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Article

Titanium(IV) and Zirconium(IV) Amido Complexes Derived from the Azaoxa Macrocycle 3,3-Dimethyl-1,5-diaza-8-oxacyclodecane

Robin M. Porter, Andreas A. Danopoulos,* and Gillian Reid*

School of Chemistry, University of Southampton, Highfield,
Southampton SO17 1BJ, United Kingdom

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The novel tridentate azaoxa macrocycle [O(NH)$_2$], 3,3-dimethyl-1,5-diaza-8-oxacyclodecane, can be singly or doubly lithiated with ^{n}BuLi at the secondary amine N atoms, giving [O(NH)N]Li and [O(N)$_2$]Li$_2$, respectively, and further elaborated with introduction of TMS substituents via reaction with (TMS)Cl. Aminolysis of [Ti(NMe$_2$)$_2$Cl$_2$] or [Zr(NR$_2$)$_2$Cl$_2$(THF)$_2$] with [O(NH)$_2$] in toluene gave the distorted octahedral M[O(NH)N](NR$_2$)Cl$_2$ (M = Ti, R = Me; M = Zr, R = Me or Et), in which the macrocycle functions as a monoanionic ligand via an amido, an amine, and an ether functionality. Salt metathesis of [Zr(NEt$_2$)$_2$Cl$_2$(THF)$_2$] with [O(NH)N]Li in toluene afforded Zr[(O(NH)N)](NEt$_2$)$_2$Cl, the structure of which also confirms tridentate macrocycle coordination via one amido, one amine, and one ether group; in contrast, analogous salt metathesis involving [Zr(NEt$_2$)$_2$Cl$_2$(THF)$_2$] and [O(N)$_2$Li$_2$] gave the "sandwich" complex [(ON$_2$)$_2$Zr], with the macrocycle behaving as a dianionic ligand (Porter, R. M.; et al. *Dalton Trans.* **2005**, 427). Finally, treatment of [O(NH)$_2$] with AlMe$_3$ gave the simple donor–acceptor adduct [O(NH)$_2$]AlMe$_3$, which resisted alkanolysis by prolonged heating. In the presence of MAO the new zirconium, titanium, and aluminum complexes show low activity in the polymerization of ethylene.

Introduction

Medium-size tridentate macrocycles have been used extensively in coordination and organometallic chemistry to block three facial coordination sites on transition-metal centers. This chemistry has been largely dominated by neutral, formally 6e$^-$ donor ligands based upon amine, ether, and/or thioether functions with middle or late transition metals,[1] and recently peralkylated aza macrocycles with or without pendant groups have been used with early transition metals and lanthanides.[2] However, incorporation of secondary amine functions within the macrocyclic framework opens the possibility of forming anionic amido-based macrocyclic ligands upon deprotonation at N. The harder nature and different donor characteristics of the amido functions[3] suggest that such ligands are potentially well-suited for the much harder and electrophilic, high-oxidation-state early-transition-metal centers, e.g., those from groups 4−6. Tridentate macrocycles which occupy three facial coordination sites and incorporate anionic amido functional groups are of interest as versatile, tunable (by virtue of ring size, donor types, substituents on the macrocycle rim, etc.) ligands, which may be suitable as replacements for the widely studied cyclopentadienyls in early-transition-metal chemistry, and indeed it has been shown that early-transition-metal amido complexes can catalyze processes such as alkene polymerization and hydroamination of alkynes and allenes.[4] Attempts to explore this ligand family were initiated by Arnold and coworkers, who have used tacn-based macrocyclic ligands, such as ^{i}Pr$_2$-tacn, involving one anionic amido function, and demonstrated that they can lead to rich and diverse organometallic chemistry with Li, Al, Zr, Ta, and Mo precursors.[5]

As part of our program of work to investigate the preparation and chemistry of tridentate anionic amido-based macrocyclic ligands which also incorporate other neutral donor groups, we prepared the novel oxaaza macrocycle 3,3-dimethyl-1,5-diaza-8-oxacyclodecane (denoted [O(NH)$_2$]),

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* To whom correspondence should be addressed. Phone: +44(0)23 8059 4116 (A.A.D.), +44(0)23 8059 3609 (G.R.). E-mail: ad1@soton.ac.uk (A.A.D.), gr@soton.ac.uk (G.R.).

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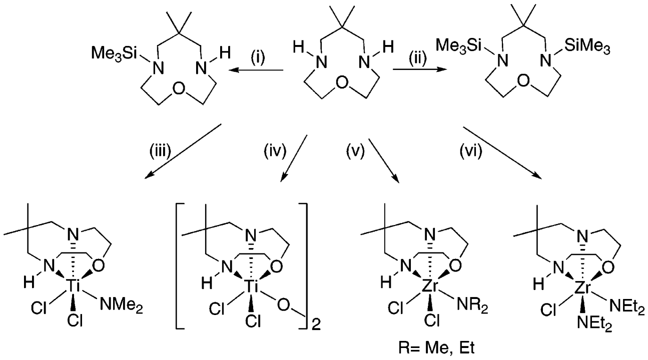
Scheme 1[a]



[a] Reagents and conditions: (i) 1 equiv of ^{n}BuLi (−78 °C), 1 equiv of Me$_3$SiCl, toluene; (ii) 2 equiv of ^{n}BuLi (−78 °C), 2 equiv of Me$_3$SiCl, toluene; (iii) Ti(NMe$_2$)$_2$Cl$_2$, toluene; (iv) Ti(NMe$_2$)$_2$Cl$_2$, H$_2$O, toluene; (v) Zr(NR$_2$)$_2$Cl$_2$(THF)$_2$, toluene, R = Me, Et; (vi) [O(NH)$_2$], 1 equiv of ^{n}BuLi followed by Zr(NEt$_2$)$_2$Cl$_2$(THF)$_2$.

which can act as a precursor to the dianionic [O(N$^-$)$_2$] by deprotonation of both secondary amines incorporated in the macrocyclic ring, giving rise to a 10e$^-$ mixed-donor macrocyclic ligand. In our preliminary work[6] we described the reaction of the dilithiated derivative O(NLi)$_2$ with [Zr(NEt$_2$)$_2$Cl$_2$(THF)$_2$] in toluene to give [Zr(ON$_2$)(NEt$_2$)$_2$] initially, in which the macrocycle behaves as a dianionic ligand. This compound underwent disproportionation to the bismacrocyclic [Zr(ON$_2$)$_2$] (and [Zr(NEt$_2$)$_4$]), the structure of which showed tridentate coordination of each dianionic macrocycle (albeit with rather long Zr−O distances), giving a formally 20e$^-$ complex with a very distorted octahedral geometry. We also reported that alkanolysis of [Ti(benzyl)$_4$] with [O(NH)$_2$] gave an unexpected species in which the macrocycle is metalated on the rim α to the amine.

