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Synthesis and Group 4 Complexes of Tris(pyrrolyl- α -methyl)amine

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The tetradentate, trianionic ligand tris(pyrrolyl- α -methyl)amine (H_3tpa) is available in 84% yield in a single step by a triple Mannich reaction involving 3 equiv of pyrrole, 3 equiv of formaldehyde, and ammonium chloride. The new ligand is readily placed on titanium by transamination on $Ti(NMe_2)_4$, which generates $Ti(NMe_2)(tpa)$ (**1**) in 73% yield. Treating **1** with 1 equiv of 1,3-dimethyl-2-iminoimidazolidine ($H-imd$) in toluene provided a rare example of a titanium 2-iminoimidazolidinide, which displays some interesting structural features. Of note is the $Ti-N(imd)$ distance of 1.768(2) Å, a typical $Ti-N$ double to triple bond distance. Reaction of $Zr(NMe_2)_4$ with H_3tpa gave a complex of variable composition, probably varying in the amount of labile dimethylamine retained. However, stable discreet compounds were available by addition of THF, pyridine, or 4,4'-di-*tert*-butyl-2,2'-bipyridine (Bu^tbp) to in situ generated $Zr(NMe_2)(NHMe_2)_x(tpa)$. Three chloro zirconium complexes were generated using three different strategies. Treating $Zr(tpa)(NMe_2)(Bu^tbp)$ (**5**) with $ClSiMe_3$ afforded $Zr(tpa)(Cl)(Bu^tbp)$ (**6**) in 92% yield. Reaction of Li_3tpa with $ZrCl_4 \cdot (THF)_2$ in THF gave a 72% yield of $ZrCl(tpa)(THF)_2$ (**7**). In addition, treatment of $ZrCl(NMe_2)_3$ with H_3tpa cleanly generated $ZrCl(NHMe_2)_2(tpa)$ (**8**) in 95% yield. An organometallic zirconium complex was generated on treatment of **6** with $LiC\equiv CPh$; alkynyl $Zr(C\equiv CPh)(tpa)(Bu^tbp)$ (**9**) was isolated in 62% yield. **1**, $Ti(imd)(tpa)$ (**2**), **6**, and **9** were characterized by X-ray diffraction.

Introduction

Multidentate ligands of approximate C_3 symmetry have been of particular recent interest in coordination chemistry and include a diverse class of ligand structures (Chart 1) including triazacyclononanes (**A**),¹ tris(pyrazolyl)borates (**B**),² tris(dialkylphosphinomethyl)borates (**C**),³ tris(alkylthiomethyl)borates (**D**),⁴ tris[2-(*N*-alkylamido)ethyl]amine (tren) derivatives (**E**),⁵ and several others.⁶ These C_3 ancillary ligands have been especially useful in the stabilization of metal–ligand multiple bonds in transition-metal systems

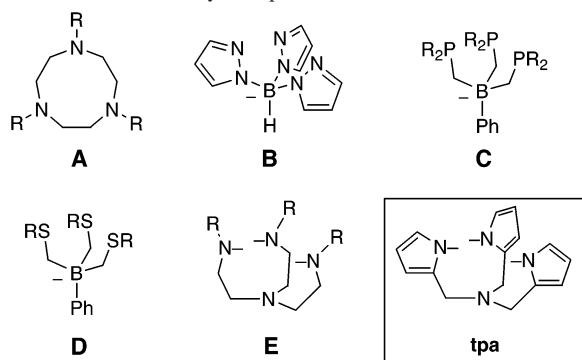
across the periodic table, including rare examples of multiple bonds where late-transition metals are in relatively low oxidation states.⁷

We have been examining the applications of pyrrolyl-based ligands in early transition metal mediated C–N bond formation,⁸ e.g., hydroamination⁹ and iminoamination¹⁰ of alkynes. For these reactions, we sought ancillary ligands that were readily prepared and that would afford Lewis acidic metal centers. Multidentate amido ligands such as the well-

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Chart 1. Examples of Some Common C_3 Ligands Employed in Transition-Metal Chemistry and tpa

explored tren derivatives are readily prepared, but alkylamido substituents can be quite π -basic, which quenches the Lewis acidity of the metal. While the π -donating ability of the amido substituents of tren ligands can be effectively tuned by changing R, a different strategy where the amido nitrogen is incorporated into a pyrrole ring also greatly reduces the π -basicity of the nitrogen.^{11,12} Here we report the one-step synthesis of a tetradentate, trianionic derivative of the tren framework (Chart 1) incorporating pyrrolyl substituents into the amido sites, tris(pyrrolyl- α -methyl)amine (H_3tpa).¹³

Experimental Section

General Considerations. All manipulations of air-sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Anhydrous ether (Columbus Chemical Industries Inc.), THF (JADE Scientific), dichloromethane (EM Science), and toluene (Spectrum Chemical Manufacturing Corp.) were sparged with dry N_2 and dried by being passed through solvent-drying columns purchased from Solv-Tek. Pentane (Spectrum Chemical Manufacturing) and benzene (EM Science) were distilled from purple sodium benzophenone ketyl. Acetonitrile (Spectrum Chemical Manufacturing) was distilled from calcium hydride. Deuterated solvents were dried over purple sodium benzophenone ketyl (C_6D_6) or phosphoric anhydride ($CDCl_3$) and distilled under nitrogen. 1H and ^{13}C spectra were recorded on Inova-300 and VXR-500 spectrometers. 1H and ^{13}C assignments were confirmed when necessary with the use of two-dimensional 1H - ^{13}C and ^{13}C - 1H correlation NMR experiments. All spectra were referenced internally to residual protiosolvent (1H) or solvent (^{13}C)

resonances. Chemical shifts are quoted in ppm and coupling constants in hertz. $Zr(NMe_2)_4$ and $Ti(NMe_2)_4$ were prepared from $LiNMe_2$ and MCl_4 using the literature procedure.¹⁴ 1,3-Dimethyl-2-iminoimidazolidine was synthesized using the literature preparation¹⁵ for the hydrochloride, which was basified by shaking with aqueous K_2CO_3 and vacuum distilled. Pyrrole was purchased from Fisher and distilled prior to use.

