

## **[2+2] Cycloaddition Reactions with a Tungsten-Stabilized 2H-Phenol**

Michael A. Todd, Michal Sabat, William H. Myers<sup>#</sup>, W. Dean Harman<sup>\*</sup>

*Contribution from the Department of Chemistry, University of Virginia Charlottesville, VA 22904-4319*

*<sup>#</sup> Department of Chemistry, University of Richmond, Richmond, Virginia 23173  
wdh5z@virginia.edu*

### **Supplementary Material**

#### Contents:

Experimental Details.....	S2-S6
Spectra for compounds <b>6</b> and <b>8</b> .....	S7-S9

## Experimental Details.

**General Methods.** All NMR spectra were obtained on either a 300 or 500 MHz Varian INOVA spectrometer, or on a 300 or 500 MHz Bruker Avance spectrometer. All chemical shifts are reported in ppm versus tetramethylsilane using residual shifts of the deuterated solvent as the internal standard. All coupling constants (J) are reported in hertz (Hz). All  $^{31}\text{P}$  NMR data is reported versus an external standard in acetone (Trimethylphosphate,  $\delta$ -16.58 ppm). Infrared spectra were obtained on a MIDAC Prospect Series spectrometer as a glaze on a Horizontal Attenuated Total Reflectance (HATR) cell from Pike Industries. Electrochemical measurements were taken under a nitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data were obtained in a three electrode cell from +1.7 to -1.7 V, with a glassy carbon working electrode, a platinum wire auxiliary electrode and a platinum wire reference electrode. All data were obtained using a 100 mv/s scan rate with tetrabutylammonium hexafluorophosphate (TBAH) as the electrolyte in N,N-dimethylacetamide (DMA) unless otherwise noted. All potentials were reported versus the Normal Hydrogen Electrode (NHE) using cobaltocenium hexafluorophosphate ( $E_{1/2} = -0.78$  V) as an internal standard. For reversible waves the peak to peak separation was less than 100 mV. All HRMS data was obtained using a 1:1 water:acetonitrile solution with sodium trifluoroacetate as a standard. The data for metal complexes is reported using the five most intense peaks from the isotopic envelope, and is listed as m/z with the intensity relative to the most abundant peak of the isotopic envelope given in parentheses for both the calculated and observed peaks. The difference between calculated and observed peaks is reported in ppm. For isolated organic products, the monoisotopic peak is reported, with observed, calculated, and ppm difference again provided. Thin layer chromatography was performed on a Uniplat silica gel GF from Analtech Inc. Methylene chloride and benzene were all run down a column packed with activated alumina and purged with nitrogen prior to use. All other solvents and chemicals were used as received from Sigma-Aldrich, Acros Chemicals or Fischer Scientific. Compound **1** was previously reported.<sup>1</sup>

### **TpW(NO)(PMe<sub>3</sub>)( $\eta^2$ -phenol) (**1b**)**

In an Erlenmeyer flask with a ground glass joint 40 mL methanol was purged for 10 min with argon. TpW(NO)(PMe<sub>3</sub>)( $\eta^2$ -phenol) (**1a,b**) (4.068g, 6.814 mmol) and a stir bar were added. The reaction was purged for 5 min and DBU (0.249g, 1.596 mmol) was added. The flask was sealed with a glass stopper. After 3 d the reaction was filtered and washed with 2 mL methanol and dried *in vacuo*. A light yellow precipitate was collected **1b** (3.298g, 81% yield.) Since ketenes react with methanol the solid was reprecipitated using methylene chloride (10 mL) and hexanes (400 mL) to remove any remaining methanol prior to the synthesis of **2a,b**, **3a,b**, **4a,b** and **5**.

### **TpW(NO)(PMe<sub>3</sub>)( $\eta^2$ -4,5-(7-chlorobicyclo[4.2.0]oct-4-ene-3,8-dione)) (**2a,b**)**

In a glovebox under a dinitrogen atmosphere, using flame dried glassware, a solution of chloroacetylchloride (0.140g, 1.24 mmol) in 75 mL CH<sub>2</sub>Cl<sub>2</sub> was slowly added drop-wise to a well stirred solution of **1b** (0.500g, 0.838 mmol) and DIEA (0.167g, 1.29

