Titanium η^1-Pyrrolyl Complexes: Electronic and Structural Characteristics Imposed by the *N,N*-Di(pyrrolyl-α-methyl)-*N*-methylamine (dpma) Ligand

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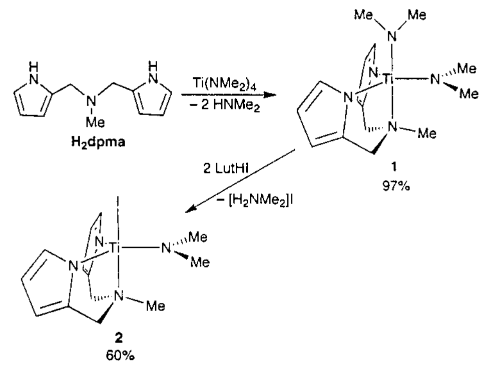
Many common organic transformations require catalytic or stoichiometric amounts of an early transition metal complex.[1] In many of these reactions, the Lewis acidity of the metal is essential for catalytic viability.[2] Despite this fact, some of the most common monoanionic monodentate ligands for early metals that provide the possibility of rational ligand alteration are alkoxide and amide, both of which are π-basic.[3] Other common monoanionic ligands, such as Cp, can be sterically encumbering and donate strongly into several orbitals, lowering acidity. Common acids such as $TiCl_4$, $SnCl_4$, and $AlCl_3$, along with the more exotic $Sc(OTf)_3$[4] and $Hf(OTf)_4$,[5] have shown broad appeal. However, halide ligands offer little in the way of tunability, and asymmetric transformations rely on the coordination of chiral auxiliaries, which can lower the activity of the metal.

While electron-withdrawing substituents are sometimes used to lower the π-basicity of alkoxide and amide substituents, we are developing a new set of ligands that utilize a different and versatile approach to monoanionic σ-only donation. To this end, η^1-pyrrolyl-based ligands appeared to be promising alternatives. Pyrrole has an aromatic stabilization energy of ~23 kcal/mol,[6] and the participation of the nitrogen lone pair is required to form an aromatic 6π-electron system. η^1-Pyrrolyl ligands, therefore, contain two competing systems involving the nitrogen lone pair: delocalization of the nitrogen lone pair into the aromatic π-system of the pyrrole ring and nitrogen-to-metal π-donation. This competition greatly decreases the amount of donation from the pyrrolyl nitrogen relative to more common dialkylamides.

Pyrrole-based ligands can have several complicating features however. Deprotonated pyrrole is a competent η^5-ligand.[7] Prevalence of η^5- over η^1-coordination in our complexes would result in an undesired increase in electron density at the metal. In addition, early metal complexes with several η^1-pyrrolyl ligands are relatively rare,[8] especially complexes that are coordinatively unsaturated. The scarcity of members in this class may be associated with the very characteristic we wish to encourage; namely, high Lewis acidity of early metal η^1-pyrrolyl complexes may make them prone to unwanted decomposition pathways. To increase the stability of the compounds, we have turned to chelating pyrrolyl-based ligands. Thus far, chelation has thwarted η^5-coordination of the pyrrolyl substituents and has allowed isolation of stable complexes.

Scheme 1. Syntheses of $Ti(NMe_2)_2(dpma)$ (**1**) and $Ti(I)(NMe_2)(dpma)$ (**2**)[a]



[a] The symbol LutHI represents anhydrous 2,6-lutidinium iodide.

To prepare the first generation of these ligands,[9] a Mannich reaction involving 2 equiv of pyrrole, 2 equiv of formaldehyde, and 1 equiv of methylamine hydrochloride at ~45 °C was used to yield the ligand in a single step. After workup, *N*,*N*-*d*i(*p*yrrolyl-α-*m*ethyl)-*N*-*m*ethyl*a*mine (H_2dpma) is isolated in ~23% yield. In our largest reactions thus far, ~40 g of H_2dpma may be synthesized in under 24 h.

Large reaction scales and inexpensive starting materials make H_2dpma one of the more readily prepared tridentate ligands available.[10] Furthermore, numerous derivatives of the ligand framework can be envisioned.

