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The coordination chemistry of iminoxosulphuranes

VIII *. The coupling of tosyliminoxosulphurane with ethylene, allene, and alkynes coordinated to osmium

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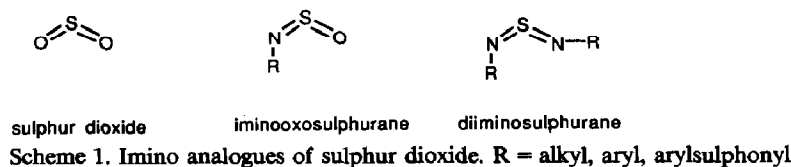
Abstract

The reactions of the zerovalent osmium nitrosyl complexes $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{L})]$ ($\text{L} = \text{CH}_2\text{CH}_2$, CH_2CCH_2 , $\text{PhC}\equiv\text{CPh}$, $\text{PhC}\equiv\text{CH}$, $\text{CH}_3\text{C}\equiv\text{CCH}_3$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$) with toluene sulphonyliminoxo- λ^4 -sulphurane, $\text{OSNSO}_2\text{C}_6\text{H}_4\text{Me-4}$ (OSNSO_2R) have been investigated. The ethylene complex reacts either by ethylene substitution to provide $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNSO}_2\text{R})]$ or by formation of the metallacyclic complex $[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$, which has been crystallographically characterised. The allene complex reacts in a similar manner, also forming a metallacycle $[\text{Os}\{\text{C}(\text{=CH}_2)\text{CH}_2\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$. The reactivity of the alkyne complexes depends upon the nature of the alkyne substituents: the strongly bound hexafluorobut-2-yne complex is unreactive, the but-2-yne complex reacts by alkyne substitution (i.e., formation of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNSO}_2\text{R})]$), and the aryl alkyne complexes react by metallacycle formation to give $[\text{Os}\{\text{CPh}=\text{CR}'\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ ($\text{R}' = \text{H}, \text{Ph}$). The metallacyclic derivatives are readily and reversibly protonated (HBF_4) at the exocyclic sulphimine substituent.

Introduction

Despite the vast amount of knowledge about the interaction of sulphur dioxide with metal alkyl and aryl complexes [2] very little is known about how this simple

* For Part VII see ref. 1.



molecule or its sulphur(IV) analogues react with more complicated ligands. The catalytic coupling of sulphur dioxide with ethylene by palladium chloride has been described [3], and the coupling of butadiene and SO_2 on an iron tricarbonyl centre has been shown to proceed in the presence of BF_3 [4]. Clearly these results indicate that unusual carbon-sulphur bond-forming reactions may be induced at metal centres ligated by unsaturated organic substrates. This possibility has been examined in the present study involving investigation of the reactions of electron-rich zerovalent osmium π -adducts of ethylene, allene and a range of alkynes with the very electrophilic tosyliminooxosulphurane, OSNSO_2R (tosyl-NSO, $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) [5]. Iminooxosulphuranes are analogues of sulphur dioxide (Scheme 1) in which one oxo group of the heterocumulene is replaced by an imino group.