mmol) in 25 mL CH<sub>2</sub>Cl<sub>2</sub>. After about 1 hour the addition was complete and the reaction was removed from the glovebox. HCl<sub>(aq)</sub> (1M, 100 mL) was added and the CH<sub>2</sub>Cl<sub>2</sub> layer was extracted, dried with MgSO<sub>4</sub>, filtered and evaporated by rotatory evaporation. The residue was dissolved in 1 mL CH<sub>2</sub>Cl<sub>2</sub>. Diethyl ether (10 mL) was slowly added and the resulting precipitate was filtered, washed with five 10 mL portions of ether and dried *in vacuo*. The light beige precipitate was isolated as a mixture of two diastereomers (**2a,b**, 1.4:1 dr, 0.517g, 92 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.12 (d, 9H, J=8.4 Hz, PMe<sub>3</sub> A), 1.17 (d, 9H, J=8.7 Hz, PMe<sub>3</sub> B), 2.01 (d, 1H, J=9.6 Hz, H4 A), 2.18 (d, 1H, J=9.6 Hz, H4 B), 2.58 (d, 1H, J=18.0, H2 B), 2.64 (d, 1H, J=16.8, H2 A), 2.87 (m, 2H, H2 A and B), 3.26 (dd, 1H, J=13.2, 9.6 Hz, H5 A), 3.35 (dd, 1H, J=9.3, 6.9 Hz, H6 B), 3.46 (dd, 1H, J=12.6, 9.6 Hz, H5 B), 3.69 (br t, J=9.3 Hz, H1 A), 3.87 (m, 2H, H6 A, H1 B) 4.77 (dd, J=6.9, 3.0 Hz, H7 B), 5.22 (dd, J=9.0, 2.1 Hz, H7 A), 6.09 (t, 1H, J=2.4 Hz, Tp), 6.11 (t, 1H, J=2.4 Hz, Tp), 6.22 (t, 1H, J=2.4 Hz, Tp), 6.24 (t, 1H, J=2.4 Hz, Tp), 6.34 (t, 1H, J=2.4 Hz, Tp), 6.35 (t, 1H, J=2.4 Hz, Tp), 7.31 (d, 1H, J=2.4 Hz, Tp), 7.36 (d, 1H, J=2.4 Hz, Tp), 7.42 (d, 1H, J=2.4 Hz, Tp), 7.45 (d, 1H, J=2.4 Hz, Tp), 7.54 (d, 1H, J=2.4 Hz, Tp), 7.68 (d, 1H, J=2.4 Hz, Tp), 7.70 (d, 1H, J=2.4 Hz, Tp), 7.76 (d, 1H, J=2.4 Hz, Tp), 8.09 (d, 1H, J=2.4 Hz, Tp). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.5 (d, J=32 Hz, PMe<sub>3</sub> A), 12.9 (d, J=30 Hz, PMe<sub>3</sub> B), 31.8 (s, C2 B), 32.3 (s, C2 A), 32.9 (d, J=4.0 Hz, C6 A) 41.4 (d, J=3.0 Hz, C6 B), 54.7(s, C1 B), 55.1 (s, C1 A), 57.3 (d, J=12 Hz, C5 A), 59.4 (s, C4 B), 60.6 (s, C4 A), 65.1 (d, J=13, C5 B), 68.5 (s, C7 A), 73.1 (s, C7 B), 106.1 (s, Tp), 106.2 (s, Tp), 106.8 (s, Tp), 106.9 (s, Tp), 107.3 (s, Tp), 107.4 (s, Tp), 136.3 (s, Tp), 136.4 (s, Tp), 136.9 (s, Tp), 137.2 (s, 2Tp), 139.9 (s, Tp), 140.0 (s, Tp), 142.7 (s, Tp), 143.1 (s, 2Tp), 143.6 (s, 2Tp), 202.0 (s, C8 A), 203.8 (s, C3 B), 204.2 (s, C8 A), 205.7 (s, C3 B). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -8.0 (A), -8.8 (B). IR: ν<sub>NO</sub> = 1567, ν<sub>CO</sub> = 1621, ν<sub>CO</sub> = 1787 cm<sup>-1</sup>. CV: E<sub>p,a</sub> = +1.14 V. Anal Calc'd for C<sub>20</sub>H<sub>26</sub>BCIN<sub>7</sub>O<sub>3</sub>PW·CH<sub>2</sub>Cl<sub>2</sub>: C, 33.25; H, 3.72; N, 12.93. Found: C, 33.72; H, 3.78; N, 13.00. HRMS:[M + H]<sup>+</sup> obs'd (%), calc'd (%), diff. in ppm: 672.11771 (65.9), 672.11807 (67.1), -0.5; 673.11983 (62.5), 673.12046 (67.0), -0.9; 674.11835 (100.0), 674.11931 (100.0), -1.4; 675.12128 (49.3), 675.12207 (52.8), -1.2; 676.12037 (89.6), 676.12200 (91.4), -2.4.

**TpW(NO)(PMe<sub>3</sub>)(η<sup>2</sup>-4,5-(7-(3-methoxyphenyl)bicyclo[4.2.0]oct-4-ene-3,8-dione))**  
**(3a,b)**

In a glovebox under a dinitrogen atmosphere, using flame dried glassware, a solution of oxalyl chloride (1.608g, 12.66 mmol) in 1 mL benzene was added to 3-methoxyphenylacetic acid (0.128g, 0.771 mmol). After 4 h the solvent was removed via evacuation. 1 mL benzene was added, evacuated to remove any remaining oxalyl chloride. The resulting oil was dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub> and slowly added dropwise to a well stirred solution of **1b** (0.199g, 0.333 mmol) and DIEA (0.101g, 0.783 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub>. After about 30 minutes the addition was complete and the reaction was removed from the glovebox. HCl<sub>(aq)</sub> (1M, 40 mL) was added and the CH<sub>2</sub>Cl<sub>2</sub> layer was extracted, dried with MgSO<sub>4</sub>, filtered and evaporated using rotatory evaporation. Acetone (15 mL) was added to the residue and the mixture was vigorously stirred. After 15 minutes the reaction was filtered and washed with 1 mL acetone, yielding an off-white solid (**3a**, 0.072 g, 29 %yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.09 (d, 9H, J=8.7 Hz, PMe<sub>3</sub>), 2.26 (d, 1H, J=9.3 Hz, H4), 2.72 (d, 1H, J=18.0 Hz, H2), 2.98 (dd, 1H, J=18.0, 12.0 Hz, H2),

