Electronic Supporting Information for

## Heterobimetallic complexes of palladium and platinum containing a redoxactive W[SNS]<sub>2</sub> metalloligand

Kyle E. Rosenkoetter, Joseph W. Ziller, and Alan F. Heyduk\*

Department of Chemistry, University of California, Irvine, California, 92697, United States Contents:

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**General Considerations.** The compounds and reactions reported below show various levels of air- and moisturesensitivity, therefore all manipulations were carried out using standard vacuum-line, Schlenk-line and glovebox techniques unless otherwise noted. Hydrocarbon and ethereal solvents were sparged with argon before being deoxygenated and dried by passage through Q5 and activated alumina columns, respectively. Halogenated solvents were sparged with argon and dried by passage through two activated alumina columns. To test for effective oxygen and water removal, aliquots of each solvent were treated with a few drops of a purple solution of sodium benzophenone ketyl radical in THF. CDCl<sub>3</sub> was dried over CaH<sub>2</sub> and vacuum distilled prior to use. PdCl<sub>2</sub> (sigma), K<sub>2</sub>PtCl<sub>4</sub> (Fisher), and 1,2-bis(diphenylphosphino)ethane (dppe) (Fisher) were all used as received. The ligand [SNS<sup>cat</sup>]H<sub>3</sub><sup>1</sup> in addition to complexes W[SNS]<sub>2</sub><sup>1</sup>, Cl<sub>2</sub>Pd(dppe)<sup>2</sup>, (DMSO)<sub>2</sub>PtCl<sub>2</sub><sup>3</sup>, and Cl<sub>2</sub>Pt(dppe)<sup>4</sup> were all prepared according to previously reported procedures.

**Spectroscopic Methods.** Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. NMR spectra were collected on a Bruker Avance 600 MHz spectrometer in dry, degassed CDCl<sub>3</sub> or C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. All <sup>31</sup>P NMR spectra were referenced with an external standard of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%). Chemical shifts are reported using the standard  $\delta$  notation in parts per million. Electronic absorption spectra were recorded with a Perkin-Elmer Lambda 900 UV-vis spectrophotometer and a Jasco V-670 absorption spectrometer as solutions in dry, degassed THF contained in 1-cm quartz cells. Electrospray ionization mass spectrometry (ESI-MS) data were collected on a Waters LCT Premier mass spectrometer using dry, degassed CH<sub>2</sub>Cl<sub>2</sub> or THF.

**Electrochemical Methods.** Electrochemical data were collected with a Gamry Series G 300 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA) using a 3.0 mm glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver wire pseudo-reference electrode. Electrochemical experiments were performed at 25°C in a glovebox under an atmosphere of N<sub>2</sub>. Electrochemical samples were 1.0 mM analyte solutions in THF containing 0.3 M [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte. All potentials were referenced to the [Cp<sub>2</sub>Fe]<sup>0/+</sup> couple using ferrocene or decamethylferrocene as an internal standard. Ferrocene and decamethylferrocene (Acros) were purified by sublimation under reduced pressure and tetra-*n*-butylammonium hexafluorophosphate (Acros) was recrystallized from ethanol three times and dried under vacuum.

**Crystallographic Methods.** X-ray diffraction data was collected on a single crystal mounted on a glass fiber using paratone oil. Data was acquired using a Bruker SMART APEX II diffractometer equipped with a CCD detector at 88 K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), which was wavelength selected with a single-crystal graphite monochromator. The SMART program package was used to determine unit-cell parameters and for data collection. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program suite. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. Analytical scattering factors for neutral atoms were used throughout the analyses. Hydrogen atoms were generated in calculated positions and refined using a riding model. ORTEP diagrams were generated using *ORTEP-3* for Windows.

**Computational Methods.** All calculations were performed employing the non-empirical tpss density functional theory using the quantum chemistry program package TURBOMOLE.<sup>7</sup> For computational efficiency, initial geometry optimizations were performed using moderate split-valence plus polarization basis sets (def2-SVP).<sup>8</sup> Structures were refined using basis sets of triple zeta valence plus polarization (def2-TZVP) quality.<sup>9</sup> Crystal structures obtained from X-ray diffraction experiments were used as starting points for the geometry optimization; no molecular symmetry was imposed. Energies and minimum energy structures were evaluated self-consistently to tight convergence criteria (energy converged to 0.1 µHartree, maximum norm of the Cartesian gradient  $\leq 10^{-4}$  a.u.).