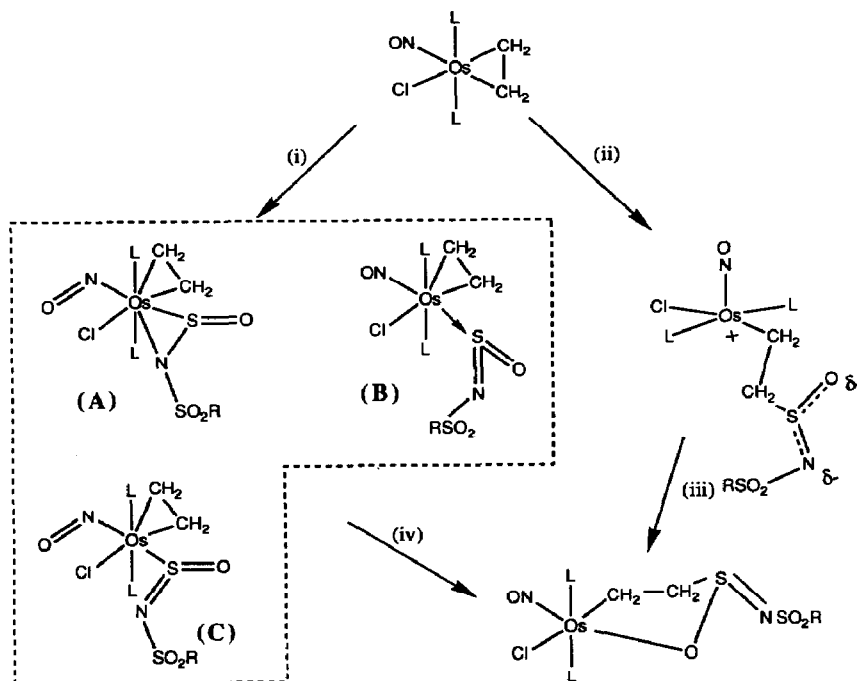
Results and discussion

Ethylene

The ethylene complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2)]$, originally obtained by Roper and Wright [6] via the reaction of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_3]$, may be prepared in a one-pot procedure from the peroxy carbonyl complex $[\text{OsCl}(\text{OOCO})(\text{NO})(\text{PPh}_3)_2]$ by heating it with one equivalent of triphenylphosphine under an atmosphere of ethylene, thereby avoiding the isolation of air-sensitive intermediates. The orange ethylene complex is partially dissociated in solution and a brown colour develops when the solutions are kept, owing to the accumulation of a species assumed to be the 16-electron complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2]$. In keeping with this assumption, the brown colour is discharged when ethylene is bubbled through the solution. This behaviour is important in the reactions of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2)]$ in that the complex serves as a suitable precursor for the convenient in situ preparation of other complexes of the form $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{L})]$ ($\text{L} = \text{CH}_2\text{CCH}_2$, $\text{RC}\equiv\text{CR}$, CS_2 , SO_2 etc).

It therefore appears unlikely that a complex containing such a weakly held olefin ligand would provide a useful model complex for the reactions of coordinated ethylene. Indeed treatment of tetrahydrofuran solutions of the complex with the iminooxosulphuranes $\text{R}'\text{NSO}$ ($\text{R}' = \text{R}$, $\text{C}_6\text{H}_4\text{Me-2}$, SO_2R) leads to essentially quantitative formation of the π -coordinated iminooxosulphurane complexes $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNR}')]$. The preparation and properties of these complexes have been discussed previously [7]. If, however, the reaction of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2)]$ and $\text{OSNSO}_2\text{C}_6\text{H}_4\text{Me-4}$ is carried out in toluene suspension, only ca. 5% of the π -adduct $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNSO}_2\text{R})]$ is obtained, and the major product (90%) is a 5-membered osmacycle derived from the coupling of the osmium-alkene moiety with the sulphur-oxygen multiple bond (Scheme 2).

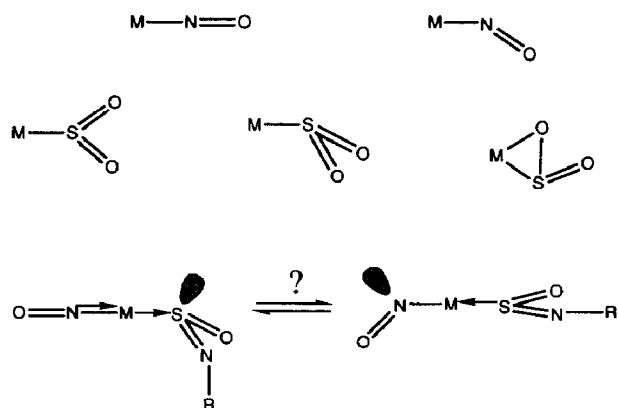
The metallacyclic complex $[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ is characterised by an infrared frequency (1805 cm^{-1}) typical of a nitrosyl ligand



Scheme 2. Mechanism for formation of $[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$. (i) Coordination of the iminoxosulphurane directly to the osmium centre. (ii) Electrophilic "backside attack" at one carbon of the coordinated olefin. (iii) Coupling of the SO and CC double bonds with metallacycle formation. (iv) Intramolecular ion-pair-collapse ring closure.

bound to divalent osmium [8], as compared to 1768 cm^{-1} for the formally zerovalent π -adduct. The osmacycle gives rise to bands at 1026 , 1010 , and 830 cm^{-1} , which are quite distinct from those observed for the π -adduct at 1088 and 921 cm^{-1} . Multiplet resonances are observed in the ^1H NMR spectrum at δ 1.64 and 2.69 ppm, shifts typical of transition metal alkyls and metallacyclic alkylsulphinates [9–11]. These resonances show some simplification upon $\{^{31}\text{P}\}$ or selective $\{^1\text{H}\}$ decoupling, but not sufficient to allow resolution of the complicated ABCDXY spin system. The characterisation of $[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ included a single crystal X-ray diffraction analysis which confirmed the coordination spheres of osmium and sulphur, and also the metallacycle connectivity and aplanarity.

