Mononuclear Amido and Binuclear Imido Zirconium Complexes Supported by Dibenzotetraaza[14]annulene Ligands. X-ray Structure of [$(Me_4taa)Zr(\mu\text{-}NR)_2Zr(NHR)_2$] (R = Bu^t or 2,6-$C_6H_3Me_2$)

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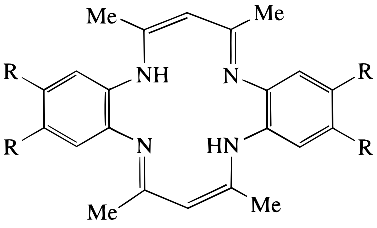
Reaction of 2 equiv of Li[NH-2,6-$C_6H_3R_2$] with [$(Me_4taa)ZrCl_2$] (Me_4taaH_2 = tetramethyldibenzotetraaza[14]annulene) gives the bis(amido) derivatives [$(Me_4taa)Zr(NH\text{-}2,6\text{-}C_6H_3R_2)_2$] [R = Pr^i (**1**) and Me (**2**)]. Addition of Me_4taaH_2 to [$Zr(N\text{-}2,6\text{-}C_6H_3Pr^i{}_2)(NH\text{-}2,6\text{-}C_6H_3Pr^i{}_2)_2(py)_2$] also affords **1**. The reaction of 2 equiv of aryl or alkyl amines H_2NR with the bis(alkyl) complex [$(Me_4taa)Zr(CH_2SiMe_3)_2$] is the most versatile method for preparing [$(Me_4taa)Zr(NHR)_2$] (R = 2,6-$C_6H_3Pr^i{}_2$, 2,6-$C_6H_3Me_2$, Ph, or Bu^t). Reaction of 1 equiv of Me_4taaH_2 with the binuclear complexes [$(Bu^tNH)_2Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2$] or [$(py)(HN\text{-}2,6\text{-}C_6H_3Me_2)_2Zr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Zr(NH\text{-}2,6\text{-}C_6H_3Me_2)_2(py)$] gives the asymmetrically substituted derivatives [$(Me_4taa)Zr(\mu\text{-}NR)_2Zr(NHR)_2$] [R = Bu^t (**6**) or 2,6-$C_6H_3Me_2$ (**8**)], which have been crystallographically characterized.

Introduction

The tetraazaannulene systems Me_ntaa (n = 4 or 8 = tetra- and octamethyldibenzotetraaza[14]annulene, respectively) have attracted renewed interest recently as useful coligands in early transition metal chemistry.[1−12] The Me_ntaa ligands differ from the porphyrins in having a saddle-shaped, nonplanar conformation and a slightly smaller (by *ca.* 0.1 Å) coordination cavity. Consequently, transition metal complexes of the type [$(Me_n$-taa)$M(L)_n$] invariably have the $M(L)_n$ fragment lying out of the N_4 plane of the Me_ntaa ring, and, in addition, $(L)_n$ ancilliary ligands adopt a mutually *cis*-configuration. Partly because of these characteristics, the Me_ntaa (and closely related[13]) ligands have recently been studied as alternatives to the bis(cyclopentadienyl) ancilliary ligand set in group 4 chemistry.[2,3,6,7,9]



Me_4taaH_2, R = H; Me_8taaH_2, R = Me

The Me_ntaa ligands are also valuable supporting groups for transition[8,10,11,14−17] metal−ligand and main group[18,19] metal−ligand multiple bonds. We have been developing group 4 imido chemistry[14−16,20−23] and were interested in comparing the chemistry and properties of Me_ntaa-supported imido compexes with those of the bis(cyclopentadienyl)-supported complexes so successfully exploited by Bergman[24−27] and others.[28−30] In pursuit of these objectives we recently reported the first tetraaza macrocycle-supported group 4 imido complexes [$(Me_n$taa)Ti-

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(NR)] (n = 4 or 8; R = Bu^t or aryl) and [(Me$_4$taa)Zr(N-2,6-C$_6$H$_3$Pr$^i_2$)(py)] (py = pyridine) together with some theoretical and reactivity studies.[14−16] In parallel studies we have developed other new Me$_4$taa-supported amido and imido zirconium chemistry and report here the synthesis and characterization of mononuclear bis(amido) and binuclear bis(μ-imido) derivatives.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out under an atmosphere of argon or dinitrogen using standard Schlenk-line or drybox techniques. Solvents, *tert*-butylamine and pyridine were predried over activated molecular sieves and distilled from the appropriate drying agent under an atmosphere of dinitrogen. Anilines were predried over calcium hydride and distilled under reduced pressure. C$_6$D$_6$ was dried over molten potassium, distilled under reduced pressure, and stored under N$_2$ in a Young's ampule. NMR samples were prepared in the drybox in 5 mm Wilmad tubes equipped with a Young's NMR/5 valve. Celite 545 filtration aid was dried at 150 °C for at least 48 h before use.

^{1}H and ^{13}C NMR spectra were recorded on either a Bruker WM 250, DPX 300, or AM 400 spectrometer. The spectra were referenced internally to residual protiosolvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Elemental analyses were carried out by the analysis department of this laboratory.

Literature Preparations. Li[NH-2,6-C$_6$H$_3$Pr$^i_2$],[31] Li[CH$_2$SiMe$_3$],[32] [Zr(CH$_2$SiMe$_3$)$_4$],[33] [Zr(N-2,6-C$_6$H$_3$Pr$^i_2$)(NH-2,6-C$_6$H$_3$Pr$^i_2$)$_2$(py)$_2$],[34] [(Bu^{t}NH)$_2$Zr(μ-NBu^t)$_2$Zr(NHBu^t)$_2$],[35] Me$_4$taaH$_2$,[36] [ZrCl$_4$(THF)$_2$][37] (THF = tetrahydrofuran), and [(Me$_4$taa)ZrCl$_2$][3] were prepared according to literature methods. Li[NH-2,6-C$_6$H$_3$Me$_2$] and Li[NH-2,4,6-C$_6$H$_2$Bu$^t_3$] were prepared in a way analogous to that used for Li[NH-2,6-C$_6$H$_3$Pr$^i_2$].

