

Communications

Coupling versus Substitution of Coordinated Ethylene with Iminooxosulfanes: Crystal Structure of $[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$

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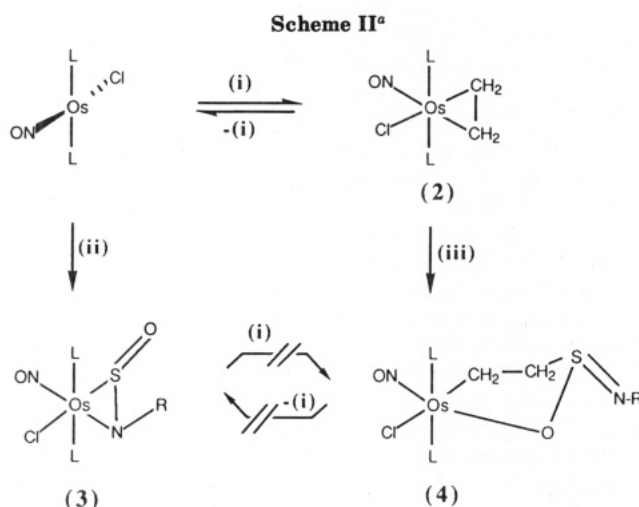
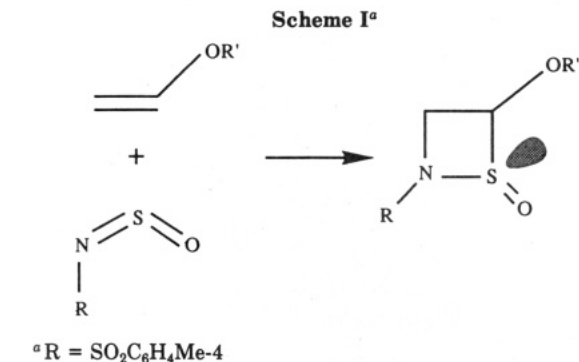
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Summary: The osmium ethylene complex $[\text{OsCl}(\text{NO})(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ reacts with (*p*-tolylsulfonyl)iminooxo- λ^4 -sulfane ($\text{O}=\text{S}=\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4}$) by either substitution of or electrophilic attack at the coordinated ethylene ligand to provide respectively $[\text{OsCl}(\text{NO})(\eta^2\text{-OSNSO}_2\text{C}_6\text{H}_4\text{Me-4})(\text{PPh}_3)_2]$ or the structurally characterized osmacycle $[\text{Os}\{\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O}\}\text{Cl}(\text{NO})(\text{PPh}_3)_2]$.

Transition-metal olefin complexes often serve as sources of coordinatively unsaturated metal-ligand fragments by virtue of the lability of the olefin ligation.¹ Alternatively, more strongly bound olefins may be induced to react with either external^{2a} or internal^{2b} substrates, thereby achieving transition-metal-mediated chemical modification of the alkene. Iminooxosulfanes, $\text{R}-\text{N}=\text{S}=\text{O}$, react with electron-rich olefins by [2 + 2] cycloaddition of carbon-carbon and nitrogen-sulfur multiple bonds³ (Scheme I).

We report herein the reaction of (*p*-tolylsulfonyl)iminooxo- λ^4 -sulfane, $\text{O}=\text{S}=\text{N}-\text{SO}_2\text{C}_6\text{H}_4\text{Me-4}$ (**1**),^{3b} with an olefin within the coordination sphere of a transition-metal complex whereby coupling of carbon-carbon and sulfur-oxygen bonds occurs, a reaction which competes with simple substitution of the olefin.

The ethylene ligand in $[\text{OsCl}(\text{NO})(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ (**2**) is labile and is readily displaced by SO_2 ,⁴ PhCCPh , $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, HCl ,⁵ CS_2 ,⁶ $\text{O}=\text{NC}_6\text{H}_5$,⁷ and diazoalkanes.⁸



^a L = PPh_3 ; R = $\text{SO}_2\text{C}_6\text{H}_4\text{Me-4}$; (i) C_2H_4 ; (ii) $\text{R}-\text{NSO}$, thf solution, 25 °C; (iii) $\text{R}-\text{NSO}$, toluene suspension, 25 °C.

