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The Preparation of $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)S_4$ from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(SH)_2$ and SO_2

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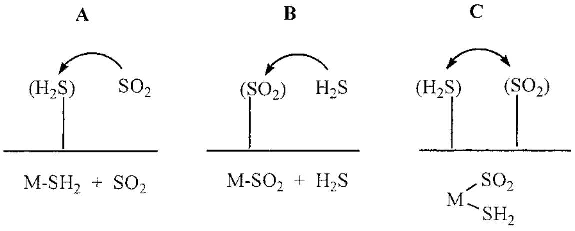
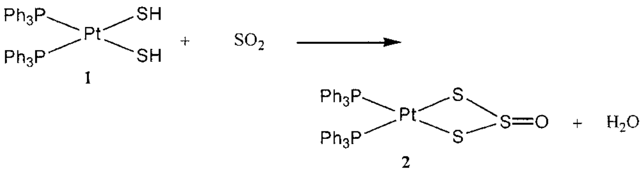
Introduction

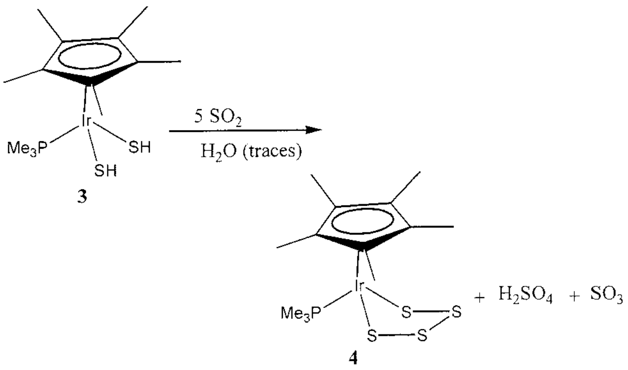
A problem associated with burning petroleum and natural gas is air pollution due to the presence of sulfur compounds which must be removed. Hydrodesulfurization (HDS)[1] gives hydrocarbons and the toxic gas H_2S, which is treated by the Claus process to give sulfur and water.[2] Three simple conceptual models of the heterogeneously catalyzed Claus reaction can be described. Model **A** depicts attack of chemisorbed H_2S by free SO_2, model **B** represents the attack of chemisorbed SO_2 by free H_2S, and in model **C**, both SO_2 and H_2S are adsorbed before reaction. These three models are easily translated to homogeneous system as shown.



With respect to model **A**, we recently reported[3] that *cis*-$(PPh_3)_2Pt(SH)_2$, **1**, homogeneously catalyzes the Claus Reaction. The catalytically active intermediate $(PPh_3)_2PtS_3O$, **2**, was isolated. The reaction of **1** with a molecule of SO_2 to give **2** and a molecule of H_2O may be the first step in the catalytic cycle.



The trans isomer of **1** was not catalytically active, which highlights the significance of the cis arrangement of the SH^- ligands. This created interest in the reactivity of other complexes which contain two adjacent SH^- ligands. Here we report the reaction of $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(SH)_2$, **3**, with excess SO_2 which, unexpectedly, gave a polysulfido complex, **4**.



Results and Discussion

Treatment of **3** in benzene or CH_2Cl_2 at room temperature with excess SO_2 led to a color change from yellow to dark red within 10 min. Subsequent work up gave red, air stable crystals of **4** in good yield. Sensitive TLC methods which have been developed[3] to detect the presence of sulfur were applied, but no traces of sulfur were detected. Complex **3** reacts with sulfur to give **4**, but the reaction takes 24 h to go to completion. This is consistent with the direct reaction between **3** and SO_2 to produce the tetrasulfido ring.

This complex has been reported as a member of a mixture of the polysulfide complexes of the type[4a] $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)S_x$, where $x = 4, 5, 6$, prepared from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)Cl_2$ and ammonium polysulfide. The analogous complex $(\eta^5\text{-}C_5Me_5)Ir(CO)S_4$, obtained by photolysis of $(\eta^5\text{-}C_5Me_5)$ $Ir(CO)_2$ in the presence of S_8,[4b] and the rhodium complexes, $CpRh(PPh_3)S_x$, where $x = 4, 5, 6$, are also known.[5] X-ray crystallographic analysis of **4** (Figure 1) showed that it is isomorphous with its selenium analogue.[6]

The reaction of **3** with SO_2 in CD_2Cl_2 was monitored by proton NMR. When excess SO_2 was injected, the only peaks observed where those due to **4** and one at 11.6 ppm, presumably due to sulfuric acid. Addition of a drop of a dilute solution of H_2SO_4 in CD_2Cl_2 to the NMR tube confirmed the assignment of this peak to H_2SO_4. Control experiments confirmed that its presence was due to the reaction of SO_2 with **3**. SO_3 is extremely difficult to directly detect in these kind of reactions. We assume that the production of H_2SO_4 is indirect evidence of SO_3 formation during the reaction, especially in the presence of traces of water. When the SO_2 was carefully dried prior to injection

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[1] (a) Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice,* 2nd ed., McGraw-Hill: New York, 1991; p 378. (b) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; p 390. (c) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905.

