

## Surprising Titanium Complexes Bearing $\eta^2$ -Pyrazolato Ligands: Synthesis, Structure, and Molecular Orbital Studies

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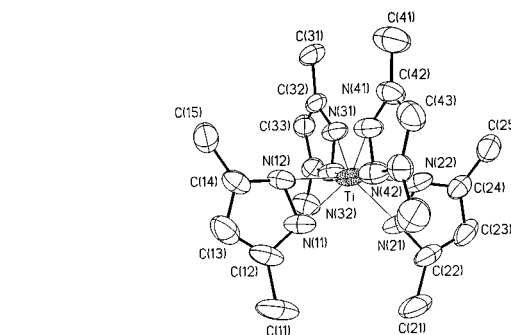
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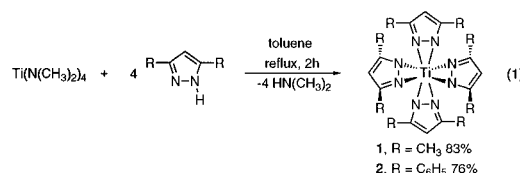
As part of a program relating to the preparation of molecular precursors to early transition metal nitride films,<sup>2</sup> we have been pursuing the synthesis of complexes that possess only nitrogen ligands in the coordination sphere. Pyrazolato (pz) ligands are particularly attractive nitrogen donors,<sup>3</sup> since the ligands themselves are easily prepared and the properties of resultant complexes should be readily modified by appropriate choice of substituents at the carbon atoms. However, application of such complexes as CVD precursors requires monomeric species to achieve the highest possible volatility. Monomeric metal complexes with  $\eta^2$ -pz ligands are known for lanthanide and actinide complexes,<sup>4,5</sup> but there is only one example of a d-block complex ( $[\text{Cp}_2\text{Zr}(\text{C}_3\text{H}_3\text{N}_2)(\text{THF})]^+\text{BPh}_4^-$ ) bearing an  $\eta^2$ -pz ligand.<sup>6</sup> All other structurally characterized d-block metal complexes have shown the ligand to be present either in the bridging mode or with only one nitrogen atom coordinated to the metal.<sup>7</sup> With these considerations in mind, we report the synthesis and characterization of several homoleptic pz complexes of titanium(IV). These species are the first homoleptic monomeric pz complexes of any metal and contain exclusively  $\eta^2$ -pz ligands. The results of molecular orbital calculations rationalize why the  $\eta^2$ -bonding mode is preferred and suggest that  $\eta^2$ -pz complexes should be common in early to middle transition metals.

Treatment of tetrakis(dimethylamido)titanium(IV) with 4 equiv of 3,5-dimethylpyrazole<sup>8</sup> or 3,5-diphenylpyrazole<sup>8</sup> in refluxing toluene afforded tetrakis(3,5-dimethylpyrazolato)-titanium(IV) (**1**; 83%) and tetrakis(3,5-diphenylpyrazolato)-



**Figure 1.** Molecular structure of **1**. Selected bond lengths (Å): Ti–N(11) 2.025(5), Ti–N(12) 2.046(6), Ti–N(21) 2.020(5), Ti–N(22) 2.086(6), Ti–N(31) 2.016(5), Ti–N(32) 2.111(6), Ti–N(41) 2.011(6), Ti–N(42) 2.061(6), N(11)–N(12) 1.371(5), N(21)–N(22) 1.357(6), N(31)–N(32) 1.368(6), N(41)–N(42) 1.360(6).

titanium(IV) (**2**; 76%) as yellow and light red solids, respectively (eq 1).<sup>9</sup> Compounds **1** and **2** were characterized by spectro-



scopic and analytical techniques, and by crystal structure determinations (vide infra). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **1** and **2** at ambient temperature showed one type of pz ligand. The mass spectrum of **1** showed a molecular ion. Complex **1** is monomeric in benzene, as determined by freezing point depression measurements.

