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Thermochemistry of $Pt(PPh_3)_3SO_2$ and the Reaction of SO_2 with $IrCl(N_2)(PPh_3)_2$

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As part of an extensive investigation into the bonding properties of ambidentate ligands[1-3] the strength of the $Pt–SO_2$ bond in $Pt(PPh_3)_3SO_2$ was studied. An interesting reaction of SO_2 with $IrCl(N_2)(PPh_3)_2$ was found to occur.

$Pt(PPh_3)_3SO_2$

This compound was prepared according to the procedure of Levison and Robinson.[4] Decomposition of this compound was studied with a Mettler TA-1 thermobalance. At 170 °C SO_2 had disappeared quantitatively according to reaction (1):

$$Pt(PPh_3)_3SO_2(cryst) \rightarrow Pt(PPh_3)_3(cryst) + SO_2(g) \quad (1)$$

At 180 °C further decomposition of $Pt(PPh_3)_3$ 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 ± 1.0 kcal/mol. The heating rate was 2 degrees per minute. Heat capacities were measured for $Pt(PPh_3)_3SO_2$ and $Pt(PPh_3)_3$, and together with the literature value for the heat capacity of SO_2 [5], the heat of reaction at 25 °C was calculated to be 14.5 ± 1.0 kcal/mol.

In the table some important structural data are collected for $Pt(PPh_3)_3SO_2$ and $IrCl(CO)(PPh_3)_2SO_2$, which latter compound also loses SO_2 on heating according to reaction (2):[6]

$$IrCl(CO)(PPh_3)_2SO_2(cryst) \rightarrow IrCl(CO)(PPh_3)_2(cryst) + SO_2(g) \quad (2)$$

According to the crystallographic results,[8] SO_2 is coordinated to Pt via the lone pair of sulfur, while it is bonded in a bent configuration to Ir in $IrCl(CO)(PPh_3)_2SO_2$.[9]

The metal–SO_2 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[8] concluded from the structural results that, contrary to the Ir complex, SO_2 is bonded purely as a base to Pt. This, however, is very unlikely in view of the nucleophilic nature of Pt^0 and the lowering of the SO_2 stretching frequencies by 100–150 cm^{-1} with respect to the free molecule. This latter behaviour is only found when SO_2 is bonded as a Lewis acid to the metal as *e.g.* in $IrCl(CO)(PPh_3)_2SO_2$. The SO_2 frequencies of the Pt and Ir complexes hardly differ from each other, which means that π-bonding with SO_2 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 σ-bonding between Pt and SO_2 has to be assumed.

$IrCl(N_2)(PPh_3)_2$

$IrCl(N_2)(PPh_3)_2$, prepared as described by Collmann *et al.*,[11], easily decomposes in solution and therefore the reaction with SO_2 was performed between the solid complex and gaseous SO_2.

During this reaction N_2 is replaced by SO_2 as seen from the simultaneous disappearance of $\nu(N\equiv N)$ at 2105 cm^{-1} and appearance of SO_2 stretching frequencies at 1272 and 1125 cm^{-1}. These frequencies show that SO_2 is coordinated to Ir as a base just as in the complex $[RuCl(NH_3)_4(SO_2)]Cl$.[12]

TABLE. Some Relevant Data for SO_2 and Its Complexes of Pt^0 and Ir^I.

Compound	Metal–Sulfur Distance (Å)	Heat of Reaction at 25 °C (kcal/mol)	SO_2 Stretching Frequencies (cm^{-1})	
			ν_{as}	ν_s
Free SO_2[a]			1340	1150
$Pt(PPh_3)_3SO_2$	2.399[b]	14.5	1202	1051
$IrCl(CO)(PPh_3)_2SO_2$	2.488[c]	9.6[d]	1198, 1185	1048[e]

[a] Ref. 7. [b] Ref. 8. [c] Ref. 9. [d] Ref. 6. [e] Ref. 10.

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On further reaction two extra SO_2 vibrations appear at 1198 and 1050 cm^{-1} which are also present in the IR spectrum of $IrCl(CO)(PPh_3)_2SO_2$.[8] Thus a second SO_2 molecule is bonded as a Lewis acid to Ir. This resulting complex can be formulated as $IrCl(PPh_3)_2(SO_2)_2$, which is the first complex reported in which two SO_2 molecules are bonded to the metal in different ways.

At ambient temperature the reaction proceeds very slowly and only the complex $IrCl(PPh_3)_2(SO_2)_2$ can be isolated. At temperatures above 120 °C only the complex $IrCl(PPh_3)_2SO_2$ is formed. Careful heating is necessary however, as the complex easily undergoes a metallation reaction as shown by the appearance of a ν(Ir–H) absorption at 2080 cm^{-1}.[13]

Both complexes are red-brown, decompose in solution and cannot easily be purified, so that analytical data are not accurate. The solid $IrCl(PPh_3)_2SO_2$ reacts with CO at higher temperatures with formation of Vaska's compound, $IrCl(CO)(PPh_3)_2$.

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