

Supporting Information for

Reactivity of a Biomimetic W(IV) Bis-Dithiolene Complex with CO₂ Leading to Formate Production and Structural Rearrangement

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General

All syntheses and manipulations prior to the addition of carbon dioxide gas were performed under an Argon atmosphere using an MBraun glovebox (<0.1 ppm O₂, <0.1 ppm H₂O) or standard Schlenk techniques. Solvents were purified by passing through alumina columns under an Argon atmosphere (MBraun solvent purification system) and stored over 4 Å molecular sieves. ¹³CO₂ (91.2 % ¹³C enriched) and C¹⁸O₂ (98 % ¹⁸O enriched) were purchased from ICON and used as received. CO₂ (99.998%) was purchased from Specialty Gases of America and used after passing through oxygen scrubber (RESTEK) and the activated molecular sieves. Complex (Et₄N)₂[WO(S₂C₂Me₂)₂] (**1**) was synthesized following the literature procedure.¹ Elemental analysis was carried out by Columbia Analytical Services (Tucson, AZ). UV-Vis spectrum was recorded on a Varian Cary 50 Bio spectrometer. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. GC-MS data were recorded using a Hewlett-Packard (Agilent) GCD 1800C GC-MS spectrometer. ¹H and ¹³C NMR spectra were recorded on Bruker Advance DRX-400 MHz NMR spectrometer. ¹H and ¹³C chemical shift are referenced to residual protio solvent signals.

(1) C. A. Goddard, and R. H. Holm, *Inorg. Chem.*, 1999, **38**, 5389.

Synthesis of (Et₄N)₂[W₂O₂(μ-S)(μ-S₂C₂Me₂)(S₂C₂Me₂)₂] (**2**)

A solution of 20 mg (0.029 mmol) of (Et₄N)₂[W^{IV}O(S₂C₂Me₂)₂] (**1**) in 3 mL of MeCN was placed in a 50 mL Schlenk flask, and the headspace gas was removed under vacuum. One atmosphere of CO₂ was prepared in a separate 100 mL Schlenk flask. The two flasks were connected inside a glove box under argon through tubing. The 50 mL flask was cooled at ~77 K (liquid N₂) to transfer CO₂ from the 100 mL flask. During the time, the dry ice was formed inside the 50 mL flask. After closing the stopcock of the 50 mL flask, the reaction flask was warmed to room temperature. Thereby, ~2 atm of CO₂ was prepared in the reaction flask. After heating at 90 °C for 4 days, the reaction solution was dried under vacuum, and the residue was washed with THF (3 × 3 mL). The product was re-dissolved in 0.5 mL of MeCN, where diethyl ether vapor was diffused to provide the brown solid product. Yield: 13 mg (86 %). The red brown needle-like crystals suitable for X-ray analysis were obtained overnight. ¹H NMR (CD₃CN, 400 MHz) 1.19 (t, 24H) 2.16 (s, 15H), 2.25 (s, 3H), 3.14 (q, 16H) ppm. ¹³C NMR (400 MHz; CD₃CN) 8.2, 21.3, 23.0, 23.1, 23.8, 53.4, 129.6, 132.2, 132.6, 138.8 ppm. UV-Vis (MeCN) 261 (ε/dm³ mol⁻¹ cm⁻¹ 32000), 328 (sh, 9800), 396 (7100) nm. IR (Nujol): ν_{W=O} 918 cm⁻¹. Anal. Calc. for C₂₈H₅₈N₂O₂S₇W₂: C, 32.12; H, 5.58; N, 2.68. Found: C, 31.80; H, 5.46; N, 2.97.

Reaction of [WO(S₂C₂Me₂)₂]²⁻ (**1**) with isotope gas, ¹³CO₂

A solution of 20 mg (0.029 mmol) of (Et₄N)₂[W^{IV}O(S₂C₂Me₂)₂] (**1**) in 3 mL of MeCN was prepared in a 50 mL Schlenk flask. The headspace gas of the reaction flask was removed under

vacuum. The $^{13}\text{CO}_2$ -filled 100 mL flask was connected to the reaction flask inside a glove box. The 50 mL flask was cooled at $\sim 77\text{ K}$ (liquid N_2) to transfer $^{13}\text{CO}_2$ from the 100 mL flask. During the time, the dry ice was formed inside the 50 mL flask. After closing the stopcock of the 50 mL flask, the reaction flask was warmed to room temperature and heated at $90\text{ }^\circ\text{C}$ for 4 days.

Reaction of $[\text{WO}(\text{S}_2\text{C}_2\text{Me}_2)_2]^{2-}$ (**1**) with another isotope gas (C^{18}O_2): All the experimental details are similar as the above procedures except for using the C^{18}O_2 gas.