[(Me$_4$taa)Zr(NH-2,6-C$_6$H$_3$Pr$^i_2$)$_2$] (1). Method a. A solution of Li[NH-2,6-C$_6$H$_3$Pr$^i_2$] (0.360 g, 1.96 mmol) in THF (15 mL) was added dropwise to a stirred, cold (0 °C) suspension of [(Me$_4$taa)ZrCl$_2$] (0.499 g, 0.989 mmol) in THF (25 mL). The resultant red-cherry mixture was stirred for 16 h at room temperature, the volatiles were removed under reduced pressure, and the residue was extracted into diethyl ether (50 mL). The solution was filtered, concentrated, and placed at −25 °C overnight. Red crystals were filtered off and dried *in vacuo*; yield, 0.332 g (43%). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K): δ 7.22 (d, 4 H, J = 5.9 Hz, *m*-C$_6$*H*$_3$Pr$^i_2$), 7.00−7.10 (m, 10 H, overlapping *p*-C$_6$*H*$_3$Pr$^i_2$ and C$_6$H$_4$ of Me$_4$taa), 5.65 (br s, 2 H, NH), 5.20 (s, 2 H, C(=N)C*H*C(=N) of Me$_4$taa), 2.95 (sept, 4 H, J = 7.1 Hz, C*H*Me$_2$), 2.09 (s, 12H, *Me*C(=N) of Me$_4$taa), 1.19 (d, 24 H, J = 7.1 Hz, CH*Me$_2$*); ^{13}C−{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ 160.0 (Me*C*=N of Me$_4$taa), 150.9 (ipso-*C*$_6$H$_3$Pr$^i_2$), 139.8 (*C*-N of C$_6$H$_4$ of Me$_4$taa), 137.8 (*o*-*C*$_6$H$_3$Pr$^i_2$), 125.4, 125.0 (2 × *C*—H of C$_6$H$_4$ of Me$_4$taa), 122.0 (*m*-*C*$_6$H$_3$Pr$^i_2$), 120.0 (*p*-*C*$_6$H$_3$Pr$^i_2$), 105.6 (C(=N)*C*HC(=N) of Me$_4$taa), 28.1 (*C*HMe$_2$), 24.0 (CH*Me*$_2$), 22.5 (*Me*C(=N) of Me$_4$taa). Anal. Calcd for C$_{46}$H$_{58}$N$_6$Zr: C, 70.3; H, 7.4; N, 10.7%. Found: C, 69.3; H, 7.9; N, 11.4%.

Method b. A mixture of [Zr(N-2,6-C$_6$H$_3$Pr$^i_2$)(NH-2,6-C$_6$H$_3$Pr$^i_2$)$_2$(py)$_2$] (1.247 g, 1.156 mmol) and Me$_4$taaH$_2$ (0.318 g, 1.156 mmol) in toluene (80 mL) was heated at 70 °C for 16 h, affording a dark red solution. Removal of the volatiles under reduced pressure and recrystallization from diethyl ether at room temperature afforded **1** as a yellow-orange powder; yield, 0.680 g (66%).

Method c. A solution of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (0.983 g, 0.331 mmol) and H$_2$N-2,6-C$_6$H$_3$Pr$^i_2$ (0.573 g, 0.333 mmol) in toluene (30 mL) was stirred for 16 h at room temperature. The volatiles were removed under reduced pressure to leave an orange oil to which was added hexane (15 mL). The mixture was stirred rapidly for 30 min, and the supernatant was filtered off, leaving **1** as a yellow-orange powder; yield, 1.027 g (81%).

[(Me$_4$taa)Zr(NH-2,6-C$_6$H$_3$Me$_2$)$_2$] (2). Method a. A mixture of Li[NH-2,6-C$_6$H$_3$Me$_2$] (0.5150 g, 2.027 mmol) and [(Me$_4$taa)ZrCl$_2$] (1.023 g, 4.051 mmol) in THF (20 mL) was stirred for 3 h. The volatiles were removed under reduced pressure and the residue was extracted into toluene (45 mL) and filtered to remove LiCl. Removal of the volatiles under reduced pressure gave **2** as a yellow-orange powder; yield, 0.517 g (38%). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K): δ 7.0−7.15 (m, 12 H, overlapping *m*-C$_6$*H*$_3$Me$_2$ and C$_6$H$_4$ of Me$_4$taa), 6.85 (t, 2 H, J = 5.8 Hz, *p*-C$_6$*H*$_3$Me$_2$), 5.34 (br s, 2 H, NH), 5.21 (s, 2 H, C(=N)C*H*C(=N) of Me$_4$taa), 2.08 (s, 12 H, *Me*C(=N) of Me$_4$taa), 1.93 (s, 12 H, C$_6$H$_3$*Me*$_2$). ^{13}C−{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 298 K): δ 159.9 (Me*C*=N of Me$_4$taa), 153.5 (ipso-*C*$_6$H$_3$Me$_2$), 137.4 (overlapping *C*—N of C$_6$H$_4$ of Me$_4$taa and *o*-*C*$_6$H$_3$Me$_2$), 125.3—125.4 (overlapping 2 × *C*—H of C$_6$H$_4$ of Me$_4$taa and *m*-*C*$_6$H$_3$Me$_2$), 118.4 (*p*-*C*$_6$H$_3$Me$_2$), 105.1 (C(=N)*C*HC(=N) of Me$_4$taa), 22.8 (*Me*C(=N) of Me$_4$taa), 18.3 (C$_6$H$_3$*Me*$_2$). Anal. Calcd for C$_{38}$H$_{42}$N$_6$Zr: C, 67.5; H, 6.3; N, 12.1%. Found: C, 68.7; H, 6.9; N, 12.2%.

Method b. To a solution of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (0.095 g, 0.156 mmol) in toluene (10 mL) was added H$_2$N-2,6-C$_6$H$_3$Me$_2$ (0.10 mL, 0.81 mmol). The solution was stirred for 3 h, and the volatiles were removed under reduced pressure. The resultant red oil was vigorously stirred with pentane (5 mL) to afford **2** as a red-orange powder which was filtered off and dried *in vacuo*; yield, 0.050 g (47%).

[(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (3). Method a. A mixture of [(Me$_4$taa)ZrCl$_2$] (0.694 g, 1.38 mmol) and Li[CH$_2$SiMe$_3$] (0.259 g, 2.75 mmol) in toluene (20 mL) was stirred for 3 h. As the reaction proceeded, a further volume of toluene (120 mL) was added to ensure complete dissolution of the product. The solution was filtered, and the volume was reduced to *ca.* 10 mL. Pentane (5 mL) was added, and the resultant yellow-orange precipitate was filtered off, washed with pentane (5 mL), and dried *in vacuo*; yield, 0.475 g (53%). ^{1}H NMR (C$_6$D$_6$, 250 MHz, 298 K): δ 7.40−7.50 and 7.10−7.20 (2 × m, 2 × 4 H, C$_6$H$_4$ of Me$_4$taa), 5.14 (s, 2 H, C(=N)C*H*C(=N) of Me$_4$taa), 2.13 (s, 12 H, *Me*C(=N) of Me$_4$taa), 0.25 (s, 4 H, C*H*$_2$SiMe$_3$), 0.21 (s, 18 H, SiMe$_3$). ^{13}C−{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 298 K): δ 159.3 (Me*C*=N of Me$_4$taa), 134.5 (*C*—N of C$_6$H$_4$ of Me$_4$taa), 103.7 (C(=N)*C*HC(=N) of Me$_4$taa), 46.5 (*C*H$_2$SiMe$_3$), 23.3 (*Me*C(=N) of Me$_4$taa), 3.8 (SiMe$_3$) (2 × *C*—H of C$_6$H$_4$ of Me$_4$taa obscured by solvent). Anal. Calcd for C$_{30}$H$_{44}$N$_4$Si$_2$Zr: C, 59.3; H, 7.3; N, 9.2%. Found: C, 60.4; H, 7.3; N, 9.4%.