Power and co-workers were the first to report two structurally characterized complexes obtained by the reaction of Ti(NMe$_2$)$_4$ with 1,5,9,13-tetraaza[16]ane in which the macrocycle ligand was coordinated to the metal via anionic amido bonds.[7] Berg and co-workers have utilized the doubly deprotonated form of an 18-membered N$_2$O$_4$-donor macrocycle as a hexadentate ligand for zirconium(IV) dialkyls and alkyl cations, as well as yttrium(III) alkyls,[8,9] while the elegant work of Fryzuk and co-workers has developed the early-transition-metal chemistry of the dianionic form of their P$_2$N$_2$-donor macrocycle with various organometallic Zr species.[10]

Here we describe Ti(IV) and Zr(IV) complexes obtained by aminolysis and salt elimination reactions using [O(NH)$_2$] and [O(NH)N]Li, respectively, in which the macrocycle acts as a monoanionic tridentate donor (Scheme 1). The products obtained have been characterized by NMR spectroscopy, microanalyses, and X-ray crystallography.

Experimental Section

General Procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using a Bruker AV300 spectrometer and are referenced to the residual proton signals from the deuterated solvent (C$_6$D$_6$ unless otherwise stated). Microanalyses were undertaken by the London Metropolitan University microanalytical service.

Solvents were dried over appropriate drying agents and distilled prior to use. All preparations involving metal amides were carried out under a N$_2$ atmosphere using standard Schlenk techniques or in a Braun glovebox. The starting materials Ti(NMe$_2$)Cl$_2$,[11] Zr(NMe$_2$)$_2$Cl$_2$(THF)$_2$, and Zr(NEt$_2$)Cl$_2$(THF)$_2$[12] were prepared following literature procedures. Me$_2$C(CH$_2$NHTs)$_2$[13] and O{(CH$_2$)$_2$OTs}$_2$[14] were prepared by the established general methods.

[O(NTs)$_2$]. To a mechanically stirred solution of Na$_2$[Me$_2$C(CH$_2$NTs)$_2$] (150.5 g, 0.331 mol) (prepared by treatment of Me$_2$C(CH$_2$NHTs)$_2$ with sodium ethoxide in ethanol at 0 °C and isolated by filtration) in DMF (6 L) maintained at 110 °C was added dropwise a solution of O{(CH$_2$)$_2$OTs}$_2$ (137.2 g, 0.331 mol) in the same solvent (1.5 L) over 10 h. After completion of the addition and stirring at 110 °C for 4 h, the mixture was cooled to room temperature, and the DMF was removed under reduced pressure to leave a brown oil which was extracted into dichloromethane (ca. 2.5 L) and washed with water (3 × 500 mL). Drying of the organic phase (MgSO$_4$) followed by evaporation of the volatiles under reduced pressure gave a yellow oil which was washed with MeOH to give the product as a colorless solid, which was isolated by filtration and dried under vacuum. Yield: 86 g, 54%.

[O(NH)$_2$]. The tosylated macrocycle obtained above, [O(NTs)$_2$] (89.8 g, 0.186 mol), was added to ^{n}BuOH (600 mL) and ^{n}Bu$_2$O (400 mL). After the mixture was heated to 125 °C, sodium (68.55 g, 3.27 mol, 17.5 equiv) was added in small chunks. Heating at 125 °C was maintained overnight. The resulting mixture was then cooled to room temperature, acidified to pH $<$ 3 with concentrated hydrochloric acid, and stirred overnight again. Removal of the volatiles under reduced pressure gave a pink-colored solid which was dissolved in the minimum volume of boiling water and filtered to remove a small amount of brown residue. NaOH was added until pH $>$ 13, and the solution was filtered again. The free base was then extracted into toluene by mixing the aqueous solution with toluene and removing the water azeotropically. The resulting crusty solid was broken up and extracted again with toluene. Removal of the toluene from the combined extracts under reduced pressure gave an oil. Distillation under reduced pressure (100−120 °C, 2×10^{-2} Torr) gave the product as a colorless oil. Yield: 22.4 g, 72%.

Prior to using [O(NH)$_2$] for further metalation reactions, it was subjected to further drying by stirring overnight a toluene solution of the macrocycle and ~10% of KN(SiMe$_3$)$_2$. After removal of the toluene, the macrocycle was distilled from the potassium salts and stored in a silylated and flame-dried ampule in the glovebox. ^{1}H NMR (δ, C$_6$D$_6$): 0.79 (6H, s, CH$_3$), 1.37 (2H, br s, NH), 2.46 (4H, d, J = 7.5 Hz, NCH_2C(CH$_3$)$_2$), 2.59 (4H, virtual q, J = 5.3 Hz, OCH$_2$CH_2), 3.45 (4H, t, J = 5.1 Hz, OCH_2CH$_2$). ^{13}C NMR (δ, C$_6$D$_6$): 24.98 (CH$_3$), 35.79 (quaternary C), 50.05 (NCH$_2$C(CH$_3$)$_2$), 57.25 (OCH$_2$$CH_2$), 71.23 (O$CH_2CH_2$).

[O(NH)(NMe$_3$Si)]. To a solution of [O(NH)$_2$] (2.9 g, 16.9 mmol) in toluene (50 mL) at −78 °C was added ^{n}BuLi (2.5 M, 1.0 mol equiv, 16.9 mmol, 6.75 mL). The reaction was allowed to reach

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room temperature within 30 min of the addition and stirred for 5 h. The reaction was cooled again to −78 °C, treated with Me_3SiCl (2.0 g, 16.9 mmol), allowed to reach room temperature within 30 min, and stirred for a further 5 h. The LiCl was removed by filtration and the filtrate transferred to a distillation apparatus. Removal of the volatiles under reduced pressure was followed by fractionation under vacuum to yield the product as a colorless oil (50−60 °C, 2 × 10^{-2} Torr). Yield: 2.1 g, 51%. ^1H NMR (δ, C_6D_6): 0.11 (9H, s, $SiMe_3$), 0.76 (6H, s, CH_3), 1.06 (1H, br s, NH), 2.46 (2H, virtual q, CH_2), 2.73 (2H, s, CH_2), 2.78 (2H, d, CH_2), 3.17 (2H, t, CH_2), 3.44 (2H, t, CH_2), 3.52 (2H, t, CH_2). ^{13}C NMR (δ, C_6D_6): 0.5 ($SiMe_3$), 25.9 (CH_3), 37.4 (quaternary C), 48.6, 53.4, 57.6, 61.0, 71.2, 74.1 (CH_2).