The reaction in which $[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ is formed may possibly proceed via direct electrophilic attack at the coordinated olefin, formation of the zwitterion $[\text{Os}^+\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}^-\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$, and subsequent intramolecular ion-pair-collapse cyclisation, a process described previously for transition-metal alkyls [13]. The specificity of this ring-closure (O exclusively *trans* to NO) is presumably due to steric control. Thus the formation of the osmacycle, rather than the substitution product $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNSO}_2\text{R})]$, predominates in situations in which olefin-dissociation (leading to the 16-electron intermediate ' $\text{OsCl}(\text{NO})(\text{PPh}_3)_2$ ') is less favoured, i.e., in a non-donor solvent (toluene vs. tetrahydrofuran) and at a high relative concentration of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$, this being obtained when the ethylene complex is suspended rather than completely dissolved. However, an alternative interpretation should also be



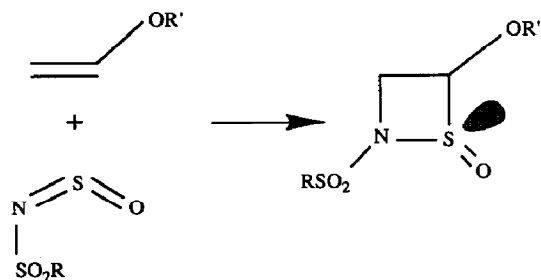
Scheme 3. Nitrosyl bending vs. iminoxosulphurane pyramidalisation.

noted. The ability of nitrosyl complexes to expand their coordination spheres by bending is well documented, and such a tautomerism in $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ would, according to Hoffmann's treatment [14], provide a square pyramidal complex with an apical nitrosyl ligand. Coordination of the iminoxosulphurane would then be expected to occur *trans* to the apical nitrosyl ligand of a square pyramidal complex, thereby resulting in the observed stereochemistry. This possibility raises some intriguing questions concerning the nature of the intermediate "super-saturated" complex. The nitrosyl ligand has two modes of coordination (linear and bent), whilst iminoxosulphurane ligands have three possible coordination geometries (Scheme 3), all of which have been observed for tosyl-NSO [15]. The factors suggested by Hoffmann et al. to favour the bending of nitrosyl ligands [14] have been shown by Ryan and Eller [16] to be identical with those that induce pyramidalisation of coordinated sulphur dioxide. These ideas extend automatically to the behaviour of iminoxosulphurane complexes, and thus the nature of the intermediate complex "[$\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2)(\text{OSNSO}_2\text{R})$]" (if formed) is not clear. It is fairly unlikely that there would be sufficient d_π -electron density in such a complex to allow π -coordination of the iminoxosulphurane (Scheme 2, A) (cf. ref. 15) and so the two remaining possibilities involve either 1-electron nitrosyl and 2-electron iminoxosulphurane ligands (C) or 3-electron nitrosyl and 0-electron (Lewis-acid) iminoxosulphurane ligands (B) (Scheme 3). The actual situation may be a compromise, but it should be noted that, e.g. in the complex cation $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+$ [17], there are two structurally distinct nitrosyls and not an averaging of coordination modes.

Attempts to induce a similar cyclisation of sulphur dioxide with coordinated ethylene led to simple substitution and formation of the known complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{SO}_2)]$ [15,18] which has a π -bound SO_2 ligand, and is isostructural with $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNR}')]$. It is noteworthy that the reactions of OSNSO_2R with free electron-rich olefins (in the uncomplexed state) lead to cycloaddition of C=C and S=N double bonds (Scheme 4) [5]. Thus prior coordination of the olefin diverts the course of the reaction.

Allene

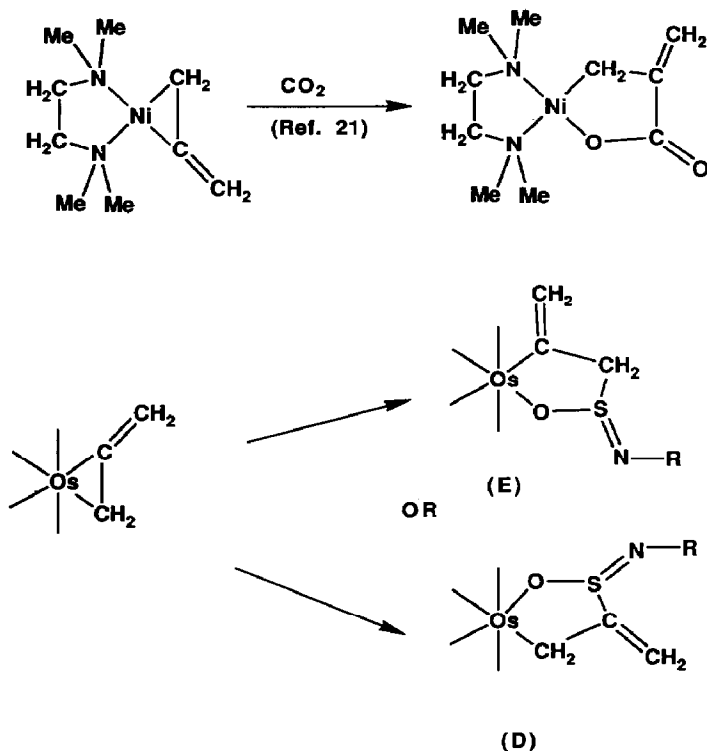
An interesting variation on simple π -olefin coordination arises when the double bond is part of an extended π -system, as is the case with allene. Allene and its



