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Homogeneous Catalysts for Claus Chemistry: The Preparation and Structure of *cis*-[(PPh₃)₂PtS₃O], a Catalytically Active Intermediate**

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The removal of sulfur from petroleum and natural gas may be the most important pollution abatement process in place today. Hydrodesulfurization (HDS)^[1] of sulfur compounds gives hydrocarbons and the toxic gas H_2S , which is disposed of by the Claus process.^[2] This reaction combines H_2S and SO_2 , obtained by partial oxidation, over alumina at 300 °C, to give sulfur and

$2 H_2 S + SO_2 \longrightarrow 3/8 S_8 + 2 H_2 O$

water with very high efficiencies. Many materials catalyze the reaction, which is also observed in water. Studies of the sequential adsorption and reactions of SO_2 and H_2S on alumina are, for the most part inconclusive.^[3] While the details of the mechanism(s) of the Claus process are only partly understood, sulfur-sulfur bond formation and oxygen transfer must be involved—processes that have few precedents in homogeneous transition metal sulfur chemistry.

We are interested in Claus-like chemistry with soluble metal complexes and to that end have developed three conceptual models for the surface-catalyzed process and translated these into the appropriate reactions of homogeneous metal complexes. Model A depicts attack of H_2S on adsorbed SO₂, model B



represents attack by SO₂ on adsorbed H_2S , and in C both gases are adsorbed before reaction. In this report we describe the reaction of *cis*-[(PPh₃)₂Pt(SH)₂] (*cis*-2) with SO₂ (model B) to give [(PPh₃)₂PtS₃O] (1) and water. This represents a step in the Claus reaction. Moreover, both the complexes 1 and 2 catalyze the Claus reaction, whereas *trans*-2 does not.

Treatment of $cis-2^{[4]}$ in CH_2Cl_2 with one equivalent of SO_2 gave 1 in 82% yield [Eq. (a)]. H_2O was observed in the NMR spectrum of the reaction mixture in the correct relative ratio by



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Fig. 1. ORTEP drawing of the structure of $[(PPh_3)_2Pt(S_3O)] \cdot CH_2Cl_2 (1 \cdot CH_2Cl_2),$ excluding the phenyl rings of the PPh_3 ligands and the solvent atoms. Selected bond lengths [Å] and angles [7]: Pt-S1, 2.341(3); Pt-S3, 2.318(2); Pt-P1, 2.271(2); Pt-P2, 2.299(2); S1-S2, 2.042(2); S2-S3, 2.110(4); S2-O, 1.436(7); S1-Pt-S3, 80.73(9); P1-Pt-P2, 98.47(8); S1-Pt-P2, 88.37(8); S3-Pt-P1, 92.33(8); Pt-S1-S2, 91.3(1); S1-S2-S3, 93.2(2); Pt-S3-S2, 90.3(1).

integration. The structure of 1 is shown in Figure 1.^[5] The Pt-S1-S2-S3 ring is not planar: the dihedral angle between the plane formed by P1-P2-Pt-S1-S3 and the plane formed by S1-S2-S3 is 22.3° .^[6]

Complex 1 reacts with H₂S at room temperature in THF to give the starting thiol complex cis-2 which was identified in solution by NMR and also isolated. This regeneration prompted treatment of cis-2 and of 1 with a 2:1 mixture of H₂S and SO₂. The reaction was conducted in dry CH₂Cl₂, in very dry flasks that had been previously treated with Me₂SiCl, (unsilylated glass catalyzes the reaction). The gases were added to the solution by syringe, and the molar ratio of the catalyst to SO, was 1:20. Sulfur, identified by thin layer chromatography, formed after 3 hours.^[7] The yields of sulfur were high for complexes cis-2, 1, and cis-[(PPh₃)₂Pt(SCHMe₂)₂], whereas those for cis-[(PPh₃)₂PtCl₂] were moderate and for trans-[(PPh₃)₂Pt(SH)₂]^[8] negligible. The latter complex was recovered unchanged after treatment with pure SO2. Addition of further aliquots of gases to solutions containing the active catalysts produced more sulfur. Peaks due to cis-2 were found in the ¹H and ³¹P NMR spectra of *cis*-[(PPh₃)₂Pt(SCHMe₂)₂] upon treatment with H₂S. ³¹P NMR spectra of the solid residues of the catalytic reactions identified the presence of the starting complex and also 1 in the cases of cis-2 and cis- $[(PPh_3)_2Pt(SCHMe_2)_2]$; peaks due to Ph_3PS were also present.

Eller and Kubas^[9] showed that treatment of $[(PPh_3)_2Pt-(SPh)_2]$ with liquid SO₂ gave labile adducts of the type $[(PPh_3)_2Pt(S(SO_2)Ph)_2]$. We observed that the complexes $[(PPh_3)_2Pt(SR)_2]$, R = CMe₃, CHMe₂, and 4-C₆H₄Me, change color in CH₂Cl₂ from yellow to deep red upon treatment with SO₂. Addition of SO₂-saturated hexanes gave red-orange solids, which could only be characterized in solution because of facile loss of SO₂, which regenerates the thiolato complexes. These complexes are therefore formulated as bis(SO₂) adducts of the type $[(PPh_3)_2Pt(S(SO_2)R)_2]$.