**W[SNS]<sub>2</sub>Pd(dppe) (1).** In a 100 mL Schlenk flask, potassium metal (40 mg, 1.0 mmol, 2.0 equiv.) and graphite (99 mg, 1.0 mmol, 2.0 equiv.) were heated with a heat gun to form two equiv. of KC<sub>8</sub> as a bronze powder. The flask was charged with 30 mL of dry THF and frozen in a liquid nitrogen cold well. Upon thawing, W[SNS]<sub>2</sub> (362 mg, 0.518 mmol, 1.04 equiv.) was added to the stirring solution to generate K<sub>2</sub>W[SNS]<sub>2</sub> *in situ.* as a dark maroon solution with a yellow hue around the rim. After 10 minutes, Cl<sub>2</sub>Pd(dppe) (298 mg, 0.518 mmol, 1.04 equiv.) was added to the solution and stirred at room temperature for 1 hour. The solution was filtered from graphite and KCl through a celite plug on a glass frit to yield a dark green filtrate. The filtrate was concentrated to roughly 10 mL and a solid was crashed out of solution using pentane. The solid was filtered and washed with pentane (2 x 10 mL) followed by Et<sub>2</sub>O (2 x 20 mL). The solid was collected as a dark green powder (430 mg, 70%). X-ray quality crystals were obtained by slow diffusion of pentane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex at ambient temperature, dark green crystals obtained. Anal. Calc.  $C_{54}H_{48}N_2PdP_2S_4W$ •CH<sub>2</sub>Cl<sub>2</sub>: C, 51.19; H, 3.91; N, 2.17%. Found: C, 51.29;

H, 3.72; N, 2.16%. <sup>31</sup>P {<sup>1</sup>H}-NMR (236 MHz, CDCl<sub>3</sub>)  $\delta$  / ppm: 56.60 (<sup>2</sup>*J*<sub>PP</sub> = 123.5 Hz), 82.10 (<sup>2</sup>*J*<sub>PP</sub> = 123.5 Hz). UV-Vis (THF)  $\lambda_{max}$  / nm ( $\epsilon$  / M<sup>-1</sup> cm<sup>-1</sup>): 633 (14,000), 430 (20,000), 381 (18,000). ESI-MS(+) (THF): *m*/*z* 1238.91 ((M+MeOH)<sup>+</sup>).

**W[SNS]<sub>2</sub>Pt(dppe) (2).** In a similar manner as that described for **1**, a 100 mL Schlenk flask was charged with potassium metal (31 mg, 0.78 mmol, 2.0 equiv.) and graphite (74 mg, 0.77 mmol, 2.0 equiv.) and heated with a heat gun to form two equiv. of KC<sub>8</sub> as a bronze powder. The flask was charged with 30 mL of dry THF and frozen in a liquid nitrogen cold well. Upon thawing, W[SNS]<sub>2</sub> (273 mg, 0.390 mmol, 1.00 equiv.) was added to the stirring solution to generate K<sub>2</sub>W[SNS]<sub>2</sub> *in situ.* as a dark maroon solution with a yellow hue around the rim. After 10 minutes, Cl<sub>2</sub>Pt(dppe) (265 mg, 0.380 mmol, 0.974 equiv.) was added to the solution and stirred at room temperature for 1 hour. The solution was filtered from graphite and KCl through a celite plug in a glass frit to yield a dark blue-green filtrate. The filtrate was concentrated to roughly 10 mL and a solid was crashed out of solution using pentane. The solid was filtered and washed with pentane (2 x 10 mL) followed by Et<sub>2</sub>O (2 x 20 mL). The solid was collected as a black powder (420 mg, 81%). X-ray quality crystals were obtained by diffusion of pentane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex at ambient temperature, purple crystals obtained. Anal. Calc. C<sub>54</sub>H<sub>48</sub>N<sub>2</sub>PtP<sub>2</sub>S<sub>4</sub>W•CH<sub>2</sub>Cl<sub>2</sub>: C, 47.94; H, 3.66; N, 2.03%. Found: C, 47.95; H, 3.50; N, 1.86%. <sup>31</sup>P {<sup>1</sup>H}-NMR (236 MHz, CDCl<sub>3</sub>)  $\delta$  / ppm: 51.34 (<sup>1</sup>J<sub>PtP</sub>= 4191 Hz), 83.40 (<sup>1</sup>J<sub>PtP</sub>= 2954 Hz). UV-Vis (THF)  $\lambda_{max}$  / nm ( $\epsilon$  / M<sup>-1</sup> cm<sup>-1</sup>): 582 (14,000), 414 (19,000). ESI-MS(+) (CH<sub>2</sub>Cl<sub>2</sub>): *m/z* 1325.16 ((M+MeOH)<sup>+</sup>).

