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Polyamidoimidonitride Clusters of Zirconium

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Abstract: Nitrogen-based polyoxoanion analogues that contain nitride (N^{3-}), imide (NH^{2-}), and amide (NH_2^-) ligands have been prepared via ammonolysis of $(\text{tritox})Zr(CH_2Ph)_3$ (**1**). Cluster formation is apparently directed by the steric bulk of tritox ($^tBu_3CO^-$). Treatment of **1** with 1.0 equiv of NH_3 in benzene for ~5 days at 25 °C provided colorless crystals of a ~0.6:1.0 composite of pseudooctahedral, C_2 $[(\text{tritox})Zr]_6(\mu_6\text{-}N)(\mu_3\text{-}NH)_6(\mu_2\text{-}NH_2)_3$ (**2**) and square pyramidal $[(\text{tritox})Zr]_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu_2\text{-}NH_2)_4$ (**3**), according to X-ray studies and ^{1}H, ^{13}C{^{1}H}, and crucial ^{15}N NMR investigations. A cross-polarization magic angle spinning (CPMAS) ^{15}N NMR spectrum of the crystals verified their composition. Addition of 1.75 equiv of NH_3 to benzene solutions of **1** at 25 °C generated pure, colorless crystals of **3** (32%), whose structure was determined by X-ray crystallography: orthorhombic, $Pbca$, $a = 15.554$ (3) Å, $b = 25.804$ (5) Å, $c = 40.406$ (8) Å, $Z = 8$, $V = 16217$ (5) Å^3, $T = 293$ K, $R = 11.3\%$, $R_w = 11.2\%$, GOF = 1.77 for 3729 reflections (data-to-parameter = 8.6:1) with $|F_o| \geq 3\sigma(F_o)$. Exposure of **1** to 2.6 equiv of NH_3 or treatment of **3** with excess ammonia produced the dodecaamido cluster $[(\text{tritox})Zr]_5(\mu_5\text{-}N)(\mu_2\text{-}NH_2)_{12}$ (**4**). In solution, **4** was observed in equilibrium with **3** and 4.0 equiv of NH_3. The cluster cores are related to simple cubic lattices, and the ^{15}N NMR shifts of the μ-N_6 (**2**, δ −40.6) and μ-N_5 (**3**, δ −62.6; **4**, δ −6.5) ligands are comparable to that of cubic ZrN (CPMAS ^{15}N NMR: δ −20).

Introduction

Central to the chemistry of the early transition metals are poly- and heteropolyoxoanions,[1-3] complexes whose topologies resemble the oxide networks common to solid-state compounds. Isoelectronic or isostructural nitrogen-based analogues containing nitride (N^{3-}), imide (NH^{2-}), and amide (NH_2^-) ligands are far less prevalent. Representative polynuclear early transition metal nitrides[4] include linear polymers (e.g., $[(^tBuO)_3MoN]_n$,[5] $[Cl_2(py)_2VN]_n$[6]),[7-10] trinuclears (e.g., $[Cp^*Ta(X)N]_3$ (X = Cl,[11] Me);[12] $[Cp^*Ti]_3(\mu_2\text{-}NH)_3(\mu_3\text{-}N)$[13]), planar tetramers (e.g., $[LCl_3MoN]_4$),[14] and ladder oligomers (e.g., $Mo_4(N)_2(O^iPr)_{12}$,[15] $W_4N_4(NPh_2)_6(O^nBu)_2$[16]).[17]

In these laboratories, ammonolysis of $(^tBuCH_2)_3Ta{=}CH^tBu$ was recently shown to produce $[(^tBuCH_2)_2TaN]_5$, a molecular ladder whose square Ta_2N_2 subunits are proposed to account for its ultimate conversion to metastable, cubic TaN ($Fm3m$), rather than the expected hexagonal ($P\bar{6}2m$) form.[18] In $[(^tBuCH_2)_2TaN]_5$, the neopentyl groups occupy equatorial positions of the trigonal bipyramids comprising the inner segments of the ladder, leaving one equatorial and two axial sites for Ta–N bonds. This conformation effectively limits the growth of an X_2MN oligomer to two dimensions, and one direction is further restricted to a single M–N bond length. A three-dimensional nitrogen network was envisaged to result from condensation of XMN fragments, provided the ancillary ligand is bulky enough to direct the aggregation. In accord with this reasoning, tritox ($^tBu_3CO^-$)[19,20] was considered to direct the formation of zirconium clusters.

Results and Discussion

Synthesis of Nitride Clusters. Ammonolysis of $(\text{tritox})Zr(CH_2Ph)_3$ (**1**),[19] a logical precursor to "(tritox)ZrN", was chosen as an appropriate route to nitride-based clusters, as illustrated in Scheme I. When exposed to 1.0 equiv of NH_3, benzene solutions of **1** deposited colorless crystals (A) over a ~5 day period at 25 °C. Single-crystal X-ray diffraction studies (rhombohedral, $R\bar{3}$) indicated an octahedral cluster of (tritox)Zr groups linked by a central nitride and facial nitrogens, but dissolution of A afforded complicated ^{1}H and ^{15}N NMR[21] spectra that were incompatible with the crystallographic symmetry. Additional electron density was detected in electron difference maps, but satisfactory disorder models were not found and the discrepancy remained unresolved. Further studies indicated that the crystals (A) were a ~0.6:1.0 composite of $[(\text{tritox})Zr]_6(\mu_6\text{-}N)(\mu_3\text{-}NH)_6(\mu_2\text{-}NH_2)_3$ (**2**) and $[(\text{tritox})Zr]_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu_2\text{-}NH_2)_4$ (**3**).[22]

Addition of 1.75 equiv of NH_3 to benzene solutions of $(\text{tritox})Zr(CH_2Ph)_3$ (**1**) at 25 °C generated colorless crystals of **3**

