The coordination chemistry of iminooxosulphuranes

VI *. Factors affecting coordination geometry in complexes of tosyliminooxosulphurane

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Abstract

The complexes $[ML_n(PPh_3)_2(OSN-SO_2C_6H_4Me-4)]$ (M = Ru, Rh, Os, Ir) have been prepared from the 16-electron complex $[ML_n(PPh_3)_2]$ or the corresponding tris(phosphine)compounds $[ML_n(PPh_3)_3]$. The sulphinylamine cumulene adopts one of three possible bonding geometries (pyramidal, or coplanar through sulphur, or π-coordination through sulphur and nitrogen). The preference for a particular mode in a given complex is discussed in terms of metal electron density, *d*-orbital occupancy, oxidation state and frontier orbital symmetry. Treatment of the complex $[RhCl(PPh_3)_2(OSNSO_2C_6H_4Me-4)]$ (prepared from tosyliminooxosulphurane and $[RhCl(PPh_3)_3]$) with carbon monoxide results in a rearrangement of the π-bond cumulene in the precursor to a pyramidally bound ligand in the CO adduct $[RhCl(CO)(PPh_3)_2(OSN-SO_2C_6H_4Me-4)]$.

Introduction

The coordination of sulphur dioxide to a transition metal results in an overwhelming array of possible bonding geometries [2]. In particular, there are three modes of coordination which predominate: coplanar $\{\eta^1\text{-}(S)\}$ (A), monodentate pyramidal $\{\eta^1\text{-}(S)\}$ (B) and bidentate pseudo-olefinic $\{\eta^2\text{-}(S, O)\}$ (C) (Scheme 1). Empirical rules have been developed to allow the prediction of bonding-mode

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* For Part V see ref. 1.
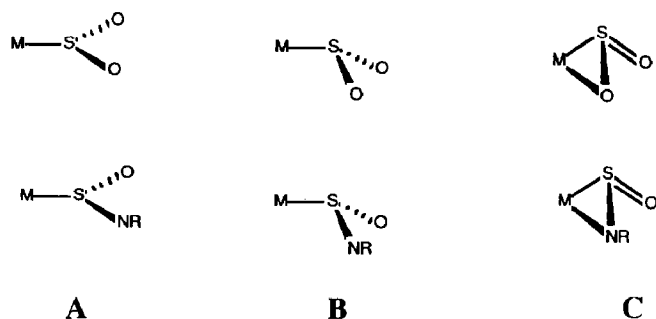
Scheme 1: Coordination modes for SO_2 and iminooxosulphuranes (R=aryl, alkyl, arylsulphonyl).

sulphur dioxide   iminooxosulphurane   diiminosulphurane
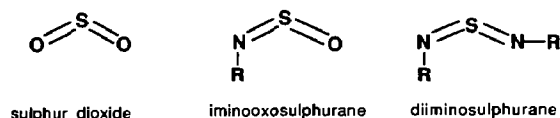
Scheme 2: Imino analogues of sulphur dioxide (R=alkyl, aryl, arylsulphonyl).

preference for a given complex but these have proven less than general [2]. Nevertheless, molecular orbital considerations have shed light on some of the factors which may be important in determining coordination geometries for a given d-configuration [3].

Iminooxosulphuranes and diiminosulphuranes have heterocumulenic functional groups (Scheme 2) which are isoelectronic with SO_2 and are obtained (formally) by replacing one or both oxo substituents by imino groups [4,5]. As might therefore by anticipated, these cumulenes have been observed to coordinate to low-valent metal centres in modes analogous to each of the above three geometries (Scheme 1) [1,6–11]. The bidentate mode of coordination has been observed to only involve the nitrogen–sulphur linkage [1,6–9] consistent with a comparison of the molecular orbitals of the parent molecule H–N=S=O [12] and those of SO_2 [13].

The paucity of examples of iminooxosulphurane complexes has precluded any detailed analysis of factors which might be important in discriminating between possible modes of coordination. Herein we describe a series of tosyliminooxo-sulphurane complexes of low-valent platinum group metals which may be prepared in high yield. The ligand geometry adopted by the sulphinylamine heterocumulene is recognisable from the infrared activity associated with the bent N=S=O unit, this
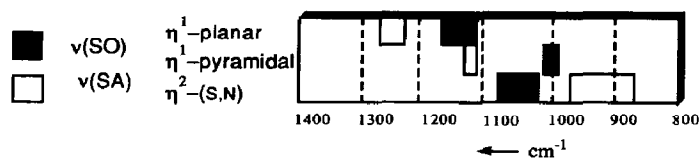

Fig. 1. Diagnostic infrared regions for O=S=NR bound to a transition metal.

being sensitive to the mode of coordination (Fig. 1). The observed preferences for a particular bonding mode are then discussed in terms of the variation in properties of the central metal.

