

# Sulphur Dioxide Complexes of the Platinum Metals\*

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## Summary

The structural, chemical and theoretical aspects of the coordination chemistry of sulphur dioxide complexes of the platinum metals have been reviewed. A detailed evaluation of the analogy between nitric oxide and sulphur dioxide ligands has been made, and it has been concluded that although the structural properties of complexes of these ligands are closely related, their oxidative-addition and oxidation reactions differ in many important respects.

## Introduction

The first sulphur dioxide-transition metal complex was reported almost forty years ago by Gleu in 1938<sup>(1)</sup>, but it was not until the mid-nineteen sixties<sup>(2–4)</sup> that an extensive series of platinum-metal sulphur dioxide complexes were synthesised and characterised by spectroscopic and x-ray crystallographic studies. The latter demonstrated that the sulphur dioxide ligand has a variable coordination geometry<sup>(5–7)</sup>, which parallels that displayed by the more extensively studied nitrosyl ligand<sup>(8–10)</sup>. In 1967 Cook<sup>(11)</sup> and Robinson<sup>(3, 12)</sup> demonstrated that, when coordinated to zero-valent platinum metal complexes, the sulphur dioxide ligand is oxidised aerobically to sulphate, and the possible relevance of this to the platinum catalysed SO<sub>2</sub> oxidation in the contact process was noted. During the last two years the detrimental environmental effects of sulphur dioxide has resulted in a renewed interest in the chemistry of this ligand, particularly by Ryan and his co-workers<sup>(13–15)</sup> in the United States.

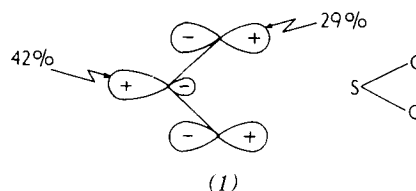
The coordination chemistry of sulphur dioxide has not been reviewed previously and therefore before discussing the detailed properties of specific complexes, some general aspects of the structures of, and bonding in, these complexes will be described. In particular the coordination chemistry of this ligand will be related to the electronic characteristics of the parent molecule.

## Structure and Electronic Properties of Sulphur Dioxide

Electron diffraction<sup>(16)</sup>, x-ray diffraction<sup>(17)</sup> and microwave studies<sup>(18)</sup> have established that SO<sub>2</sub> has an angular C<sub>2v</sub> geometry with an O–S–O bond angle of 119° and S–O bond length of 1.431(1) Å. The molecule has a dipole moment<sup>(19)</sup> of 1.61 D and first ionization potential of 12.34 eV<sup>(20)</sup>. This value is contrasted with that for some other common ligands below<sup>(21)</sup>.

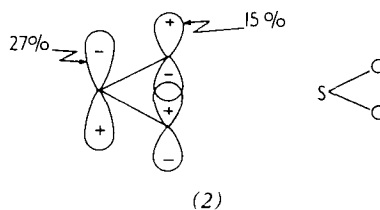
Ligand	SO <sub>2</sub>	N <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	NH <sub>3</sub>	OH <sub>2</sub>
1st I.P. (eV)	12.34	15.58	14.00	10.52	10.85	12.61

The ionization potential of SO<sub>2</sub> is comparable to that of water and smaller than those reported for N<sub>2</sub> and CO and therefore, in a naive way, if the formation of coordinate bonds is associated with the ionization process a reasonably extensive coordination chemistry for SO<sub>2</sub> is anticipated. *Ab initio* molecular orbital calculations by Hillier, Dacre, Siegbahn and their co-workers<sup>(22–24)</sup> have indicated that for SO<sub>2</sub> the ionization process described above originates from an orbital of a<sub>1</sub> symmetry which is concentrated primarily on the sulphur atom but also has contributions from the oxygen 2p orbitals. This orbital, which may be loosely described as the SO<sub>2</sub> "lone pair" orbital, *n*, is illustrated schematically in (1).



This molecular orbital is weakly antibonding between sulphur and oxygen but bonding between oxygen atoms, therefore electron donation from this orbital to an empty orbital on the metal with the appropriate symmetry could result in some shortening of the S–O bond length and opening up of the O–S–O bond angle.

The theoretical studies noted above have also indicated that SO<sub>2</sub> has a low lying empty orbital of b<sub>1</sub> symmetry suitable for back donation from a metal atom with filled d orbitals. This orbital which is represented schematically



in (2) is thought to lie at ca. –9.00 eV relative to the free electron. This energy is approximately the same as that for the π\* levels in N<sub>2</sub> (–7.1 eV) and CO (–6.0 eV). Therefore the SO<sub>2</sub> ligand is expected to show some π-acceptor properties when coordinated to low valent transition metals. The sulphur d<sub>yz</sub> orbital also makes a contribution to this molecular orbital, and has the effect of rehybridising the sulphur p<sub>y</sub> orbital away from the oxygen atoms. The b<sub>1</sub> acceptor orbital (2) is also S–O antibonding and oxygen-oxygen

\* Reprints of this article are not available.

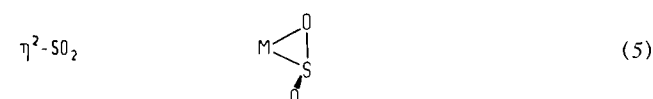
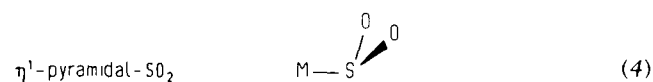
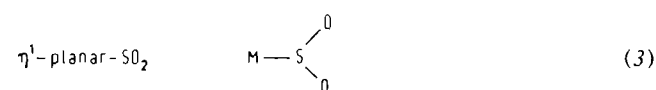
bonding and therefore back donation into this orbital could result in a lengthening of a S-O bond and a decrease in the O-S-O bond angle. It follows from the discussion above that structural studies on the coordinated SO<sub>2</sub> ligand could lead to a clear separation of competing forward and back donation effects.

Before considering in detail specific bonding situations for the SO<sub>2</sub> ligand, it must be emphasised that the above discussion based as it is on relative energies must be tempered by the knowledge that the overlap integrals between the sulphur orbitals and a transition metal are probably significantly smaller than those for a first row donor atom (e.g. O or N).

## Bonding in Sulphur Dioxide Transition Metal Complexes

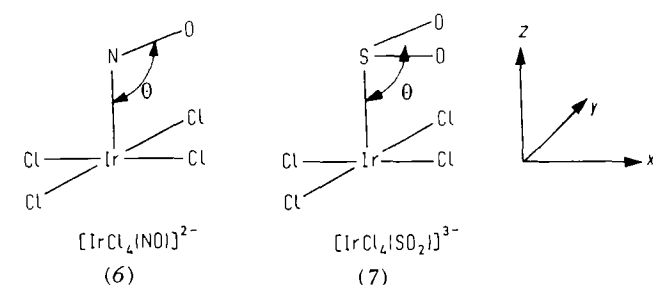
### (a) Mononuclear complexes

Three distinct coordination modes have been identified for the SO<sub>2</sub> ligand and these are illustrated in (3-5). For the purposes of this review these geometries will be distinguished by the following names based on the *hapto* (or *eta*) nomenclature schemes<sup>(25)</sup>.



Structures (3) and (4) closely resemble the *linear* and *bent* geometries which have been observed for coordinated nitric oxide and several workers<sup>(23, 26, 27)</sup> have noted that the ambistructural behaviour exhibited by these and related ligands has its origins in the presence of low lying acceptor levels [e.g. the  $\pi^*$  for NO, and the  $b_1$  orbital shown in (2) for SO<sub>2</sub>]. The  $\eta^2$ -coordination mode has not been identified for nitric oxide, but has been established for other triatomic ligands, e.g. CS<sub>2</sub><sup>(28)</sup>.

Figure 1 illustrates schematically the bonding interactions for the square-pyramidal complexes [IrCl<sub>4</sub>(NO)]<sup>2-</sup> and [IrCl<sub>4</sub>(SO<sub>2</sub>)]<sup>3-</sup> with the nitrosyl and sulphur dioxide ligands coordinated in linear and  $\eta^1$ -planar geometries respectively, i.e. the  $\theta$  angle defined in (6) and (7) is equal to 180°. The major bonding interactions for the nitrosyl complex arises from the overlap of the metal  $z^2$  orbital with the nitrosyl



"lone pair" orbital,  $n$ , and the metal  $xz$  and  $yz$  orbitals with  $\pi^*(NO)$ . The sulphur dioxide ligand can enter into a similar  $\sigma$ -type interaction which utilizes its "lone pair" orbital,  $n$ , but it has only a single molecular orbital of  $\pi$ -pseudosymmetry,  $b_1$ , as illustrated in (2), and therefore it can only interact with one component of the degenerate metal  $xz, yz$  orbital pair. If the SO<sub>2</sub> ligand is taken to lie in the  $yz$  plane then the  $b_1$  orbital interacts exclusively with the metal  $xz$  orbital as shown in Figure 1. In such a conformation the metal  $yz$  orbital remains essentially non-bonding.

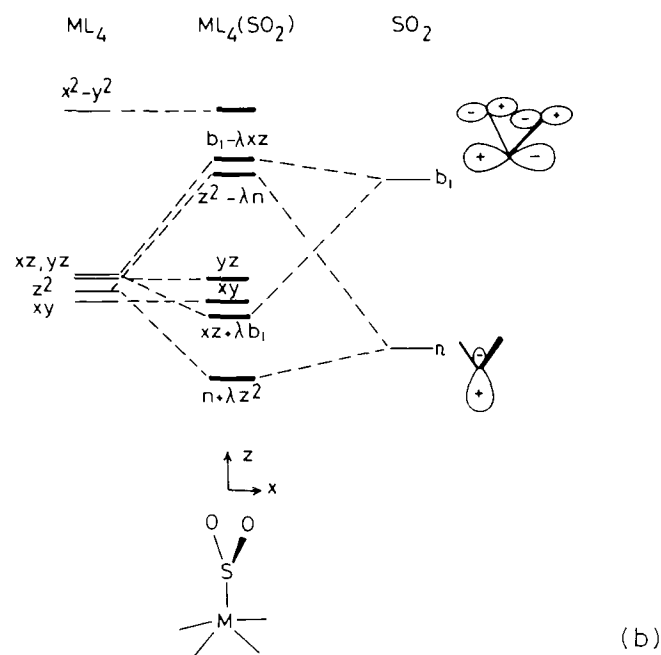
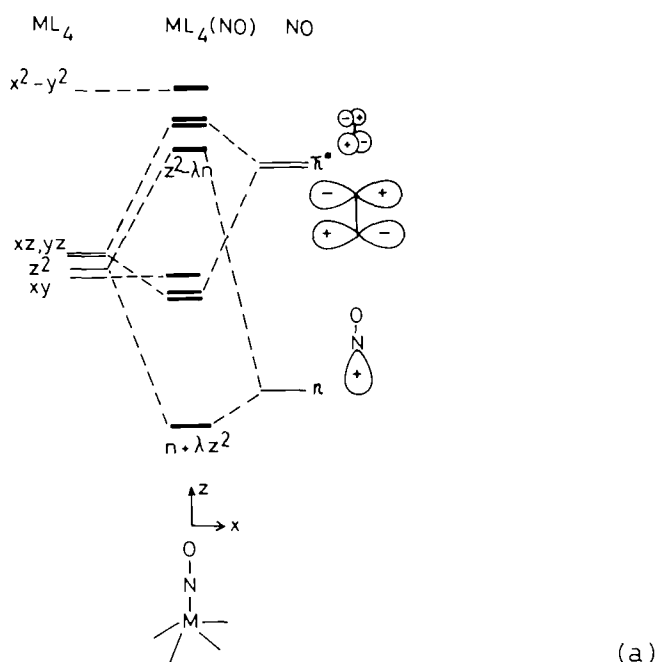
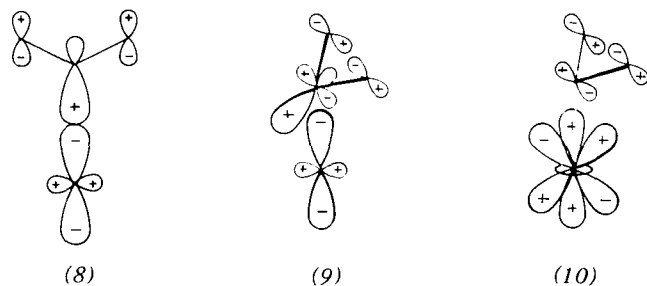


Figure 1. The molecular orbital interaction diagrams for the square-pyramidal complexes [IrCl<sub>4</sub>(NO)]<sup>2-</sup> (1a) and [IrCl<sub>4</sub>(SO<sub>2</sub>)]<sup>3-</sup> (1b) derived from extended Hückel calculations<sup>(26, 29)</sup>.

