Two Routes to Bis(μ-diphenylphosphino)methane Diplatinum Halides Bridged by Sulfur Monoxide

Ruili Huang, Ilia A. Guzei, and James H. Espenson*

Ames Laboratory and Department of Chemistry,
Iowa State University of Science and Technology, Ames, Iowa 50011

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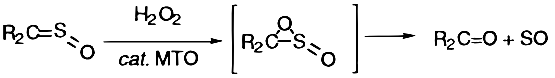
Summary: The new compounds $Pt_2(\mu$-diphenylphosphinomethane$)_2(\mu$-SO$)X_2$, with X = Cl and I, have been prepared and characterized. One route was to use $Pt_2(\mu$-dppm$)_2X_2$ to trap the sulfur monoxide liberated from decomposition of a sultine intermediate formed from the oxidation of a thioketone sulfoxide with hydrogen peroxide, catalyzed by CH_3ReO_3 (MTO). The second and preferable route consists of the oxidation of $Pt_2(\mu$-dppm$)_2(\mu$-S$)X_2$ with hydrogen peroxide, catalyzed by CH_3ReO_3 (MTO). The X-ray structural analysis of $Pt_2(\mu$-dppm$)_2(\mu$-SO$)Cl_2$ showed that it has an "A-frame" structure in which the bridge sulfur atom has the geometry of a distorted trigonal bipyramid.

The use of simple chemical methods to generate and study reactive molecules has attracted some attention, but relatively little attention has been paid to sulfur monoxide.[1,2] Until now, the main method for generating SO has been the pyrolysis of episulfoxides[1,3−5] and other sulfoxides of varying structures.[6,7] The reactive SO molecule has been trapped as a thiophene-1-oxide with dienes and trienes.[8,9] Certain transition metal complexes have also been used to trap SO.[10] Atoms and small molecules are known to insert into the Pt−Pt bond of the platinum(I) complex $Pt_2(\mu$-dppm$)_2X_2$, **1** (X = Cl, Br, I), to produce so-called A-frame molecules $Pt_2(\mu$-dppm$)_2X_2(\mu$-Y), **2**, Y = S, SO_2, CH_2 (from CH_2N_2), CO, etc.[11−15]

We recently uncovered a reaction (eq 1) that gradually generates SO in solution.[16] Sulfur monoxide was then either oxidized or, in separate experiments, trapped with a diene. We reasoned that SO logically could also be trapped by the Pt(I) complex **1**, eq 2, to form $Pt_2(\mu$-dppm$)_2(\mu$-SO), **3**.



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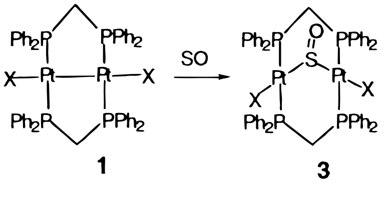

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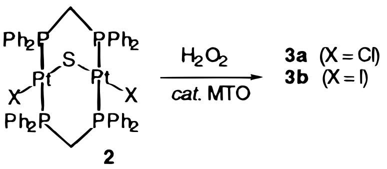
This reaction was successful, providing what we believe is the first μ-SO complex of platinum. Related complexes have been made with Pd[17,18] and Ni,[19] not through direct SO insertion but by oxidation of a μ-S complex. With that in mind, we carried out a parallel (and superior) synthesis of **3** based on an oxidation reaction, eq 3.



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The lemon-yellow compounds **1** and the yellow **2** (μ-S) were prepared by established procedures.[20,21] From reaction 3[22] a pure yellow product, **3a**, was isolated in 92% yield. Recrystallization from chloroform−hexane afforded yellow crystals. The product was identified and characterized by elemental analysis, NMR,[23] and single-crystal X-ray diffraction.[24] The iodide derivative **3b** was similarly obtained in 86% yield as a yellow solid and

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[1] Abu-Yousef, I. A.; Harpp, D. N. *J. Org. Chem.* **1997**, *62*, 8366.

[2] Abu-Yousef, I. A.; Harpp, D. N. *Tetrahedron Lett.* **1995**, *36*, 201.

[3] Hartzell, G. E.; Paige, J. N. *J. Am. Chem. Soc.* **1966**, *88*, 2616.

[4] Hartzell, G. E.; Paige, J. N. *J. Org. Chem.* **1967**, *32*, 459.

[5] Saito, S. *Tetrahedron Lett.* **1968**, 4961.

[6] Dover, F. H.; Solomon, K. E. *J. Phys. Chem.* **1980**, *84*, 3024.

[7] Chow, Y. L.; Tam, J. N. S.; Blier, J. W. *J. Chem. Soc., Chem. Commun.* **1970**, 1604.

[8] Dodson, R. M.; Sauers, F. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1189.

