Journal of Organometallic Chemistry, 90 (1975) C13—C16

Preliminary communication

FLUXIONAL BEHAVIOUR OF μ_3-(ETHAN-1-YL-2-YLIDYNE)-DI-μ-HYDRIDO-*triangulo*-TRIS(TRICARBONYLOSMIUM)(3 Os—Os)

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(Received February 22nd, 1975)

Summary

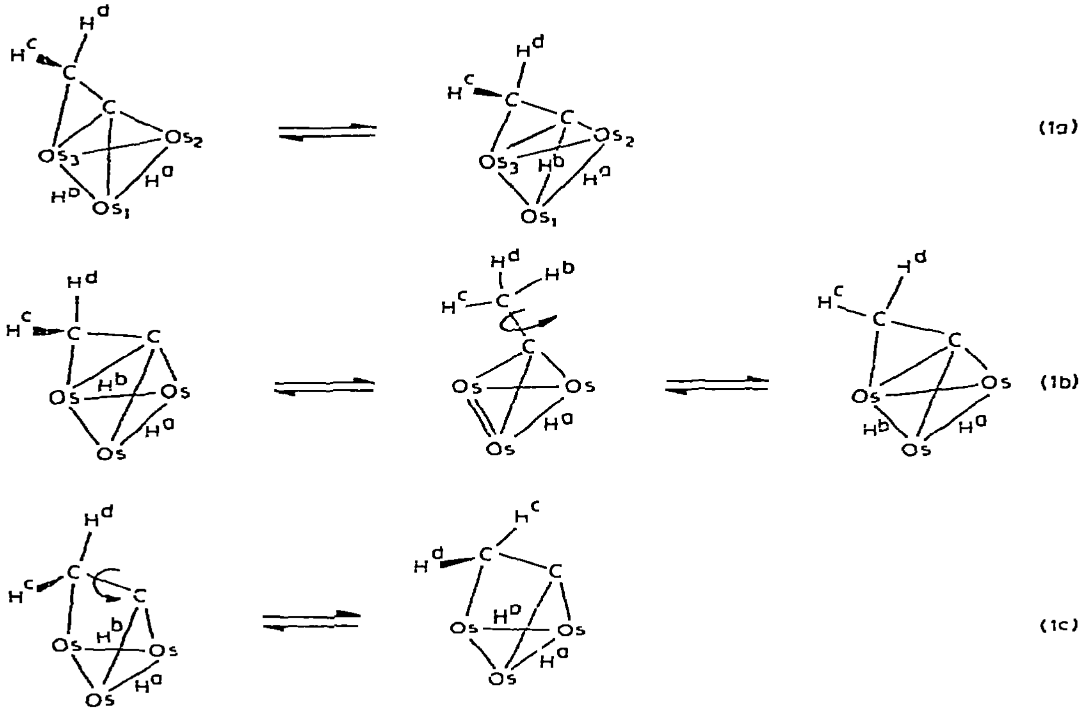
The two H-exchange phenomena observed with $H_2Os_3(CO)_9(C{=}CH_2)$ have been shown to occur by the interchange of Os—H—Os bridges.

Deeming and Underhill [1] have shown that the complex $H_2Os_3(CO)_9(C{=}CH_2)$ (I) undergoes two independent fluxional processes. First there is the interchange of the two olefinic protons H^c and H^d (Scheme 1) and secondly the interchange of the two hydrides H^a and H^b (Scheme 2). Although several mechanisms were proposed [1] to account for these phenomena, none have been substantiated by experiment. We now report experiments which support the view that each process occurs via the movement of bridging hydride ligands between the edges of the Os_3 triangle.