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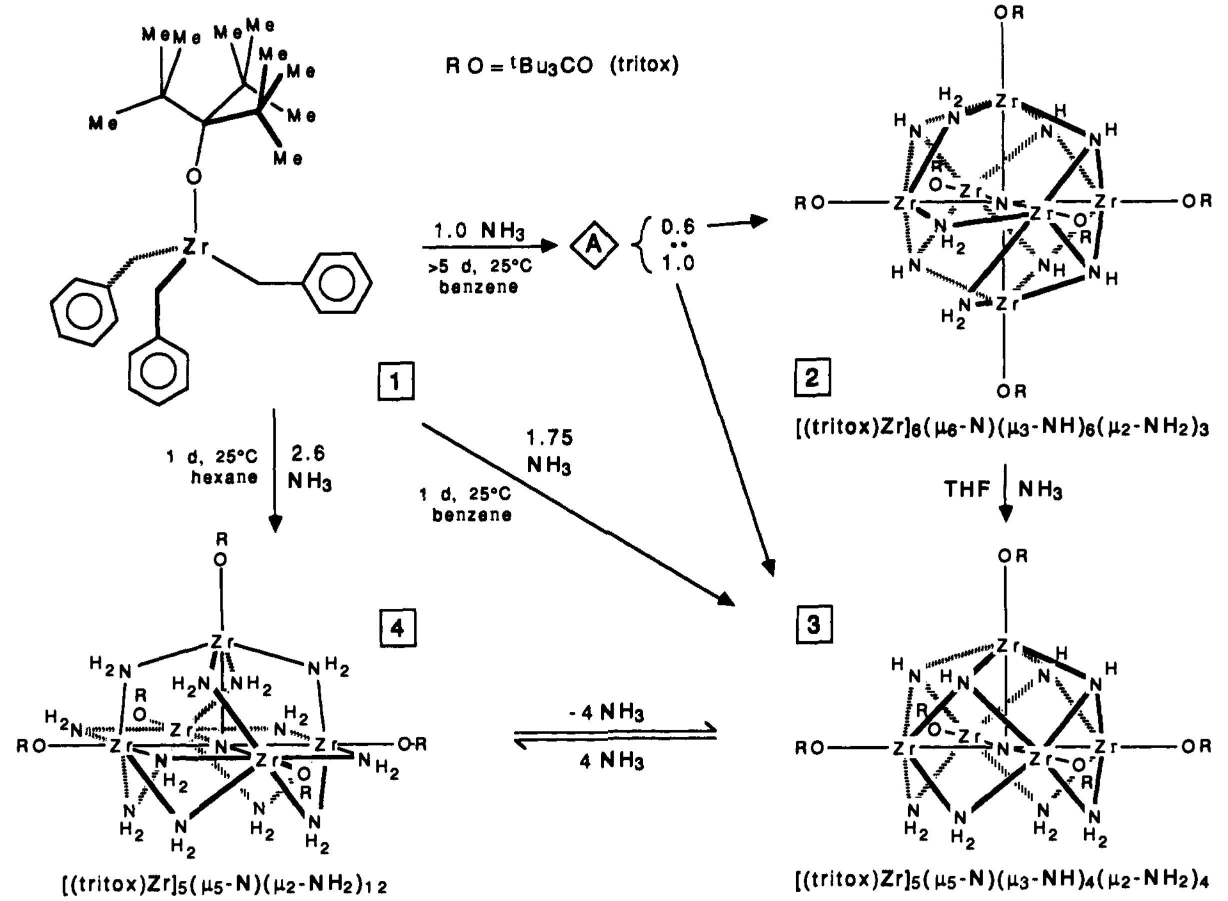
Scheme I



(32%), a square pyramid of (tritox)Zr fragments surrounding a nitride, with μ_3-NH groups capping the triangular faces and μ_2-NH_2 units girding the basal zirconiums. ^{15}N NMR spectra (C_6D_6, external CH_3NO_2 reference)[21] of material prepared from $^{15}NH_3$ (**3**-$^{15}N_9$) proved critical in identifying the nitride (δ −62.6, s), imide (δ −141.1, d, J_{NH} = 61 Hz), and amide (δ −302.2, t, J_{NH} = 60 Hz) ligands, while $^{13}C\{^1H\}$ and ^1H NMR spectra manifested a 4:1 ratio of tritox groups. Resonances for the μ_3-NH (δ 6.40) and inequivalent μ_2-NHH′ protons (δ 0.87, 1.63, J = 8.5 Hz) completed the characterization, which was subsequently verified by X-ray crystallography (vide infra).

Treatment of (tritox)Zr(CH_2Ph)$_3$ (**1**) with 2.6 equiv of NH_3 produced opaque white crystals of the dodecaamido square pyramid [(tritox)Zr]$_5$(μ_5-N)(μ_2-NH_2)$_{12}$ (**4**). Although the ^{15}N NMR spectrum[21] of **4**-$^{15}N_{13}$ (THF-d_8) clearly exhibited a nitride (δ −6.5, s) and three different amide (δ −274.4, t, J_{NH} = 62 Hz; −292.1, t, J_{NH} = 62 Hz; −295.9, t, J_{NH} = 60 Hz) resonances, some ambiguity in the structure persists. The 4:1 ratio of tritox groups observed in $^{13}C\{^1H\}$ and ^1H NMR (C_6D_6) spectra of **4** corroborated the square pyramidal configuration, but the bonding of the amides is less straightforward. In THF-d_8, the ^1H NMR spectrum revealed two sets of broad resonances tentatively assigned to diastereotopic protons of Zr_b(μ_2-NHH′)Zr_b units that bridge basal zirconiums (δ 1.09, 1.54, J = 8 Hz), and Zr_a(μ_2-NHH′)Zr_b groups bridging apical and basal sites (δ 1.48, 1.52, J = 10 Hz). The diastereotopic Zr_a(μ_2-NHH′)Zr_b protons may be rationalized by invoking a 4-fold twist along the apical Zr-(μ_5-N) axis of C_4 dodecaamide **4**.