Scheme 4. Cycloaddition of tosyl-NSO with olefins.

derivatives form a large number of complexes with transition metals [19], some of which involve the rapid migration of the metal between the two orthogonal double bonds [20]. The complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CCH}_2)]$ [6] is not fluxional on the ^1H NMR time scale at room temperature and so has two chemically distinct osmium-carbon bonds. Should a similar reaction occur as for ethylene, two possible metallacycles can be expected, depending on which of the two bonds is involved in C-S bond formation (Scheme 5, D or E).

Treatment of a toluene solution of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CCH}_2)]$ with tosyl-NSO leads to slow formation of a pale orange compound, which was isolated in high yield after chromatographic purification. Data for the complex are given in Tables 1 and 2. In this case no competing substitution of the allene ligand was



Scheme 5. Allene-heterocumulene coupling.

Table 1

Infrared data for the new complexes

Complex	Infrared (Nujol)(cm ⁻¹)		
	$\nu(\text{NO})(\text{vs})$	$\nu(\text{SO}_2)$	other
[Os] = OsCl(NO)(PPh ₃) ₂ ; R = C ₆ H ₄ Me-4			
[Os]{CH ₂ CH ₂ S(NSO ₂ R)O} (orange)	1805	1297, 1284, 1145	1026, 1010, 830, 280(OsCl)
[Os]{C(CH ₂)CH ₂ S(NSO ₂ R)O} (orange)	1809	1310, 1297 1285, 1144	991, 936, 882, 829, 811, 802
[Os]{CPh=CHS(NSO ₂ R)O} (brown/orange)	1820	1338, 1319, 1306, 1152	996, 871, 837, 809
[Os]{CPh=CPhS(NSO ₂ R)O} (orange)	1821	1295, 1283, 1142	1023, 985, 960, 851, 816

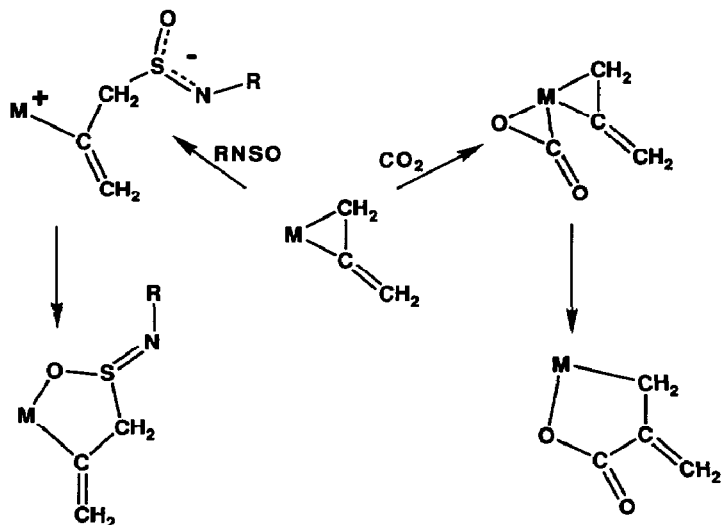
observed. The infrared data are consistent with a divalent osmium complex ($\nu(\text{NO})$ 1809 cm⁻¹, Nujol) which contains a toluene sulphonyl group (1310, 1297, 1285 and 1144 cm⁻¹). Furthermore, bands at 991 and 829 cm⁻¹ are similar to those observed for the ethylene derived metallacycle, and lead to the formulation of the product as [Os{C(=CH₂)CH₂S(NSO₂R)O}Cl(NO)(PPh₃)₂]. Additional bands are observed at 936 and 882 cm⁻¹ and are presumably also due to the metallacycle, however no band could be unequivocally assigned to the vinylic C=C stretch. The infrared data could not distinguish between the two possible metallacycles (**D** and **E**) (Scheme 5), but ¹H NMR evidence suggests that it is in fact that deriving from attack at the "alkyl" Os-C bond (**E**) and not at the "vinyl" Os-C bond (**D**) which is formed. Metallacycle **D** would be expected to show ³¹P-¹H coupling in its ¹H NMR spectrum such that the methylene group bound to osmium appears either as an AA'XX' or ABXY multiplet depending upon the extent to which the asymmetry of the distant sulphimine group is felt. Furthermore, even with the expected allylic shift, the observed chemical shift of the osmium-bound methylene protons in