3.51 (m, 2H, H6, H5), 3.80 (m buried, H1), 3.80 (s, 3H, OMe), 4.41 (dd, 1H, J=7.2, 2.4 Hz, H7), 6.16 (d, 1H, J=2.4 Hz, Tp), 6.23 (d, 1H, J=2.4 Hz, Tp), 6.37 (d, 1H, J=2.4 Hz, Tp), 6.78-6.88 (m, 3H), 7.27 (m, 1H), 7.33 (t, 1H, J=2.4 Hz, Tp), 7.53 (t, 1H, J=2.4 Hz, Tp), 7.56 (t, 1H, J=2.4 Hz, Tp), 7.70 (t, 1H, J=2.4 Hz, Tp), 7.77 (t, 1H, J=2.4 Hz, Tp), 8.13 (t, 1H, J=2.4 Hz, Tp). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.7 (d, J=29 Hz), 32.7 (s), 37.8 (s), 55.5 (s), 56.5 (s), 60.2 (s), 67.9 (d, J=13 Hz), 78.3 (s), 106.4 (s), 106.7 (s), 107.4 (s), 112.6 (s), 113.3 (s), 119.6 (s), 130.2 (s), 136.2 (s), 137.0 (s), 137.1 (s), 138.5 (s), 140.0 (s), 143.0 (s), 143.6 (s), 160.2 (s), 206.7 (s), 210.8 (s).

The filtrate was added to 50 mL hexane and the resulting precipitate was collected by filtration (**3b**, 0.128g, 52% yield.) <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.97 (d, 9H, J=8.4 Hz, PMe<sub>3</sub>), 2.04 (d, 1H, J=9.6 Hz, H4), 2.66 (dd, 1H, J=13.8, 9.6 Hz, H5), 2.80 (d, 1H, J=17.1 Hz, H2), 2.98 (dd, 1H, J=17.1, 7.5 Hz, H2), 3.72 (s, 3H, OMe), 3.92 (m, 2H, H1, H6), 4.90 (dd, 1H, J=9.0, 3.0 Hz, H7), 6.11 (t, 1H, J=2.1 Hz, Tp), 6.14 (t, 1H, J=2.1 Hz, Tp), 6.35 (t, 1H, J=2.1 Hz, Tp), 6.65 (d, 1H, J=2.1 Hz, Tp), 6.83-6.92 (m, 3H), 7.24 (m, 1H), 7.52 (d, 1H, J=2.1 Hz, Tp), 7.53 (d, 1H, J=2.1 Hz, Tp), 7.62 (d, 1H, J=2.1 Hz, Tp), 7.74 (d, 1H, J=2.1 Hz, Tp), 8.11 (d, 1H, J=2.1 Hz, Tp). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.7 (d, J=29 Hz, PMe<sub>3</sub>), 32.9 (s, C2), 33.3 (d, J=4 Hz, C6), 55.4 (s, OMe), 57.1 (s, C1), 61.2 (s, C4), 61.5 (d, J=12.0, C5), 71.4 (s, C7), 106.0 (s, Tp), 106.7 (s, Tp), 107.3 (s, Tp), 114.2 (s, Ph), 114.8 (s, Ph), 122.6 (s, Ph), 129.4 (s, Ph), 135.2 (s, Ph), 136.2 (s, Tp), 136.8 (s, Tp), 137.1 (s, Tp), 139.2 (s, Tp), 143.1 (s, Tp), 143.6 (s, Tp), 159.5 (s, Ph), 205.4 (s, C3), 210.1 (s, C8). IR: ν<sub>NO</sub> = 1565, ν<sub>CO</sub> = 1600, ν<sub>CO</sub> = 1766 cm<sup>-1</sup>. CV: E<sub>p,a</sub> = +0.94 V. Anal Calc'd for C<sub>27</sub>H<sub>33</sub>BN<sub>7</sub>O<sub>4</sub>PW·CH<sub>2</sub>Cl<sub>2</sub>: C, 40.51; H, 4.25; N, 11.91. Found: C, 40.82; H, 4.25; N, 11.81.

