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Titanium and Zirconium Amido Complexes Ligated by 2,2′-Di(3-methylindolyl)methanes: Synthesis, Characterization, and Ethylene Polymerization Activity

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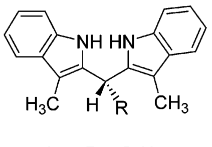
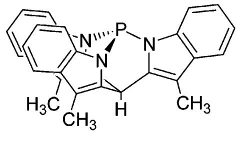
2,2′-Di(3-methylindolyl)methanes (L_2H_2) are introduced as dianionic, bidentate ligands of reduced π-donating ability. Four complexes of the type $L_2Ti(NEt_2)_2$ and $L_2Zr(NEt_2)_2(THF)$ have been synthesized and characterized by elemental analysis, NMR (^1H, ^{13}C) spectroscopy, and X-ray crystallography. Structural data confirm the reduced π-donating ability of the η^1-indolyl moiety compared to that of diethylamido. Preliminary catalytic activities of these group 4 complexes for the polymerization of ethylene are reported.

Numerous 2,2′-diindolylmethanes are reported in the literature that could serve as bidentate or, for those with an additional ligating substituent, tridentate ligands for transition and main group elements.[1] Deprotonated 2,2′-diindolylmethanes can be regarded as dianionic analogues of scorpionate bis(pyrazolyl)borate ligands,[2] although with greater steric requirement. In addition, 2,2′-diindolylmethanes are appealing ligand candidates since pyrrolyl,[3−5] indolyl,[1,6−8] and carbazolyl[9] groups are now recognized to impart significantly different electronic and steric properties to complexes of main group and transition metals than those offered by traditional amido ligands. Specific advantages of indolyl ligands include strong electron-withdrawing ability when bound in an η^1-N mode, reduced tendency for η^5 coordination and M−N−M bridging, and reduced N→M π-donation. These properties are attributable to the high electronegativity of nitrogen, significantly enhanced by extensive delocalization of the nitrogen lone pair into the aromatic π system and onto the indolyl carbons. Delocalization reduces the availability of the nitrogen lone pair for π-donation to the metal and also limits M−N−M bridging capability.

Surprisingly, 2,2′-diindolylmethanes and related 2,2′,2″-triindolylmethanes are unexplored as ligands for main group and transition elements, aside from our recent work on these readily synthesized compounds.[1] We recently demonstrated bidentate coordination of **1a**−**c** to aluminum, boron, and silicon,[1] and showed that tri(3-methylindol-2-yl)methane is an effective framework for the construction of the very bulky and π-acidic phosphine **2**.[6,7]



1a R = C_6H_5
1b R = 4-C_6H_4Br
1c R = 2-$C_6H_4(OCH_3)$



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Here we introduce deprotonated 2,2′-di(3-methylindolyl)arylmethanes **1a** and **1b** as dianionic, bidentate ligands of reduced π-donating ability for applications to the coordination chemistry of transition metals. Representative diethylamido complexes of titanium and zirconium are reported, along with their catalytic activities for the polymerization of ethylene.

Reactions of $Ti(NEt_2)_4$[10] with **1a**[11,12] and **1b**[12] in refluxing toluene, followed by concentration of the reaction solutions and cooling at −20 °C overnight, yielded brick red crystals of **3a** and **3b**, respectively (eq 1). The ^1H and ^{13}C NMR

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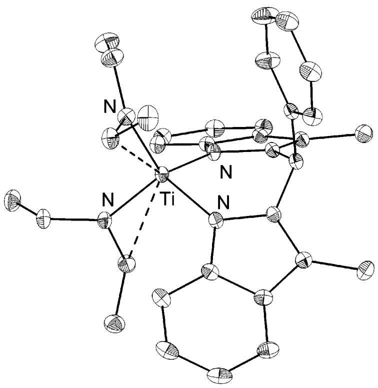


Figure 1. ORTEP drawing of **3a**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

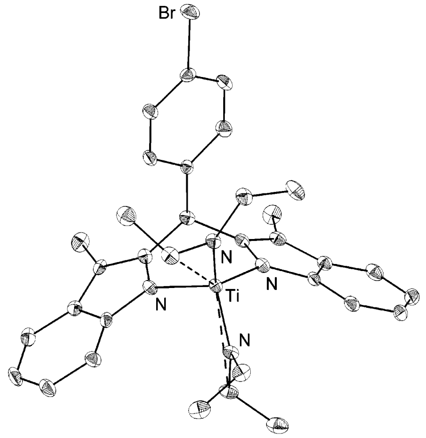
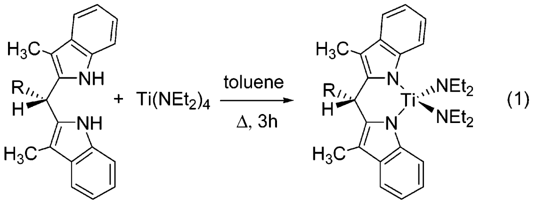


Figure 2. ORTEP drawing of **3b**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

spectra of **3a** and **3b** exhibit all expected ligand resonances and indicate that both indolyl moieties of the 2,2′-di(3-methylindolyl)methane are equivalent. Indolyl NH resonances are absent in the ^{1}H NMR spectra. Two sets of methylene and methyl resonances are observed in the ^{1}H and ^{13}C NMR spectra for each complex due to the chemically inequivalent diethylamido groups.