Preparation of $ClZr(NMe_2)_3$. This compound was obtained using the procedure of Johnson and Cummins, which is reproduced in brief.¹⁶ In an inert atmosphere drybox, a 250 mL Schlenk flask was loaded with 75 mL of toluene, $Zr(NMe_2)_4$ (1.10 g, 4.11 mmol), $ZrCl_4$ (0.32 g, 1.37 mmol), and a stir bar. The vessel was removed from the box and heated in a 95 °C oil bath for 5 min. The solution was cooled to room temperature and then returned to the drybox. The clear, yellow solution was concentrated in vacuo and then cooled to -30 °C, which generated colorless crystals in 72% yield. 1H NMR (300 MHz, 23 °C, C_6D_6): δ = 2.80 ppm. $^{13}C\{^1H\}$ NMR (75 MHz, 23 °C, C_6D_6): δ = 43.4 ppm.

Preparation of H_3tpa . A 250 mL flask was charged with a stir bar, pyrrole (18 g, 0.268 mol), formaldehyde (20 mL of a 37% solution in water, 0.268 mol), NH_4Cl (4.78 g, 0.0894 mol), 60 mL of ethanol, and 20 mL of water. The reaction was heated at 40 °C in an oil bath with stirring for 40 min. Volatiles were then removed by rotary evaporation with the aid of an aspirator. To the residue were added 40 mL of ether, 40 mL of THF, and 40 mL of NaOH (20%). The organic layer was separated. The aqueous layer was extracted three times with ether (20 mL). The combined organic layers were dried over $MgSO_4$. Volatiles were removed in vacuo. The product was washed with 10 mL of pentane/ether (v:v = 1:1), which afforded H_3tpa as a colorless solid. The product was recrystallized from THF/pentane (19.20 g, 84%). Mp = 137–8 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 8.12 (br s, 3 H, NH), 6.70 (m,

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3 H, 5-C₄H₃N), 6.15 (m, 3 H, 4-C₄H₃N), 6.06 (app s, 3 H, 3-C₄H₃N), 3.57 (s, 6 H, CH₂). ¹³C{¹H} NMR (CDCl₃): δ = 128.7 (2-C₄H₃N), 117.6 (5-C₄H₃N), 108.2 (4-C₄H₃N), 107.9 (3-C₄H₃N), 49.8 (CH₂). Anal. Found (Calcd) for C₁₅H₁₈N₄: C, 70.84 (70.74); H, 7.13 (7.14); N, 22.03 (22.24). MS (EI): m/z = 254.2 (M⁺).

Preparation of Li₃tpa. To a -95 °C suspension of H₃tpa (0.5086 g, 2 mmol) in 30 mL of toluene was added LiBuⁿ (3.75 mL, 1.6 M in hexanes, 6 mmol) slowly. The mixture was allowed to warm to room temperature and stir for 2 h. Then, 20 mL of pentane was added. The product was filtered, washed (3 × 20 mL of pentane), and dried in vacuo, which yielded a white solid (0.52 g, 95%) that was used without further purification.

Preparation of Ti(NMe₂)(tpa) (1). Under an inert atmosphere of purified nitrogen, a nearly frozen solution of Ti(NMe₂)₄ (0.2242 g, 1 mmol) in 3 mL of Et₂O was treated with a cooled solution of H₃tpa (0.2513 g, 1 mmol) in 3 mL of Et₂O and 3 mL of CH₂Cl₂. The reaction mixture was stirred at room temperature for 3 h. Volatiles were removed in vacuo to generate a black solid. The solid was dissolved in 3 mL of CH₂Cl₂ and layered with 3 mL of Et₂O. The layered solution was stored at -35 °C, which gave the product as a dark red solid. A second recrystallization of the crude product with CH₂Cl₂ and Et₂O afforded dark red crystals (73%, 0.25 g). MW = 343.29. ¹H NMR (300 MHz, C₆D₆): δ = 7.07 (m, 3 H, 5-C₄H₃N), 6.28 (m, 3 H, 4-C₄H₃N), 6.01 (m, 3 H, 3-C₄H₃N), 3.60 (s, 6 H, CH₂), 3.14 (s, 6 H, NCH₃). ¹³C{¹H} NMR (300 MHz, C₆D₆): δ = 139.2 (2-C₄H₃N), 126.7 (5-C₄H₃N), 108.5 (4-C₄H₃N), 105.2 (3-C₄H₃N), 55.4 (C₄H₃NCH₂N), 42.5 (N(CH₃)₂). Anal. Found (Calcd) for C₁₇H₂₁N₅Ti: C, 59.82 (59.48); H, 6.28 (6.17); N, 20.12 (20.40).

Preparation of Ti(imd)(tpa) (2). A solution of Ti(tpa)(NMe₂) (0.1716 g, 0.5 mmol) in 10 mL of toluene was cooled to -35 °C. To the stirring cold solution was added 1,3-dimethyl-2-iminoimidazolidine (H-imd) (0.0566 g, 0.5 mmol). The reaction mixture was allowed to warm to room temperature and stir overnight. The volatiles were removed in vacuo to give a light brown solid. The solid was recrystallized at -35 °C in CH₂Cl₂ layered with toluene, which afforded the product as a yellow powder (0.191 g, 93%). M = 411.35. ¹H NMR (300 MHz, CDCl₃): δ = 7.16 (q, 3 H, J = 1 Hz, 5-C₄H₃N), 5.94 (t, 3 H, J = 3 Hz, 4-C₄H₃N), 5.88 (q, 3 H, J = 1 Hz, 3-C₄H₃N), 4.11 (d, 6 H, J = 1 Hz, C₄H₃NCH₂N), 3.57 (s, 4 H, NCH₂CH₂N), 3.16 (s, 6 H, CH₃). ¹³C NMR (CDCl₃): δ = 139.6 (2-C₄H₃N), 129.4 (5-C₄H₃N), 107.1 (4-C₄H₃N), 103.3 (3-C₄H₃N), 55.6 (C₄H₃NCH₂N), 46.7 (CH₃), 33.6 (NCH₂CH₂N). Anal. Found (Calcd) for C₂₀H₂₅N₇Ti: C, 58.17 (58.40); H, 6.28 (6.13); N, 23.48 (23.83).