From the Figure it is clear that the metal-nitrosyl and metal-sulphur dioxide  $\sigma$  and  $\pi$  bonding interactions will be maximised for  $\{MB\}^6$  complexes. In this review we will follow the suggestion of Enemark and Feltham<sup>(30)</sup> and denote the MB fragment (where B = NO or SO<sub>2</sub>) by  $\{MB\}^r$ , where r is the number of electrons associated with the metal d orbitals and the  $\pi^*$  orbitals of the ligand B.

If the number of electrons, r, exceeds six then for both the nitrosyl and SO<sub>2</sub> complexes the additional electrons must be accommodated in the low lying but antibonding orbitals  $z^2-\lambda n$  shown in Figure 1 and (8). The energies of these molecular orbitals are particularly sensitive to a bending distortion which reduces their antibonding character.



If the angle  $\theta$  defined in (6) and (7) is reduced from its initial value of 180° (the SO<sub>2</sub> bisecting vector moving in the  $xz$  plane) then  $z^2$  will reduce its antibonding interaction with  $n$  which is no longer colinear with the M–S bond [see (9)]. This distortion also removes the symmetry distinction between the  $z^2-\lambda n$  and  $b_1-xz$  orbitals, which both have  $a'$  symmetry when  $\theta \neq 180^\circ$ . These orbitals also lie close in energy and therefore mix extensively as the distortion proceeds. The lower component of this interacting pair is stabilised by the constructive overlap between  $z^2$  and the SO<sub>2</sub>  $b_1$  level as illustrated in (9), an interaction which is clearly forbidden for the  $\eta^1$ -planar geometry. The upper component of the interacting pair is likewise destabilised by the destructive overlap between  $z^2$  and the  $\pi$ -like orbital

of SO<sub>2</sub>,  $b_1$ , as illustrated in (10). The importance of these orbital mixings is confirmed by the Walsh diagram for the bending process [derived from extended Hückel calculations<sup>(26)</sup>] which is illustrated in Figure 2b.

The corresponding Walsh diagram for the bending distortion in  $[\text{IrCl}_4(\text{NO})]^{2-}$ , which is illustrated in Figure 2a<sup>(29)</sup>, indicates that a very similar energetic and symmetry situation exists. On bending, the  $z^2-\lambda n$  orbital mixes with one component of the  $\pi^*-xz, yz$  orbital pair to give one component of lower energy and one of higher energy. The other component of the  $\pi^*-xz, yz$  pair,  $\pi^*-yz$ , remains essentially unaffected by the distortion mode. The large similarities in the Walsh diagrams for the two complexes suggest that the rules which have been developed for predicting the geometries of NO complexes are generally transferable to SO<sub>2</sub> complexes and the following conclusions may be proposed from the work of Mingos and Hoffmann<sup>(29)</sup> and Ryan and Eller<sup>(26)</sup>.

1. In  $\{M(B)\}^6$  (B = SO<sub>2</sub> or NO) complexes based on the octahedron or the square-pyramid with B occupying an apical site, the linear and  $\eta^1$ -planar geometries are energetically preferred. For  $\{M(B)\}^8$  complexes the bent or  $\eta^1$ -pyramidal geometries are more stable

These conclusions follow from the Walsh diagrams illustrated in Figures 2a and 2b and have been confirmed by the following x-ray crystallographic analyses:

Complex	Electronic Configuration	Ligand Geometry	Ref.
$[\text{RuCl}_5(\text{NO})]\text{Cl}_2$	$\{M(\text{NO})\}^6$	NO linear	(8, 30)
$[\text{RuCl}(\text{NH}_3)_4\text{SO}_2]\text{Cl}$	$\{M(\text{SO}_2)\}^6$	SO <sub>2</sub> $\eta^1$ -planar	(5)
$[\text{IrCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2]^+$	$\{M(\text{NO})\}^8$	NO bent	(9, 30)
$\text{IrCl}_2(\text{NO})(\text{PPh}_3)_2$	$\{M(\text{NO})\}^8$	NO bent	(10, 30)
$\text{IrCl}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$	$\{M(\text{SO}_2)\}^8$	SO <sub>2</sub> $\eta^1$ -pyramidal	(6)
$\text{RhCl}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$	$\{M(\text{SO}_2)\}^8$	SO <sub>2</sub> $\eta^1$ -pyramidal	(7)

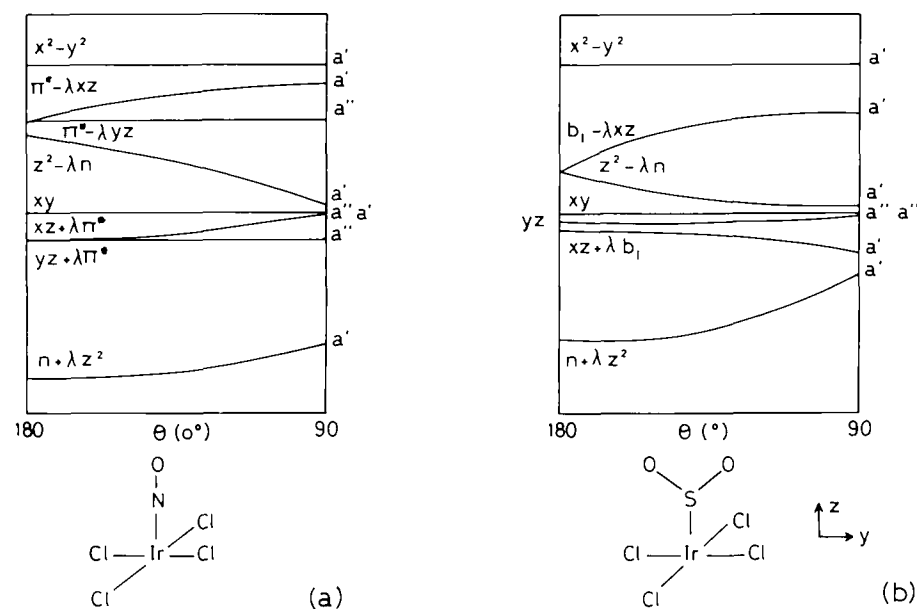
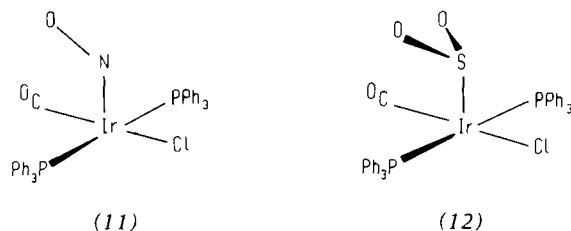


Figure 2. Walsh diagrams for the bending distortion in  $[\text{IrCl}_4(\text{NO})]^{2-}$  (2a) and  $[\text{IrCl}_4(\text{SO}_2)]^{3-}$  (2b)<sup>(26, 29)</sup>.

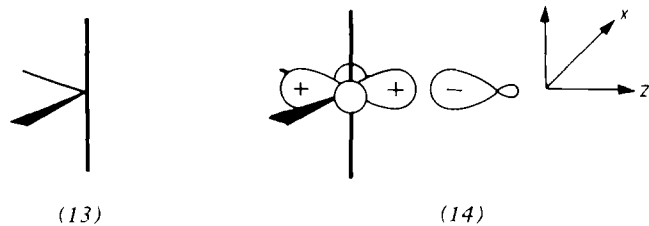
2. In square-pyramidal  $\{M(B)\}^8$  complexes of the type  $ML_2DA(B)$  where  $D$  is  $\pi$ -donor *trans* to  $A$  a  $\pi$ -acceptor, the  $NO$  or  $SO_2$  group will bend in the  $DMA$  plane towards the  $\pi$ -acceptor

The x-ray analyses of  $[\text{IrCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2]^+$  (11)<sup>(9)</sup> and  $\text{IrCl}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$  (12)<sup>(7)</sup> by Ibers and his co-workers have shown that in both complexes the ligand bends towards the  $\pi$ -accepting carbonyl group.



3. In related  $\{M(B)\}^8$  trigonal-bipyramidal nitrosyl and sulphur dioxide complexes, the ligand is less likely to bend than when occupying the apical site of the corresponding square-pyramid

The antibonding  $z^2-\lambda n$  combination in the square-pyramid, which it will be recalled was the controlling factor for nitrosyl and sulphur dioxide bending, is significantly higher in energy than in the trigonal-bipyramid geometry. The reason for this can be traced to the reduced symmetry of the trigonal bipyramid fragment [ $C_{2v}$ , as shown in (13)]. In the square-pyramid the  $z^2$  orbital is the only metal orbital of  $a_1$  symmetry. In the trigonal bipyramid fragment both  $z^2$  and  $x^2-y^2$  are of  $a_1$  symmetry. They mix slightly in the fragment but more so when the ligand comes in. The primary interaction in both the square pyramid and the trigonal bipyramid is between  $n$  and  $z^2$  and it is antibonding. In the square-pyramid that antibonding cannot be effectively avoided, but in the trigonal bipyramid  $x^2-y^2$  can be utilized. The linear combination " $z^2 + (x^2-y^2)$ " shown in (14) takes some of the electron density from the metal-ligand axis and puts it into the relatively harmless region along the  $y$  axis, and consequently the driving force towards distortion is diminished<sup>(29)</sup>.



4. Nitrosyl and  $SO_2$  ligands in axial positions in trigonal bipyramidal and basal sites in a square-pyramidal  $\{M(B)\}^8$  complexes prefer to be linearly (or  $\eta^1$ -planar) coordinated

The well established energy levels for a trigonal bipyramidal fragment (15) are illustrated in Figure 3. There is a low lying degenerate  $xz, yz$  set, followed by the  $x^2-y^2, xy$  orbitals, which are slightly metal-ligand antibonding and finally the more strongly antibonding metal  $z^2$  orbital. As the nitrosyl or  $SO_2$  ligand approaches to complete the axially substituted trigonal-bipyramid, the ligand orbitals of  $\pi$ -pseudosymmetry will interact with and stabilise one or

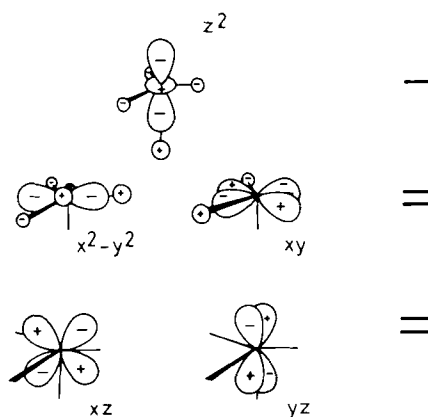
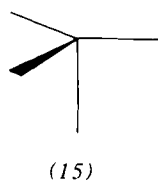


Figure 3. Schematic representation of the energy levels of a  $C_{3v}$   $ML_4$  fragment<sup>(29)</sup>.

both components of the  $xz, yz$  set. For five coordinate  $\{M(B)\}^8$  complexes the fragment  $z^2$  is unfilled. This is a very different situation from the apical-square-pyramid and the equatorial trigonal-bipyramid complexes, and there is no analogue of (8) which stimulates the bending distortion.



