

## Experimental Procedures.

### Physical Techniques.

X-band EPR spectra were recorded using a Bruker ESP300 Electron Spin Resonance Spectrometer. Temperature regulation was achieved using a Bruker Variable Temperature Unit.  $\text{I}^+\text{PF}_6^-$  was generated *in situ* by reacting **I** with 0.95 equivalents of  $\text{Cp}_2\text{Fe}^+\text{PF}_6^-$  in 2-Me-THF.

UV/Vis/NIR spectra were recorded using a PerkinElmer Lambda 900 UV/Vis/NIR spectrometer, with nitrogen purging. A 1.00 mm or 10.00 mm IR quartz cell was employed. A spectrum of the neat solvent (THF) was subtracted.

Raman spectra were recorded using a Renishaw System 1000 and its associated He/Ne laser operating at 632.8 nm using a sample of **I** packed in a capillary and sealed under an inert atmosphere.

The  $^1\text{H}$  NMR spectrum of **I** was recorded on a 400 MHz Bruker DPX Avance spectrometer and referenced to residual proton signals of  $d_8$ -THF at  $\delta = 3.58$ . Values are quoted in ppm.

The Cyclic voltammogram and differential pulse voltammogram of **I** were collected with a scan rate of  $100 \text{ mVs}^{-1}$  and  $5 \text{ mVs}^{-1}$  respectively, using a Princeton Applied Research (PAR) 173A potentiostat-galvanostat equipped with a PAR 176 current-to-voltage converter. Electrochemical measurements were performed under an inert atmosphere in a 0.5 M solution of  $^n\text{Bu}_4\text{NPF}_6$  in THF inside a single-compartment voltammetric cell, equipped with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode.. The potential values are

referenced to the Fc/Fc<sup>+</sup> couple, obtained by addition of a small amount of FeCp<sub>2</sub> to the solution.

Microanalysis was performed by Atlantic Microlab, Inc.

### Synthesis.

All manipulations were performed in a nitrogen-filled glovebox, or by using standard Schlenk line techniques. All solvents were dried using standard procedures, and degassed prior to use.

#### **[(<sup>t</sup>BuCO<sub>2</sub>)<sub>3</sub>W<sub>2</sub>]<sub>2</sub>(μ-H<sub>2</sub>C<sub>4</sub>N<sub>2</sub>O<sub>2</sub>) (I).**

A Schlenk tube was charged with 1.50g of W<sub>2</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>4</sub> (1.94 mmol) and 109mg of 3,6-dihydroxypyridazine (0.97 mmol). Toluene (5ml) was added and the suspension stirred for 6 days, during which time the solution turned purple. The microcrystalline product was isolated by filtration and washed with toluene (1 x 5ml) and hexanes (2 x 5ml) then dried *in vacuo* to yield 835mg of a purple solid.

**Yield:** 64%

**d<sup>1</sup>H (d<sub>8</sub>-THF):** 6.19 (2H, s), 1.34 (36H, s), 1.29 (18H, s).

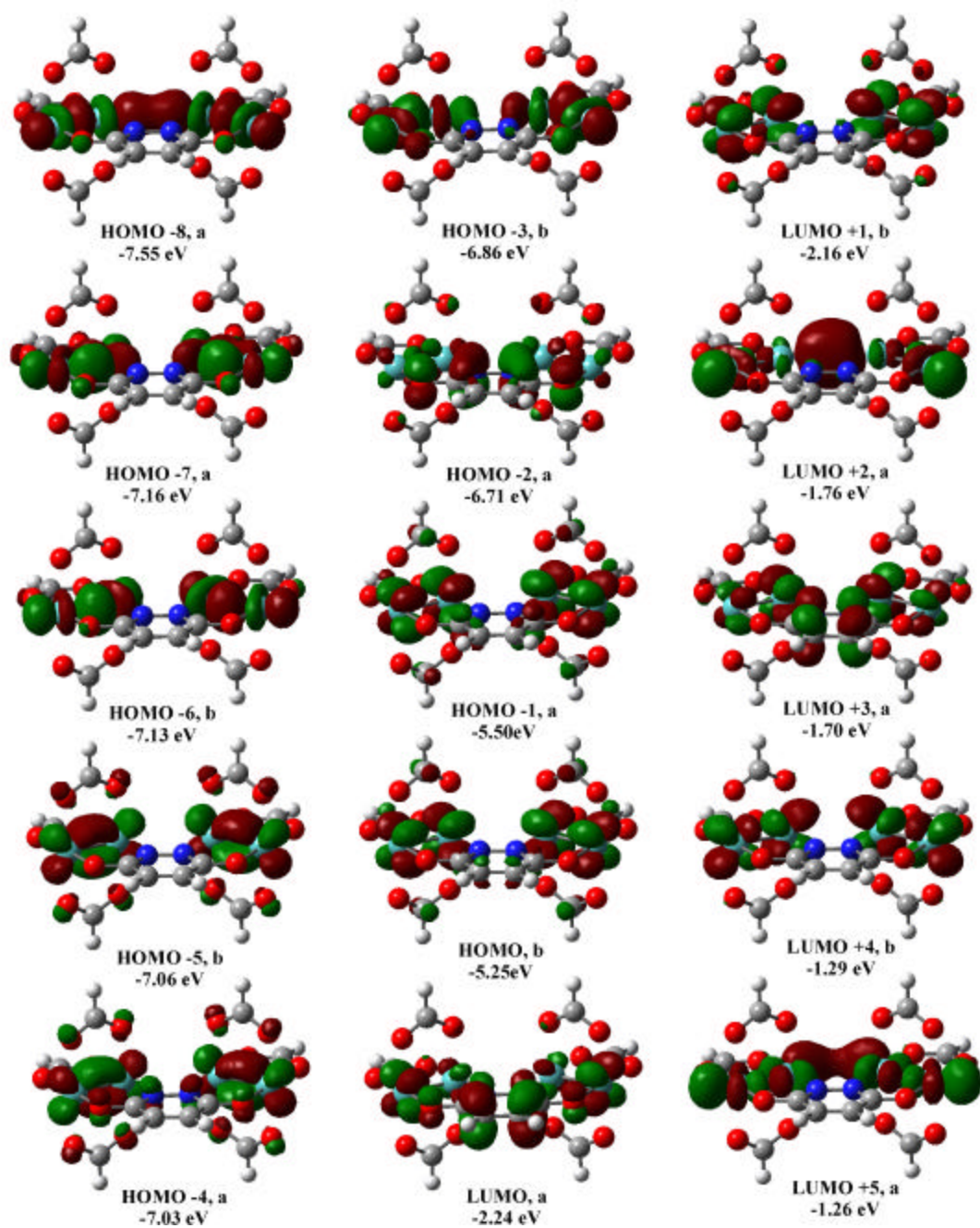
**Microanalysis:** Found, C 26.28, H 3.89, N 1.82%. Calcd. For C<sub>30</sub>H<sub>56</sub>N<sub>2</sub>O<sub>10</sub>W<sub>4</sub>, C 26.88, H 4.21, N 2.09%.