Preparation of Zr(NMe₂)(tpa)(THF) (3). To a nearly frozen solution of H₃tpa (0.127 g, 0.5 mmol) in 3 mL of THF was added Zr(NMe₂)₄ (0.134 g, 0.5 mmol) in 10 mL of THF. The reaction mixture was allowed to warm to room temperature and stir for 4 h, after which time the volatiles were removed in vacuo, providing product as a colorless solid (98%, 0.224 g). ¹H NMR (300 MHz, CDCl₃): δ = 6.90 (q, 3 H, J = 1 Hz, 5-C₄H₃N), 6.07 (t, 3 H, J = 3 Hz, 4-C₄H₃N), 5.97 (t, 3 H, J = 1 Hz, 3-C₄H₃N), 4.10 (s, 6 H, C₄H₃NCH₂N), 3.41 (m, 4 H, 2-C₄H₈O), 3.37 (s, 6 H, N(CH₃)₂), 1.67 (m, 4 H, 3-C₃H₈O). ¹³C{¹H} NMR (300 MHz, CDCl₃): δ = 138.1 (2-C₄H₃N), 125.2 (5-C₄H₃N), 108.8 (4-C₄H₃N), 104.6 (3-C₄H₃N), 70.9 (2-C₄H₈O), 55.8 (C₄H₃NCH₂N), 39.1 (N(CH₃)₂), 25.1 (3-C₄H₈O). Anal. Found (Calcd) for C₂₁H₂₉N₅OZr (MW = 458.71): C, 54.49 (54.99); H, 6.29 (6.37); N, 15.27 (15.27).

Preparation of Zr(NMe₂)(tpa)(pyridine)₂ (4). To a -90 °C suspension of H₃tpa (0.127 g, 0.5 mmol) and pyridine (1 mmol, 81 μ L) in 10 mL of toluene was added Zr(NMe₂)₄ (0.134 g, 0.5 mmol) in 10 mL of toluene dropwise. The reaction mixture was

allowed to warm to room temperature and stir for 2 h. Volatiles were removed in vacuo to generate a yellow solid. Recrystallization from toluene at -35 °C provided yellow microcrystals of **4** (68%, 0.185 g). ¹H NMR (300 MHz, CDCl₃): δ = 8.02 (d, J = 2 Hz, 4 H, 2-C₅H₅N), 7.71 (t, J = 6 Hz, 2 H, 4-C₅H₅N), 7.26 (t, J = 6 Hz, 4 H, 3-C₅H₅N), 6.39 (d, J = 1 Hz, 3 H, 5-C₄H₃N), 5.95 (dd, J = 1 Hz, 3 H, 4-C₄H₃N), 5.92 (d, J = 1 Hz, 3 H, 3-C₄H₃N), 4.15 (s, 6 H, C₄H₃NCH₂N), 3.16 (s, 6 H, CH₃). ¹³C NMR{¹H} (300 MHz, CDCl₃): δ = 150.1 (2-C₅H₅N), 138.1 (4-C₅H₅N), 137.8 (2-C₄H₃N), 126.1 (3-C₅H₅N), 124.5 (5-C₄H₃N), 108.9 (4-C₄H₃N), 104.3 (3-C₄H₃N), 56.3 (C₄H₃NCH₂N), 41.4 (CH₃). Anal. Found (Calcd) for C₃₄H₃₉N₇Zr (MW = 636.95): C, 63.60 (64.11); H, 6.41 (6.17); N, 14.95 (15.39).

Preparation of Zr(NMe₂)(tpa)(Bu^bbpy) (5). To a -90 °C suspension of H₃tpa (0.127 g, 0.5 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (Bu^bbpy) (0.134 g, 0.5 mmol) in 10 mL of toluene was added Zr(NMe₂)₄ 0.134 g (0.5 mmol) in 10 mL of toluene dropwise. The reaction mixture was allowed to warm to room temperature and stir for 2 h. The volatiles were removed in vacuo to generate a dark red solid. Recrystallization from toluene at -35 °C provided microcrystals of **5** (78%, 0.253 g). ¹H NMR (300 MHz, C₆D₆): δ = 8.89 (d, 6,6'-C₅H₃N, J = 6 Hz, 2 H), 7.98 (d, 3,3'-C₅H₃N, J = 2 Hz, 2 H), 7.15 (dd, 5,5'-C₅H₃N, J = 2 and 1 Hz, 2 H), 6.73 (dd, 5-C₄H₃N, J = 2 and 1 Hz, 2 H), 6.49 (dd, 4-C₄H₃N, J = 2 and 4 Hz, 2 H), 6.43 (dd, 3-C₄H₃N, J = 1 and 2 Hz, 2 H), 6.16 (t, 5-C₄H₃N, J = 1 Hz, 1 H), 6.10 (t, 4-C₄H₃N, J = 2 Hz, 1 H), 5.42 (t, 3-C₄H₃N, J = 1 Hz, 1 H), 4.58-3.86 (br m, C₄H₃-NCH₂N, 6 H), 2.65 (s, N(CH₃)₂, 6 H), 0.89 (s, 4,4'-C₅H₃NC(CH₃)₃, 18 H). ¹³C{¹H} NMR (300 MHz, CDCl₃): δ = 164.4 (2,2'-C₅H₃N), 152.9 (6,6'-C₅H₃N), 150.6 (4,4'-C₅H₃N), 139.3 (2-C₄H₃N), 137.6 (2-C₄H₃N), 127.8 (5-C₄H₃N), 125.8 (5-C₄H₃N), 123.2 (3-C₅H₃N), 117.8 (5-C₅H₃N), 108.7 (4-C₄H₃N), 106.8 (4-C₄H₃N), 103.4 (3-C₄H₃N), 102.5 (3-C₄H₃N), 56.6 (C₄H₃NCH₂N), 56.5 (C₄H₃NCH₂N), 44.2 (br s, N(CH₃)₂), 35.5 (4,4'-C₅H₃NC(CH₃)₃), 30.4 (4,4'-C₅H₃-NC(CH₃)₃). Anal. Found (Calcd) for C₃₅H₄₅N₇Zr·2CH₂Cl₂: C, 54.20 (53.88); H, 6.25 (5.99); N, 11.81 (11.89).