Method b. A mixture of [Zr(CH$_2$SiMe$_3$)$_4$] (3.76 g, 8.54 mmol) and Me$_4$taaH$_2$ (2.86 g, 8.30 mmol) were stirred in toluene (40 mL) for 6 days at room temperature. The supernatant was separated, and the yellow-orange residue was washed with hexane (10 mL) and dried *in vacuo*; yield, 4.72 g (94%).

[(Me$_4$taa)Zr(NHPh)$_2$] (4). To a solution of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (0.514 g, 0.845 mmol) in toluene (20 mL) was added H$_2$NPh (0.3 mL, 3.29 mmol). The solution was stirred for 24 h, and the volatiles were removed under reduced pressure. The oily residues were vigorously stirred with pentane (10 mL), filtered, and dried *in vacuo* to give **4** as a yellow powder; yield, 0.250 g (48%). ^{1}H NMR (C$_6$D$_6$, 250 MHz, 298 K): δ 7.00−7.25 (m, 12 H, overlapping *m*-C$_6$H$_5$ and C$_6$H$_4$ of Me$_4$taa), 6.95 (t, 2 H, J = 6.1 Hz, *p*-C$_6$H$_5$), 6.34 (d, 4 H, J = 5.9 Hz, *o*-C$_6$H$_5$), 5.75 (br s, 2 H, NH), 5.35 (s, 2 H, C(=N)C*H*C(=N) of Me$_4$taa), 2.08 (s, 12 H, *Me*C(=N) of Me$_4$taa). ^{13}C−{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 298 K): δ 159.7 (Me*C*=N of Me$_4$taa), 147.1 (ipso-*C*$_6$H$_5$), 141.4 (*C*—N of C$_6$H$_4$ of Me$_4$taa), 129.4 (*o*-C$_6$H$_5$), 124.4, 123.3 (2 × C$_6$H$_4$ of Me$_4$taa), 118.3, 115.1 (*m*- and *p*-C$_6$H$_5$), 104.8 (C(=N)*C*HC(=N) of Me$_4$taa), 23.2 (*Me*C(=N) of Me$_4$taa). Satisfactory elemental analysis was not obtained.

[(Me$_4$taa)Zr(NHBu^t)$_2$] (5). To a solution of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (1.512 g, 2.486 mmol) in toluene (20 mL) was added H$_2$NBu^t (1.0 mL, 9.5 mmol).The solution was stirred for 5.5 h, and the volatiles were removed under reduced pressure. The residues were washed with pentane (5 mL) and dried *in vacuo* to give **5** as a red-orange powder; yield, 1.36 g (95%). ^{1}H NMR (C$_6$D$_6$, 250 MHz, 298 K): δ 7.28, 7.12 (2 × m, 2 × 4 H, C$_6$H$_4$ of Me$_4$taa), 5.16 (s, 2 H, C(=N)C*H*C(=N) of Me$_4$taa), 4.40 (br s, 2 H, NH), 2.13 (s, 12 H, *Me*C-

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(=N) of Me$_4$taa), 1.30 (s, 18 H, Bu^t). ^{13}C−{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 298 K): δ 158.9 (Me*C*=N of Me$_4$taa), 125.2, 124.8 (2 × *C*—H of C$_6$H$_4$ of Me$_4$taa), 103.2 (C(=N)*C*HC(=N) of Me$_4$taa), 54.0 (*C*Me$_3$), 34.6 (C*Me*$_3$), 23.2 (*Me*C(=N) of Me$_4$taa) (*C*—N of C$_6$H$_4$ of Me$_4$taa not observed). Anal. Calcd for C$_{30}$H$_{42}$N$_6$Zr: C, 62.4; H, 7.3; N, 14.5%. Found: C, 64.0; H, 7.4; N, 14.0%.

Reaction of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] with 1 equiv of H$_2$N-2,6-C$_6$H$_3$Pr$^i_2$. A mixture of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (0.201 g, 0.331 mmol) and H$_2$N-2,6-C$_6$H$_3$Pr$^i_2$ (0.059 g, 0.333 mmol) in toluene (10 mL) were stirred for 14 h. The volatiles were removed under reduced pressure to yield an orange solid (0.151 g) shown by ^{1}H NMR to be a *ca*. 50:50 mixture of [(Me$_4$taa)Zr(NH-2,6-C$_6$H$_3$Pr$^i_2$)$_2$] (**1**) and unreacted [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (**3**).

NMR Tube Reaction of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] with 1 equiv of H$_2$N-2,6-C$_6$H$_3$Pr$^i_2$ in the Presence of Pyridine. To a mixture of [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (9.9 mg, 1.6 μmol) and pyridine (2.7 μL, 3.2 μmol) in C$_6$D$_6$ (0.75 mL) was added H$_2$N-2,6-C$_6$H$_3$Pr$^i_2$ (3 μL, 1.6 μmol). After 3 h the ^{1}H NMR spectrum revealed a *ca*. 50:50 mixture of [(Me$_4$taa)Zr(NH-2,6-C$_6$H$_3$Pr$^i_2$)$_2$] (**1**), unreacted [(Me$_4$taa)Zr(CH$_2$SiMe$_3$)$_2$] (**3**), and pyridine.

[(Me$_4$taa)Zr(μ-NBu^t)$_2$Zr(NHBu^t)$_2$] (6). A mixture of [(Bu^{t}NH)$_2$Zr(μ-NBu^t)$_2$Zr(NHBu^t)$_2$], (0.480 g, 0.783 mmol) and Me$_4$taaH$_2$ (0.271 g, 0.787 mmol) in toluene (25 mL) was heated for 1 h at 80 °C. Cooling the solution afforded **6** as well-shaped yellow crystals (0.292 g) which were separated, washed with toluene (*ca.* 5 mL), and dried *in vacuo*. Concentration of the combined washings and mother liquors to *ca.* 10 mL gave a second crop of **6** (0.062 g); combined yield, 0.354 g (56%). Careful recrystallization from toluene afforded diffraction quality crystals which were also suitable for elemental analysis. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ 7.27, 7.12 (2 × m, 2 × 4 H, C$_6$H$_4$ of Me$_4$taa), 5.06 (s, 2 H, s, 2 H, C(=N)C*H*C(=N) of Me$_4$taa), 2.82 (br s, 2 H, NH), 2.04 (s, 12 H, *Me*C(=N) of Me$_4$taa), 1.65 (s, 18 H, μ-N*Bu*^{t}), 1.30 (s, 18 H, NH*Bu*^{t}). ^{13}C−{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): δ 160.1 (Me*C*=N of Me$_4$taa), 137.4 (*C*—N of C$_6$H$_4$ of Me$_4$taa), 125.6, 125.1 (2 × *C*—H of C$_6$H$_4$ of Me$_4$taa), 102.5, (C(=N)*C*HC(=N) of Me$_4$taa), 61.2 (μ-N*C*Me$_3$), 52.5 (NH*C*Me$_3$), 35.6, 34.5 (μ-NC*Me*$_3$ and NHC*Me*$_3$), 22.7 (*Me*C(=N) of Me$_4$taa). Anal. Calcd for C$_{38}$H$_{60}$N$_8$Zr$_2$·C$_7$H$_8$: C, 59.8; H, 7.6; N, 12.4%. Found: C, 58.9; H, 7.7; N, 12.6%.

