

Zirconium complexes of a tacn-derived amido ligand and ring-opening to form a new diamido-amino pincer

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The tribenzyl complex $(\text{Pr}_2\text{tacn})\text{Zr}(\text{CH}_2\text{Ph})_3$ eliminates toluene upon heating with concomitant ring-opening of the anionic ancillary macrocycle to yield $[\text{CH}_2=\text{CHNCH}_2\text{CH}_2\text{N}(\text{Pr}^i)\text{CH}_2\text{CH}_2\text{NPr}^i]\text{Zr}(\text{CH}_2\text{Ph})_2$; the latter features a new class of dianionic pincer ligand.

Non-metallocene complexes of Group IV metals have recently been the subject of renewed interest due to the realization that new ligand environments might result in novel patterns of reactivity.^{1–3} For example, Group IV metal complexes bearing bi-^{4–8} or tridentate^{9–15} diamide ligands have attracted attention as potential alternatives to the classical homogeneous Ziegler–Natta polymerization catalysts that are mostly based on bis- or monocyclopentadienyl ligands. In contrast, tridentate mono-amide ligands have received scant attention, an exception being the tridentate, acyclic monoanion, $[(\text{Me}_2\text{NCH}_2\text{SiMe}_2)_2\text{N}]^-$, for which Ti, Zr and Hf derivatives have been described.¹⁶

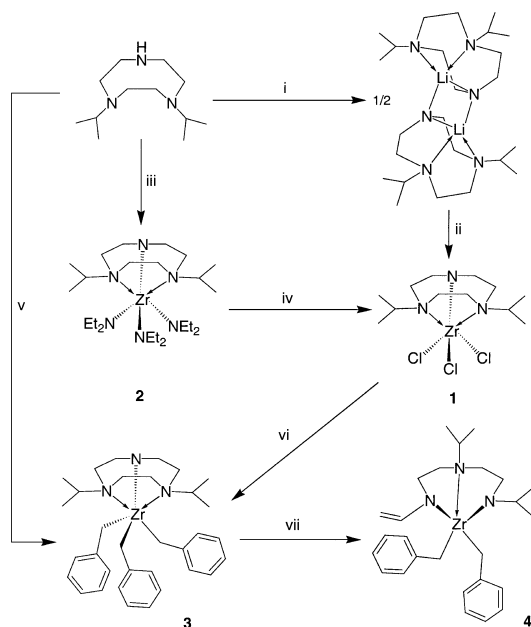
We¹⁷ and others¹⁸ recently described the use of the lithium salt of diisopropyltriazacyclononane as a synthon in the development of new constrained-geometry ligand systems.^{17,18} By utilizing a ligand system in which the nitrogen donors are part of a macrocycle, we reasoned that metal complexes would necessarily bind the azamacrocycle facially, in closer analogy to cyclopentadienyl complexes. Here we report the use of this fragment as an anionic, tridentate diamino-amido ancillary ligand for the stabilization of zirconium complexes and the conversion of this ligand into a dianionic acyclic variant.

As shown in Scheme 1, $\{(\text{Pr}_2\text{tacn})\text{Li}\}_2$ reacts with $\text{ZrCl}_4(\text{THF})_4$ in THF to yield the mono-ligand complex,

$(\text{Pr}_2\text{tacn})\text{ZrCl}_3$ **1** as an analytically-pure pale yellow solid in low yield. Alternately, **1** can be synthesized *via* a two-step process in nearly 90% overall yield: reaction of $(\text{Pr}_2\text{tacn})\text{H}$ with $\text{Zr}(\text{NEt}_2)_4$ quantitatively generates $(\text{Pr}_2\text{tacn})\text{Zr}(\text{NEt}_2)_3$ **2** as a yellow oil which is sufficiently clean to be used without further purification. The latter reacts smoothly with excess Me_3SiCl in hot toluene to give **1**, which precipitates in pure form. Compound **1** is soluble in methylene chloride and only sparingly soluble in solvents such as THF, diethyl ether or toluene.