Readily accessible titanium complexes (see Scheme 1) with intriguing structural features have been realized. Addition of 1 equiv of ethereal H_2dpma to ethereal $Ti(NMe_2)_4$ yields pseudo-trigonal-bipyramidal (tbp) $Ti(NMe_2)_2(dpma)$ (**1**) with loss of 2

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(6) The aromatic stabilization energy (ASE) for benzene has been estimated to be ~35 kcal/mol. For pyrrole, there is greater contention over the ASE. References in the literature often place the value between 19 and 30 kcal/mol. However, most seem to place the energy near ~24 kcal/mol. See p 45 of ref 1 and references therein.
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(8) We exclude complexes of porphyrin, phthalocyanine, etc. from the term "pyrrolyl" because of their drastically different electronic structure caused by extended π-systems present. We also exclude the fascinating work of Floriani and co-workers on the porphyrinogen ligand because of its cyclic nature and redox-induced modifications. Even so, interesting parallels to our ligand system may be drawn. For a recent communication: (a) Bonomo, L.; Solari, E.; Martin, G.; Scopelliti, R.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1999**, 2319. Four complexes incorporating group-4 metals with an η^1-pyrrolyl ligand are in the Cambridge Structural Database at the date of submission. (b) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 21. (c) Atwood, J. L.; Rogers, R. D., Bynum, R. V. *Acta Crystallogr., Sect. C* **1984**, *40*, 1812. (d) Bynum, R. V.; Zhang, H.-M.; Hunter, W. E.; Atwood, J. L. *Can. J. Chem.* **1986**, *64*, 1304. For one of the few crystal structures of an η^1-pyrrolyl ligand on titanium: (e) Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368−2374.
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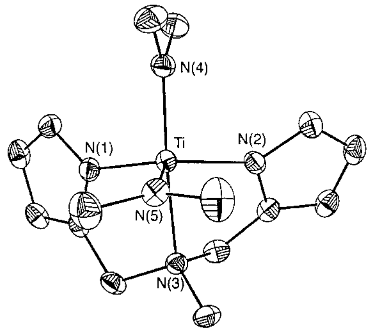

Figure 1. ORTEP structural drawing of $Ti(NMe_2)_2$(dpma) (**1**) with thermal ellipsoids at the 25% probability level. Selected bond lengths (Å) and angles (deg): Ti−N(5) 1.859(3), Ti−N(4) 1.888(3), Ti−N(1) 2.015(3), Ti−N(2) 2.017(3), Ti−N(3) 2.312(3), N(5)−Ti−N(4) 100.74(13), N(5)−Ti−N(1) 115.95(14), N(4)−Ti−N(1) 97.88(14), N(5)−Ti−N(2) 118.21(14), N(4)−Ti−N(2) 94.96(13), N(1)−Ti−N(2) 120.37(12), N(5)−Ti−N(3) 95.59(12), N(4)−Ti−N(3) 163.58(12), N(1)−Ti−N(3) 76.16(12), N(2)−Ti−N(3) 75.67(12).

equiv of $HNMe_2$. Yellow **1** was synthesized in 97% of the theoretical yield.[11]

An ORTEP structural representation derived from single-crystal X-ray diffraction[12] on **1** (Figure 1) displays several interesting features. The overall structure is remarkably close to tbp, considering the presence of the chelating ligand. Angles between equatorial nitrogens add to 354.53(14)°, and the nitrogen of the axial amine donor is restricted by chelation to be ∼76° from the N4−N1−N2 plane. The axial position occupied by dimethylamide is nearer to perpendicular with respect to the equatorial plane, having angles of 100.74(13)°, 97.88(14)°, and 94.96(13)° relative to those equatorial nitrogens. Perhaps most interesting is the range of Ti−N distances displayed by the complex. As expected, the donor amine exhibits the longest Ti−N bond in the complex: 2.312(3) Å. A surprisingly large difference between Ti−N(pyrrolyl) and Ti−N(dimethylamide) bond lengths is observed. The average pyrrolyl Ti−N bond distance, which is less likely to be attenuated by metal−ligand π-bonding, is found to be 0.143 Å longer than the average distance of the amide Ti−N bonds. An analysis of known $Ti-N(NMe_2)$ crystallographically determined bond lengths reveals that the $Ti-N(NMe_2)$ distances in **1** are relatively short,[13] averaging 1.874(3) Å. The axial $Ti-N(NMe_2)$ bond is 1.888(3) Å and is 0.03 Å longer than the equatorial $Ti-N(NMe_2)$ distance of 1.859(3) Å.