In addition to these amides, which account for 8 of the necessary 12 NH_2 groups, an apparent dd at δ 2.29 (J = 3.5, 7 Hz, ~4 H) was observed. While it is tempting to include terminal amides in the structure in order to keep the basal zirconiums 6-coordinate, it is difficult to reconcile the couplings of the latter resonance. An accompanying J of 3.5 Hz may be unresolved within one of the broad doublets of the aforementioned bridging amides, but the 8-Hz coupling signifies another μ_2-NHH′ group, especially considering the similarities in ^{15}N-amide chemical shifts and ^{15}NH-coupling constants.[23] As a consequence, the structure of C_4 dodecaamide **4** is considered to possess three sets of μ_2-NHH′ groups and 7-coordinate basal zirconiums about the μ_5-nitride, as if NH_3 adds symmetrically across four Zr_b-(μ_3-NH) bonds. Complexation of zirconium by seven or more ligands is common, and the distantly related oxide–alkoxide cluster $Zr_{13}O_8(OMe)_{36}$, which contains 12 7-coordinate zirconium atoms,[24] provides appropriate precedent. In solution, the dodecaamido nitride (**4**) is prone to ammonia loss, as evidenced by its equilibration with **3** and 4.0 equiv of NH_3, thereby hampering variable temperature NMR experiments.

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(21) ^1H NMR spectra of ^{15}N-containing samples revealed J_{NH} values for μ_3-^{15}NH and μ_2-$^{15}NH_2$ groups that were virtually indistinguishable. Furthermore, the resonances were typically broad and difficult to integrate relative to tritox, and the amides reside in the tritox region of the spectrum and were not always identified, even for clusters prepared with $^{15}NH_3$. These problems were exacerbated by low solubilities of the clusters, particularly **2**. For ^{15}N NMR spectra of nitrides, see: (a) von Philipsborn, W.; Muller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383–406. (b) Mason, J. *Chem. Rev.* **1981**, *81*, 205–227. (c) Mason, J. *J. Am. Chem. Soc.* **1991**, *113*, 24–26. (d) Mason, J. *J. Am. Chem. Soc.* **1991**, *113*, 6056–6062. (e) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41–86.

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(23) For example, the ^{15}N shifts for the terminal amides in ($^tBu_3SiO$)$_2$Ta(CH_2Ph)$_2$(NH_2) and ($^tBu_3SiO$)$_2$Ta(CH_2Ph)(NH_2)$_2$ are δ −194.5 (t, J_{NH} = 72 Hz) and −226.3 (t, J_{NH} = 70 Hz), respectively. Banaszak Holl, M. M. Ph.D. Thesis, Cornell University, 1991.

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(25) $R = \sum||F_o| - |F_c||/(\sum|F_o|)$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2\}^{1/2}$; GOF = $\{\sum[\text{weight} \times (|F_o| - |F_c|)^2]\}/(M - N)$ where M is the number of observations and N is the number of parameters; 3729 reflections (data-to-parameter = 8.6:1) with $|F_o| \geq 3\sigma(F_o)$.

Table I. Average[a] Interatomic Distances (Å) and Angles (deg) for $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu_2\text{-NH}_2)_4$ (**3**)

$\text{Zr}_a\text{–Zr}_b$	3.146 (2)	$\text{Zr}_b\text{–Zr}_b$	3.146 (9)	$\text{Zr}_a\text{–}(\mu_5\text{-N})$	2.35 (3)
$\text{Zr}_a\text{–}(\mu_3\text{-NH})$	2.27 (5)	$\text{Zr}_b\text{–}(\mu_5\text{-N})$	2.23 (2)	$\text{Zr}_b\text{–}(\mu_3\text{-NH})$	2.19 (3)
$\text{Zr}_b\text{–}(\mu_2\text{-NH}_2)$	2.31 (2)	$\text{Zr}_1\text{–O}$	1.90 (2)	$\text{Zr}_b\text{–O}$	1.935 (12)
$\text{Zr}_a\text{–Zr}_b\text{–Zr}_b$	60.00 (12)	$\text{Zr}_b\text{–Zr}_b\text{–Zr}_b$	89.98 (30)	$\text{Zr}_b\text{–Zr}_a\text{–Zr}_b$	60.00 (22), 90.00 (14)
$\text{Zr}_a\text{–O–C}$	179.8 (22)	$\text{Zr}_b\text{–O–C}$	177.2 (6)	$\text{Zr}_a(\mu_5\text{-N})\text{Zr}_b$	86.9 (4)
$\text{Zr}_b\text{–}(\mu_5\text{-N})\text{–Zr}_b$	89.8 (7), 173.7 (1)	$\text{Zr}_a\text{–}(\mu_3\text{-NH})\text{–Zr}_b$	90.6 (7)	$\text{Zr}_b(\mu_3\text{-NH})\text{Zr}_b$	92.1 (11)
$\text{Zr}_b\text{–}(\mu_2\text{-NH}_2)\text{–Zr}_b$	85.9 (4)	$(\mu_3\text{-NH})\text{–Zr}_a\text{–}(\mu_3\text{-NH})$	82.7 (12), 138.3 (4)	$(\mu_3\text{-NH})\text{Zr}_b(\mu_3\text{-NH})$	85.3 (7)
$(\mu_2\text{-NH}_2)\text{–Zr}_b\text{–}(\mu_2\text{-NH}_2)$	95.7 (12)	$(\mu_2\text{-NH}_2)\text{–Zr}_b\text{–}(\mu_3\text{-NH})$	80.5 (7), 147.1 (7)	$(\mu_2\text{-NH}_2)\text{Zr}_b(\mu_5\text{-N})$	75.1 (9)
$(\mu_3\text{-NH})\text{–Zr}_b\text{–}(\mu_5\text{-N})$	72.3 (7)	$(\mu_3\text{-NH})\text{–Zr}_a\text{–}(\mu_5\text{-N})$	69.1 (12)	$\text{O–Zr}_b\text{–}(\mu_3\text{-NH})$	106.8 (14)
$\text{O–Zr}_a\text{–}(\mu_3\text{-NH})$	110.9 (20)	$\text{O–Zr}_b\text{–}(\mu_2\text{-NH}_2)$	105.7 (8)	$\text{O–Zr–}(\mu_5\text{-N})$	177.9 (8)