[9] Dodson, R. M.; Nelson, J. P. *J. Chem. Soc., Chem. Commun.* **1969**, 1159.

[10] Schenk, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 98.

[11] Puddephatt, R. J. *J. Chem. Soc. Rev.* **1983**, *12*, 99.

[12] Balch, A. L. *Adv. Chem. Ser.* **1982**, *196*, 243.

[13] Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Thomson, M. A. *Adv. Chem. Ser.* **1982**, *196*, 231.

[14] Muralidharan, S.; Espenson, J. H.; Ross, S. A. *Inorg. Chem.* **1986**, *25*, 2557.

[15] Brant, P.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1979**, *18*, 3422.

[16] Huang, R.; Espenson, J. H. *J. Org. Chem.* **1999**, *64*, 6374.

[17] Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1175.

[18] Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622.

[19] Gong, J. K.; Fanwick, P. E.; Kubiak, C. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1190.

[20] Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1977**, 951.

[21] Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1978**, 749.

[22] Compound **2a** (250 mg, 0.20 mmol) and MTO (2.5 mg, 10 μmol) in 15 mL of chloroform were treated with 1 equiv of hydrogen peroxide. ^{1}H NMR showed that reaction 3 was complete upon mixing. The product was obtained by column chromatography on silica gel with chloroform as eluent.

[23] ^{1}H NMR ($CDCl_3$) of **3a**: δ 7.00−7.90 (aromatic, m, 40 H); 4.12 (CH_2, m, 2 H); 2.87 (CH_2, m, 2H). ^{31}P: δ 16.12, 13.51 ppm. Elemental analysis for $Pt_2Cl_2P_4C_{50}H_{44}SO$: C, found 46.00 (calcd 46.99), H 3.61 (3.47), S 1.85 (2.51), P 10.14 (9.69). The calcd values assume the analyzed compound is solvent (chloroform) free, whereas the crystallographic sample contained 3.3 $CHCl_3$, to which we attribute the figure for C being low. As little as 0.14 $CHCl_3$ would make the comparison of C be 46.00 (46.52 calcd).

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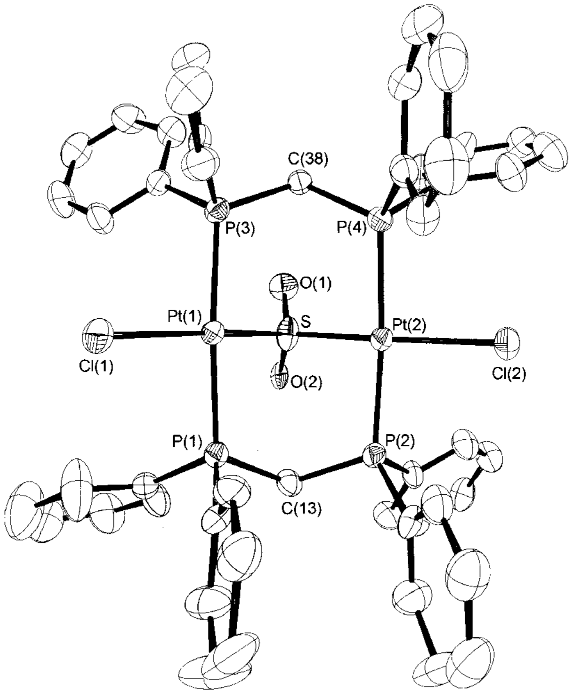

Figure 1. Perspective view of $Pt_2(dppm)_2Cl_2(\mu\text{-}SO)$, **3a**, with thermal ellipsoids at the 30% probability level. The two fractionally occupied oxygen positions are shown as O(1) and O(2). Selected bond lengths (pm) and bond angles (deg): Pt(1)−Pt(2) = 326.9(2); Pt(1)−Cl(1) = 240.98(19); Pt(2)−Cl(2) = 241.13(18); Pt(1)−S = 226.2(2); Pt(1)−P(1) = 231.5(2); Pt(1)−P(3) = 231.54(19); Pt(2)−S = 226.2(2); Pt(2)−P(2) = 231.5(2); Pt(2)−P(4) = 231.2(2); S−O(1) = 142.8(7); S−O(2) = 142.8(7); Cl(1)−Pt(1)−S = 172.22(7); P(1)−Pt(1)−P(3) = 176.32(7); Cl(2)−Pt(2)−S = 171.26(8); P(2)−Pt(2)−P(4) = 174.26(7); Pt(1)−S−Pt(2) = 92.57(7); Pt(1)−S−O(1) = 118.2(4); Pt(1)−S−O(2) = 120.2(5); Pt(2)−S−O(1) = 118.4(4); Pt(2)−S−O(2) = 120.4(6); O(1)−S−O(2) = 89.8(7).

characterized by NMR.[25] Without the MTO catalyst, the reaction under similar conditions is $>10^3$ times slower.