Table 2

Hydrogen-1 and phosphorus-31 NMR data for the new complexes ^a

Complex	$\delta(^1\text{H})$ (ppm)	$\delta(^{31}\text{P})$ (ppm)
[Os] = OsCl(NO)(PPh ₃) ₂ ; R = C ₆ H ₄ Me-4		
[Os]{CH ₂ CH ₂ S(NSO ₂ R)O} (orange)	1.64 [m, 2H, OsCH ₂], 2.38 [s, 3H, CH ₃], 2.69, 2.62 [m, 2 H, SCH ₂]	-5.6
[Os]{C(CH ₂)CH ₂ S(NSO ₂ R)O} (orange)	2.42 [s, 3H, CH ₃], 2.86, 3.16 [AB, 2H, J(AB) 12.5, SCH ₂], 4.09, 5.29 [s(br)x2, 2H, =CH ₂]	-6.8
[Os]{CPh=CHS(NSO ₂ R)O} (brown/orange)	2.14 [s, 3H, CH ₃] 5.22 [s, 1H, CH]	-5.9 -11.8 ^b
[Os]{CPh=CPhS(NSO ₂ R)O} (orange)	2.32 [s, 3H, CH ₃]	-5.6 -15.6 ^c

^a Data obtained from saturated solutions in CDCl₃ at ambient temperature. ¹H chemical shifts are given in ppm relative to internal SiMe₄ (δ 0.00). ³¹P-¹H chemical shifts are given in ppm relative to external D₃PO₄ (δ 0.00). ^b Inner pair of lines of an AB quartet for which the outer lines were not observed. ^c AB quartet, chemical shifts corrected for 'roof effects'; J(PP) 371 Hz.



Scheme 6. Alternative mechanisms for allene-heterocumulene coupling.

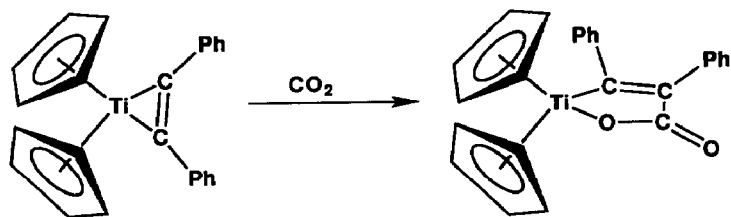
$[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ (1.64 ppm) would suggest that the signal for such a group in metallacycle **D** would appear to much higher field than the AB multiplet that is observed at δ 2.86 and 3.16 ppm.

This result may be contrasted with the observations of Hoberg et al. for the reaction of $[\text{Ni}(\text{tmen})(\text{CH}_2\text{CCH}_2)]$ ($\text{tmen} = N,N,N',N'$ -tetramethylethylenediamine) with carbon dioxide (Scheme 5) [21]. The product of this reaction would appear to involve the formation of a metallacycle in which the carbon of CO_2 becomes bound to the central allene carbon (Scheme 6). It is not clear why there is a difference in preference for the formation of metallacycles between the two cumulenes, but the metal centres involved have quite different frontier orbital symmetry and this may contribute. Alternatively the reaction of the osmium complex may involve outer-sphere electrophilic attack by the iminoxosulphurane, in which case the more electron rich "alkyl" bond would be expected to be more susceptible to attack than the "vinylic" Os-C bond. The reaction in the nickel case would almost certainly proceed via an increased coordination number at nickel (Scheme 6).

