to 113.3(2)°. The (Me$_4$taen)Hf unit adopts a basket-like conformation similar to that in **4**. The N(1)−N(2)−N(4)/N(2)−N(4)−N(3) fold angle is 28.7°, and the N(1)−N(2)−N(3)−N(4) dihedral angle, which defines the relative twisting of the diiminato planes, is −20.6°. The atoms Hf, N(2), N(4), N(5), and N(6) are planar to within 0.1 Å. The Hf−N$_{\text{macrocycle}}$ bonds *cis* to the amide groups are shorter (2.176(5) Å average) than those *trans* to the amides (2.278(6) Å average) as a result of the *trans* influence of the amide ligands.

The Hf−N$_{\text{amide}}$ distances in **5** (2.091(5), 2.093(5) Å) are within the range reported for the few other Hf(IV) amides which have been crystallographically characterized (2.03−2.12 Å).[17] These distances are shorter than the sum of the Hf and N covalent radii (ca. 2.19−2.24 Å),[15] again reflecting ionic and π contributions to the Hf−NR$_2$ bonds. The NMe$_2$ groups in **5** are flat (sum of angles around N = 359.7°), consistent with a N−Hf π interaction.[18] The amide ligands are oriented over the Hf−N(2) and Hf−N(4) bonds and are rotated an average of 33° out of the Hf−N(2)−N(4)−N(5)−N(6) plane.[19]

Structural Trends in Group 4 Metal (Me$_4$taen)MX$_2$ Complexes. The group 4 metal (Me$_4$taen)MX$_2$ complexes described here and earlier[2] may be grouped into two structural types (Chart 1): distorted trigonal prismatic structures (**1**, **2**; X = Cl, CH$_2$Ph) and distorted octahedral structures (**3**−**5**; X = NMe$_2$, O^{t}Bu). As there is no evidence that interligand steric interactions strongly influence the structures of any of these species, it is believed that the structures are determined primarily by the electronic properties of the X ligands. As noted above, the conformational properties of the Me$_4$taen^{2-} macrocycle and the covalent character of and absence of a strong π-component in the M−X bonds favor trigonal prismatic structures for **1** and **2**. In contrast, M−NR$_2$ and M−OR π-bonding in **3**−**5** promotes distortion toward an octahedral structure. The constraints imposed by the tetradentate Me$_4$taen^{2-} ligand prevent **3**−**5** from achieving more ideal octahedral structures.[20]

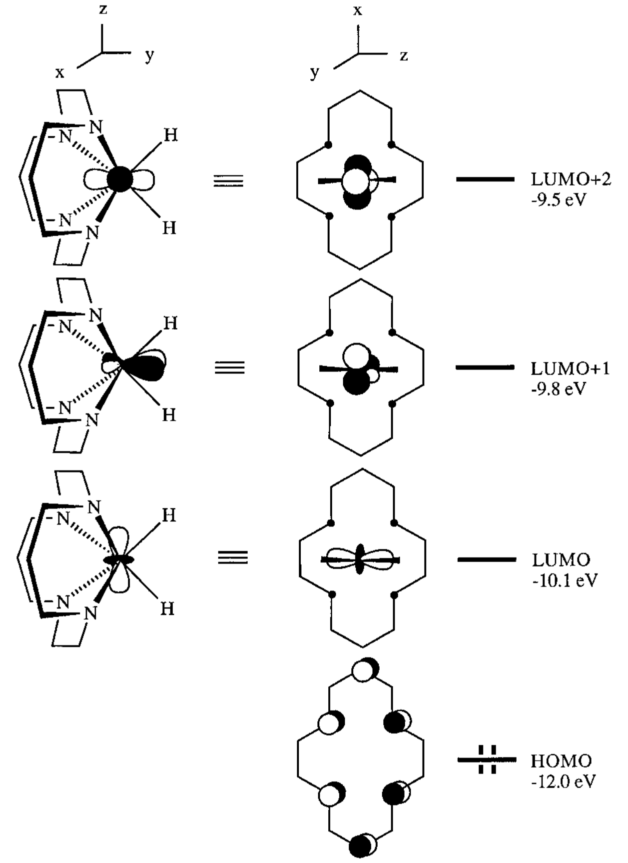

Figure 3. Frontier orbitals for the model complex (taen)ZrH$_2$ (**6**) with a trigonal prismatic structure derived from that of (Me$_4$taen)ZrCl$_2$ (**1**) as described in the text.