#### **TpW(NO)(PMe<sub>3</sub>)(η<sup>2</sup>-4,5-(7,7-dichlorobicyclo[4.2.0] oct-4-ene-3,8-dione)) (4)**

Diisopropylethylamine (0.043g, 0.34 mmol) was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>, added to **1b** (0.100g, 0.168 mmol) and stirred. Dichloroacetylchloride (0.049g, 0.34 mmol) was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> and slowly added dropwise via a separatory funnel over about 20 minutes. The reaction was removed from the glovebox and HCl<sub>(aq)</sub> (1M, 20 mL) was added. The reaction was extracted, dried with MgSO<sub>4</sub> and evaporated using rotatory evaporation. 2 mL EtOAc was added and the reaction was stirred. After 5 minutes the reaction was filtered, washed twice with 1 mL EtOAc, dried *in vacuo*. A light beige precipitate was isolated (**4**, 0.077g, 65% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.18 (d, 9H, J=8.4 Hz, PMe<sub>3</sub>), 2.18 (d, 1H, J=9.6 Hz, H4), 2.74 (d, 1H, J=17.5 Hz, H2), 2.89 (dd, 1H, J=17.5, 10.4 Hz, H2), 3.34 (dd, 1H, J=12.9, 9.6 Hz, H5), 3.95 (d, 1H, J=10.4 Hz, H6), 4.27 (t, 1H, J=10.4 Hz, H1), 6.14 (t, J=2.1 Hz, Tp), 6.28 (t, J=2.1 Hz, Tp), 6.39 (t, J=2.1 Hz, Tp), 7.37 (d, J=2.1 Hz, Tp), 7.43 (d, J=2.1 Hz, Tp), 7.56 (d, J=2.1 Hz, Tp), 7.72 (d, J=2.1 Hz, Tp), 7.79 (d, J=2.1 Hz, Tp), 8.13 (d, J=2.1 Hz, Tp). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.6 (d, J=29 Hz), 32.0 (s), 49.3 (d, J=4 Hz), 54.9 (s), 59.5 (d, J=12 Hz), 60.1 (s), 93.3 (s), 106.3 (s), 107.0 (s), 107.5 (s), 136.5 (s), 137.1 (s), 137.3 (s), 139.9 (s), 143.2 (s), 143.7 (s), 197.1 (s), 203.8 (s). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -10.1. IR: ν<sub>NO</sub> = 1563, ν<sub>CO</sub> = 1621, ν<sub>CO</sub> = 1798 cm<sup>-1</sup>. CV: E<sub>p,a</sub> = +1.18 V. Anal Calc'd for C<sub>20</sub>H<sub>25</sub>BCl<sub>2</sub>N<sub>7</sub>O<sub>3</sub>PW: C, 33.93; H, 3.56; N, 13.85. Found: C, 33.65; H, 3.61; N, 13.36.

**TpW(NO)(PMe<sub>3</sub>)( $\eta^2$ -4,5-(8-hydroxy-7-(3-methoxyphenyl)bicyclo[4.2.0] oct-4-ene-3-one)) (5)**

A solution of **3a** (0.050g, 0.067 mmol) in 0.5 mL of 1:1 CH<sub>2</sub>Cl<sub>2</sub> : MeOH was added to NaBH<sub>4</sub>. After 5 minutes 1 mL H<sub>2</sub>O was added. The CH<sub>2</sub>Cl<sub>2</sub> layer was extracted, dried over MgSO<sub>4</sub> and evaporated by rotatory evaporation. The residue was dissolved in 0.25 mL CH<sub>2</sub>Cl<sub>2</sub>, precipitated into 50 mL hexanes, filtered and dried *in vacuo*. The precipitate was isolated as an off-white solid (**5**, 0.33g, 66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 0.87 (d, 9H, J=8.1 Hz, PMe<sub>3</sub>), 2.23 (d, 1H, J=9.6 Hz, H4), 2.41 (d, 1H, J=2.7 Hz, OH), 2.50 (d, 1H, J=17.1 Hz, H2), 3.00 (dd, 1H, J=17.1, 7.8 Hz, H2), 3.09 (dd, 1H, J=14.1, 9.6 Hz, H5), 3.27 (q, 1H, J= 7.8 Hz, H1), 3.74 (s, OMe), 3.93 (m, 2H, H6, H7), 4.79 (m, 1H, H8), 6.14 (m, 2H), 6.32 (t, 1H, J=2.1 Hz), 6.83 (m, 1H), 6.91 (d, 1H, J= 2.1 Hz), 7.18 (m, 1H), 7.52 (m, 2H), 7.62 (m, 2H), 7.72 (d, J=2.1 Hz), 8.08 (d, J=2.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 12.7 (d, J=29 Hz, PMe<sub>3</sub>), 33.5 (s, C2), 39.6 (s, C3), 39.8 (d, J=4 Hz, C4), 51.7 (s, C8), 55.4 (s, OMe), 61.6 (s, C6), 63.9 (d, J=11 Hz, C5), 73.5 (s, C7), 106.2 (s, Tp), 106.6 (s, Tp), 107.1 (s, Tp), 113.7 (s), 116.3 (s), 124.0 (s), 128.8 (s, 2C), 135.9 (s), 136.6 (s), 136.8 (s), 143.6 (s, 3C), 159.0 (s), 210.6 (s). IR:  $\nu_{\text{NO}}$  = 1563,  $\nu_{\text{CO}}$  = 1595,  $\nu_{\text{OH}}$  = 3498 cm<sup>-1</sup>. CV: E<sub>p,a</sub> = +0.74 V. Anal Calc'd for C<sub>27</sub>H<sub>35</sub>BN<sub>7</sub>O<sub>4</sub>PW: C, 43.40; H, 4.72; N, 13.12. Found: C, 43.02; H, 4.66; N, 12.83.