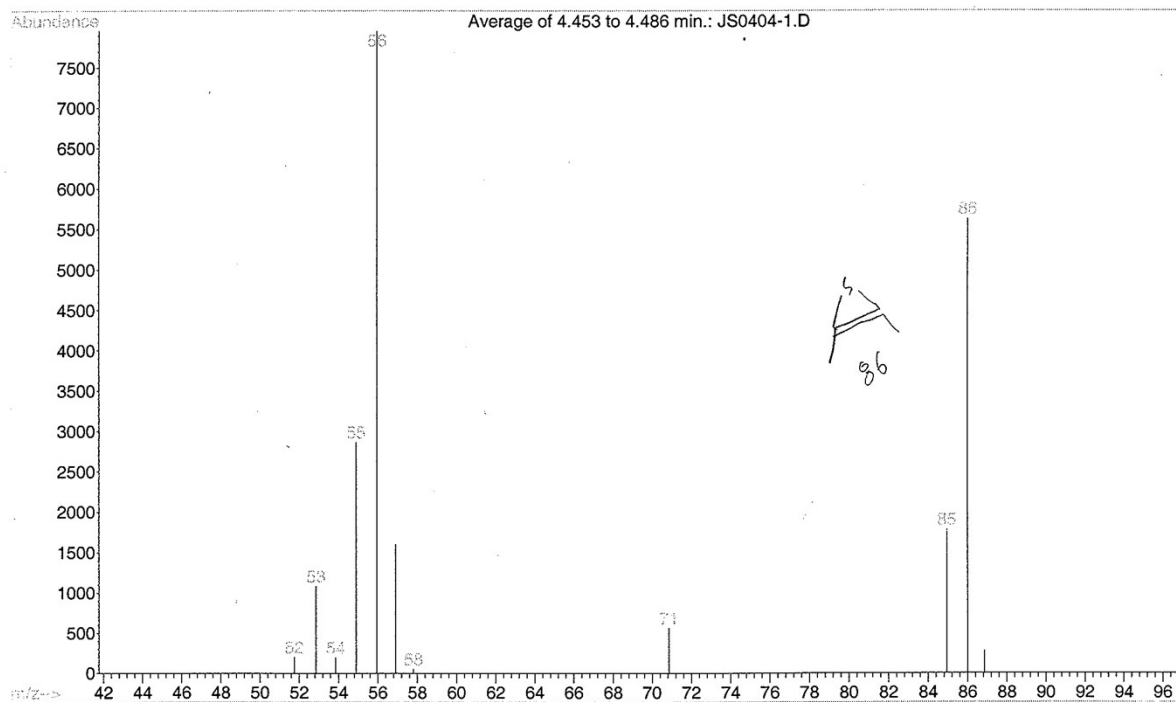


Figure S1. Detection of dimethylthiirene fragment by GC-MS

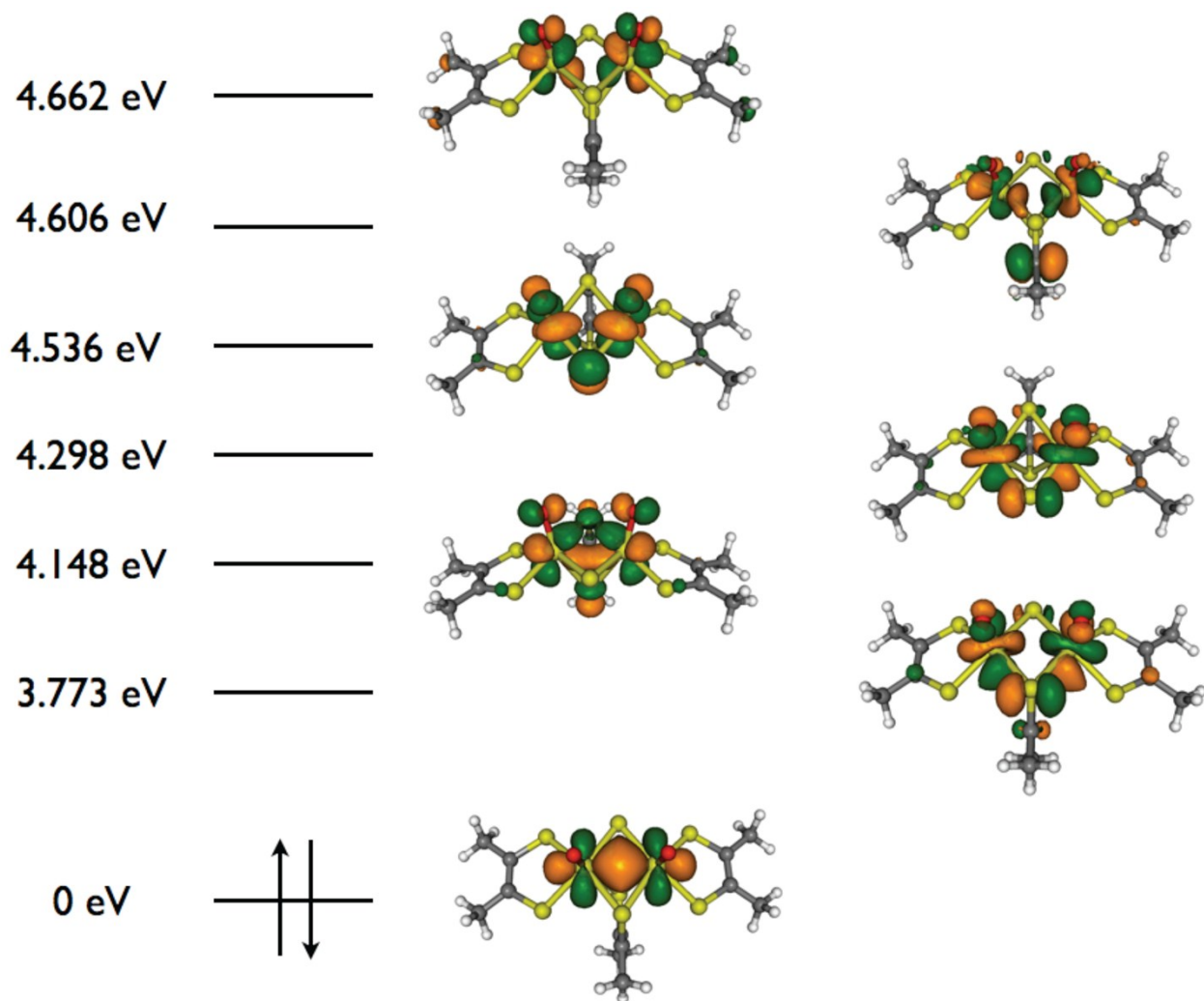


Figure S2. DFT calculations for the molecular “d” type orbitals of **2**

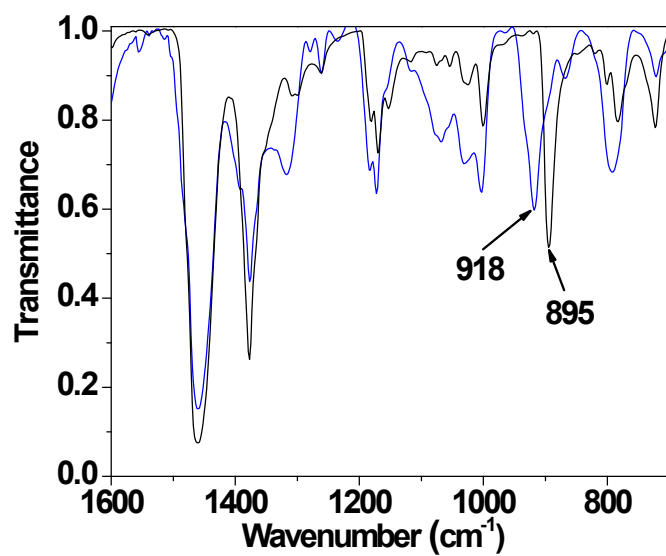


Figure S3. IR (Nujol) spectra of $[\text{WO}(\text{S}_2\text{C}_2\text{Me}_2)_2]^{2-}$ (**1**, black line, $\nu(\text{W}(\text{IV})=\text{O})$ 895 cm^{-1}) and $[\text{W}^{\text{V}}_2\text{O}_2(\mu\text{-S})(\mu\text{-S}_2\text{C}_2\text{Me}_2)(\text{S}_2\text{C}_2\text{Me}_2)_2](\text{NEt}_4)_2$ (**2**, blue line, $\nu(\text{W}(\text{V})=\text{O})$ 918 cm^{-1})