	W[SNS] <sub>2</sub> Pd(dppe)	W[SNS] <sub>2</sub> Pt(dppe)
	(1)	(2)
empirical formula	$C_{54}H_{48}N_2PdP_2S_4W{\bullet}CH_2Cl_2$	$C_{54}H_{48}N_2PtP_2S_4W{\bullet}CH_2Cl_2$
formula weight [g/mol]	1290.29	1378.99
crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_{1}/n$
T [K]	88(2) K	143(2)
a [Å]	14.0682(13)	14.0874(8)
b [Å]	15.7304(14)	15.6390(9)
c [Å]	24.270(2)	24.3593(14)
a [deg]	90	90
b [deg]	104.3314(11)	104.6962(6)
g [deg]	90	90
V [Å <sup>3</sup> ]	5203.86	5191.1(5)
Ζ	4	4
refl collected	63378	58665
data/restr/param	13098 / 0 / 626	12232/0/608
$R_1 [I > 2\sigma(I)]^a$	0.0185	0.0203
wR <sub>2</sub> (all data) <sup>a</sup>	0.0444	0.0482
GOF <sup>a</sup>	1.033	1.025

Table S1. X-ray Diffraction Data-Collection and Refinement Parameters.

<sup>a</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}, GOF = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ 



**Figure S1.** ORTEP diagram for complex 1 with thermal ellipsoids shown at 50% probability. Hydrogen atoms and a solvent molecule ( $CH_2Cl_2$ ) have been omitted for clarity.



Figure S2. <sup>1</sup>H NMR spectra for (top) W[SNS]<sub>2</sub>Pd(dppe) (1) and (bottom) W[SNS]<sub>2</sub>Pt(dppe) (2) in CDCl<sub>3</sub>.



Figure S3. <sup>31</sup>P NMR spectra for (top) W[SNS]<sub>2</sub>Pd(dppe) (1) and (bottom) W[SNS]<sub>2</sub>Pt(dppe) (2) in CDCl<sub>3</sub>.



**Figure S4.** (*top*) <sup>31</sup>P VT NMR studies of complex **1** in tetrachloroethane- $d_2$  at elevated temperatures (340 K – 390 K) and (*bottom*) <sup>31</sup>P NMR spectra collected of **1** at 298 K before applying heat (black) and 298 K after applying heat (red). Signal observed at 64.3 ppm is consistent with sample decomposition to (dppe)PdCl<sub>2</sub>.

Temp	k (sec <sup>-1</sup> )	Type of Exchange Observed
298 K	0	No Exchange
340 K	1820	Slow exchange
345 K	2680	$k = \pi^*(h_e - h_o)$ $h_e = peak$ width mid height at temp T $h_o = peak$ width mid height at no exchange
350 K	5270	Intermediate Exchange
355 K	7210	$\mathbf{k} = (\pi / (2^{1/2}))^* ((\Delta v_o^2 - \Delta v_e^2))^{1/2}$
360 K	9160	$\Delta v_0$ = frequency in Hz at no exchange $\Delta v_e$ = frequency in Hz of peaks at temp T
370 K	14800	Coalescense $k = \pi^* (\Delta v_o)/(2)^{1/2}$ $\Delta v_o =$ frequency in Hz at no exchange
380 K	22000	Fast Exchange
390 K	36000	$\mathbf{k} = \pi^* (\Delta v_o^2) / (2^* \mathbf{h}_e - \mathbf{h}_o)$