#### **[(<sup>t</sup>BuCO<sub>2</sub>)<sub>3</sub>W<sub>2</sub>]<sub>2</sub>(μ-H<sub>2</sub>C<sub>4</sub>N<sub>2</sub>O<sub>2</sub>)<sup>+</sup>PF<sub>6</sub><sup>-</sup> (I<sup>+</sup>PF<sub>6</sub><sup>-</sup>).**

A Schlenk tube was charged with 300mg of I (0.22mmol) and 57mg of AgPF<sub>6</sub> (0.22mmol) and THF (5ml) added. The solution turned blue and was stirred for one hour,

then filtered through celite. The solvent was removed *in vacuo* to yield 280mg of a dark blue solid.

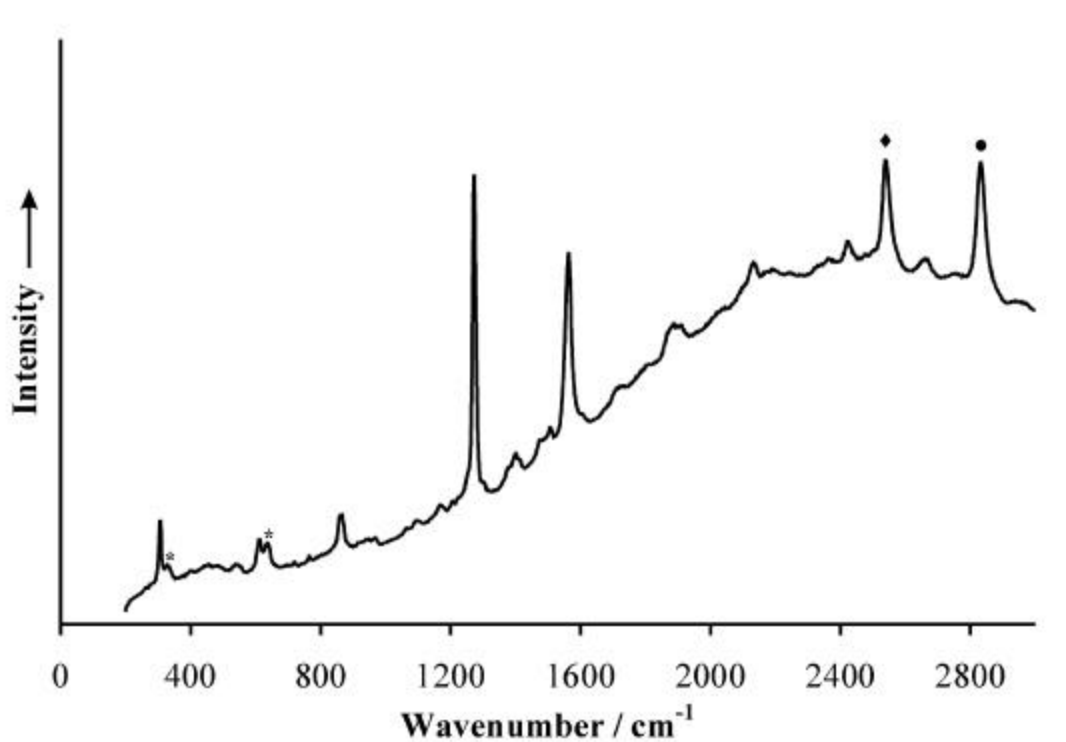
**Yield:** 84%



**Fig. S1** Frontier molecular orbital plots calculated for  $[(t\text{BuCO}_2)_3\text{Mo}_2](\mu\text{-H}_2\text{C}_4\text{N}_2\text{O}_2)$ .

Orbitals are drawn at an isosurface value of 0.04.

**Fig. S2** The differential pulse voltammogram (top) and cyclic voltammogram (bottom) of **I** recorded in THF.



**Fig. S3** Resonance Raman spectrum of **I** recorded with 632.8 nm excitation. Satellite peaks marked with \* denote unidentified bands. Peaks marked by ? and ? are an overtone of the band at 1273  $\text{cm}^{-1}$  and a combination of the 1273 and 1566  $\text{cm}^{-1}$  bands respectively. Assignments of the remaining resonance enhanced bands are given in the main text (table 2). They are assigned by inspection of the calculated frequencies that correspond to vibrations of the  $W_2$  bond or 3,6-dioxypyridazine bridge.