Results and discussion

Molecular orbital calculations on the parent compound HNSO, supported by photoelectron spectroscopic results [12], give an indication of how the coordination chemistry of iminooxosulphuranes might vary from that of sulphur dioxide: Firstly the molecular orbital corresponding primarily to the lone pair on oxygen in SO_2 raises in energy upon substituting NH for O. Similarly the lone pair on sulphur, of primary importance in bonding mode (**B**), also increases in energy. Finally, the π-bonding orbital associated with the N=S double bond in HNSO is of higher energy than the corresponding S=O π-bonding orbital in SO_2. These changes in the energy of the orbitals associated with donation to the metal suggest that in all cases (A–C) the σ-donation component will become more efficient upon replacing O with NH.

An important possibility which arises from these considerations is that the lone pair on the nitrogen atom may act as a donor to a transition metal. Coordination of sulphur dioxide to a metal through the lone electron pairs on oxygen is extremely rare and occurs only in cases where the metal is very oxophilic and devoid of d-electron density for retrodative bonding. A manifestation of this energy difference on replacing oxygen with an imino group involves the complex [W(CO)$_4${S(= N^{t}Bu)$_2$}] which has the diiminosulphurane bound to tungsten in a bidentate manner through both nitrogen atoms forming a four membered metallacycle [14]. It should be pointed out that the orbital which shows the greatest relative increase in energy is that associated with the π-system. We might therefore expect that iminooxosulphuranes might show a more pronounced tendency to form π-complexes than sulphur dioxide.

Tosyliminooxosulphurane (OSN-SO$_2$C$_6$H$_4$Me-4, tosyl-NSO)

Tosyl-NSO was chosen for this study because of the previously established thermal stability of its adducts [1,6,9]. This choice introduces a bias, in that the strongly electron withdrawing nature of the toluenesulphonyl substituent will reduce the importance of bonding mechanisms involving donation of electron density to the metal, whilst favouring any retrodative electron transfer from the metal to the antibonding π-orbitals of the NSO cumulene. However, if this prejudice is born in mind, useful conclusions may nevertheless be drawn.

Ruthenium complexes

Wilkinson's compound [RuCl$_2$(PPh$_3$)$_3$] has been reported to react with sulphur dioxide to provide a 16-electron SO_2 complex, [RuCl$_2$(SO$_2$)(PPh$_3$)$_2$] [15]. This is perhaps surprising since there is no obvious mechanism whereby sulphur dioxide may stabilise reduced coordination, yet there is no evidence to suggest coordination of a second molecule of SO_2. On the basis of its infrared data it would appear that the sulphur dioxide ligand in [RuCl$_2$(SO$_2$)(PPh$_3$)$_2$] coordinates in a coplanar mode (A, Scheme 1). The correlation of infrared frequencies with the coordination mode is well developed and reliable [2]. In this and further reports we will employ exten-
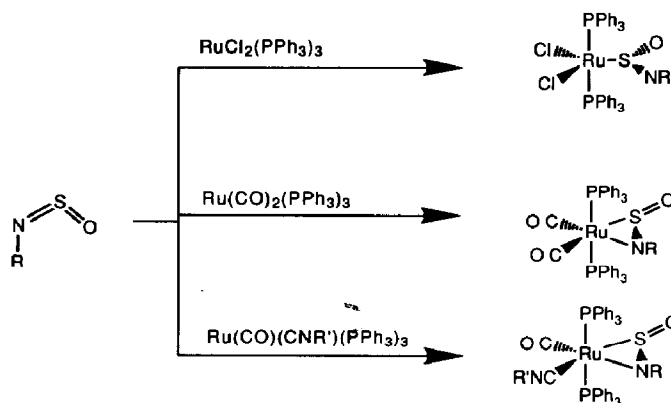
Scheme 3: Ruthenium tosyliminooxosulphurane complexes ($R=SO_2C_6H_4Me-4$; $R'=C_6H_3Me_2-2,6$, ^tBu).

sively a similar qualitative treatment of the group frequencies in the infrared activity associated with the N=S=O moiety. In our experience the three distinct frequency ranges shown in Fig. 1 do not overlap, and reliable coordination mode assignments can be obtained.