[a] Zr_a = Zr1, Zr_b = Zr2, Zr3, Zr4, Zr5; μ_3-NH = N2, N3, N4, N5; $\mu_2\text{-NH}_2$ = N6, N7, N8, N9; O_a = O1; O_b = O2, O3, O4, O5; μ_5-N = N1.

^{15}N NMR spectra (THF-d_8)[21] of dissolved crystals A revealed nitride (δ −40.6, s), three imide (δ −110.9, d, J_{NH} = 57 Hz; −145.4, d, J_{NH} = 62 Hz; −149.6, d, J_{NH} = 63 Hz) and two amide (δ −294.3, t, J_{NH} = 60 Hz; −296.0, t, J_{NH} = 61) resonances attributed to $[(\text{tritox})\text{Zr}]_6(\mu_6\text{-N})(\mu_3\text{-NH})_6(\mu_2\text{-NH}_2)_3$ (**2**), in addition to those of **3**. The ^{13}C {^{1}H} NMR spectrum of **2** manifested three tritox groups (~1:1:1), and ^{1}H NMR spectra (THF-d_8) exhibited three imide resonances (δ 5.03, 5.37, and 8.03) plus one doublet assigned to an amide proton (δ 2.07, J = 8 Hz).[21] Using rough integrations, the nitrogen-based ligands possess a total charge ($\text{N}^{3-} + 6\text{NH}^{2-} + 3\text{NH}_2^- = 18^-$) commensurate with six $(\text{tritox})\text{Zr}^{3+}$ fragments. The proposed structure for **2**, illustrated in Scheme I, contains a C_2 axis through the unique $\mu_2\text{-NH}_2$ and μ_6-N ligands of a Zr_6 octahedron. Consequently, three distinct symmetry-equivalent pairs of imides and two symmetry-related μ_2-NHH′ groups are generated along with the nitride and unique amide, in accord with the spectra.

In order to verify the mixed composition of crystalline A, its cross-polarization magic angle spinning (CPMAS) ^{15}N NMR spectrum was taken (Figure 1). A broad amide resonance at δ −300 (CH_3NO_2 reference), and accompanying imide (δ −138) and nitride (δ −60) signals are spectral features ascribed to $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu_2\text{-NH}_2)_4$ (**3**). Amide resonances attributable to **2** are also within the envelope at δ −300, and corresponding imide signals are clearly observed at δ −115, δ −147 (shoulder), and δ −160. The lack of a signal for the μ_6-N of **2** is not surprising, since no nearby protons are available for cross polarization to be effective. In contrast, **3** contains a set of μ_2-NH*H* protons that are directed toward the inside of the square pyramid, enabling observation of its μ_5-N resonance. A rough estimate of the intensities in the imide region indicated that the ratio of square pyramid **3** to octahedron **2** was ~1.0:0.6, consistent with solution data.

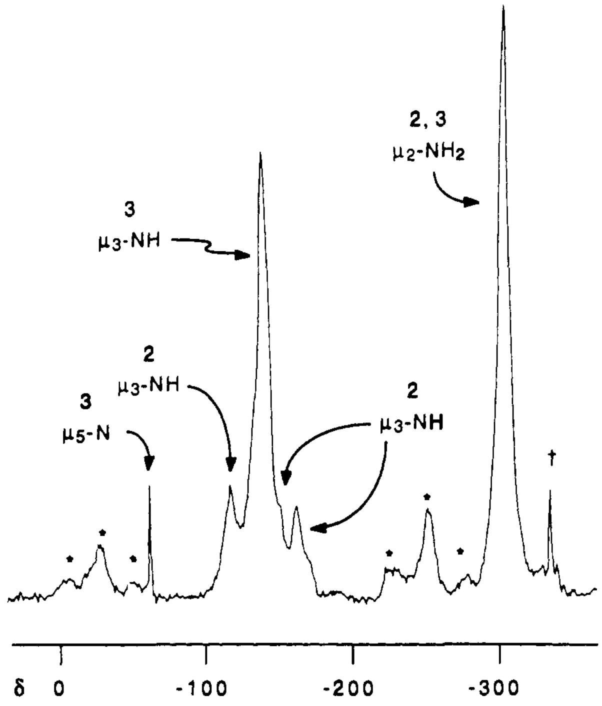

Figure 1. CPMAS ^{15}N NMR spectrum of crystalline A showing its composition of ~1.0 $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu_2\text{-NH}_2)_4$ (**3**) to 0.6 $[(\text{tritox})\text{Zr}]_6(\mu_6\text{-N})(\mu_3\text{-NH})_6(\mu_2\text{-NH}_2)_3$ (**2**). The spectrum was acquired in reference to external $^{15}\text{NH}_4\text{Cl}$, but the above spectrum is corrected in reference to $\text{CH}_3{}^{15}\text{NO}_2$ (δ 0.0) for comparison to the solution spectra. Asterisks indicate spinning sidebands. Dagger (†) indicates unidentified resonance.

