

Supplementary information for

**New alkylzinc Complexes with Bulky Tris(triazoly)borate Ligands:  
Surprising Water Stability and Reactivity**

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**Experimental section**

**General Procedures.** Compounds **3-5** were prepared under N<sub>2</sub> atmosphere using an M. Braun UNILAB glove-box and Schlenk techniques. The ligands, K(Ttz<sup>R,Me</sup>), were prepared by following known procedures.<sup>1</sup> TiNO<sub>3</sub>, Et<sub>2</sub>Zn and Me<sub>2</sub>Zn were purchased from Acros and Aldrich and used without further purification. Solvents were dried using an M. Braun solvent purification system with alumina columns or were freshly distilled from drying agents using standard methods. NMR spectra were recorded using either a 300 MHz or a 500 MHz Varian Unity Inova NMR spectrophotometer. IR spectra were recorded on a Perkin-Elmer Spectrum one Fourier-transform IR absorption spectrophotometer. High resolution mass spectrometry was performed on VG70SE double focusing, triple quadruple mass spectrometer equipped with FAB or CI ionization capability. Elemental analyses were performed by Robertson Microlit.

**Single crystal X-ray diffraction studies.** Diffraction data for all compounds were collected using a Bruker AXS SMART APEX CCD diffractometer using monochromatic Mo K $\alpha$  radiation with the omega scan technique. Single crystals were mounted on Mitegen micromesh mounts and data were collected at 100 K. Data were collected, unit cells determined, and the data integrated and corrected for absorption and other

systematic errors using the Apex2 suite of programs.<sup>2</sup> The structures were solved by direct methods and refined by full matrix least squares against  $F^2$  with all reflections using SHELXTL 6.14<sup>3</sup> All non-hydrogen atoms were refined anisotropically. Water hydrogen atoms were located in difference density Fourier maps and were refined with an O-H distance restraint of 0.84(2) Å. All other hydrogen atoms were placed in calculated positions and were refined with isotropic displacement parameters 1.2 (C-H) or 1.5 (CH<sub>3</sub>) times that of the adjacent carbon atom. Unit cell parameters, atomic coordinates and other crystallographic data are given in cif file format as supporting material.

### Synthesis

**Synthesis of Tl(Ttz<sup>tBu,Me</sup>) (1).** To a MeOH (2.0 mL) and H<sub>2</sub>O (6.0 mL) solution of K(Ttz<sup>tBu,Me</sup>) (0.411 g, 0.883 mmol) was added a solution of TlNO<sub>3</sub> (0.470 g, 1.76 mmol), separately prepared in 7 mL H<sub>2</sub>O. A white precipitate formed immediately which was collected by filtration and dried under vacuum for 24 hours. The yield of **1** was 0.280 g, 50.3%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.45 (s, 27H, (CH<sub>3</sub>)<sub>3</sub>C), 2.25 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>): δ 13.99 (CH<sub>3</sub>), 30.85, 32.13 C(CH<sub>3</sub>)<sub>3</sub>, 33.65 C(CH<sub>3</sub>)<sub>3</sub>, 158.20 (5-tz), 173.33 (3-tz); IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2530.0 (νB-H); FAB MS: m/z = 632.314473 [M+H]<sup>+</sup> (experimental), 632.315720 [M+H]<sup>+</sup> (calculated); all peaks showed the expected isotopic pattern.

**Synthesis of Tl(Ttz<sup>Ph,Me</sup>) (2).** To a MeOH (5.0 mL) and H<sub>2</sub>O (5.0 mL) solution of K(Ttz<sup>Ph,Me</sup>) (0.396 g, 0.754 mmol) was added a solution of TlNO<sub>3</sub> (0.200 g, 0.751 mmol) separately prepared in 5 mL H<sub>2</sub>O. A white precipitate formed immediately which was collected by filtration and dried under vacuum for 24 hours. The yield of **2** was 0.321g, 61.9%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.69 (s, 9H, CH<sub>3</sub>), 7.45 (m, 9H, meta, para-Ph), 7.87 (m, 6H, ortho-Ph); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 13.79 (CH<sub>3</sub>), 126.48, 128.02, 129.18, 129.69, 131.15

(Ph), 158.64 (5-tz), 162.73, 163.30 (3-tz); IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2516.7 (ν<sub>B-H</sub>); CI MS: m/z = 692.212247 [M+H]<sup>+</sup> (experimental), 692.214832 [M+H]<sup>+</sup> (calculated); all peaks showed the expected isotopic pattern.