Preparation of ZrCl(tpa)(Bu^bbpy) (6). To a nearly frozen solution of **5** (0.655 g, 1.00 mmol) in 25 mL of THF was added ClSiMe₃ (127 μ L, 1.00 mmol) dropwise. The reaction mixture was allowed to warm to room temperature and stir for 3 h, after which the volatiles were removed in vacuo to generate a yellow solid. Purification was accomplished by recrystallization from THF/toluene at -35 °C, which provided yellow microcrystals of **6** (92%, 0.59 g). ¹H NMR (300 MHz, CDCl₃): δ = 8.92-7.78 (br s, 3,3'-C₅H₃N, 2 H), 8.20 (d, 6,6'-C₅H₃N, J = 1 Hz, 2 H), 7.44 (d, 5,5'-C₅H₃N, J = 4 Hz, 2 H), 7.10 (s, br s 5-C₄H₃N, 2 H), 6.08 (t, 4-C₄H₃N, J = 2 Hz, 2 H), 5.97 (dd, 3-C₄H₃N, J = 1 and 1 Hz, 2 H), 5.85 (t, 5-C₄H₃N, J = 2 Hz, 1 H), 5.63 (t, 4-C₄H₃N, J = 2 Hz, 1 H), 5.35 (dd, 3-C₄H₃N, J = 1 and 1 Hz, 1 H), 5.12-3.72 (br s, C₄H₃NCH₂N, 6 H), 1.44 (s, 4,4'-C₅H₃NC(CH₃)₃, 18 H). ¹³C{¹H} NMR (300 MHz, CDCl₃): δ = 165.3 (2,2'-C₅H₃N), 153.0 (6,6'-C₅H₃N), 150.2 (br, 4-C₄H₃N), 138.7 (5-C₄H₃N), 130.6 (br, 5-C₄H₃N), 126.6 (5-C₄H₃N), 123.2 (3,3'-C₅H₃N), 118.8 (5,5'-C₅H₃N), 109.6 (4-C₄H₃N), 108.7 (4-C₄H₃N), 104.3 (br, 3-C₄H₃N), 103.9 (3-C₄H₃N), 57.0 (C₄H₃NCH₂N), 35.7 (4,4'-C₅H₃NC(CH₃)₃), 30.4 (C₄H₃NC(CH₃)₃). Anal. Found (Calcd) for C₄₀H₄₇N₆ClZr (MW = 738.52): C, 65.05 (64.79); H, 6.41 (6.47); N, 11.38 (11.01).

Preparation of ZrCl(tpa)(THF)₂ (7). To a nearly frozen suspension of ZrCl₄(THF)₂ (0.377 g, 1 mmol) in 20 mL of toluene was added cold Li₃tpa (0.272 g, 1 mmol) suspended in 20 mL of toluene. The reaction mixture was allowed to warm to room temperature. A yellow solution was isolated after filtration. Volatiles

were removed under reduced pressure to give a yellow solid. The product was recrystallized from CH_2Cl_2 at -35°C (72%, 0.376 g). ^1H NMR (300 MHz, CDCl_3): δ = 6.99 (s, 3H, 5- $\text{C}_4\text{H}_3\text{N}$), 6.07 (t, 3 H, 4- $\text{C}_4\text{H}_3\text{N}$, J = 2 Hz), 5.94 (t, 3H, 3- $\text{C}_4\text{H}_3\text{N}$, J = 2 Hz), 4.27 (s, 6H, $\text{C}_4\text{H}_3\text{NCH}_2\text{N}$), 3.88 (m, 8H, 2- $\text{C}_4\text{H}_8\text{O}$), 1.94 (m, 8H, 3- $\text{C}_4\text{H}_8\text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3): δ = 137.9 (5- $\text{C}_4\text{H}_3\text{N}$), 127.7 (2- $\text{C}_4\text{H}_3\text{N}$), 109.7 (3- $\text{C}_4\text{H}_3\text{N}$), 103.7 (4- $\text{C}_4\text{H}_3\text{N}$), 69.9 (2- $\text{C}_4\text{H}_8\text{O}$), 57.1 (CH_2), 25.5 (3- $\text{C}_4\text{H}_8\text{O}$). Anal. Found (Calcd) for $\text{C}_{23}\text{H}_{31}\text{ClN}_4\text{O}_2\text{Zr}$ (MW = 522.19): C, 52.76 (52.90); H, 5.93 (5.98); N, 10.66 (10.73).

Preparation of $\text{ZrCl}(\text{NHMe}_2)_2(\text{tpa})$ (8). To a nearly frozen suspension of H_3tpa (0.102 g, 0.4 mmol) in 5 mL of CH_2Cl_2 was added a cold solution of $\text{ZrCl}(\text{NMe}_2)_3$ (0.104 g, 0.4 mmol) in 5 mL of CH_2Cl_2 . The reaction mixture was allowed to warm to room temperature and stir for 2 h. Volatiles were removed in vacuo, which provided a yellow solid. Then, the solid was dissolved in CH_2Cl_2 , which was layered by a mixture of Et_2O and toluene (v:v = 1:1). The layered solution was stored at -35°C , which gave the product as light yellow crystals (95%, 0.177 g). ^1H NMR (300 MHz, CDCl_3): δ = 7.00 (br s, 3 H, 5- $\text{C}_4\text{H}_3\text{N}$), 6.11 (d, 3 H, J = 2 Hz, 4- $\text{C}_4\text{H}_3\text{N}$), 5.94 (d, J = 2 Hz, 3 H, 3- $\text{C}_4\text{H}_3\text{N}$), 4.24 (s, 6 H, $\text{C}_4\text{H}_3\text{NCH}_2\text{N}$), 3.08 (s, 2 H, NHMe_2), 2.18 (br s, 12 H, $\text{NH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3): δ = 138.1 (2- $\text{C}_4\text{H}_3\text{N}$), 126.8 (br, 5- $\text{C}_4\text{H}_3\text{N}$), 110.5 (4- $\text{C}_4\text{H}_3\text{N}$), 104.4 (3- $\text{C}_4\text{H}_3\text{N}$), 57.1 ($\text{C}_4\text{H}_3\text{NCH}_2\text{N}$), 39.3 (CH_3). Anal. Found (Calcd) for $\text{C}_{20}\text{H}_{29}\text{Cl}_3\text{N}_6\text{Zr}$ (MW = 555.06): C, 43.45 (43.59); H, 5.70 (5.30); N, 15.05 (15.25).