(1)

1a R = C_6H_5
1b R = 4-C_6H_4Br

3a R = C_6H_5
3b R = 4-C_6H_4Br

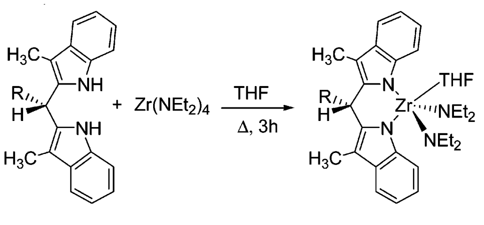
The molecular structures of **3a** and **3b** were further confirmed by X-ray crystallography (Figures 1, 2). Each structure consists of an approximately tetrahedral titanium ligated by two inequivalent diethylamido groups and a chelating, bidentate 2,2′-di(3-methylindolyl)methane. Each deprotonated indolyl ring of the latter is η^1-coordinated to titanium. The orientation of the 2,2′-di(3-methylindolyl)methane aryl group is reminiscent of the coordination mode of scorpionate bis(pyrazolyl)borates,[2] in that the aryl group is poised for coordination to the metal.

Table 1. Selected Distances (Å) and Angles (deg) for **3a**,**b** and **4a**,**b**

	M−N$_{indolyl}$	M−N$_{amido}$	N$_{indolyl}$−M−N$_{indolyl}$
3a	1.977(1), 1.987(2)	1.865(1), 1.867(2)	97.79(6)
3b	1.968(3), 1.994(3)	1.862(3), 1.863(3)	96.32(14)
4a	2.198(2), 2.218(2)	2.013(2), 2.019(2)	82.95(7)
4b	2.185(3), 2.203(3)	2.014(4), 2.030(3)	83.39(12)

The average Ti−N$_{indolyl}$ distances (Table 1) for **3a** (1.982 Å) and **3b** (1.981 Å) fall slightly short of the range of Ti−N distances (2.00−2.10 Å) observed for pyrrolyl[4,13,14] and carbazolyl[9] complexes of titanium. The average Ti−N$_{amido}$ distances for **3a** (1.866 Å) and **3b** (1.863 Å) are significantly shorter than the Ti−N$_{indolyl}$ distances as a result of greater N→M π-donation for the amido ligands than for the 2,2′-di(3-methylindolyl)methanes.

Reactions of $Zr(NEt_2)_4$[10] with **1a** and **1b** in refluxing THF, followed by removal of volatiles in vacuo and recrystallization of the remaining residue from hot toluene, yielded nearly colorless crystals of toluene solvates of **4a** and **4b**, respectively (eq 2). In contrast to the apparent four-coordinate titanium in **3a**−**b**, the zirconium atoms in **4a** and **4b** are each five-coordinate with a coordinated THF based on ^{1}H and ^{13}C NMR chemical shifts. The OCH_2 resonances of the THF are broadened considerably in the ^{13}C NMR spectrum, suggesting the occurrence of a dynamic process on the NMR time scale. The ^{1}H NMR spectrum exhibits a sharp quartet and triplet for one set of the chemically equivalent diethylamido groups. The second diethylamido group exhibits a broad resonance for the methylene protons and a broadened triplet for the methyl protons, again suggesting a dynamic process in solution. The methylene resonances of both diethylamido groups of **4a** and **4b** are broad in the ^{13}C NMR spectrum, whereas those for **3a** and **3b** are relatively sharp.



(2)

1a R = C_6H_5
1b R = 4-C_6H_4Br

4a R = C_6H_5
4b R = 4-C_6H_4Br

The molecular structures of **4a** and **4b** were confirmed by X-ray crystallography (Figures 3, 4). Each structure consists of a five-coordinate zirconium ligated by two inequivalent diethylamido groups, a chelating bidentate 2,2′-di(3-methylindolyl)methane, and a molecule of THF. The 2,2′-di(3-methylindolyl)methanes are folded to a greater extent in **4a** and **4b** than in **3a** and **3b**, resulting in greatly reduced N$_{indolyl}$−Zr−N$_{indolyl}$ angles of 82.95(7)° and 83.39(12)°, respectively (Table 1). The average Zr−N$_{indolyl}$ distances for **4a** (2.208 Å) and **4b** (2.194 Å) are in the range observed for

