

Preliminary communication

AN UNUSUAL NITROSYL-DIAZOALKANE COUPLING REACTION. SYNTHESIS, STRUCTURE AND REACTIVITY OF THE ALDOXIME-DINITROGEN COMPLEX, $\text{OsCl}_2(\text{N}_2)[\text{N}(\text{OH})\text{CHCO}_2\text{Et}](\text{PPh}_3)_2$

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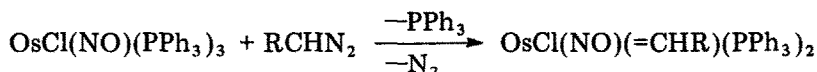
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(Received April 10th, 1984)

Summary

Reaction of $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ with $\text{IC}(\text{N}_2)\text{CO}_2\text{Et}$ gives a purple species which, on treatment with HCl , affords $\text{OsCl}_2(\text{N}_2)[\text{N}(\text{OH})\text{CHCO}_2\text{Et}](\text{PPh}_3)_2$. This aldoxime-dinitrogen complex, structurally characterised by X-ray crystallography, is thought to arise from a coupling reaction of the diazoalkane with the nitrosyl ligand in the substrate. Dehydrating agents convert the osmium-bound aldoxime to a nitrile ligand.

We recently observed the formation of osmium carbene complexes from reactions of the zerovalent compound $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ (**1**) with diazoalkanes [1,2]:

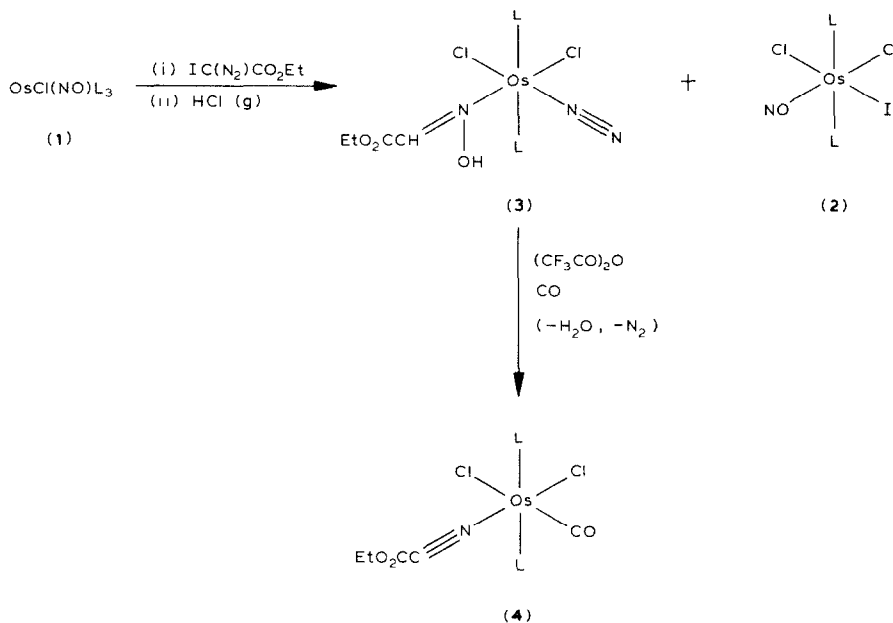


($\text{R} = \text{H}, p\text{-tolyl}, \text{CO}_2\text{Et}$)

The synthetic utility of halocarbene complexes is well established [3–5] and the potential of this diazoalkane reaction as a preparative route to these compounds was of interest. We now report that the reaction of **1** with the halogenated diazoalkane $\text{IC}(\text{N}_2)\text{CO}_2\text{Et}$ does not form an isolable halocarbene complex, but rather yields an unstable adduct that reacts with HCl to form $\text{OsCl}_2(\text{N}_2)[\text{N}(\text{OH})\text{CHCO}_2\text{Et}](\text{PPh}_3)_2$, an aldoxime-dinitrogen complex that has been structurally characterised by X-ray crystallography.

When a THF solution of **1** is treated with one molar equivalent of $\text{IC}(\text{N}_2)\text{CO}_2\text{Et}$ [6] at -78°C an intensely violet-coloured solution is formed, from which a purple solid is precipitated on the addition of pre-cooled *n*-hexane. The thermal instability of this compound has prevented its characterisation.

An orange solution is rapidly generated on treating a THF solution of the purple compound with HCl gas at -78°C . A red-brown crystalline solid is easily isolated from the reaction mixture and chromatographic separation of this material on a silica-gel column affords nearly equal quantities of $\text{OsCl}_2\text{I}(\text{NO})(\text{PPh}_3)_2$ (**2**) ($\nu(\text{NO})$ 1848 vs cm^{-1}) and $\text{OsCl}_2(\text{N}_2)[\text{N}(\text{OH})\text{CHCO}_2\text{Et}](\text{PPh}_3)_2$ (**3**), ($\nu(\text{NN})$ 2139 vs, $\nu(\text{CO})$ 1667 m, $\nu(\text{CN})$ 1600 m cm^{-1} , $\delta(\text{OH})$ 14.7 ppm, s) (see Scheme 1).



SCHEME 1. Synthesis and reactivity of $\text{OsCl}_2(\text{N}_2)[\text{N}(\text{OH})\text{CHCO}_2\text{Et}]\text{L}_2$ ($\text{L} = \text{PPh}_3$).