[(py)(NH-2,6-C$_6$H$_3$Me$_2$)$_2$Zr(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Zr(NH-2,6-C$_6$H$_3$Me$_2$)$_2$(py)] (7). To a suspension of [ZrCl$_4$(THF)$_2$] (2.30 g, 6.10 mmol) in THF (20 mL) at 0 °C was added a cold solution of Li[NH-2,6-C$_6$H$_3$Me$_2$] (2.86 g, 22.5 mmol) in THF (20 mL). The mixture was stirred for 3 h, and an excess of pyridine (4 mL, 50 mmol) was added. After stirring for a further 16 h, the volatiles removed under reduced pressure and the residues were extracted into toluene (300 mL) and filtered through Celite. Removal of the toluene under reduced pressure gave **7** as a yellow solid, which was washed with diethyl ether (10 mL) and dried *in vacuo*; yield, 2.313 g (78%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ 8.41 (d, 4 H, J = 5.1 Hz, *o*-NC$_5$H$_5$), 7.03, 6.96 (2 × d, 8 H and 4 H, J = 5.8 and 5.9 Hz, *m*-NH-2,6-C$_6$*H*$_3$Me$_2$ and *m*-(μ-N-2,6-C$_6$*H*$_3$Me$_2$)), 6.81, 6.78 (2 × t, 4 H and 2 H, J = 5.8 and 5.9 Hz, *p*-NH-2,6-C$_6$*H*$_3$Me$_2$ and *p*-(μ-N-2,6-C$_6$*H*$_3$Me$_2$)), 6.71 (t, 2 H, J = 5.8 Hz, *p*-NC$_5$H$_5$), 6.55 (br s, 4 H, NH), 6.32 (apparent t, 4 H, apparent J = 5.8 Hz, *m*-NC$_5$H$_5$), 2.70 (s, 12 H, μ-(N-2,6-C$_6$H$_3$*Me*$_2$)), 2.33 (s, 24 H, NH-2,6-C$_6$H$_3$*Me*$_2$). Anal. Calcd for C$_{58}$H$_{68}$N$_8$Zr$_2$: C, 65.7; H, 6.5; N, 10.6%. Found: C, 66.7; H, 6.8; N, 10.6%.

[(Me$_4$taa)Zr(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Zr(NH-2,6-C$_6$H$_3$Me$_2$)$_2$] (8). A mixture of **7** (0.108 g, 0.102 mmol) and Me$_4$taaH$_2$ (0.035 g, 0.102 mmol) in toluene (10 mL) was stirred for 8 h at 70 °C, and the volatiles were removed under reduced pressure. The NMR spectrum of the residue was interpreted as a mixture of [(Me$_4$taa)Zr(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Zr(NH-2,6-C$_6$H$_3$Me$_2$)$_2$], [(Me$_4$taa)$_2$Zr],[3] and **8**. Macroscopic separation of the components of this mixture was not possible. However, a few crystals of **8**·C$_7$H$_8$ suitable for ^{1}H NMR and X-ray analyses separated at room temperature from the reaction mixture. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ 6.85−7.30 (overlapping m, 20 H, C$_6$H$_4$ of Me$_4$taa, *m*- and *p*-NH-2,6-C$_6$*H*$_3$Me$_2$ and *m*- and *p*-(μ-N-2,6-C$_6$*H*$_3$Me$_2$)), 5.59 (br s, 2 H, NH), 5.04 (s, 2 H, C(=N)C*H*C(=N) of Me$_4$taa), 2.18 (s, 12 H, *Me*C(=N) of Me$_4$taa), 1.93, 1.89 (2 × s, 2 × 12 H, μ-(N-2,6-C$_6$H$_3$*Me*$_2$) and NH-2,6-C$_6$H$_3$*Me*$_2$). Insufficient quantities of pure material for elemental analysis were obtained.

Table 1. X-ray Data Collection and Processing Parameters for [(Me$_4$taa)Zr(μ-NBu^t)$_2$Zr(NHBu^t)$_2$]·C$_7$H$_8$ (**6**·C$_7$H$_8$) and [(Me$_4$taa)Zr(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Zr(NH-2,6-C$_6$H$_3$Me$_2$)$_2$]·C$_7$H$_8$ (**8**·C$_7$H$_8$)

	6·C$_7$H$_8$	**8**·C$_7$H$_8$
mol form	C$_{38}$H$_{60}$N$_8$Zr$_2$·C$_7$H$_8$	C$_{54}$H$_{60}$N$_8$Zr$_2$·C$_7$H$_8$
fw	903.51	1095.7
temp/K	150.0(2)	150.0(2)
cryst syst	orthorhombic	monoclinic
space group	*Pnma*	*C*2/*c*
unit cell dimens:		
a/Å	19.286(7)	25.353(11)
b/Å	12.662(6)	15.394(4)
c/Å	18.260(8)	16.423(4)
β/deg		123.75(2)
vol/Å^3	4459	5332
Z	4	4
density(calcd)/(mg·m^{-3})	1.346	1.366
absorpn coeff/mm^{-1}	0.510	0.440
cryst size/mm	0.75 × 0.75 × 0.45	0.60 × 0.53 × 0.45
independ reflcns	3797	4339
reflcns with [$I > 2\sigma(I)$]	3240	3515
R,[a] R_w[b]	0.044, 0.043	0.042, 0.047
goodness-of-fit	0.952	1.196

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum(w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$.

Crystal Structure Determinations of [(Me$_4$taa)Zr(μ-NBu^t)$_2$Zr(NHBu^t)$_2$]·C$_7$H$_8$ (6·C$_7$H$_8$) and [(Me$_4$taa)Zr(μ-N-2,6-C$_6$H$_3$Me$_2$)$_2$Zr(NH-2,6-C$_6$H$_3$Me$_2$)$_2$]·C$_7$H$_8$ (8·C$_7$H$_8$). Data collection and processing parameters are given in Table 1. Crystals were mounted on a glass fiber with RS3000 oil and transferred to the goniometer head of a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[38] Absorption corrections based on ψ scans were applied to the data, and equivalent reflections were merged and systematically absent reflections rejected. The structures were solved by direct methods (SIR92[39]) followed by difference Fourier syntheses which revealed the positions of all other non-hydrogen atoms: these were refined anisotropically. In both instances the dizirconium species lies on a crystallographic symmetry element. Further Fourier difference syntheses revealed residual electron density which was modeled as a half-occupancy (per asymmetric unit) toluene molecule of crystallization that was sucessfully refined in the anisotropic approximation (subject to bond length and angle restraints[40] for the toluene molecule in **8**·C$_7$H$_8$). H atoms were placed in calculated positions and were refined using a "riding" model. For **6**·C$_7$H$_8$ a Chebychev[41] weighting scheme was applied in the final stages of refinement. For both **6**·C$_7$H$_8$ and **8**·C$_7$H$_8$, examination of the refined secondary extinction parameter[42] and comparison of $|F_o|$ and $|F_c|$ for the strongest reflections suggested that no extinction correction was required.

