Novel Synthetic Routes to Disulphur and Disulphur Monoxide Ligands: Nucleophilic Attack at Co-ordinated Imino-oxo-λ^4-sulphanes†

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The reactions of [$OsCl(NO)(C_2H_4)(PPh_3)_2$] and [$IrCl(CO)(PPh_3)_2$] with oxo-4-tosylimino-$\lambda^4$-sulphane (4-$MeC_6H_4SO_2NSO$) lead quantitatively to the adducts [{ML}$Cl(PPh_3)_2$(4-Me-$C_6H_4SO_2NSO$)] [{ML} = Os(NO) or Ir(CO)] which in turn are hydrolysed to the corresponding sulphur dioxide complexes [{ML}$Cl(PPh_3)_2(SO_2)$]. The iridium compound [$IrCl(CO)(PPh_3)_2$(4-Me-$C_6H_4SO_2NSO$)] reacts cleanly with hydrogen sulphide to provide the disulphur monoxide complex [$IrCl(CO)(PPh_3)_2(S_2O)$] whilst [$OsCl(NO)(PPh_3)_2$(4-$MeC_6H_4SO_2NSO$)] with hydrosulphide leads to the disulphur complex [$OsCl(NO)(PPh_3)_2(S_2)$] which may be oxidised to the corresponding S_2O complex [$OsCl(NO)(PPh_3)_2(S_2O)$] with 3-chloroperbenzoic acid. Alternatively, [$OsCl(NO)(PPh_3)_2$-(S_2)] is accessible *via* the reaction of [$OsCl(NO)(PPh_3)_3$] with cyclo-octasulphur.

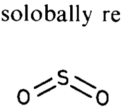
The co-ordination chemistry of reactive sulphur oxide molecules such as SO, S_2O, and S_2O_2, which are unstable in the free state, has enjoyed some systematisation in recent years due, in particular, to the efforts of the groups of Rauchfuss,[1] Schenk,[2] and Lorenz[3] and to our own studies.[4,5]

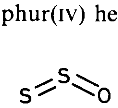
Amongst the molecules investigated, disulphur monoxide, S_2O,[6] is particularly interesting as an isolobal analogue of sulphur dioxide, SO_2. We have recently described the synthesis and structural characterisation of a manganese complex of this unstable molecule, *viz.* [$Mn(CO)_2(S_2O)(\eta^5$-$C_5Me_5)$].[4] Other complexes containing terminal S_2O ligands include [$NbCl(S_2O)(\eta^5$-$C_5H_5)_2$],[1] [$M(CO)_2(S_2O)(\eta^5$-$C_5H_5)$] (M = Mn or Re),[7] [$Re(CO)_2(S_2O)(\eta^5$-$C_5Me_5)$],[5] and the cation [$Ir(dppe)_2(S_2O)$]$^+$ [8] [dppe = 1,2-bis(diphenylphosphino)ethane]. A binuclear complex [{$Mo(\mu$-$S_2O)(S_2CNEt_2)_2$}$_2$] involving S_2O bridges is also known.[9] However, to date the only successful strategy for the synthesis of complexes of disulphur monoxide (S_2O) has been the oxidation of complexes of disulphur (S_2) with reagents capable of transferring an oxygen atom, *e.g.* periodate, IO_4^-,[8] organic peracids such as peracetic[1] and 3-chloroperbenzoic acid,[1,5] and even dioxygen itself.[4,7,9] The obvious drawback with this methodology is the lack of any general synthetic route to the required disulphur complex precursors.

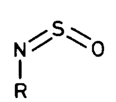
We describe here a rational synthesis of co-ordinated S_2O and an unexpected route to a complex of disulphur. Both procedures make use of nucleophilic attack at a co-ordinated imino-oxo-λ^4-sulphane.

Results and Discussion

Preparation of Complexes of Oxo-4-tosylimino-λ^4-sulphane.— The isolobally related sulphur(IV) heterocumulenes SO_2, S_2O,

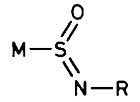




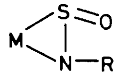


and RNSO have all been observed to co-ordinate to low-valent transition-metal centres.[2,10,11] Surprisingly, there are, prior to this report, no analogous series of compounds [ML_n(A=S=O)] (A = O, S, or N–R), the members of which are isostructural, *i.e.* in which the sulphur(IV) cumulenes are bound to the metal in the same manner for all three complexes.