[2] (a) Yanxin, C.; Yi, J.; Wenhafo, L.; Rongchao, J.; Shaozhen, T.; Wenbin, H. *Catal. Today* **1999**, *50*, 39. (b) Stern, D. L.; Nariman, K. E.; Buchanan, J. S.; Bhore, N. A.; Johnson, D. L.; Grasselli, K. R. *Catal. Today*. **2000**, *55*, 311. (c) Grancher, P. *Hydrocarbon Process.* **1978**, *57*, 155. (d) Grancher, P. *Hydrocarbon Process.* **1978**, *57*, 257. (e) George, Z. M.; Tower, R. W. *Can. J. Chem. Eng.* **1985**, *63*, 618. (f) Datta, A.; Cavell, R. G.; Tower, T. W.; George, Z. M. *J. Phys. Chem.* **1985**, *89*, 443. (g) Datta, A.; Cavell, R. G. *J. Phys. Chem.* **1985**, *89*, 450. (h) Datta, A.; Cavell, R. G. *J. Phys. Chem.* **1985**, *89*, 454. (i) Karge, H. G.; Dalla Lana, I. G. *J. Phys. Chem.* **1984**, *88*, 1958.

[3] Shaver, A.; El-khateeb, M.; Lebuis, A.-M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2362.

[4] (a) Herberhold, M.; Jin, G.-X.; Rheingold, A. L. *Chem. Ber*. **1991**, *124*, 2245. (b) Herberhold, M.; Jin, G.-X.; Milius, W. *Chem. Ber*. **1995**, *128*, 557.

[5] Wakatsuki, Y.; Yamazaki, H.; Cheng, C. *J. Organomet. Chem*. **1989**, *372*, 437.

[6] Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022.

10.1021/ic001385p CCC: $20.00

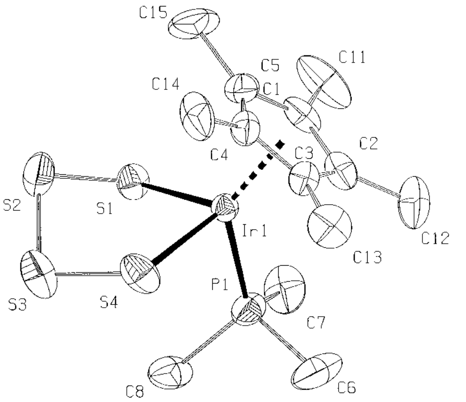

Figure 1. Platon drawing (40%) of (η^5-C_5Me_5)Ir(PMe_3)S_4. Selected bond lengths (Å) and angles (deg): Ir−S(1), 2.359(3); Ir−S(4), 2.365(4); Ir−P, 2.258(4); S(1)−S(2), 2.057(6); S(2)−S(3), 2.034(8); S(3)−S(4), 2.065(7); P−Ir−S(1), 86.53(14); P−Ir−S(4), 90.57(16); S(1)−Ir−S(4), 92.41(15); S(3)−S(4)−Ir, 107.9(2).

Table 1. Crystallographic Data for Complex **4**

chemical formula	$C_{13}H_{24}IrPS_4$
fw	531.75
cryst syst	orthorhombic
space group	$P2_12_12_1$
a	8.767(3) Å
b	13.443(5) Å
c	15.447(4) Å
V	1820.5(10) Å
$Z=$	1.940 g/cm^{-3}
d_{calc}	4
λ	0.70930 Å
T	293(2) K
R_1[a]	0.053, 0.063 ($I > 2\sigma(I)$,all)
ωR_2 (on F_2)[b]	0.126, 0.133 ($I > 2\sigma(I)$,all)
Flack[11d]	−0.01(2)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)/\Sigma(\omega(F_o^2)^2]^{1/2}$.

in excess, several peaks were observed, suggesting the presence of many products including **4**. Injection of unpurified SO_2 in 1, 2, 3, or 4 equiv gave peaks due to **3** and **4** in the ratio consistent with the stoichiometry; no intermediates were observed. Addition of 5 equiv of SO_2 gave complete conversion, giving rise to the assigned stoichiometry of the reaction. Complex **4** does not react with H_2S or H_2 and, therefore, perhaps not surprisingly, neither **3** nor **4** catalyses the Claus process.