All crystallographic calculations were performed using SIR92[39] and CRYSTALS.[43] A full listing of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, of this Journal.

Results and Discussion

Floriani has recently described the multigram synthesis of [(Me$_4$taa)ZrCl$_2$], which is a useful entry point to new Me$_4$taa-supported zirconium complexes.[3] Treatment of [(Me$_4$taa)ZrCl$_2$]

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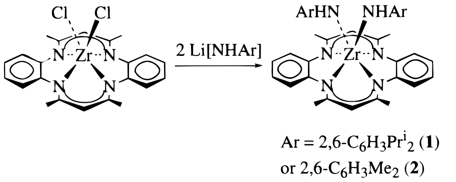
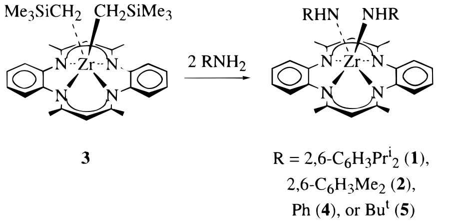
with 2 equiv of Li[NH-2,6-$C_6H_3Pr^i_2$] afforded the bis(arylimido) derivative [(Me_4taa)Zr(NH-2,6-$C_6H_3Pr^i_2$)$_2$] (**1**) in 43% recrystallized yield (eq 1). Similarly, Li[NH-2,6-$C_6H_3Me_2$] reacts smoothly with [(Me_4taa)$ZrCl_2$] to afford [(Me_4taa)Zr(NH-2,6-$C_6H_3Me_2$)$_2$] (**2**). However, attempts to extend this route to the synthesis of *ortho*-unsubstituted aryl or *tert*-butyl amido derivatives were not successful, and addition of Li[NHC_6H_5] or Li[$NHBu^t$] to [(Me_4taa)$ZrCl_2$] afforded mixtures of several products (although the bis(phenyl) amido complex [(Me_4taa)-Zr(NHPh)$_2$] (**4**; *vide infra*) was present by ^{1}H NMR spectroscopy).



(1)

We have not been able to obtain good quality crystals of any of the Me_4taa-supported bis(amido) complexes. However, preliminary results for twinned crystals of **1** did show the Zr atom lying *ca.* 1.12 Å from the N_4 plane of the Me_4taa ligand, with the two aryl amide ligands mutually *cis* as anticipated.[44] We note that Jordan *et al.* have very recently reported the related tetraazamacrocycle-supported complex [(Me_4taen)Zr(NMe_2)$_2$] (prepared from [Zr(NMe_2)$_4$] and Me_4taenH_2; Me_4taenH_2 = tetramethyltetraazacyclotetradecatetraene) which is proposed to have *cis*-coordinated dimethyl amido ligands.[13]

A more general route to Me_4taa-supported bis(amide) complexes is by alkane elimination from [(Me_4taa)Zr(CH_2SiMe_3)$_2$] (**3**) on treatment with primary aryl or *tert*-butylamines (eq 2).



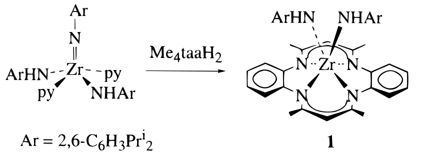
(2)

Thus, addition of H_2NR to **3** gave [(Me_4taa)Zr(NHR)$_2$] [R = 2,6-$C_6H_3Pr^i_2$ (**1**), 2,6-$C_6H_3Me_2$ (**2**), C_6H_5 (**4**), or Bu^t (**5**)] in 47–95% yield. When the reaction between H_2N-2,6-$C_6H_3Pr^i_2$ and **3** was followed by ^{1}H NMR in C_6D_6, the expected $SiMe_4$ side product was observed. The bis(*ortho*-substituted arylamido) complexes **1** and **2** are stable at 70 °C in C_6D_6 solution, whereas the bis(*tert*-butylamido) homologue **5** decomposes to a mixture of products similar in composition to that obtained from [(Me_4taa)$ZrCl_2$] and 2 equiv of Li[$NHBu^t$]. The bis(phenylamido) complex **4** decomposes slowly in solution at room temperature, and this has hampered attempts to obtain analytically pure samples.

The new compound [(Me_4taa)Zr(CH_2SiMe_3)$_2$] (**3**) is analogous to previously described complexes of the type [(ring)Zr-(R)$_2$] (ring = Me_4taa, R = Me or CH_2Ph;[7] ring = Me_8taa, R = CH_3 or CH_2SiMe_3;[9] ring = Me_4taen, R = CH_2Ph or CH_2SiMe_3[13]) and may be prepared either by addition of 2 equiv of Li[CH_2SiMe_3] to [(Me_4taa)$ZrCl_2$] (53%) or by treating [Zr(CH_2SiMe_3)$_4$][33] with Me_4taaH_2 (94%). Complex **3** is stable in C_6D_6 solution at room temperature but slowly decomposes at *ca.* 80 °C, possibly *via* an alkyl group migration reaction of the type described previously by Floriani for [(Me_4taa)$ZrMe_2$].[7]

Although the quantitative formation of [(Me_4taa)Zr(NH-2,6-$C_6H_3Pr^i_2$)$_2$] (**1**) from [(Me_4taa)Zr(CH_2SiMe_3)$_2$] (**3**) and H_2N-2,6-$C_6H_3Pr^i_2$ proceeds readily at room temperature over 16 h, attempts to form the "super-mesityl" homologue [(Me_4taa)Zr-(NH-2,4,6-$C_6H_2Bu^t_3$)$_2$] from **3** and H_2N-2,4,6-$C_6H_2Bu^t_3$ were unsuccessful and no reaction was observed in C_6D_6 at room temperature. Heating this mixture led eventually only to decomposition of **3**, as described above. Treatment of [(Me_4taa)$ZrCl_2$] with Li[NH-2,4,6-$C_6H_2Bu^t_3$)$_2$] gave a mixture of unidentified products.