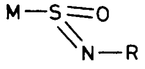
Two modes of co-ordination have been observed for imino-oxo-λ^4-sulphanes bound to transition-metal centres: σ-S-coplanar[12] and η^2-N,S-bidentate[13] in which the heterocumulene is π-bound through the nitrogen–sulphur multiple bond. A further mode of co-ordination, σ-S-pyramidal, in which the metal atom is displaced from the plane of the cumulene, has been proposed for the complex [$IrCl(CO)(PPh_3)_2$(4-NO_2-C_6H_4NSO)].[14] The same co-ordination modes are known for complexes of sulphur dioxide, SO_2.[10] The disulphur monoxide ligand has only been observed to adopt the bidentate (S, S′) mode of co-ordination.[2]



σ-S-coplanar



η^2-N,S-bidentate



σ-S-pyramidal

Iridium complexes. Vaska and Bath[15] and LaPlaca and Ibers[16] have described the synthesis and molecular structure, respectively, of [$IrCl(CO)(PPh_3)_2(SO_2)$], the complex formed upon treating [$IrCl(CO)(PPh_3)_2$] with sulphur dioxide. The SO_2 molecule is bound in a pyramidal manner through sulphur, occupying the apex of the tetragonal pyramid. This co-ordination is reversible, and it is therefore not surprising that early attempts to prepare an adduct of [$IrCl(CO)(PPh_3)_2$] with an imino-oxo-λ^4-sulphane were complicated by the ready dissociation of the cumulene.[14]

We find that the highly electrophilic imino-oxo-λ^4-sulphane, oxo-4-tosylimino-λ^4-sulphane (4-$MeC_6H_4SO_2NSO$), forms a thermally stable 1:1 adduct with [$IrCl(CO)(PPh_3)_2$]. The bright yellow-orange complex is very sensitive to hydrolysis by traces of moisture, the ultimate product being the corresponding green SO_2 complex [$IrCl(CO)(PPh_3)_2(SO_2)$] [equation (1)].[15]

Spectroscopic data for the new imino-oxo-λ^4-sulphane complex (Table) indicate that the mode of co-ordination of the –N=S=O moiety is neither σ-S-coplanar nor η^2-N, S-bidentate, the former giving rise to two strong bands in the vicinity of 1 300

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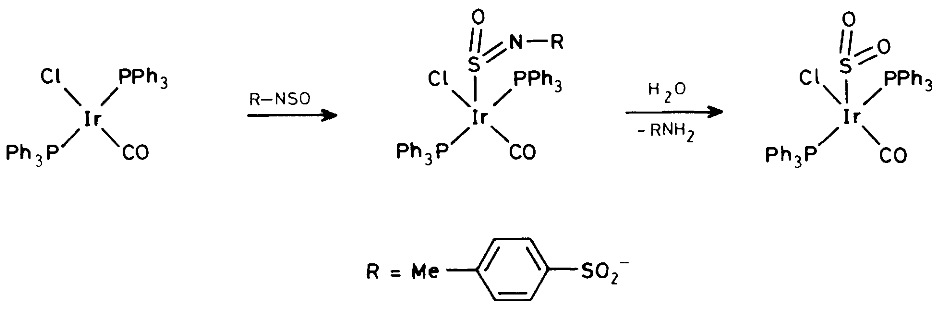
† The term *N*-sulphinylamine is also frequently used for imino-oxo-λ^4-sulphanes, R–NSO.