Treatment of (η^5-C_5Me_5)Ir(PMe_3)(SH)(H) with SO_2 gave decomposition while (η^5-C_5Me_5)Ir(PMe_3)(SH)Cl gave (η^5-C_5Me_5)Ir(PMe_3)Cl_2 and **4**, which is consistent with metathesis to form the dichloride and **3**. Similar treatment of (η^5-C_5Me_5)Ir(PMe_3)(SH)(Br) gave **4**, some of the hexasulfide (η^5-C_5Me_5)Ir(PMe_3)S_6,[4a] and (η^5-C_5Me_5)Ir(PMe_3)Br_2.

Kubas and co-workers have summarized the structure, bonding,[7a] and reactivity[7b] of SO_2 containing complexes. The formation of sulfato complexes has been observed previously via unusual reactions, such as that[7c] between SO_2 and Ru(H)$_2$(PR_3)$_x$, where x = 3 or 4, to give Ru(SO_4)(SO_2)(PPh_3)(H_2O) wherein SO_2 disproportionation was proposed. SO_2 reacted with (η^6-C_6H_6)$_2$Cr to give[8] the salt [(η^6-C_6H_6)$_2$Cr]S_4O_{10}, which contains the anion $S_2O_6 \cdot 2SO_2^{2-}$. The complex (dppe)$_2$Mo(N_2)$_2$ reacted[9] with SO_2 to give *trans*-(dppe)$_2$Mo(S)O, the crystal structure of which contained SO_2 and H_2SO_4 in stoichiometric proportion in the lattice. Oxygen transfer from SO_2 has been observed[10] in the reaction of SO_2 with (η^5-C_5Me_5)Ru(CO)$_2$H to give (η^5-C_5Me_5)Ru(CO)$_2SO_3$H and [(η^5-C_5Me_5)Ru(CO)$_2$]$_2$(μ-S_2O_3). The reaction between (η^5-C_5Me_5)Ir(PMe_3)(SH)$_2$ and SO_2 reported here has few precedents and represents another interesting example[3] of Claus-like chemistry induced by a metal complex with two cis-oriented SH^- ligands.

Experimental Section

Cp*Ir(PMe$_3$)S$_4$, 4. (η^5-C_5Me_5)Ir(PMe_3)(SH)$_2$ (0.17 g, 0.36 mmol) was dissolved in CH_2Cl_2 (3 mL), and an excess of SO_2 was added by syringe. The reaction changed color immediately from yellow to red−orange. After 15 min, hexane (1.5 mL) was added, and the reaction was cooled to −15 °C. The red oil thus obtained was dissolved in methanol (5 mL) and left standing at room temperature to give large red crystals. Yield: 89%. The spectroscopic data was the same as that published in the literature.[4a]

X-ray Structure Determination for 4 (Table 1). A red crystal of **4** (0.65 × 0.57 × 0.25 mm), obtained by slow evaporation of a methanolic solution, was mounted on a glass fiber. Intensity measurements were made using a Rigaku AFC6S diffractometer with Mo Kα radiation. A total of 14 258 reflections were collected ($-10 \le h \le 10$, $-16 \le k < 16$, $-19 \le l < 19$) using $\omega/2\theta$ scan mode to a maximum 2θ value of 52°; of these 3 584 were unique (merging R_{int} = 0.12, decay = 0.8%). The number of reflections observed ($I > 2\sigma(I)$) was 3 157. The data were processed and corrected for absorption (ψ scans, transmission range 0.26−1.00 μ = 7.826 mm^{-1}). The structure was solved by direct methods using SHELXS[11a] and difmap synthesis using SHELXL 96.[11b] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were calculated at idealized positions using riding model with different C−H distances for each type of hydrogen. Atomic scattering factors are from the usual sources.[11c]

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Supporting Information Available: Deposited material includes a complete table of X-ray data and references, final refined atomic, anisotropic thermal parameters, calculated hydrogen atom coordinates, complete table of bond lengths and angles, torsion angels, least-squares planes for complex **4**, and an X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) (a) Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller P. G. *Struct. Bonding* **1981**, *46*, 48. (b) Kubas, G. J. *Acc. Chem. Res.* **1994**, *27*, *183*. (c) Ghatak, I.; Mingos, D. M. P.; Hursthouse, M. B.; Abdul-Malik, K. M. *Transition Met. Chem.* (London) **1979**, *4*, 260.

(8) Elschenbroich, C.; Gondrum, R.; Massa, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 11.

(9) Lorenz, I.-P.; Walter, G.; Hiller, W. *Chem. Ber.* **1990**, *123*, 979.

(10) Kubat-Martin, K. A.; Kubas, G. J.; Ryan, R. R. *Organometallics*, **1989**, *8*, 1910.

(11) (a) Sheldrick, G. M. *SHELXS*, Program for the solution of crystal structures; University of Gottingen: Germany, 1990. (b) Sheldrick, G. M. *SHELX1-96*, Program for structure analysis; University of Gottingen: Germany, 1996. (c) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, Tables 4, 2, and 6. (d) Flack, H. D. *Acta Cryst.* **1983**, *A39*, 876−881.