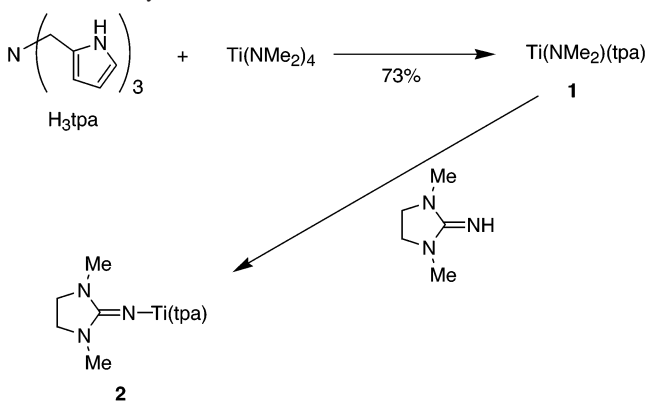
Preparation of $\text{Zr}(\text{C}\equiv\text{C}-\text{Ph})(\text{tpa})(\text{Bu}^i\text{bpy})$ (9). To a nearly frozen suspension of $\text{LiC}\equiv\text{CPh}$ (0.025 g, 0.5 mmol) in 10 mL of toluene was added a cold solution of **6** (0.3232 g, 0.5 mmol) in 5 mL of THF dropwise. The reaction mixture was allowed to warm to room temperature and stir overnight. Then, volatiles were removed in vacuo. The residue was dissolved in 20 mL of toluene and filtered, which provided a yellow solution. Concentration of the resulting solution in vacuo and cooling to -35°C afforded **9** as yellow microcrystals (0.221 g, yield 62%). ^1H NMR (300 MHz, CDCl_3): δ = 8.48 (d, J = 5 Hz, 6,6'- $\text{C}_5\text{H}_3\text{N}$, 2 H), 8.18 (s, 3,3'- $\text{C}_5\text{H}_3\text{N}$, 2 H), 7.41 (d, J = 5 Hz, 5,5'- $\text{C}_5\text{H}_3\text{N}$, 2 H), 7.25 (br s, 5- $\text{C}_4\text{H}_3\text{N}$, 2 H), 6.99 (m, 3,4-Ph, 3 H), 6.85 (m, 2-Ph, 2 H), 6.05 (m, 4- $\text{C}_4\text{H}_3\text{N}$, 2 H), 5.98 (d, J = 2 Hz, 3- $\text{C}_4\text{H}_3\text{N}$, 2 H), 5.85 (d, J = 2 Hz, 5- $\text{C}_4\text{H}_3\text{N}$, 1 H), 5.65 (m, 4- $\text{C}_4\text{H}_3\text{N}$, 1 H), 5.42 (d, J = 2 Hz, 3- $\text{C}_4\text{H}_3\text{N}$, 1 H), 4.42–4.18 (br, $\text{C}_4\text{H}_3\text{NCH}_2\text{N}$, 6 H), 1.44 (d, 4,4'- $\text{C}_5\text{H}_3\text{NC}(\text{CH}_3)_3$, 18 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3): δ = 164.7 (2,2'- $\text{C}_5\text{H}_3\text{N}$), 153.4 (6,6'- $\text{C}_4\text{H}_3\text{N}$), 150.6 (4,4'- $\text{C}_4\text{H}_3\text{N}$), 139.2 (2- $\text{C}_4\text{H}_3\text{N}$), 138.6 (2- $\text{C}_4\text{H}_3\text{N}$), 131.5 (2-Ph), 130.5 (3-Ph), 127.5 (2-Ph), 125.8 (5- $\text{C}_4\text{H}_3\text{N}$), 125.7 (5- $\text{C}_4\text{H}_3\text{N}$), 122.9 (3,3'- $\text{C}_5\text{H}_3\text{N}$, 1-Ph), 118.4 (5,5'- $\text{C}_5\text{H}_3\text{N}$), 109.1 (4- $\text{C}_4\text{H}_3\text{N}$), 108.2 (4- $\text{C}_4\text{H}_3\text{N}$), 104.3 (3- $\text{C}_4\text{H}_3\text{N}$), 104.1 (3- $\text{C}_4\text{H}_3\text{N}$), 80.8 ($\text{C}_6\text{H}_5\text{C}_2$), 56.8 ($\text{C}_4\text{H}_3\text{NCH}_2\text{N}$), 35.6 (4,4'- $\text{C}_5\text{H}_3\text{NC}(\text{CH}_3)_3$), 30.4 (4,4'- $\text{C}_5\text{H}_3\text{NC}(\text{CH}_3)_3$). Anal. Found (Calcd) for $\text{C}_{41}\text{H}_{44}\text{N}_6\text{Zr}$ (MW = 712.06): C, 69.35 (69.16); H, 6.36 (6.23); N, 11.81 (11.80).