(1)

Table. Physical data for the iridium and osmium complexes

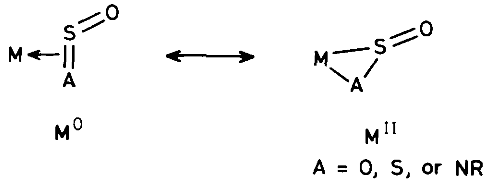
Complex	M.p. (θ/°C)	Colour	Yield (%)	ν(CO/NO)[a]	ν(SO, SN)[a]	^{31}P(δ)[b]/ p.p.m.	^2J(PP′)/ Hz
				cm^{-1}			
[IrCl(CO)(PPh$_3$)$_2$(4-MeC$_6$H$_4$SO$_2$NSO)]	126 (decomp.)	Yellow-orange	>95	2 034	1 118, 1 014, 1 023	7.0	
[OsCl(NO)(PPh$_3$)$_2$(4-MeC$_6$H$_4$SO$_2$NSO)]	149 (decomp.)	Yellow	92	1 768	1 088, 920	9.1, −15.5	350
[IrCl(CO)(PPh$_3$)$_2$(S$_2$O)]	168	Yellow	76	2 038	1 040	11.6, −11.6	397
[OsCl(NO)(PPh$_3$)$_2$(S$_2$O)]	187 (decomp.)	Orange	93	1 744	1 063	4.7, −12.5	372
[OsCl(NO)(PPh$_3$)$_2$(S$_2$)]	153	Green	73	1 746		−4.0	

[a] In Nujol mull. [b] In CDCl$_3$, 25 °C, relative to external D$_3$PO$_4$. Values reported are corrected for 'roof effects'.

and 1 120 cm^{-1} and the latter resulting in two bands in the regions 1 080—1 120 and 880—950 cm^{-1} in the i.r. spectra. The appearance of two absorptions at 1 118 and 1 023 cm^{-1}, in addition to those derived from the –SO$_2$– group of the sulphonyl substituent (1 317, 1 155 cm^{-1}), suggests that [IrCl(CO)(PPh$_3$)$_2$(4-MeC$_6$H$_4$SO$_2$NSO)] features a pyramidally co-ordinated –N=S=O group.

The factors dictating the bonding geometry of sulphur dioxide in a given complex have been investigated both empirically[10] and theoretically[17] (*cf.* ref. 2). The feature determining which of the two possible monodentate tautomers, pyramidal or coplanar, is preferred is suggested to be the population of an antibonding orbital of σ symmetry with respect to the metal–sulphur vector. This unfavourable interaction is reduced by pyramidalisation at the sulphur. The orbital is only populated for d^n complexes where $n \geqslant 8$. The arguments outlined were derived by extrapolation of results obtained for the more familiar linear–bent tautomerism observed in nitrosyl co-ordination,[18] and as such give no indication about the preference for the third mode of co-ordination, *i.e.* η^2-bidentate through oxygen and sulphur. Intuitively, it might be expected that, as the electron density of a metal ligand fragment increases, a co-ordination mode becomes favoured which may oxidatively reduce the excessive negative charge on the metal *via* contribution from a metallacyclic resonance form [in which the formal oxidation state of the central metal increases by two units (Scheme 1)]. These arguments, presented to rationalise and predict co-ordination geometries for ligating sulphur dioxide, may be extended to describe the co-ordination of imino-oxo-λ^4-sulphanes as well, provided that the relevant differences in the frontier orbitals[19] of R–N=S=O and O=S=O are taken into account.

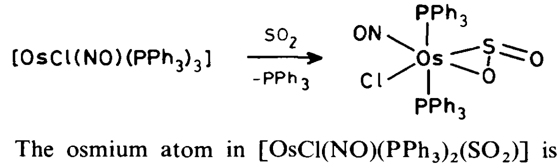
In general, as the *d*-orbital occupancy of the complex increases, so does the electron density. Thus, the complex [IrCl(CO)(PPh$_3$)$_2$(4-MeC$_6$H$_4$SO$_2$NSO)] represents a fine balance such that the *d* configuration is high enough to destabilise coplanar co-ordination but the electron density is not sufficient to cause bidentate co-ordination.



Scheme 1.

In a similar manner to Vaska's complex, [IrCl(CO)(PPh$_3$)$_2$],[15] the corresponding rhodium complex [RhCl(CO)(PPh$_3$)$_2$] forms an analogous 1:1 adduct with 4-MeC$_6$H$_4$SO$_2$NSO. The i.r. data associated with the NSO cumulene system are evident at 1 126 and 1 007 cm^{-1}, and two structured absorptions, typical of the SO$_2$ (λ^4) group, are observed at 1 316, 1 306, 1 293 and 1 161, 1 154 cm^{-1}; the ν(CO) band appears at 2 047 cm^{-1}. The adduct [RhCl(CO)(PPh$_3$)$_2$(4-MeC$_6$H$_4$SO$_2$NSO)] therefore would also appear to contain a pyramidally co-ordinated imino-oxo-λ^4-sulphane.