Instead the  $z^2$  orbital actually helps to make the nitrosyl linear and the  $SO_2$  planar by virtue of its strong bonding interaction with the lone pair orbital  $n$ . The basal site of a square-pyramid represents a perturbation on the above scheme and the same arguments favouring the linear geometry apply.

The available nitrosyl structures are in accord with these conclusions<sup>(28)</sup>. In  $[\text{IrH}(\text{NO})(\text{PPh}_3)_3]^+$ <sup>(10)</sup> the hydride ligand was not specifically located but was inferred to lie *trans* to the  $NO$  along the axis of a distorted trigonal-bipyramid. In this complex the nitrosyl ligand is linearly coordinated. Structural studies on the  $\{M(\text{NO})\}^8$  square-pyramidal dinitrosyl complexes  $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+$ <sup>(31)</sup> and  $[\text{Os}(\text{NO})_2(\text{OH})(\text{PPh}_3)_2]^+$ <sup>(32)</sup> have shown that the basal  $NO$  has a linear geometry and the apical  $NO$  a bent geometry. These conclusions remain to be tested for  $SO_2$  complexes, and an x-ray crystallographic analysis of  $\text{IrH}(\text{PPh}_3)_3(\text{SO}_2)$ , for example, would be most helpful in this regard.

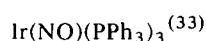
An x-ray structural determination of  $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-Cp})(\text{SO}_2)^{14*}$ , which is an  $\{M(\text{SO}_2)\}^8$  complex has shown that the  $SO_2$  ligand has an  $\eta^1$ -planar  $SO_2$  geometry. Ryan, Eller and Kubas<sup>(14)</sup> have noted that this rhodium cyclopentadienyl complex has a molecular orbital splitting diagram which is closely related to that of  $[\text{IrCl}_4(\text{SO}_2)]^{2-}$  with the  $SO_2$  occupying the axial site of a trigonal bipyramid and have rationalised the observed  $SO_2$  geometry in terms of a high lying and unoccupied orbital ( $z^2-\lambda n$ ) similar to that described for the iridium complex above and illustrated in Figure 3.

\* Cp = cyclopentadienyl.

5. Good  $\pi$ -acceptor ligands,  $L$ , in  $\{L_4M(B)\}^8$  and  $\{L_3M(B)\}^{10}$  complexes in general encourage linear (or  $\eta^1$ -planar) geometries, whereas good  $\pi$ -donors encourage the bent (or  $\eta^1$ -planar) geometries

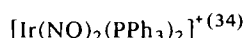
In nitrosyl complexes this conclusion has been supported by x-ray crystallographic analyses on  $[Mn(CO)_4(NO)]^8$  and  $[Ir(NO)Cl_2(PPh_3)_2]^8$ , for example, but an insufficient number of sulphur dioxide structures has been determined to support or refute this conclusion.

Ryan's extended Huckel calculations on related NO and  $SO_2$  complexes<sup>(13)</sup> have suggested that for  $\{L_3M(B)\}^{10}$  complexes the bending process is energetically more favourable when  $B = SO_2$  than when  $B = NO$ . X-ray structural studies on some triphenylphosphine platinum metal complexes which are summarised below seem to confirm this conclusion.



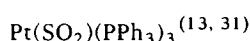
$$Ir-N = 1.67 \text{ \AA}$$

$$\theta = 180^\circ$$



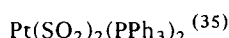
$$Ir-N = 1.77 \text{ \AA}$$

$$\theta = 164^\circ$$



$$Pt-S = 2.36 \text{ \AA}$$

$$\theta = 120^\circ$$

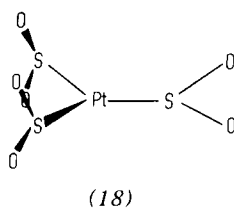
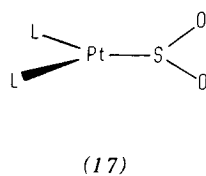
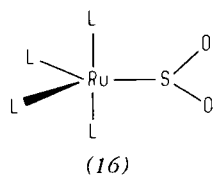


$$Pt-S = 2.45 \text{ \AA}$$

$$\theta = 117^\circ$$

Ryan has noted<sup>(13)</sup> that the  $n$  and  $b_1$  molecular orbitals of  $SO_2$  lie closer in energy than the  $n$  and  $\pi^*$  orbitals of NO, and has suggested that if this trend is maintained in complexes of these ligands then the  $SO_2$  ligand will show the greater tendency to distort, because the smaller energy difference will permit more extensive orbital mixings as the bending distortion proceeds.

The discussion above has highlighted some important similarities between  $SO_2$  and NO. There are, however, some important differences which must also be borne in mind. The  $n$  and  $\pi$  interactions for NO with a transition metal will generally be stronger than those for  $SO_2$  because the metal-ligand overlaps are larger in the former case and therefore smaller metal-ligand bond dissociation energies are predicted for the  $SO_2$  ligand. The presence of only a single acceptor orbital of  $\pi$ -pseudosymmetry in the case of  $SO_2$  also has some interesting conformational and energetic consequences for  $\eta^1$ -planar and  $\eta^1$ -pyramidal  $SO_2$  complexes. For example, if the  $SO_2$  ligand is coordinated to an  $ML_n$  fragment which does not have axial symmetry then the  $SO_2$  ligand will have a preferred conformation which maximises the bonding interaction between the  $SO_2$   $b_1$  orbital (2) and the donor orbital on the metal. The following equi-

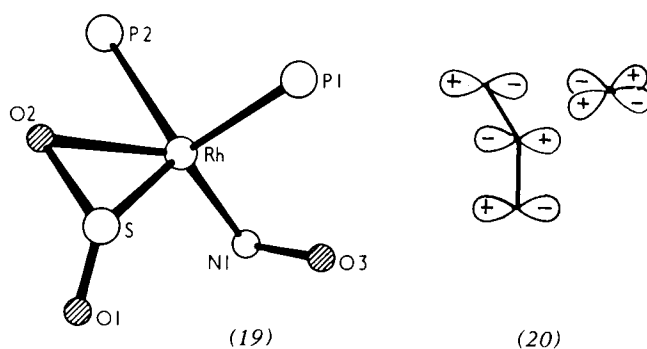


$L =$  a two electron ligand such as  $PR_3$ ,  $CO$ , etc.

librium conformations may be predicted for  $\eta^1$ -planar  $SO_2$  complexes from a knowledge of the bonding characteristics of  $ML_n$  fragments<sup>(37)</sup>.

### $\eta^2$ - $SO_2$ complexes

The only structure reported to date where  $SO_2$  is coordinated to the metal through the sulphur atom and one of the oxygen atoms is  $Rh(NO)(SO_2)(PPh_3)_2$  (19)<sup>(16)</sup>. The coordination geometry around the metal is tetrahedral if the adjacent sulphur and oxygen atoms bonded to the metal are considered as a monodentate ligand. The nitrosyl ligand is also non-linear in this compound. The coordinated S–O bond is longer than the uncoordinated S–O bond by ca. 0.07 Å in this compound. The bonding in this complex can be viewed in terms of electron donation from a metal orbital to the  $b_1$   $SO_2$  acceptor orbital as illustrated in (20).



### Bond length and angle parameters for mononuclear $SO_2$ complexes

The important bond lengths and angles for those  $SO_2$  complexes whose structures have been determined x-ray crystallographically are summarised in Tables 1 and 2 below. The following trends are apparent from the structural data:

1. The metal-sulphur bond length is significantly longer (ca. 0.3 Å) in  $\eta^1$ -pyramidal than  $\eta^1$ -planar  $SO_2$  complexes.
2. The O–S–O bond angle is consistently smaller for the coordinated  $SO_2$  ligand than for the free ligand, irrespective of whether it coordinated in a planar or pyramidal mode. This consistent trend follows from the nodal characteristics of the lowest occupied orbital of the  $SO_2$  ligand and has been discussed above.
3. The limited number of very accurate structural determinations on metal- $SO_2$  complexes precludes any definitive statements about the changes in S–O bond lengths which accompany coordination.
4. In the  $\eta^1$ -pyramidal complexes the angle between the M–S vector and the  $SO_2$  plane is close to  $120^\circ$  for all those complexes which have been studied to date.

### (b) Polynuclear Complexes

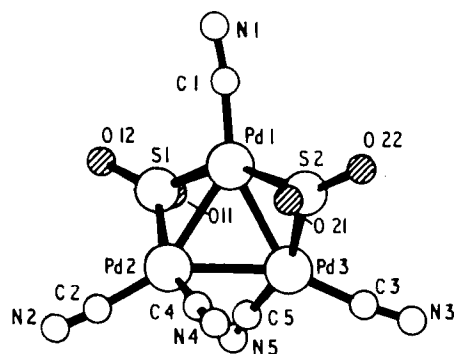
Single crystal x-ray structure analyses on  $Pd_3(\tau\text{-BuNC})_5(SO_2)_2$ <sup>(40)</sup> and  $Ir(CO)_2H(PPh_3)_2(SO_2)$ <sup>(41)</sup> have shown that  $SO_2$  can act as a bridging ligand in some platinum metal complexes. Illustrations of these structures are given in (21) and (22) below, and the relevant structural

Table 1. Structural parameters for SO<sub>2</sub> complexes

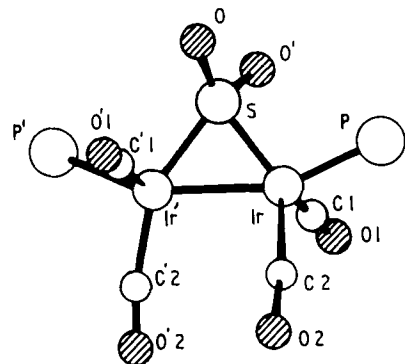
Compound	Coordination Type	{M(SO <sub>2</sub> )} <sup>f</sup>	M-S distance (Å)	Angle between M-S vector and SO <sub>2</sub> plane (degrees)	Ref.
[RuCl(NH <sub>3</sub> ) <sub>4</sub> SO <sub>2</sub> ]Cl	Octahedral	6	2.072(3)	180	(5)
Rh(η-C <sub>2</sub> H <sub>4</sub> )(η-C <sub>5</sub> H <sub>5</sub> )(SO <sub>2</sub> )	Trigonal bipyramidal	8	2.096(2)	180	(14)
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	Tetragonal pyramidal	8	2.49(1)	121.5(1.5)	(6)
RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	Tetragonal pyramidal	8	2.45(2)	120.3(3)	(7)
Pt(PPh <sub>3</sub> ) <sub>3</sub> (SO <sub>2</sub> )	Tetrahedral	10	2.368(3)	120.3(3)	(13)
Pt(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> ) <sub>2</sub>	Tetrahedral	10	2.43(1)	117.0(3)	(35)
Rh(NO)(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	Tetrahedral	10	2.33		(15)