Compound 1 is synthesized by a direct reaction between SO₂ and the thiolato complex 2, which leads to sulfur-sulfur bond formation and oxygen transfer, thus mimicking a fundamental step in the Claus process.^[10] The regeneration of the starting thiolato complex upon treatment of 1 with H₂S is consistent with the proposed catalytic cycle for the Claus reaction shown in Scheme 1. The first step is adduct formation between *cis*-2 and SO₂, followed by insertion of SO₂ into the SH bond. Subsequent elimination of H₂O gives 1, which reacts with H₂S to cleave the Pt-S

bonds and regenerate cis-2. The other cleavage product is designated as " H_2S_3O " simply on the basis of the stoichiometry and was not detected. It is significant, however, that " H_2S_3O " is believed to be a key intermediate in the Claus process^[111] and is expected to react rapidly with H_2S to give water and sulfur. These studies open a new chapter in the Claus process by introducing homogeneously catalyzed Claus chemistry.

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Scheme 1. Potential mechanism for Claus chemistry catalyzed by $cis_{[(PPh_3)_2Pt(SH)_2]}$.

Experimental Procedure

1: In a 100 mL Schlenk flask, *cis*-2 (0.050 g, 0.064 mmol) in dichloromethane (5.0 mL) was treated with SO₂ gas for 30 minutes at room temperature and stirred thereafter for another 3 h. The volatiles were removed under vacuum, and the resulting yellow solid was recrystallized from in dichloromethane/hexanes. The yellow crystals were isolated by the removal of the mother liquor with a syringe (0.043 g, 82%). M.p. 262–263 °C. IR (Nujol): \tilde{v} (SO) = 1065(s) cm⁻¹. ¹H NMR (CDCl₃): 7.26 (m, PPh₃). ³¹P NMR (CDCl₃): 18.5 (*J*(Pt,P) = 3200 Hz). Mass spectrum (FAB in NBA): *m/z* 832 [*M*⁺], 784 [*M*⁺ - SO], 752 [*M*⁺ - S₂O], 720 [*M*⁺ - S₃O]. C,H analysis calcd. for (C₃₆H₃₀OP₂PtS₃·CH₂Cl₂): 48.47% C, 3.52% H.

Catalyzed reactions of H_2S with SO_2 : H_2S was dried by passage through a column of P_2O_5 , and SO_2 was purified by bubbling through concentrated sulfuric acid and then by passage through a column of P_2O_5 . The Schlenk flasks (100 mL) were silylated by treatment of the flask with Me_2SiCl_2 (30 mL) for 12 h under a nitrogen atmosphere. Then the Me_2SiCl_2 was removed by syringe, and the flask dried under vacuum overnight. Sulfur produced from these reactions was identified by TLC (alumina) and mass spectroscopy.

The flask was charged with the solid catalyst $(5.15 \times 10^{-2} \text{ mmol})$, evacuated, filled with N₂ twice, and weighed. CH₂Cl₂ (20.0 mL) was added, and H₂S (2.06 mmol, 50.0 mL) was bubbled slowly (syringe) into the mixture, followed by the addition (by syringe) of SO₂ (1.03 mmol, 25.0 mL). The resulting solution was stirred at room temperature for 3 h, and then purged with nitrogen for 30 min. The volatiles were removed under vacuum, and the resulting solid was dried under vacuum for 4 days. The flask and its contents was weighed again to estimate the amount of sulfur formed.

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(TEXSAN): linear decay correction -0.6% and absorption (psi scans, transmission range from 0.81 to 1.00), solution by the Patterson method. The central sulfur atom of the PtS, ring is disordered over two sites S2 and S2a at 0.73 and 0.27 occupancies, respectively, corresponding to positions above and below the plane formed by PtS1S3. The position of the oxygen atom corresponding to the minor orientation (O₃) could not be resolved so the oxygen atom of the major orientation was assigned full occupancy. Distances given in the figure refer only to the major orientation. The carbon atom in the CH2Cl2 solvent is also disorded over two sites at 0.66 and 0.33 occupancies. All non-H atoms except S2a and the two solvent carbon atoms CS1 and CS2 were refined anisotropically, H-atoms were introduced in idealized positions. Final agreement factors: R = 0.040, Rw = 0.037 (418 parameters), S = 1.04. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-179-94. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: teched@chemcrvs.cam.ac.uk).

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Catalytic, Enantioselective Addition of Allylsilanes to Aldehydes: Generation of a Novel, Reactive Ti^{IV} Complex from TiF_4

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The stereoselective addition of allylmetal reagents to aldehydes is a powerful and important reaction for the preparation of homoallylic alcohols and has been extensively employed for the synthesis of stereochemically complex natural products.^[1,2] Recently, catalytic versions of this process that utilize Ti^{IV} complexes and allyl- or methallyltin reagents have been reported, which afford homoallylic alcohols with high enantioselectivities and yields.^[3] However, additions involving the corresponding inexpensive, nontoxic allyltrimethylsilane to give protected homoallylic alcohols in useful yields and enantioselectivities have not been reported [Eq. (a)]. As a part of our interest in developing chiral complexes that function competently as catalysts in aldehyde additions, we have studied Ti^{IV} complexes prepared



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