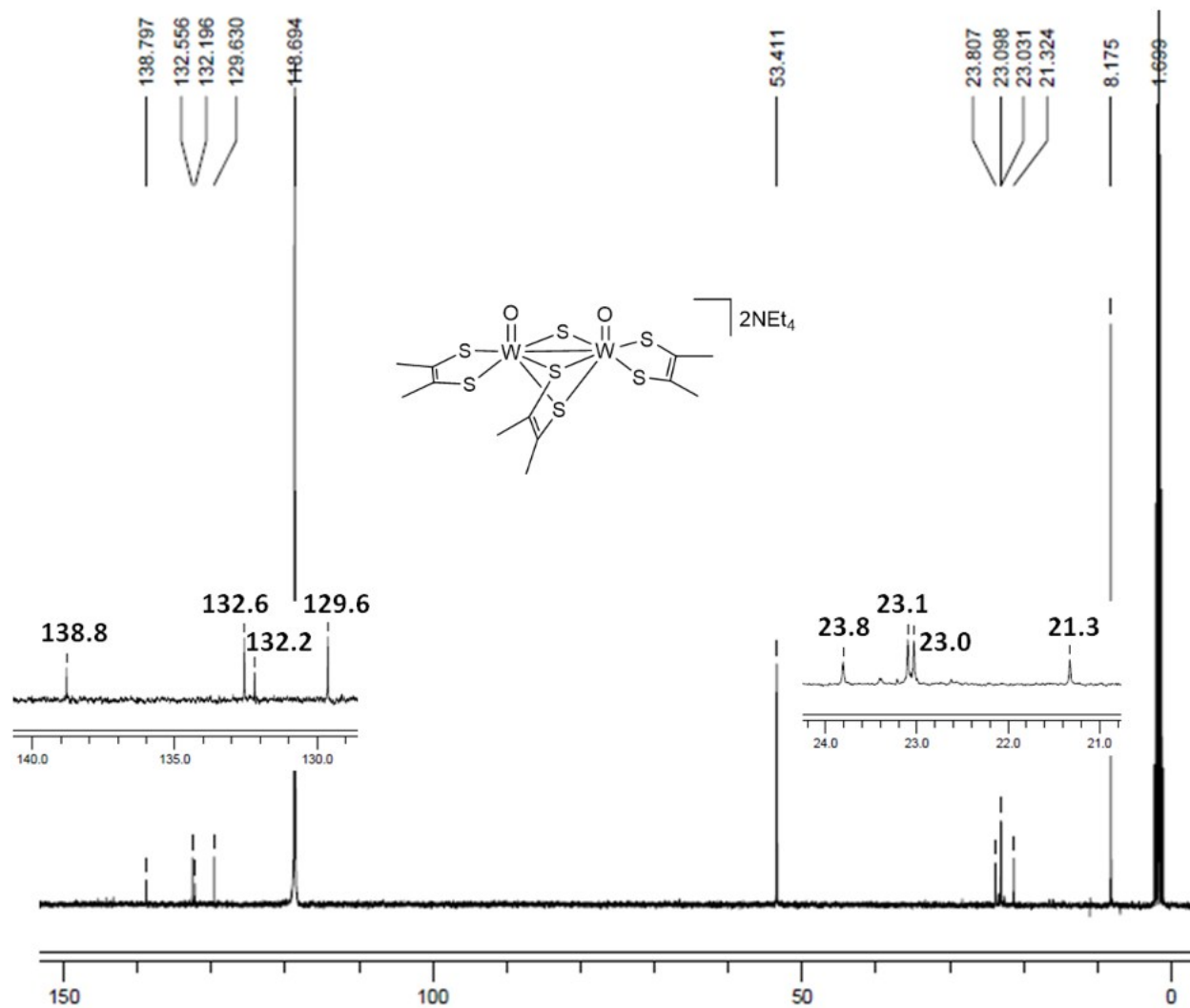


Figure S4. ^{13}C NMR spectrum of $(\text{Et}_4\text{N})_2[\text{W}_2\text{O}_2(\mu\text{-S})(\mu\text{-S}_2\text{C}_2\text{Me}_2)(\text{S}_2\text{C}_2\text{Me}_2)_2]$ (2) in CD_3CN .

