Oxygen-transfer Reactions in Platinum Metal Complexes of Nitric Oxide and Sulphur Dioxide

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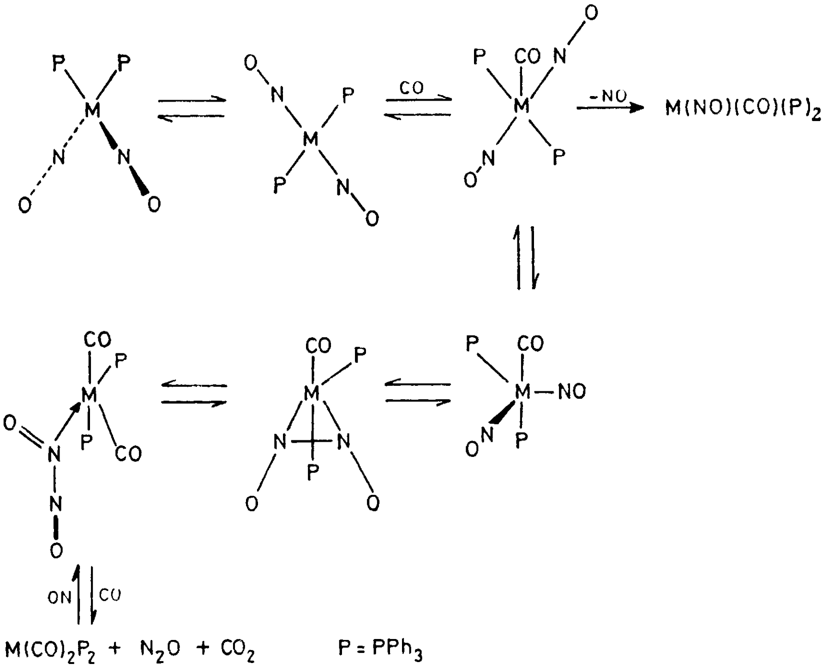
The reactions of SO_2 with $[Pt(N_2O_2)(PPh_3)_2]$ and NO with $[Pt(PPh_3)_3(SO_2)]$ have been shown to result in the formation of $[Pt(NO_2)_2(PPh_3)_2]$ and $[Pt(PPh_3)_2(SO_3)]$, which arise from ready oxygen-transfer reactions. A compound which analyses correctly for $[Pt(N_2O_2)(PPh_3)_2(SO_2)]$ has also been isolated from these reactions and is formulated as an insertion product on the basis of i.r. and chemical studies. The reaction of $[Ru(NO)_2(PPh_3)_2]$ with SO_2 proceeds in a quite different fashion and gives an SO_2 adduct $[Ru(NO)_2(PPh_3)_2(SO_2)]$ which has both a linear and a bent NO ligand. This complex is readily oxidised to the corresponding sulphato-complex in air.

In 1973 it was reported[1] that the cationic dinitrosyl complex ion $[Ir(NO)_2(PPh_3)_2]^+$ reacts with carbon monoxide to generate CO_2 and N_2O according to equation (1). Subsequent work on this and related complexes,

$$[Ir(NO)_2(PPh_3)_2]^+ + 4CO \longrightarrow [Ir(CO)_3(PPh_3)_2]^+ + N_2O + CO_2 \quad (1)$$

and ^{15}N labelling studies led Bhaduri and Johnson[2] to suggest a mechanism involving a dinitrogen dioxide intermediate for this reaction (see Scheme 1). Related studies by Eisenberg, Ibers and their co-workers[3-6] have substantiated the generality of the overall reaction and led to the development of platinum metal catalysts for the overall reaction involving CO and NO, *i.e.* equation (2).



SCHEME 1

The role of the dinitrogen dioxide intermediate is still controversial and, as Meyer and Eisenberg have commented in a recent paper,[4] it is impossible to conclude on the basis of published data whether the dinitrogen dioxide is acting as a ligand in a stable intermediate, a transition state in the conversion of two-co-ordinate

$$2NO + CO \longrightarrow CO_2 + N_2O \quad (2)$$

nitrosyls into a hyponitrite derivative, or simply unimportant in the above mechanism. To understand this aspect of the mechanism Johnson and co-workers[7] have investigated the reactions of $[Pt(N_2O_2)(PPh_3)_2]$, which was first prepared by Robinson, Ugo, and their co-workers[8] and has been recently characterised as a *cis-OO'*-dinitrogen dioxide complex (1) by crystallographic methods.[9] They have shown that (1) reacts stoicheiometrically with CO according to equation (3),[7] however,