**8-hydroxy-7-(3-methoxyphenyl)bicyclo[4.2.0] oct-4-ene-3-one (6)**

A solution of N-Bromosuccinimide (0.019g, 0.11 mmol) in 0.5 mL CH<sub>3</sub>CN and 0.5 mL CH<sub>2</sub>Cl<sub>2</sub> was added to **6** (0.040g, 0.054 mmol). After 10 minutes the solvent was removed by rotatory evaporation. The reaction was chromatographed using a 20 x 20, 500  $\mu$ M preparatory TLC plate using 1:1 EtOAc:hexanes as the eluent. Compound **7** (0.0063g, 48%, R<sub>f</sub> = 0.24) was isolated as a colorless oil. The recovery of the metal complex was not attempted. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 1.95 (br s, 1H), 2.49 (dd, 1H, J=18.0, 7.8 Hz), 2.64 (dd, 1H, J=18.0, 1.8 Hz), 3.25 (q, 1H, J=6.3 Hz), 3.49 (m, 1H), 3.79 (s, 3H), 4.00 (dd, 1H, J=9.3, 5.7 Hz), 4.71 (td, 1H, J=5.7, 2.7 Hz), 6.18 (dd, 1H, J=10.5, 2.1 Hz), 6.80-6.95 (m, 4H), 7.24 (t, 1H, J=8.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 33.8 (s), 35.1 (s), 38.4 (s), 49.5 (s), 55.4 (s), 74.7 (s), 112.5 (s), 115.7 (s), 122.1 (s), 129.6 (s), 130.5 (s), 137.3 (s), 149.7 (s), 159.8 (s), 198.4 (s). IR:  $\nu_{\text{CO}}$  = 1662,  $\nu_{\text{OH}}$  = 3415 cm<sup>-1</sup>. HRMS: [C<sub>15</sub>H<sub>16</sub>O<sub>3</sub> + Na<sup>+</sup>] obs'd (%), calc'd (%), diff. in ppm: 267.09938 (100), 267.09917 (100), 0.8.

**TpW(NO)(PMe<sub>3</sub>)( $\eta^2$ -4,5-(3-oxobicyclo[4.1.0]hept-4-ene-7-carboxylic acid methyl ester)) (7)**

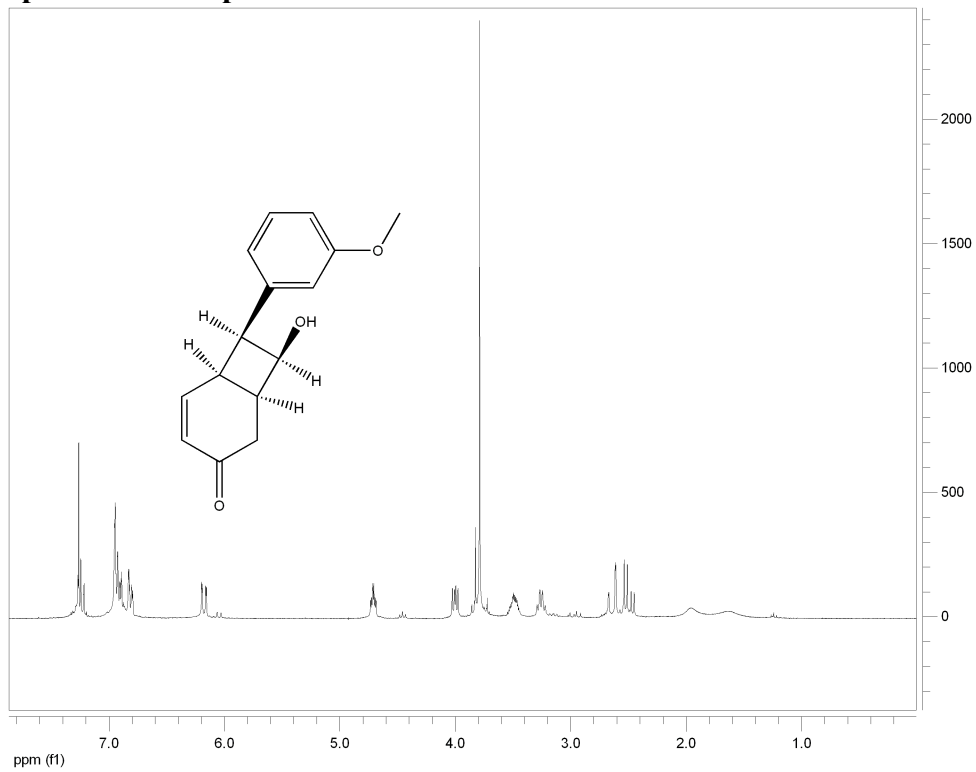
A mixture of LiOMe (0.005g, 0.13 mmol) in 0.25 mL methanol was added to a solution of **2a,b** (0.050g, 0.074 mmol) in 0.25 mL CH<sub>2</sub>Cl<sub>2</sub>. After 3 hours the solvent was removed by rotatory evaporation. The residue was dissolved in 1 mL CH<sub>2</sub>Cl<sub>2</sub> and extracted with 3 mL water. The organic layer was dried with MgSO<sub>4</sub>, filtered and removed by rotatory evaporation. The residue was dissolved in 0.25 mL methylene chloride, then 2 mL Et<sub>2</sub>O and 4 mL hexanes were added. The reaction was filtered and dried *in vacuo*. An off-white precipitate (**7**, 0.029g, 58% yield) was isolated. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 1.21 (d, 9H, J=8.7 Hz, PMe<sub>3</sub>), 1.65 (dd, 1H, J=4.5, 3.6 Hz, H7), 1.97 (d, 1H, J=9.6 Hz, H4), 2.08 (m,