When a second equivalent of peroxide was used, the μ-S compounds were further oxidized to the previously known $\mu\text{-}SO_2$ complexes,[14,20] **4a** (X = Cl) and **4b** (X = I). These yellow compounds were isolated and purified by column chromatography on silica gel with 5% methyl alcohol in chloroform as eluent. The spectroscopic data matched the known materials.[26]

The A-frame structure of **3a** is depicted by the ORTEP diagram shown in Figure 1. The platinum atoms exhibit a distorted square-planar geometry, in which the bond angles for Cl−Pt−S and P−Pt−P are 171−177°, slightly deviant from linearity. The Pt−Pt distance in **3a**, 326.9 pm, indicates the absence of direct Pt−Pt bonding. The Pt−S distances, 226.2 pm, are equal. Structures of these binuclear A-frame bis(diphenylphosphino)methane (dppm) complexes have been reported: $Pd_2Cl_2(\mu\text{-}SO)(\mu\text{-}dppm)_2$ (**5**),[17,18] $Pd_2Cl_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$ (**6**),[27] $Pd_2Cl_2(\mu\text{-}S)(\mu\text{-}dppm)_2$ (**7**),[27] $Ni_2Cl_2(\mu\text{-}SO)(\mu\text{-}dppm)_2$ (**8**),[19] $Ir_2(CO)_2(\mu\text{-}N\text{-}tol)(\mu\text{-}dppm)_2$,[26] and $Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2$.[28] Their Pt analogues, however, have not been structurally characterized.

Complexes **3a** and **5**−**8** exhibit very similar structural features, Table 1. In **3a**, two different tilt geometries of the SO oxygen atom were observed. The occupancy factors for oxygen atom disorder were refined to 0.66 for O(1) and 0.34 for O(2), a feature also observed for **5** and **8**. The S−O bond distance is 142.8 pm, comparable to those found for **5** (140 pm)[17,18] and **8** (144, 146 pm). Complex **3a** contains pyramidal S, located equidistant from both metal centers. The O−S−O and Pt−S−Pt angles about the S atom are close to 90°, while the Pt−S−O angles are near 120°. These values are in excellent agreement with the bond angle in **5**, but the same angles in **6**−**8** (except for O−S−O) were much closer to 111°. The two six-membered rings Pt−S−Pt−P−C−P exhibit boat conformations similar to those in **5** and **8**, with atoms C(13) and C(38) on the same side of the P−Pt−P−P−Pt−P plane. Two Pt and four P atoms are planar within 9 pm. The coordination environment about Pt(1) and Pt(2) is that of a slightly distorted square plane with the coordination angles in the range 87.81(8)−92.99(7)° and 87.60(8)−92.84(7)°, respectively. The ligating atoms lie alternatively 9 pm around Pt(1) and 14 pm around Pt(2) above and below the least-squares planes of PtP_2SCl. This diagonal twist toward tetrahedral geometry has also been observed in **5**−**8**. The platinum−chlorine and platinum−phosphorus parameters are similar to those for the palladium and nickel complexes.

Preparation of SO-bridged dimetallic complexes by oxidation of the corresponding S-bridged complexes has limited precedent. In addition to the palladium complex **5**, one also finds $Mo_2(NTol)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)(\mu\text{-}SR)(\mu\text{-}SO)$ **9**[29] and $Mn_2Cp_2(CO)_4(\mu\text{-}SO)$ **10**.[30,31] Compounds **3a**, **5**, the nickel complex **8** (from $Ni(cod)_2$, dppm, and thionyl chloride), and **9** all have pyramidal M_2SO units, whereas compound **10** has a planar M_2SO unit. The locations of the oxygen atom were disordered in **3a**, **5**, and **8** but not in **9** and **10**. In **10** the planar Mn_2SO unit renders it incapable of that disorder; the lack of disorder in compound **9** was due to the two orientations being grossly inequivalent.

Previous methods used for the preparation of the SO-bridged complexes **5**,[17,18] **8**,[19] **9**,[29] and **10**[30,31] usually needed very low temperature (−20 to −95 °C), an inert atmosphere (under N_2, **8** and **9**), the avoidance of light (**9**), and/or the use of a concentrated oxidizing reagent (30% H_2O_2, **5**). The nickel complex **8** was obtained in

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[24] Crystallographic data for **3a**: $C_{53.33}H_{17.33}Cl_{12}OP_4Pt_2S$, tetragonal, $P4_1$, $a = 21.1745(8)$ Å, $b = 21.1745(8)$ Å, $c = 14.2897(8)$ Å, $V = 6406.9(5)$ Å^3, $Z = 4$, $T = 183(2)$ K, $D_{calcd} = 1.737$ Mg/m^3, $R(F) = 3.89\%$ for 14518 independently observed ($I \geq 2\sigma(I)$) reflections ($3° \leq 2\theta \leq 57°$). All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The oxygen atom is disordered over two positions in a 66:34 ratio. There are also 3.33 solvate molecules of chloroform in the asymmetric unit. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI, 1988).