$(\text{Pr}_2\text{tacn})\text{H}$ reacts with $\text{Zr}(\text{CH}_2\text{Ph})_4$ in diethyl ether to form the tribenzyl species $(\text{Pr}_2\text{tacn})\text{Zr}(\text{CH}_2\text{Ph})_3$ **3** in good yield. Compound **3** may also be synthesized from the trichloride **1** and 3 equiv. of benzyl Grignard, although the former reaction is substantially cleaner. The ^1H NMR spectrum of **3** shows a doublet for the diastereotopic isopropyl resonances and the methylene protons of the triazacyclononane ring appear as broad singlets. Also, the two isopropyl methyl groups give rise to a single peak in the $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum (18.9 ppm) in contrast to the two distinct singlets observed for **1** (19.5 and 18.1 ppm). The six benzylic protons are equivalent on the NMR time scale, resulting in a singlet in the ^1H NMR spectrum (2.71 ppm) and a broad resonance in the $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum (76.1 ppm).

Compound **3** is monomeric in the solid-state (see Fig. 1)[†] with the triazacyclononane ring attached facially to the metal through all three nitrogen atoms. The zirconium center is best described as distorted octahedral, with the $\text{N–Zr–C}_{\text{trans}}$ angles ranging from $152.06(8)$ to $159.46(7)^\circ$; additionally, the three C–Zr–C angles vary from $91.10(8)$ to $96.33(9)^\circ$. Two of the benzyl



Scheme 1 i, BuLi, Et₂O, -78°C ; ii, $\text{ZrCl}_4(\text{THF})_2$, THF, rt; iii, $\text{Zr}(\text{NEt}_2)_4$, Et₂O, -78°C ; iv, xs Me_3SiCl , toluene, 90°C ; v, $\text{Zr}(\text{CH}_2\text{Ph})_4$, Et₂O, -78°C ; vi, 3 BzMgCl , Et₂O, -78°C ; vii, 90°C , benzene, 24 h.

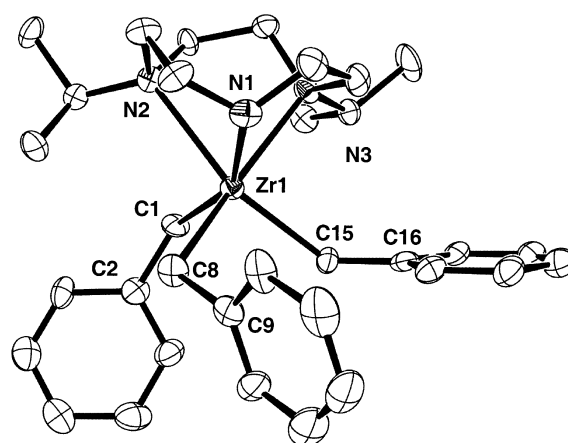


Fig. 1 ORTEP view of $(\text{Pr}_2\text{tacn})\text{Zr}(\text{CH}_2\text{Ph})_3$ **3** drawn with 50% probability ellipsoids. Selected bond distances (Å) and angles ($^\circ$): Zr1–N1 2.073(2), Zr1–N2 2.604(2), Zr1–N3 2.479(2), Zr1–C1 2.347(2), Zr1–C8 2.326(2), Zr1–C15 2.303(2); N1–Zr1–N2 70.00(7), N1–Zr1–N3 73.04(7), N1–Zr1–C1 152.06(8), N1–Zr1–C8 88.12(8), N1–Zr1–C15 115.99(8), N2–Zr1–N3 73.01(6), N2–Zr1–C1 82.50(7), N2–Zr1–C8 108.67(8), N2–Zr1–C15 155.46(7), N3–Zr1–C1 104.15(8), N3–Zr1–C8 159.46(7), N3–Zr1–C15 85.79(7), C1–Zr1–C8 96.33(9), C1–Zr1–C15 91.10(8), C8–Zr1–C15 95.54(8), Zr1–C1–C2 116.3(2), Zr1–C8–C9 113.7(2), Zr1–C15–C16 133.5(2).