Similarly, treatment of **2** with **1** in dilute tetrahydrofuran solution (0.1 mol dm^{-3} in each reagent, 25 °C) leads to quantitative formation of the complex $[\text{OsCl}(\text{NO})(\text{OSNSO}_2\text{C}_6\text{H}_4\text{Me-4})(\text{PPh}_3)_2]$ (**3**) which we have previously prepared from the reaction of $[\text{OsCl}(\text{NO})(\text{PPh}_3)_3]$ with **1**.⁴ The $-\text{N}=\text{S}=\text{O}$ cumulene in **3** is bound in a pseudoolefinic mode through the nitrogen-sulfur multiple bond (cf. ref 9) as indicated by infrared [$\nu(\text{SO})$ 1088, $\nu(\text{SN})$ 921 cm^{-1}] and $^{31}\text{P}\{^1\text{H}\}$ NMR [9.1, -15.5 ppm {AB, $J(\text{AB}) = 350 \text{ Hz}$ }] spectroscopic data.

If, however, the reaction of **1** and **2** is carried out in toluene suspension, only ca. 5% of **3** is obtained and the major product formed (90%) is a 5-membered osmacycle

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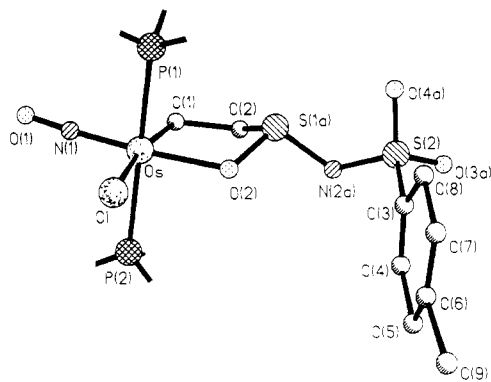


Figure 1. The molecular geometry of **4** showing the (a) arrangement of the sulfane group. Bond distances: Os–P(1), 2.447 (2); Os–P(2), 2.450 (2); Os–Cl, 2.460 (2); Os–N(1), 1.706 (9); Os–O(2), 2.035 (7); Os–C(1), 2.158 (10) Å. S(1a) is displaced from the plane defined by Os, C(1), C(2), O(2), and N(2a) by 0.69 Å while in the (b) molecule this distance is –0.23 Å.

which derives from the coupling of the osmium–alkene moiety with the sulfur–oxygen multiple bond. The complex $[\text{Os}(\text{CH}_2\text{CH}_2\text{S}(\text{NSO}_2\text{C}_6\text{H}_4\text{Me-4})\text{O})\text{Cl}(\text{NO})(\text{PPh}_3)_2]$ (**4**) is characterized by infrared activity (1805 cm^{-1}) typical of a nitrosyl ligand bound to divalent osmium¹⁰ while the osmacycle gives rise to bands at 1026, 1010, and 830 cm^{-1} . Multiplet resonances are observed in the ^1H NMR spectrum of **4** at δ 1.64 and 2.69 ppm, regions typical of transition-metal alkyls and metallacyclic alkylsulfonates.^{8b,11,12} These resonances show some simplification upon $\{^{31}\text{P}\}$ or selective $\{^1\text{H}\}$ decoupling, but not sufficient to resolve the ABCDXY spin system. The characterization of **4**¹³ included a single-crystal X-ray diffraction analysis (Figure 1) that confirmed the coordination spheres of osmium and sulfur, the metallacycle connectivity, and aplanarity.