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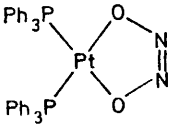
the facile conversion of $[Pt(CO)_2(PPh_3)_2]$ into the cluster compound $[Pt_3(CO)_4(PPh_3)_3]$ limits the catalytic potential of this system.[2] In this paper we report the reaction of

$$[Pt(N_2O_2)(PPh_3)_2] + 3CO \longrightarrow [Pt(CO)_2(PPh_3)_2] + N_2O + CO_2 \quad (3)$$

$[Pt(N_2O_2)(PPh_3)_2]$ with SO_2 which was of particular interest because of the structural similarities which exist between SO_2 and NO when co-ordinated to transition metals.[10] We have also investigated the related reaction of $[Pt(PPh_3)_3(SO_2)]$ with NO as part of a more general study of the reactions of the co-ordinated SO_2 ligand.[10] A previous paper [11] has described the oxidation of co-ordinated CS_2 to dithiocarbonate by SO_2 according to equations (4) and (5), and thereby establishing the ability of SO_2 to act as an oxygen-transfer reagent.



(1)

$$[Pt(PPh_3)_3(SO_2)] + CS_2 \longrightarrow [Pt(\eta^2\text{-}CS_2)(PPh_3)_2] + SO_2 + PPh_3 \quad (4)$$

$$[Pt(\eta^2\text{-}CS_2)(PPh_3)_2] + 2SO_2 \longrightarrow [Pt(CS_2O)(PPh_3)_2] + S + SO_3 \quad (5)$$

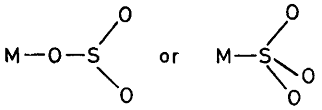
RESULTS AND DISCUSSION

Reaction of $[Pt(PPh_3)_3(SO_2)]$ *with Nitric Oxide.*—As nitric oxide and sulphur dioxide are both able to act as oxidising agents when co-ordinated to platinum, as described above, it was of interest to examine their mutual chemical interactions on a single metal centre. When NO was bubbled through a benzene solution of $[Pt(PPh_3)_3(SO_2)]$ a mixture of products was obtained, the relative proportions of which were found to depend markedly on the rate at which NO was bubbled through the solution. When NO was bubbled slowly through the solution the predominant product was $[Pt(NO_2)_2(PPh_3)_2]$. This compound, which was originally prepared by Levison and Robinson [12] from the reaction of $[PtCl_2(PPh_3)_2]$ with sodium nitrite, was identified by its melting point (258 °C, reported 260 °C) and characteristic i.r. bands: $\nu(NO_2)$ 1 410, 1 330, and 825 cm^{-1}. When NO was bubbled rapidly through the solution a mixture of products was obtained. The components of this mixture were separated by fractional crystallisation and characterised as $[Pt(PPh_3)_2(SO_3)]$ (2) and $[Pt(N_2O_2)(PPh_3)_2(SO_2)]$ (3) on the basis of elemental analysis and i.r. studies. Complex (3) was also isolated from the reaction of $[Pt(N_2O_2)(PPh_3)_2]$ with SO_2 and will be discussed in more detail below.

An authentic sample of $[Pt(PPh_3)_2(SO_3)]$ was prepared from $Ag_2[SO_3]$ and $[PtCl_2(PPh_3)_2]$, and shown to have properties identical with those found for (2). An alternative synthesis of this compound from molecular SO_3 [equation (6)] failed to produce a tractable product.

$$[Pt(PPh_3)_3] + SO_3 \longrightarrow [Pt(PPh_3)_2(SO_3)] + PPh_3 \quad (6)$$

The sulphito-ligand has the ability to co-ordinate to a transition-metal ion in a unidentate or bidentate fashion. Furthermore, it is an ambidentate ligand which can co-ordinate either through sulphur or oxygen as illustrated below. The latter has been more extensively characterised using *X*-ray crystallographic techniques.[13-15] *S*-Sulphito-complexes retain the C_{3v} symmetry elements of the parent anion and therefore four normal modes of vibration $\nu_1(A_1)$, $\nu_2(E)$, $\delta(A_1)$, and $\delta(E)$ which are both i.r. and Raman active are anticipated and indeed observed in complexes such as $[Co(NH_3)_5(SO_3)]Cl$ (see Table).