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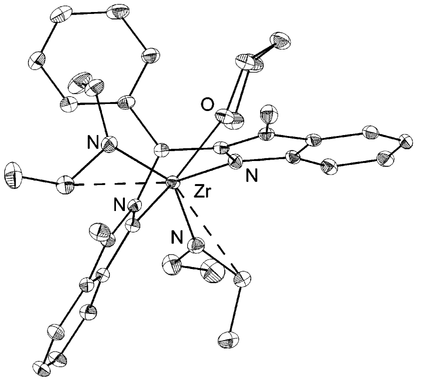

Figure 3. ORTEP drawing of **4a**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

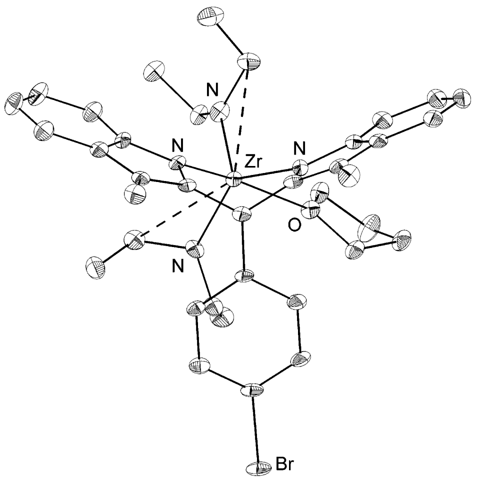

Figure 4. ORTEP drawing of **4b**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

representative pyrrolyl[4b,13−16] and carbazolyl[9] complexes of zirconium (2.07−2.33 Å). The greater Zr−$N_{indolyl}$ distances compared to the average Zr−N_{amido} distances (2.019 Å) substantiate the reduced π-donating ability of η^1-indolyl ligands.

Another feature of the molecular structures of **3a**,**b** and **4a**,**b** is the close proximity of the metal to one methylene carbon per diethylamido group. In the structure of **3a**, for example, two short Ti−C distances of 2.709(2) and 2.771(3) Å are observed, whereas the other two Ti−C distances are substantially longer at 3.107(4) and 3.044(3) Å. The short Ti−C distances are accompanied by one short Ti−H distance per methylene (2.56(2), 2.58(3) Å), and small Ti−N−C angles (108.0(1)°, 111.6(1)° vs 132.3(1)°, 138.2(1)°). Ti−C and Ti−H distances observed for **3b** are comparable with those observed for **3a**. Similarly, the zirconium complexes **4a** and **4b** each show two short Zr−C distances (2.838(3)−2.958(3) Å), two short Zr−H distances (2.56(3)−2.83(3) Å), and two small Zr−N−C angles (108.1(2)−115.5(2)°). Comparison of these data to those for diethylamido complexes of titanium and zirconium listed in the Cambridge Structural Database strongly supports the presence of two agostic interactions in each of the structures **3a**,**b** and **4a**,**b**. Huang et al. previously assigned a Zr−C distance of 2.808(3) Å and a Zr−H distance of 2.526(3) Å to an agostic interaction.[17] Tanski and Parkin similarly assigned comparable distances in a dimethylamido complex of zirconium to an agostic interaction.[16] NMR spectra of **3a**,**b** and **4a**,**b** do not support retention of static agostic interactions in solution. Although broadened methylene resonances were observed in the ^{1}H and ^{13}C NMR spectra of **4a** and **4b**, $^1J_{CH}$ values for the amido methylenes are normal[18] and in the range of 122−133 Hz. As is often the case,[18] IR data were inconclusive as to the presence of agostic interactions in **3a**,**b** and **4a**,**b**.

Considering the recent interest in non-metallocene catalysts for the polymerization of alkenes, we tested **3a**,**b** and **4a**,**b** for catalytic activity for the polymerization of ethylene. Upon activation with methylaluminoxane, **3a** and **3b** polymerized ethylene at 25 °C in toluene with activities of 1.1 and 8.4 kg of polymer/mol of Ti/h, respectively. Activities were slightly greater for **4a** (13.0 kg of polymer/mol of Zr/h) and **4b** (36.1 kg of polymer/mol of Zr/h). These activities are approximately 2 orders of magnitude less than those obtained for Cp_2TiCl_2 (2100 kg of polymer/mol of Ti/h) and Cp_2ZrCl_2 (3900 kg of polymer/mol of Zr/h) under the same conditions.

In conclusion, 2,2′-di(3-methylindolyl)methanes have been demonstrated to serve as dianionic, bidentate ligands of reduced π-donating ability for support of transition metal complexes. The coordination chemistry of 2,2′-diindolylmethanes bearing additional ligating substituents will be reported in the near future.

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Supporting Information Available: Experimental details of the syntheses, characterization, X-ray analyses (CIF, fully labeled ORTEPs), and polymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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