

The coordination chemistry of iminoxosulphuranes

II*. The interaction of tosyl-NSO with osmium-alkylidene complexes

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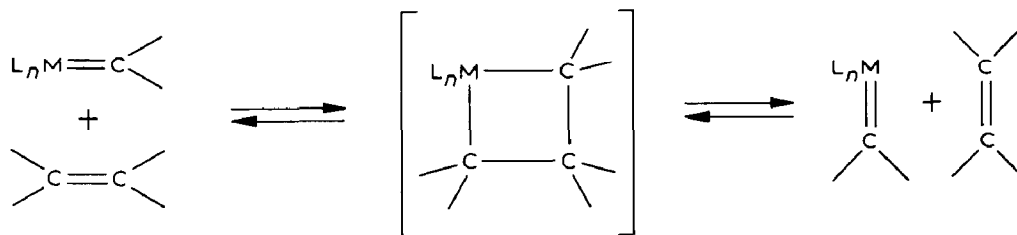
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Abstract

The low-valent osmium alkylidene complexes $\text{Os}(=\text{CHR})\text{Cl}(\text{NO})(\text{PPh}_3)_2$ ($\text{R} = \text{H}, \text{CO}_2\text{Et}$) react with 4-tosyliminoxosulphurane, $4\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{S}=\text{O}$, to give the four-membered metallacyclic complexes $\text{Os}[\text{CHRS}(=\text{N}-\text{SO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$ which provide models for intermediates proposed in the pseudo-Wittig synthesis of alkylideniminosulphuranes from iminoxosulphuranes and phosphorus ylides.

Introduction

The transition metal alkylidene catalysed metathesis of olefins is now a well understood and increasingly exploited reaction [2,3]. Fundamental to the currently accepted mechanism is the formation of a four-membered metallacycle derived from the cycloaddition of $\text{M}=\text{C}$ and $\text{C}=\text{C}$ double bonds [4].

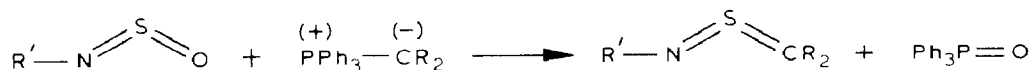


* For Part I see ref. 1.

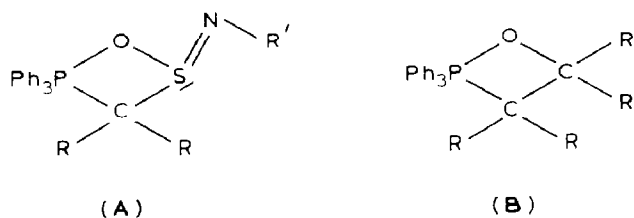
Surprisingly in view of the current interest in isolobal mappings [5], the extension of this reaction to the synthesis of more exotic ring systems, in particular inorganic analogues, has received little attention. Roper et al. [6] have described the interaction of a low-valent osmium methylene complex with sulphur dioxide to provide a complex of sulphene, $[\text{CH}_2=\text{SO}_2]$. We describe here the reaction of osmium alkylidene complexes with iminoxosulphuranes, sulphur(IV) heterocumulenes in which one oxygen atom of SO_2 has been replaced by an imino group.

Results and discussion

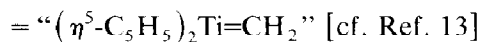
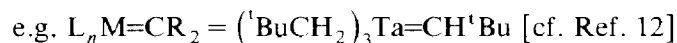
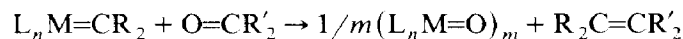
The synthesis of alkylideniminosulphuranes, $\text{R}_2\text{C}=\text{S}=\text{NR}'$, by an inorganic "pseudo-Wittig" reaction has been reported [7]:



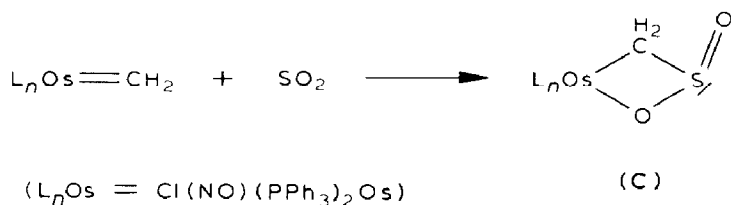
An attractive intermediate in this process is the heterocycle **A**, by analogy with the Wittig intermediate **B**.



A transition metal alkylidene complex may, depending upon the nature of metal and alkylidene substitution, display ylidic character, as, e.g., in $\text{Ta}(\text{=CH}^t\text{Bu})(\text{CH}_2\text{-}^t\text{Bu})_3$ [8], $\text{Ta}(\text{=CH}_2)(\text{CH}_3)(\eta^5\text{-C}_5\text{H}_5)_2$ [9] and $\text{Os}(\text{=CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ [10], and may act as an alkylidene transfer reagent in a manner reminiscent of the Wittig reaction [11].