$[O(NMe_3Si)_2]$. The method was similar to the one described above for $[O(NH)(NMe_3Si)]$, but using $[O(NH)_2]$ (2.9 g, 16.9 mmol), toluene (50 mL), ^nBuLi (2.5 M, 2.1 mol equiv, 35.5 mmol, 14.2 mL), and Me_3SiCl (4.0 g, 36 mmol). The product was vacuum distilled at 50−60 °C, 2 × 10^{-2} Torr. Yield: 3.0 g, 55%. ^1H NMR (δ, C_6D_6): 0.09 (18H, s, $SiMe_3$), 0.88 (6H, s, CH_3), 2.91 (4H, s, CH_2), 2.94−3.00 (4H, m, CH_2), 3.48−3.52 (4H, m, CH_2). ^{13}C NMR (δ, C_6D_6): 0.1 ($SiMe_3$), 28.0 (CH_3), 39.4 (quaternary C), 52.2, 59.9, 76.5 (CH_2).

$AlMe_3[[O(NH)_2]$. The reagents $[O(NH)_2]$ (0.38 g, 2.2 mmol) and $AlMe_3$ (2.0 mol·dm^{-3}, 1.13 mL, 2.25 mmol) were mixed together at room temperature in toluene (25 mL) and refluxed overnight. The volatiles were removed, and the residue was extracted into petrol and allowed to stand at room temperature to yield crystals suitable for single-crystal X-ray diffraction. Yield: 0.36 g, 67%. ^1H NMR (δ, C_6D_6): 0.36 (9H, s, $AlMe_3$), 0.43 (3H, s, CH_3), 0.79 (3H, s, CH_3), 1.70−2.00 (6H, m, CH_2, NH), 2.10−2.40 (2H, m, CH_2), 2.80−3.30 (6H, m, CH_2). ^{13}C NMR (δ, C_6D_6): −7.5 ($AlMe_3$), 24.7, 27.3 (CH_3), 33.1 (quaternary C), 48.1, 53.0, 55.9, 61.9, 66.9, 68.7 (CH_2).

$Ti[(O(HN)N](NMe_2)Cl_2$. $[O(NH)_2]$ (0.22 g, 1.3 mmol) in toluene (20 mL) was added to $Ti(NMe_2)_2Cl_2$ (0.26 g, 1.3 mmol) in toluene (20 mL), and within 10 min a brown precipitate was produced. The reaction was stirred at room temperature for a further 3 h before the product was collected by filtration, washed with toluene (20 mL) and petrol (20 mL), and dried in vacuo. Yield: 0.41 g, 95%. Crystals suitable for single-crystal X-ray diffraction analysis were grown by mixing the two reagents in C_6D_6. Anal. Found: C, 39.50; H, 7.51; N, 12.68. Calcd for $C_{11}H_{25}Cl_2N_3Oti$: C, 39.54 H, 7.54, N, 12.58. ^1H NMR (δ, C_6D_5N): 0.91 (3H, s, CH_3), 1.07 (3H, s, CH_3), 2.65−3.15 (5H, m, CH_2), 3.45−3.65 (2H, m, CH_2), 3.66 (6H, s, NMe_2), 3.85−3.95 (1H, m, CH_2), 4.6−4.75 (2H, m, CH_2), 4.9−5.05 (2H, m, CH_2), 6.28 (1H, br s, NH). ^{13}C NMR (δ, C_6D_5N): 30.1, 30.3 (CH_3), 38.7 (quaternary C), 48.1 (CH_2), 49.0 (NMe_2), 59.3, 59.5, 69.8, 72.6, 77.3 (CH_2).

$\{Ti[O(HN)N]Cl_2\}_2(\mu\text{-}O)$. A solution of $[O(NH)_2]$ (0.12 g, 0.70 mmol) and two drops of H_2O in toluene (20 mL) was added to $Ti(NMe_2)_2Cl_2$ (0.15 g, 0.72 mmol) in toluene (20 mL). The reaction mixture was stirred for 90 min and filtered from the orange precipitate that was formed. The supernatant was cooled to −35 °C to give light yellow crystals of the product. Yield: 0.08 g, 38%. ^1H NMR (δ, C_5D_5N): 1.15 (3H, s, CH_3), 1.52 (2H, m, CH_2), 1.68 (3H, s, CH_3), 2.80−3.25 (2H, m, CH_2), 3.55−4.05 (2H, m, CH_2), 3.85−3.95 (2H, m, CH_2), 4.50−4.75 (2H, m, CH_2), 4.05−4.35 (2H, m, CH_2), 11.30 (1H, br s, NH). ^{13}C NMR (δ, C_6D_5N): 25.7, 29.7 (CH_3), 34.8 (quaternary C), 49.4 (CH_2), 58.9, 67.8, 68.3, 79.6, 90.6 (CH_2).

$Zr[(O(HN)N](NMe_2)Cl_2$. $[O(NH)_2]$ (2.0 g, 1.17 mmol) in toluene (20 mL) was added to $Zr(NMe_2)_2Cl_2(THF)_2$ (0.46 g, 1.17 mmol) in toluene (20 mL), and within 10 min a colorless precipitate was produced. The reaction was stirred at room temperature for a further 3 h before the product was collected by filtration, washed with toluene (20 mL) and petrol (20 mL), and dried in vacuo. Yield: 0.28 g, 63%. Crystals suitable for single-crystal X-ray diffraction analysis were grown by mixing the two reagents in C_6D_6. Anal. Found: C, 34.95; H, 6.61; N, 11.07. Calcd for $C_{11}H_{25}Cl_2N_3Ozr$: C, 35.00; H, 6.68; N, 11.13. ^1H NMR (δ, C_4D_8O): 1.11 (3H, s, CH_3), 1.20 (3H, s, CH_3), 2.75−3.00 (4H, m, CH_2), 3.19 (6H, s, NMe_2) 3.40−3.55 (1H, m, CH_2), 3.60−3.75 (1H, m, CH_2), 3.95−4.20 (4H, m, CH_2), 4.50−4.60 (2H, m, CH_2), 4.90−5.05 (1H, m, CH_2); note that the assignment of the NH resonance is unclear as it is under one of the CH_2 resonances. ^{13}C NMR (δ, C_4D_8O): 28.3, 32.1 (CH_3), 37.1 (quaternary C), 43.6 (NMe_2), 49.1, 56.6, 58.0, 63.8, 70.7, 75.8 (CH_2).