Structural Study of $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu_2\text{-NH}_2)_4$ (3). An X-ray structure determination of $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu_2\text{-NH}_2)_4$ (**3**) confirmed its square pyramidal geometry (Figure 2), although the tritox groups were disordered. The C–C distances of the tritox ligands were constrained according to those found in previous structures,[19,20] and the carbons refined isotropically, whereas the remaining non-hydrogen atoms were subjected to anisotropic refinement (crystal data for **3**: orthorhombic, *Pbca*, a = 15.554 (3) Å, b = 25.804 (5) Å, c = 40.406 (8) Å, Z = 8, V = 16217 (5) Å^3, T = 293 K, R = 11.3%, R_w = 11.2%, GOF = 1.77).[25]

One striking aspect of the cluster concerns the proximity of the $\text{Zr}_a(\text{Zr}_b)_4$ core to an ideal square pyramid, as evidenced by the 3.146 (9) Å Zr–Zr distances and the 60.0 (3)° or 90.0 (4)° Zr–Zr–Zr angles. Because of the regularity of the Zr_5-core and surrounding nitrogens, most of the structural features are best considered in terms of average interatomic distances and angles (Table I). The nitride ligand extends below the basal plane by 0.12 Å, thus the apical $\text{Zr}_a\text{–}(\mu_5\text{-N})$ bond length is 2.35 (3) Å, while the $\text{Zr}_a\text{–}(\mu_3\text{-NH})$ distances average 2.27 (5) Å. Basal $\text{Zr}_b\text{–}(\mu_5\text{-N})$, $\text{Zr}_b\text{–}(\mu_3\text{-NH})$, and $\text{Zr}_b\text{–}(\mu_2\text{-NH}_2)$ distances average 2.23 (2), 2.19 (3), and 2.31 (2) Å, respectively, in accord with Zr–N single bonds.[26] The Zr–O distances (1.927 (19) Å) and accompanying nearly linear Zr–O–C angles (∠Zr–O–C = 177.7 (13)° (average)) reflect strong O(pπ) → Zr(dπ) bonding.[19,20] The $\text{Zr}_a(\mu_3\text{-NH})\text{Zr}_b$, $\text{Zr}_b(\mu_3\text{-NH})\text{Zr}_b$, and $\text{Zr}_b(\mu_2\text{-NH}_2)\text{Zr}_b$ angles average 90.6 (7)°, 92.1 (11)°, and 85.9 (4)°, consistent with substantial p-orbital contributions to the Zr–N σ-bonds, as evidenced by the similar J_{NH} values for the amide and imide ligands. Since the nitride distends the basal plane, the amides splay slightly at the base (cf. $\angle(\mu_3\text{-NH})\text{Zr}_b(\mu_3\text{-NH})$ = 85.3 (7)° vs $\angle(\mu_2\text{-NH}_2)\text{Zr}_b(\mu_2\text{-NH}_2)$ = 95.7 (12)°). Perhaps the C_2 geometry of **2** is a consequence of a similar distortion due to encapsulating a μ_6-N with six zirconiums linked by eight face caps; $\mu\text{-NH}_2$ edge-bridges formed via the addition of another nitrogen (i.e., NH_3) may relieve the strain. The remaining angles of **3** reflect the square pyramidal distortion of the 6-coordinate pseudo-C_{4v} zirconium centers imposed by the bonding constraints of the bridges.

Related Compounds. As in polyoxoanions (POA),[1-3] the polyamidoimidonitrides (PAIN) possess geometries and spectral characteristics common to related solid-state species. Each cluster embodies the core of a simple bcc cubic lattice, albeit with minor variants, and the nitride chemical shifts are similar to cubic ZrN (*Fm3m*), whose CPMAS ^{15}N NMR spectrum consists of a broad singlet at δ −20.[23] Polyamidoimidonitrides are more tangibly related to oxide/alkoxide complexes, such as Caulton's square pyramidal, μ_5-O-centered cluster, $[(^i\text{PrO})\text{Y}]_5(\mu_5\text{-O})(\mu_3\text{-O}^i\text{Pr})_4(\mu_2\text{-O}^i\text{Pr})_4$,[27] which is an analogue of **3**. Ammonolysis methods

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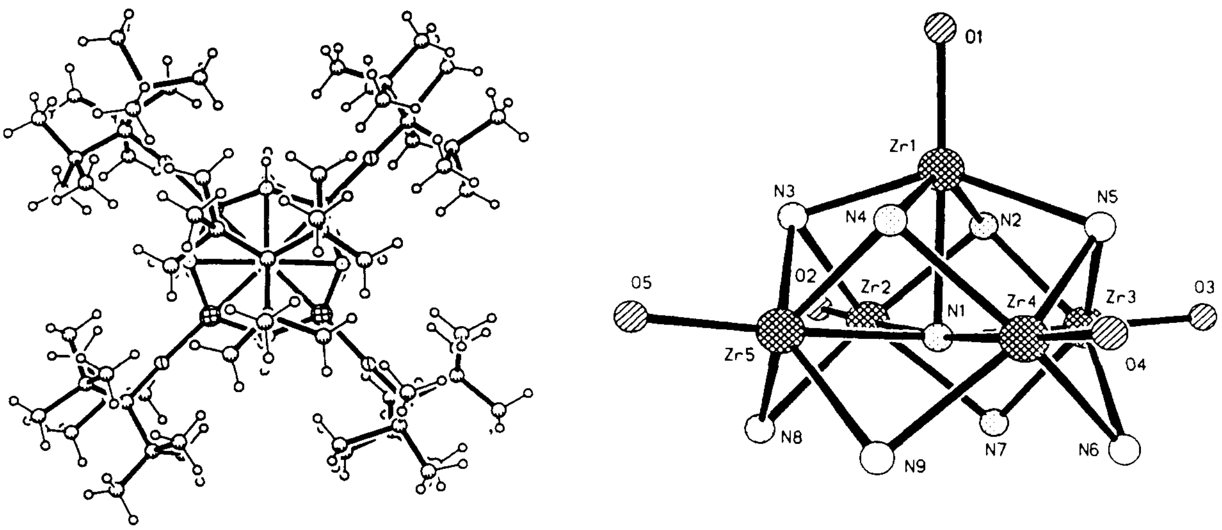