Alkynes

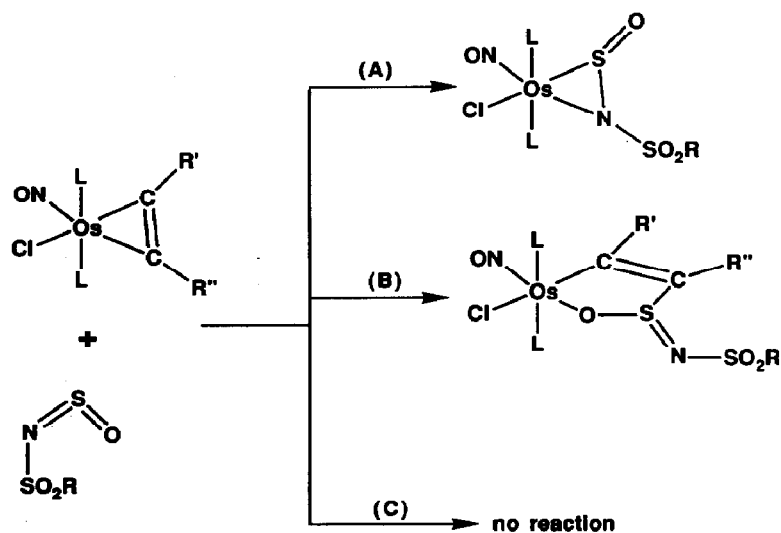
To our knowledge there are no reports of reactions of simple alkyne complexes with sulphur dioxide. However, the reactions of early transition metal alkyne complexes [22,23] with CO_2 (Scheme 7) may serve as an indication of what might be expected from the reaction of a coordinated alkyne with other electrophilic cumulenes.

The red or purple alkyne complexes $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{R}'\text{C}\equiv\text{CR}'')]$ ($\text{R}' = \text{R}'' = \text{Ph}, \text{CH}_3, \text{CF}_3$; $\text{R}' = \text{H}, \text{R}'' = \text{Ph}, \text{CO}_2\text{Me}$), originally obtained from the reaction of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_3]$ with the appropriate alkyne [6], may more conveniently be prepared in situ spectroscopically quantitative yield from the ethylene complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ and one equivalent of alkyne. The violet diphenylacetylene complex reacts slowly with tosyl-NSO to give an orange 1/1 adduct. The reaction is accompanied by an increase in the nitrosyl stretching frequency to a

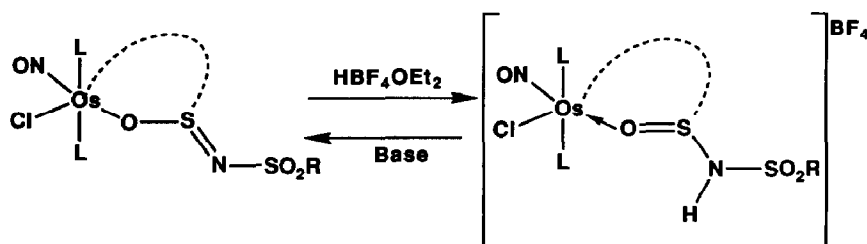
Scheme 7. Coupling of tolane with CO_2 .

value (1821 cm^{-1} , Nujol) typical of divalent osmium and consistent with the formation of a metallacycle $[\text{Os}\{\text{CPh}=\text{CPhS}(\text{N}-\text{SO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$. Infrared bands due to the tosyl group are evident in addition to bands at $985(\text{s})$ and $851(\text{m})\text{ cm}^{-1}$. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum consists of an AB system, but the chemical shifts of the two phosphorus nuclei differ only slightly (-10.8 and -7.2 ppm, corrected for 'roof' effects), suggesting that the difference in chemical environments is small compared to that, in e.g., $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNSO}_2\text{R})]$ (9.1 , -15.5 ppm), in which the centre of asymmetry is much closer to the metal. If the sulphur–nitrogen bond were involved in metallacyclisation (i.e., formation of $[\text{Os}\{\text{CPh}=\text{CPhS}(\text{O})\text{NSO}_2\text{R}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$), the steric bulk of the tosyl group would be expected to be more strongly felt. The structure proposed for the metallacycle (Scheme 8) is in keeping with that observed in the $[\text{Ti}(\text{PhC}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)_2]/\text{CO}_2$ reaction.

The generality of the reaction was investigated briefly. The reaction outcome is strongly dependent on the nature of the alkyne substitution. Thus $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{HC}\equiv\text{CPh})]$ reacts to form, in lower yield, the metallacycle $[\text{Os}\{\text{CPh}=\text{CHS}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ in which the unsubstituted end of the alkyne apparently ends up β to the metal, as judged from the absence of observable phosphorus–proton coupling in the ^1H NMR spectrum. However, the monosub-



Scheme 8. Reactions of alkyne complexes with RSO_2NSO , $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$. (A) $\text{R}' = \text{R}'' = \text{CH}_3$. (B) $\text{R}' = \text{Ph}$; $\text{R}'' = \text{H}$, Ph . (C) $\text{R}' = \text{R}'' = \text{CF}_3$; $\text{R}' = \text{H}$, $\text{R}'' = \text{CO}_2\text{Me}$.