$Zr[(O(HN)N](NEt_2)Cl_2$. $[O(NH)_2]$ (0.44 g, 2.5 mmol) in toluene (20 mL) was added to $Zr(NEt_2)_2Cl_2(thf)_2$ (1.13 g, 2.5 mmol) in toluene (20 mL), and within 10 min a colorless precipitate was produced. The reaction was stirred at room temperature for a further 3 h before the product was collected by filtration, washed with toluene (20 mL) and petrol (20 mL), and dried in vacuo. Yield: 0.68 g, 67%. Crystals suitable for single-crystal X-ray diffraction were grown by mixing the two reagents in C_6D_6. Anal. Found: C, 38.64; H, 7.16; N, 10.27. Calcd for $C_{13}H_{29}Cl_2N_3Ozr$: C, 38.50; H, 7.21; N, 10.36. ^1H NMR (δ, C_6D_6): 0.70 (6H, s, CH_3), 1.21 (6H, t, NCH_2CH_3), 1.95−2.20 (2H, m, CH_2), 2.40−2.55 (2H, m, CH_2), 2.60−2.75 (2H, m, CH_2), 2.80−3.05 (3H, m, CH_2), 3.40−3.50 (1H, m, CH_2), 3.63 (2H, overlapping q, NCH_2CH_3), 3.80, (2H, overlapping q, NCH_2CH_3), 4.05 (1H, d, CH_2), 4.15−4.25 (1H, m, CH_2), 4.35−4.45 (1H, m, CH_2); note that the assignment of the NH resonance is unclear as it is under one of the CH_2 resonances. ^{13}C NMR (δ, C_6D_6) 14.8 (NCH_2CH_3), 29.8, 31.5 (CH_3), 36.1 (quaternary C), 43.5 (NCH_2CH_3), 47.2, 55.5, 58.3, 64.0, 71.6, 76.5 (CH_2).

$Zr[(O(HN)N](NEt_2)_2Cl$. $[O(NH)_2]$ (0.12 g, 0.69 mmol) was placed in a Schlenk tube and dissolved in toluene (25 mL). The solution was cooled to −78 °C and treated with ^nBuLi (2.5 M, 1.0 mol equiv, 0.28 mL). The reaction was allowed to reach room temperature within 30 min of the addition and stirred for 5 h. The reaction was then recooled to −78 °C, treated with $Zr(NEt_2)_2Cl_2(THF)_2$ (0.31 g, 0.69 mmol), allowed to reach room temperature slowly, and stirred for 12 h. The LiCl was removed by filtration, and the volatiles were removed from the filtrate in vacuo before the residue was dissolved in petrol (50 mL). The solution was concentrated and cooled to −35 °C to yield the product as a yellow crystalline solid. Yield: 0.15 g, 50%. Crystals suitable for single-crystal X-ray diffraction were grown from a petrol solution. Anal. Found: C, 46.22; H, 8.52; N, 12.37. Calcd for $C_{17}H_{38}ClN_4Ozr$: C, 46.28; H, 8.68; N, 12.70. ^1H NMR (δ, C_6D_6): 0.71 (3H, s, CH_3), 0.78 (3H, s, CH_3), 1.20−1.35 (12H, m, NCH_2CH_3), 1.95−2.20 (2H, m, CH_2), 2.25−2.80 (7H, m, CH_2, NH), 2.90−3.10 (2H, m, CH_2), 3.5−3.95 (8H, m, NCH_2CH_3), 4.10−4.20 (2H, m, CH_2). ^{13}C NMR (δ, C_6D_6): 15.4, 15.8 (NCH_2CH_3), 29.7, 31.3 (CH_3), 35.9 (quaternary C), 43.5, 44.4 (NCH_2CH_3), 46.6, 55.9, 57.9, 65.6, 70.0, 76.0 (CH_2).

X-ray Crystallography. Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals of $M[(O(HN)N](NMe_2)Cl_2$ (M = Ti or Zr), $\{Ti[O(HN)N]Cl_2\}_2(\mu\text{-}O)$, $Zr[(O(HN)N](NEt_2)Cl_2$, $Zr[(O(HN)N](NEt_2)_2Cl$, and $AlMe_3[[O(NH)_2]$ were obtained as described above. All data sets were collected on a Bruker Nonius KappaCCD area detector diffractometer with rotating anode FR591 and an Oxford Cryosystems low-temperature device, operating in ω scanning mode with ϕ and ω scans to fill the Ewald sphere. The crystals were mounted on a glass fiber with silicon grease, from Fomblin vacuum oil. The

Table 1. Crystallographic Data

	$Ti[O(HN)N](NMe_2)Cl_2$	$\{Ti[O(HN)N]Cl_2\}_2(\mu\text{-}O)$	$Zr[O(HN)N](NMe_2)Cl_2$	$Zr[O(HN)N](NEt_2)Cl_2\cdot$ toluene	$Zr[O(HN)N](NEt_2)_2Cl$	$AlMe_3[O(NH)_2]$
empirical formula	$C_{11}H_{25}Cl_2N_3OTi$	$C_{18}H_{38}Cl_4N_4O_3Ti_2$	$C_{11}H_{25}Cl_2N_3OZr$	$C_{33}H_{66}Cl_4N_6O_2Zr_2$	$C_{17}H_{39}ClN_4OZr$	$C_{12}H_{29}AlN_2O$
mol wt	334.14	596.12	377.46	903.16	442.19	244.35
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	*Pbca*	*Pbca*	$P2_1/n$	*Pbca*	$P2_1/c$
a/Å	11.5966(9)	11.5453(15)	8.598(5)	10.5836(7)	13.485(5)	8.383(5)
b/Å	9.8494(6)	17.8984(14)	12.572(4)	8.6093(4)	19.862(5)	23.561(16)
c/Å	13.8793(9)	24.843(3)	28.968(19)	23.0627(16)	16.344(5)	7.9470(18)
α/deg	90	90	90	90	90	90
β/deg	96.639(6)	90	90	97.982(6)	90	105.88(3)
γ/deg	90	90	90	90	90	90
V/Å^3	1574.66(19)	5133.6(10)	3131(3)	2081.1(2)	4378(2)	1509.7(14)
Z	4	8	8	2	8	4
μ(Mo Kα)/mm^{-1}	0.876	1.066	1.037	0.793	0.636	0.121
total no. of reflns	13660	41423	14562	21369	22079	19583
no. of unique reflns	3624	5891	3580	4764	5053	3478
R_{int}	0.0578	0.1156	0.0927	0.0655	0.1322	0.0490
no. of params	171	292	171	222	223	158
R1[a] $[I_o > 2\sigma(I_o)]$	0.0420	0.0428	0.0630	0.0427	0.0660	0.0391
R1[a] (all data)	0.0652	0.0945	0.1263	0.0654	0.1215	0.0603
wR2[a] $[I_o > 2\sigma(I_o)]$	0.0856	0.0722	0.1088	0.0772	0.1008	0.0866
wR2[a] (all data)	0.0933	0.0847	0.1246	0.0837	0.1150	0.0948

[a] $R1 = \sum||F_o| - |F_c||_i/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_{o,i}^4]^{1/2}$.

programs used for control and integration were Collect, Scalepack, and Denzo.[15] All solutions and refinements were performed using the WinGX package and all software packages within.[16] Selected bond lengths and angles are given in Tables 2−7.