In an analogous manner, $[RuCl_2(PPh_3)_3]$ reacts with tosyl-NSO to provide a khaki substitution product of composition $[RuCl_2(PPh_3)_2(OSNSO_2C_6H_4Me-4)]$ (Scheme 3). Spectroscopic data for this and subsequent complexes are collected in Table 1. The infrared spectrum (Nujol mull) of the product thus formed shows five strong bands in the region typical of $\nu(S=O)$ and $\nu(S=N)$ activity, two due to the sulphonyl group (1355 and 1154 cm^{-1}), and two which correspond to $\nu(S=O)$ and $\nu(S=N)$ of the NSO cumulene, the higher of which shows solid state splitting (1292/1266 and 1120 cm^{-1}). As with the sulphur dioxide complex, the mode of coordination would appear to be monodentate through sulphur with the metal and cumulene coplanar (A, Scheme 1), and as with the SO_2 complex, the reason for coordinative unsaturation is not clear and excess iminooxosulphurane does not lead to increased coordination.

The compound $[RuCl_2(PPh_3)_2(OSN-tosyl)]$ is air sensitive, though the decomposition products have not been identified. Solutions of the complex in solvents which have not been scrupulously dried are smoothly converted to the sulphur dioxide complex $[RuCl_2(PPh_3)_2(SO_2)]$ and toluenesulphonamide (tosyl-NH_2). We have also observed this type of hydrolysis with complexes of tosyl-NSO in which the iminooxosulphurane cumulene is bound in modes B and C, and have extended the reaction to hydrogen sulphide [1,9a].

In the case of SO_2, coplanar coordination is considered to be an essentially dative process with some synergistic compensation being achieved by retrodative electron transfer from the metal d-orbitals to a vacant p_z orbital on sulphur (z normal to the plane of the cumulene). A similar mechanism is employed in describing metal-alkylidene interactions. A more efficient method of transferring electron density to the cumulene is via displacement of the metal from the plane of the cumulene (pyramidalisation, B) however the most efficient method involves π-coordination of the N=S double bond allowing a Dewar–Chatt–Duncanson or pseudo-olefinic type of interaction. A divalent resonance form, a metallaazathiirane-S-oxide, may be envisaged to rationalise this effect.

Table 1

Infrared data for iminooxosulphurane complexes (L=PPh_3, R=$SO_2C_6H_4$Me-4)

Complex	Yield (%)	Infrared (cm^{-1}) [a]			
		ν(SO)	ν(NS)	ν(SO$_2$)	other
$RuCl_2L_2$(OSNR) (khaki)	72	1120	1292, 1266	1355, 1154	
Ru(CO)(CN^{t}Bu)L$_2$(OSNR) (colourless)	84	1039	947	1277, 1132	2157(CN) 1946(CO)
Ru(CO)$_2$L$_2$(OSNR) (colourless)	92	1058	957, 935	1316, 1283, 1141	2031, 1971(CO)
$OsCl_2L_2$(OSNR) (green/khaki)	76	1119	1278	1355, 1154	
OsCl(NO)L$_2$(OSNR) (yellow)	92	1088	920	1316, 1302, 1150	1768(NO)
$RhClL_2$(OSNR) (orange)	79	1029	950	1268, 1149	
RhCl(CO)L$_2$(OSNR) (orange)	94	1126	1007	1306, 1161	2047(CO)
IrCl(CO)L$_2$(OSNR) (yellow)	95	1118	1023, 1014	1317, 1155	2034(CO)
IrCl(CN^{t}Bu)L$_2$(OSNR) (yellow)	80	1080	961	1319, 1261, 1158	2183(CN)
Ir(NO)L$_2$(OSNR) (yellow)	67	1088	877	1310, 1253, 1150	1759(NO)
PtL$_2$(OSNR) (colourless)	94	1066	898	1310, 1253, 1150	

[a] Data were obtained from nujol mulls between KBr discs in the region 4000–400 cm^{-1}.

The electron density at the central metal should play an important part in determining coordination mode preference and accordingly, the synthesis of zerovalent ruthenium complexes of tosyl-NSO was addressed. We have previously described [9b] the preparation of adducts of simple aryliminooxosulphuranes with the zerovalent ruthenium-ligand fragments Ru(CO)(L)(PPh$_3$)$_2$ (L=CO, CN^{t}Bu, CNC$_6$H$_3$Me$_2$-2,6). Thus the tris(phosphine) complexes [Ru(CO)(L)(PPh$_3$)$_3$] react with OSN–R (R=C$_6$H$_4$Me-2, C$_6$H$_4$Me-4) via displacement of a phosphine ligand (labilised by steric pressures) to provide the complexes [Ru(CO)(L)(PPh$_3$)$_2$(OSNR)] [9b]. In a similar manner the more electrophilic iminooxosulphurane tosyl-NSO readily replaces a triphenylphosphine ligand from [Ru(CO)(L)(PPh$_3$)$_3$] giving the complexes [Ru(CO)(L)(PPh$_3$)$_2$(OSN-tosyl)] (L=CO, CN^{t}Bu) in high yield. The aryliminooxosulphurane complexes contain the cumulenes OSNR bound to the electron rich centre in a bidentate manner through sulphur and nitrogen and a similar mode of coordination is seen for the sulphonyl substituted derivatives: Infrared activity due to ν(SO) and ν(SN), at 1039 and 947 cm^{-1}, respectively, for the complex [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(OSN-tosyl)] (Table 1) indicates that the N=S=O cumulene is π-bound to ruthenium(0). These data agree well with analogous

