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The coordination chemistry of iminooxosulphuranes

X *. Pseudo-olefinic coordination of OSNC₆H₄Me-4 to zerovalent osmium. Crystal structure of [OsCl(NO)(PPh₃)₂(OSNC₆H₄Me-4)]

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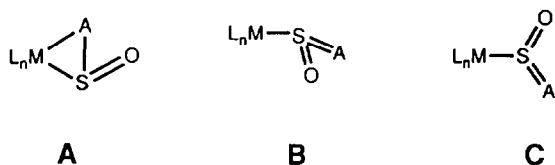
Abstract

The crystal structure of the complex *trans*-[OsCl(NO)(PPh₃)₂(OSNC₆H₄Me-4)] has been determined and confirms that the sulphur(IV) heterocumulene adopts a pseudo-olefinic mode of coordination (η^2 -NS), with the pyramidal sulphur *trans* to chloride.

Introduction

Our investigations of the parallels between the coordination chemistries of sulphur(IV) cumulenes have involved the synthesis of a range of complexes of the general form [L_nM(O=S=A)] which allowed a study of the effect of varying the cumulene (A = O, S, CH₂, NC₆H₄Me-4, NSO₂C₆H₄Me-4) [2] and the metal and ancillary ligands ML_n [3]. Of particular importance is the series of compounds [OsCl(NO)(PPh₃)₂(O=S=A)] which on the basis of infrared data would appear to be isostructural as distinct from the formally isoelectronic series [IrCl(CO)(PPh₃)₂(O=S=A)] wherein the cumulene is either bound in a pseudo-olefinic mode (A, Scheme 1) for A = S or pyramidal mode (B, Scheme 1) for A = O, NSO₂C₆H₄Me-4 [2]. Because of the central importance of the osmium complexes we

* For Part IX see ref. 1.



Scheme 1. Coordination geometries for sulphur(IV) heterocumulenes.

were eager to firmly establish the “metallathirane-*S*-oxide” mode of coordination for this series in addition to addressing questions of metal centre stereochemistry raised by the analogy with sulphur dioxide [4].

Experimental

The compound $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$ was prepared according to the procedure outlined previously [2] and in Scheme 2. Crystals suitable for

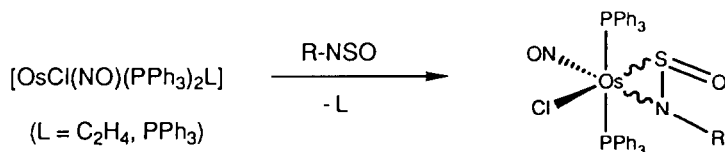
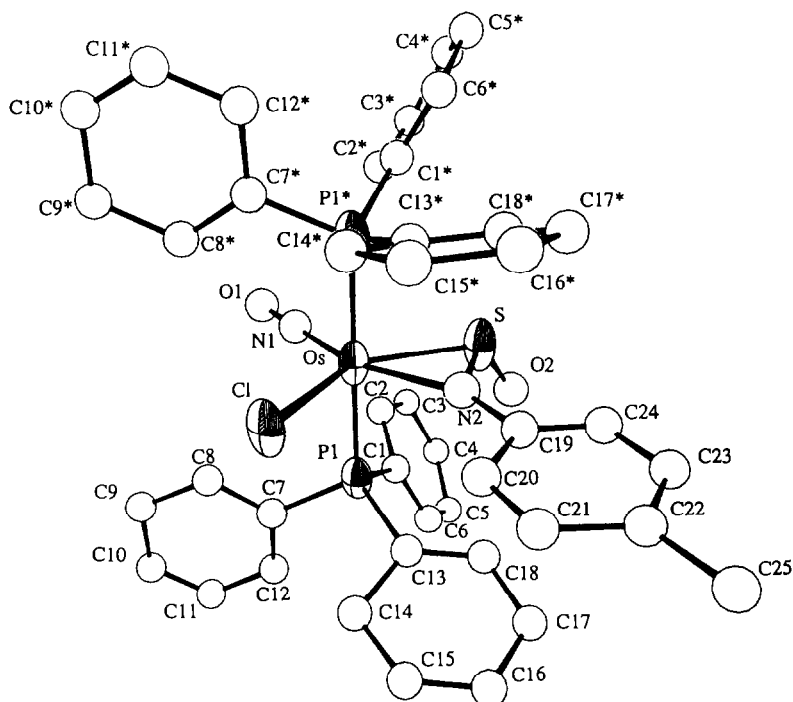
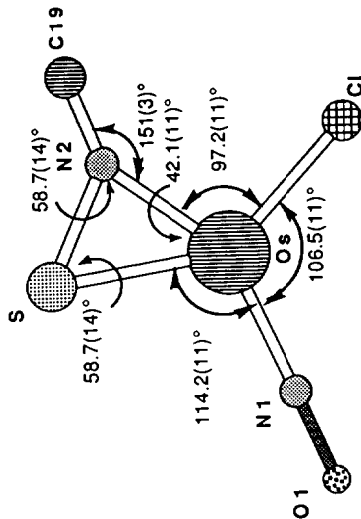
Scheme 2. Synthesis of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$.