The crystal structure of **1** was determined to understand the molecular geometry (Figure 1).<sup>10</sup> Analysis of the nitrogen atom coordinates using criteria presented by Muetterties<sup>11</sup> shows that **1** possesses a distorted dodecahedral geometry. The titanium–nitrogen bond lengths in **1** fall between 2.011 and 2.111 Å. Only one pz ligand shows a significant difference in the titanium–nitrogen bond lengths (Ti–N(31) = 2.016(5) Å, Ti–N(32) = 2.111(6) Å). The other titanium–nitrogen bond lengths are identical within experimental error. The nitrogen–nitrogen bond lengths range between 1.357 and 1.371 Å. The bond lengths in **1** are similar to values for titanium–nitrogen single bonds found in other titanium(IV) complexes (1.99–2.07 Å).<sup>12</sup> The only other known titanium complex with bonds to eight

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(9) Spectroscopic and analytical data for **1**: mp 147 °C; <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 22 °C) δ 5.86 (s, 4 H), 2.19 (s, 24 H); <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 22 °C, ppm) δ 145.33 (8 C-CH<sub>3</sub>), 112.83 (4 ring CH), 12.78 (8 CH<sub>3</sub>). Anal. Calcd for C<sub>20</sub>H<sub>28</sub>N<sub>8</sub>Ti: C, 56.07; H, 6.59; N, 26.16. Found: C, 55.62; H, 6.51; N, 25.76. Molecular weight measurement for **1** in freezing benzene (MW of monomer 428): 426 (0.090 m), 407 (0.246 m). Spectroscopic and analytical data for **2**: mp 252–253 °C; <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 22 °C) δ 7.78 (m, 16 H), 7.11 (s, 4 H), 7.05 (m, 24 H); <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 22 °C, ppm) δ 150.25 (8 ring C-Ph), 132.59 (8 Ph *ipso*-C), 128.83 (16 Ph *o*-CH), 128.01 (16 Ph *m*-CH), 126.42 (8 Ph *p*-CH), 108.89 (4 ring C-H). Anal. Calcd for C<sub>60</sub>H<sub>44</sub>N<sub>8</sub>Ti: C, 77.91; H, 4.79; N, 12.11. Found: C, 77.52; H, 4.69; N, 12.04.

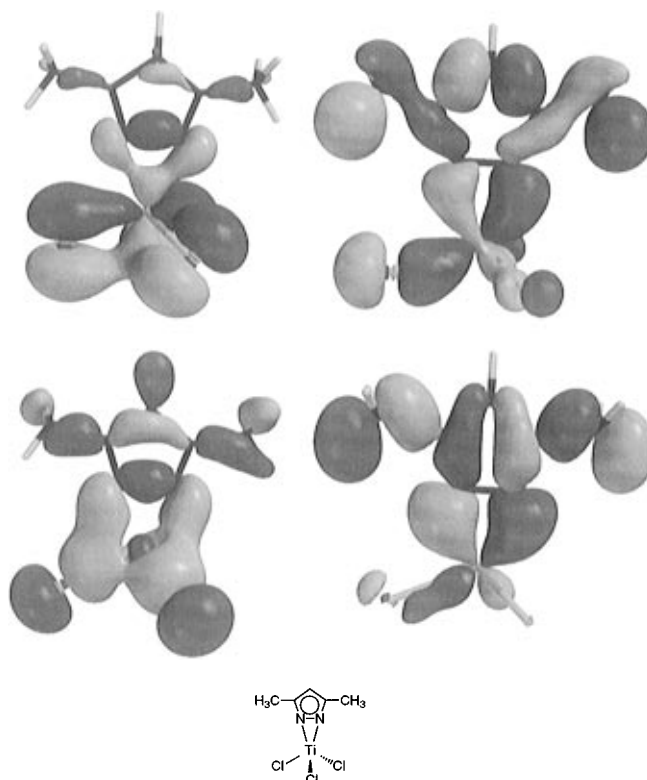
(10) Crystal data for **1**: crystals grown from hexane at –20 °C, C<sub>20</sub>H<sub>28</sub>N<sub>8</sub>Ti, triclinic, group P1, *a* = 8.339(4) Å, *b* = 9.029(4) Å, *c* = 16.208(7) Å, α = 94.39(4)°, β = 100.02(4)°, γ = 93.14(4)°, *V* = 1195.4(9) Å<sup>3</sup>, *Z* = 2, *T* = 256 K, *D*<sub>calcd</sub> = 1.190 g cm<sup>–3</sup>, *R*(*F*) = 5.84% for 2884 independent observed reflections (4.0° ≤ 2θ ≤ 44.0°). Crystal data for **2**: C<sub>60</sub>H<sub>44</sub>N<sub>8</sub>Ti, monoclinic, group C2/c, *a* = 23.713(4) Å, *b* = 16.179(3) Å, *c* = 15.752(2) Å, β = 129.48(8)°, *V* = 4664(1) Å<sup>3</sup>, *Z* = 4, *T* = 241 K, *D*<sub>calcd</sub> = 1.317 g cm<sup>–3</sup>, *R*(*F*) = 5.36% for 3051 independent observed reflections (2.23° ≤ 2θ ≤ 22.50°). All non-hydrogen atoms in **1** and **2** were refined with anisotropic displacement parameters. Full data for the X-ray crystal structure of **2** are enclosed in the Supporting Information and will be described in a future full paper.