Scheme 9. Protonation of the metallacycles, R = C₆H₄Me-4.

stituted alkyne complex, [OsCl(NO)(PPh₃)₂(HC≡CCO₂Me)], showed no reaction. Similarly the adduct of the very electron-withdrawing alkyne CF₃C≡CCF₃ was unreactive towards tosyl-NSO, whilst the electron releasing alkyne but-2-yne was quantitatively eliminated from its adduct [OsCl(NO)(PPh₃)₂(CH₃C≡CCH₃)] with formation of [OsCl(NO)(PPh₃)₂(OSNSO₂R)]. Thus it appears that it is necessary for the alkyne to bind strongly enough to prevent dissociation, but not so strongly that the metal centre is deactivated towards electrophilic attack. The results are summarised in Scheme 8.

Protonation of the metallacycles

Treatment of the metallacycles [Os{CPh=CPhS(NSO₂R)O}Cl(NO)(PPh₃)₂] and [Os{C(=CH₂)CH₂S(NSO₂R)O}Cl(NO)(PPh₃)₂] with tetrafluoroboric acid diethyl etherate in toluene leads to the formation of colourless ionic precipitates that show a sharp band in the region assignable to toluenesulphonamide ν(NH) activity. The infrared peaks due to the SO₂ group of the tosyl substituent near 1300 and 1150 cm⁻¹ are also perturbed, and presumably moved below other strong bands in the region. The ¹H NMR pattern for the allene-derived metallacycle is virtually unchanged upon protonation, suggesting that there is very little structural reorganisation. Furthermore, treatment with a non-nucleophilic base or simply chromatography on silica gel leads to clean reformation of the neutral starting complexes. Three possible sites of protonation may be considered: the metal-bound oxygen, the SO₂ group, or the sulphimine nitrogen atom. We suspect that in view of its reactivity that it is the last of these that is the site of protonation. We have previously observed protonation of the nitrogen atom of coordinated iminoxosulphuranes [1].

Concluding remarks

The reaction of tosyliminoxosulphurane with electron-rich olefins involves the formal [2 + 2] cycloaddition of C=C and N=S double bonds (Scheme 4 [24]). Indeed, virtually all the known organic chemistry of iminoxosulphuranes centres around the very reactive nitrogen-sulphur multiple bond [5]. It is therefore somewhat surprising to note that the metallacycles observed here, including the crystallographically characterised complexes [Os{(CH₂)_nS(NSO₂R)O}Cl(NO)(PPh₃)₂] (*n* = 1 [9], 2 [25]), all involve the sulphur oxygen multiple bond, with the N=S bond retaining its integrity. We can offer no obvious explanation for this phenomenon; but we note that the complexes involved have very sterically crowded coordination spheres. It may simply be that the bulk of the toluene sulphonylimine group prevents competitive Os-N vs. Os-O ring closure of a zwitterionic intermediate.

Secondly, we are unable to distinguish between two plausible mechanisms for the formation of the metallacycles described here and previously [9]. The non-innocent participation of the nitrosyl ligand (3-electron \leftrightarrow 1-electron ligand), allowing prior coordination of the iminooxosulphurane, would explain some but not all of the observations and the stereoselectivity of metallacycle formation. Perhaps the most significant-point arguing against this mechanism is the observation that $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNSO}_2\text{R})]$ does not react with ethylene even though the "virtual" coordination site provided by a nitrosyl ligand should also be present here, and give rise to the same intermediate " $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2)(\text{OSNSO}_2\text{R})]$ " upon ethylene coordination, notwithstanding the fact that iminooxosulphuranes are better π -acids than ethylene and less likely to facilitate nitrosyl bending.

The importance of the nitrosyl ligand will need to be investigated by extending these reactions to other metal-ligand systems which have no possible way of increasing their coordination number (e.g., complexes of the form $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{L})]$). Nevertheless the results described here indicate that a range of unsaturated organic ligands may be coordinatively activated towards iminooxo- λ^4 -sulphuranes, and that the reactivity thus observed is distinct from that observed in the absence of metal-coordination. We have recently extended these reactions to include inorganic substrates coordinated to a metal, i.e., nitrosobenzene and aryliminooxosulphuranes themselves [26].

Experimental

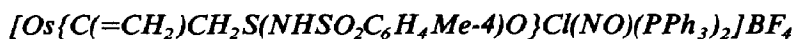
General experimental procedures and instrumentation [7] and the compounds $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{L})]$ [6] and OSNSO_2R [5] have been described elsewhere. Light petroleum refers to that fraction of b.p. 40–60°C. Physical data for the complexes are listed in Table 1 and 2. Representative compounds gave satisfactory elemental microanalyses.

