

Pyridine-catalysed *cis*-*trans*-Isomerisation of a μ,η^2 -Vinyl Ligand in a Triosmium Cluster

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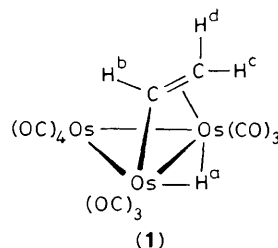
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Stereospecific *cis*-addition of $[\text{Os}_3\text{D}_2(\text{CO})_{10}]$ to C_2H_2 and of $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ to C_2D_2 gives partially deuterated samples of $[\text{Os}_3\text{H}(\mu,\eta^2\text{-CH=CH}_2)(\text{CO})_{10}]$ which undergo pyridine-catalysed *cis*-*trans*-isomerisation about the carbon-carbon double bond *via* the intermediate zwitterionic alkylidene complex $[\text{Os}_3\text{H}(\mu,\eta^1\text{-CHCH}_2\text{NC}_5\text{H}_5)(\text{CO})_{10}]$.

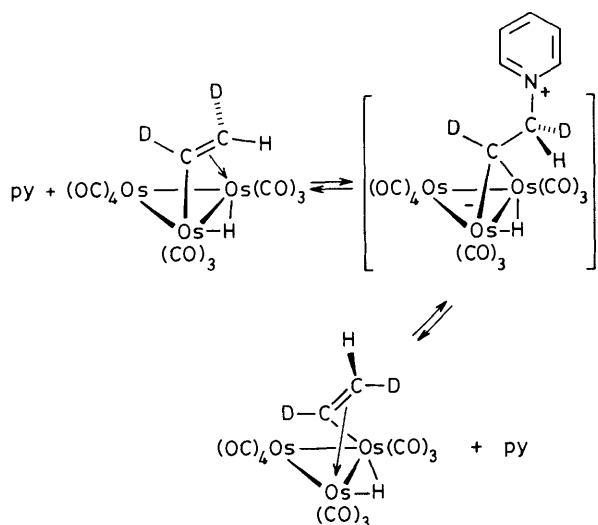
The dihydride $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ reacts at room temperature with ethyne to give a high yield of the μ,η^2 -vinyl complex $[\text{Os}_3\text{H}(\text{CH=CH}_2)(\text{CO})_{10}]$ (**1**),^{1,2} the structure of which has been determined by *X*-ray and neutron diffraction.³ Evans *et al.*⁴ reported that reactions of partially deuterated ethyne with $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ and of C_2H_2 with partially deuterated dihydrido-complex led to a mixture of isotopomers, and tentative assignments of i.r. absorptions of the eight possible isotopomers of the vinyl ligand $\text{C}_2\text{H}_{3-x}\text{D}_x$ ($x = 0, 1, 2$ or 3) were made.⁴ We have now shown by ^1H and ^2H n.m.r. methods that the vinyl product (A) from C_2D_2 (100% D) and $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ and the vinyl product (B) from C_2H_2 and $[\text{Os}_3\text{D}_2(\text{CO})_{10}]$ (80–90% D) are as expected for stereospecific *cis*-addition of Os-H or Os-D across the carbon-carbon multiple bond. Complex (**1**) gave well separated ^1H n.m.r. signals in CDCl_3 at 20 °C: δ 7.58 (H^b), 5.01 (H^d), 3.43 (H^c), and -19.39 (H^a). For product (A), ^2H n.m.r. signals

were observed at δ 7.6 and 5.0 with no signals at δ 3.5 or -19.7 p.p.m., totally consistent with the product $[\text{Os}_3\text{H}(\text{cis-CD=CHD})(\text{CO})_{10}]$. Likewise for product (B), the only ^2H n.m.r. signals were at δ 3.5 and -19.7 p.p.m. Since the reaction leading to these compounds was extremely clean, no chromatography was necessary and the only impurity was a small amount of the starting dihydride or dideuteride.