Figure 2. Molecular and skeletal views of $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu_2\text{-NH}_2)_4$ (**3**).

utilized to prepare **2**–**4** are related to alkoxide hydrolyses of the sol–gel process,[28] which produce intermediate oxide/alkoxide aggregates. Klemperer[29] and Mosset[30] have generated oxide-centered clusters of titanium alkoxides (e.g., $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$ and $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$) by such techniques, and Hollingshead and McCarley[31] have synthesized a distorted octahedral cluster of reduced molybdenum centers surrounding a μ_6-O ligand, $[(\text{EtO})\text{Mo}]_6(\mu_6\text{-O})(\mu_2\text{-OEt})_{12}$. Certain chalcogenides (e.g., $\text{Cp}_6\text{Zr}_6\text{S}_9$)[32] and polyamides (e.g., $\text{Ni}_6(\text{NH}_2)_{12}$[33]) possess structural features related to the polyamidoimidonitrides, which are also reminiscent of $\text{Zr}_6(\text{Z})\text{Cl}_{12}\text{·L}/\text{X}_6^{\,n-}$[34,35] clusters, except that μ_n-N, μ_3-NH, and μ_2-NH$_2$ bridges compensate for Zr–Zr bonding evident in the reduced halides.[36] The scope and reactivity of PAIN are currently under investigation.

Experimental Section

General Considerations. All manipulations were performed with use of either glovebox or high vacuum line techniques. Ethereal and hydrocarbon solvents were distilled under nitrogen from purple benzophenone ketyl and vacuum transferred from the same prior to use. Small amounts of tetraglyme (2–5 mL/mL of solvent) were added to hydrocarbons to solubilize the ketyl. Benzene-d_6 was dried over activated 4-Å molecular sieves, vacuum transferred, and stored under N$_2$; THF-d_8 was dried over sodium benzophenone ketyl. Anhydrous ammonia was purchased from Matheson and distilled from sodium. $^{15}\text{NH}_3$ (98%, Aldrich) was dried over sodium, and $(\text{tritox})\text{Zr}(\text{CH}_2\text{Ph})_3$ (**1**) was prepared via literature methods.[19]

NMR spectra were obtained using Varian XL-200 (^{1}H) and XL-400 (^{1}H, ^{13}C {^{1}H}, ^{15}N) spectrometers. Chemical shifts are reported relative to TMS (^{1}H) or benzene-d_6 (^{1}H, δ 7.15; ^{13}C {^{1}H}, δ 128.00). ^{15}N spectra were referenced to natural abundance CH$_3$NO$_2$ (neat, δ 0.00) using a coaxial 5-mm tube containing the lock solvent; a delay of 40 s and a pulse width of 30° were employed. ^{15}N NMR spectra were obtained on samples prepared via ^{15}NH$_3$. ^{1}H NMR spectra of ^{15}N-labeled material enabled identification of μ_3-^{15}NH and μ_2-^{15}NH$_2$ groups, but the resonances were often broad and difficult to integrate relative to tritox, and their respective J_{NH} values were virtually indistinguishable. Low solubilities exacerbated these problems, particularly for **2**. The CPMAS spectrum of A was obtained on a Bruker 300-MHz MSL spectrometer. Infrared spectra were recorded on a Mattson FT-IR interfaced to a AT&T PC7300 computer or a Perkin-Elmer 299B instrument. Mass spectra were obtained on a Kratos MS89OMS. Analyses were obtained by Oneida Research Services, Whitesboro, NY.

Procedures. 1. $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu_2\text{-NH}_2)_4$ (3). To a 100-mL flask charged with 607 mg (1.08 mmol) of $(\text{tritox})\text{Zr}(\text{CH}_2\text{Ph})_3$ (**1**) was distilled 60 mL of hexane. Ammonia (1.75 equiv, 1.94 mmol) was condensed into the flask at 77 K, and the mixture was allowed to warm to 25 °C. After the mixture was stirred for 18 h, the volatiles were removed from the clear colorless solution. The resulting white solid was dissolved twice in hexane followed by removal of the solvent to expel residual ammonia. The material was redissolved in hexane, the solution was filtered, and the solvent was reduced to 8 mL and cooled to −78 °C. A snow white solid was isolated by filtration (108 mg, 32%). ^{1}H NMR (C$_6$D$_6$) δ 0.87 (d, μ_2-N*H*H′, J = 8.5 Hz, 4 H), 1.39 (s, C(CH$_3$)$_3$, 27 H), 1.43 (s, C(CH$_3$)$_3$, 108 H), 1.63 (d, μ_2-NH*H*′, J = 8.5 Hz, 4 H), 6.40 (s, μ_3-NH, 4 H); ^{13}C {^{1}H} NMR (C$_6$D$_6$) δ 33.5, 33.7 (C{C(*C*H$_3$)$_3$}$_3$, ~4:1), 45.6, 45.9 (C{*C*(CH$_3$)$_3$}$_3$, ~4:1), 94.3, 94.8 (*C*{C(CH$_3$)$_3$}$_3$, ~4:1); ^{15}N NMR (C$_6$D$_6$) δ −62.6 (s, μ_5-N), −141.1 (d, μ_3-NH, J_{NH} = 61 Hz), −302.2 (t, μ_2-NH$_2$, J_{NH} = 60 Hz). IR (Nujol, cm^{-1}) 1531 (w), 1500 (m), 1480 (m), 1390 (s)†, 1200 (vw)†, 1182 (w)†, 1070 (s)†, 1018 (s)†, 920 (m)†, 880 (m)†, 740 (m), 705 (s); (halocarbon oil) 1540 (w), 1395 (s)†, 1371 (m). IR (**3**-$^{15}N_9$) (Nujol, cm^{-1}) 1395 (m)†, 1190 (w)†, 1182 (w)†, 1072 (s)†, 1020 (s)†, 925 (m), 888 (m), 745 (m), 722 (m), 650 (m); (halocarbon oil) 1540 (w), 1480 (m), 1460 (m), 1410 (w), 1395 (m)†, 1371 (m). Absorptions marked with a dagger (†) are believed to derive from the tritox ligand. Anal. Calcd for $\text{C}_{65}\text{H}_{147}\text{N}_9\text{O}_5\text{Zr}_5$: C, 49.07; H, 9.31; N, 7.92. Found: C, 50.12; H, 9.43; N, 7.78.