An X-ray crystal structure determination of **3** was undertaken to confirm the aldohime-dinitrogen formulation. Bright red **3** crystallises in the monoclinic space group $P2_1/n$, with four molecules in a unit cell with dimensions a 17.236(2), b 12.273(8), c 18.811(2) Å, β 108.46(1) $^{\circ}$. The structure was solved by conventional Patterson and difference Fourier techniques and refined by full-matrix least squares employing anisotropic thermal parameters for all atoms except phenyl carbon. Hydrogen atoms were included in calculated positions, but were not refined. The final residual, R , was 0.038 for 3156 observed [$F > 3\sigma(F)$] reflections. The molecular geometry and pertinent bond lengths and angles are depicted in Fig. 1.

The aldohime $\text{EtO}_2\text{CCH}=\text{NOH}$ acts as a neutral, monodentate ligand in this complex and is *cis* to coordinated dinitrogen. The $\text{Os}-\text{N}(1)$ bond length of 2.026(4) Å is typical for an $\text{Os}-\text{N}$ single bond while the $\text{N}(2)-\text{N}(3)$ distance at 1.063(5) Å is shorter than the $\text{N}-\text{N}$ distance in dinitrogen itself (1.0976 Å [7]). Wilkinson et al. have also recently observed very short $\text{N}-\text{N}$ bond lengths in $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$ [8].

A mechanism that accounts for the formation of **2** and **3** and proposes a reasonable structure for the initial purple compound has yet to be verified.

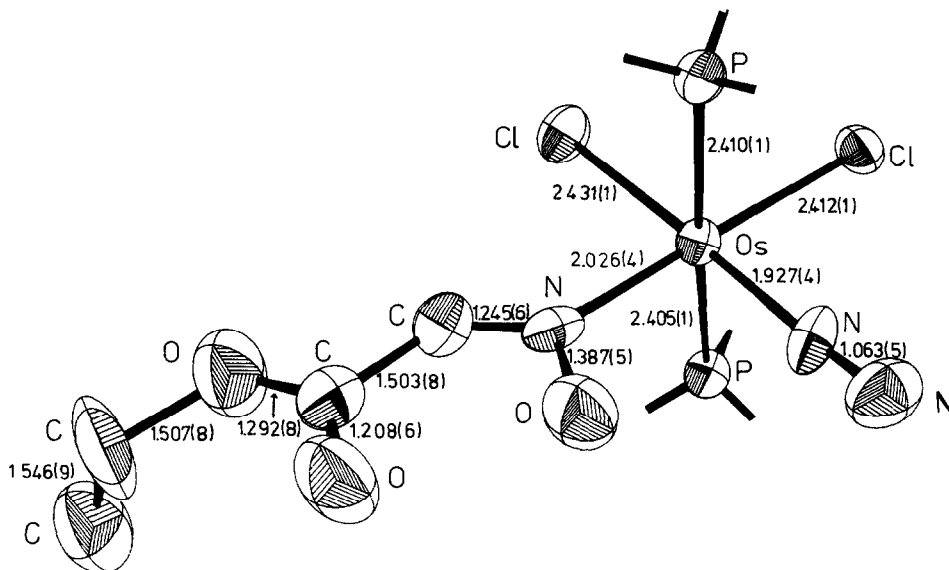
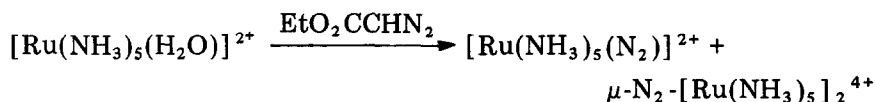


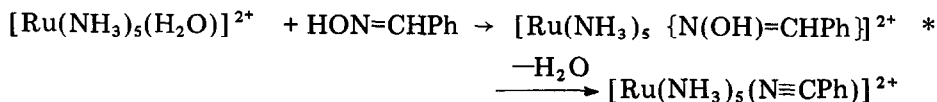
Fig. 1. Molecular structure of $\text{OsCl}_2(\text{N}_2)[\text{N}(\text{OH})\text{CHCO}_2\text{Et}](\text{PPh}_3)_2$ with phenyl groups omitted for clarity.

The aldoxime ligand is almost certainly derived from a coupling reaction between the diazoalkane (or related carbenoid fragment) and the nitrosyl ligand in the substrate. Alkylation of a nitrosyl ligand to form a transient oxime species has been proposed to explain the outcome of the reaction of $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ with PhCH_2Br in a CO atmosphere [9].

The dinitrogen ligand in **3** is derived from $\text{IC}(\text{N}_2)\text{CO}_2\text{Et}$, since the same product distribution is obtained when the reaction is performed in an argon or a nitrogen atmosphere. Transfer of diazonitrogen from diazoalkanes to metal centres has been previously observed, e.g. [10].



Schug et al. have recently reported the facile dehydration of aldoximes at ruthenium(II) centres [11]. The reaction products were ruthenium nitrile complexes and the intermediacy of ruthenium-bound oxime species was proposed, e.g.,



Complex **3** is considerably more inert than these ruthenium aldoxime species, probably because of hydrogen-bonding of the OH group to the ester function, nevertheless, **3** is dehydrated by treatment with trifluoroacetic an-

*Proposed intermediate — not detected.

hydride in a CO atmosphere. The principal product is the nitrile complex $\text{OsCl}_2(\text{CO})(\text{N}\equiv\text{CCO}_2\text{Et})(\text{PPh}_3)_2$ (4), ($\nu(\text{CN})$ 2220s, $\nu(\text{CO})$ 1952vs, $\nu(\text{CO}_2\text{Et})$ 1728s cm^{-1}) (see Scheme1).

Acknowledgement. We thank the N.Z. Universities Grants Committee for grants towards instrumental facilities and Johnson-Matthey Ltd. for a generous loan of OsO_4 .

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