General Considerations for X-ray Diffraction. Crystals grown at -35°C were quickly moved from a scintillation vial to a microscope slide containing Paratone N. Samples were selected and mounted onto a glass fiber in wax and Paratone. The data collections were carried out at a sample temperature of 173(2) K on a Bruker AXS platform three-circle goniometer with a CCD detector. The incident radiation was of wavelength 0.71073 Å, which was selected with a graphite monochromator. The data were processed and reduced utilizing the program SAINTPLUS supplied by Bruker AXS. The structures were solved by direct methods (SHELXTL v5.1, Bruker AXS) in conjunction with standard difference Fourier techniques. Absorption corrections were done empirically using the

Table 1. Structural Parameters for **1**, **2**, **6**·2 CH_2Cl_2 , and **9**· CH_2Cl_2

	1	2	6	9
empirical formula	$\text{C}_{17}\text{H}_{21}\text{N}_5\text{Ti}$	$\text{C}_{20}\text{H}_{25}\text{N}_7\text{Ti}$	$\text{C}_{37}\text{H}_{49}\text{Cl}_4\text{N}_7\text{Zr}$	$\text{C}_{20}\text{H}_{29}\text{Cl}_3\text{N}_6\text{Zr}$
fw	343.29	411.37	824.85	551.06
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	12.588(4)	10.728(3)	8.5527(18)	12.468(3)
<i>b</i> (Å)	12.147(4)	10.672(3)	23.370(5)	15.019(3)
<i>c</i> (Å)	22.353(7)	17.655(4)	20.101(4)	13.703(3)
β (deg)	99.518(6)	95.078(4)	99.270(4)	107.116(3)
vol (Å ³)	3370.9(18)	2013.3(8)	3965.1(14)	2452.5(9)
<i>Z</i>	8	4	4	4
μ (mm ⁻¹)	0.514	0.446	0.583	0.794
<i>D</i> _{calcd} (g cm ⁻³)	1.353	1.357	1.382	1.492
no. of total reflns	15191	16570	17955	10930
no. of unique reflns (<i>R</i> _{int})	4852 (0.1658)	2890 (0.082)	5704 (0.1419)	3522 (0.269)
extinction	0.0005(3)	0.0021(5)	0.0043(6)	0.0006(3)
<i>R</i> (<i>F</i> _o) (<i>I</i> > 2σ)	0.0576	0.0419	0.0623	0.0372
<i>R</i> _w (<i>F</i> _o ²) (<i>I</i> > 2σ)	0.1332	0.0879	0.1557	0.0923

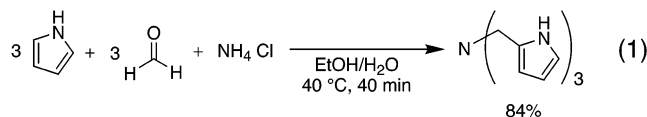
Scheme 1. Synthesis of **1** and **2**



program xprep. Some details on the structure refinement are found in Table 1.

Results and Discussion

The tetradentate ligand H_3tpa was prepared in 84% yield on a 20 g scale by a triple Mannich reaction of 1 equiv of ammonium chloride, 3 equiv of formaldehyde, and 3 equiv of pyrrole in 3:1 ethanol/water (eq 1). The correct temperature and time for the reaction are crucial for obtaining a satisfactory quality and yield of the product.



Recently, a similar ligand, tris(indolyl- α -methyl)amine, using indolyl instead of pyrrolyl groups was synthesized by Tanski and Parkin through a multistep procedure.¹⁷ Several tantalum complexes incorporating this tetradentate indolyl ligand were reported.

Addition of an ethereal solution of H_3tpa to a cold solution of $\text{Ti}(\text{NMe}_2)_4$ afforded pseudo-trigonal-bipyramidal **1** in 73% recrystallized yield (Scheme 1). The dark red complex was structurally characterized by single-crystal X-ray diffraction (Figure 1). The pseudo-trigonal-bipyramidal complex has

(17) Tanski, J. M.; Parkin, G. *Inorg. Chem.* **2003**, *42*, 264–266.

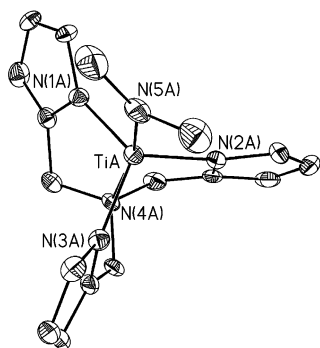


Figure 1. Structure of **1** found by X-ray diffraction. Only one of the two chemically identical but crystallographically distinct molecules in the asymmetric unit is shown. Ellipsoids are at the 25% probability level.

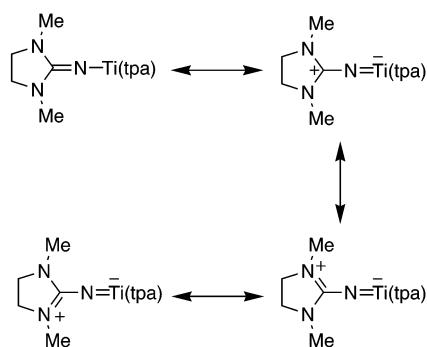


Figure 2. Possible resonance forms for **2** leading to the observed Ti–N multiple bond. A second π -bond due to donation of the lone pair on the imid imino nitrogen is not shown.

Table 2. Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on **1**

Ti(A)–N(1A)	1.992(6)	N(5A)–Ti(A)–N(1A)	98.3(3)
Ti(A)–N(2A)	2.000(5)	N(5A)–Ti(A)–N(2A)	111.7(2)
Ti(A)–N(3A)	1.977(5)	N(5A)–Ti(A)–N(3A)	99.3(2)
Ti(A)–N(4A)	2.275(5)	N(5A)–Ti(A)–N(4A)	169.3(2)
Ti(A)–N(5A)	1.843(6)	N(1A)–Ti(A)–N(2A)	111.4(2)
		N(1A)–Ti(A)–N(3A)	119.8(2)
		N(3A)–Ti(A)–N(2A)	114.2(2)

structural features common for titanium pyrrolyl compounds of this class. The titanium dimethylamido, Ti(A)–N(5A), has a distance consistent with significant π -bonding at 1.843–(6) Å due to amido lone pair to titanium donation (Table 2). The three pyrrolyl nitrogens reside in the approximate trigonal plane with an average Ti–N(pyrrolyl) distance of 1.989(6) Å, consistent with the much lower π -donating ability of pyrrolyl versus dimethylamido. The donor amine occupies the other axial position 169.3(2)° away from the dimethylamido and has a Ti(A)–N(4A) distance of 2.275–(5) Å.