2. $[(\text{tritox})\text{Zr}]_5(\mu_5\text{-N})(\mu_2\text{-NH}_2)_{12}$ (4). To a 25-mL flask charged with 747 mg (1.32 mmol) of $(\text{tritox})\text{Zr}(\text{CH}_2\text{Ph})_3$ (**1**) was distilled 15 mL of hexane. Ammonia (4.00 equiv, 5.30 mmol) was condensed into the flask at 77 K, and the mixture was allowed to warm to 25 °C and was stirred for 24 h, resulting in a clear, colorless solution. After 24 h, the mixture acquired a slight opalescence. All volatiles were stripped and 5 mL of THF was added to give a clear, colorless solution. The mixture was filtered, the solvent reduced to 3 mL, and the solution cooled to −78 °C, resulting in a microcrystalline white solid isolated via filtration (247 mg, 56%). The crystals rapidly became opaque and thus were stored at −20 °C in the drybox. ^{1}H NMR (THF-d_8) δ 1.09 (d, Zr$_\text{b}$(μ_2-N*H*H′)Zr$_\text{b}$, J = 8 Hz, 4 H), 1.32 (s, C(CH$_3$)$_3$, 108 H), 1.38 (s, C(CH$_3$)$_3$, 27 H), 1.48 (d, Zr$_\text{a}$(μ_2-N*H*H′)Zr$_\text{b}$, J = 10 Hz), 1.52 (d, Zr$_\text{a}$(μ_2-NH*H*′)Zr$_\text{b}$, J = 10 Hz), 1.54 (d, Zr$_\text{b}$(μ_2-NH*H*′)Zr$_\text{b}$, J = 8 Hz, 4 H), 2.29 (dd, N*H*H′, J = 3.5, 7 Hz, ~4 H). ^{1}H NMR (C$_6$D$_6$) δ 1.08 (dd, μ_2-N*H*H′, J = ~4, 7 Hz, ~4 H), 1.14 (tentative d, μ_2-N*H*H′, J = 8.0 Hz), 1.32 (s, C(C*H*$_3$)$_3$,

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27 H), 1.45 (s, $C(CH_3)_3$, 108 H), 1.79 (d, μ_2-NH*H′*, J = 8.0 Hz, ~4 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 33.8, 34.9 ($C\{C(CH_3)_3\}_3$, ~4:1), 46.9, 47.4 ($C\{C(CH_3)_3\}_3$, ~4:1), the $C\{C(CH_3)_3\}_3$ resonances were not resolved; ^{15}N NMR (THF-d_8) δ –6.47 (s, μ_5-N, ~1 N), –274.4 (t, NH_2, J_{NH} = 62 Hz, ~4 N), –292.1 (t, NH_2, J_{NH} = 62 Hz, ~4 N), –295.9 (t, NH_2, J_{NH} = 60 Hz, ~4 N). IR (Nujol, cm^{-1}) 1590 (w)†, 1385 (m)†, 1200 (w)†, 1180 (w)†, 1052 (s), 1000 (s), 920 (w)†, 880 (w)†, 712 (m), 628 (m). IR (**4**-$^{15}N_{13}$) (Nujol, cm^{-1}) 1600 (m), 1588 (m)†, 1390 (m)†, 1058 (s), 1006 (s), 925 (m)†, 908 (m), 720 (m), 695 (w), 622 (w); (halocarbon oil) 3380 (w), 1592 (m)†, 1580 (m), 1530 (vw), 1475 (m), 1400 (w), 1388 (s)†, 1366 (m). Absorptions marked with a dagger (†) are believed to be derived from the tritox ligand. Anal. Calcd for $C_{65}H_{159}N_{13}O_5Zr_5$: C, 47.05; H, 9.66; N, 10.97. Found: C, 47.66; H, 9.67; N, 11.37. It is not clear that these numbers are meaningful since spectral analysis of **4** revealed some loss of ammonia and reversion to **3**.