We have explored potential routes to imido zirconium complexes starting from [(Me_4taa)$ZrCl_2$] and [(Me_4taa)Zr(CH_2SiMe_3)$_2$] (**3**). However, addition of 1 equiv of Li[NH-2,6-$C_6H_3Pr^i_2$] to [(Me_4taa)$ZrCl_2$] in THF gave only the bis(arylamide) [(Me_4taa)Zr(NH-2,6-$C_6H_3Pr^i_2$)$_2$] (**1**) in *ca.* 50% yield—rather than the desired monosubstituted derivative [(Me_4taa)Zr(Cl)-(NH-2,6-$C_6H_3Pr^i_2$)] which might have served as a precursor to an imido complex *via* dehydrohalogenation methodologies. Similarly, addition of 1 equiv of H_2N-2,6-$C_6H_3Pr^i_2$ to [(Me_4taa)Zr(CH_2SiMe_3)$_2$] (**3**) again gave only the bis(amide) **1** together with unreacted **3**. No evidence for an imido complex of the type [(Me_4taa)Zr(N-2,6-$C_6H_3Pr^i_2$)]$_n$ or an amido–alkyl derivative such as [(Me_4taa)Zr(NH-2,6-$C_6H_3Pr^i_2$)(CH_2SiMe_3)] was found. Repeating this reaction in C_6D_6 in an NMR tube experiment in the presence of added pyridine again gave **1** in *ca.* 50% yield, together with unreacted **3** and free pyridine. The known imido–pyridine complex [(Me_4taa)Zr(N-2,6-$C_6H_3Pr^i_2$)(py)][16] was not obtained under these conditions. Addition of Me_4taaH_2 to the previously-described[34] mononuclear imido–bis(amido) zirconium complex [Zr(N-2,6-$C_6H_3Pr^i_2$)(NH-2,6-$C_6H_3Pr^i_2$)$_2$(py)$_2$] only afforded [(Me_4taa)Zr(NH-2,6-$C_6H_3Pr^i_2$)$_2$] (**1**) with free pyridine and free H_2N-2,6-$C_6H_3Pr^i_2$ being the only detectable side-products in an NMR tube experiment in C_6D_6 (eq 3).



(3)

The formation of the complexes [(Me_4taa)Zr(NHR)$_2$] *via* our halide metathesis (eq 1) or alkane elimination (eq 2) routes are analogous to those described by Bergman and co-workers for the synthesis of [Cp_2Zr(NHR)$_2$] (R = alkyl or aryl).[26] Bergman's studies of the alkane elimination route for the zirconocene system established that the intermediate [Cp_2Zr(NHR)(Me)] undergoes methane elimination at elevated temperatures to form transient [Cp_2Zr(NR)], which may then add H_2NR across the Zr=NR multiple bond. It is possible that some or all of the reactions described in eqs 1–3 involve the formation of transient [(Me_4taa)Zr(NR)] (or a Lewis base adduct thereof) but that the unavoidable presence of free anilines in these reaction mixtures leads to the apparently irreversible formation of the bis(amides) [(Me_4taa)Zr(NHR)$_2$] (**1**–**5**). In support of this hypothesis we have recently shown[16] that the imido zirconium complex [(Me_4taa)Zr(N-2,6-$C_6H_3Pr^i_2$)(py)] reacts immediately and quantitatively with H_2N-2,6-$C_6H_3Pr^i_2$ to form the six-coordinate [(Me_4taa)Zr(NH-2,6-$C_6H_3Pr^i_2$)$_2$] (**1**). Furthermore, attempts to prepare imido zirconium complexes from [(Me_4taa)Zr(NHR)$_2$] (**1**–**5**) *via* aniline elimination reactions in the presence of an excess of pyridine in C_6D_6 gave no new products, again consistent with our previous obvservations.[16]

Although mononuclear zirconium imido complexes are not accessible using the synthetic approaches described in eqs 1–3,

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(44) Naumov, D. Yu.; Nikonov, G. I.; Mountford, P. Unpublished results.

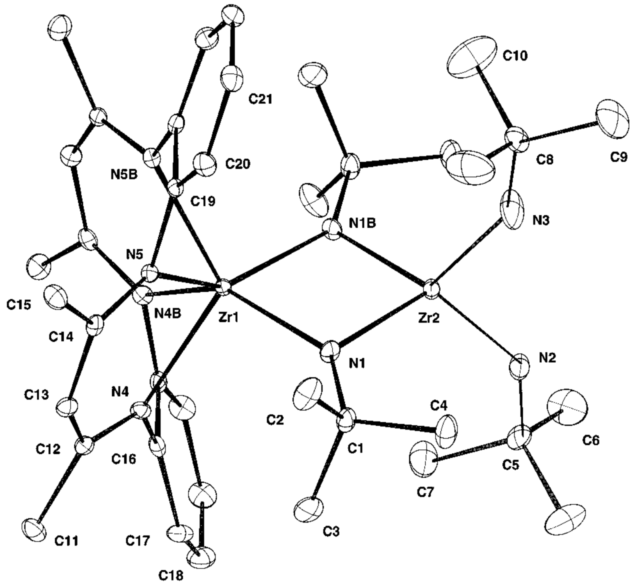
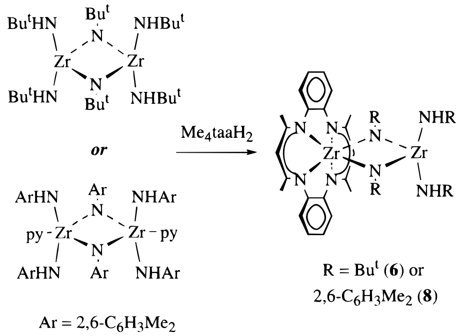


Figure 1. Molecular structure of $[(Me_4taa)Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2]$ (**6**). Hydrogen atoms and the toluene molecule of crystallization are omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level. Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator [*x*, $^1/_2 - y$, *z*].

we have successfully isolated binuclear bis(μ-imido) derivatives (eq 4). Addition of 1 equiv of Me_4taaH_2 to the previously described dizirconium complex $[(HNBu^t)_2Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2]$[35] afforded the novel, binuclear bis(μ-imido) complex $[(Me_4taa)Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2]$ (**6**). The NMR spectra for **6** support the structure shown in eq 4. Diffraction quality crystals of toluene-solvated **6** were obtained, and the molecular structure is shown in Figure 1, selected bond lengths and angles are given in Table 2, and data collection and processing parameters are given in Table 1. The structural data for **6** are discussed below along with those of **8**. Interestingly, reaction of $[(HNBu^t)_2Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2]$ with *2* equiv of Me_4taaH_2 gave only a mixture of **6** and the previously described[3] sandwich compound $[(Me_4taa)_2Zr]$.