Frontier Orbital Properties of Model (taen)ZrH$_2$ Complexes. A corollary to the conclusion that M−X π bonding strongly influences the structures of (Me$_4$taen)MX$_2$ complexes is that the structure of the (Me$_4$taen)M unit should influence its π-acceptor properties. To probe the nature of the metal π-acceptor orbitals in (Me$_4$taen)MX$_2$ complexes, we performed extended Hückel molecular orbital analyses for the model compound (taen)ZrH$_2$ in two geometries.[21] In **6**, (taen)ZrH$_2$ is given the trigonal prismatic structure of (Me$_4$taen)ZrCl$_2$ (**1**), while in **7**, it is given the distorted octahedral structure of (Me$_4$taen)Zr(O^{t}Bu)$_2$ (see Figures 3 and 4). In both **6** and **7**, the macrocycle methyl groups were replaced with hydrogens to simplify the calculations, and the Zr−H distances were set at

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(17) (a) Cp$_2$*Hf(H)NHMe, 2.027(8) Å; Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309. (b) *rac*-(EBI)Hf(NMe$_2$)$_2$, 2.07 Å average: Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics*, in press. (c) Hf{NH(2,6-^{i}Pr$_2$-C$_6$H$_3$)}$_2${=N(2,6-^{i}Pr$_2$-C$_6$H$_3$)}(4-pyrrolidinopyridine)$_2$, 2.12 Å average: Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689.

(18) (a) Andersen, R. A.; Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1985**, *24*, 4741. (b) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. (c) Lukens, W. W.; Smith, M. R.; Anderson, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 1719.

(19) Angles between planes: Hf−N2−N4−N5−N6/C17−N6−C18, 37.3°; Hf−N2−N4−N5−N6/C15−N5−C16, 28.3°.

(20) It is possible that differences in the ionic character of the M−X bonds may influence the structures of (Me$_4$taen)MX$_2$ complexes. However if this were the case, **1** would be expected to adopt a distorted octahedral structure similar to those of **3**−**5**, as revised Pauling electronegativity values suggest that the Zr−Cl bonds in this species are probably more polar than the M−NR$_2$ bonds in **3** and **5**. χ values: N, 3.04; Cl, 3.16; O, 3.44.

(21) Extended Hückel calculation were performed on a CaChe system (CaChe Scientific, Inc.), release 3.6, version number CA45R. The Alvarez parameter set included in this version was used; parameter *K* was set to 1.75.

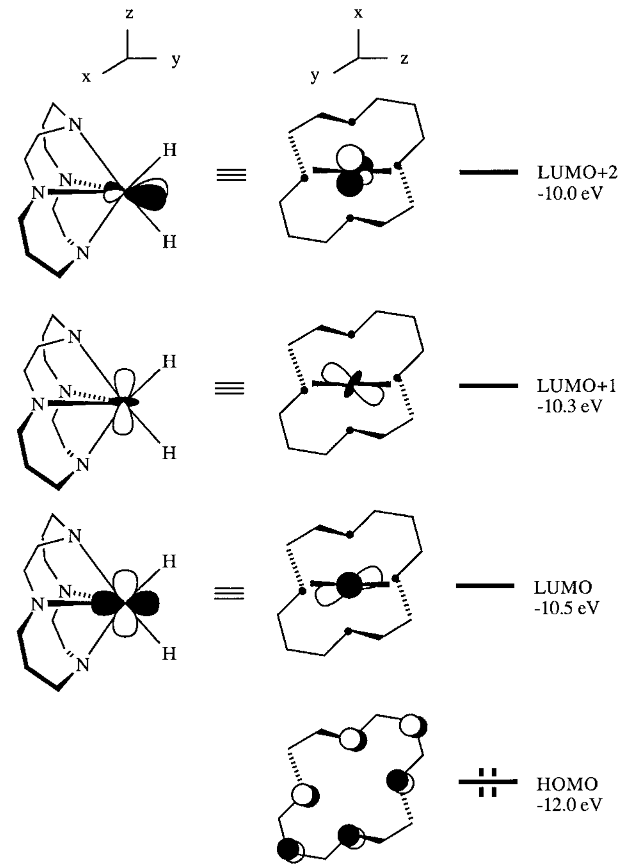

Figure 4. Frontier orbitals for the model complex (taen)ZrH$_2$ (**7**) with a distorted octahedral structure derived from that of (Me$_4$taen)Zr(O^t-Bu)$_2$ (**4**) as described in the text.