An electronically interesting ligand that has been little used in titanium chemistry is the 2-iminoimidazolidinide, especially where the imidazolidine is substituted with donating alkyl substituents in the 1- and 3-positions. Because of the significant stabilization of the carbocation resulting from Ti–N triple bond formation due to donation from the adjacent nitrogens (Figure 2) and relatively high Lewis acidity of the metal center due to poor π -donation from the pyrrolyl ligands (vide supra), we expected a short Ti–N(imd) bond. Reaction of H-imd with **1** generated **2** as a red crystalline solid (Scheme 1).

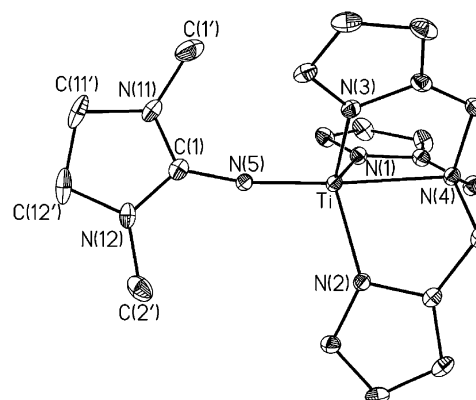
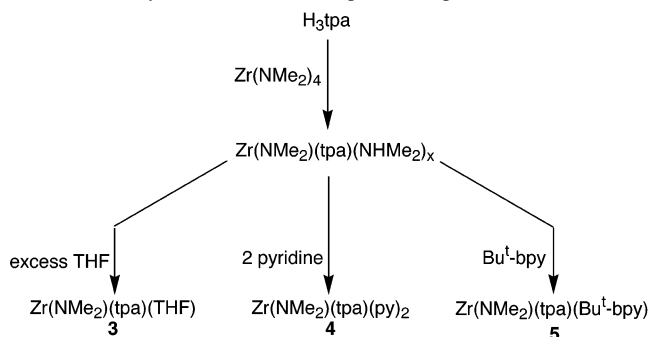


Figure 3. Structure of **2** found by X-ray diffraction. Ellipsoids are at the 25% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on **2**

Ti–N(1)	1.995(3)	N(5)–Ti–N(1)	103.1(1)
Ti–N(2)	2.009(2)	N(5)–Ti–N(2)	106.6(1)
Ti–N(3)	1.996(3)	N(5)–Ti–N(3)	99.6(1)
Ti–N(4)	2.296(2)	N(5)–Ti–N(4)	175.7(1)
Ti–N(5)	1.768(2)	N(1)–Ti–N(2)	112.9(1)
N(5)–C(1)	1.321(4)	N(1)–Ti–N(3)	114.2(1)
N(11)–C(1)	1.341(4)	N(3)–Ti–N(2)	117.9(1)
N(11)–C(1)	1.440(4)	C(1)–N(5)–Ti	169.1(2)
N(12)–C(1)	1.367(4)		
N(12)–C(2)	1.434(4)		

Scheme 2. Synthesis of Zr(NMe₂)(tpa)_L_x Complexes from Zr(NMe₂)₄



The first X-ray diffraction study on a iminoimidazolidinide titanium complex was recently reported by Kretschmer and co-workers on Ti(Cp)Cl₂(N=C[N(Ph)CH₂]₂), which exhibited a Ti–N(imd) distance of 1.792(2) Å.¹⁸ Titanium tpa **2** was also characterized by X-ray diffraction (Figure 3, Table 3) and exhibited a short Ti–N(imd) distance of 1.768(2) Å. The slightly shorter distance in **2** versus reported Ti(Cp)Cl₂(N=C[N(Ph)CH₂]₂) may be a result of the more basic methyl substituents on the imidazoline moiety and/or greater Lewis acidity of the tpa ligand set. The typical Ti–N(imido) bond length range is approximately 1.65–1.78 Å, which can be thought of as a Ti–N double to triple bond distance.¹⁹ The Ti–N(imd) bond of **2** is in the typical titanium–imido bond range, suggestive of some triple bond character. Indeed, the Ti–N(imd) bond distance is similar to the Ti–N(imido) bond distances in Ti(NSiBu^t)(OSiBu^t)(THF),¹⁹ⁿ [Ti(NSiMe₃)(CH₂SiR₃)(N(SiMe₃)₂)][–],^{19t} and Ti(N–C₆H₃–2,6-Me)(OPMe₃)(Cp)(NHC₆H₃–2,6-Me)^{19ai} at 1.772(3), 1.751(5), and 1.752–

(18) Kretschmer, W. P.; Dijkhuis, C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2002**, 608–609.

(8) Å, respectively. In addition, the Ti–N(imd) bond is ~0.1 Å shorter than the Ti–N(NMe₂) bond in **1**, suggestive of significant additional bonding in the iminoimidazolidinide complex.

That the nitrogens of the imidazoline strongly participate in π -bonding is also apparent from the solid-state structure of **2**. The N(11)–C(1) and N(12)–C(1) bond distances of 1.341(4) and 1.367(4) Å, respectively, are indicative of significant multiple bond character; cf. the C–N bond distance in pyridine of 1.339(5) Å.²⁰ By comparison, the imidazolidine N–Me average single bond distance, i.e., N(11)–C(1') and N(12)–C(2'), is much longer at 1.437(4) Å.

We also explored the use of tpa in related zirconium chemistry. Because of the larger van der Waals radius of zirconium, additional donors on the metal center were invariably present in these initial studies. Several donors with variable lability were studied to provide a selection of starting materials. For example, reaction of H₃tpa with Zr(NMe₂)₄

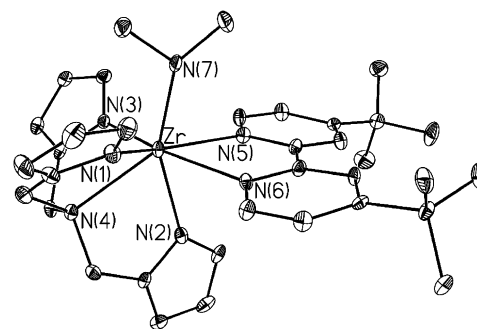


Figure 4. Structure of **5** found by X-ray diffraction. The compound crystallized with 2 equiv of CH₂Cl₂ per Zr complex. Ellipsoids are at the 25% probability level.

