

### Thermochemistry of $\text{Pt}(\text{PPh}_3)_3\text{SO}_2$ and the Reaction of $\text{SO}_2$ with $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$

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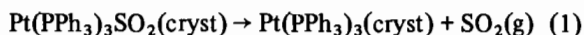
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As part of an extensive investigation into the bonding properties of ambidentate ligands<sup>1-3</sup> the strength of the Pt-SO<sub>2</sub> bond in  $\text{Pt}(\text{PPh}_3)_3\text{SO}_2$  was studied. An interesting reaction of SO<sub>2</sub> with  $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$  was found to occur.

#### $\text{Pt}(\text{PPh}_3)_3\text{SO}_2$

This compound was prepared according to the procedure of Levison and Robinson.<sup>4</sup> Decomposition of this compound was studied with a Mettler TA-1 thermobalance. At 170 °C SO<sub>2</sub> had disappeared quantitatively according to reaction (1):



At 180 °C further decomposition of  $\text{Pt}(\text{PPh}_3)_3$  occurred.

Calorimetric measurements of the heat of reaction by a Dupont 990 DSC apparatus showed that reaction (1) starts at 117 °C and is complete at 166 °C with a peak temperature of 143 °C and a heat of reaction of  $14.6 \pm 1.0$  kcal/mol. The heating rate was 2 degrees per minute. Heat capacities were measured for  $\text{Pt}(\text{PPh}_3)_3\text{SO}_2$  and  $\text{Pt}(\text{PPh}_3)_3$ , and together with the literature value for the heat capacity of SO<sub>2</sub><sup>5</sup>, the heat of reaction at 25 °C was calculated to be  $14.5 \pm 1.0$  kcal/mol.

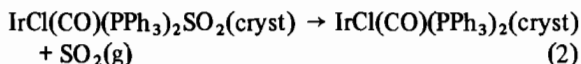
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TABLE. Some Relevant Data for SO<sub>2</sub> and Its Complexes of Pt<sup>0</sup> and Ir<sup>I</sup>.

Compound	Metal-Sulfur Distance (Å)	Heat of Reaction at 25 °C (kcal/mol)	SO <sub>2</sub> Stretching Frequencies (cm <sup>-1</sup> )	
			$\nu_{\text{as}}$	$\nu_{\text{s}}$
Free SO <sub>2</sub> <sup>a</sup>			1340	1150
$\text{Pt}(\text{PPh}_3)_3\text{SO}_2$	2.399 <sup>b</sup>	14.5	1202	1051
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{SO}_2$	2.488 <sup>c</sup>	9.6 <sup>d</sup>	1198, 1185	1048 <sup>e</sup>

<sup>a</sup> Ref. 7. <sup>b</sup> Ref. 8. <sup>c</sup> Ref. 9. <sup>d</sup> Ref. 6. <sup>e</sup> Ref. 10.

In the table some important structural data are collected for  $\text{Pt}(\text{PPh}_3)_3\text{SO}_2$  and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{SO}_2$ , which latter compound also loses SO<sub>2</sub> on heating according to reaction (2):<sup>6</sup>



According to the crystallographic results,<sup>8</sup> SO<sub>2</sub> is coordinated to Pt via the lone pair of sulfur, while it is bonded in a bent configuration to Ir in  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{SO}_2$ .<sup>9</sup>

The metal-SO<sub>2</sub> bond is found to be stronger in the Pt complex, as can be seen from the smaller metal-sulfur distance and the larger heat of reaction.

Linsky and Pierpont<sup>8</sup> concluded from the structural results that, contrary to the Ir complex, SO<sub>2</sub> is bonded purely as a base to Pt. This, however, is very unlikely in view of the nucleophilic nature of Pt<sup>0</sup> and the lowering of the SO<sub>2</sub> stretching frequencies by 100-150 cm<sup>-1</sup> with respect to the free molecule. This latter behaviour is only found when SO<sub>2</sub> is bonded as a Lewis acid to the metal as e.g. in  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{SO}_2$ . The SO<sub>2</sub> frequencies of the Pt and Ir complexes hardly differ from each other, which means that  $\pi$ -bonding with SO<sub>2</sub> is equally strong in both complexes. On the other hand, owing to the much higher heat of reaction of the Pt complex, a higher contribution of  $\sigma$ -bonding between Pt and SO<sub>2</sub> has to be assumed.

#### $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$

$\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ , prepared as described by Collmann *et al.*,<sup>11</sup> easily decomposes in solution and therefore the reaction with SO<sub>2</sub> was performed between the solid complex and gaseous SO<sub>2</sub>.

During this reaction N<sub>2</sub> is replaced by SO<sub>2</sub> as seen from the simultaneous disappearance of  $\nu(\text{N}\equiv\text{N})$  at 2105 cm<sup>-1</sup> and appearance of SO<sub>2</sub> stretching frequencies at 1272 and 1125 cm<sup>-1</sup>. These frequencies show that SO<sub>2</sub> is coordinated to Ir as a base just as in the complex  $[\text{RuCl}(\text{NH}_3)_4(\text{SO}_2)]\text{Cl}$ .<sup>12</sup>

On further reaction two extra  $\text{SO}_2$  vibrations appear at 1198 and  $1050\text{ cm}^{-1}$  which are also present in the IR spectrum of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{SO}_2$ .<sup>8</sup> Thus a second  $\text{SO}_2$  molecule is bonded as a Lewis acid to Ir. This resulting complex can be formulated as  $\text{IrCl}(\text{PPh}_3)_2(\text{SO}_2)_2$ , which is the first complex reported in which two  $\text{SO}_2$  molecules are bonded to the metal in different ways.

At ambient temperature the reaction proceeds very slowly and only the complex  $\text{IrCl}(\text{PPh}_3)_2(\text{SO}_2)_2$  can be isolated. At temperatures above  $120^\circ\text{C}$  only the complex  $\text{IrCl}(\text{PPh}_3)_2\text{SO}_2$  is formed. Careful heating is necessary however, as the complex easily undergoes a metallation reaction as shown by the appearance of a  $\nu(\text{Ir-H})$  absorption at  $2080\text{ cm}^{-1}$ .<sup>13</sup>

Both complexes are red-brown, decompose in solution and cannot easily be purified, so that analytical data are not accurate. The solid  $\text{IrCl}(\text{PPh}_3)_2\text{SO}_2$  reacts with CO at higher temperatures with formation of Vaska's compound,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ .

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