1H, H1), 2.21 (dd, 1H, J=9.3, 3.6 Hz, H6), 2.68 (d, 1H, J=18.0 Hz, H2), 3.01 (dd, 1H, J=18.0, 5.4 Hz, H2), 3.47 (dd, 1H, J=12.0, 9.6 Hz, H5), 3.68 (s, 3H, OMe), 6.12 (t, 1H, J=2.4 Hz, Tp), 6.21 (t, 1H, J=2.4 Hz, Tp), 6.36 (t, 1H, J=2.4 Hz, Tp), 7.28 (d, 1H, J=2.4 Hz, Tp), 7.53 (d, 2H, J=2.4 Hz, Tp), 7.68 (d, 1H, J=2.4 Hz, Tp), 7.75 (d, 1H, J=2.4 Hz, Tp), 8.15 (d, 1H, J=2.4 Hz, Tp). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ13.1 (d, J=29 Hz, PMe<sub>3</sub>), 24.7 (s, C1), 29.6 (d, J=3 Hz, C6), 31.9 (s, C7), 35.4 (c, C2), 51.7 (s, Me), 60.2 (s, C4), 63.9 (s, C5), 106.1 (s, Tp), 106.5 (s, Tp), 107.3 (s, Tp), 136.0 (s, Tp), 140.0 (s, Tp), 143.0 (s, Tp), 143.8 (s, Tp), 174.7 (s, C8), 207.2 (s, C3). IR: ν<sub>NO</sub> = 1571, ν<sub>CO</sub> = 1598 ν<sub>CO</sub> = 1712 cm<sup>-1</sup>. CV: E<sub>p,a</sub> = +0.86 V. Anal Calc'd for C<sub>21</sub>H<sub>29</sub>BN<sub>7</sub>O<sub>4</sub>PW: C, 37.69; H, 4.37; N, 14.65. Found: C, 37.34; H, 4.49; N, 14.23.

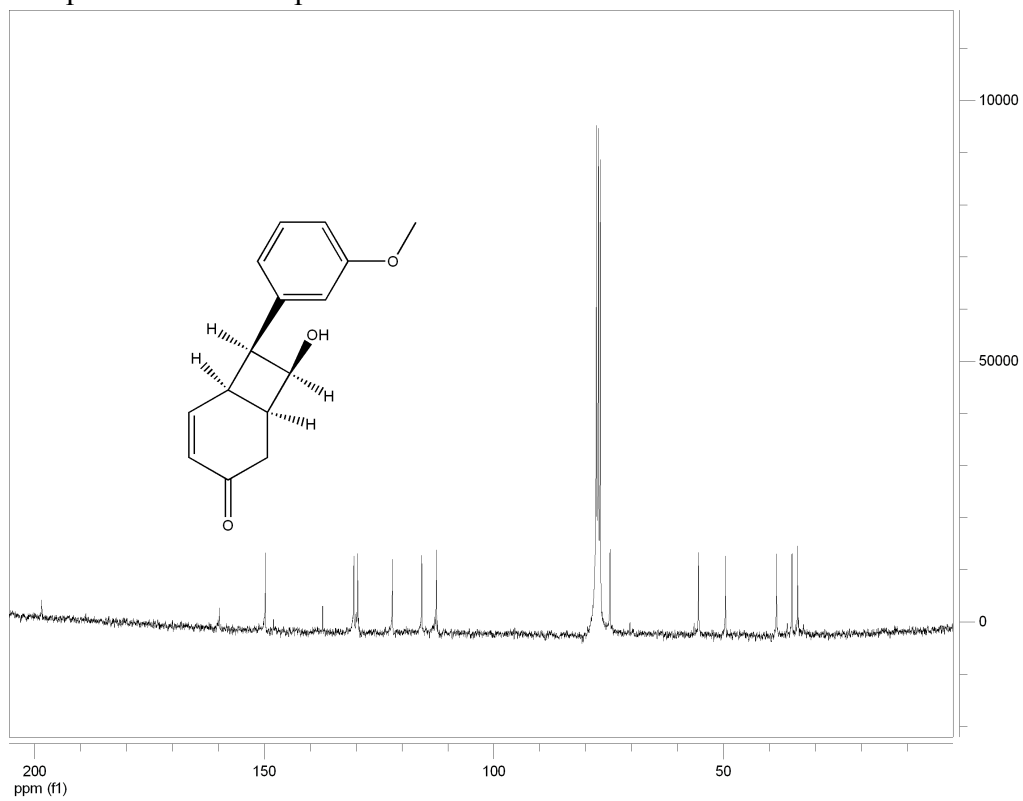
**TpW(NO)(PMe<sub>3</sub>)(η<sup>2</sup>-4,5-(3-Oxo-bicyclo[4.2.0]octa-4,7-diene-7,8-dicarboxylic acid dimethyl ester)) (8)**