[25] ^1H NMR/$CDCl_3$: δ 7.00−7.90 (aromatic, m, 40 H), 4.48 (CH_2, m, 2 H), 2.61 (CH_2, m, 2 H) ppm. ^{31}P NMR/$CDCl_3$: δ 12.66, 9.88 ppm.

[26] Changquing, Y.; Sharp, P. R. *Inorg. Chem.* **1995**, *34*, 55.

[27] Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

[28] Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 6129.

[29] Wang, R.; Mashuta, M. S.; Richardson, J. F.; Noble, M. E. *Inorg. Chem.* **1996**, *35*, 3022.

[30] Lorenz, I.-P.; Messelhäuser, J.; Hiller, W.; Conrad, M. *J. Organomet. Chem.* **1986**, *316*, 228.

[31] Lorenz, I.-P.; Messelhäuser, J.; Hiller, W.; Haug, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 228.

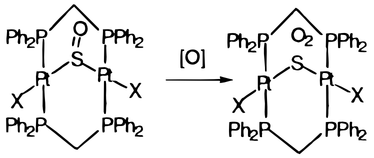
Table 1. Selected Structural Parameters for 3a and 5−8

	d_{M-X}/pm				
complex	M···M	M−Cl	M−S	M−P	M−S−M
$Pt_2Cl_2(\mu\text{-}SO)(\mu\text{-}dppm)_2$ **3a**	327.0(2)	241.1(1)	226.2(2)	231.5(2)	92.57(7)
$Pd_2Cl_2(\mu\text{-}SO)(\mu\text{-}dppm)_2$ **5**[a]	322.5(4)	240.2(9)	227.3(5)	233.7(7)	90.4(3)
$Pd_2Cl_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$ **6a**[b,c]	338.3(4)	238.1(4)	223.4(4)	234.4(4)	98.4(4)
$Pd_2Cl_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$ **6b**[b,c]	322.0(4)	238.1(4)	224.1(4)	235.9(19)	91.9(4)
$Pd_2Cl_2(\mu\text{-}S)(\mu\text{-}dppm)_2$ **7**[c]	325.8(2)	237.2(5)	229.8(5)	231.6(13)	90.3(2)
$NiCl_2(\mu\text{-}SO)(\mu\text{-}dppm)_2$ **8**[d]	330.8(1)	237.2(5)	212.7(2)	222.7(12)	101.98(7)

[a] References 17, 18. [b] **6a, 6b**—two independent molecules. [c] Reference 27. [d] Reference 19.

20−25% yield, compared to 60−95% for the others. Complexes **5** and **9** decompose quickly when taken out of solution or exposed to air or light. The μ-SO complexes of platinum, **3a** and **3b**, are very stable as crystals and in solution. They are not sensitive to laboratory light or oxygen and can be kept unchanged for months. The oxidation of the μ-S complexes by H_2O_2/MTO provides the superior means for generating them. This reaction proceeds in air in a few minutes at room temperature, affording a product that can be isolated and purified in high yield.

Complexes **1** are known to react with S and SO_2 to yield, respectively, **2,** Y = S, and **4**, Y = SO_2. Trapping by **1** of the SO released during reaction 1 also provides the μ-SO product, confirmed by comparison of the ^{1}H NMR spectra. In a typical experiment 4,4′-difluorothiobenzophenone *S*-oxide (40 mM) and MTO (12 mM) were dissolved in acetonitrile containing 0.1 M trifluoromethanesulfonic acid. Hydrogen peroxide (80 mM) was added, followed by **1a** (7.5 mM). After 1.5 h, during which time the ^{1}H spectrum was monitored, 1.0 mM **3a** was found in the reaction mixture. The various reactions are shown in eqs 1, 2, and 4. The low yield of the desired product is a consequence of the SO trap, **1a**, itself being rapidly oxidized by H_2O_2/MTO, a point that was independently confirmed.



(4)

Summary. This research has provided the first examples of sulfur monoxide-bridged diplatinum phosphines. Direct insertion of sulfur monoxide was used, as was the oxidation of the μ-S compound with hydrogen peroxide in an MTO-catalyzed reaction. To our knowledge, this is the first μ-SO compound prepared by direct insertion of sulfur monoxide into a metal−metal bond. The structure was confirmed spectroscopically and crystallographically.

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Supporting Information Available: Experimental procedures for the synthesis of and spectroscopic data for **3a**,**b** and **4a**,**b**, and X-ray diffraction data for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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