(4)

We also wished to prepare other aryl imido/amido zirconium compexes as potential precursors to tetraaza macrocycle-supported complexes. Thus, treatment of $[ZrCl_4(THF)_2]$ with 3−4 equiv of $Li[NH\text{-}2,6\text{-}C_6H_3Me_2]$ followed by addition of an excess of pyridine afforded the binuclear complex $[(py)(NH\text{-}2,6\text{-}C_6H_3Me_2)_2Zr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Zr(NH\text{-}2,6\text{-}C_6H_3Me_2)_2(py)]$ (**7**) according to NMR and analytical data. The ^1H NMR spectrum of **7** in C_6D_6 shows a py:NH-2,6-$C_6H_3Me_2$:N-2,6-$C_6H_3Me_2$ ratio of 1:2:1. Although these data could, in principle, indicate the four-coordinate mononuclear species $[Zr(N\text{-}2,6\text{-}C_6H_3Me_2)(NH\text{-}2,6\text{-}C_6H_3Me_2)_2(py)]$, we consider the binuclear structure shown in eq 4 to be the most likely on the basis of the reactivity of **7** toward Me_4taaH_2 (*vide infra*) and the observation that the monomeric isopropylphenyl imido/amido complex $[Zr(N\text{-}2,6\text{-}C_6H_3Pr^i_2)(NH\text{-}2,6\text{-}C_6H_3Pr^i_2)_2(py)_2]$ exists as the bis(pyridine) adduct.[34] The structure of the valence isoelectronic, dititanium aryloxo−μ-oxo complex[45] $[(py')(NH\text{-}2,6\text{-}C_6H_3Pr^i_2)_2Ti(\mu\text{-}O)_2Ti(NH\text{-}2,6\text{-}C_6H_3Pr^i_2)_2(py')]$ (py′ = 4-NC_5H_4-NC_4H_8) is analogous to that proposed for **7**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(Me_4taa)Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2]$ (**6**)[a]

Zr(1)···Zr(2)	3.1575(6)	Zr(2)−N(3)	2.065(5)
Zr(1)−N(1)	2.129(3)	N(1)−C(1)	1.490(4)
Zr(1)−N(4)	2.250(3)	N(2)−C(5)	1.461(6)
Zr(1)−N(5)	2.248(3)	N(3)−C(8)	1.448(7)
Zr(2)−N(1)	2.048(3)	Zr(1)···N_4	1.17
Zr(2)−N(2)	2.082(4)		
Zr(2)···Zr(1)−N(1)	39.95(8)	N(1)−Zr(2)−N(3)	117.0(1)
N(1)−Zr(1)−N(1B)	79.8(2)	N(2)−Zr(2)−N(3)	104.0(2)
Zr(1)···Zr(2)−N(1)	41.86(8)	Zr(1)−N(1)−Zr(2)	98.2(1)
N(1)−Zr(2)−N(1B)	83.7(2)	Zr(1)−N(1)−C(1)	140.2(2)
Zr(1)···Zr(2)−N(2)	130.1(1)	Zr(2)−N(1)−C(1)	121.6(2)
N(1)−Zr(2)−N(2)	117.6(1)	Zr(2)−N(2)−C(5)	140.3(4)
Zr(1)···Zr(2)−N(3)	125.9(2)	Zr(2)−N(3)−C(8)	146.6(4)

[a] Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator [*x*, $^1/_2 - y$, *z*]. N_4 denotes the computed least squares plane for the Me_4taa N atoms.

Treatment of complex **7** with either 1 or 2 equiv of Me_4taaH_2 gave mixtures of compounds including $[(Me_4taa)_2Zr]$ and an analogue of **6**, namely, $[(Me_4taa)Zr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Zr(NH\text{-}2,6\text{-}C_6H_3Me_2)_2]$ (**8**; see eq 4). The reactivity of **7** toward Me_4taaH_2 is more like that of binuclear $[(HNBu^t)_2Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2]$ than of mononuclear $[Zr(N\text{-}2,6\text{-}C_6H_3Pr^i_2)(NH\text{-}2,6\text{-}C_6H_3Pr^i_2)_2(py)_2]$, thus supporting the binuclear structure proposed for **7**.

The formation of $[(Me_4taa)_2Zr]$ in the reactions of $[(HNBu^t)_2Zr(\mu\text{-}NBu^t)_2Zr(NHBu^t)_2]$ or **7** with Me_4taaH_2 is consistent with the formation of transient $[(Me_4taa)Zr(\mu\text{-}NR)_2Zr(Me_4taa)]$ (formed from **6** or **8**), which could then dissociate to give mononuclear $[(Me_4taa)Zr(NR)]$. Attack of Me_4taaH_2 at the (presumably highly reactive) terminal imido linkage in this latter species would account for the formation of $[(Me_4taa)_2Zr]$. This mechanism for the formation of $[(Me_4taa)_2Zr]$ is probably more likely than direct attack of Me_4taaH_2 at the μ-imido group in **6** or **8**. We have attempted to cleave the μ-imido bridges in **6** with an excess of pyridine, but unfortunately no reaction was observed in C_6D_6 at 70 °C.

It was possible to separate a few crystals of the toluene solvate of **8** for ^1H NMR spectroscopic and X-ray crystal structure analyses. The molecular structure of **8** is shown in Figure 2, and selected bond lengths and angles are given in Table 3. Complexes **6** and **8** are the first binuclear group 4 bis(μ-imido) species with different terminal ligand sets. Three dizirconium, bis(μ-imido) derivatives have been crystallographically characterized previously, namely, $[Cp_2Zr(\mu\text{-}N\text{-}4\text{-}C_6H_4Bu^t)_2ZrCp_2]$,[26] $[Cp'ClZr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Pr^i_2)_2ZrCp'Cl]$ (Cp′ = η^5-C_5H_4Me),[34] and $[(Me_2N)_2Zr(\mu\text{-}NBu^t)_2Zr(NMe_2)_2]$.[46]

The molecular structures of **6** and **8** show comparable features. Molecules of **6** are bisected by a crystallographic mirror plane containing Zr(1), Zr(2), N(3), and N(4); molecules of **8** lie on a 2-fold axis which passes through Zr(1) and Zr(2). The structures have Zr(1) lying out of the N_4 plane of the Me_4taa ligand by *ca.* 1.17 and 1.09 Å for **6** and **8**, respectively. These Zr(1)···N_4 displacements are somewhat larger than those found for the two previously structurally characterized six-

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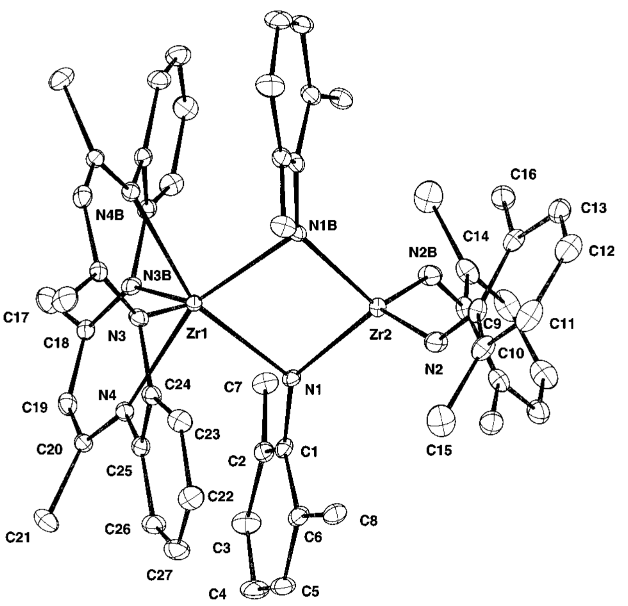