Results and Discussion

Ligand Syntheses. The 10-membered ring macrocyclic donor ligand $[O(NH)_2]$ was obtained as an oil through high-dilution cyclization of $K_2[Me_2C(CH_2NTs)_2]$ and $O\{(CH_2)_2OTs\}_2$ in DMF solution at 110 °C, followed by deprotection with sodium in 1-butanol/dibutyl ether at 125 °C, following a modification of the methods described in the literature.[17] The Me groups in the backbone were introduced to enhance the solubility of the macrocycle for the ensuing reaction chemistry, and the 10-membered ring with the C_3 linkage positioned between the N atoms was identified as the minimum ring size which would accommodate the trigonal planar amido groups ligated to a metal center. The neutral macrocycle has a significant affinity for water and must be rigorously dried prior to reaction with the titanium(IV) and zirconium(IV) dialkylamides to facilitate clean aminolysis to the desired products. This was accomplished by treatment of a toluene solution of $[O(NH)_2]$ with ca. 10% $KN(SiMe_3)_2$ at room temperature overnight, followed by distillation. The dry $[O(NH)_2]$ was stored in a silylated and flame-dried ampule in the glovebox.

The NH functions may be readily and sequentially deprotonated by the addition of either 1 or 2 mol equiv of ^nBuLi to a toluene solution of $[O(NH)_2]$. Treatment of toluene suspensions of the resulting $LiHN_2O$ or Li_2N_2O with 1 or 2 mol equiv, respectively, of Me_3SiCl at −78 °C affords the N-silylated derivatives $[O(NH)(NMe_3Si)]$ and $[O(NMe_3Si)_2]$, which were obtained in 50−55% yield following workup and purification by vacuum distillation.

Complexes. In an attempt to prepare $[O(N)_2]MCl_2$, M = Ti, Zr, which would serve as a desirable starting material for further derivatization by alkyls, amido groups, etc., we decided to employ an aminolysis methodology starting from $M(NR_2)_2Cl_2$, R = Me, Et. Our previous results[6] showed that the alkanolysis of $Ti(benzyl)_4$ with $[O(NH)_2]$ and the salt metathesis of $Zr(NEt_2)_2Cl_2(THF)_2$ with $[O(N)_2Li_2]$ did not stop at the desired monosubstitution stage but were followed by a rim metalation or a disproportionation reaction, respectively.

The aminolysis reaction between $[O(NH)_2]$ and 1 mol equiv of $[Ti(NMe_2)_2Cl_2]$ in toluene led to the formation of $[O(NH)N]Ti(NMe_2)Cl_2$ as a brown solid in nearly quantitative yield, together with production of the expected Me_2NH. The formulation follows from ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and microanalysis. The low symmetry of the NMR patterns and the integration are consistent with a singly deprotonated macrocycle coordinated to the Ti via one amido N, one neutral amine N, and the ether O atom. Crystals of this product were obtained from C_6D_6 solution. The structure shows (Figure 1, Table 2) the distorted octahedral coordination environment consistent with that anticipated from the spectroscopic data.

The macrocycle is clearly monoanionic, with Ti−N(1) (amide) = 1.911(2) Å, Ti−N(2) (amine) = 2.210(2) Å, and Ti−O = 2.2407(16) Å.[18] The Ti−N bond in the coordinated NMe_2 residue is 1.8804(19) Å, and the Cl ligands completing the coordination set give Ti−Cl = 2.2422(7) and 2.3441(7) Å. The angles are also in line with this assignment, with the angles at N(1) and N(3) approximating trigonal planar, while N(2) is approximately tetrahedral as expected.

It is interesting to notice that the reaction of $[Ti(NMe_2)_2Cl_2]$ with $[O(NH)_2]$ stored over activated 4 Å molecular

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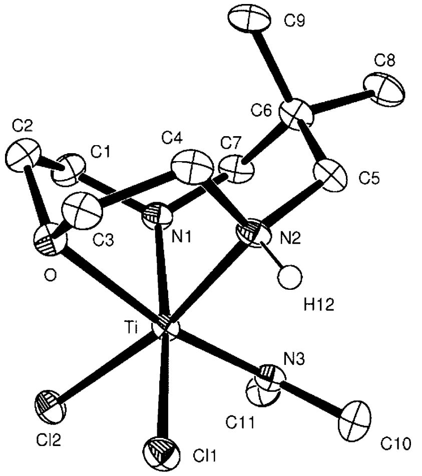

Figure 1. ORTEP representation of the structure of Ti[O(HN)N](NMe$_2$)Cl$_2$ with the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ti[O(HN)N](NMe$_2$)Cl$_2$

N(1)−Ti	1.911(2)	N(2)−Ti	2.210(2)
N(3)−Ti	1.8804(19)	O−Ti	2.2407(16)
Cl(1)−Ti	2.4622(7)	Cl(2)−Ti	2.3441(7)
C(7)−N(1)−C(1)	119.5(2)	C(7)−N(1)−Ti	122.34(16)
C(1)−N(1)−Ti	115.82(16)	C(4)−N(2)−C(5)	113.13(19)
C(4)−N(2)−Ti	114.07(15)	C(5)−N(2)−Ti	114.25(15)
C(10)−N(3)−C(11)	112.4(2)	C(10)−N(3)−Ti	127.22(17)
C(11)−N(3)−Ti	119.58(16)	C(3)−O−C(2)	113.17(18)
C(3)−O−Ti	109.57(13)	C(2)−O−Ti	112.16(13)
N(3)−Ti−N(1)	97.49(9)	N(3)−Ti−N(2)	94.52(8)
N(1)−Ti−N(2)	85.07(8)	N(3)−Ti−O	169.59(8)
N(1)−Ti−O	77.96(7)	N(2)−Ti−O	75.86(7)
N(3)−Ti−Cl(2)	99.62(6)	N(1)−Ti−Cl(2)	95.63(6)
N(2)−Ti−Cl(2)	165.62(6)	O−Ti−Cl(2)	90.20(5)
N(3)−Ti−Cl(1)	95.83(6)	N(1)−Ti−Cl(1)	163.57(6)
N(2)−Ti−Cl(1)	84.33(6)	O−Ti−Cl(1)	87.29(5)
Cl(2)−Ti−Cl(1)	91.58(3)		

sieves, but which had not been exhaustively dried as described in the Experimental Section, gave rise to good yields of the dimeric oxo-bridged complex {Ti[O(HN)N]-Cl$_2$}$_2$(μ-O), which is shown in Figure 2 (metrical data in Table 3).