Table S2. Calculated values for the rate of exchange for complex 1 in tetrachloroethane- $d_2$ .<sup>5,6</sup>



$$ln\left(\frac{kobs}{T}\right) = \frac{-\Delta H^{\ddagger}}{R} * \left(\frac{1}{T}\right) + ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$$

$$slope = \frac{-\Delta H^{\ddagger}}{R} \qquad y - intercept = ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$$

$$\Delta H^{\ddagger} = -(-7240) * R \qquad \Delta S^{\ddagger} = \left(23.22 - ln\left(\frac{k_B}{h}\right)\right) * R$$

$$\Delta H^{\ddagger} = -14.6 \ kcal \ mol^{-1} \qquad \Delta S^{\ddagger} = -0.8 \ cal \ mol^{-1} \ K^{-1}$$

**Figure S5.** Eyring plot and equations for calculating the activation parameters for complex 1. R is the gas constant in cal K<sup>-1</sup> mol<sup>-1</sup>,  $k_B$  is the Boltzmann constant in J K<sup>-1</sup>, and h is planks constant in J sec<sup>-1</sup>.



**Figure S6.** (*top*) <sup>31</sup>P VT NMR studies of complex **2** in tetrachloroethane- $d_2$  at elevated temperatures (298 K – 390 K) and (*bottom*) <sup>31</sup>P NMR spectra collected of **2** at 298 K before applying heat (black) and 298 K after applying heat (red). Signal observed at 41.4 ppm is consistent with sample decomposition to (dppe)PtCl<sub>2</sub>.



Figure S7. Electronic absorption spectra of W[SNS]<sub>2</sub>Pd(dppe) (1) (black) and W[SNS]<sub>2</sub>Pt(dppe) (2) (red) in THF.

Table S3.	Electronic	absorpt	ion data	for com	plexes 1	and <b>2</b> .

	$\lambda / nm (\epsilon / M^{-1}cm^{-1})$
W[SNS] <sub>2</sub> Pd(dppe) (1) (black)	381 (18,000), 430 (20,000), 633 (14,000)
$W[SNS]_2Pt(dppe)$ (2) (red)	414 (19,000), 582 (14,000)



**Figure S8.** Individual scan rate dependencies for (*top*) oxidative events and (*bottom*) reductive events of  $W[SNS]_2Pd(dppe)$  (1). CVs were recorded with 1 mM analyte concentration in 0.3 M [NBu<sub>4</sub>][PF<sub>6</sub>] in dry, degassed THF under a nitrogen atmosphere using a 3 mm glassy carbon working electrode, Pt wire counter electrode, and silver wire pseudo-reference electrode at room temperature.



**Figure S9.** Individual scan rate dependencies for (top) oxidative events and (bottom) reductive event of W[SNS]<sub>2</sub>Pt(dppe) (2). CVs were recorded with 1 mM analyte concentration in 0.3 M [NBu<sub>4</sub>][PF<sub>6</sub>] in dry, degassed THF under a nitrogen atmosphere using a 3 mm glassy carbon working electrode, Pt wire counter electrode, and silver wire pseudo-reference electrode at room temperature.

	W[SNS	$S]_2Pd(dp)$	pe)	
	W	Pd	Р	[SNS]
	(%)	(%)	(%)	〔 <b>%</b> 〕
HOMO-1	13.37	9.02	8.40	69.21
HOMO	13.49	6.94	5.57	74.00
LUMO	34.69	12.19	8.50	44.62
LUMO+1	52.89	1.20	0.00	45.91

 Table S4. Mulliken population analysis distributions for (*left*) 1 and (*right*) 2.



Figure S10. Lewis structures for the possible electron arrangements in  $W[SNS]_2M(dppe)$  (M = Pd (1), Pt (2)).

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