

One-Pot Oxidation and Protonation of Bridging Sulfide and Crystallographic Evidence of the Rare Coordinated [SO] Complex in $[\text{Pt}_2(\mu\text{-S}_2\text{O}_2\text{H})(\text{PPh}_3)_4]^+$

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Experimental

General Methods and Materials

All manipulations were carried out in ambient conditions. Solvents used were generally analytical grade (Tedia). $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ (**1**) was synthesized by metathesis of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Riedel-de Haën) in benzene. ESI-MS (80% MeOH/20% H_2O): m/z 1504 $[\text{M} + \text{H}^+]$. $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SH})(\text{PPh}_3)_4]^+$ (**2**) was synthesized by $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ (**1**) with HCl (3% w.t). The following chemicals were used as supplied from Aldrich: triphenylphosphine (PPh_3), H_2O_2 (35% in water), and ammonium hexafluorophosphate (NH_4PF_6).

Elemental analyses were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. ^1H NMR spectra were recorded at 25°C on a Bruker ACF 300 and Bruker AMX 500 spectrometers with Me_4Si as internal standard. The ^{31}P NMR spectra were recorded at 25°C at 212.46 MHz with 85% H_3PO_4 as external reference. Electrospray mass spectra were obtained in the positive-ion mode with a Finnigan/MAT LCQ mass spectrometer coupled with a TSP4000 HPLC system and the crystal 310 CE system. The mobile phase was 80% methanol / 20% H_2O (flow rate: 0.4 mL min^{-1}). The capillary temperature was 150°C. Peaks were assigned from the m/z values and from the isotope-distribution patterns.

Synthesis

$[\text{Pt}_2(\mu\text{-S}_2\text{O}_2\text{H})(\text{PPh}_3)]][\text{PF}_6]$ (**3**):

Procedure 1: Excess 35% w.t H_2O_2 (0.1 ml) was added to the suspension of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ (**1**) (20 mg, 0.013 mmol) in MeOH (10 ml). The mixture was stirred for 1 h and

filtered over celite to obtain a clear yellow solution. Excess NH_4PF_6 was added to the resultant solution to give a suspension. The light orange precipitate was isolated by suction filtration and washed with deionized water (50 ml) and Et_2O (50 ml) to yield a pale red powder of **3** (19 mg, 94%). ESI-MS (MeOH/ H_2O): m/z (%) 1534 ($[\text{M}]^+$, 100%); ^{31}P -NMR(CDCl_3): δ (ppm) = 20.2 ($J_{\text{Pt-P}} = 2705$ Hz); IR (KBr pellet; cm^{-1}): 834 ($\nu_{\text{s}}(\text{S-O})$); 3413, 3553, 3642 ($\nu_{\text{w}}(\text{O-H})$); Element analysis: calcd (%) for $\text{C}_{72}\text{H}_{61}\text{F}_6\text{O}_2\text{P}_5\text{Pt}_2\text{S}_2 \cdot 3\text{CH}_2\text{Cl}_2$ (1936): C 46.5, H 3.5, S 3.3; Found (%): C 46.7, H 3.7, S 3.5.

Procedure 2: Similar to procedure 1. Excess *tert*-butyl hydroperoxide (TBHP) and **1** (20 mg, 0.013 mmol) was mixed and stirred for 1 h, with excess NH_4PF_6 added to yield **3** (19 mg, 87%).

Procedure 3: Excess 35% w.t H_2O_2 (0.1 ml) was added to the suspension of $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SH})(\text{PPh}_3)_4][\text{PF}_6]$ (**2**) (20 mg, 0.012 mmol) in MeOH (10 ml). The mixture was stirred for 1 h and filtered over celite to obtain a clear yellow solution. Excess NH_4PF_6 was added to the resultant solution to give a suspension. The light orange precipitate was isolated by suction filtration and washed with deionized water (50 ml) and Et_2O (50 ml) to yield a pale red powder of **3** (18 mg, 91%).

Procedure 4: Similar to procedure 3. Excess *tert*-butyl hydroperoxide (TBHP) and **2** (20 mg, 0.012 mmol) was mixed and stirred for 1 h, with excess NH_4PF_6 added to yield **3** (17 mg, 89%).

X-ray Crystal Structure Determination and Refinement

All measurements were made on a Bruker AXS SMART APEX diffractometer equipped with a CCD area detector by using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The software SMART¹ was used for the collection of data frames, for indexing reflections, and to determine lattice parameters; SAINT¹ was used for the integration of the intensity of the reflections and for scaling; SADABS² was used for empirical absorption correction; and SHELXTL³ was used for space group and structure determination, refinements, graphics, and structure reporting. The structure was refined by full-matrix least squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms.

References:

1. SMART & SAINT Software Reference Manuals, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI (USA), (1996).
2. S. G. M. Sheldrick, software for empirical adsorption correction, University of Göttingen, Göttingen (Germany), (1993).
3. S. G. M. Sheldrick, VERSION 5.03, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI (USA), (1996).