Co-ordination through oxygen leads to a reduction of symmetry to C_s and a removal of the degeneracy of the degenerate vibrations of *E* symmetry. $Tl_2[Cu(SO_3)_2]$ provides an example of such a complex, and suggests that this mode of co-ordination is characterised by three $\nu(SO_3)$ vibrations in the 850—1 000 cm^{-1} region. On the other hand for the bidentate *OO'*-sulphito-ligand, which also has C_s local symmetry, three bands in the 940—1 200 cm^{-1} region are expected for the $\nu(SO_3)$ stretching vibrations. In some complexes, *e.g.* $K_2[Pt(SO_3)_2]\cdot 2H_2O$ and $K_3[Rh(SO_3)_3]\cdot 2H_2O$, the highest frequency band shows an additional splitting. The complex $[Pt(PPh_3)_2(SO_3)]$ has bands at 1 210, 1 065, 890, 620, and 535 cm^{-1} which are consistent with its formulation as an *OO'*-sulphito-complex.

Infrared data (cm^{-1}) for sulphito-complexes *

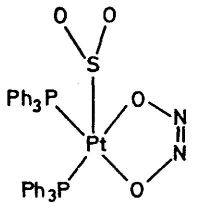
Species	Symmetry	$\nu_1(A_1)$	$\nu_2(E)$	$\delta(A_1)$	$\delta(E)$
SO_3^{2-}	C_{3v}	970		633	498
$[Co(NH_3)_5(SO_3)]Cl$	C_{3v}(*S*-bonded)	1 110	985	633	519
$Tl_2[Cu(SO_3)_2]$	C_s(*O*-bonded)	989	902, 862	673	506, 460
$K_2[Pt(SO_3)_2]\cdot 2H_2O$	C_s(*OO'*-bonded)	1 166, 1 092			
$K_3[Rh(SO_3)_3]\cdot 2H_2O$	C_s(*O'O'*-bonded)	1 157, 1 113	1 058, 939	690	647, 527
$[Pt(PPh_3)_2(SO_3)]$		1 210	1 065, 890		620, 535

* See refs. 14—16.

Reaction of $[Pt(N_2O_2)(PPh_3)_2]$ *with Sulphur Dioxide.*—When SO_2 was bubbled through a suspension of $[Pt(N_2O_2)(PPh_3)_2]$ in toluene a mixture of two products was obtained which were separated by fractional recrystallisation. The products were shown to be identical with the samples of $[Pt(PPh_3)_2(SO_3)]$ (2) and $[Pt(N_2O_2)(PPh_3)_2(SO_2)]$ (3) isolated from the reaction of $[Pt(PPh_3)_3(SO_2)]$ with NO. It proved to be impossible to obtain analytically pure samples of (3) under these conditions; however, when the reaction was repeated at a temperature of −78 °C samples which gave satisfactory chemical analyses were obtained. The complex (3) is a white microcrystalline solid and chemical analyses and proton n.m.r. studies indicated that it is partially solvated, *i.e.* it has the molecular formula $[Pt(PPh_3)_2(N_2O_2)(SO_2)]\cdot 0.5(C_7H_8)$. A molecular weight determination in $CHCl_3$ solution indicated that it was monomeric ($M = 781$; calculated 843). This compound gave no signs of oxidation or SO_2 dissociation even when exposed to air for several months and only lost N_2O when heated *in vacuo* at 120 °C. The platinum–sulphito-complex (2) resulted from the decomposition process (7). This

$$[Pt(N_2O_2)(PPh_3)_2(SO_2)] \xrightarrow[\textit{in vacuo}]{120\,^{\circ}C} [Pt(PPh_3)_2(SO_3)] + N_2O \quad (7)$$

behaviour may be contrasted with that reported for $[Pt(PPh_3)_3(SO_2)]$ which is almost instantaneously oxidised by atmospheric oxygen to $[Pt(PPh_3)_2(SO_4)]$,[17] and $[Pt(CH_3)(ISO_2)(PPh_3)_2]$ which readily loses SO_2 to give the parent methyl–platinum complex $[Pt(CH_3)I(PPh_3)_2]$.[18] Those observations imply that the SO_2 ligand in (3) is not co-ordinated either directly to the metal as in (4) or to the ligand by a simple dative bond as in (5).