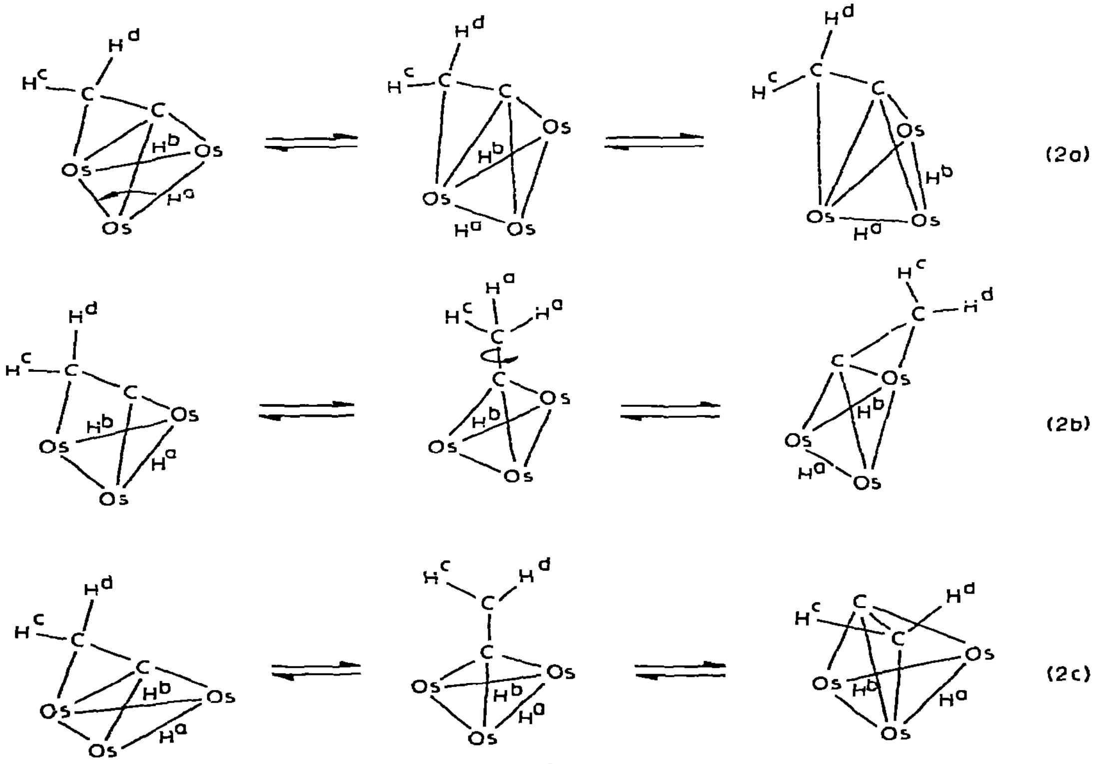
In their report, Deeming and Underhill suggested that the equilibration of the olefinic protons H^c and H^d was brought about by the process shown in Scheme 1 in which hydride transfer from one edge (Os(1)—Os(3)) of the osmium triangle to a vacant edge (Os(2)—Os(3)) occurred. This could come about by one of three processes: (*i*) the direct movement of the bridging hydrido-ligand between the two edges (eqn. 1a) (i.e. via the intermediacy of a terminal Os—H arrangement or by tunnelling); (*ii*) H-migration first to the bound $C{=}CH_2$ fragment and then to the vacant edge (eqn. 1b); or (*iii*) rotation about the olefinic C—C bond (eqn. 1c).

Similar processes may also be considered as a means of equilibration of protons H^a and H^b (eqns. 2a-2c) although the processes 1 and 2 must be mutually exclusive since two different equilibration temperatures are observed. We now report experiments which clearly show that mechanisms 1b, 1c, 2b and 2c may be excluded.

The complex $HDOs_3(CO)_9(C{=}CH_2)$ (II) has been prepared by the method outlined in Scheme 3. On the basis of ^1H NMR and mass spectroscopic evidence we have been able to demonstrate that in this complex the D-ligand is equally distributed between the two available proton sites H^a and