No hydrogen scrambling between the hydride and the vinyl ligand nor within the vinyl ligand was observed for ethanol-free chloroform solutions kept at room temperature in the dark for several weeks. However, when a chloroform solution



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Scheme 1

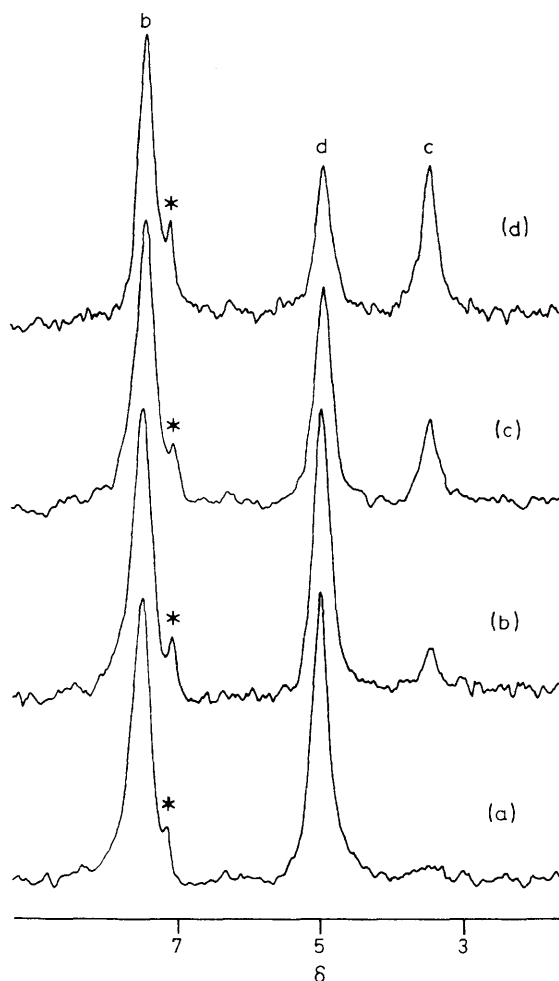


Figure 1. ^2H N.m.r. spectra of product (A) in ethanol-free chloroform before the addition of pyridine (a) and after the addition at successive intervals (b) and (c) and at equilibrium (d). (* CDCl_3 , natural abundance).

of product (A) was treated with pyridine (1 mol per mol of Os_3) the ^2H n.m.r. spectrum showed that the deuterium in site d had completely scrambled between sites c and d without there being any exchange with the other hydrogen or deuterium atoms in sites a and b. No observable reaction with pyridine (py) occurred on the addition of an excess of pyridine to a chloroform solution, on the basis of the i.r. spectrum around 2000 cm^{-1} which remains unchanged except for some broadening. The rate of scrambling between sites c and d depends upon the pyridine concentration. For a cluster concentration of $2.78 \times 10^{-2}\text{ mol dm}^{-3}$ in chloroform at 22°C , $t_{1/2}$ values for the exchange are 2.25 min (0.04 mol), 9.5 min (0.01 mol), and 30 min (0.007 mol of py per mol of Os_3) \ddagger (See Figure 1 for an example set of spectra).

We propose that reversible addition of pyridine at the β -carbon atom is the origin of the exchange (Scheme 1) even though the equilibrium position is essentially totally in favour of (1). Similar equilibria for other nucleophiles (PMe_2Ph , CN^- , or OMe^-) favour adduct formation. 5,6 Scheme 1 shows that the interchange of c and d is accompanied by an interchange of the η^1 and η^2 interactions between the metal atoms. We have, however, no way of detecting this because the vinyl ligand is known to oscillate rapidly between the metal atoms intramolecularly. 7 In one other case, $[\text{Mo}_2(\mu, \eta^2\text{-CH=CH}_2)(\text{CO})_4(\text{C}_5\text{H}_5)_2]^+$, it was shown that vinyl oscillation between the molybdenum atoms occurred at the same rate as the exchange of the terminal CH_2 hydrogen atoms. 8 Rather than occurring intramolecularly as proposed, this process could have taken place by reversible nucleophilic addition of water, perhaps, at the β -carbon atom which would be very favourable for a cationic compound. Addition of $\text{CF}_3\text{CO}_2\text{D}$ to $[\text{Mo}_2(\text{C}_2\text{H}_2)(\text{CO})_4(\text{C}_5\text{H}_5)_2]^+$ gave $[\text{Mo}_2(\mu, \eta^2\text{-CH=CHD})(\text{CF}_3\text{CO}_2)(\text{CO})_4(\text{C}_5\text{H}_5)_2]$ with ^2H distributed equally between the two terminal sites so that in the neutral case the *cis-trans*-isomerisation of the vinyl is chemically fast but not fast enough to give coalescence. 9

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\ddagger The rate of isomerisation at the very lowest pyridine concentrations decreases with time to zero so that equilibrium is not totally reached. Possibly traces of acid are generated in ethanol-free chloroform which neutralise the pyridine (only 0.0405 mg in 2.5 cm^3 , lowest concentration used).