Table 2. SO<sub>2</sub> Bond angles and bond lengths in SO<sub>2</sub> complexes

Compound	Coordination mode	O-S-O (degrees)	S-O <sub>1</sub> (Å)	S-O <sub>2</sub> (Å)	Ref.
free SO <sub>2</sub>		119.0(5)	1.43(1)	1.43(1)	(17)
[RuCl(NH <sub>3</sub> ) <sub>4</sub> (SO <sub>2</sub> )Cl]	η <sup>1</sup> -planar	113.8(6)	1.462(1)	1.394(1)	(5)
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	η <sup>1</sup> -pyramidal	117.1(1.5)	1.41(2)	1.47(2)	(6)
RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	η <sup>1</sup> -pyramidal	113.8(3)	1.446(4)	1.456(4)	(7)
Pt(PPh <sub>3</sub> ) <sub>3</sub> (SO <sub>2</sub> )	η <sup>1</sup> -planar	122(4)	1.51(5)	1.47(5)	(36)
Pt(PPh <sub>3</sub> ) <sub>3</sub> (SO <sub>2</sub> ) (re-examination)	η <sup>1</sup> -pyramidal	114.2(5)	1.428(8)	1.453(7)	(13)
Pt(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> ) <sub>2</sub>	η <sup>1</sup> -pyramidal	114.5(3)	1.453(5)	1.416(5)	(35)
		116.9(5)	1.381(6)	1.368(8)	
Rh(η-C <sub>2</sub> H <sub>4</sub> )(η-Cp)(SO <sub>2</sub> )	η <sup>1</sup> -planar	114.4(5)	1.442(7)	1.430(8)	(14)
Rh(NO)(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	η <sup>2</sup>	115	1.41	1.48	(15)
Pt(Me)(I-SO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	η <sup>1</sup> - to I	116.1(5)	1.406(8)	1.400(8)	(39)
Pd <sub>3</sub> (t-BuNC) <sub>5</sub> (SO <sub>2</sub> ) <sub>2</sub>	bridging	(i) 113(2) (ii) 109(2)	1.49(3) 1.47(3)	1.45(3) 1.49(2)	(40)
Ir(CO) <sub>2</sub> H(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	bridging	113.7(2)	1.457(7)		(41)



(21)



(22)

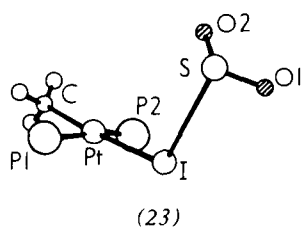
parameters are presented in Table 2. The average Pd-S bond distance in (21) is 2.26 Å, which is slightly shorter than the values commonly found for chalcogenide palladium complexes (av. 2.30 Å), implying a strong bonding interaction with the metal for the SO<sub>2</sub> bridging ligand<sup>(40)</sup>.

Each iridium atom in {Ir(CO)<sub>2</sub>H(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)<sup>(41)</sup> is at the centre of a distorted octahedron whose apices are occupied by the other iridium and by atoms S, P, C(1), C(2) and H, the latter is thought to lie at the apex *trans* to C(1). An important feature in this structure is the lengthening of the M-M bond due to the presence of the bridging SO<sub>2</sub>, as in the absence of such a bridge a formal covalent bond connects the two metal atoms. The Ir-Ir distance observed here 2.759 Å is longer than those observed in Ir<sub>4</sub>(CO)<sub>12</sub>, 268 Å; in Ir<sub>4</sub>(CO)<sub>12-m</sub>(PPh<sub>3</sub>)<sub>m</sub><sup>(42)</sup>, 2.72 Å, and in Ir<sub>2</sub>(NO)<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub><sup>(43)</sup>, 2.717 Å. This elongation has been rationalised in terms of the π acid character of the bridging ligand<sup>(41)</sup>.

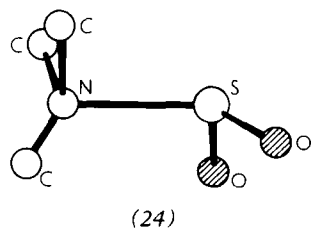
### (c) Coordination of SO<sub>2</sub> to a ligand in a transition metal complex

A novel mode of coordination of SO<sub>2</sub> has been revealed by the crystal structure determination of PtMe(I-SO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub><sup>(9)</sup>, and is illustrated in (23).

The structure shows that the SO<sub>2</sub> ligand is coordinated to the iodide ligand in the complex. The I-S distance of 3.391 Å is significantly shorter than the Van der Waal's radii sum (3.78 Å) but much longer than their single bond radii sum (2.36 Å). Presumably, SO<sub>2</sub> is acting as a weak Lewis acid in this complex. Similar Lewis acid bonding has



been observed in the trimethylamine adduct of  $\text{SO}_2$  (44), which is illustrated in (24). The important structural parameters for the  $\text{PtMe}(\text{ISO}_2)(\text{PPh}_3)_2$  complex are given in Table 2.

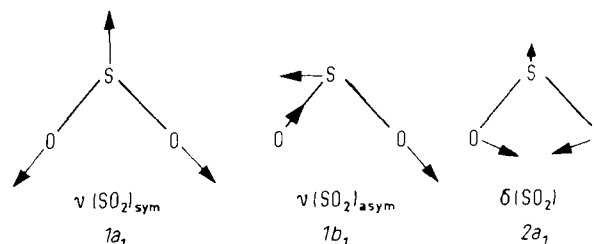


Ibers and Snow<sup>(39)</sup> have noted that this coordination mode might be present in other halo-transition metal complexes, e.g.  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)_2$ , and that it may be recognised by characteristic bands in the i.r. and u.v. spectra of these adducts. A preliminary communication has shown that the solid samples of  $\text{MX}(\text{CO})(\text{PPh}_3)_2$  ( $X = \text{Cl, Br or I}$ ;  $M = \text{Rh or Ir}$ ) are capable of picking up gaseous  $\text{SO}_2$  over the temperature range  $-5$  to  $-180^\circ$  at 1 atmosphere pressure. The maximum amount of  $\text{SO}_2$  taken up by  $\text{IrI}(\text{CO})(\text{PPh}_3)_2$  is, for example, 2.30 mol. at  $-5^\circ$  and 1.98 mol. at  $25^\circ$ <sup>(45)</sup>. This behaviour must be related to the formation of weak  $\text{I}-\text{SO}_2$  bonds such as those described for the platinum complex above.

### Infrared Studies

The symmetric and asymmetric stretching modes for the free  $\text{SO}_2$  ligand have been observed at 1151 and

$1362\text{ cm}^{-1}$ <sup>(46)</sup> respectively and the bending mode has been assigned to a band at  $518\text{ cm}^{-1}$ . These modes together with their group theoretical symmetry designations are illustrated below:



Coordination of  $\text{SO}_2$  to a metal atom generally results in a decrease in the  $\nu(\text{SO}_2)_{\text{sym}}$  and  $\nu(\text{SO}_2)_{\text{asym}}$  frequencies, and two bands in the  $1330-1030\text{ cm}^{-1}$  region are observed. To evaluate whether the positions of the  $\text{SO}_2$  stretching vibrations can be used as a diagnostic test for the coordination mode of the ligand, the i.r. data of  $\text{SO}_2$  complexes whose structures have been unambiguously determined by x-ray studies are summarised in Table 3.

On the limited data available, it appears that for  $\eta^1$ -planar complexes the  $\text{SO}_2$  frequencies lie in the range,  $\nu(\text{SO}_2)_{\text{asym}}$   $1250-1300\text{ cm}^{-1}$  and  $\nu(\text{SO}_2)_{\text{sym}}$  at  $1090-1105\text{ cm}^{-1}$  and  $\eta^1$ -pyramidal complexes  $\nu(\text{SO}_2)_{\text{asym}}$   $1185-1214\text{ cm}^{-1}$  and  $\nu(\text{SO}_2)_{\text{sym}}$   $1045-1057\text{ cm}^{-1}$ . Therefore the latter are characterised by somewhat lower frequencies. It is doubtful, however, whether the small differences involved provide a satisfactory basis for a general and reliable assignment of bonding mode from i.r. data. When the  $\text{SO}_2$  ligand is coordinated in an  $\eta^2$  mode the  $\nu(\text{SO}_2)$  frequencies are about  $100\text{ cm}^{-1}$  lower than expected for  $\eta^1$ -planar or  $\eta^1$ -pyramidal  $\text{M}-\text{SO}_2$  complexes. When  $\text{SO}_2$  is acting as a bridging ligand the  $\nu(\text{SO}_2)$  bands are not very different from those observed for  $\eta^1$ -pyramidal  $\text{M}-\text{SO}_2$  complexes.  $\nu(\text{SO}_2)$  is approximately  $100\text{ cm}^{-1}$  higher when  $\text{SO}_2$  is coordinated to the metal through a ligand such as iodide. Clearly, i.r. data on  $\text{SO}_2$  complexes contain little structural information, and must be treated with caution.

**Table 3.** I.r. data for  $\text{SO}_2$  complexes whose structures have been determined by x-ray crystallography

Compound	$\nu(\text{SO}_2)$ ( $\text{cm}^{-1}$ )	Mode of $\text{SO}_2$ attachment	Ref.
$[\text{RuCl}(\text{NH}_3)_4(\text{SO}_2)]\text{Cl}$	1301, 1100 1278	$\eta^1$ -planar	(5)
$\text{Rh}(\eta\text{-C}_2\text{H}_4)(\eta\text{-Cp})(\text{SO}_2)$	1258, 1105–1093	$\eta^1$ -planar	(14)
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$	1198, 1185, 1048	$\eta^1$ -pyramidal	(2, 6)
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$	1208, 1053	$\eta^1$ -pyramidal	(2, 7)
$\text{Pt}(\text{PPh}_3)_3(\text{SO}_2)$	1195, 1045	$\eta^1$ -pyramidal	(3, 13, 36)
$\text{Pt}(\text{PPh}_3)_2(\text{SO}_2)_2$	1223, 1215, 1050, 1038	$\eta^1$ -pyramidal	(11, 35)
$\text{Rh}(\text{NO})(\text{PPh}_3)_2(\text{SO}_2)$	1138, 948	$\eta^2$	(15)
$\text{Pt}(\text{CH}_3)(\text{I}-\text{SO}_2)(\text{PPh}_3)_2$	1322, 1138	$\text{SO}_2$ bonded through iodine	(39)
$\text{Pd}_3(\text{t-BuNC})_5(\text{SO}_2)_2$	1208, 1060	bridging $\text{SO}_2$	(40)
$[\text{Ir}(\text{CO})_2\text{H}(\text{PPh}_3)_2]_2(\text{SO}_2)$	1190, 1177 1046, 1037	bridging $\text{SO}_2$	(41)

### Thermochemical Studies on Sulphur Dioxide Complexes

Calorimetric studies for the dissociation process:  $ML_n(SO_2)(\text{cryst}) \rightarrow ML_n(\text{cryst}) + SO_2(\text{g})$  (where  $ML_n = RhCl(CO)(PPh_3)_2$ ,  $IrCl(CO)(PPh_3)_2$  or  $Pt(PPh_3)_3$ ) have yielded important thermodynamic data on the nature of the metal-ligand bond in sulphur-dioxide complexes. The  $\Delta H_{298}^\circ$  values for the process indicated by the equations are summarised in Table 4 and contrasted with those reported for the related dioxygen ligand<sup>(47)</sup>.