Table 2

Infrared data ^{a} for the complexes [Ru(CO)$_2$(PPh$_3$)$_2$(L$'$)]

| L$'$ | ν(CO) (cm^{-1}) | | k (N cm^{-1}) ^{b} |
	ν1	ν2	[27]
CNC$_6$H$_4$Me-4 [16]	1899,	1865	14.30
Ph-C≡C-Ph [17]	1950,	1895	14.93
CH$_2$=CH$_2$ [17]	1955,	1900	15.01
CS [18]	1962,	1900	15.06
CSe [19]	1979,	1926	15.40
CF$_2$ [20]	1982,	1912	15.31
SO$_2$ [21]	2000,	1932	15.61
O$_2$ [17]	2005,	1945	15.76
S$_2$ [22]	2000,	1955	15.79
OSN-tolyl	2015,	1941	15.80
CS$_2$ [23]	2010,	1945	15.80
CSe$_2$ [24]	2020,	1950	15.92
OSN-tosyl	2031,	1971	16.17
NNC$_6$H$_5{}^+$	2060,	1970	16.40
NO$^+$	2065,	2014	16.80

^{a} Measured as Nujol mulls between KBr discs. ^{b} Cotton–Kraihanzel force constants as given by $k = 2.0191 \times 10^{-6}$ mN $\times [(\nu_1)^2 + (\nu_2)^2]$.

activity at 1029 and 928 cm^{-1} in the infrared spectrum of the complex [Ru(CO)(CN^{t}Bu)(PPh$_3$)$_2$(OSNC$_6$H$_4$Me-4)], whilst the band attributed primarily to ν(SO) may also be compared with other three-membered metallacycles with exocyclic sulphoxide units, e.g., [Ru(CO)$_2$(PPh$_3$)$_2$(SO$_2$)] (1066) [21], [IrCl(CO)(PPh$_3$)$_2$(S$_2$O)] (1040) [9a] and [OsCl(NO)(PPh$_3$)$_2$(CH$_2$SO)] (1035 cm^{-1}) [1,28]. However, the infrared activity associated with the isonitrile and carbonyl co-ligands is more disparate: Whilst the aryl substituted complex has bands at 2155 and 1920 cm^{-1}, the related bands in the sulphonyl derivative appear at 2157 and 1946 cm^{-1}. Thus tosyl-NSO is a significantly stronger π-acid ligand than simple aryliminooxosulphuranes and the imino substituent is therefore important in determining the electron density at the metal and the resulting coordination geometry.

A more complete series of compounds for comparison is provided by the complexes [Ru(CO)$_2$(PPh$_3$)$_2$(L$'$)] where L$'$ is a range of common π-acid ligands. Infrared data and Cotton-Kraihanzel ν(CO) force constants [27] for these complexes are collected in Table 2 and show that tosyl-NSO is an exceedingly strong π-acceptor ligand, whilst simple aryliminosulphuranes are comparable in π-acidity to carbon disulphide.

The pale cream complexes, whilst being air-sensitive, have indefinite thermal stability when stored under an inert atmosphere and are comparatively resistant towards hydrolysis. The enhanced stability towards hydrolysis is compatible with the idea of significant transfer of electron density from the metal and the resulting deactivation of the cumulene towards nucleophilic attack. Indeed, the complexes [Ru(CO)(L)(PPh$_3$)$_2$(OSNR)] have proven ideal model compounds for studying the coordinative activation of iminooxosulphuranes towards electrophiles [29].