Dimethyl acetylenedicarboxylate (0.146g, 1.03 mmol) was dissolved in 0.25 mL CH<sub>2</sub>Cl<sub>2</sub> and added to **1b** (0.050g, 0.084 mmol) and heated at 50 °C. After 6.5 h the solvent was removed by applying a N<sub>2</sub> stream under vacuum. When the residue was completely dry 0.25 mL CH<sub>2</sub>Cl<sub>2</sub> was added and this solution was added to 50 mL hexanes. The yellow precipitate was collected by filtration and dried *in vacuo*. The precipitate (0.057g) contained mostly **9** with traces of several other very minor complexes. This mixture was purified by preparatory thin layer chromatography using a 20 x 20 cm, 500 μM silica plate with ethyl acetate as the mobile phase. **8** (0.0085g) was isolated from a band (R<sub>f</sub> = 0.49) that contained a 40% paramagnetic impurity by electrochemistry. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ1.19 (d, 9H, J=8.7 Hz, PMe<sub>3</sub>), 1.75 (d, 1H, J=9.9 Hz), 2.59 (d, 1H, J=16.8 Hz), 3.08 (dd, 1H, J=16.8, 9.0 Hz), 3.47 (dd, 1H, J=9.0, 4.2 Hz), 3.53 (dd, 1H, J=12.9, 9.9 Hz), 3.76 (s, 3H), 3.82 (s, 3H), 3.92 (d, 1H, J=4.2), 6.18 (t, 1H, J=2.4 Hz, Tp), 6.31 (t, 1H, J=2.4 Hz, Tp), 6.45 (t, 1H, J=2.4 Hz, Tp), 7.44 (d, 1H, J=2.4 Hz, Tp), 7.46 (d, 1H, J=2.4 Hz, Tp), 7.73 (d, 1H, J=2.4 Hz, Tp), 7.88 (d, 1H, J=2.4 Hz, Tp), 7.93 (d, 1H, J=2.4 Hz, Tp), 8.17 (d, 1H, J=2.4 Hz, Tp). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ13.0 (d, J=29 Hz), 31.2 (s), 36.3 (s), 41.9 (s), 42.5 (s), 52.0 (s), 52.2 (s), 60.8 (s), 62.3 (d, J=12 Hz), 106.3 (s), 106.6 (s), 107.3 (s), 136.1 (s), 136.8 (s), 137.0 (s), 140.1 (s), 143.0 (s), 143.5 (s), 145.2 (s), 149.6 (s), 161.7 (s), 162.4 (s), 208.0 (s). <sup>31</sup>P NMR (CD<sub>3</sub>CN): δ-8.0. IR: ν<sub>NO</sub> = 1567, ν<sub>CO</sub> = 1618, ν<sub>CO</sub> = 1713 cm<sup>-1</sup>. CV: E<sub>p,a</sub> = +1.03 V. Ms (ESI): [MH<sup>+</sup>] = 740.