These reactions presumably proceed through four-membered ring species like **A** and **B**, isolobally related to the olefin metathesis intermediate. An indication that main group multiple-bond systems could also participate in similar reactions was provided by the reaction between $\text{Os}(\text{=CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ and sulphur dioxide to give the cyclic adduct **C** [6]:



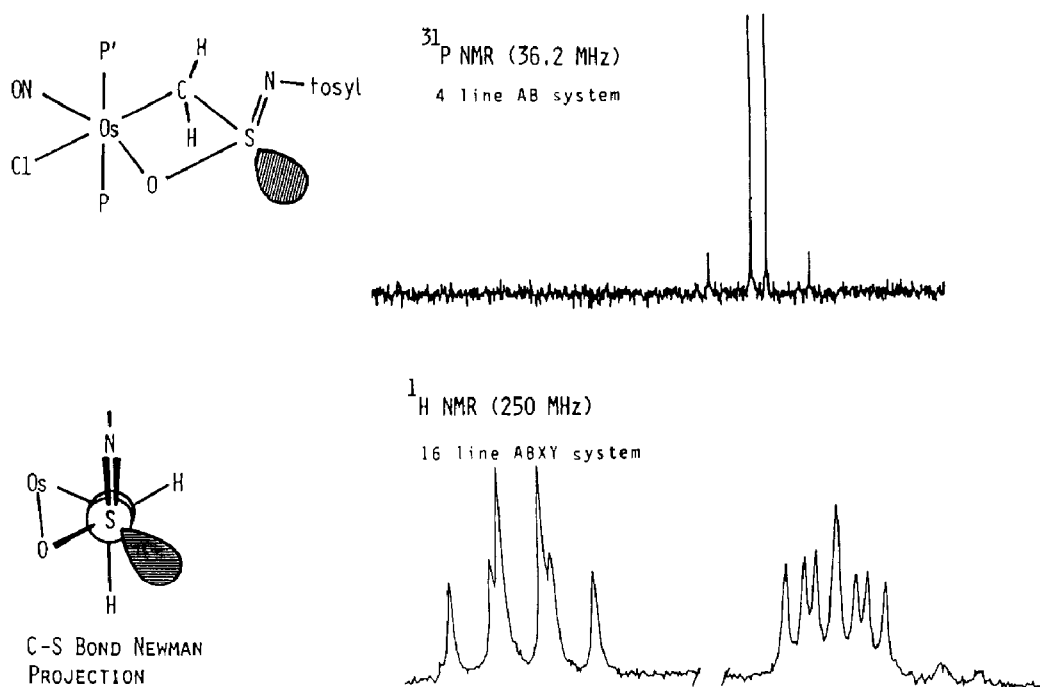
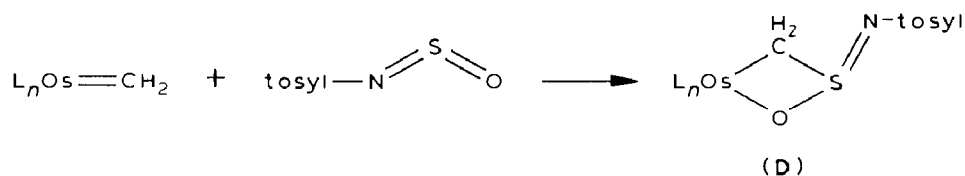


Fig. 1. ^1H and ^{31}P NMR spectra of $\text{Os}[\text{CH}_2\text{S}(=\text{N-tosyl})-\text{O}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$.

It was therefore reasonable to expect that replacing SO_2 with iminoxosulphuranes might lead to stable metallacycles isolobal with **A**. Indeed, whilst simple iminoxosulphuranes ($\text{MeC}_6\text{H}_4\text{NSO}$, $^t\text{BuNSO}$) fail to provide the desired products (**C** being the only isolated complex), the highly electrophilic tosyliminoxosulphurane, $\text{MeC}_6\text{H}_4\text{SO}_2\text{NSO}$, reacts smoothly with $\text{Os}(=\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ to provide the cycloadduct **D**:



The asymmetry of the chiral sulphur atom in **D** imposes chemical inequivalence upon both the methylenic protons and the phosphane phosphorus atoms, giving rise to an ABXY spin system, manifest in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum as an AB quartet and in the ^1H NMR spectrum as a 16-line pattern (Fig. 1).