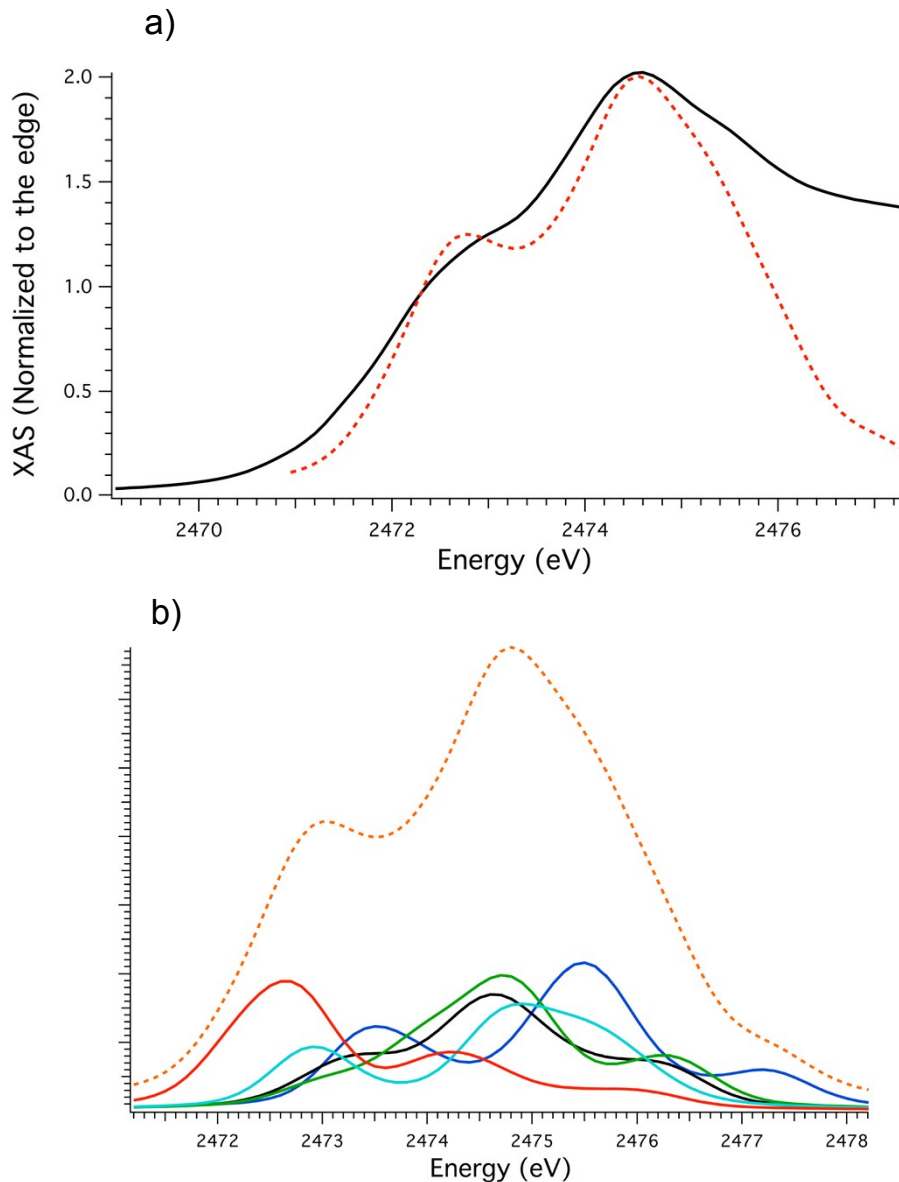


Figure S5. a) Experimental (black solid line) and calculated (red dashed line) S K-edge X-ray absorption spectra, b) deconvolution of the TD-DFT generated S K-edge spectrum with the individual S-atom components. The dashed orange spectrum is the sum of the individual components, the solid red spectrum is the contribution from the sulfide sulfur, the light blue spectrum is the contribution from the terminal dithiolene sulfurs *trans* to the bridging dithiolene atom, the dark blue spectrum is the contribution from the terminal dithiolene sulfurs *trans* to the bridging sulfide, the black spectrum is the contribution from the bridging dithiolene sulfur *trans* to “vacant site” and the green spectrum is the contribution from the bridging dithiolene sulfur *trans* to the sulfide.