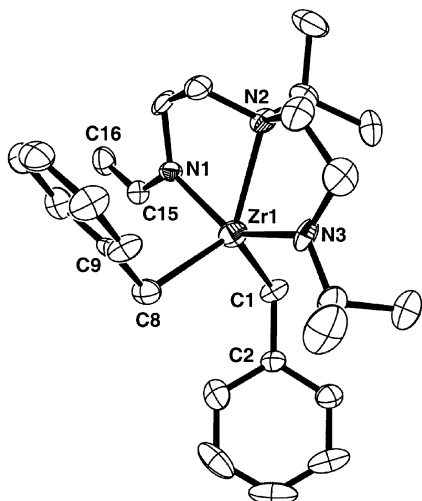


Fig. 2 ORTEP view of $[\text{CH}_2=\text{CHNCH}_2\text{CH}_2\text{N}(\text{Pr}^i)\text{CH}_2\text{CH}_2\text{N}-\text{Pr}^i]\text{Zr}(\text{CH}_2\text{Ph})_2$ **4** drawn with 50% probability ellipsoids. Selected bond distances (Å) and angles ($^\circ$): Zr1–N1 2.131(5), Zr1–N2 2.410(5), Zr1–N3 2.043(5), Zr1–C1 2.289(6), Zr1–C8 2.295(6), C15–C16 1.317(9); N1–Zr1–N2 71.3(2), N1–Zr1–N3 142.3(2), N1–Zr1–C1 100.5(2), N1–Zr1–C8 94.3(2), N2–Zr1–N3 71.5(4), N2–Zr1–C1 124.3(2), N2–Zr1–C8 125.1(2), N3–Zr1–C1 105.3(2), N3–Zr1–C8 101.9(2), C1–Zr1–C8 110.2(2), Zr1–C1–C8 114.7(2), Zr1–C8–C9 109.2(4).

ligands are positioned with their phenyl rings pointing downwards with respect to the tacn ring, while the third has its phenyl ring pointing upwards, being disposed almost parallel to the azamacrocyclic. Two of the benzyl groups possess normal Zr–C–C bond angles (113.7(2) and 116.3(2) $^\circ$) while the third displays an angle that is larger than expected (Zr1–C15–C16 = 133.5(2) $^\circ$). The disposition of the benzyl groups is similar to that found for $\text{Cp}^*\text{Ti}(\text{CH}_2\text{Ph})_3$, in which a single anomalous Ti–C–C angle is a consequence of a double agostic $\text{CH}_2\text{--Ti}$ interaction.¹⁹ Owing to the broadness of the peak arising from the benzylic methylene groups in the $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum, we were unable to extract the C–H coupling constant to determine if any additional interaction was present in our case; it is likely that this unusually large angle is a result of packing forces in the crystal.

Heating $(\text{Pr}^i_2\text{tacn})\text{Zr}(\text{CH}_2\text{Ph})_3$ **3** for 24 h at 80 $^\circ\text{C}$ results in elimination of one equiv. of toluene and complete conversion to a new metal complex. The ^1H NMR spectrum reveals a total lack of symmetry in solution as evidenced by the presence of four isopropyl methyl doublets and separate multiplets for each of the methylene protons of the ligand backbone. Particularly diagnostic of this new species are resonances consistent with a vinyl group; a doublet of doublets corresponding to one olefinic proton is present at 7.92 ppm ($^3J_{\text{H-H}'} = 8.4$, $^3J_{\text{H-H}''} = 14.8$ Hz) with the other two protons of the vinyl unit giving rise to two doublets farther upfield (4.12 ppm, $^3J_{\text{H-H}'} = 8.4$ Hz; 3.93 ppm, $^3J_{\text{H-H}''} = 14.8$ Hz). These conclusions are supported by $\{^1\text{H}\}^{13}\text{C}$ NMR spectroscopy which shows four separate isopropyl methyl peaks, two isopropyl methine resonances and distinct peaks for four methylene groups of the ancillary ligand. ^{13}C DEPT experiments allowed the vinyl resonances to be assigned (143.1 and 79.0 ppm); the presence of a vinyl group is visible in the IR spectrum which shows a strong absorption in the olefinic region (ca. 1600 cm^{-1}).