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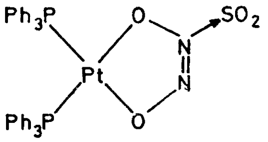
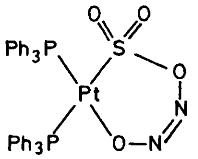


(5)

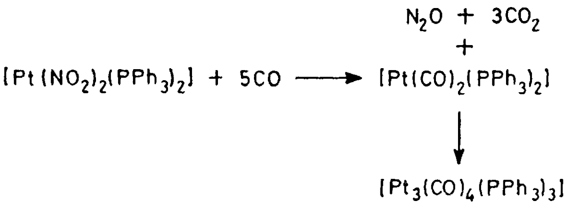
The i.r. spectrum of $[Pt(PPh_3)_2(N_2O_2)(SO_2)]$ (3) has bands at 1 345, 1 295, 1 128, 1 090, 925, and 625 cm^{-1} which cannot be assigned to the triphenylphosphine ligands. The i.r. spectrum of the corresponding labelled compound $[Pt(^{15}N_2O_2)(PPh_3)_2(SO_2)]$ demonstrated that the bands at 1 295, 1 127, 1 090, and 628 cm^{-1} showed no isotopic shifts to lower frequencies. These bands are therefore attributed to those vibrational modes associated predominantly with the SO_2 moiety. These SO_2 frequencies are intermediate between those reported for $[Pt(PPh_3)_3(SO_2)]$ (1 195, 1 065, and 525 cm^{-1}) and $[Pt(CH_3)(ISO_2)(PPh_3)_2]$ (1 322, 1 138, and 630 cm^{-1}). The $-SO_2(OMe)$ ligand when co-ordinated to platinum metals has bands at 1 240—1 270, 1 110, and 595—690 cm^{-1} [19,20] which have been assigned to $\nu_{sym}(SO_2)$, $\nu_{asym}(SO_2)$, and $\delta(SO_2)$ respectively. This together with the chemical evidence described above suggests that the complex (3) may have a $Pt{-}SO_2{-}O$ fragment resulting from insertion of SO_2 into the Pt–O bond of the dinitrogen dioxide complex. A possible structure for (3) is illustrated above. The bands at 1 345 and 896 cm^{-1} in (3) which showed isotopic shifts are therefore attributed to the N_2O_2 moiety. The parent dinitrogen dioxide complex, $[Pt(N_2O_2)(PPh_3)_2]$, has bands at 1 285, 1 240, and 1 060 cm^{-1} which have been assigned to the N_2O_2 ligand.[8]



Conversion of $[Pt(NO_2)_2(PPh_3)_2]$ *into* $[Pt(PPh_3)_2(SO_3)]$.—The isolation of both $[Pt(NO_2)_2(PPh_3)_2]$ and $[Pt(PPh_3)_2(SO_3)]$ from the reaction of NO with $[Pt(PPh_3)_3(SO_2)]$ led us to investigate the reaction of $[Pt(NO_2)_2(PPh_3)_2]$ with SO_2. When dioxygen-free SO_2 was allowed to react with a solution of $[Pt(NO_2)_2(PPh_3)_2]$ in benzene for 24 h, the product was found to be identical with the sample of $[Pt(PPh_3)_2(SO_3)]$ as prepared above. Furthermore, N_2O was identified as the major volatile product from the reaction. Therefore reaction (8) may

$$[Pt(NO_2)_2(PPh_3)_2] + 3SO_2 \longrightarrow [Pt(PPh_3)_2(SO_3)] + N_2O + 2SO_3 \quad (8)$$

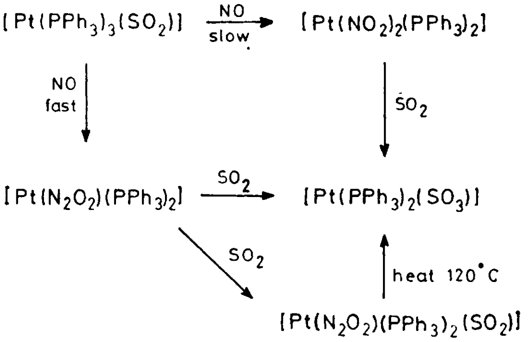
be proposed, which is closely related to that proposed earlier for the reaction of $[Pt(NO_2)_2(PPh_3)_2]$ with CO,[7] *i.e.* equation (9).