**Table 4.** Thermochemical data on metal-sulphur dioxide complexes

Complex	Ligand removed	$\Delta H/\text{kJ mol}^{-1}$ at 298 K	Metal-sulphur distance (Å)
$IrCl(CO)(PPh_3)_2(SO_2)$	$SO_2$	35.00	2.49
$RhCl(CO)(PPh_3)_2(SO_2)$	$SO_2$	33.00	2.45
$IrCl(CO)(O_2)(PPh_3)_2$	$O_2$	97.00	—
$Pt(PPh_3)_3(SO_2)$	$SO_2$	60.60	2.40

These  $\Delta H^\circ$  values, which can be approximately equated to metal-ligand bond dissociation energies, clearly indicate that the metal- $SO_2$  bond in these  $\eta^1$ -pyramidal complexes is much weaker than the reported value for the related dioxygen complex<sup>(47)</sup>. This data is consistent with the long metal-sulphur bond lengths reported for these complexes. The corresponding data on a  $\eta^1$ -planar  $SO_2$  complex, which is known to have a much shorter metal-sulphur bond length, would certainly be most interesting and contribute to an understanding of the different bonding modes in these complexes.

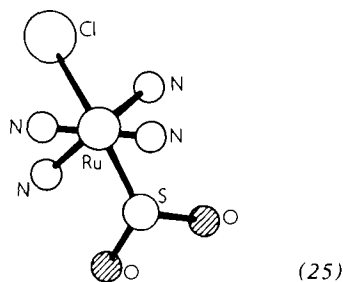
### Preparation and Properties of Sulphur Dioxide Complexes

In general, sulphur dioxide complexes have been prepared using the free ligand which is readily available as a starting material. Other potential routes to  $SO_2$  complexes using for example dithionite  $[S_2O_4]^{2-}$  or organic sulphones as sources of  $SO_2$  have been little studied. The reactions of the coordinated  $SO_2$  ligand have similarly received little attention. In this section the preparation and properties of sulphur dioxide complexes of the platinum metals will be reviewed. The classification has been made on the basis of the central metal atom.

#### Ruthenium-sulphur dioxide complexes

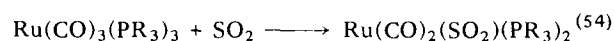
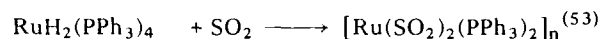
A wide range of ruthenium(II) and ruthenium(0) sulphur dioxide complexes have been prepared and studied. Indeed the first  $SO_2$  complex,  $[RuCl(NH_3)_4(SO_2)]Cl$  was prepared by Gleu *et al.* in 1938<sup>(1)</sup>. It was obtained by reacting  $Ru(HSO_3)_2(NH_3)_4$  with 1 : 1 HCl. The molecular structure of this compound has been established by x-ray analysis and is illustrated in (25).

The coordination geometry about the ruthenium is octahedral and the  $SO_2$  and Cl ligands occupy *trans*-positions. The  $SO_2$  has a  $\eta^1$ -planar coordination geometry, which is consistent with the  $d^6$  electronic configuration of the metal. The closely related  $[Ru(NH_3)_5(SO_2)]X_2$  ( $X = Cl, Br$  or  $I$ ) complexes have been reported and the iodide has also been



(25)

prepared directly from  $[Ru(NH_3)_5(N_2)]^{2+}$  and sulphur dioxide<sup>(49)</sup>. The insoluble red phosphine ruthenium(II) complex  $RuCl_2(PPh_3)_2(SO_2) \cdot Me_2CO$  is formed when  $SO_2$  is bubbled through an acetone solution of  $RuCl_2(PPh_3)_3$ <sup>(50)</sup>. The octahedral complexes  $RuHX(CO)(PCy_3)_2(SO_2)^*$  ( $X = Cl$  or  $Br$ ) are formed similarly from the five coordinate complexes  $RuHX(CO)(PCy_3)_2$ <sup>(51)</sup>. Spencer and Wilkinson<sup>(52)</sup> have reported that the  $\mu^3$ -oxo complex  $[Ru_3O(O_2CMe)_6(MeOH)_3]^+$  reacts slowly with  $SO_2$  to give a variety of blue and green complexes. In one of these complexes it has been proposed that the  $SO_2$  is coordinated directly to the central oxo-ligand. Zerovalent ruthenium sulphur dioxide complexes have been prepared by the following routes:



$R = Ph$  or *p*- $MeC_6H_4$

The dicarbonyl complex reacts readily with dioxygen to form the sulphato-complex  $Ru(CO)_2(PPh_3)_2(SO_4)^{(54)}$ . The bright yellow complex  $[Ru(SO_2)_2(PPh_3)_2]_n$  has not been fully characterised and could well be polymeric<sup>(53)</sup>.

In the presence of traces of water it has been shown that the ruthenium dihydride complex  $RuH_2(PPh_3)_4$  reacts with  $SO_2$  to give the sulphato-sulphur dioxide ruthenium(II) complex illustrated in (26). This molecule is polymeric and linked by bridging sulphato-ligands<sup>(38, 55)</sup>. Wilkinson and

**Table 5.** I.r. data for ruthenium complexes

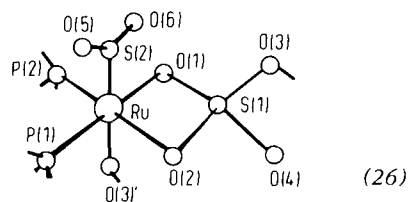
Compound	$\nu(SO_2)$ ( $cm^{-1}$ )	Colour	Ref.
$[RuBr(NH_3)_4(SO_2)]Br$	1303, 1255 1098	brown	(1)
$[Ru(NH_3)_5(SO_2)]Cl_2$	1303, 1255 1098	red brown	(1)
$[Ru(NH_3)_5(SO_2)]Br_2$	1327, 1301 1117	red brown	(1)
$[Ru(NH_3)_5(SO_2)]I_2$	not reported	red brown	(49)
$Ru(PPh_3)_2(SO_2)_2$	not reported	bright yellow	(53)
$[RuCl_2(PPh_3)_2(SO_2)] \cdot Me_2CO$	1276, 1117 562	red	(50)
$Ru(CO)_2(PPh_3)_2(SO_2)$	1212, 1144 1066	mustard yellow	(54)
$RuHCl(CO)(PCy_3)_2(SO_2)$	1290, 1110	yellow	(51)
$RuHBr(CO)(PCy_3)_2(SO_2)$	1292, 1110	yellow	(51)
$Ru(CO)_2\{P(p\text{-tolyl})_3\}_2(SO_2)$	1229, 1160, 1072	yellow	(54)

\* Cy = cyclohexyl



Cole-Hamilton have established that  $\text{RuH}_2(\text{PPh}_3)_4$  is very sensitive to traces of moisture forming the hydroxy-hydride complex  $\text{Ru}(\text{H})(\text{OH})(\text{PPh}_3)_4$  which is presumably an intermediate in the above reaction<sup>(56)</sup>.

The i.r. frequencies and colours of the ruthenium compounds discussed above are given in Table 5.

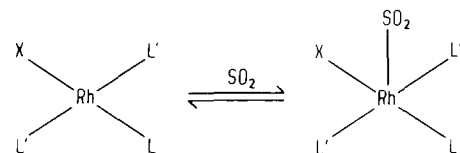


### Osmium-sulphur dioxide complexes

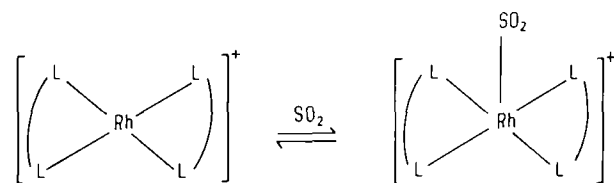
The osmium sulphur dioxide complexes  $\text{OsXH}(\text{PCy}_3)_2(\text{SO}_2)$  ( $X = \text{Cl}$  or  $\text{Br}$ ) have been prepared by bubbling  $\text{SO}_2$  through a benzene solution of  $\text{OsX}(\text{CO})\text{H}(\text{PCy}_3)_2$ <sup>(51)</sup>. These yellow crystalline compounds are stable under an  $\text{N}_2$  atmosphere and the peaks at  $1284$  and  $1109 \text{ cm}^{-1}$  in the i.r. spectrum have been attributed to the coordinated  $\text{SO}_2$  group. The complexes are analogous to the ruthenium complexes described above.

### Rhodium-sulphur dioxide complexes

The majority of sulphur dioxide complexes of rhodium have the metal in the +1 oxidation state and have tertiary phosphines also coordinated to the metal. The most common route into the five coordinate complexes has been the addition of  $\text{SO}_2$  to coordinatively unsaturated square-planar rhodium(I) complexes as shown below:



	X	L	L'	Ref.
1.	halide or pseudohalide	CO	$\text{PPh}_3$	(57)
2.	$\text{C}\equiv\text{CR}$	CO	$\text{PPh}_3$	(58)
3.	$\text{SC}_6\text{F}_5$	CO	$\text{PPh}_3$	(59)
4.	Cl	$\text{PF}_3$	$\text{PPh}_3(\text{AsPh}_3)$	(60)
5.	Cl	$\text{PPh}_3$	diolefin (e.g. $\text{C}_6\text{H}_4$ )	(61)
6.	Cl	pipiperidinel	CO	(61)



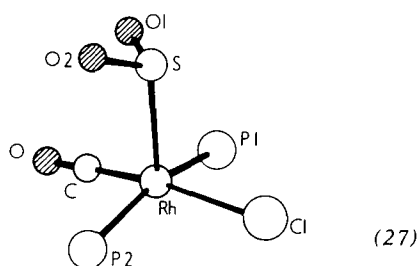
$\text{L'L} = o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$ <sup>(62)</sup>

These reactions are generally reversible and the  $\text{SO}_2$  ligand can frequently be displaced by heating the complex or by bubbling an inert gas through a solution of the complex. Palazzi *et al.*<sup>(61)</sup> have studied the desorption temperatures

of some of these  $\text{SO}_2$  complexes and concluded that the stabilities of the complexes are related to the basicities of the other ligands coordinated to the metal atom. It was also noted that the sulphur dioxide ligand was more readily lost from the rhodium complexes than the corresponding iridium complexes.

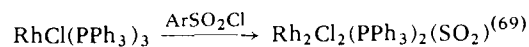
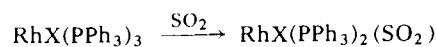
I.r. spectral studies<sup>(57, 58)</sup> of the rhodium complexes have shown that  $\nu(\text{CO})$  increases markedly when  $\text{SO}_2$  coordinates to the metal indicative of a substantial increase in the positive charge on the metal atom resulting from effective metal- $\text{SO}_2$  electron donation. Interestingly the  $\text{SO}_2$  adduct of  $\text{RhCl}(\text{PF}_3)(\text{PPh}_3)_2$  has been reported<sup>(60)</sup> to be thermally less stable than that of  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ .

The x-ray crystallographic analysis of  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$  by Muir and Ibers<sup>(7)</sup> has established that this adduct has the square-pyramidal geometry shown in the diagram below (27):

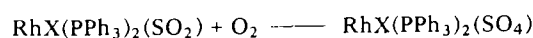


The electronic factors responsible for  $\text{SO}_2$  geometry and the rather long rhodium-sulphur bond in this molecule ( $2.450 \text{ \AA}$ ) have been discussed above. Presumably, the other five coordinate complexes listed in Table 6 have similar geometries.