The infrared spectrum of **D** features a strong nitrosyl stretching absorption at 1799 cm^{-1} , a value typical of divalent osmium, and two structured bands at ca. 1300 and 1144 cm^{-1} which may be assigned to the SO_2 group of the toluene sulphonyl substituent. The remaining infrared bands not attributable to ligands present in the precursor methylene complex, appearing at 1026 , 1008 and 661 cm^{-1} , are difficult to assign, and certainly do not unequivocally discriminate between alternative formulations of the adduct “ $\text{Os}(=\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2/(\text{tosyl-NSO})$ ” given by **E** and **F**. Accordingly, an X-ray diffraction study was performed on

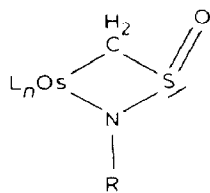
Table 1

Spectroscopic data for the osmium complexes

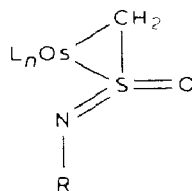
Complex R = SO ₂ C ₆ H ₄ Me-4	Infrared (Nujol) (cm ⁻¹)		NMR (ppm)	
	$\nu(\text{NO})$	Other	$\delta(^1\text{H})^a$	$\delta(^{31}\text{P}\{^1\text{H}\})^b$ [$^2J(\text{P,P})$] (Hz)
$\text{Os}[\overline{\text{CH}_2\text{S}(=\text{O})\text{O}}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$ (C) (ref. 6)	1797	1120, 1100, 709	3.01(m)	-2.2, -11.0 [382]
$\text{Os}[\overline{\text{CH}_2\text{S}(=\text{NR})\text{O}}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$ (D)	1799	1309, 1299, 1284, 1144, 1026, 1008, 661	3.77 ^c 3.16 ^d 2.37(s)	-0.4, -9.9 [369]
$\text{Os}[\overline{\text{CH}(\text{CO}_2\text{Et})\text{S}(=\text{NR})\text{O}}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$	1794	1283, 1143, 1023, 990, 813, 791	6.02(t) ^e 3.67(q) ^f 2.37(s) 1.00(t) ^f	-4.4, 0.0 [371]

^a ¹H NMR data determined from saturated solutions in CDCl₃ at 25 °C (250 MHz) relative to internal SiMe₄. ^b Determined at 25 °C in CDCl₃ solution relative to external D₃PO₄. ^c ²J(P,H) 7.2, 9.0 Hz; ²J(H,H) 8.2 Hz. ^d ³J(P,H) 3.2, 5.6 Hz; ²J(H,H) 8.2 Hz. ^e ³J(P,H) 7.3 Hz. ^f ³J(H,H) 7.2 Hz.

crystals of the adduct [14]. Unfortunately, due to a disorder problem arising from the aplanarity of the metallacyclic ring involving the large tosyl substituent, the structure determination could not be taken to completion. The preliminary results indicate, however, that the metallacycle **D** is indeed formed, and that an exocyclic tosylimino group is present.



(E)



(F)

The carboethoxymethylene complex $\text{Os}(=\text{CHCO}_2\text{Et})\text{Cl}(\text{NO})(\text{PPh}_3)_2$ [15] prepared from $\text{Os}(\text{CH}_2\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ and ethyl diazoacetate, also reacts with tosyl-iminoxosulphurane to provide an adduct with spectroscopic data similar to **D** (Table 1). Only one isomer is formed (³¹P{¹H} NMR) and, assuming steric factors to be dominant in the congested coordination sphere, an antiperiplanar disposition of tosylimino and carboethoxy groups is most likely.

Experimental

General experimental techniques and instrumentation have been described previously [1]. The compounds $\text{Os}(=\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ [10], $\text{Os}(\text{CH}_2\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ [16] and tosyliminoxosulphurane [17] were prepared by published procedures. All manipulations were carried out under purified nitrogen. Characteris-

tic data for the new cycloadducts are compiled in Table 1 in addition to those for the related complex $\text{Os}[\text{CH}_2\text{S}(=\text{O})\text{O}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$ (C) [6].

Preparation of the cycloadducts

$\text{Os}[\text{CH}_2\text{S}(=\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$ (D). A suspension of $\text{Os}(=\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ (0.40 g, 0.50 mmol) in toluene (20 cm³) was treated with a solution of tosyliminooxosulphurane in toluene (0.10 mol/l, 5.3 ml, 0.53 mmol) and stirred for 2 h. The solvent was removed in vacuo and the yellow residue recrystallised from dichloromethane/ethanol as yellow needles. Yield 0.41 g (81%). M.p. 212°C. Anal. Found: C, 51.68; N, 2.85. $\text{C}_{44}\text{H}_{39}\text{ClN}_2\text{O}_4\text{OsP}_2\text{S}_2$ calc: C, 52.25; N, 2.77%. The complex was also characterised by a partially resolved crystallographic structural determination [14].

$\text{Os}[\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)\text{S}(=\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}]\text{Cl}(\text{NO})(\text{PPh}_3)_2$. A solution of $\text{Os}[\text{CH}_2\text{CH}_2]\text{Cl}(\text{NO})(\text{PPh}_3)_2$ (0.40 g, 0.50 mmol) in tetrahydrofuran (30 ml) was treated with commercial (Fluka) ethyl diazoacetate, $\text{N}_2\text{CHCO}_2\text{C}_2\text{H}_5$ (2 drops), followed by a solution of tosyliminooxosulphurane in toluene (0.10 mol/l, 5.3 ml, 0.53 mmol) and the mixture stirred for 1 h. The solvent was then removed under reduced pressure and the bright yellow residue recrystallised from tetrahydrofuran/ethanol. Yield 0.44 g (82%). M.p. 194°C.

Acknowledgements

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