The course of the reaction $1 + 2 \rightarrow 4$ presumably proceeds 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 cyclization, a process described previously for transition-metal alkyls.¹⁴ The specificity of this ring closure [O(2) exclusively trans to N(1)] is presumably due to steric control. Thus the for-

mation of **4** rather than **3** predominates in situations where olefin dissociation (leading to **3**) is less favored, i.e., a nondonor solvent (toluene vs tetrahydrofuran) and a high relative concentration of **1**, this being obtained when **2** is suspended rather than completely dissolved. An alternative interpretation should also be noted. The ability of nitrosyl complexes to expand their coordination spheres by bending is well documented, and such a tautomerism in **2** would, according to Hoffmann's treatment,¹⁵ provide a square-pyramidal complex with an apical nitrosyl ligand. Nucleophilic attack at osmium by the oxygen of the iminoxosulfurane moiety would therefore occur trans to the nitrosyl ligand, giving the observed stereochemistry.

The novel formation of **4** involves the combination of an olefin and iminoxosulfane within a transition-metal coordination sphere in a manner which constrains markedly with that occurring in the absence of ligation and illustrates the control of the fine balance between the processes of substitution or chemical modification of coordinated olefins.

Preliminary results with the alkyne complexes $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{PhC}\equiv\text{CR})]$ (R = H, Ph) and the allene complex $[\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{C}=\text{CH}_2)]$ suggest the formation 5-membered metallacycles similar to **4**, indicating that the reaction may have some generality.¹⁶

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An Unexpected Isotope Scrambling Process Accompanies Hydrozirconation of Styrene[†]

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Summary: Treatment of Cp_2ZrHCl with styrene leads to a mixture of terminal (85%) and internal (15%) insertion products. Attempts to prepare stereospecifically labeled deuterioorganozirconium derivatives result in scrambling of the β -positions of both isomers, yielding a statistical distribution of isotopomers. The features of this scrambling process are described, and a mechanism is proposed.

The use of NMR stereochemical probes such as $\text{Me}_3\text{CCHDCHDX}$ as a mechanistic tool was introduced to organometallic chemistry by Whitesides.¹ In subsequent application of this technique to electrophilic cleavage reactions of organozirconium compounds, it was recognized that hydrozirconation itself provides a particularly con-

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(13) Spectroscopic data for **4**: IR (Nujol) 1805 [$\nu(\text{NO})$], 1299 , 1284 , 1145 ($-\text{SO}_2$), 1026 , 1010 , 830 (metallacycle), 280 cm^{-1} [$\nu(\text{OsCl})$]; ^1H NMR (CDCl_3) δ 1.64 (m, 2 H, OsCH_2), 2.38 (s, 3 H, Me-4), 2.62–2.69 (m, 2 H, SCH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3), –5.6 (s). Crystal data for $\text{C}_{45}\text{H}_{41}\text{ClN}_2\text{O}_4\text{OsP}_2\text{S}_2$: $M_r = 1025.56$; monoclinic, $P2_1/n$; $a = 10.329$ (2), $b = 33.273$ (3), $c = 12.600$ (1) Å; $\beta = 99.76$ (1)°; $V = 4267.7$ Å³; $Z = 4$, $D_{\text{calc}} = 1.596\text{ g cm}^{-3}$; yellow prisms; $F(000) = 2048$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 34.44\text{ cm}^{-1}$; $\theta_{\text{max}} = 25^\circ$; 5111 observed reflections [$I > 3\sigma(I)$] were collected on a Nonius CAD4 diffractometer and corrected for absorption. The structure was solved by conventional Patterson and Fourier techniques and by full-matrix least-squares refinement. It was found that the SNSO_2 -component of the sulfane moiety adopted one of two alternative arrangements while common positions for atoms C(1)–C(9), O(2), and S(2) were maintained. Refinement of the occupancy factors for alternative half atoms indicated that one arrangement (a) occurred two thirds of the time, and the other arrangement (b) occurred one third of the time. Figure 1 shows arrangement a, but there is no significant chemical difference between the two arrangements. Refinement of this model converged with $R = 0.050$. The crystals contain one molecule per asymmetric unit. The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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