Osmium complexes

The complexes [OsCl(L$''$)(PPh$_3$)$_3$] (L$''$ = Cl, NO) react rapidly with tosyl-NSO to provide, via substitution of a labile phosphine, the complexes [OsCl(NO)-
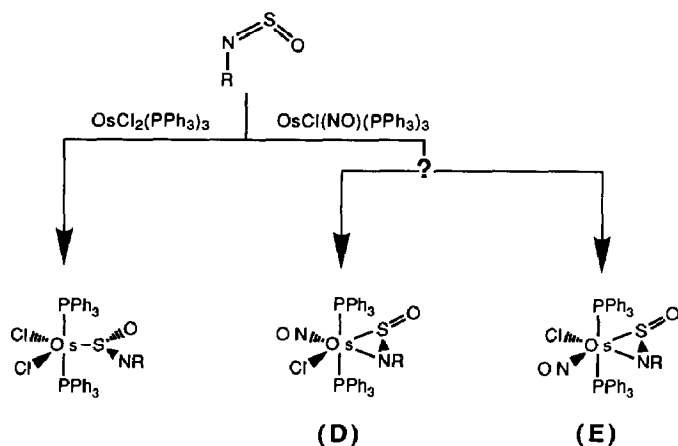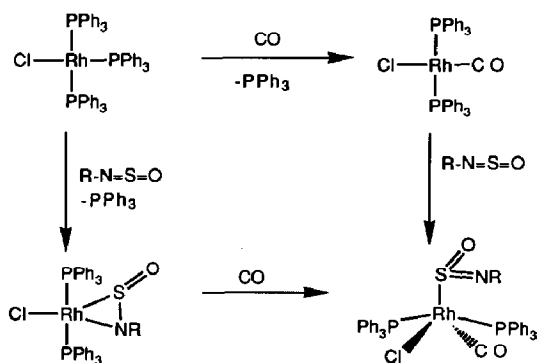
Scheme 4: Osmium tosyliminooxosulphurane complexes ($R=SO_2C_6H_4Me-4$).

$(PPh_3)_2(OSN-tosyl)]$ [9a], and $[OsCl_2(PPh_3)_2(OSN-tosyl)]$ (Scheme 4). The bonding modes adopted by the tosyl-NSO cumulene in the two complexes reflect the available electron density. Thus the green divalent d^6-16-electron complex $[OsCl_2(PPh_3)_2(OSN-tosyl)]$ features coplanar-monodentate (A) coordination, paralleling that found in the ruthenium analogue, whilst the cumulene in the yellow, formally zerovalent [NO considered as NO^+] 18-electron complex $[OsCl(NO)-(PPh_3)_2(OSN-tosyl)]$ is bound in a bidentate manner (C). In the latter case there exists the possibility of isomers with respect to the orientation of the Cl ligand *cis* or *trans* to the sulphur (Scheme 4). The ^{31}P-$\{^1H\}$ NMR data for the complex indicate that the OsNS metallacycle is rigid and that rotation does not occur under ambient conditions. Extension of ideas proposed for the coordination preferences of SO_2 [3] suggest that the ligand will ideally coordinate such that the π-acceptor orbital based primarily on sulphur will compete with the least efficient π-acceptor ligand, i.e., *trans* to the poorest π-acid, in this case the chloride ligand (D). The complex has been discussed in a previous report [9a] and will not be described here in detail other than to reinforce what was shown in the case of the ruthenium complexes: Reduction of the metal centre facilitates bidentate coordination. Both of the complexes $[OsCl(L'')(PPh_3)_2(OSN-tosyl)]$ (L''=NO, Cl) are hydrolysed to the corresponding sulphur dioxide complexes in moist solvent, the dichloro complex being the more reactive.

Rhodium complexes

The complexes $[RhCl(P^iPr_3)_2(OSN-aryl)]$ have been described previously by Meij et. al. [10] and a structure determination of $[RhCl(P^iPr_3)_2(OSNC_6H_4Me-4)]$ indicates that the sulphur(IV) cumulene in these complexes is bound in a monodentate coplanar fashion (*A*), as might also be inferred from the infrared data associated with the NSO moiety (1268 and 1148 cm^{-1}) [10,11], in addition to the mode of coordination observed for the corresponding sulphur-oxide complexes $[RhCl(P^iPr_3)_2(SO_x)]$ ($x = 1$, $\nu(SO)$, 1075 [30]; $x = 2$, $\nu(SO)$ 1268 and 1120 cm^{-1}) [10]. In contrast to this class of compounds, Wilkinson's catalyst $[RhCl(PPh_3)_3]$ reacts with tosyl-NSO to provide the 16-electron complex $[RhCl(PPh_3)_2(OSN-tosyl)]$ (Scheme 5), the infrared data of which indicate that the iminooxosulphurane is
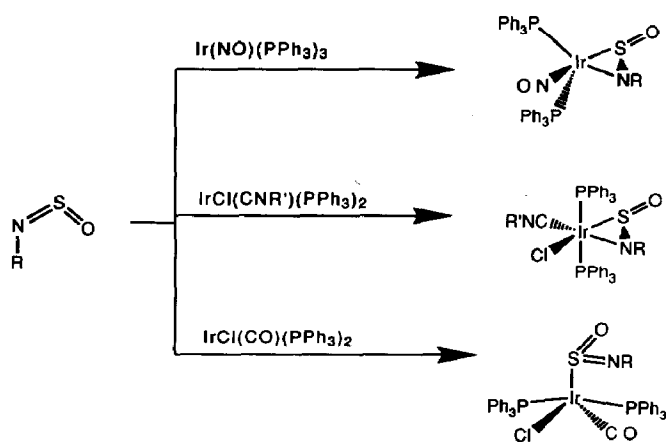
Scheme 5: Rhodium tosyliminooxosulphurane complexes ($R=SO_2C_6H_4Me-4$).