Fig. 1. The structure of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$. Important distances and angles are Os–P 2.421(9), Os–Cl 2.449(12), Os–NO 1.78(3), Os–S 2.354(13), Os–N2 2.05(4), S–N2 1.61(4) Å; Cl–Os–N1 106(1)°, Cl–Os–N2 97(1)°, N1–Os–S 114(1)°.

Table 1

Selected bond lengths (Å) and angles (°) for the complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$

	Os-S	Os-P1
Os-Cl	2.449(12)	2.354(13)
Os-N1	1.78(3)	N1-O1
N2-S	1.61(4)	N2-C19
S-Os-Cl	139.4(4)	
P1-Os-Cl	88.5(2)	
P1-Os-S	90.3(2)	
N1-Os-Cl	106.5(11)	
N1-Os-S	114.2(11)	
N1-Os-P1	91.7(2)	
N2-Os-Cl	97.2(11)	
N2-Os-S	42.1(11)	
N2-Os-P1	88.9(2)	
N2-Os-N1	156.3(14)	
O2-S-Os	121.6(19)	
N2-S-Os	58.7(14)	
N2-S-O2	114(2)	
O2-S-O2*	114(4)	
O1-N1-Os	179(3)	
S-N2-Os	79.1(16)	
C19-N2-Os	151(3)	
C19-N2-S	130(3)	



diffraction were obtained by slow diffusion of hexane into a dichloromethane solution of the compound.

Crystal data. $C_{43}H_{37}ClN_2O_2OsP_2S$, $M = 933.40$, orthorhombic intensely-red irregular fragments, $Pnma$, $a = 15.173(10)$, $b = 15.461(4)$, $c = 20.584(3)$ Å; $V = 4828.8$ Å³; $Z = 4$; $D_c = 1.28$ g cm⁻³; $F(000) = 1856$; $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å; $\mu = 29.58$ cm⁻¹; $\theta_{\text{max}} = 23^\circ$ (Table 1). A total of 2487 unique reflections of which 1117 were deemed to be observed [$I > 3\sigma(I)$], were collected on a Nonius CAD-4 diffractometer, and corrected for absorption [5]. The maximum and minimum correction factors were 1.0000 and 0.9397 respectively. The structure was solved by conventional Patterson and Fourier techniques, and refined using full-matrix least-squares equations employing the program SHELX-76 [6]. The molecule lies on the crystallographic mirror plane with the oxygen atom attached to the sulphur statistically lying above or below the equatorial plane. Only one of the two possible oxygen positions is shown in the figure. Final residuals, $R = 0.0790$ and 0.0792 . Least squares weighting scheme [$\sigma^2(F) + 0.0114 F^2$]⁻¹. No attempt was made to locate

Table 2

Atomic coordinates for [OsCl(NO)(PPh₃)₂(OSNC₆H₄-4)] (standard deviations in parentheses)

Atom	x	y	z
Os	0.10121(12)	0.25000(0)	0.18853(9)
Cl	0.2325(8)	0.25000(0)	0.2577(6)
S	0.0642(8)	0.25000(0)	0.0774(6)
P1	0.1068(6)	0.0935(6)	0.1882(4)
O1	-0.053(3)	0.25000(0)	0.2753(19)
O2	0.038(3)	0.1720(18)	0.0443(19)
N1	0.008(2)	0.25000(0)	0.2418(16)
N2	0.165(2)	0.25000(0)	0.1009(19)
C1	0.012(2)	0.039(2)	0.1493(14)
C2	-0.071(3)	0.077(3)	0.1620(18)
C3	-0.145(3)	0.044(3)	0.132(2)
C4	-0.140(3)	-0.040(3)	0.099(2)
C5	-0.053(3)	-0.083(3)	0.090(2)
C6	0.024(6)	-0.039(2)	0.1164(19)
C7	0.109(2)	0.043(2)	0.2675(14)
C8	0.104(2)	0.093(2)	0.3242(16)
C9	0.099(3)	0.051(2)	0.3897(18)
C10	0.103(3)	-0.046(3)	0.3883(18)
C11	0.109(3)	-0.088(3)	0.3326(19)
C12	0.108(3)	-0.048(3)	0.2696(19)
C13	0.207(2)	0.059(2)	0.1463(15)
C14	0.281(3)	0.034(3)	0.192(2)
C15	0.359(3)	0.013(3)	0.1539(18)
C16	0.362(3)	0.001(3)	0.0878(19)
C17	0.285(3)	0.018(3)	0.048(2)
C18	0.208(3)	0.049(3)	0.080(2)
C19	0.246(3)	0.25000(0)	0.063(2)
C20	0.326(3)	0.25000(0)	0.099(2)
C21	0.408(4)	0.25000(0)	0.069(3)
C22	0.406(4)	0.25000(0)	-0.002(2)
C23	0.320(4)	0.25000(0)	-0.036(3)
C24	0.241(3)	0.25000(0)	-0.002(2)
C25	0.491(5)	0.25000(0)	-0.041(3)

hydrogen atoms. Os, Cl, S and P atoms were assigned anisotropic thermal parameters. Maximum value on a final difference map is $1.85 \text{ e } \text{\AA}^{-3}$ near Os. Atomic positions are listed in Table 2. Tables of thermal parameters, and complete bond lengths and angles and a list of observed and calculated structure factors are available from the authors (G.R.C.).