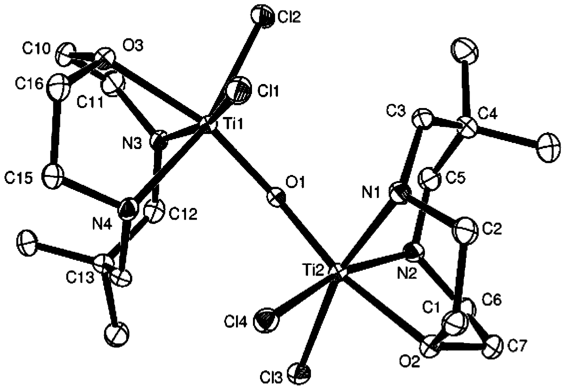

Figure 2. ORTEP representation of the structure of {Ti[O(HN)N]Cl$_2$}$_2$(μ-O) with the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for {Ti[O(HN)N]Cl$_2$}$_2$(μ-O)

N(3)−Ti(1)	1.874(2)	O(1)−Ti(1)	1.8162(19)
O(3)−Ti(1)	2.214(2)	N(4)−Ti(1)	2.216(2)
Cl(1)−Ti(1)	2.4425(9)	Cl(2)−Ti(1)	2.3315(9)
N(3)−Ti(1)−Cl(1)	162.18(8)	O(3)−Ti(1)−Cl(1)	84.87(6)
N(4)−Ti(1)−Cl(1)	84.89(7)	Cl(2)−Ti(1)−Cl(1)	90.30(3)
O(1)−Ti(1)−O(3)	165.61(8)	N(3)−Ti(1)−O(3)	78.32(9)
O(1)−Ti(1)−N(4)	90.33(9)	N(3)−Ti(1)−N(4)	85.21(10)
O(3)−Ti(1)−N(4)	75.43(8)	Ti(2)−O(1)−Ti(1)	155.54(12)

The complex is a centrosymmetric oxo-bridged dimer with distorted octahedral six-coordinate titanium centers. The macrocycle is bound to the metal via a short [1.874(2) Å] anionic amide bond and two longer dative bonds [amine, 2.216(2) Å; ether, 2.214(2) Å]. This binding mode is analogous to the one observed in the monomeric [O(NH)N]-Ti(NMe$_2$)Cl$_2$ described earlier. The Ti−O bonds to the bridging oxo ligand [1.8162(19) Å] are shorter than a typical single Ti−O bond (ca. 1.9 Å). This, in combination with the Ti−O−Ti angle [155.54(12) Å], indicates some degree of π-bonding. The Ti−O−Ti structural motif has been previously observed in the product obtained from the reaction of Ti(NMe$_2$)$_4$ with the tetraaza macrocycle 1,5,9,13-tetraaza-[16]ane.[7]

The analogous Zr(IV) species Zr[O(NH)N](NMe$_2$)Cl$_2$ and Zr[O(NH)N](NMe$_2$)Cl$_2$ were obtained similarly and in good yield as colorless solids by reaction of [Zr(NR$_2$)$_2$Cl$_2$(THF)$_2$] (R = Me or Et) with 1 mol equiv of [O(NH)$_2$] in toluene. There is no evidence for the formation of the dianionic form of the macrocycle in any of these reactions even upon prolonged reaction or heating the reaction solution in toluene or THF. The crystal structures of Zr[O(NH)N](NR$_2$)Cl$_2$ (R = Me, Figure 3, Table 4; R = Et, Figure 4, Table 5) show similar trends in the bond lengths and angles, albeit the bond lengths at Zr are ~0.15 Å longer than in the Ti species, consistent with the increased radius of Zr.[19a,b]

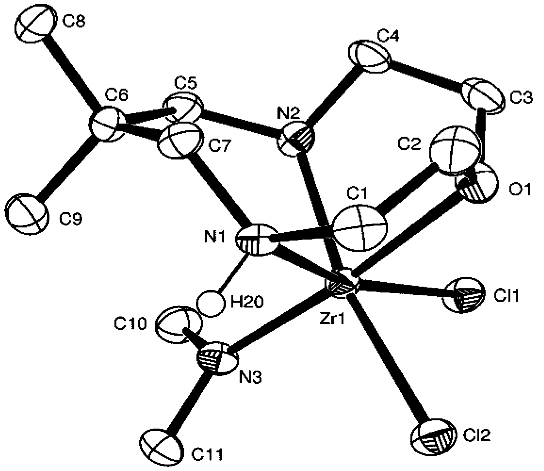

Figure 3. ORTEP representation of the structure of Zr[O(HN)N]-(NMe$_2$)Cl$_2$ with the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

The Zr−O distances (2.346(4) and 2.362(2) Å) in these formally 16e$^-$ species are considerably shorter than Zr−O in [Zr(ON$_2$)$_2$] in which each macrocycle functions as a

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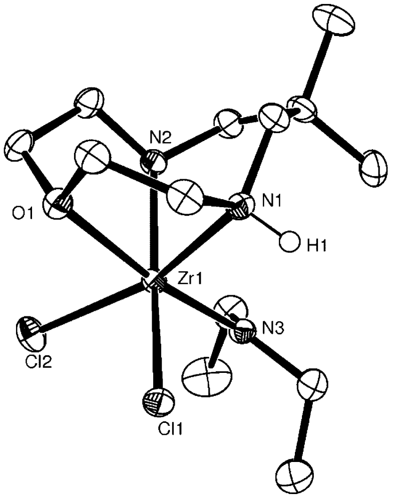

Figure 4. ORTEP representation of the structure of Zr[O(HN)N](NEt$_2$)-Cl$_2$ with the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms and toluene solvent molecules are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Zr[O(HN)N](NMe$_2$)Cl$_2$