**Synthesis of (Ttz<sup>tBu,Me</sup>)ZnEt (3) in C<sub>6</sub>D<sub>6</sub>.** To a 2 mL C<sub>6</sub>D<sub>6</sub> solution of Tl(Ttz<sup>tBu,Me</sup>) (0.028 g, 0.044 mmol) in a flask under N<sub>2</sub> atmosphere was added Et<sub>2</sub>Zn (100 μL, 0.100 mmol, 1.0 M in hexanes) via syringe. The reaction mixture turned gray immediately and formation of a silver-black precipitate (Tl<sub>(s)</sub>) was observed. The progress of the reaction was monitored by recording <sup>1</sup>H-NMR spectra at different time intervals. After 2 h, the reaction was complete and the contents were filtered. The volatiles were removed under vacuum from the filtrate and a white solid, (Ttz<sup>tBu,Me</sup>)ZnEt, was isolated and purified by recrystallization from a mixture of dichloromethane and hexanes (1:1). The yield of **3** was 0.016 g, 69.2%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.21 (q, 2H, ZnCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.49 Hz), 1.57 (s, 27H, (CH<sub>3</sub>)<sub>3</sub>C), 1.88 (t, 3H, ZnCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H-H</sub> = 7.99 Hz), 2.10 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.46 (ZnCH<sub>2</sub>CH<sub>3</sub>), 13.34 (CH<sub>3</sub>), 13.77 (ZnCH<sub>2</sub>CH<sub>3</sub>), 30.72 C(CH<sub>3</sub>)<sub>3</sub>, 33.43 C(CH<sub>3</sub>)<sub>3</sub>, 156.81 (5-tz), 173.91 (3-tz); IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2543.4 (ν<sub>B-H</sub>); FAB-MS: m/z = 520.303013 [M+H]<sup>+</sup> (experimental), 520.302593 [M+H]<sup>+</sup> (calculated); 490.2510 [M-Et]<sup>+</sup> (experimental), 490.2556 [M-Et]<sup>+</sup> (calculated); all peaks showed the expected isotopic pattern. Elemental analysis, found C 51.99, H 8.16, N 22.96, calcd. for **3**•H<sub>2</sub>O C 51.27, H 8.23, N 23.39.

**Synthesis of (Ttz<sup>tBu,Me</sup>)ZnEt (3) in CH<sub>2</sub>Cl<sub>2</sub>.** To a 5 mL CH<sub>2</sub>Cl<sub>2</sub> solution of Tl(Ttz<sup>tBu,Me</sup>) (0.107 g, 0.170 mmol) in a flask under N<sub>2</sub> atmosphere was added Et<sub>2</sub>Zn (340 μL, 0.340 mmol, 1.0 M in hexanes) via syringe. The reaction mixture turned gray immediately and formation of a black precipitate was observed. After 3 hours, the contents were filtered

and the volatiles of the filtrate were removed under vacuum and a white solid was isolated. The yield of **3** was 0.066 g, 74.7%. Spectra were identical to those for **3** prepared in C<sub>6</sub>D<sub>6</sub>.

**Synthesis of (Ttz<sup>tBu,Me</sup>)ZnMe (4).** Compound **4** was prepared in a similar manner to **3** from the appropriate starting materials. Starting materials and solvent: Tl(Ttz<sup>tBu,Me</sup>) (0.037 g, 0.059 mmol), Me<sub>2</sub>Zn (100 μL, 0.120 mmol, 1.2 M in toluene), C<sub>6</sub>D<sub>6</sub> (2 mL). The yield of **4** was 0.024g, 80.7%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.43 (s, 3H, ZnCH<sub>3</sub>), 1.56 (s, 27H, (CH<sub>3</sub>)<sub>3</sub>C), 2.11 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>): δ -4.07 (ZnCH<sub>3</sub>), 13.24 (CH<sub>3</sub>), 30.63 (C(CH<sub>3</sub>)<sub>3</sub>), 33.43 (C(CH<sub>3</sub>)<sub>3</sub>), 156.83 (5-tz), 173.78 (3-tz); IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2547.9 (νB-H); FAB-MS: m/z = 506.291444 [M+H]<sup>+</sup> (experimental), 506.293931 [M+H]<sup>+</sup> (calculated); 490.2585 [M-Me]<sup>+</sup> (experimental), 490.2556 [M-Me]<sup>+</sup> (calculated); all peaks showed the expected isotopic pattern. Elemental analysis, found C 50.18, H 7.84, N 22.00, calcd. for **4**•H<sub>2</sub>O C 50.35, H 8.07, N 24.02.

**Synthesis of (Ttz<sup>Ph,Me</sup>)ZnEt (5).** To a 5 mL CH<sub>2</sub>Cl<sub>2</sub> solution of Tl(Ttz<sup>Ph,Me</sup>) (0.080 g, 0.116 mmol) in a flask under N<sub>2</sub> atmosphere was added Et<sub>2</sub>Zn (230 μL, 0.230 mmol, 1.0 M in hexanes) via syringe. The reaction mixture turned gray immediately and formation of a black precipitate was observed. After 3 h, the contents were filtered and the volatiles removed from the filtrate under vacuum. A white solid, (Ttz<sup>Ph,Me</sup>)ZnEt (**5**), was isolated and was purified by recrystallization from a mixture of dry dichloromethane and hexanes (1:1). The yield of **5** was 0.055g, 81.7%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.39 (m, 5H, ZnCH<sub>2</sub>CH<sub>3</sub>), 2.73 (s, 9H, CH<sub>3</sub>), 7.44 (m, 9H, meta, para-Ph), 7.90 (m, 6H, ortho-Ph); <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.98 (m, 5H, ZnCH<sub>2</sub>CH<sub>3</sub>), 2.22 (s, 9H, CH<sub>3</sub>), 7.07-7.18 (m, 9H, meta, para-Ph), 8.23 (m, 6H, ortho-Ph). Note that the ethyl hydrogen atoms appear at nearly<sup>4</sup> the same