(9)

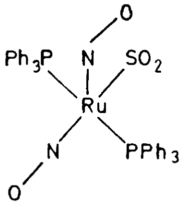
The wide range of products obtained from the reaction of $[Pt(PPh_3)_3(SO_2)]$ with NO and $[Pt(N_2O_2)(PPh_3)_2]$ with SO_2 makes it impossible to suggest a simple mechanism for the oxygen-transfer reactions involving the co-ordinated NO and SO_2 ligands and clearly further kinetic, structural, and chemical studies are required in this field. The formation of $[Pt(PPh_3)_2(SO_3)]$ (2) and $[Pt(N_2O_2)(PPh_3)_2(SO_2)]$ (3) from $[Pt(PPh_3)_3(SO_2)]$ and NO could perhaps arise from an initial displacement of the labile SO_2 ligand by NO and result in the formation of $[Pt(N_2O_2)(PPh_3)_2]$ which has been shown to react with SO_2 to give $[Pt(PPh_3)_2(SO_3)]$, in which case the observed products could be summarised as shown in Scheme 2. The ability of platinum to facilitate these oxygen-transfer reactions for the co-ordinated SO_2 and NO is fascinating and could have wide implications if it could be coupled to a metal centre which simultaneously co-ordinated olefins in addition to these ligands.

Reaction of $[Ru(NO)_2(PPh_3)_2]$ *with* SO_2.—In $[Ru(NO)_2(PPh_3)_2]$ the nitrosyl ligands are co-ordinated to the metal in a conventional linear fashion (Ru–N–O = 168—178°).[21] We have studied the reaction of this 18-electron complex with SO_2 because it provided an interesting comparison to that of the platinum dinitrogen dioxide complex $[Pt(N_2O_2)(PPh_3)_2]$. The complex $[Ru(NO)_2(PPh_3)_2]$ and the related osmium complex react with CO only under forcing conditions and in accordance with equation (10).[2,*] The reaction of $[Ru(NO)_2(PPh_3)_2]$ with SO_2 occurs much more slowly than that with $[Pt(N_2O_2)(PPh_3)_2]$. After leaving a solution of $[Ru(NO)_2(PPh_3)_2]$ under an SO_2 atmosphere for several weeks a dark green (almost black) crystalline air-sensitive solid separated from the solution. The i.r. spectrum of this compound showed bands at 1 820—1 830 cm^{-1} and 1 620 cm^{-1} which were attributed to a linear and bent nitrosyl group respectively,[22] and bands at 1 235 and 1 135 cm^{-1} which were assigned to $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ respectively.[10] These results suggest the illustrated formulation for compound (6). In air the compound rapidly takes on a yellow appearance and the resulting compound has been characterised as $[Ru(NO)_2(PPh_3)_2(SO_4)]$ (7) on the basis of chemical analyses and i.r. spectral studies. In particular it has bands at 1 860 and 1 620 cm^{-1} which are assigned to linear and bent nitrosyl ligands and bands at 1 300, 1 170, 900, and 800 cm^{-1} due to an *OO'*-sulphato-ligand. In the related complex $[RuCl(NO)(PPh_3)_2(SO_4)]$,[23] which has been characterised by *X*-ray crystallography, bands at 1 300, 1 170, 885, and 860 cm^{-1} have been assigned to the bidentate sulphato-group. The dinitrosyl complex $[RuCl(NO)_2(PPh_3)_2][PF_6]$ which has been shown to have linear and bent nitrosyl ligands and a square-pyramidal geometry about the metal has bands at 1 845 and 1 687 cm^{-1} which have been attributed to ν(NO).[24] The oxidation of co-ordinated SO_2 to sulphate has many precedents and two illustrative examples are given in equations (11) and (12).[12,25,26]



SCHEME 2

$$[Ru(NO)_2(PPh_3)_2] \xrightarrow[24\,h]{CO\ (100\ atm)} [Ru(CO)_4(PPh_3)] \quad (10)$$



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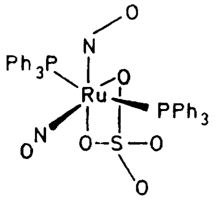