Square-planar rhodium(I) sulphur-dioxide complexes have been isolated<sup>(12)</sup> from the following reactions of Wilkinson's compound  $\text{RhX}(\text{PPh}_3)_3$  ( $X = \text{Cl}, \text{Br}$  or  $\text{I}$ ).



In the latter reaction the rhodium(I) complex is behaving as a desulphonating agent<sup>(69)</sup> and similar decarbonylations have also been reported<sup>(66)</sup>. The  $\text{RhX}(\text{PPh}_3)_2(\text{SO}_2)$  complexes, which may also be prepared from  $[\text{RhX}(\text{PPh}_3)_2]_2$ , are brown crystalline solids which are air-stable in the solid state but react in solution with dioxygen to yield rhodium(III) sulphato complexes:

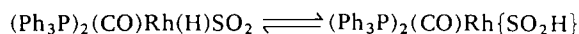


Meek and Napier<sup>(67)</sup> have shown that the tridentate phosphine complex  $\text{RhCl}\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}$  forms more stable adducts with  $\text{SO}_2$ ,  $\text{CO}$  and  $\text{O}_2$  than the related Wilkinson compound. They have noted that the formation of the rhodium(III) sulphato-complex proceeds more slowly when  $\text{O}_2$  is added to  $\text{RhCl}\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}(\text{SO}_2)$  than when  $\text{SO}_2$  is added to

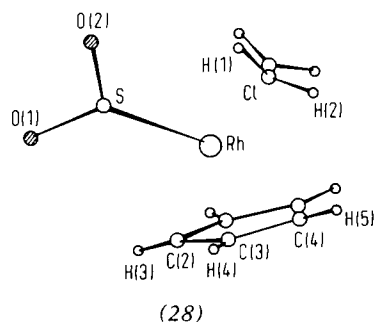
$\text{RhCl}\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}\text{O}_2$ . Collman and his co-workers have observed similar effects for iridium complexes, and attributed them to the greater Lewis acidity of  $\text{SO}_2$ .

One of the phosphine ligands is displaced from  $\text{Rh}(\text{CO})\text{H}(\text{PPh}_3)_3$  by  $\text{SO}_2$  to give  $\text{Rh}(\text{CO})\text{H}(\text{PPh}_3)_2(\text{SO}_2)$ .

The absence of peaks in the i.r. and n.m.r. spectra of this compound, which can be attributed to a metal-hydrogen bond, has led Robinson and Levison<sup>(64)</sup> to propose the following tautomeric equilibrium:



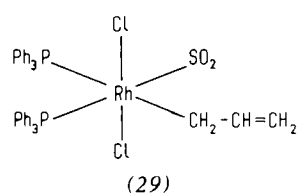
In chloroform solutions a weak band is observed at  $2020\text{ cm}^{-1}$ , which indicates that the equilibrium lies further to the left in solution. The corresponding iridium complex has an i.r. band at  $1965\text{ cm}^{-1}$  in the solid state and is therefore formulated as a hydrido-sulphur dioxide complex.  $\text{SO}_2$  also displaces one of the ethylene ligands from  $\text{Rh}(\eta\text{-C}_2\text{H}_4)_2(\eta\text{-Cp})$  to give  $\text{Rh}(\eta\text{-C}_2\text{H}_4)(\eta\text{-Cp})(\text{SO}_2)$ . Structural studies<sup>(14)</sup> have shown that this is an example of a  $d^8$  complex with  $\eta^1$ -planar  $\text{SO}_2$  group [see (28)] which is in contrast to the two previously reported structures of  $d^8$ -metal complexes where  $\text{SO}_2$  is  $\eta^1$ -pyramidal. Solid and solution samples of  $\text{Rh}(\eta\text{-C}_2\text{H}_4)(\eta\text{-Cp})(\text{SO}_2)$  are robust towards aerial oxidation, which suggests that the  $\eta^1$ -pyramidal  $\text{SO}_2$  geometry may be an important prerequisite for facile oxidation to sulphate.



A significant feature of the structures of  $\text{Rh}(\eta\text{-C}_2\text{H}_4)(\eta\text{-Cp})(\text{SO}_2)$  and  $\text{Rh}(\eta\text{-C}_2\text{H}_4)(\eta\text{-Cp})(\eta\text{-C}_2\text{F}_4)$  is the rotational angle about the  $\text{Rh-SO}_2$  and  $\text{Rh-C}_2\text{F}_4$  bonds. In these two compounds the  $\pi$ -acceptor orbitals have exactly the same orientation with respect to the metal-ethylene and Cp ring. Extended Huckel m.o. calculations favour the observed conformation by  $21\text{ kJ mol}^{-1}$  over the hypothetical orientation with the  $\text{SO}_2$  plane parallel to that of the ethylene.

Sulphur dioxide has been shown to interact reversibly with  $\text{Rh}(\text{NO})(\text{PPh}_3)_3$ , crystals of  $\text{Rh}(\text{NO})(\text{PPh}_3)_2(\text{SO}_2)$  thus formed are stable in air for several days and have been characterised by x-ray analysis<sup>(15)</sup>. The compound has an  $\eta^2$ -coordination mode and has been discussed above (see 19).

The rhodium(III) complex  $\text{RhCl}_2(\eta\text{-C}_3\text{H}_5)(\text{PPh}_3)_2$  dissolves in liquid  $\text{SO}_2$  to yield a compound which is 1:1 adduct<sup>(65)</sup>. The following structure (29) has been proposed for the complex on the basis of i.r. studies:



The characteristic  $\text{SO}_2$  i.r. frequencies for rhodium complexes are summarised in Table 6.

Table 6. I.r. data for rhodium  $\text{SO}_2$  complexes

Compound	$\nu(\text{SO}_2)$ ( $\text{cm}^{-1}$ )	Colour	Ref.
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$	1208, 1053	green	(2)
$\text{RhCl}(\text{PF}_3)(\text{PPh}_3)_2(\text{SO}_2)$	1222, 1194, 1064		(60)
$\text{RhCl}(\eta\text{-C}_8\text{H}_{12})(\text{PPh}_3)(\text{SO}_2)$	1218, 1050	red	(61)
$\text{RhCl}(\eta\text{-C}_7\text{H}_8)(\text{PPh}_3)(\text{SO}_2)$	1215, 1050	red	(61)
$\text{RhCl}(\eta\text{-C}_8\text{H}_{12})(\text{pip})(\text{SO}_2)$	1200, 1050	red	(61)
$\text{RhCl}(\text{CO})_2(\text{pip})(\text{SO}_2)$	1200, 1050	red	(61)
$\text{Rh}(\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$ R = Me or Et	1200, 1044	bright yellow	(58)
$\text{RhCl}(\text{PPh}_3)_2(\text{SO}_2)$	1172, 1038, 1033	brown	(12)
$\text{RhBr}(\text{PPh}_3)_2(\text{SO}_2)$ <i>cis-trans-</i>	1177, 1036 1288, 1124	brown	(12)
$\text{RhI}(\text{PPh}_3)_2(\text{SO}_2)$ <i>cis-trans-</i>	1173, 1030 1287, 1121	brown	(12)
$\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_2(\text{SO}_2)$	1090	not reported	(12)
$\text{Rh}(\text{CO})\text{H}(\text{PPh}_3)_2(\text{SO}_2)$	1183, 1038	orange yellow	(64)
$[\text{Rh}(\text{SO}_2)(\text{VP})_2]\text{BPh}_4^{\text{a}}$	1161, 1140, 1060	yellow	(62)
$\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{SC}_6\text{F}_5)(\text{SO}_2)$	1217, 1052	orange	(59)
$\text{Rh}(\eta\text{-C}_3\text{H}_5)\text{Cl}_2(\text{PPh}_3)_2(\text{SO}_2)$	1164, 1120, 1095	—	(65)

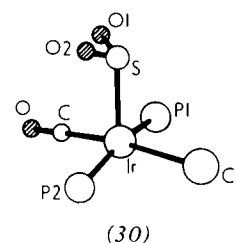
a) VP = *o*-vinylphenyl(diphenyl)phosphine.

### Iridium-sulphur dioxide complexes

The first reported iridium- $\text{SO}_2$  complex was prepared by Vaska<sup>(2)</sup> according to the following equation:



The  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$  complex has the following square-pyramidal structure<sup>(6)</sup> in the solid state:



The related  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$  complexes (where X = Br, I<sup>(2)</sup>,  $\text{SC}_6\text{F}_5$ <sup>(59)</sup> or  $\text{C}\equiv\text{CR}$ <sup>(58)</sup>) have also been prepared and their characteristic  $\text{SO}_2$  frequencies are reported in Table 7.

Reactions involving addition of  $\text{SO}_2$  to  $\text{Ir}^1$  complexes containing  $\pi$ -ligands coordinated to the metal have been studied by Palazzi *et al.*<sup>(61)</sup>, e.g.



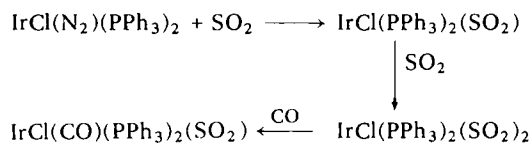
(where diene = 1,5 cyclooctadiene or norbornadiene).

When piperidine replaced the phosphine,  $\text{SO}_2$  adducts were formed more easily, suggesting an electrophilic attack by  $\text{SO}_2$  on the metal, which was made more basic by the coordinated piperidine.

Table 7. I.r. data for iridium-SO<sub>2</sub> complexes

Compound	$\nu(\text{SO}_2)$ ( $\text{cm}^{-1}$ )	Colour	Ref.
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$	1198, 1185, 1048	green	(2)
$\text{IrBr}(\text{CO})(\text{PPh}_3)_2(\text{SO}_2)$	1213, 1055	green	(2)
$\text{Ir}(\text{CO})\text{I}(\text{PPh}_3)_2(\text{SO}_2)$	1188, 1041	green	(2)
$\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{SC}_6\text{F}_5)(\text{SO}_2)$	1202, 1187, 1047	yellow green	(59)
$\text{IrCl}(\text{PPh}_3)_2(\text{SO}_2)$	1272, 1125	red brown	(63)
$\text{IrCl}(\text{PPh}_3)_2(\text{SO}_2)_2$	1272, 1125, 1198, 1050	red brown	(56, 50 48, 54)
$\text{IrCl}(\text{CO})(\text{C}\equiv\text{CR})(\text{PPh}_3)_2(\text{SO}_2)$ (R = Me or Et)	1190, 1042	green	(58)
$\text{Ir}(\eta\text{-C}_8\text{H}_{12})\text{Cl}(\text{PPh}_3)(\text{SO}_2)$	1200, 1050	red	(61)
$\text{IrCl}(\text{CS})(\text{PPh}_3)_2(\text{SO}_2)$	1205, 1050	green	(70)
$\text{Ir}(\eta\text{-C}_2\text{H}_4)\text{Cl}(\text{PPh}_3)_2(\text{SO}_2)$	1215, 1190, 1063	yellow green	(71)
$\text{Ir}(\eta\text{-C}_3\text{H}_4)\text{Cl}(\text{PPh}_3)_2(\text{SO}_2)$	1215, 1190, 1040	yellow green	(71)
$\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_2(\text{SO}_2)$	1175, 1037	lime green	(64)
$\{\text{IrCl}(\text{PPh}_3)_2\}_2(\text{SO}_2)$	1120, 980, 907	yellow	(54)
$\text{Ir}(\text{CO})(\text{ISO}_2)(\text{PPh}_3)_2(\text{SO}_2)$	1323, 1185, 1156, 1040, 1140	yellow green	(39)
$\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2(\text{SO}_2)_2\text{Cl}$	1276, 1163	white	(4)

An interesting reaction of SO<sub>2</sub> with IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> has been observed by two independent groups of workers<sup>(48, 54)</sup>. Sulphur dioxide can replace dinitrogen in IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> forming IrCl(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>), which further interacts with SO<sub>2</sub> yielding IrCl(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)<sub>2</sub>. One of the SO<sub>2</sub> groups can be replaced by CO forming IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>). The overall reaction can be written as follows:

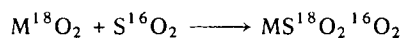


The IrCl(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)<sub>2</sub> complex is oxidised by oxygen in the presence of CO to give the sulphato-complex IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>). Treatment of solutions of IrCl(PPh<sub>3</sub>)<sub>3</sub> with SO<sub>2</sub> gives an incompletely characterised yellow solid which has tentatively been assigned the dimeric structure {IrCl(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(SO<sub>2</sub>). Surprisingly, this complex does not react with oxygen under mild conditions.