bound to rhodium via both nitrogen and sulphur: Activity due to the NSO system occurs at 1029 and 950 cm^{-1}, in regions clearly indicative of π-coordination. Thus we have an example of the effect of the imino substituent upon coordination geometry, consistent with the idea of tosyl-NSO requiring the more retrodative electron density for bonding than the less electrophilic aryliminooxosulphuranes. This effect is even more notable in that the differences in phosphine basicity for the two examples (PPh_3 vs. P^iPr_3) should disfavour the observed dichotomy.

A surprising change in coordination geometry occurs upon treating the 16-electron complex $[RhCl(PPh_3)_2(OSN-tosyl)]$ with one atmosphere of carbon monoxide. An immediate reaction occurs and the orange 18-electron complex $[RhCl(CO)(PPh_3)_2(OSN-tosyl)]$ is obtained quantitatively. The infrared data (1126, $\nu(SN)$, and 1007 cm^{-1}, $\nu(SO)$) for the new carbonyl complex indicate that the iminooxosulphurane is bound in neither mode A nor C but rather that the rhodium atom is displaced from the plane of the monodentate-coordinated NSO group (B, Scheme 1). The complex $[RhCl(CO)(PPh_3)_2]$ reacts immediately to also give the hydrolytically sensitive complex $[RhCl(CO)(PPh_3)_2(OSN-tosyl)]$, providing an alternative synthetic route (Scheme 5).

The result, at first surprising, may be rationalised with reference to the frontier orbitals of the two metal ligand fragments $RhCl(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$. These metal-ligand fragments may be simplified by relating them to the hypothetical isolobal groups $[IrCl_3]^{2-}$ (ML_3-C_{2v}-d^8) and $[IrCl_4]^{3-}$ (ML_4-C_{4v}-d^8). The important orbital interactions have been outlined for the combination of these complexes with sulphur dioxide [3]. The case of iminooxosulphuranes does not differ significantly from that of SO_2 and a detailed discussion is not required other than a brief summary of the basic principles. As with the well established tautomerism involving linear and bent nitrosyl coordination [31], the important interaction which favours sulphur dioxide or iminooxosulphurane pyramidalisation or nitrosyl bending in the ML_4-C_{4v} complex, is a closed shell 4-electron interaction between an orbital of a_1 symmetry on the metal and the σ-donor orbital on sulphur (or nitrogen in the nitrosyl case). This antibonding orbital is populated for d^8-electron counts and may be minimised by pyramidalisation (or bending) by which this orbital may feed electron density into an empty orbital on the ligand, which was previously engaged in retrodative π-acceptance. This pyramidalisation destroys the retrodative $d\pi$–$p\pi$ interaction, however if this was significant enough to be determinant, one

Scheme 6: Iridium tosyliminooxosulphurane complexes (R=$SO_2C_6H_4$Me-4; R′=^{t}Bu).

assumes that the cumulene would coordinate in a pseudo-olefinic manner to maximise this effect.

In the ML_4-C_{4v}-d^6 case the unfavorable interaction is irrelevant because, due to the shortage of electrons, the orbital is not occupied. Accordingly the 16-electron complexes [$MCl_2(PPh_3)_2$(OSN-tosyl)] (M = Ru, Os) are seen to display coplanar coordination of the SO_2 and -NSO cumulenes. In the case of the 16-electron complexes [$RhCl(PPh_3)_2$(OSN-tosyl)] (cf. [$IrCl_3$]$^{2-}$) the frontier orbitals are of different symmetry. The only orbital of suitable symmetry to induce pyramidalisation, the $2a_1$ level, is unoccupied.

