Modeling the Claus Reaction: Preparation of *trans*-Pt(PPh$_3$)$_2$(phthalimido)S(O)$_2$SR

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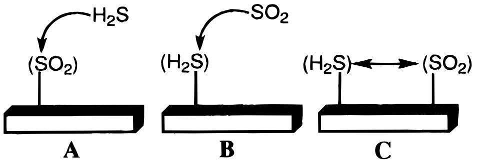
The removal of sulfur from crude oil is accomplished by hydrodesulfurization (HDS)[1] followed by the Claus process,[2] which converts the H_2S produced by HDS to sulfur and water (eq 1). Natural gas contaminated by H_2S is purified by direct

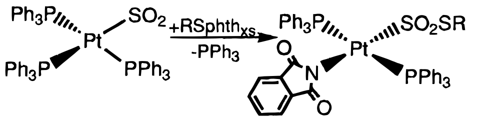
$$2H_2S + SO_2 \xrightarrow{\text{catalyst}} {}^{3}/_{8}S_8 + 2H_2O \qquad (1)$$

application of the Claus process. The Claus reaction is conducted at 300 °C using alumina as a catalyst although other materials also catalyze the reaction. The mechanism is unknown, but the reaction must involve the formation of sulfur−sulfur bonds and oxygen transfer, a suite of reactions with few precedents in homogeneous catalysis. Three simple conceptual models of the Claus reaction can be described. Model **A** depicts



attack by H_2S on adsorbed SO_2, model **B** represents attack by SO_2 on adsorbed H_2S,[3] and in **C** both the H_2S and the SO_2 are adsorbed before reaction.[4] Studies of the sequential adsorption and reactions of SO_2 and H_2S on alumina[5] are for the most part inconclusive; however, preadsorbed SO_2 is reactive toward H_2S.[5d] Therefore, the complex Pt(PPh$_3$)$_3$SO$_2$,[6] chosen as an example of preadsorbed SO_2, was treated with a source of RS^+ as a simulation of model **A**.

Treatment of Pt(PPh$_3$)$_3$SO$_2$ with RSphth[7] gave pale yellow complexes of the type *trans*-Pt(PPh$_3$)$_2$(phth)S(O)$_2$SR, **1a−f**, where phth = phthalimido (eq 2). The IR and NMR (^{1}H and



(2)

1a, R= CH_3
b, R= CH_2CH_3
c, R= n-C_3H_7
d, R= $CHMe_2$
e, R= 4-C_6H_4Me
f, R= CH_2Ph

^{31}P) spectra of **1a−f** are consistent with their formulation,[8] and the structure of **1f**, shown in Figure 1, confirms the presence of the PtS(O)$_2$SCH$_2$Ph moiety.[9] Interestingly, while organic thiosulfonates (RS(O)$_2$SR′) are known,[10] few structures have been reported;[11] complexes **1a−f** are the first to contain an RSS(O)$_2^-$ ligand.[12] Sulfito groups are the parent ligands of this new class.[3k,13]

Attachment of the RS^+ residue to the SO_2 ligand of Pt(PPh$_3$)$_3$-SO$_2$ and oxidation of the metal center result in a much shorter Pt−S distance (2.261(3) Å) in **1f** than in the precursor (2.368-(3) Å).[14] The Pt−S distance in **1f** is also shorter than those in *cis*-Pt(PPh$_3$)$_2$(phth)SSCHMe$_2$ (2.353(3) Å),[15] [Pt(PPh$_3$)$_2$(S(O)-

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(8) Preparative procedures and characterization data are given in the Supporting Information.

(9) Crystal data for *trans*-Pt(PPh$_3$)$_2$(phth)S(O)$_2$SCH$_2$Ph·0.75CH$_2$Cl$_2$ **1f**: monoclinic $P2_1/c$ (No. 14), a = 21.212(4) Å, b = 13.996(2) Å, c = 17.789(3) Å, V = 4868.9(14) Å^3, β = 112.79(1)°, Z = 4, D_c = 1.524 g/cm^3, μ(Mo Kα) = 3.190 mm^{-1}, λ(Mo Kα) = 0.709 30 Å (graphite monochromated); $2\theta_{max}$ = 50°, 32 688 measured reflections (8585 unique, R(int) = 0.133); R = 0.063, R_w = 0.108, GOF = 0.887 (4409 reflections with $I > 2.00\sigma(I)$). A complete structural report is included in the Supporting Information.

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(12) The RSS(O)$_2^-$ ligands in **1a−f** are isomeric with those in (a) CpRu-(PPh$_3$)(CO)SS(O)$_2$-4-C$_6$H$_4$Me (Shaver, A.; Plouffe, P. Y. *J. Am. Chem. Soc.* **1991**, *113*, 7780) and (b) CpRu(CO)$_2$SS(O)$_2$Ph (Trojansek, D. Ph.D. Thesis, McGill University, 1995).