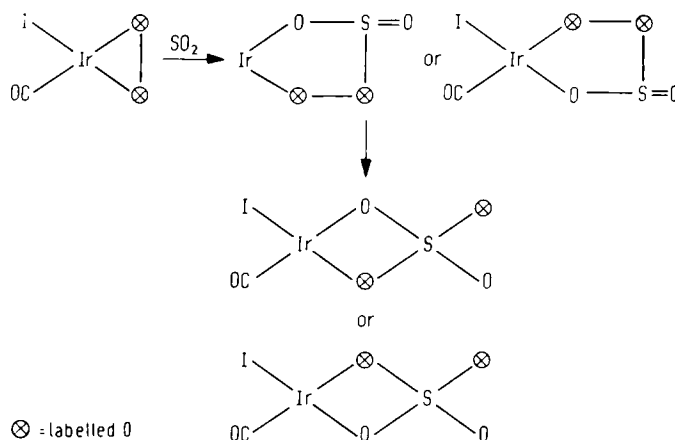
When the carbonyl ligand in Vaska's compound is replaced by C<sub>2</sub>H<sub>4</sub>, allene or CS the resultant complexes also form adducts with SO<sub>2</sub><sup>(70, 71)</sup>. The complex [Ir(Ph<sub>2</sub>P)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>]<sub>2</sub>Cl picks up two moles of SO<sub>2</sub>, however, the structure of the resultant six-coordinate complex has not been confirmed by a single crystal x-ray analysis<sup>(4)</sup>.

The i.r. frequencies of the iridium-SO<sub>2</sub> complexes are summarised in Table 7.

An <sup>18</sup>O study of the reaction between iridium and platinum-oxygen complexes and SO<sub>2</sub> to form coordinated sulphate has been reported by Collman *et al.*<sup>(63)</sup>. They accomplished oxidation of SO<sub>2</sub> using the <sup>18</sup>O isotopic labelling experiments given below:



The highest frequency band in the i.r. spectrum of the iridium sulphate appeared at 1296 cm<sup>-1</sup> which was attributed to the antisymmetric stretch of the two external, uncoordinated oxygen atoms. They observed three peaks after isotopic substitution of the iridium-sulphate, at 1296 cm<sup>-1</sup>, 1280 cm<sup>-1</sup> and 1257 cm<sup>-1</sup>. These three bands were assigned to the external <sup>16</sup>O<sup>16</sup>O, <sup>16</sup>O<sup>18</sup>O, <sup>18</sup>O<sup>18</sup>O isotopic species. The iridium sulphate resulting from reactions (1) and (2) did not have a band at 1257 cm<sup>-1</sup> which was attributed to two external <sup>18</sup>O atoms. They concluded therefore that intramolecular rearrangement of sulphate had not taken place since this would scramble the oxygen atoms and afford 20.5% of the species containing two external <sup>18</sup>O atoms (starting with 90.0% O<sub>2</sub> or SO<sub>2</sub> statistically labelled with <sup>18</sup>O). Metal-oxygen bond cleavage must have taken place during the reaction and they propose the following reactions to account for the identical isotopic substitution pattern observed for the two external oxygens, starting from either doubly labelled O<sub>2</sub> or doubly labelled SO<sub>2</sub>.



#### Palladium-sulphur dioxide complexes

Few palladium sulphur dioxide complexes have been isolated to date. The Pd(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>) complex has been prepared simply by bubbling SO<sub>2</sub> through a solution of Pd(PPh<sub>3</sub>)<sub>3</sub> in benzene<sup>(3)</sup>. An alternative formulation [Pd(PPh<sub>3</sub>)<sub>4</sub>(SO<sub>2</sub>)]<sub>n</sub> has been proposed<sup>(72)</sup> for this compound but it is not consistent with more recent x-ray fluorescence studies<sup>(64)</sup>. In the solid state this palladium complex is less air sensitive than its solvated platinum analogue, and undergoes aerobic oxidation only over a period of weeks. In solution, however, oxidation to the sulphato-complex Pd(SO<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> occurs rapidly. The palladium complex Pd{(Ph<sub>2</sub>P)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>}<sub>2</sub>, like its platinum analogue, reacted with sulphur dioxide, but the resultant complexes were too air-sensitive to characterise completely<sup>(64)</sup>.

The Pd(NCO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> complex reacts with SO<sub>2</sub> in methanol to give the polynuclear complex [Pd(PPh<sub>3</sub>)(SO<sub>2</sub>)]<sub>3</sub><sup>(73)</sup>. The related orange diamagnetic cluster complex [Pd<sub>3</sub>(t-BuNC)<sub>5</sub>(SO<sub>2</sub>)<sub>2</sub>] · 2C<sub>6</sub>H<sub>6</sub> has been prepared from Pd(t-BuNC)<sub>2</sub> and an excess of SO<sub>2</sub>. The structure of

this complex has been solved using single crystal techniques and is illustrated (21)<sup>(40)</sup>. The sulphur dioxide ligand in this and other polynuclear complexes, is inactive towards oxygen, which is perhaps a reflection of the coordinative saturation of a bridging SO<sub>2</sub> group<sup>(40)</sup>.

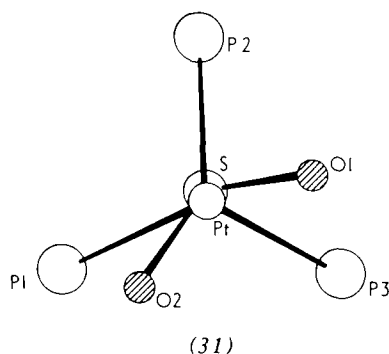
The i.r. frequencies for palladium SO<sub>2</sub> complexes are given in Table 8.

Table 8. I.r. data for palladium-SO<sub>2</sub> complexes

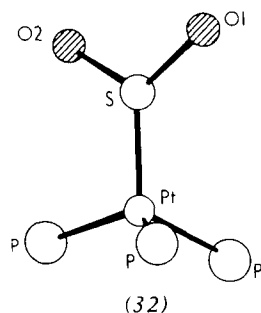
Compound	$\nu(\text{SO}_2)$ (cm <sup>-1</sup> )	Colour	Ref.
Pd(PPh <sub>3</sub> ) <sub>3</sub> (SO <sub>2</sub> )	1195, 1045	purple red	(3)
[Pd(PPh <sub>3</sub> )(SO <sub>2</sub> )] <sub>n</sub>	1252, 1237, 1064	—	(73)
Pd <sub>3</sub> (t-BuNC) <sub>5</sub> (SO <sub>2</sub> ) <sub>2</sub>	1208, 1060	orange	(40)

### Platinum-sulphur dioxide complexes

The first well characterised SO<sub>2</sub> complex of platinum, Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>), was prepared by Robinson and Levison<sup>(3)</sup>. The x-ray crystallographic analysis by Ryan and his co-workers<sup>(13)</sup> of this compound has established that the SO<sub>2</sub> ligand is coordinated to the metal in  $\eta^1$ -pyramidal mode (31).



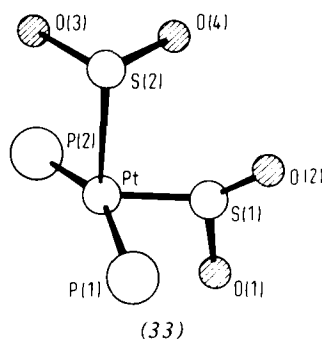
This result contradicted previous work which proposed a structure<sup>(6)</sup> with SO<sub>2</sub> coordinated to the metal in a  $\eta^1$ -planar-coordination mode (32).



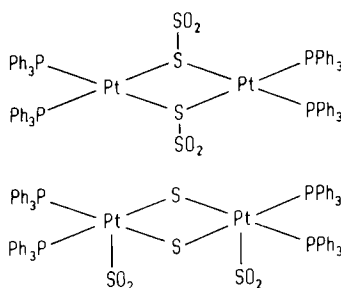
An interesting reaction was observed by Cook and Jauhal<sup>(11)</sup>; when they reacted SO<sub>2</sub> with Pt( $\eta$ -C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>, Pt(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)<sub>2</sub> was obtained. The x-ray structural analysis<sup>(35)</sup> of this compound has established that coordination geometry around platinum is best described as a severely distorted tetrahedron. Both the SO<sub>2</sub> groups are pyramidal with the average angle between the M-S vector and SO<sub>2</sub> plane being 119° and the average M-S distance is 2.43 Å

[see (33)]. The P-Pt-P angle (158.6°) is noticeably larger than the S-Pt-S angle (106.3°) and is the largest P-M-P angle reported for a tetrahedral d<sup>10</sup> complex. The structure has the two SO<sub>2</sub> ligands bent towards opposite Pt-P bonds, a tendency which has also been noted for Os(NO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>(35)</sup>.

The Pt(SO<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub> and Pt(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)<sub>2</sub> compounds show a ready reactivity towards dioxygen to form Pt(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>) and Ryan has pointed out that all structurally characterised complexes with the  $\eta^1$ -planar coordination mode are, on the other hand, remarkably inert to this reaction. However, the  $\eta^1$ -pyramidal geometry is commonly associated with the more basic transition metals which might also promote the attack of electrophiles such as dioxygen. On heating, Pt(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)<sub>2</sub><sup>(11)</sup> loses one molecule of SO<sub>2</sub> and gives the green complex Pt(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>).

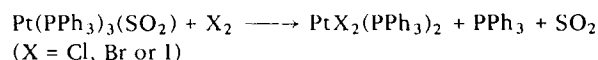


The [Pt(PPh<sub>3</sub>)<sub>2</sub>(S)(SO<sub>2</sub>)]<sub>2</sub> complex has been obtained by reacting [Pt(PPh<sub>3</sub>)<sub>2</sub>S]<sub>2</sub> with SO<sub>2</sub>. Weak bonds between SO<sub>2</sub> and platinum have been proposed for this compound as bubbling O<sub>2</sub> or N<sub>2</sub> through a solution of [Pt(PPh<sub>3</sub>)<sub>2</sub>(S)(SO<sub>2</sub>)]<sub>2</sub> results in the displacement of SO<sub>2</sub> and the sulphato-complex is not formed. The following two structures have been proposed for this complex:



Ghatak and Mingos<sup>(55)</sup> have established that an identical product results from the reaction of Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>) with elemental sulphur. It is interesting to note that this reaction is not analogous to that reported for dioxygen which results in the formation of a sulphato-complex. The i.r. data on this and other platinum-SO<sub>2</sub> complexes are summarised in Table 9.