$[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{R})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$

Toluene (5.0 cm³) was added to a mixture of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ (0.60 g, 0.75 mmol) and OSN-tosyl (0.20 g, 0.92 mmol). The suspension was stirred for 1 h and then ethanol (20 cm³) added to complete precipitation of the yellow product. In cases in which the product was contaminated with traces of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNSO}_2\text{C}_6\text{H}_4\text{Me-4})]$, recrystallisation from dichloromethane/ethanol removed the latter complex, which is slightly soluble in alcohols. Yield 0.72 g (94%). M.p. 202°C.

$[\text{Os}\{\text{C}(=\text{CH}_2)\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$

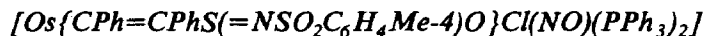
A suspension of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CCH}_2)]$ (0.50 g, 0.62 mmol) in toluene (0.20 cm³) was treated with a solution of OSN-tosyl (0.10 mol/l, 6.5 cm³, 0.65 mmol) and the mixture was stirred for 1 h. The solvent was removed in vacuo and the orange residue recrystallised twice from dichloromethane/ethanol. Yield 0.60 g (95%). M.p. 191°C. Anal. Found: C, 53.21; N, 2.66; S, 6.17. $\text{C}_{46}\text{H}_{41}\text{ClN}_2\text{O}_4\text{OsP}_2\text{S}_2$ calcd.: C, 53.25; N, 2.70; S, 6.18%.



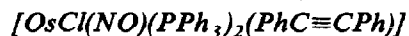
A solution of the adduct $[\text{Os}\{\text{C}(\text{=CH}_2)\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ (0.20 g, 0.19 mmol) in dichloromethane (20 cm³) was titrated with $\text{HBF}_4 \cdot \text{OEt}_2$ dissolved in dichloromethane (ca. 0.1 mol/l), and the reaction was monitored by infrared spectroscopy in the range 1750–1850 cm⁻¹. When one equivalent of acid had been added the solution was concentrated under reduced pressure and pentane added dropwise to effect precipitation of the pale orange, salt which was then isolated by decantation, washed twice with pentane (2 × 10 cm³), and recrystallised from dichloromethane/pentane at -78°C. Yield 0.19 g (91%). M.p. 184°C. Chromatography of the product on silica gel (CH_2Cl_2 as eluant) returned the starting complex $[\text{Os}\{\text{C}(\text{=CH}_2)\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$.



A solution of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{HC}\equiv\text{CPh})]$ (0.40 g, 0.45 mmol) in toluene (50 cm³) was treated with a solution of OSN-tosyl in toluene (0.10 mol/l, 4.8 cm³, 0.48 mmol) and the mixture stirred for 2 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of dichloromethane and placed on a TLC plate coated with silica gel (Merck, Kieselgel TLC-60 GF₂₅₄, layer thickness 0.5 mm). Elution with dichloromethane then with a mixture of dichloromethane/thf (10/1) allowed isolation of a major brown-orange zone, the solid from which was recrystallised from dichloromethane/hexane. Yield 0.19 g (38%). The complex decomposes without melting at 92°C.



A solution of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh})]$ (0.40 g, 0.42 mmol) in toluene (50 cm³) was treated with a solution of OSN-tosyl in toluene (0.10 mol/l, 4.50 cm³, 0.45 mmol) and the mixture stirred for 2 h by which time the solution had become orange. The solvent was removed under reduced pressure and the residue recrystallised from dichloromethane/ethanol as orange needles. Yield 0.42 g (86%). M.p. 182°C decomp.



This complex has been previously prepared from the reaction of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_3]$ with toluene [6]. The method described here is a variation involving a significant improvement in yield.

A suspension of $[\text{OsCl}(\text{OOCO})(\text{NO})(\text{PPh}_3)_2]$ (0.50 g, 0.60 mmol) and triphenylphosphine (0.20 g, 0.76 mmol) in toluene (8 cm³) was refluxed for 5 min and then left to cool to room temperature. Diphenylacetylene (0.12 g, 0.67 mmol) was added, the suspension stirred for 5 min, and ethanol (50 cm³) added. The mixture was cooled to -30°C for 2 h to allow complete crystallisation of the red-violet compound, which was isolated by filtration. Yield 0.54 g (94%). The compound was characterised by comparison of spectroscopic data with those of an authentic sample prepared as described previously. An alternative method of preparation involves the quantitative reaction between the ethylene complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2)]$ and diphenylacetylene in tetrahydrofuran. In this case the alkyne complex is not normally isolated but used in situ.

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