N(1)−Zr(1)	2.377(4)	N(2)−Zr(1)	2.067(4)
N(3)−Zr(1)	2.027(4)	O(1)−Zr(1)	2.346(4)
Cl(1)−Zr(1)	2.4871(16)	Cl(2)−Zr(1)	2.5150(17)
C(1)−N(1)−C(7)	108.8(4)	C(1)−N(1)−Zr(1)	107.0(3)
C(7)−N(1)−Zr(1)	118.8(3)	C(4)−N(2)−C(5)	112.6(4)
C(4)−N(2)−Zr(1)	119.7(4)	C(5)−N(2)−Zr(1)	122.3(3)
C(11)−N(3)−C(10)	111.2(5)	C(11)−N(3)−Zr(1)	130.4(4)
C(10)−N(3)−Zr(1)	118.4(3)	C(2)−O(1)−C(3)	113.1(4)
C(2)−O(1)−Zr(1)	116.9(3)	C(3)−O(1)−Zr(1)	102.4(3)
N(3)−Zr(1)−N(2)	102.75(18)	N(3)−Zr(1)−O(1)	169.05(16)
N(2)−Zr(1)−O(1)	74.83(16)	N(3)−Zr(1)−N(1)	97.33(17)
N(2)−Zr(1)−N(1)	78.62(15)	O(1)−Zr(1)−N(1)	71.75(14)
N(3)−Zr(1)−Cl(1)	100.48(13)	N(2)−Zr(1)−Cl(1)	97.97(12)
O(1)−Zr(1)−Cl(1)	90.46(9)	N(1)−Zr(1)−Cl(1)	162.18(12)
N(3)−Zr(1)−Cl(2)	95.25(13)	N(2)−Zr(1)−Cl(2)	157.28(13)
O(1)−Zr(1)−Cl(2)	84.88(11)	N(1)−Zr(1)−Cl(2)	85.49(10)
Cl(1)−Zr(1)−Cl(2)	92.19(5)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Zr[O(HN)N](NEt$_2$)Cl$_2$•Toluene

Cl(1)−Zr(1)	2.5438(8)	Cl(2)−Zr(1)	2.4644(8)
N(1)−Zr(1)	2.406(2)	N(2)−Zr(1)	2.069(2)
N(3)−Zr(1)	2.011(2)	O(1)−Zr(1)	2.362(2)
C(7)−N(1)−C(1)	108.4(2)	C(7)−N(1)−Zr(1)	118.69(17)
C(1)−N(1)−Zr(1)	107.24(17)	C(4)−N(2)−C(5)	113.1(2)
C(4)−N(2)−Zr(1)	119.83(18)	C(5)−N(2)−Zr(1)	121.50(18)
C(10)−N(3)−C(12)	113.8(3)	C(10)−N(3)−Zr(1)	133.1(2)
C(12)−N(3)−Zr(1)	113.01(19)	C(2)−O(1)−C(3)	112.5(2)
C(2)−O(1)−Zr(1)	118.14(17)	C(3)−O(1)−Zr(1)	103.12(16)
N(3)−Zr(1)−N(2)	101.87(9)	N(3)−Zr(1)−O(1)	171.72(9)
N(2)−Zr(1)−O(1)	74.63(8)	N(3)−Zr(1)−N(1)	101.08(9)
N(2)−Zr(1)−N(1)	78.40(9)	O(1)−Zr(1)−N(1)	70.98(8)
N(3)−Zr(1)−Cl(2)	101.24(7)	N(2)−Zr(1)−Cl(2)	100.37(7)
O(1)−Zr(1)−Cl(2)	86.85(5)	N(1)−Zr(1)−Cl(2)	157.40(6)
N(3)−Zr(1)−Cl(1)	93.67(7)	N(2)−Zr(1)−Cl(1)	156.03(7)
O(1)−Zr(1)−Cl(1)	87.43(5)	N(1)−Zr(1)−Cl(1)	80.80(6)
Cl(2)−Zr(1)−Cl(1)	94.27(3)		

dianionic ligand via two amido units and one ether oxygen, giving Zr−O = 2.519(2) Å, in a formally 20e$^-$ species.[6]

Reaction of the monolithiated macrocycle [O(NH)N]Li with [Zr(NEt$_2$)$_2$Cl$_2$(THF)$_2$] in toluene solution at −78 °C gave the 18e$^-$ triamido species Zr[O(NH)N](NEt$_2$)$_2$Cl via a salt elimination reaction. This formulation follows from NMR spectroscopic studies and microanalysis and has been confirmed unequivocally through a crystal structure determination. The structure (Figure 5, Table 6) shows that the macrocycle adopts a facial bonding mode similar to the one observed in the previous complexes, via one amido, one amine, and the ether O atom, with two NEt$_2$ ligands and a Cl ligand completing the distorted octahedral coordination sphere. Retention of one amine function in the coordinated macrocycle and a coordinated Cl ligand on the Zr center leads to this species being stable with respect to disproportionation.

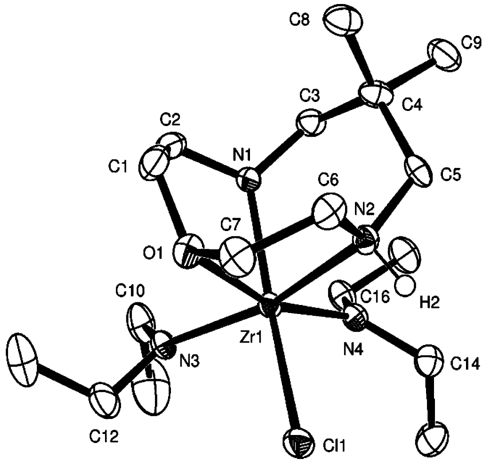

Figure 5. ORTEP representation of the structure of Zr[O(HN)N](NEt$_2$)$_2$-Cl with the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Zr[O(HN)N](NEt$_2$)$_2$Cl