Iridium complexes

We have suggested above that of the three modes of coordination, the pseudo-olefinic mode (C) should be the most efficient for relieving electron-rich metal centres of excess charge. By replacing the carbonyl ligand in Vaska's complex, [$IrCl(CO)(PPh_3)_2$], for an isonitrile ligand, the electron density at the metal may be significantly increased. Thus the complex [$IrCl(CN^tBu)(PPh_3)_2$], obtained by treating [$IrHCl_2(PPh_3)_3$] successively with t-butyl isonitrile and DBU, (1,8-diazabicyclo[5.4.0]undec-7-ene), reacts with tosyl-NSO to give a 1:1 adduct in a manner completely analogous to Vaska's complex [9a] (Scheme 6). However, infrared data for the complex [$IrCl(CN^tBu)(PPh_3)_2$(OSN-tosyl)] clearly indicate that the cumulene is π-bound to the metal (1080 ν(SO), 961 ν(SN)). The isonitrile gives rise to a peak at 2183 cm^{-1} indicating a comparatively elecron-deficient metal centre. Furthermore the complex is significantly more stable towards hydrolysis than is the carbonyl analogue.

The complex [$Ir(NO)(PPh_3)_3$] has a formally d^{10} electronic configuration (NO bound as NO$^+$) and reacts readily with tosyl-NSO via substitution of one labile phosphine to provide the tetrahedral complex [$Ir(NO)(PPh_3)_2$(OSN-tosyl)]. The iminooxosulphurane ligand in this complex is bound to iridium in a bidentate manner (1088 ν(SO), 877 cm^{-1} ν(SN)), consistent with the high electron density at the iridium(−I) centre. The related sulphur dioxide complex [$Rh(NO)(PPh_3)_2(SO_2)$] was the first in which the bidentate mode of coordination was recognised [32].

A platinum complex

Blake and Reynolds reported the first complex of tosyliminooxosulphurane, a complex of zerovalent platinum obtained from [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] and tosyl-NSO [6]. The infrared absorptions of the complex (1028, 940 cm^{-1}) due to the cumulene show that coordination occurs through both sulphur and nitrogen. We find that this complex and the simple aryliminooxosulphurane complexes may be obtained directly from the tris(phosphine) complex [Pt(PPh$_3$)$_3$], simplifying their preparation.

Conclusions and summary

A wide range of bis(triphenylphosphine)iminooxosulphurane metal complexes have been prepared with metals from groups 8–10, spanning oxidation states $-$I to $+$II and d-orbital occupancies of 6, 8 and 10. The results are summarised in Fig. 2. Sufficient examples have been prepared to allow some generalisations to be put forward: (i) Three modes of coordination are observed which may be clearly distinguished on the basis of solid-state infrared data associated with the NSO group. As the electron density at the metal centre increases, the preferred mode of
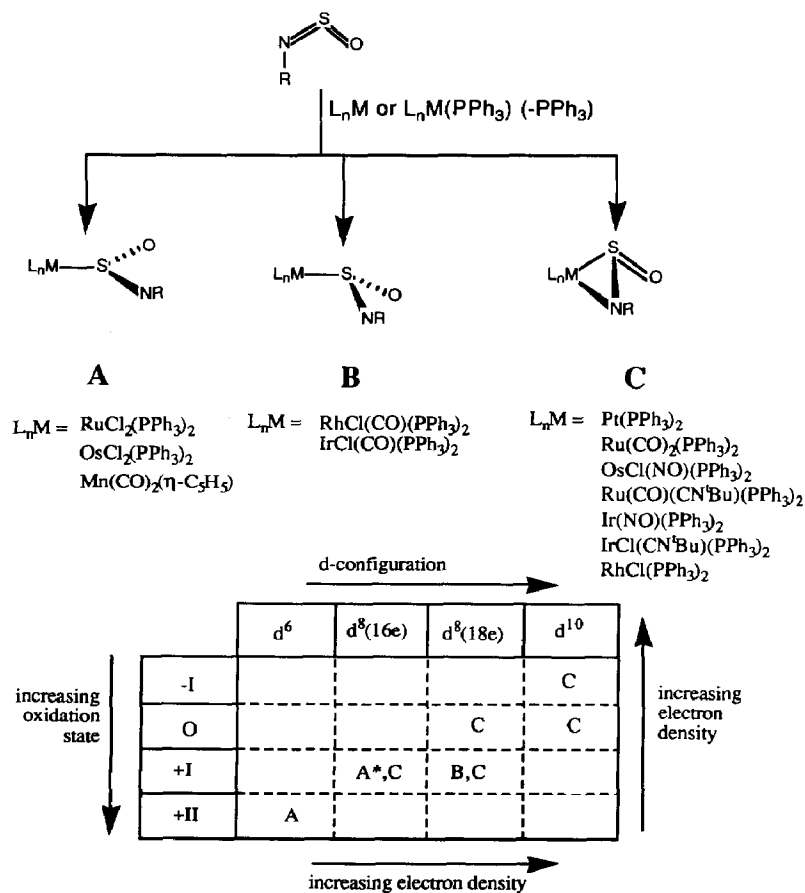

Fig. 2. Correlation of coordination mode and electronic properties of iminooxosulphurane complexes. R=SO$_2$C$_6$H$_4$Me-4, * = observed for aryliminooxosulphuranes.