Osmium complexes. We have recently described[20] the synthesis of [OsCl(NO)(PPh$_3$)$_2$(SO$_2$)] *via* substitution of a labile phosphine ligand in [OsCl(NO)(PPh$_3$)$_2$] by SO$_2$, equation (2).



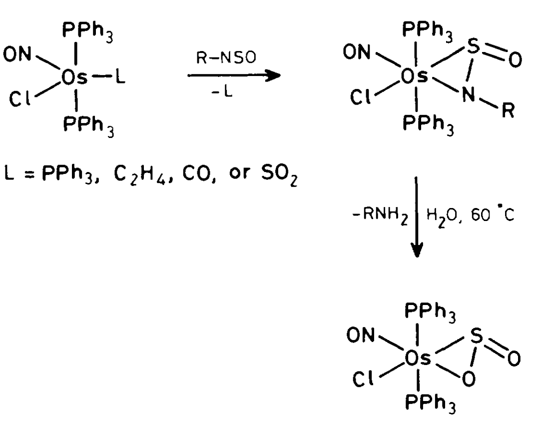
(2)

The osmium atom in [OsCl(NO)(PPh$_3$)$_2$(SO$_2$)] is formally zerovalent (nitrosyl considered as NO$^+$), and accordingly the electron density at the metal is somewhat higher than that in the iridium complex [IrCl(CO)(PPh$_3$)$_2$(SO$_2$)]. Thus, the observation that the SO$_2$ molecule is bound in a bidentate manner in the osmium complex is consistent with the arguments outlined above. The organosulphur(IV) cumulene, $CH_2{=}S{=}O$ binds to the $[OsCl(NO)(PPh_3)_2]$ fragment in the bidentate, η^2-C, S manner,[20] and so it might be expected that the imino-oxo-λ^4-sulphanes co-ordinate through both nitrogen and sulphur.

The complexes $[OsCl(NO)(PPh_3)_3]$[21] and $[OsCl(NO)(C_2H_4)(PPh_3)_2]$[22] may serve as sources for the complex fragment $[OsCl(NO)(PPh_3)_2]$, and both these complexes react rapidly with $4\text{-}MeC_6H_4SO_2NSO$ in toluene or tetrahydrofuran to provide, in high yield, the adduct $[OsCl(NO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$. Surprisingly, the substitution-inert complexes $[OsCl(NO)(CO)(PPh_3)_2]$[23] and $[OsCl(NO)(PPh_3)_2(SO_2)]$[20] also react with $4\text{-}MeC_6H_4SO_2NSO$ with substitution of CO and SO_2, respectively. The substitution of CO in $[OsCl(NO)(CO)(PPh_3)_2]$ is slow (1 week) and accompanied by side reactions. In view of the usual inertness of $[OsCl(NO)(CO)(PPh_3)_2]$ towards dissociative CO substitution, it is tempting to propose an electrophilic associative mechanism. In support of this, we note that $[OsCl(NO)(CO)(PPh_3)_2]$ dissolves slowly in liquid SO_2 to give $[OsCl(NO)(PPh_3)_3(SO_2)]$. The self activation of liquid SO_2, enhancing its electrophilic reactivity, has been noted.[24]

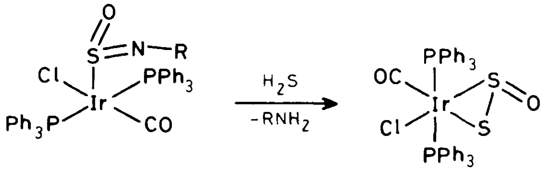
The complex $[OsCl(NO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ gives rise to a strong peak at 1 768 cm^{-1} due to the nitrosyl ligand (Table). In addition to the activity arising from the tosyl group (1 312, 1 303, and 1 149 cm^{-1}), absorptions at 1 088 and 920 cm^{-1} attest to the presence of a bidentate-co-ordinated imino-oxo-λ^4-sulphane. The π co-ordination of the $-N{=}S{=}O$ moiety through the nitrogen–sulphur multiple bond leads to a significant reduction in the N–S bond order. This is evident in the low energy of the ν(NS)-derived i.r. absorption at 920 cm^{-1} which contrasts with that observed for the iridium complex $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ [ν(NS,OS) 1 118, 1 023 cm^{-1}] wherein the N–S bond remains essentially double.