1.90 Å.[22] In **6** and **7**, the X groups are σ-donor hydride ligands, so the metal π-acceptor orbitals (which would be used for M−X π-bonding in (Me$_4$taen)MX$_2$ species containing potential π-donor X ligands) can be easily indentified and visualized.

The frontier orbitals of **6** are shown schematically in Figure 3. The HOMO is localized on the taen ligand. The LUMO has mainly d$_{z^2}$ character, as expected from the ligand field splitting diagram for a trigonal prismatic structure. The next two unoccupied orbitals have mainly d$_{xy}$ and d$_{x^2-y^2}$ character respectively. The LUMO and LUMO+1 are potential π-acceptor orbitals, but neither is oriented for optimum π-interaction with potential π-donor ligands at the H sites. The LUMO+2 has δ symmetry with respect to the Zr−H sites. The taen CN π^* orbitals lie at higher energy. The frontier orbitals of **6** are similar to those of (Me$_4$taa)ZrX$_2$ species.[23]

The frontier orbitals of **7** are shown in Figure 4. The ligand based HOMO is very similar to that of **6**. The three lowest unoccupied orbitals are 0.4 eV lower in energy than the corresponding orbitals in **6**, as expected since the Zr−N$_{\mathrm{macrocycle}}$ distances are shorter in **7** than in **6**, and the metal center is correspondingly more electron deficient. The LUMO is a d hybrid orbital which is tilted ca. 20° out of the *yz* plane. Significantly, this orbital is almost ideally oriented for π-interactions with potential π-donors at the Zr−H sites. Thus, if the Zr−H ligands are replaced with π-donor ligands, a strong π-interaction with the LUMO is expected. The LUMO+1 and LUMO+2 are potentially π-acceptors, but are less optimally oriented than the LUMO.

This simple analysis suggests that distortion of a (Me$_4$taen)ZrX$_2$ complex from the trigonal prismatic structure of type **6** to a distorted octahedral structures of type **7** does indeed increase the π-acceptor ability of the metal center. In (Me$_4$taen)ZrX$_2$ species with structure **7**, the X groups may compete for π-donation to the metal LUMO, and may also engage in less effective π donation to the LUMO+1 and LUMO+2 orbitals. As noted above, the shortening of the Zr−O and Hf−NMe$_2$ bonds in **4** and **5** may be ascribed in part to such π-donation.

The orientation of the NR$_2$ groups provides an additional probe of N−M π-bonding in metal amide complexes. For a (Me$_4$taen)M(NR$_2$)X mono(amide) species with a structure similar to that of **7**, the M−NR$_2$ π-interaction is maximized with a R$_2$N−M−X/R−N−R dihedral angle of ca 70°, since the LUMO is tilted ca. 20° out of the *yz* plane (Figure 4). However, for bis(amide) complexes such as **3** and **5**, this orientational preference will be much less pronounced, since the two amide π-donors must share one π bond with the LUMO. Additionally π-interactions involving the LUMO+1 and LUMO+2 may be important. The observed R$_2$N−M−X/R−N−R dihedral angles in **5** are ca. 33°; i.e., the amide groups are rotated ca. 37° from the optimum orientation for N−Hf π bonding.

Acknowledgment. This work was supported by DOE Grant DE-FG02-88ER13935.

Supporting Information Available: Complete listings of crystallographic data, atomic coordinates and equivalent displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for **4** and **5** (15 pages). Ordering information is given on any current masthead page.

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(22) The terminal Zr−H bond length for [(η^5-C$_5$H$_4$CH$_3$)$_2$ZrH(μ-H)]$_2$ is 1.78 Å. Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

(23) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801.