Surprisingly, the five-coordinate complex **1**, which has inequivalent NMe_2 substituents in the solid state, appears to retain this structure in solution. Proton NMR of **1** reveals two inequivalent dimethylamido resonances. The peak shifts are sensitive to solvent and temperature. For example, the separation between the two resonances due to the dimethylamide protons is 0.002 ppm in $CDCl_3$ and 0.242 ppm in C_6D_6. Variable temperature ^1H NMR studies in C_6D_6 up to 90 °C were consistent with a nonfluxional system. While the more shielded dimethylamide resonance shifted from 2.873 to 2.964 ppm on raising the temperature from 25 to 90 °C, the less shielded dimethylamide resonance was temperature-independent. In addition, neither resonance broadened on changing the temperature, which is also consistent with exchanging dimethylamides.

A simple crystal field analysis of the pseudo-C_{3v} complex reveals a metal center with two low-energy orbitals (d_{xz} and d_{yz}). The two dimethylamides in the structure are oriented to maximize their nitrogen lone pair interactions with the two low-energy metal-centered orbitals.

Because dimethylamide substituents are effectively occupying the two low-energy metal orbitals in **1** through π-donation, we investigated substituting amide with halide, which would effectively open an orbital on the metal for substrate binding. Complex **1** reacts with 2 equiv of 2,6-lutidinium iodide[14] to give red $Ti(NMe_2)(I)$(dpma) (**2**) in 60% of the theoretical yield. Addition of 4 equiv of acid to **1**, even after heating and extended time periods, yields only the monoiodide **2**. This lack of reactivity with an acid suggests that the lone pair on the remaining amide is strongly occupied in π-bonding to the metal center. Similar effects have been reported for a few other amido complexes. For example, some chromium(VI) nitrido amides[15] have barriers to rotation for amido substituents in excess of 23 kcal/mol, indicative of strong amido-to-metal π-donation; consequently, $Cr(N)(NPr^i{}_2)_3$ reacts with excess lutidinium iodide to form $Cr(N)(I)(NPr^i{}_2)_2$ and no $Cr(N)(I)_2(NPr^i{}_2)$ even under forcing conditions. In the case of both $Cr(N)(I)(NPr^i{}_2)_2$ and $Ti(NMe_2)(I)$(dpma) (**2**), the lower reactivity of the remaining amido substituent could be attributable to a relatively high kinetic barrier to protonation brought about by the low electron density present on the amido nitrogen.

The structure of **2** as determined by single-crystal X-ray diffraction[16] includes a $Ti-N(NMe_2)$ bond distance of 1.849(2) Å, somewhat shorter than found for equatorial $Ti-N(NMe_2)$ of 1.859(3) Å in **1**. In fact, the $Ti-N(NMe_2)$ bond distance in **2** is comparable to that found in $[Ti(NEt_2)Cl(\mu\text{-}Cl)_2]_x$ of 1.852(4) Å.[17]

In addition to surveying the chemistry of dpma complexes on metal centers across the periodic table, we are currently exploring steric, electronic, and stereochemical modifications of this versatile ligand. The titanium complexes expounded here are interesting starting materials for a number of studies on pyrrolyltitanium chemistry, which are currently underway. Titanium dpma complexes are currently being examined for Lewis acid catalysis of organic transformations and hydroamination of alkynes.[18]

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Supporting Information Available: Synthetic details and characterization data for new complexes, two X-ray crystallographic files in CIF format, and variable temperature ^1H NMR spectra for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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