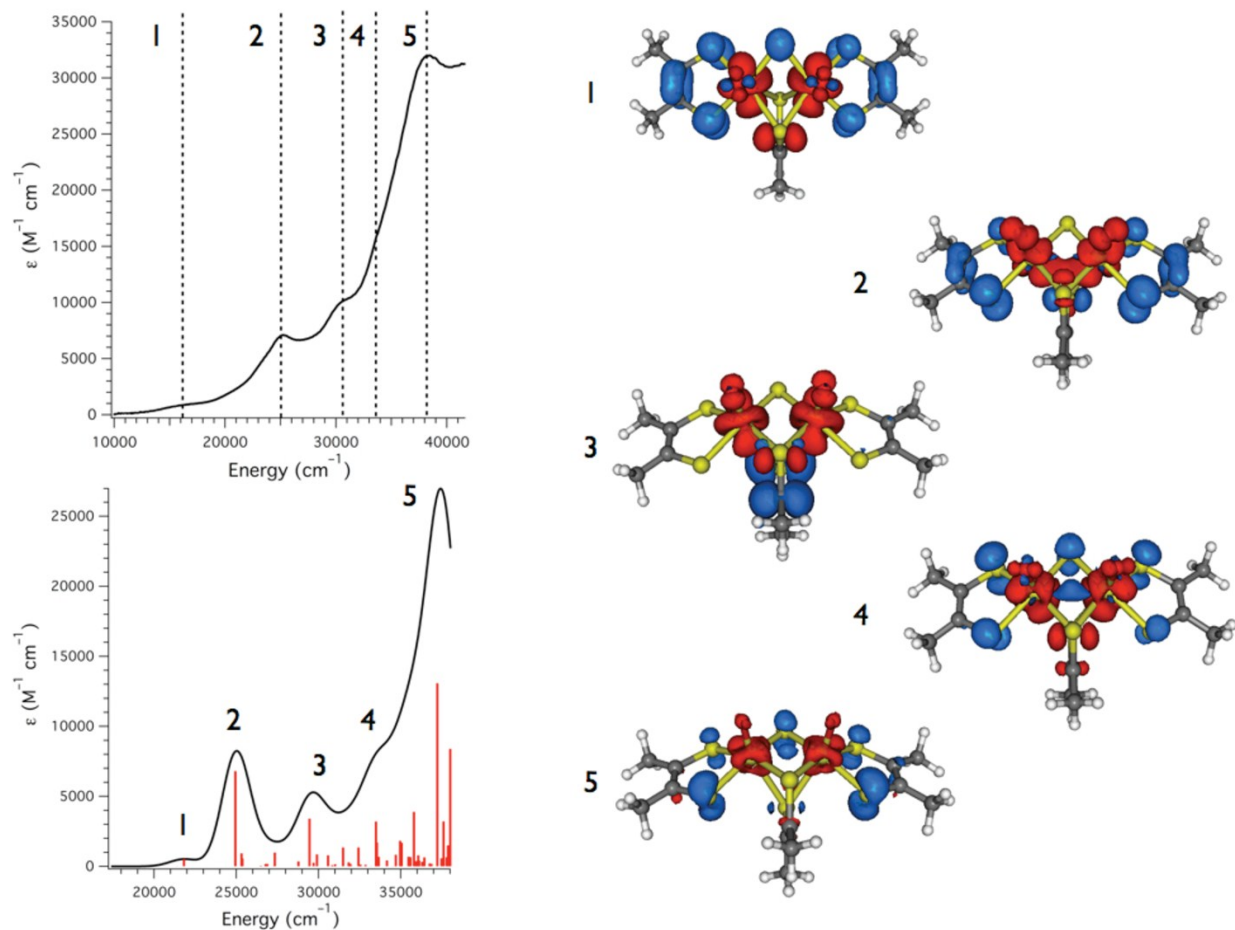


Figure S6. Experimental (top left) and simulated absorption (bottom left). The transition densities (the red represents the gaining of electron density, the blue represents the loss of electron density) for the five most prominent transitions from the TD-DFT spectrum.

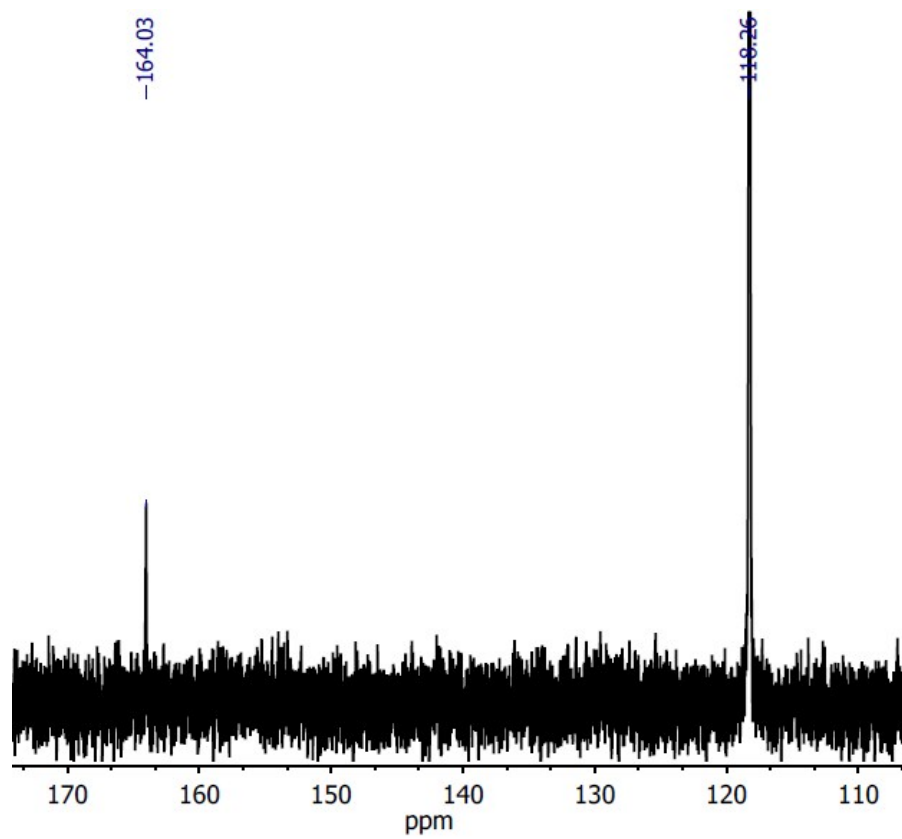


Figure S7. ^{13}C NMR (CD_3CN) spectrum of Et_4NHCO_2 (164 ppm)