The facile hydrolysis of $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ to $[IrCl(CO)(PPh_3)_2(SO_2)]$ is presumed to proceed *via* nucleophilic attack at sulphur by hydroxide or water. Consistent with the proposed increase in metal-based electron density upon going from $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ to $[OsCl(NO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$, the osmium complex is stable to atmospheric moisture and may be handled as a solid in air. Nevertheless, warming a solution of $[OsCl(NO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ in wet $[^2H_7]$-dimethylformamide to 60 °C leads to smooth conversion to the sulphur dioxide complex $[OsCl(NO)(PPh_3)_2(SO_2)]$ (as observed by $^{31}P\text{-}\{^1H\}$ n.m.r.), equation (3).

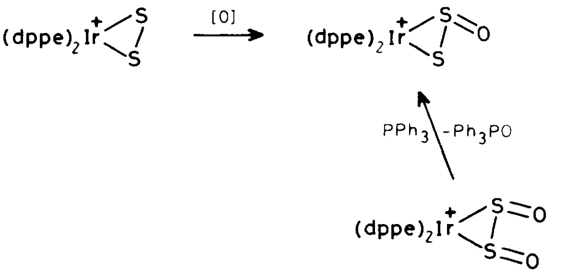


Preparation of Complexes of Disulphur Monoxide and Disulphur.—Iridium complexes. The susceptibility of the imino-oxo-λ^4-sulphane ligand in $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ towards hydrolysis, coupled with the retention of the hydrolysis product within the co-ordination sphere of the complex, suggests the possibility that treating $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ with other nucleophiles might lead to novel complexes containing unusual ligands.

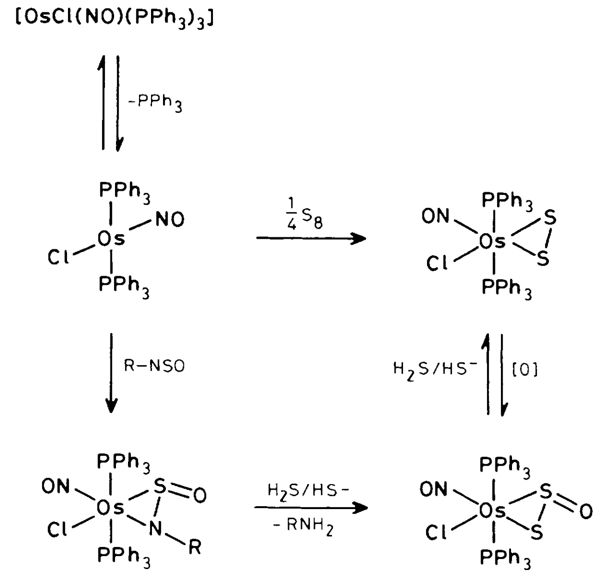
Treating a suspension of $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ in tetrahydrofuran with gaseous hydrogen sulphide leads to immediate formation of a yellow product with infrared activity due to a carbonyl ligand occurring at 2 038 cm^{-1}. This value is typical of adducts of $[IrCl(CO)(PPh_3)_2]$ with strong π-acids, whilst the disappearance of all activity due to the tosyl group and appearance of one strong band at 1 040 cm^{-1} suggests the formation of the novel complex $[IrCl(CO)(PPh_3)_2(S_2O)]$ in which the $4\text{-}MeC_6H_4SO_2NSO$ ligand has been converted to co-ordinated disulphur monoxide. The two phosphorus atoms of the triphenylphosphine ligands are chemically inequivalent, as evident from the AB quartet observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the complex (11.6, −11.6 p.p.m., $^2J(PP') = 397$ Hz). A similar AB quartet is found for the osmium complex $[OsCl(NO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ [9.1, −15.5 p.p.m., $^2J(PP') = 350$ Hz]. These inequivalencies may result from the pyramidal sulphur atom which directs the oxo group towards one phosphine and the lone electron pair towards the other [equation (4)].