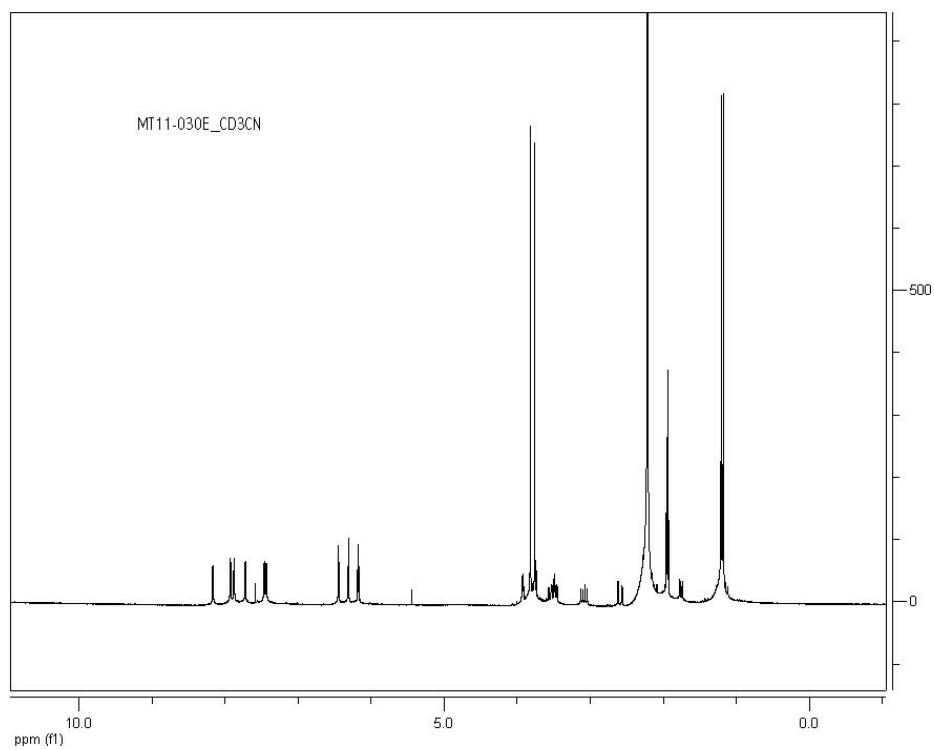
**Spectra for compounds 6 and 8.**



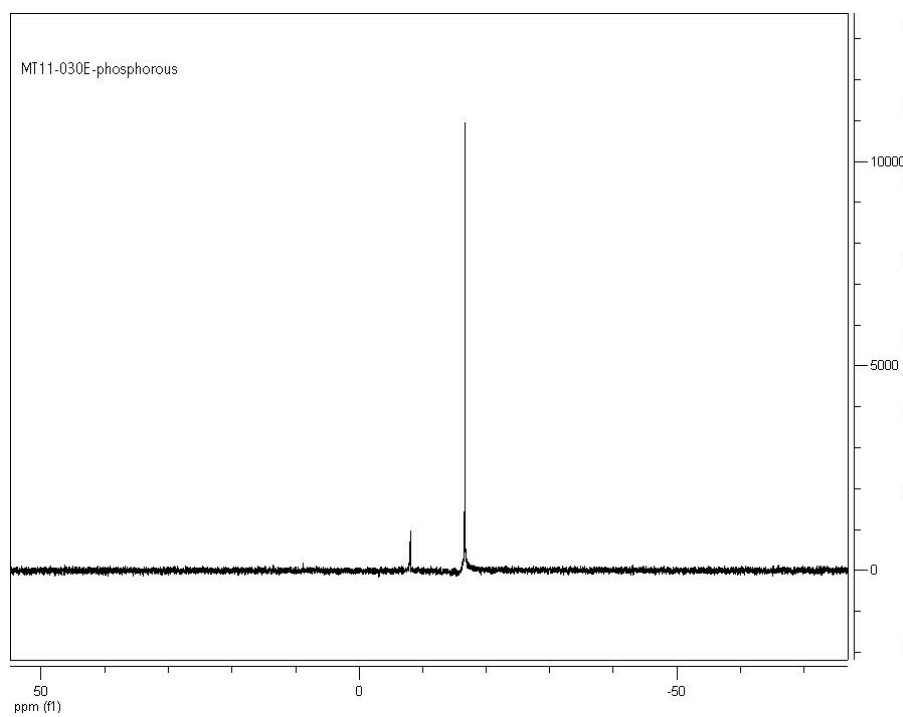
**Compound 6 HNMR spectrum.**



Compound **6**  $^{13}\text{C}$  NMR spectrum.

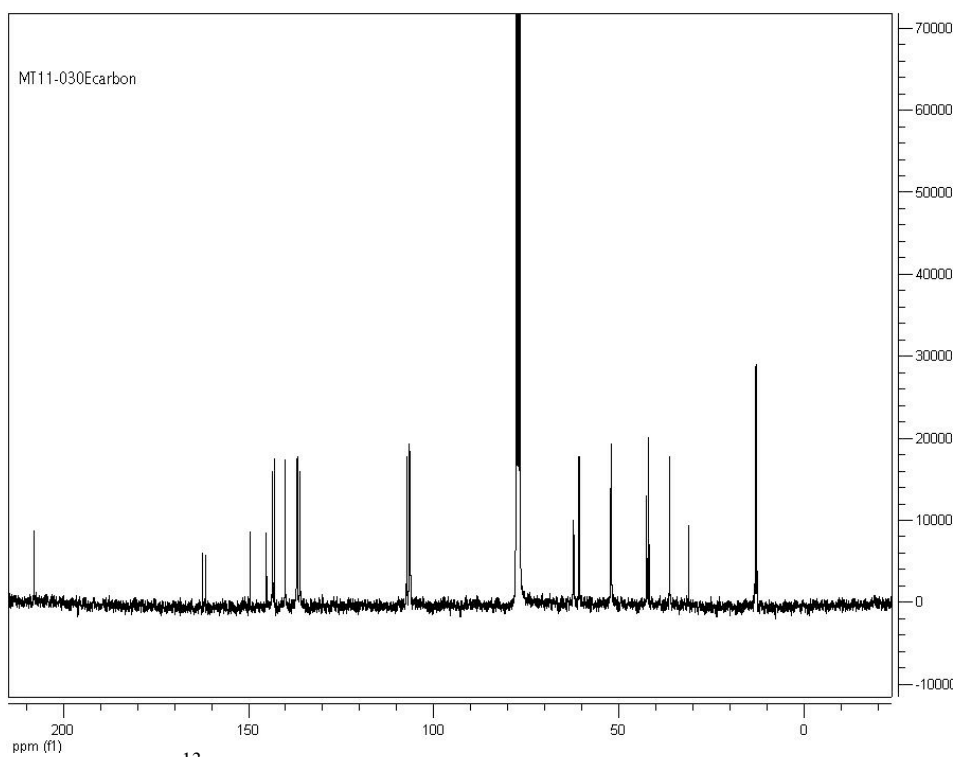


Compound **8**  $^1\text{H}$  NMR spectrum.



Compound **8**  $^{31}\text{P}$  NMR spectrum.





Compound **8**  $^{13}\text{C}$  NMR spectrum.