(7)

$$[Pt(PPh_3)_3(SO_2)] + O_2 \longrightarrow [Pt(PPh_3)_2(SO_4)] + PPh_3 \quad (11)$$

$$[Rh(NO)(PPh_3)_2(SO_2)] + O_2 \longrightarrow [Rh(NO)(PPh_3)_2(SO_4)] \quad (12)$$

It is interesting to note that the addition of SO_2 to $[Ru(NO)_2(PPh_3)_2]$ does not result in the formation of N_2O and a sulphito-complex in the manner described for $[Pt(N_2O_2)(PPh_3)_2]$. This observation strongly suggests that the coupling of two nitrosyl ligands to give a dinitrogen dioxide intermediate is an important prerequisite for the oxygen-transfer reaction. The other noteworthy point is that (6) may be viewed as a model for one of the five-co-ordinate dinitrosyl intermediates proposed for the reaction of $[M(NO)(PPh_3)_2]^+$ with CO and illustrated in Scheme 1. In (6) a 20-electron complex with two linear nitrosyl groups is avoided by a bending of one of the nitrosyl ligands. The factors regulating the coupling of adjacent nitrosyl groups to form a dinitrogen dioxide ligand remain to be elucidated, however.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. Microanalyses were determined by Mr. D. Florey of Cambridge University and the Butterworth Microanalytical Services. In reactions in which free nitric oxide was used the nitric oxide was purified by first passing the gas through a U-tube cooled at −78 °C and then through potassium hydroxide pellets. ^{15}NO was obtained from Air Products Ltd. Molecular weights were determined on a Macrolab Osmometer. The complex $[Pt(N_2O_2)(PPh_3)_2]$ was prepared by the method described by Robinson, and co-workers;[8] $[Ru(NO)_2(PPh_3)_2]$ and $[Pt(PPh_3)_3(SO_2)]$ were also prepared by standard literature methods.[6,27]

Reaction of $[Pt(N_2O_2)(PPh_3)_2]$ *with* SO_2.—Gaseous SO_2 was passed through a well stirred suspension of $[Pt(N_2O_2)(PPh_3)_2]$ (0.22 g) in toluene (70 cm^3). The yellow solid dissolved rapidly and subsequently a white microcrystalline solid precipitated leaving a colourless solution. The solid was filtered off, washed with toluene, and dried *in vacuo* (0.08 g), m.p. 170 °C (decomp.). The compound gave the following analyses (Found: C, 53.4; H, 4.1; N, 2.2; P, 6.1. $C_{79}H_{68}N_4O_8P_4Pt_2S_2$ $[Pt(PPh_3)_2(N_2O_2)(SO_2)\cdot 0.5C_7H_8]$ requires C, 53.3; H, 3.9; N, 3.1; P, 7.0%). When the reaction was repeated at −78 °C more satisfactory chemical analyses were obtained (Found: C, 53.4; H, 4.0; N, 2.9; P, 7.0%). Molecular weight in $CHCl_3$ solution 781 (calculated 890). The proton n.m.r. spectrum of the compound in CD_2Cl_2 showed in addition to the broad peak at 7.3 p.p.m. due to the triphenylphosphine protons, a peak

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[*] Throughout this paper: 1 atm = 101 325 Pa.

at 2.8 p.p.m. due to the methyl protons of the toluene of crystallization.

The corresponding labelled compound $[Pt(^{15}N_2O_2)(PPh_3)_2(SO_2)]$ was prepared from $[Pt(^{15}N_2O_2)(PPh_3)_2]$ in a similar manner. The i.r. data for $[Pt(N_2O_2)(PPh_3)_2(SO_2)]$ and $[Pt(^{15}N_2O_2)(PPh_3)_2(SO_2)]$ are 1 345s, 1 295s, 1 128s, 1 090s, 925s, and 628s cm^{-1} and 1 295s, 1 127s, 1 095s, 896s, and 628s cm^{-1} respectively.

When the filtrate from the reaction of SO_2 with $[Pt(N_2O_2)(PPh_3)_2]$ was reduced in volume white microcrystals of sulphito-*OO′*-bis(triphenylphosphine)platinum(II) toluene, $[Pt(PPh_3)_2(SO_3)]\cdot C_7H_8$, (0.12 g) separated out, m.p. 165 °C (decomp.) (Found: C, 57.7; H, 4.3; P, 6.4; S, 3.6. $C_{43}H_{38}O_3P_2PtS$ requires C, 57.9; H, 4.3; P, 7.0; S, 3.6%).