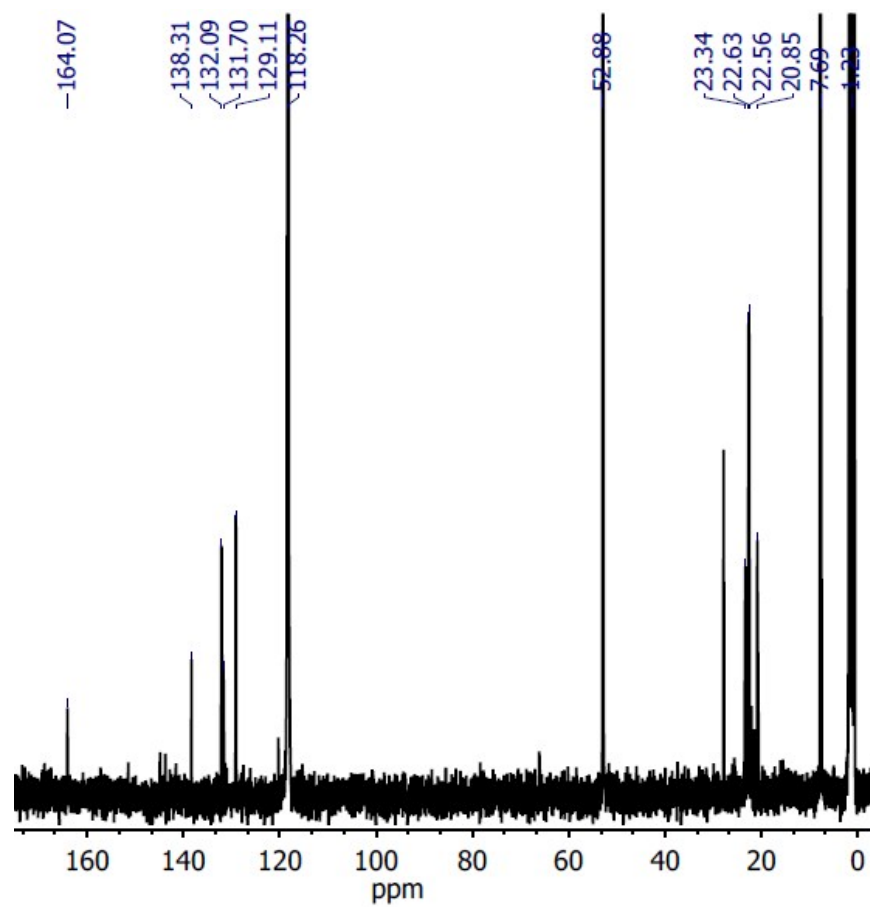


Figure S8. ^{13}C NMR (CD_3CN) spectrum of the products mixture from the CO_2 reaction of $[\text{WO}(\text{S}_2\text{C}_2\text{Me}_2)_2]^{2-}$ (**1**).

File: RQ7444

Date Run: 03-11-2011

Sample: j seo/kim, formic acid/dioxane, from reaction

Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600

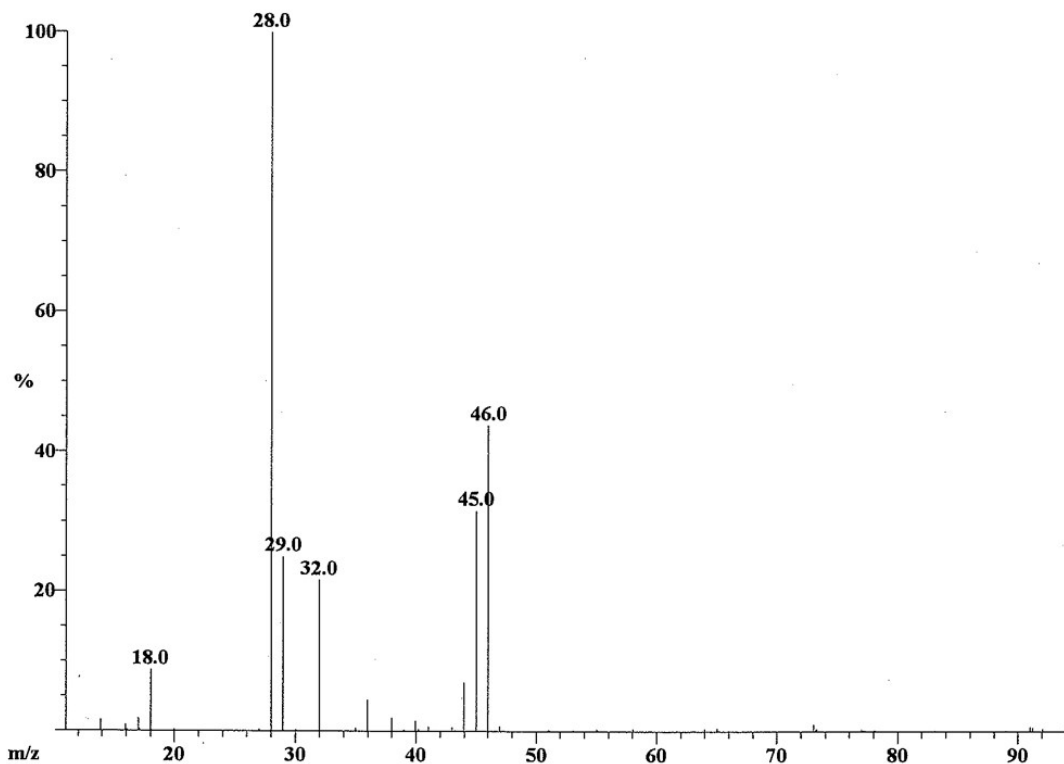
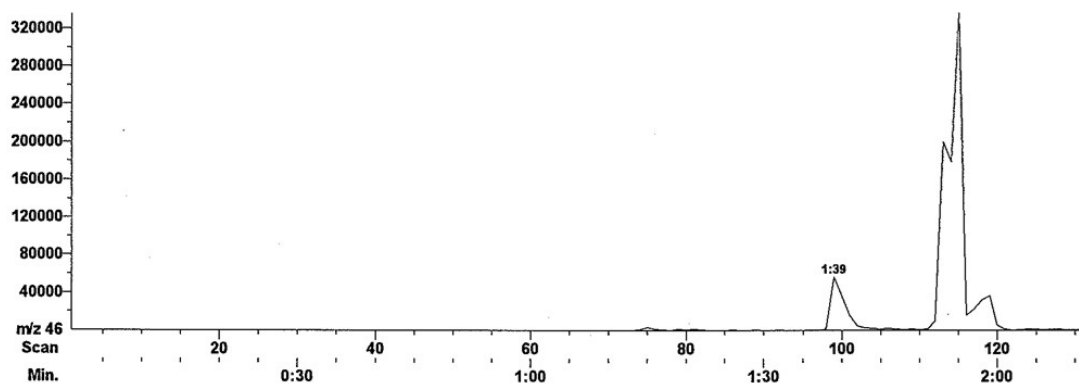