A cationic iridium complex of disulphur monoxide, $[Ir(dppe)_2(S_2O)]^+$, had been previously reported,[8] resulting either from the peracid oxidation of a disulphur ligand,[1] or the phosphine reduction of a S,S′-disulphur dioxide ligand,[8] both within the co-ordination sphere of the complex fragment $[Ir(dppe)_2]^+$ [equation (5)].



Osmium complexes. It was noted above that the osmium complex $[OsCl(NO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ was considerably more stable with respect to hydrolysis than the corresponding iridium complex $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$. In a similar manner we find that the osmium complex is also less reactive towards hydrogen sulphide and no reaction is observed at room temperature in tetrahydrofuran. If, however, a solution of $[OsCl(NO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ in tetrahydrofuran is treated with H_2S and then a non-nucleophilic base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene, is added to generate, *in situ*, the more nucleophilic hydrosulphide ion, a slow reaction ensues to provide not the S_2O complex $[OsCl(NO)(PPh_3)_2(S_2O)]$, but rather a green complex with no i.r. activity above 600 cm^{-1} other than that attributable to nitrosyl and phosphine ligands. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a singlet indicating that the phosphines are in equivalent chemical environments, *i.e.* the molecule has a plane of symmetry and therefore no ligands containing a pyramidal sulphur atom. The reaction leading to this green complex is not



Scheme 2. [O] = $3\text{-ClC}_6H_4C(O)OOH$, R = $4\text{-MeC}_6H_4SO_2^-$

clean. However, the same compound may be prepared in good yield from the reaction of $[OsCl(NO)(PPh_3)_3]$ with $\frac{3}{8}$ of an equivalent of cyclo-octasulphur with formation of one equivalent of $Ph_3P{=}S$ (Scheme 2). By analogy with the product of the reaction of $[Os(CO)_2(PPh_3)_3]$ with elemental sulphur,[25] the disulphur complex $[Os(CO)_2(PPh_3)_2(S_2)]$, the green compound is formulated as $[OsCl(NO)(PPh_3)_2(S_2)]$. The position of the nitrosyl activity in the i.r. at 1 746 cm^{-1} compares well with that observed for the related complexes $[OsCl(NO)(PPh_3)_2(O_2)]$ (1 740 cm^{-1})[22] and $[OsCl(NO)(PPh_3)_2(CH_2S)]$ (1 728 cm^{-1})[21] in which the $[OsCl(NO)(PPh_3)_2]$ fragment is co-ordinated to the 'hetero-olefins' O=O and $H_2C{=}S$.

The isolation of $[OsCl(NO)(PPh_3)_2(S_2)]$ from the reaction of $[OsCl(NO)(PPh_3)_2(4\text{-MeC}_6H_4SO_2NSO)]$ with hydrosulphide (Scheme 2) is at first surprising. However, the co-ordination of disulphur monoxide to transition metals leads to a weakening of the S–O interaction by population of an antibonding orbital which is primarily associated with the S–S 'double bond' but also extends to the exocyclic S=O bond. This weakening facilitates the reduction of the sulphoxide group and reagents which are capable of removing an oxo atom (*e.g.*, phosphines) have been observed readily to reduce co-ordinated S_2O.[1] It is therefore reasonable to expect that, should a disulphur monoxide complex be formed, it would be reduced by the basic medium in which it was synthesised. This secondary reaction is not a problem in the iridium case, where the medium is neutral.

It is well established that disulphur complexes can usually be converted to the corresponding disulphur monoxide complexes by appropriate oxygen-transfer reagents.[1,5,8] Indeed, $[OsCl(NO)(PPh_3)_2(S_2)]$ was found to be cleanly oxidised to $[OsCl(NO)(PPh_3)_2(S_2O)]$ upon treatment with $3\text{-ClC}_6H_4C(O)OOH$ in chloroform at sub-ambient temperatures. The reaction may be easily followed by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy by treating a solution of $[OsCl(NO)(PPh_3)_2(S_2)]$ in $CDCl_3$ with the peracid. The ^{31}P singlet observed for $[OsCl(NO)(PPh_3)_2(S_2)]$ at -4.0 p.p.m. is then replaced by an AB quartet (4.7, -12.5 p.p.m., $^2J(PP') = 372$ Hz) with no other phosphorus-containing products being evident.