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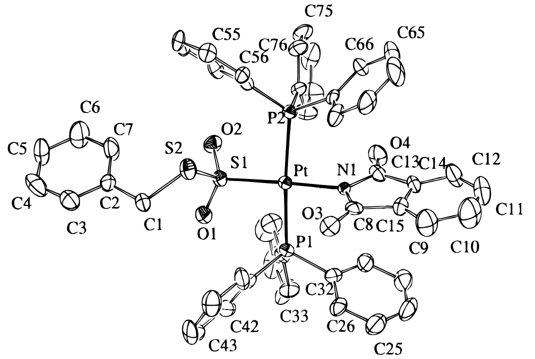

Figure 1. ORTEP drawing of *trans*-Pt$(PPh_3)_2$(phth)SO_2SCH_2Ph, **1f**. Selected bond lengths (Å) and angles (deg): Pt−S, 2.261(3); Pt−P(1), 2.341(3); Pt−P(2), 2.360(2); Pt−N, 2.061(7); S(1)−S(2), 2.154(4); S(1)−O(1), 1.446(7); S(1)−O(2), 1.451(7); Pt−S(1)−O(1), 114.4(3); Pt−S(1)−O(2), 112.5(3); Pt−S(1)−S(2), 102.3(1); O(1)−S(1)−O(2), 114.2(5); P(1)−Pt−P(2), 171.1(1); S(1)−Pt−N, 177.2(2).

$(CH_2)_4S$] (Pt−S(O) = 2.333(2) Å, Pt−S = 2.334(3) Å).[16] The S−O bond lengths are within the normal range,[17] while the S−S bond distance (2.154(4) Å) is longer[11c] than that in 4-C_6H_4BrS-$(O)_2$S-4-C_6H_4Br (2.091(6) Å)[11b] and those in *cis*-Pt$(PPh_3)_2$(phth)-SSCHMe$_2$ (2.037(4) Å)[15] and in other metal-coordinated polysulfur oxide ligands of the type RS(O)S^- and RS$(O)_2S^-$.[18]

Complex **1f** lost SO_2 at 110 °C under vacuum to give *trans*-Pt$(PPh_3)_2$(phth)SCH_2Ph, which does not react in solution with SO_2 to regenerate **1f**. This leads one to suggest that the 1,2-oxidative addition[19] of RSphth to the Pt−SO_2 bond in Pt$(PPh_3)_3$-SO_2 occurs via direct attachment of the RS^+ group to the pyramidal (nucleophilic)[17] SO_2 ligand rather than by attack at the platinum metal atom followed by insertion of SO_2 into the Pt−SR bond thus formed. While insertion reactions of SO_2 into metal−carbon bonds are well-known,[20] similar insertion reactions of SO_2 into other metal−atom bonds are rare[3fk,13ac,21] and are unknown for M−SR bonds even in complexes containing both the RS^- and SO_2 groups as ligands[4] (i.e., model **C**).

Complex **1f** reacted with ROH in $CHCl_3$ to give quantitatively the sulfito complexes *trans*-Pt$(PPh_3)_2$(phth)S$(O)_2$OR[8] (R = H, C_2H_5, CHMe$_2$). These are resistant to loss of SO_2 up to 200 °C. Exchange of **1f** with RSH is very slow, whereas treatment of **1f** with H_2S gave Pt$(PPh_3)_2$(H)(SH)[22] and $(PhCH_2S)_2$ as the major products as determined by ^{1}H NMR.

Treatment of Pt$(PPh_3)_3SO_2$ with the oxidized sulfur transfer reagent RS(O)phth[23] was expected to produce complexes containing the PtS$(O)_2$S(O)R moiety; however, complexes **1d**−**f** and PPh_3O were isolated and there was no evidence of the expected products. Since RS(O)phth is deoxygenated only very slowly by PPh_3, complexes **1d**−**f** are probably the products of deoxygenation of *trans*-Pt$(PPh_3)_2$(phth)S$(O)_2$S(O)R by free PPh_3 released from Pt$(PPh_3)_3SO_2$. The apparent activation of the oxygen atom on the *β*-sulfur atom of the RS(O)S$(O)_2^-$ ligand is noteworthy. The complexes CpRu(PPh_3)(CO)SS(O)R also undergo facile oxygen exchange to give CpRu$(PPh_3$(CO)SSR and CpRu(PPh_3)(CO)SS$(O)_2$R.[12] Kubas and co-workers have observed similar chemistry.[3h−k,24] On the other hand, complexes **1a**−**f**, which have oxygen atoms on the α-sulfur atom, are inert toward PPh_3. This observation may be useful in developing Claus-like chemistry with soluble metal complexes.

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Supporting Information Available: Text giving preparative methods, spectroscopic data, and X-ray analysis and tables of crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom coordinates for **1f** (16 pages). See any current masthead page for ordering information.

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(18) S−S bond distances are as follows. (a) CpRu(PPh_3)(CO)E:[12a] E = SS(O)CHMe$_2$, 2.076(3) Å; E = SS$(O)_2$-4-C_6H_4Me, 2.023(3) Å. (b) CpRu$(CO)_2$E:[12b] E = SS(O)Ph, 2.050(4) Å; E = SS$(O)_2$Ph, 2.037(2) Å. (c) CpRu$(PPh_3)_2$E: E = SS(O)CH_2Ph, 2.086(3) Å (Weigand, W.; Bosl, G.; Robl, C.; Kroner, J. *Z. Naturforsch., B:; Chem. Sci.* **1993**, *48B*, 627.

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