Preparation of an Authentic Sample of $[Pt(PPh_3)_2(SO_3)]$.—The complex *cis*-$[PtCl_2(PPh_3)_2]$ (0.5 g) was dissolved in CH_2Cl_2 (25 cm^3) and an excess of $Ag_2[SO_3]$ (0.3 g) was added. The reaction mixture was stirred in the dark for 2 h and then filtered. The filtrate was evaporated to a small volume yielding colourless crystals of $[Pt(PPh_3)_2(SO_3)]$ (0.3 g) which had a m.p. and i.r. characteristics identical with those reported above for this compound.

Reaction of $[Pt(PPh_3)_3(SO_2)]$ *with* NO.—A fast stream of purified NO was bubbled through a solution of $[Pt(PPh_3)_3(SO_2)]$ which had been prepared *in situ* by bubbling SO_2 gas through a solution of $[Pt(PPh_3)_3]$ (0.5 g) in benzene (30 cm^3). After 10 min the colour of the solution had been discharged and a white crystalline compound separated out, and was filtered off, washed with benzene, and dried *in vacuo* (0.34 g). The compound analysed correctly for $[Pt(NO_2)_2(PPh_3)_2]$ (Found: C, 52.5; H, 3.8; N, 2.7; P, 7.9. $C_{36}H_{30}N_2O_4Pt$ requires C, 53.2; H, 3.7; N, 3.4; P, 7.6%). This compound had a melting point (260 °C) and i.r. characteristics, ν(NO_2), 1 410s, 1 330, and 820 cm^{-1}, similar to those reported previously for $[Pt(NO_2)_2(PPh_3)_2]$ by Levison and Robinson.[12] When purified NO was bubbled slowly through a solution of $[Pt(PPh_3)_3(SO_2)]$ [17] (0.5 g) in toluene (30 cm^3) for 15 min a white solid separated from the solution, and when filtered off was shown to be identical with the product $[Pt(N_2O_2)(PPh_3)_2(SO_2)]$ prepared from the reaction of $[Pt(N_2O_2)(PPh_3)_2]$ with SO_2. When the volume of the filtrate was reduced a sample of $[Pt(PPh_3)_2(SO_3)]$ identical to that described above was isolated.

Reaction of $[Pt(NO_2)_2(PPh_3)_2]$ *with* SO_2.—One mol equivalent of SO_2 was condensed into a flask at −80 °C using a dry ice–acetone bath, the flask was evacuated to remove traces of O_2 present in commercial SO_2. This dioxygen-free SO_2 was allowed to react with a solution of $[Pt(NO_2)_2(PPh_3)_2]$ (0.2 g) in benzene (25 cm^3). After 24 g, the volatile products from the reaction mixture were collected. The major component was shown to be N_2O by i.r. The resultant solution was reduced in volume, $[Pt(PPh_3)_2(SO_3)]$ separated as a solid sample, and identified by its characteristic i.r. bands and m.p. The i.r. spectrum of this sample showed no traces of residual $[Pt(NO_2)_2(PPh_3)_2]$.

Reaction of $[Ru(NO)_2(PPh_3)_2]$ *with* SO_2.—The compound $[Ru(NO)_2(PPh_3)_2]$ (0.5 g) was dissolved in benzene (25 cm^3) and SO_2 was passed through the solution for 30 min. When this solution was left for four weeks dark green, almost black crystals of *dinitrosyl(sulphur dioxide)bis(triphenylphosphine)ruthenium* were seen to have formed in the flask and were filtered off (Found: C, 57.3; H, 4.2; N, 4.0; S, 4.0. $C_{36}H_{30}N_2O_4P_2RuS$ requires C, 57.7; H, 4.0; N, 3.7; S, 3.7%). This compound is extremely air-sensitive and aerial oxidation converted the compound into a yellow solid which was identified as *dinitrosyl(sulphato-OO′)bis(triphenylphosphine)ruthenium* on the basis of its i.r. spectrum [ν(NO), 1 860s, and 1 620s cm^{-1}; ν(SO_4) 1 300s, 1 170s, 900ms, and 800ms] and elemental analyses (Found: C, 55.1; H 4.4; N, 3.7; S, 3.2. $C_{36}H_{30}N_2O_6P_2RuS$ requires C, 55.3; H, 3.9; N, 3.6; S, 4.1%).

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