Table 3

Analytical data for the complexes [a]

Complex	C (%)	H (%)	N (%)	S (%)
Ru(CO)(CN^{t}Bu)L$_2$(OSNR)	61.4	4.6	2.8	
(C$_{49}$H$_{46}$N$_2$O$_4$P$_2$RuS$_2$)	(61.7)	(4.9)	(2.9)	
Ru(CO)$_2$L$_2$(OSNR)	59.5	4.2	1.4	
(C$_{45}$H$_{37}$NO$_5$P$_2$RuS$_2$)	(60.1)	(4.2)	(1.6)	
OsCl(NO)L$_2$(OSNR)	55.4	3.6		7.0
(C$_{43}$H$_{37}$ClN$_2$O$_4$OsP$_2$S$_2$)	(55.2)	(4.0)		(6.9)
RhCl(CO)L$_2$(OSNR)	58.4	4.3	1.6	
(C$_{44}$H$_{37}$ClNO$_4$P$_2$RhS$_2$)	(58.2)	(4.1)	(1.5)	
IrCl(CO)L$_2$(OSNR)	56.8	3.7		6.7
(C$_{44}$H$_{37}$ClIrNO$_4$P$_2$S$_2$)	(56.5)	(4.0)		(6.9)
Ir(NO)L$_2$(OSNR)	54.1	4.4	2.9	
(C$_{43}$H$_{37}$IrN$_2$O$_4$P$_2$S$_2$)	(53.6)	(3.9)	(2.9)	

[a] Calculated values given in parentheses. The complexes [MCl$_2$L$_2$(OSNR)] (M=Os, Ru) and [RhClL$_2$(OSNR)] failed to give satisfactory microanalytical data and the complex [PtL$_2$(OSNR) has been described previously and was not analysed.

coordination becomes pseudoolefinic, this being the most efficient mechanism for π-acceptor or retrodative interaction; (ii) The frontier orbital symmetry of the metal-ligand fragment may in some cases influence the choice between coplanar or pyramidal coordination through sulphur; (iii) The trend in hydrolytic sensitivity parallels that of iminooxosulphurane lability, though whether or not the latter is the cause of the former has not been established; (iv) Hydrolysis of all three types of complex leads to the corresponding sulphur dioxide complex, which in the cases studied are isostructural with respect to cumulene coordination.

Experimental

General experimental procedures and instrumentation [33] and the compounds [RuCl$_2$(PPh$_3$)$_3$] [34], [Ru(CO)$_2$(PPh$_3$)$_3$] [17], [Ru(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_3$] [29], [OsCl(NO)(PPh$_3$)$_3$] [35], [IrCl(CO)(PPh$_3$)$_2$] [36], [Ir(NO)(PPh$_3$)$_3$] [37], [Pt(PPh$_3$)$_3$] [38], [RhCl(CO)(PPh$_3$)$_2$] [39], [RhCl(PPh$_3$)$_3$] [40] and tosyl-NSO [4] are described elsewhere. Elemental analytical data are listed in Table 3.

The syntheses of the compounds [ML$_n$(PPh$_3$)$_2$(OSNR)] are completely analogous. Accordingly, only exemplary preparative details for [OsCl(NO)(PPh$_3$)$_2$(OSN-tosyl)] are given in full. Physical data for the complexes are collected in Table 1.

[OsCl(NO)(PPh$_3$)$_2$(OSN-tosyl)]

A suspension of [OsCl(NO)(PPh$_3$)$_3$] (0.26 g, 0.25 mmol) in toluene (20 cm^3) was treated with OSNSO$_2$C$_6$H$_4$Me-4 (1.15 equivalents, 0.10 mol/l in toluene) and the suspension stirred for 20 min. The solvent was removed in vacuo and the residue recrystallised from a mixture of THF/pentane at $-30°$C to give the product as pale yellow microcrystals. Yield 0.22 g (92%). M.p. 149°C (decomp.). Found: C, 55.40; H, 3.60; S, 7.00. C$_{43}$H$_{37}$ClN$_2$O$_4$OsP$_2$S$_2$ calc.: C, 55.20; H, 4.00; S, 6.85%.

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