Zr(1)−N(4)	2.049(3)	Zr(1)−N(3)	2.053(3)
Zr(1)−N(1)	2.068(3)	Zr(1)−O(1)	2.421(3)
Zr(1)−N(2)	2.424(3)	Zr(1)−Cl(1)	2.5532(14)
N(4)−Zr(1)−N(3)	110.04(14)	N(4)−Zr(1)−N(1)	96.34(14)
N(3)−Zr(1)−N(1)	95.38(14)	N(4)−Zr(1)−O(1)	161.55(12)
N(3)−Zr(1)−O(1)	86.57(12)	N(1)−Zr(1)−O(1)	73.43(12)
N(4)−Zr(1)−N(2)	94.07(12)	N(3)−Zr(1)−N(2)	155.83(13)
N(1)−Zr(1)−N(2)	79.78(12)	O(1)−Zr(1)−N(2)	69.32(10)
N(4)−Zr(1)−Cl(1)	100.43(11)	N(3)−Zr(1)−Cl(1)	96.07(11)
N(1)−Zr(1)−Cl(1)	155.03(10)	O(1)−Zr(1)−Cl(1)	85.19(8)
N(2)−Zr(1)−Cl(1)	80.70(9)	C(7)−O(1)−C(1)	113.9(3)
C(7)−O(1)−Zr(1)	111.1(2)	C(1)−O(1)−Zr(1)	112.1(3)
C(3)−N(1)−C(2)	118.9(3)	C(3)−N(1)−Zr (1)	122.9(3)
C(2)−N(1)−Zr(1)	114.6(3)	C(6)−N(2)−C(5)	113.2(3)
C(6)−N(2)−Zr(1)	116.2(2)	C(5)−N(2)−Zr(1)	113.3(2)
C(10)−N(3)−C(12)	113.2(4)	C(10)−N(3)−Zr(1)	123.4(3)
C(12)−N(3)−Zr(1)	123.3(3)	C(16)−N(4)−C(14)	114.2(3)
C(16)−N(4)−Zr(1)	124.4(3)	C(14)−N(4)−Zr(1)	120.9(3)

It is interesting to note that the sum of the angles at the macrocycle amido N atom in the four complexes involving the monoanionic macrocycle is in the range 354.4−357.6° and is significantly closer to the expected 360° for a perfectly trigonal planar amido ligand. Compared to the Zr−N bonds (2.078−2.111 Å) and angles at N (340.6−346.6°) within [Zr(ON$_2$)$_2$], in which two dianionic diamido macrocycles are involved, the observed data indicate the presence of stronger π-bonding in the former case. This may be interlinked to reduced steric constraints upon coordination of the monoanionic macrocycle, rendering the resultant complexes more stable and resistant to further deprotonation. Increasing the macrocycle ring size may allow tuning of the ligand to facilitate easier diamide formation.

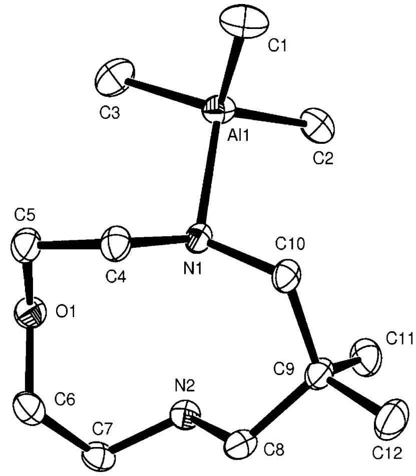

Figure 6. ORTEP representation of the structure of AlMe$_3$[O(NH)$_2$] with the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for AlMe$_3$[O(NH)$_2$]

C(1)−Al(1)	1.9785(19)	C(2)−Al(1)	1.9754(18)
C(3)−Al(1)	1.9845(19)	N(1)−Al(1)	2.0277(13)
C(4)−N(1)−C(10)	110.21(11)	C(4)−N(1)−Al(1)	113.42(9)
C(10)−N(1)−Al(1)	111.05(9)	C(7)−N(2)−C(8)	115.13(12)
C(5)−O(1)−C(6)	114.24(11)	C(2)−Al(1)−C(1)	114.48(8)
C(2)−Al(1)−C(3)	109.76(7)	C(1)−Al(1)−C(3)	114.41(9)
C(2)−Al(1)−N(1)	105.80(7)	C(1)−Al(1)−N(1)	102.55(6)
C(3)−Al(1)−N(1)	109.13(7)		

Reaction of [O(NMe$_3$Si)$_2$] with 1 mol equiv of [TiCl$_4$(THF)$_2$] or ZrCl$_4$ in refluxing toluene overnight in a sealed ampule leads to elimination of Me$_3$SiCl and production of poorly soluble solids formulated on the basis of microanalysis as [Ti(ON$_2$)Cl$_2$] and [(ZrCl$_3$)$_2$(ON$_2$)], respectively.

On the basis of the unexpected C-metalation observed following the alkanolysis reaction between [Ti(benzyl)$_4$] and [O(NH)$_2$], we have also attempted an alkanolysis reaction between [O(NH)$_2$] and 1 mol equiv of AlMe$_3$ in refluxing toluene. Following isolation of a colorless solid, ^{1}H and ^{13}C{^{1}H} NMR spectroscopic studies indicated that the product was in fact an adduct of formula [O(NH)$_2$]AlMe$_3$, involving coordination of one amine group of a neutral macrocycle to the Al center. This was confirmed by a crystal structure determination which shows (Figure 6, Table 7) a distorted tetrahedral Al carrying three Me groups and one amine (Al−N = 2.0277(13) Å).

Similar results were observed from the analogous reaction of ^{i}Pr$_2$-tacn with AlMe$_3$, giving the neutral [(^{i}Pr$_2$-tacn)AlMe$_3$].[20] Aza macrocycles with pendant groups have also been used for the synthesis of neutral and cationic aluminum complexes.[21]

Studies on the activity of the Ti and Zr complexes toward ethene polymerization were undertaken with excess MAO,[22] resulting in "low activity".[4]

Conclusions

These results show that the 10-membered [ON$_2$] donor macrocycle is a very versatile ligand capable of acting as a neutral 6e$^-$ diamine ether donor, a monoanionic 8e$^-$ N(amido)N(amine)O donor, or a dianionic 10e$^-$ N$_2$(amido)O donor depending upon the metal type, reaction conditions, and other coligands on the metal. There is a very fine balance between these factors in determining the degree of deprotonation at the macrocyclic amines and the precise coordination mode and geometry adopted by the complex. The presence of the C$_3$ linker between the N atoms allows the geometric requirements of both coordinated tetrahedral amine and trigonal planar amide to be accommodated easily, while the dimethyl ring substituents aid significantly the solubility of the products and ease of spectroscopic characterization and crystallization. We are now investigating the reactions of [O(NH)$_2$] with group 5 and group 6 metal precursor compounds and the effect of the linker between the secondary N and the ether donor on the nature of the isolated amido complexes.

Acknowledgment. We thank the EPSRC for support (Grant GR/R47134/01) and Professor M. B. Hursthouse for access to the X-ray facilities. We also thank Dr. J. A. Wright and Mr. N. Stylianides for X-ray data collection and analyses.

Supporting Information Available: Full details of the X-ray crystal structures, including complete tables of crystal data, atomic coordinates, bond lengths and angles. and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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