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nitrogen atoms is {5,5',19,19'-bis[phthalocyanito(2<sup>-</sup>)]-titanium(IV)},<sup>13</sup> which adopts square antiprismatic geometry with titanium–nitrogen bond lengths ranging between 2.17 and 2.26 Å.

To help understand the bonding, ab initio calculations<sup>14</sup> were carried out at the B3LYP/6-311G\* level of theory on a simplified model<sup>15</sup> of the complex, trichloro(3,5-dimethylpyrazolato)titanium(IV). An attempt to optimize the monodentate complex proceeded smoothly to the bidentate complex, suggesting that a stable monodentate complex does not exist at this level of theory. The optimized geometry for the model bidentate complex is in very good agreement with the results of the X-ray structure determination (Ti–N(calcd) = 1.970, 2.012 Å versus Ti–N(X-ray) = 2.01–2.11 Å; N–N(calcd) = 1.369 Å versus N–N(X-ray) = 1.357–1.371 Å). The symmetric combination of the nitrogen lone pairs mixes with the ring  $\beta$ -bonds; one of these orbitals interacts strongly with the titanium 3d<sub>z<sup>2</sup></sub> (Figure 2a) while the other interacts with the symmetric combination of the Ti–Cl  $\beta$ -orbitals (Figure 2b).<sup>16</sup> Two orbitals with large contributions from the antisymmetric combination of the nitrogen lone pairs interact strongly with an empty 3d<sub>xz</sub> orbital on the titanium (Figure 2c,d). The ring  $\pi$ -orbitals interact only weakly with the metal (not shown).

It has been proposed that the lack of d-block metal complexes bearing  $\eta^2$ -pz ligands can be attributed to the directional nature of the nitrogen lone pairs,<sup>3</sup> which does not allow simultaneous coordination of both nitrogens by a single metal. In lanthanides and actinides, the metals are larger and the bonding is ionic, thus rendering  $\eta^2$ -coordination possible.<sup>3,4</sup> However, the present results with **1** and **2** demonstrate that  $\eta^2$ -pz coordination is easily achieved. Molecular orbital calculations with a large basis set reveal that the symmetric and antisymmetric combinations of the nitrogen lone pairs interact with appropriate symmetry-hybridized d-orbitals on titanium. The presence of the empty d-orbitals on the metal strongly favors  $\eta^2$ -bonding over  $\eta^1$ -bonding, since the  $\eta^1$ -mode was not a minimum at the level of theory used. It is therefore highly likely that other early to middle transition metal transition metal complexes will favor  $\eta^2$ -pz coordination. It is interesting to compare the properties of **1** and **2** with those of tetrakis(acetylacetonato)titanium(IV) (Ti(acac)<sub>4</sub>).<sup>17</sup> Despite extensive investigations of titanium–



**Figure 2.** Calculated occupied orbitals showing the interactions between the trichlorotitanium(IV) and 3,5-dimethylpyrazolato fragments: a, top left; b, middle left; c, top right; d, middle right.

acetylacetonate complexes, the synthesis of monomeric Ti(acac)<sub>4</sub> has never been reported in the open literature and it remains an ill-defined compound with a questionable existence. By contrast, **1** and **2** are molecular and **1** sublimates at about 100 °C (0.1 mmHg). Importantly, metal–acetylacetonate complexes are widely used as source compounds in film depositions.<sup>18</sup> Analogous pz complexes are attractive potential precursors, particularly in applications where oxygen incorporation is undesired. We are continuing to explore the synthesis of metal–pz complexes and are examining their use in the fabrication of thin films. These studies will be reported in due course.

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**Supporting Information Available:** Tables listing full experimental details for data collection and refinement, atomic coordinates, bond distances and angles, and thermal parameters for **1** and **2** and calculated atomic coordinates for trichloro( $\eta^2$ -pyrazolato)titanium(IV) and a figure showing the calculated molecule for trichloro( $\eta^2$ -pyrazolato)titanium(IV) (19 pages). See any current masthead page for ordering and Internet access instructions.

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