The topographical similarity between the syntheses of $[OsCl(NO)(PPh_3)_2(S_2O)]$ and that of the complex $[OsCl(NO)(PPh_3)_2(CH_2SO)]$[20] is noted in view of the current interest in isolobal mappings.[26]

Conclusions

Novel synthetic routes to both disulphur and disulphur monoxide complexes are reported which are based on the reactivity of co-ordinated imino-oxo-λ^4-sulphanes, a subject about which very little is known. Clearly an extensive synthetic potential of $[ML_n(RNSO)]$ as a synthetic equivalent for $[ML_n(SO)]^{2+}$ can be expected. We will report on further reactions of co-ordinated imino-oxo-λ^4-sulphanes in due course.[27] The extension of the described S_2O synthesis to the preparation of the complex $[Mn(CO)_2(S_2O)(\eta\text{-}C_5H_5)]$ will be discussed subsequently.[7]

Experimental

All manipulations were carried out under an atmosphere of pre-purified dinitrogen. Hydrocarbon (pentane, toluene) and ethereal (tetrahydrofuran) solvents were pre-dried over KOH and distilled from Na–K alloy. Dichloromethane was distilled from P_4O_{10} and alcohols (ethanol) from the corresponding alkoxide. Preparative thin-layer chromatography (t.l.c.) was carried out on glass plates loaded with silica gel (Merck Kieselgel, TLC-60, GF_{254}, layer thickness 0.5 mm). Column chromatography was performed on silica gel (Matrex TM 60, 70—200 μm).

Melting or decomposition points were determined in open capillaries and are uncorrected. The following instruments were employed in the spectroscopic and physical characterization of the new complexes: i.r., Perkin-Elmer 597 and 983 G, Beckman IR 4240; n.m.r., JEOL FX 90Q; melting points, Büchi 510. The data for the complexes are collected in the Table.

The starting complexes $[IrCl(CO)(PPh_3)_2]$,[28] $[OsCl(NO)(PPh_3)_3]$,[21] and $[OsCl(NO)(C_2H_4)(PPh_3)_2]$[22] were prepared according to published procedures. The imino-oxo-λ^4-sulphane, $4\text{-MeC}_6H_4SO_2NSO$, was synthesised from tosylamine, $4\text{-MeC}_6H_4SO_2NH_2$, and thionyl chloride, $SOCl_2$, according to Kresze and Wucherphennig.[29]

$[IrCl(CO)(PPh_3)_2(4\text{-MeC}_6H_4SO_2NSO)]$.—A solution of $4\text{-MeC}_6H_4SO_2NSO$ in tetrahydrofuran (0.10 mol dm^{-3}, 10.5 cm^3, 1.05 mmol) was added dropwise to a suspension of $[IrCl(CO)(PPh_3)_2]$ (0.08 g, 1.01 mmol) in tetrahydrofuran (15 cm^3) and the suspension stirred for 5 min. The solvent was removed *in vacuo* and the bright orange-yellow microcrystalline residue recrystallised from tetrahydrofuran–pentane (*ca.* 1:4). The yield is quantitative. (In the event that the product should contain unchanged $[IrCl(CO)(PPh_3)_2]$, the mixture may be treated with further $4\text{-MeC}_6H_4SO_2NSO$ until no more starting material remains, as evident in the i.r. spectrum of the product.) (Found: C, 56.80; H, 3.70; S, 6.70. $C_{44}H_{37}ClIrNO_4P_2S_2$ requires C, 56.50; H, 4.00; S, 6.85%).