Results and discussion

The X-ray analysis (Table 1) confirms the coordination geometry and mode of coordination of the iminoxosulphurane ligand in the complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$. Thus in agreement with our original interpretation of infrared data, the sulphur(IV) heterocumulene is found to adopt a pseudo-olefinic ligation to the electron rich osmium centre. The nitrogen-sulphur bond length is extended to $1.61(4) \text{ \AA}$ as a result of this coordination, a value of ca 1.53 \AA being expected on the basis of comparison with the free compound CH_3NSO [$r_{\text{NS}} 1.524(4) \text{ \AA}$; electron diffraction] [7]. The complex $[\text{Pt}(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_2\text{Me}_3\text{-2,4,6})]$ has also been crystallographically characterised [8] and shows a similar lengthening [$r_{\text{NS}} = 1.63(1) \text{ \AA}$]. This is consistent with significant retrodonative bonding from the electron-rich centre to the electrophilic cumulene, a process not apparently operating as significantly in the case of $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$ [$1.520(9) \text{ \AA}$] [9] wherein the cumulene binds in a monodentate planar manner (C, Scheme 1).

The possibility of coordination isomers arises for a complex such as *trans*- $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$ in that the arrangement of chloride and nitrosyl ligands may place the nitrosyl ligand either *cis* or *trans* to the sulphur atom of the OsNS metallacycle. On the basis of ideas introduced by Ryan et al. to explain a similar situation for sulphur dioxide coordination [4], we had suggested that in the groundstate, the sulphur of the cumulene would lie *trans* to the chloride ligand, this being the weaker π -acceptor ligand [2]. We now find that this is indeed the case and anticipate that the rules developed for SO_2 coordination will be generally applicable to iminoxosulphurane ligation.

The geometry of the $\text{OsCl}(\text{NO})(\text{PPh}_3)_2$ fragment is essentially isostructural with that in the complex $[\text{OsAu}(\mu\text{-CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ [10], the N-Os-Cl angle being expanded some 14° in the latter (Scheme 3). This latter compound might be viewed as a complex between the $\text{OsCl}(\text{NO})(\text{PPh}_3)_2$ fragment and the hypothetical hetero-



Scheme 3. Coordination isomers of *trans*- $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNC}_6\text{H}_4\text{Me-4})]$.



Scheme 4. Coordination of the pseudo-olefins $\text{OS}=\text{NR}$ and $\text{I-Au}=\text{CH}_2$.

olefin I–Au=CH₂. The essentially linear *equatorial* nitrosyl ligand present in both *trigonal bipyramidal* complexes suggests a strong π -acceptor role for the ligands OSNC₆H₄Me-4 and “I–Au=CH₂” according to Hoffmann’s postulates on nitrosyl coordination [11]. The considerable lengthening of the N–S bond in the complex [OsCl(NO)(PPh₃)₂(OSNC₆H₄Me-4)] via retrodonative $d\pi$ –NS π suggests an activation of the iminoxosulphurane towards electrophilic attack and our preliminary reactivity studies support this [12]. This aspect of iminoxosulphurane coordination is currently under investigation.

References

- 1 Part IX: M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, 395 (1990) 327.
- 2 M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, 387 (1990) 323.
- 3 M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, 395 (1990) 195.
- 4 R.R. Ryan, G.J. Kubas, D.C. Moody and P.G. Eller, *Struct. Bonding*, 46 (1981) 47.
- 5 A.C. North, D.C. Phillips, and F.S. Matthews, *Acta Crystallogr. A*, 24 (1968) 351.
- 6 G.M. Sheldrick, *SHELX-76*. Program for Crystal Structure Determination, University of Cambridge, 1976.
- 7 B. Beagley, S.J. Chantrell, R.G. Kirby and D.G. Schmidling, *J. Mol. Struct.*, 25 (1975) 319.
- 8 R. Meij, D.J. Stufkens, K. Vrieze, E. Roosendaal and H. Schenk, *J. Organomet. Chem.*, 155 (1978) 323.
- 9 R. Meij, D.J. Stufkens, K. Vrieze, W. Van Gerresheim and C.H. Stam, *J. Organomet. Chem.*, 164 (1979) 353.
- 10 A.F. Hill, W.R. Roper, J.M. Waters and A.H. Wright, *J. Am. Chem. Soc.*, 105 (1983) 5939.
- 11 R. Hoffmann, M.M.L. Chen, M. Elian, A.R. Rossi and D.M.P. Mingos, *Inorg. Chem.*, 13 (1974) 2666.
- 12 M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, 395 (1990) 207.