The following oxidative addition reactions of Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>) have also been studied:

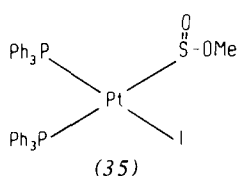


and shown to proceed with loss of SO<sub>2</sub>, even when stoichiometric quantities of halogen are used. With organic halides, Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>) gives a more complex series of oxidative

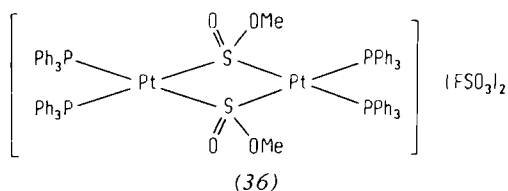
Table 9. I.r. data for platinum-SO<sub>2</sub> complexes

Compound	$\nu(\text{SO}_2)$ ( $\text{cm}^{-1}$ )	Colour	Ref.
Pt(PPh <sub>3</sub> ) <sub>3</sub> (SO <sub>2</sub> )	1195, 1045	dark purple	(3)
Pt(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> ) <sub>2</sub>	1223, 1215, 1050, 1030	brown red	(11,35)
Pt(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>2</sub> )	1182, 1149, 1035	green	(11)
{Pt(PPh <sub>3</sub> ) <sub>2</sub> (S)(SO <sub>2</sub> ) <sub>2</sub> }	1210, 1060	deep orange	(74)
Pt <sub>2</sub> Cl <sub>4</sub> (PPh <sub>3</sub> ) <sub>4</sub> (SO <sub>2</sub> )	1090, 1100	—	(75)

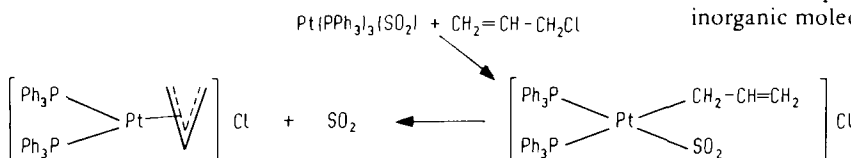
addition reactions. With methyl iodide the predominant product is *trans*-Pt(Me)I(PPh<sub>3</sub>)<sub>2</sub>, but the *S*-sulphoxylato complex (35) is also isolated in low yields from the reaction<sup>(55)</sup>:



If methyl iodide is replaced by the more strongly electrophilic MeSO<sub>3</sub>F then attack at the ligand site occurs almost exclusively to give the bridged sulphoxylato complex illustrated in (36).

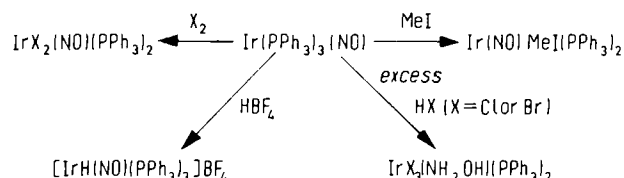


The corresponding reaction with allyl chloride gives initially an ionic  $\eta^1$ -allyl sulphur dioxide complex, which readily loses SO<sub>2</sub> to form an  $\eta^3$ -allyl complex as shown below<sup>(55)</sup>.



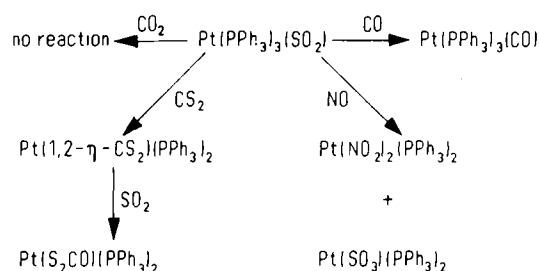
The insertion products *cis*- and *trans*-[Pt(SO<sub>2</sub>CH=CHMe)Cl(PPh<sub>3</sub>)<sub>2</sub>] were also isolated from the above reaction in low yields. Volger and Vrieze have shown that identical insertion products result when [Pt( $\eta$ -C<sub>3</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>]Cl is dissolved in liquid sulphur dioxide<sup>(75)</sup>.

In view of the similar bonding characteristics of NO and SO<sub>2</sub> in transition metal complexes, it is of interest to contrast the oxidative addition reactions of Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>) with those of the pseudo-isoelectronic nitrosyl complex Ir(NO)(PPh<sub>3</sub>)<sub>3</sub>. The latter, as shown below, generally proceed with retention of the nitrosyl coordinate bond and occur at the metal centre:

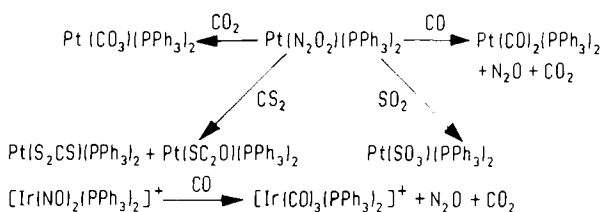


The different products observed for the nitrosyl and sulphur dioxide complexes arise primarily from the weaker metal-ligand bond in the latter case, which encourages the dissociation of the SO<sub>2</sub> ligand in the oxidative addition product. If strong electrophiles, e.g. Me<sup>+</sup> or H<sup>+</sup>, are used, attack at the ligand rather than the metal becomes preferred for both the NO and SO<sub>2</sub> complexes, although the point of attack in the two types of complexes is quite different.

The reactions of Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>) with small unsaturated molecules such as CO, CO<sub>2</sub>, CS<sub>2</sub> and NO have been studied<sup>(55, 77, 78)</sup> and are summarised below:



These reactions may be contrasted with those which have been reported for the related metal dinitrosyl and dinitrogen dioxide complexes which are illustrated below<sup>(79–83)</sup>:



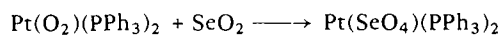
From this comparison it is clear that the platinum sulphur dioxide complex is much less effective at oxidising small inorganic molecules such as CO and CO<sub>2</sub> than are the

dinitrosyl and dinitrogen dioxide complexes. Only with CS<sub>2</sub> and NO, which are more reactive, are oxidation processes observed.

From the comparisons made above it is clear that the analogous bonding capabilities of the nitrosyl and sulphur dioxide ligand is not reflected in the chemistries of these coordinated ligands to any marked extent. In particular, the relatively weak metal-sulphur coordinate bond limits the scope of the oxidative addition reactions of complexes of this ligand, and it is only with strong electrophiles which encourage attack at the ligand rather than the metal, that interesting products are observed.

*Platinum-selenium dioxide complex*

It has recently been shown in our laboratories<sup>(55)</sup> that SeO<sub>2</sub> reacts with a benzene solution of Pt(PPh<sub>3</sub>)<sub>3</sub> to give a mononuclear selenium dioxide complex Pt(PPh<sub>3</sub>)<sub>2</sub>(SeO<sub>2</sub>), which does not react with molecular oxygen under mild conditions to give a platinum(II) selenate complex. The latter, can however, be formed in the following oxidation process:



The SeO<sub>2</sub> complex has been characterised on the basis of infrared and x-ray fluorescence data.

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## Triphenylphosphineoxide Nitrosyl Complexes of Molybdenum

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### Summary

Nitric oxide gas reacts with biscarbonyl(bisdialkyldithiocarbamate)triphenylphosphinemolybdenum complexes to give new complexes, formulated as  $\text{Mo}(\text{NO})(\text{S}_2\text{CNR}_2)_2\text{Ph}_3\text{PO}$  (R = Me and Et) on the basis of their i.r. spectra and elemental analyses. With nitrosyl bromide, the same molybdenum complexes give  $\text{Mo}(\text{NO})_2\text{Br}_2(\text{Ph}_3\text{PO})_2$ .

### Introduction

Two types of nitrosyl(dialkyldithiocarbamate)molybdenum complexes are known:

*a.* the dinitrosyldialkyldithiocarbamate molybdenum complexes of general formula  $\text{Mo}(\text{NO})_2(\text{S}_2\text{CNR}_2)_2$  (R = Me and Et); (these are considered to be octahedral in which the two nitrosyl groups are *cis* to each other), and  
*b.* the heptacoordinated mononitrosyl(trisdialkyldithiocarbamate)molybdenums,  $\text{Mo}(\text{NO})(\text{S}_2\text{CNR}_2)_3$  (R = Me, Et, and *n*-Bu), whose crystal structure has been established recently<sup>(3)</sup>. On the other hand, as far as we are aware, no metal nitrosyldialkyldithiocarbamates containing triphenylphosphine are known. Such complexes containing mixed ligands were reported for metal carbonyls, in particular the carbonyl(bisdialkyldithiocarbamate)molybdenum species,  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2\text{Ph}_3\text{P}$  (R = Me or Et)<sup>(7)</sup>. Complexes of the general formula  $\text{M}(\text{NO})_2\text{Br}_2(\text{Ph}_3\text{P})_2$  have been prepared by direct interaction of  $[\text{M}(\text{NO})_2\text{Br}_2]_n$  (where M = Mo or W) with triphenylphosphine<sup>(5)</sup>. In this work, we describe the reaction of both nitric oxide and nitrosyl bromide with the dicarbonyl(dialkyldithiocarbamate)molybdenums containing a triphenylphosphine ligand, *i.e.*  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2\text{Ph}_3\text{P}$ , where R = Me or Et.

### Results and Discussion

In the first reaction, NO gas was passed through a dichloromethane solution of  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2\text{Ph}_3\text{P}$  (R = Me or Et) and yellow crystals were obtained. The product was formulated on the basis of i.r. spectra and elemental analyses as  $\text{Mo}(\text{NO})(\text{S}_2\text{CNR}_2)_2\text{Ph}_3\text{PO}$ , where R = Me and Et. Both the methyl and ethyl derivatives exhibit a single NO stretching frequency at  $1640\text{ cm}^{-1}$  together with characteristic C–N partial double bond stretching frequencies at  $1540\text{ cm}^{-1}$ <sup>(6)</sup>. Other bands, observed in the  $1150\text{--}1190\text{ cm}^{-1}$  range, were attributed to PO stretching frequencies<sup>(7)</sup>. Since both methyl and ethyl complexes exhibit NO stretching frequencies at  $1640\text{ cm}^{-1}$ , the coordinated NO may be considered as  $\text{NO}^{+(8)}$  and molybdenum to be in a univalent state. In the other reaction, in which nitrosyl bromide was employed, both the methyl and ethyl derivatives of  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2\text{Ph}_3\text{P}$  gave the compound  $\text{Mo}(\text{NO})_2\text{Br}_2(\text{Ph}_3\text{PO})_2$ . In both cases the product was identified by its i.r. spectrum and elemental analysis. Two bands at  $1780$  and  $1670\text{ cm}^{-1}$ , due to NO stretching frequencies, were observed. This indicates, as pointed out previously, that the NO groups occupy mutually *cis* positions<sup>(5)</sup>. Bands observed in the  $1150\text{--}1190\text{ cm}^{-1}$  region were assigned to PO stretching frequencies as also pointed out for complexes previously. Although the reaction pathway is not yet known, the isolation of the pure dinitrosyldibromotriphenylphosphineoxidemolybdenum complex in each case reveals that triphenylphosphine forms complexes of superior stability to those containing the dithiocarbamate ligand.

Although these reactions were carried out in an inert atmosphere, oxidation of the coordinated triphenylphosphine occurred. This phenomenon was ascribed recently to the presence of nitric oxide or nitrosyl bromide in which NO behaves as an oxidant<sup>(9–10)</sup>.

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