Figure S9. GC-MS analysis after treatment of the reaction ($1+CO_2$) products with HCl in 1,4-dioxane. Insoluble species was filtered prior to injection. (top) Retention time of formic acid at 1:39 min; dioxane at 1:50 min, (bottom) fragmentation pattern of formic acid at 1:39.

Crystal Structure Report for (Et₄N)₂[W₂O₂(μ-S)(μ-S₂C₂Me₂)(S₂C₂Me₂)₂] (2)

A specimen of C₂₈H₅₈N₂O₄S₇W₂, approximate dimensions 0.150 mm x 0.250 mm x 0.250 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 20150 reflections to a maximum θ angle of 29.86° (0.71 Å resolution), of which 9849 were independent (average redundancy 2.046, completeness = 88.6%, R_{int} = 7.33%, R_{sig} = 9.92%) and 7931 (80.53%) were greater than 2 σ (F²). The final cell constants of $a = 11.151(3)$ Å, $b = 11.518(3)$ Å, $c = 17.444(5)$ Å, $\alpha = 92.543(3)^\circ$, $\beta = 108.567(3)^\circ$, $\gamma = 112.376(3)^\circ$, volume = 1928.6(10) Å³, are based upon the refinement of the XYZ-centroids of reflections above 20 σ (I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2988 and 0.4482. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, C₂₈H₅₈N₂O₄S₇W₂. The final anisotropic full-matrix least-squares refinement on F² with 384 variables converged at R1 = 8.67%, for the observed data and wR2 = 23.99% for all data. The goodness-of-fit was 1.030. The largest peak in the final difference electron density synthesis was 4.935 e⁻/Å³ and the largest hole was -6.657 e⁻/Å³ with an RMS deviation of 0.498 e⁻/Å³. On the basis of the final model, the calculated density was 1.858 g/cm³ and F(000), 1064 e⁻.

Table 1. Sample and crystal data for (Et₄N)₂[W₂O₂(μ-S)(μ-S₂C₂Me₂)(S₂C₂Me₂)₂] (2).

Chemical formula	C ₂₈ H ₅₈ N ₂ O ₄ S ₇ W ₂	
Formula weight	1078.88	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal size	0.150 x 0.250 x 0.250 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 11.151(3)$ Å	$\alpha = 92.543(3)^\circ$
	$b = 11.518(3)$ Å	$\beta = 108.567(3)^\circ$
	$c = 17.444(5)$ Å	$\gamma = 112.376(3)^\circ$
Volume	1928.6(10) Å ³	
Z	2	
Density (calculated)	1.858 g/cm ³	
Absorption coefficient	6.372 mm ⁻¹	
F(000)	1064	

Table 2. Data collection and structure refinement for 2.

Theta range for data collection	1.25 to 29.86°
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Index ranges	-14<=h<=14, -15<=k<=15, -24<=l<=23
Reflections collected	20150
Independent reflections	9849 [R(int) = 0.0733]
Max. and min. transmission	0.4482 and 0.2988
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	9849 / 0 / 384
Goodness-of-fit on F²	1.030
Δ/σ_{\max}	0.001
Final R indices	7931 data; I>2 σ (I) R1 = 0.0867, wR2 = 0.2256 all data R1 = 0.0978, wR2 = 0.2399
Weighting scheme	w=1/[$\sigma^2(F_o^2)+(0.1712P)^2+0.0000P$] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	4.935 and -6.657 eÅ ⁻³
R.M.S. deviation from mean	0.498 eÅ ⁻³