$[OsCl(NO)(PPh_3)_2(4\text{-MeC}_6H_4SO_2NSO)]$.—A solution of $4\text{-MeC}_6H_4SO_2NSO$ in toluene (0.10 mol dm^{-3}, 2.6 cm^3, 0.26 mmol) was added to a solution of either $[OsCl(NO)(C_2H_4)(PPh_3)_2]$ (0.20 g, 0.25 mmol) or $[OsCl(NO)(PPh_3)_3]$ (0.26 g, 0.25 mmol). The reaction mixture was stirred for 20 min and then volatile components were removed under reduced pressure. The yellow residue was recrystallised from tetrahydrofuran and pentane at -30 °C. Yield 0.22 g (92%) (Found: C, 55.40; H, 3.60; S, 7.00. $C_{43}H_{37}ClN_2O_4OsP_2S_2$ requires C, 55.20; H, 4.00; S, 6.85%).

For reactions of the complex $[OsCl(NO)(PPh_3)_2(4\text{-MeC}_6H_4SO_2NSO)]$ it was found convenient to prepare it *in situ* from the ethylene complex and 1.0 equivalents of the imino-oxo-λ^4-sulphane $4\text{-MeC}_6H_4SO_2NSO$, since this reaction is quantitative.

$[IrCl(CO)(PPh_3)_2(S_2O)]$.—A suspension of $[IrCl(CO)(PPh_3)_2(4\text{-}MeC_6H_4SO_2NSO)]$ (0.50 g, 0.50 mmol) in tetrahydrofuran (20 cm^3) was treated with a stream of hydrogen sulphide for 20 s and then the Schlenk tube was sealed. The reaction mixture was stirred for 20 min by which time the starting complex had dissolved. The solvent was removed under reduced pressure, the yellow residue dissolved in a minimum of dichloromethane and chromatographed on silica gel. Elution with dichloromethane provided $[IrCl(CO)(PPh_3)_2]$ (10—15%). The column was then eluted with dichloromethane–tetrahydrofuran (10:1) and the major yellow band collected and solvent removed. The yellow residue was subsequently purified by thin-layer chromatography on silica gel eluting with dichloromethane–tetrahydrofuran (10:1) and the bright yellow complex isolated by crystallisation from tetrahydrofuran–ethanol (*ca.* 1:4). Yield 0.33 g (76%) (Found: C, 50.90; H, 3.45; Cl, 4.20; S, 7.65. $C_{37}H_{30}ClIrO_2P_2S_2$ requires C, 51.65; H, 3.50; Cl, 4.10; S, 7.45%).

$[OsCl(NO)(PPh_3)_2(S_2)]$.—A suspension of $[OsCl(NO)(PPh_3)_3]$ (1.04 g, 1.00 mmol) and cyclo-octasulphur (S_8, 0.10 g, 0.38 mmol, $\frac{3}{8}$ equivalents) in toluene (20 cm^3) was stirred for 3 h and then solvent was removed under reduced pressure. The brown residue was chromatographed on silica gel, eluting with dichloromethane. The green band and the first third of the tailing brown band with which it elutes were collected and the solvent removed. The residue was then rechromatographed and the green band was once again collected, this time being successfully resolved from the brown, unidentified product. Addition of ethanol to the eluate and concentration of the solvent volume under reduced pressure afforded the complex $[OsCl(NO)(PPh_3)_2(S_2)]$ as dark green microcrystals. Yield 0.62 g (73%) (Found: C, 51.00; H, 3.70; S, 7.85. $C_{36}H_{30}ClNOOsP_2S_2$ requires C, 51.55; H, 3.60; S, 7.60%).

$[OsCl(NO)(PPh_3)_2(S_2O)]$.—A solution of $[OsCl(NO)(PPh_3)_2(S_2)]$ (0.25 g, 0.30 mmol) in chloroform (40 cm^3) was cooled to −40 °C and treated with solid $3\text{-}ClC_6H_4\text{-}C(O)OOH$ (0.08 g, 0.38 mmol) [the commercial peracid (Fluka) contains *ca.* 15% of the benzoic acid as stabiliser]. The dark green solution immediately decolourised to orange and was allowed to warm up to room temperature, solvent was removed under reduced pressure, and the orange residue recrystallised from dichloromethane–ethanol (*ca.* 1:4). The yield is quantitative according to the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, the isolated yield being 0.24 g (93%) (Found: C, 49.75; H, 3.25; S, 7.70. $C_{36}H_{30}ClNO_2OsP_2S_2$ requires C, 50.15; H, 3.50; S, 7.45%).

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