To further investigate the structure of the thermolysis product, we turned to X-ray diffraction (Fig. 2).[†] The ORTEP of **4** shows that the zirconium center is coordinated by two benzyl groups and a new tacn-derived pincer ligand in which the original anionic, macrocyclic, diamino-amido ligand has been transformed into a dianionic, acyclic, diamido-amino moiety. Additionally, one of the ethylene units of the triazacyclononane ring has been converted into a vinyl group (C15–C16). The zirconium center is best described as distorted trigonal bipyramidal, with N1 and N3 occupying the axial sites (N1–Zr1–N3 = 142.3(2) $^\circ$). Both amido nitrogens in **4** display trigonal planar

geometries, with the sum of the three angles subtended by nitrogen approaching 360 $^\circ$. The metal center displays two short zirconium–nitrogen bonds (Zr1–N1 = 2.131(5), Zr1–N3 = 2.043(5) Å) and one longer bond (Zr1–N2 = 2.410(5) Å) consistent with a diamido-amino ligand. The benzyl groups are unremarkable (Zr–C–C_{benzyl} = 109.2(4), 114.7(4) $^\circ$), although they are inequivalent by ^1H and ^{13}C NMR spectroscopy. This implies that the structure observed in the solid state is maintained in solution, and the benzyl groups are not averaged by some fluxional process as is observed for tribenzyl **3**.

In order to test the generality of this reaction, $(\text{Pr}^i_2\text{tacn})\text{ZrCl}_3$ **1** was reacted with three equiv. of RLi (R = Me, CH_2SiMe_3 , Ph). The NMR spectra of these products also indicate the formation of $[\text{CH}_2=\text{CHNCH}_2\text{CH}_2\text{N}(\text{Pr}^i)\text{CH}_2\text{CH}_2\text{NPr}^i]\text{ZrR}_2$ with the elimination of the corresponding alkane. A related ligand decomposition has been observed for the tantalum species $[\text{N}_3\text{N}]\text{TaMe}_2$ ($[\text{N}_3\text{N}] = [\text{N}(\text{CH}_2\text{CH}_2\text{NSiR}_3)_3]^{3-}$, R = Me²⁰, Et²¹). Thermolysis of the deuterated complex $(\text{Pr}^i_2\text{tacn})\text{Zr}(\text{CD}_2\text{C}_6\text{D}_5)_3$ affords $\text{C}_7\text{D}_7\text{H}$, ruling out α -hydrogen abstraction and a benzylidene intermediate. A more detailed study of the kinetics and mechanism of this ring-opening reaction will be reported shortly, along with other examples of the synthetic utility of $(\text{Pr}^i_2\text{tacn})^-$.

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Notes and references

[†] Crystal data: for **3**: $\text{C}_{33}\text{H}_{47}\text{N}_3\text{Zr}$, $M = 576.97$, trigonal, $a = 39.6517(3)$, $b = 39.6517(3)$, $c = 9.7469(1)$ Å, $V = 13\,271.5(2)$ Å³, $T = 173$ K, space group $R\bar{3}(h)$ (no. 148), $Z = 18$, $\mu(\text{Mo-K}\alpha) = 0.4$ mm^{−1}, 20082 reflections measured, 5097 unique ($R_{\text{int}} = 0.035$), $D_{\text{calc}} = 1.30$ g cm^{−3}, $R = 0.024$, $R_w = 0.028$. For **4**: $\text{C}_{26}\text{H}_{39}\text{N}_3\text{Zr}$, $M = 484.83$, monoclinic, $a = 8.881(5)$, $b = 25.936(2)$, $c = 11.7707(7)$ Å, $\beta = 112.017(1)^\circ$, $V = 2513.5(6)$ Å³, $T = 164$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.45$ mm^{−1}, 11 204 reflections measured, 4314 unique ($R_{\text{int}} = 0.082$), $D_{\text{calc}} = 1.28$ g cm^{−3}, $R = 0.043$, $R_w = 0.054$. CCDC 182/1783. See <http://www.rsc.org/suppdata/cc/b0/b005675h/> for crystallographic files in .cif format.

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