Figure 2. Molecular structure of $[(Me_4taa)Zr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Zr(NH\text{-}2,6\text{-}C_6H_3Me_2)_2]$ (**8**). Hydrogen atoms and the toluene molecule of crystallization are omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level. Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator $[1 - x, y, {}^{1}/_{2} - z]$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[(Me_4taa)Zr(\mu\text{-}N\text{-}2,6\text{-}C_6H_3Me_2)_2Zr(NH\text{-}2,6\text{-}C_6H_3Me_2)_2]$ (**8**)[a]

Zr(1)···Zr(2)	3.205(4)	Zr(2)−N(2)	2.14(2)
Zr(1)−N(1)	2.21(2)	N(1)−C(1)	1.39(3)
Zr(1)−N(3)	2.17(2)	N(2)−C(9)	1.39(3)
Zr(1)−N(4)	2.24(2)	Zr(1)···N_4	1.09
Zr(2)−N(1)	1.98(2)		
Zr(2)···Zr(1)−N(1)	37.5(5)	N(1)−Zr(2)−N(2B)	110.2(8)
N(1)−Zr(1)−N(1B)	75.0(10)	N(2)−Zr(2)−N(2B)	126.5(12)
Zr(1)···Zr(2)−N(1)	42.8(5)	Zr(1)−N(1)−Zr(2)	99.7(7)
N(1)−Zr(2)−N(1B)	85.7(11)	Zr(1)−N(1)−C(1)	124(2)
Zr(1)···Zr(2)−N(2)	116.8(6)	Zr(2)−N(1)−C(1)	135(2)
N(1)−Zr(2)−N(2)	108.4(8)	Zr(2)−N(2)−C(9)	140(2)

[a] Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator $[1 - x, y, {}^{1}/_{2} - z]$. N_4 denotes the computed least squares plane for the Me_4taa N atoms.

coordinate Me_4taa complexes of zirconium, namely, $[(Me_4taa)ZrCl_2]$ [Zr···N_4 = 1.071(2) Å][3] and $[(Me_4taa)Zr(CH_2Ph)_2]$ [Zr···N_4 = 1.019(2) Å].[7] Consequently, the individual Zr(1)−N(macrocycle) distances in **6** and **8** are generally longer than in these previously reported complexes [range 2.158(5)−2.193(8) Å], while the N(1)−Zr(1)−N(1B) angles [79.8(2) and 75.0(10)°] in **6** and **8** are slightly more acute than the X−Zr−X angles in $[(Me_4taa)ZrX_2]$ (X = Cl, 85.6(1)°; X = CH_2Ph, 80.2(4)°]. The remaining geometric features of the $(Me_4taa)Zr(N)_2$ fragment in **6** and **8** are very similar to those of $[(Me_4taa)ZrCl_2]$ and $[(Me_4taa)Zr(CH_2Ph)_2]$.

The $(Me_4taa)Zr$ centers in **6** and **8** are linked to bis(amido) zirconium moieties *via* μ-imido bridges. The coordination geometry at Zr(2) is approximately tetrahedral in both complexes. The N(1)−Zr(2)−N(1B) angles are slightly larger than the corresponding angles at Zr(1), but all of the N(1)−Zr−N(1B) angles in **6** and **8** are comparable to those in the three previously crystallographically characterized dizirconium bis(μ-imido) complexes.[26,34,46]

The coordination geometry at the bridging N(1) atoms is approximately trigonal-planar, and the sums of the angles subtended at N(1) are 360.0(2) and 358.7(4)° for **6** and **8**, respectively. The slightly greater pyramidalization of N(1) in compound **8** is revealed in the computed diplacements of C(1) from the [Zr(1), N(1), N(1B), Zr(1B)] least squares plane of 0.08 (for **6**) and 0.22 Å (for **8**). Due to the imposed crystallographic symmetry, the displacements of C(1) and C(1B) in **6** are in the same "direction", while in **8** the displacements are one "up" and one "down". A search of the Cambridge Structural Database[47,48] revealed similar features in most other binuclear bis(μ-imido) compexes of group 4. The partial pyramidalization of the μ-imido nitrogen atoms in the amido/bis(μ-imido) complexes $[(Me_2N)_2M(\mu\text{-}NBu^t)_2M(NMe_2)_2]$ (M = Ti or Zr) has been interpreted in terms of some lone electron pair localization at the bridging N atoms.[46,49]

The bond lengths from Zr(2) to the terminal amido nitrogen atoms in **6** and **8** are slightly longer than those to the μ-imido nitrogen atoms. In the only dizirconium terminal amido/bis(μ-imido) complex previously crystallographically characterized, namely, $[(Me_2N)_2Zr(\mu\text{-}NBu^t)_2Zr(NMe_2)_2]$, the situation is reversed.[46] In **6** and **8** the Zr(1)−N(1) bond lengths are significantly longer than the Zr(2)−N(1) distances [difference = 0.081(4) and 0.23(3) Å for **6** and **8**, respectively] which may reflect either the higher coordination number of Zr(1) and/or the greater steric influence of the Me_4taa ligand set. In both structures the μ-imido organic substituent is bent away from the Me_4taa ligand so that the Zr(1)−N(1)−C(1) angles are greater than the Zr(2)−N(1)−C(1) angles by 18.6(3) and 11(3)° for **6** and **8**, respectively. This certainly appears to be a consequence of steric effects.

Finally we report that the complexes $[(Me_4taa)Zr(NHR)_2]$ are reactive toward a range of unsaturated substrates, including alkynes and a number of different cumulenes. Unfortunately we have not yet been able to isolate any discrete metal coordination complex product from these reactions.

Summary and Conclusions

We have described the synthesis of zirconium tetraaza macrocycle-supported bis(amido) complexes from $[(Me_4taa)ZrX_2]$ [X = Cl or CH_2SiMe_3 (**3**)], together with the new bis((trimethylsilyl)methyl) species **3**. Attempts to prepare mononuclear imido complexes or suitable amido−chloride or amido−alkyl precursors to such species have so far been unsuccessful. The principal reason for the failure to produce isolable tetraaza macrocycle-supported terminal imido derivatives is probably the ready addition of free amines across the Zr=NR multiple bond of any transient imido complex formed in these reactions. However, bis(amido)−(μ-imido) dizirconium complexes react with Me_4taaH_2 to give novel asymmetrically substituted, tetraaza macrocycle-supported binuclear derivatives.

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Supporting Information Available: X-ray crystallographic files in CIF format for **6** and **8** are available on the Internet. Access information is given on any current masthead page.

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