SCHEME 1. POSSIBLE MECHANISMS FOR $H^c \rightleftharpoons H^d$ INTERCONVERSION



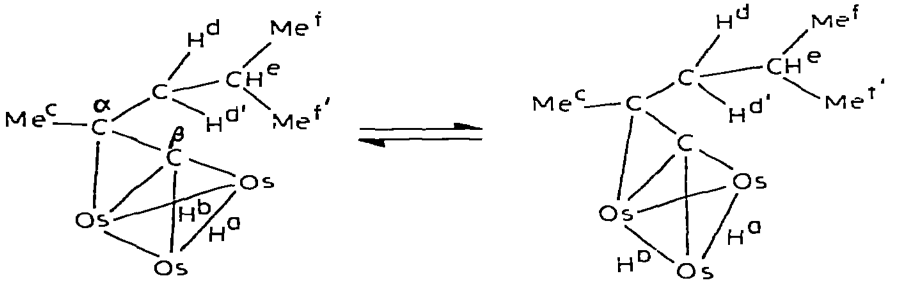
SCHEME 2. POSSIBLE MECHANISMS FOR $H^a \rightleftharpoons H^b$ INTERCONVERSION

H^b, and that no interchange of protons H^c and H^d with D occurs after several hours at 40 °C. D-scrambling amongst all from inequivalent sites occurs only on heating the complex at 100° C. The coalescence temperature for the process $H^c \rightleftharpoons H^d$ was established as 80±2° C for I and 88±2° C for II. These results clearly indicate that the exchange is an intramolecular process and rule out pathway 1b which requires instantaneous S-scrambling at temperatures well below 100° C.

$$H_2Os_3(CO)_9(C{=}CH_2) \xrightarrow{CF_3CO_2{}^2H} H_2DOs_3(CO)_9(C{=}CH_2)^+ \xrightarrow{{}^2H_2O} HDOs_3(CO)_9(C{=}CH_2) + I$$

SCHEME 3. PREPARATION OF $HDOs_3(CO)_9(C{=}CH_2)$

Process 1c which involves rotation about the C—C axis would lead to H^c and H^d interconversion but would necessitate Os(3)—C bond cleavage. This possibility cannot be excluded directly from studies on I but may be excluded from studies of complex $H_2Os_3(CO)_9[C{=}C(Me)CH_2CHMe_2]$ (III) which is structurally similar and may be prepared from the reaction of $Os_3(CO)_{12}$ with $H_2C{=}C(Me)CH_2CHMe_2$. The ^1H NMR of III in $CDCl_3$ at 60° C shows the following features: τ7.52, m, $1H^e$; τ7.54, s, $3H^c$; τ7.60, m, $H^d + H^{d'}$; τ9.05, d, $3H^f$; J_{de} = 6.5 Hz, τ9.08, d, $3H^{f'}$, J_{ef} = 6.5 Hz; and τ29.60, s, $H^a + H^b$. At —40° C the singlet at τ29.60 separates into singlets at τ28.50 ($1H^b$) and τ30.80 ($1H^a$) as expected for the two inequivalent hydride positions. The two diastereomeric forms IIIa and IIIb which arise from the presence of the two asymmetric carbon atoms C^α and C^β, are clearly apparent at —60° when two methyl resonances (H^f and $H^{f'}$) are observed at τ7.48, s, 1.5H and τ7.68, s, 1.5H. Above —40° C the isomers IIIa and IIIb undergo interconversion by hydride transfer (Os(1)—H^b—Os(3)$\rightleftharpoons$Os(2)—H^b—Os(3)) which destroys the chirality at C^β. However, the observed diastereotopic splitting (≈ 3Hz at 100 MHz) in the isopropyl methyl (H^f and $H^{f'}$) remains up to +60° C (the highest temperature studied). Thus chirality at C^α is retained. This result establishes that the Os—C^α bond is intact under the conditions of H-interchange, clearly demonstrating that the bond-breaking mechanism 1c is not operative. This result also establishes that any mechanism involving Os—C bond cleavage cannot be operative under conditions of total H-fluxionality thus ruling out the possibility that interconversion $H^a \rightleftharpoons H^b$ can occur via either mechanism 2b or 2c.



(IIIa) (IIIb)

These observations verify the initial prediction [1] that both $H^c \rightleftharpoons H^d$ and $H^a \rightleftharpoons H^b$ interconversion occur directly by hydride migration from one edge of the metal triangle to another.

We thank the SRC for financial support and Johnson Matthey and Co. Ltd. for their generous loan of osmium tetroxide.

Reference

1 A.J. Deeming and M. Underhill, J. Chem. Soc., (1974) 1415.