3. $[(tritox)Zr]_6(\mu_6\text{-}N)(\mu_3\text{-}NH)_6(\mu_2\text{-}NH_2)_3$ (2) in Composite A. To a 10-mL glass ampule charged with 375 mg (0.665 mmol) of $(tritox)Zr(CH_2Ph)_3$ (**1**) was added 2 mL of benzene. Ammonia (1.0 equiv, 0.665 mmol) was condensed into the ampule at 77 K, and the ampule was flame-sealed. Crystals (A) typically formed on the walls of the ampules over the course of 5–20 days. The ampules were broken open and the very pale yellow/colorless crystals isolated via filtration. The yellow filtrate contained primarily **1**. The crystals were sparingly soluble in both benzene and hexane and were typically washed with 5 × 2 mL benzene. Typical preparations on this scale yielded between 30 and 67 mg of crystals. The crystals (A) contained an approximately 0.6:1 ratio of $[(tritox)Zr]_6(\mu_6\text{-}N)(\mu_3\text{-}NH)_6(\mu_2\text{-}NH_2)_3$ (**2**) to $[(tritox)Zr]_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu_2\text{-}NH_2)_4$ (**3**) based upon CPMAS ^{15}N solid-state NMR, and consistent with the X-ray structural study. ^1H NMR (**2**-$^{15}N_9$, THF-d_8, assignments are tentative due to low solubility and presence of **3**) δ 2.07 (br d, μ_2-N*H*H′, 2 H, J_{NH} = 62 Hz), 5.03 (d, μ_3-NH, 2 H, J_{NH} = 63 Hz), 5.37 (dd, μ_3-NH, 2 H, J_{NH} = ~1, 63 Hz), 8.03 (dd, μ_3-NH, 2 H, J_{NH} = 3, 56 Hz). The tritox protons (tentative, δ 1.32, 1.33, 1.34) are obscured by the presence of **3** (br s, δ 1.31). Although other resonances consistent with amides were observed in the tritox region, they could not be confirmed via labeling. 2-D experiments designed to help locate other amides proved ambiguous due to the insolubility of **2**. $^{13}C\{^1H\}$ NMR (THF-d_8) δ 46.6, 46.7, 46.9 ($C\{C(CH_3)_3\}_3$, ~1:1:1), the methyl carbons (δ 33.8–34.4) overlapped with those of **3** and the $C\{C(CH_3)_3\}_3$ resonances were poorly resolved (tentative, δ 94.8, 95.9, 96.3); ^{15}N NMR (THF-d_8, integrations are estimated) δ –40.6 (s, μ_6-N, ~1 N), –100.9 (d, μ_3-NH, $^1J_{NH}$ = 57 Hz, ~2 N), –145.4 (d, μ_3-NH, $^1J_{NH}$ = 62 Hz, ~2 N), –149.6 (d, μ_3-NH, $^1J_{NH}$ = 63 Hz, ~2 N), –296.0 (t, μ_2-NH_2, $^1J_{NH}$ = 61 Hz, ~2 N), –294.3 (t, μ_2-NH_2, $^1J_{NH}$ = 60 Hz, ~1 N). IR (**4**-$^{15}N_{10}$, Nujol, cm^{-1}) 1498 (w), 1480 (m), 1410 (w), 1394 (s)†, 1372 (m); (halocarbon oil) 1401 (w), 1389 (s)†, 1200 (w)†, 1181 (w)†, 1075 (s), 1020 (s), 920 (m)†, 881 (m)†, 745 (m), 711 (w), 670 (m), 650 (m); sporadic absorptions (halocarbon oil) were also seen at 3340 (vw) (Nujol), 3358 (vw), and 3678 (vw). Absorptions marked with a dagger (†) are believed to derive from the tritox ligand. Analysis calculated for a 0.6:1 mixture of **2** and **3**: C, 49.15; H, 9.38; N, 7.71. Found: C, 49.27; H, 8.56; N, 6.90. The crystals did not analyze reproducibly; the numbers given are an average.

4. X-ray Structure Determination Summary for $[(tritox)Zr]_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu_2\text{-}NH_2)_4$ (3). A clear, colorless single-crystalline prism of $[(tritox)Zr]_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu_2\text{-}NH_2)_4$ (**3**), approximately 0.4 × 0.4 × 0.5 mm, was grown in THF via slow vapor transport of hexane into solution and sealed in a thin-walled Lindemann capillary. Precise lattice constants for an orthorhombic cell, determined from a least-squares fit of 10 diffractometer-measured 2θ values, were a = 15.554 (3) Å, b = 25.804 (5) Å, c = 40.406 (8) Å, and Z = 8. The cell volume was 16217 (5) $Å^3$ with a calculated density of 1.303 g/cm^3 and μ = 0.656 mm^{-1}. The space group was determined to be *Pbca*. Diffraction maxima (h, k, l) with $0.0 \leq 2\theta \leq 50$ were measured using variable-speed ω-scans and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). After correction for Lorentz, polarization, and background, 3729 (49.2%) of the merged unique data (7566) were judged observed ($F \geq 3.0\sigma(F)$). The zirconium, nitrogen, and oxygen positions were calculated by direct methods using the SHELXTL PLUS program. Subsequent Fourier difference maps revealed the tritox groups attached to the four zirconiums on the base of the square pyramid. Hydrogens were fixed at 0.96 Å to all *tert*-butyl groups and at 0.90 Å to the imide and amide nitrogens. Because of significant disorder present in the tritox groups, the carbon atoms were refined isotropically, all tritox methyl distances were constrained to 1.54 ± 0.03 Å, and the quaternary carbon distances were constrained to 1.63 ± 0.03 Å, an average taken from previously determined tritox-containing structures.[19,20] Full-matrix least-squares refinement of anisotropic zirconium, nitrogen, and oxygen atoms, isotropic carbon atoms, and fixed hydrogen atoms converged to crystallographic residuals of R = 0.113, R_w = 0.112, and GOF = 1.77. An obvious problem with the data collection was the relatively low number of observed reflections. This problem was particularly acute for 2θ values between 34° and 40° (1.1–1.2 Å resolution) where only 28% of the reflections were observed. An attempt to re-collect the data using copper radiation failed to result in a higher percentage of observed reflections.

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Supplementary Material Available: X-ray structural information pertaining to $[(tritox)Zr]_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu_2\text{-}NH_2)_4$ (**3**) and composite A including summaries of crystal data encompassing data collection and solution/refinement, atomic coordinates, isotropic and anisotropic temperature factors, hydrogen atom coordinates, bond lengths, and bond angles (25 pages); observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.