chemical shift in both C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub> on a 500MHz NMR. While this is surprising, a similar result was seen for <sup>1</sup>H-NMR spectra of the chemically similar compounds, (Tp<sup>Ph</sup>)ZnEt, (Tp<sup>p-tol</sup>)ZnEt, (Tp<sup>anisyl</sup>)ZnEt, and (Tp<sup>Ph,Ph</sup>)ZnEt, all of which showed just one singlet signal for the ethyl groups at δ 0.01, 0.00, 0.03, and 0.00, respectively (field strength was not reported and spectra were recorded in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub>).<sup>5</sup> <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 2.05 (ZnCH<sub>2</sub>CH<sub>3</sub>), 10.71 (ZnCH<sub>2</sub>CH<sub>3</sub>), 13.53 (CH<sub>3</sub>), 128.27, 128.74, 129.56, 130.37 (Ph), 158.34 (5-tz), 163.88 (3-tz); <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>): δ 3.25 (ZnCH<sub>2</sub>CH<sub>3</sub>), 11.67 (ZnCH<sub>2</sub>CH<sub>3</sub>), 13.45 (CH<sub>3</sub>), 128.87, 129.16, 129.27, 130.68 (Ph), 158.67 (5-tz), 164.66 (3-tz); IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2544.9 (νB-H); FAB-MS: m/z = 580.209526 [M+H]<sup>+</sup> (experimental), 580.208693 [M+H]<sup>+</sup> (calculated); 550.2 [M-Et]<sup>+</sup> (experimental), 550.161731 [M-Et]<sup>+</sup> (calculated); all peaks showed the expected isotopic pattern. Elemental analysis (glovebox handling was needed as this complex is moisture sensitive), found C 59.69, H 5.10, N 21.45, calcd. for **5** C 59.97, H 5.21, N 21.70.

**Attempts at Hydrolysis of (Ttz<sup>tBu,Me</sup>)ZnEt (3) and (Ttz<sup>tBu,Me</sup>)ZnMe (4).** In a typical experiment, complex **3** was dissolved in 1 mL of C<sub>6</sub>D<sub>6</sub> in an NMR tube and a <sup>1</sup>H-NMR spectrum was taken to confirm the presence of **3**. One drop of H<sub>2</sub>O was added to the NMR tube and <sup>1</sup>H-NMR spectra were taken immediately afterwards, hours later, days later, and finally six months later. Even after six months, spectra still showed the presence of **3** with the Zn-Et group's resonances showing the correct integration relative to the resonances from the Ttz<sup>tBu,Me</sup> ligand, indicating no detectable hydrolysis. The spectra also indicated that some water had dissolved in the C<sub>6</sub>D<sub>6</sub> solution.

In another experiment, complex **3** (0.020g) was mixed with 2 mL of water and 2 mL of methanol to form a suspension which was stirred for 48 h at room temperature.

The  $^1\text{H-NMR}$  spectrum of the resultant product showed no evidence of the hydrolysis of the Zn-Et group. Similarly, complex **3** (0.020g) was mixed with 4 mL of water and 2 mL of dichloromethane to form a clear mixture which was stirred for 24 h at room temperature. The  $^1\text{H-NMR}$  spectrum of the resultant product showed no evidence of the hydrolysis of Zn-Et group. Similar experiments with complex **4** indicated that it too was water stable.

**Formation of  $(\text{Ttz}^{\text{Ph,Me}})_2\text{Zn}$  (**6**) from  $(\text{Ttz}^{\text{Ph,Me}})\text{ZnEt}$  (**5**).** To a 2 mL  $\text{CH}_2\text{Cl}_2$  solution of **5** (0.050 g, 0.086 mmol) was added 0.5 mL of water. The contents were stirred for 24 h. Then the solvent was removed and  $^1\text{H-NMR}$  and IR spectra showed the formation of  $(\text{Ttz}^{\text{Ph,Me}})_2\text{Zn}$  (**6**). This material was purified by recrystallization from  $\text{CH}_2\text{Cl}_2$  and hexanes (1:1). The yield of **6** was 0.044 g, 49.2%. Single crystal X-ray diffraction confirmed the structure of **6**, which was identical to  $(\text{Ttz}^{\text{Ph,Me}})_2\text{Zn}$  prepared previously in our laboratory by a different route and fully characterized.<sup>6</sup>

## References

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  - 4 Since the ethyl group of **5** appears as a multiplet rather than a singlet in the  $^1\text{H-NMR}$ , the splitting indicates that while the chemical shifts of the  $\text{CH}_2$  and the  $\text{CH}_3$  group are

close in value they cannot be identical. For a discussion of ethyl groups that appear as singlets see W. Sattler, K. Yurkerwich, G. Parkin, *Dalton Trans.* 2009, 4327-4333.

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