Table 4. Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on **5**

Zr–N(1)	2.200(7)	N(7)–Zr–N(1)	87.5(2)
Zr–N(2)	2.301(6)	N(7)–Zr–N(3)	87.9(2)
Zr–N(3)	2.202(6)	N(7)–Zr–N(2)	151.6(2)
Zr–N(4)	2.462(6)	N(1)–Zr–N(4)	70.0(2)
Zr–N(5)	2.365(6)	N(2)–Zr–N(4)	70.1(2)
Zr–N(6)	2.434(6)	N(7)–Zr–N(5)	77.9(2)
Zr–N(7)	2.054(6)	N(7)–Zr–N(6)	91.5(2)
		N(3)–Zr–N(6)	162.9(2)
		N(1)–Zr–N(5)	146.1(2)

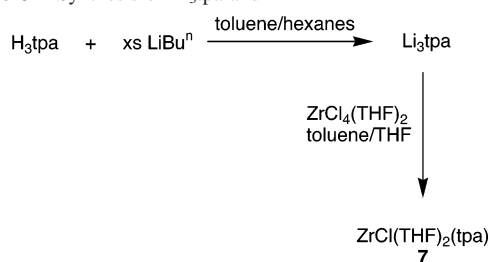
provided a complex that was of somewhat ill-defined composition, probably due to variable amounts of NHMe₂ being retained by the metal center (Scheme 2). A single compound, Zr(THF)(Cl)(tpa) (**3**), is readily prepared by addition of THF to in situ generated Zr(NMe₂)(tpa)(NHMe₂)_x.

While excess THF generates the monoadduct **3**, addition of 2 equiv of pyridine results in a stable complex with two donor ligands Zr(NMe₂)(tpa)(pyridine)₂ (**4**). Similarly, addition of 1 equiv of 4,4'-di-*tert*-butyl-2,2'-bipyridine (Bu'bpy) to in situ generated Zr(NMe₂)(tpa)(NHMe₂)_x gave Zr(NMe₂)(tpa)(Bu'bpy) (**5**).

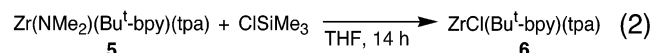
Seven-coordinate **5** was characterized by X-ray diffraction (Figure 4, Table 4) and displays a geometry most closely resembling face-capped octahedral, where the donor nitrogen of the tpa caps the trigonal face formed by the three pyrrolyl substituents. The two pyrrolyl substituents *trans* to the nitrogens of the Bu'bpy have similar zirconium–nitrogen distances of 2.200(7) and 2.202(6) Å for Zr–N(1) and Zr–N(3), respectively. However, Zr–N(2) is substantially lengthened at 2.301(6) Å, presumably due to the *trans* influence of the approximately coaxial dimethylamido ligand. Another structural feature of **5** is the unequal Zr–N distances to the two bpy nitrogens. The Zr–N(5) bond distance of 2.365(6) Å is substantially shorter than Zr–N(6) at 2.434(6) Å. The difference in bonding to the two pyridyl nitrogens may be a result of differing *trans* influences by the tpa ligand on the two sides of the bpy. The pyrrolyl nitrogen N(3) is nearly *trans* to the longer bpy nitrogen with an angle of 162.9(2)°. Conversely, the shorter pyridyl–zirconium bond, Zr–N(5), is farther from coaxial with its *trans*-pyrrolyl nitrogen, and the N(1)–Zr–N(5) angle is 146.1(2)°.

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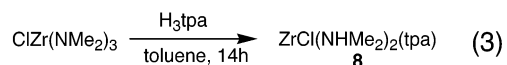
Scheme 3. Synthesis of Li₃tpa and **7**


The synthesis of potentially useful zirconium chloride tpa complexes was also explored using several different routes and donor ligands. Reaction of **5** with trimethylsilyl chloride results in the formation of **6** in 92% yield as a crystalline yellow solid (eq 2).



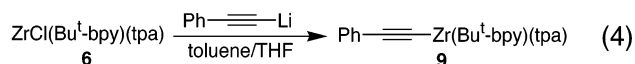
The zirconium halide complex **7** is available in 72% yield through a reaction of ZrCl₄(THF)₂ with Li₃tpa (Scheme 3). The lithium salt of the tpa ligand was prepared in near quantitative yield by deprotonation of the a toluene solution of H₃tpa with *n*-butyllithium in hexanes. Treatment of ZrCl₄(THF)₂ in THF with a toluene slurry of Li₃tpa provides ZrCl(THF)₂(tpa) in 72% recrystallized yield.

An alternative synthesis to zirconium chloride complexes was explored using the starting material ClZr(NMe₂)₃ (eq 3). Treatment of a CH₂Cl₂ solution of ClZr(NMe₂)₃ with a solution of H₃tpa provides the bis(dimethylamine) complex **8** in 95% recrystallized yield. Bis(amine) **8** was also characterized by X-ray diffraction, and the details are included in the Supporting Information.



Zirconium organometallic complexes are available through metathesis reactions involving the chloride tpa compounds. Reaction of methylolithium with **6** results in the formation of

a ZrMe(Bu^tbpy)(tpa) complex, which was unstable even at −35 °C. However, reaction of **6** with LiC≡CPh (eq 4) provided the stable alkynyl **9** in 62% yield.



Concluding Remarks

The tetradentate nitrogen ligand H₃tpa is readily available in a single step from commercially available compounds. We set out to discover if the tetradentate tpa ligand framework would provide a stable platform for group 4 complexes. A wide selection of functionality was placed on the Ti(tpa) and Zr(tpa) cores. In the zirconium system three different synthetic protocols were used for the synthesis of ZrClL₂(tpa) complexes. All the syntheses provided compounds in high yields, consistent with a robust and useful ancillary ligand set. In addition, a stable alkynyl complex of zirconium was readily generated by simple metathesis.

The tpa ligand on titanium and zirconium provided stable compounds bearing halides, amidos, 2-iminoimidazolidinide, pyridine, alkynyl, and others. Due to the low π-donating ability of the amide groups, the ligand may be useful in the generation of complexes across the transition and main group series.

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Supporting Information Available: Tables of crystallographic data including refinement parameters, coordinates, bond distances, and bond angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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