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Preliminary communication

FLUXIONAL BEHAVIOUR OF $H_2M_3(CO)_9(RR'C_2)$ (M = Ru, Os)

JOHN EVANS, BRIAN F.G. JOHNSON*, JACK LEWIS and TREVOR W. MATHESON
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)
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Summary

NMR studies on $H_2M_3(CO)_9(RR'C_2)$ (M = Ru, Os) have shown that at least three separate fluxional processes are occurring; a mechanism involving olefin rotation has to be considered.

Variable temperature ^{13}C and ^{1}H NMR studies on the products of the reaction between $M_3(CO)_{12}$ (M = Ru, Os) and olefins have shown that a minimum of three separate fluxional processes are occurring; namely restricted hydride exchange, total hydride exchange and "localised" carbonyl scrambling (Fig. 2). These compounds, of general formula $H_2M_3(CO)_9(RR'C_2)$ [1-4] exist in two distinct forms A and B (Fig. 1) distinguished by the mode of bonding of the organic moiety.

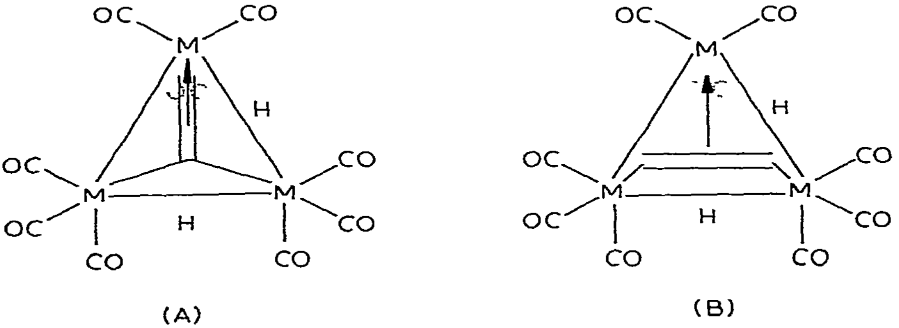

Fig.1.

Previous studies [1,2] have shown that two separate H-migration mechanisms operate in A and B (mechanisms 1 and 2, Fig. 2) and we have confirmed this by ^{13}C NMR. However, another mechanism, requiring

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[*] To whom correspondence should be addressed.

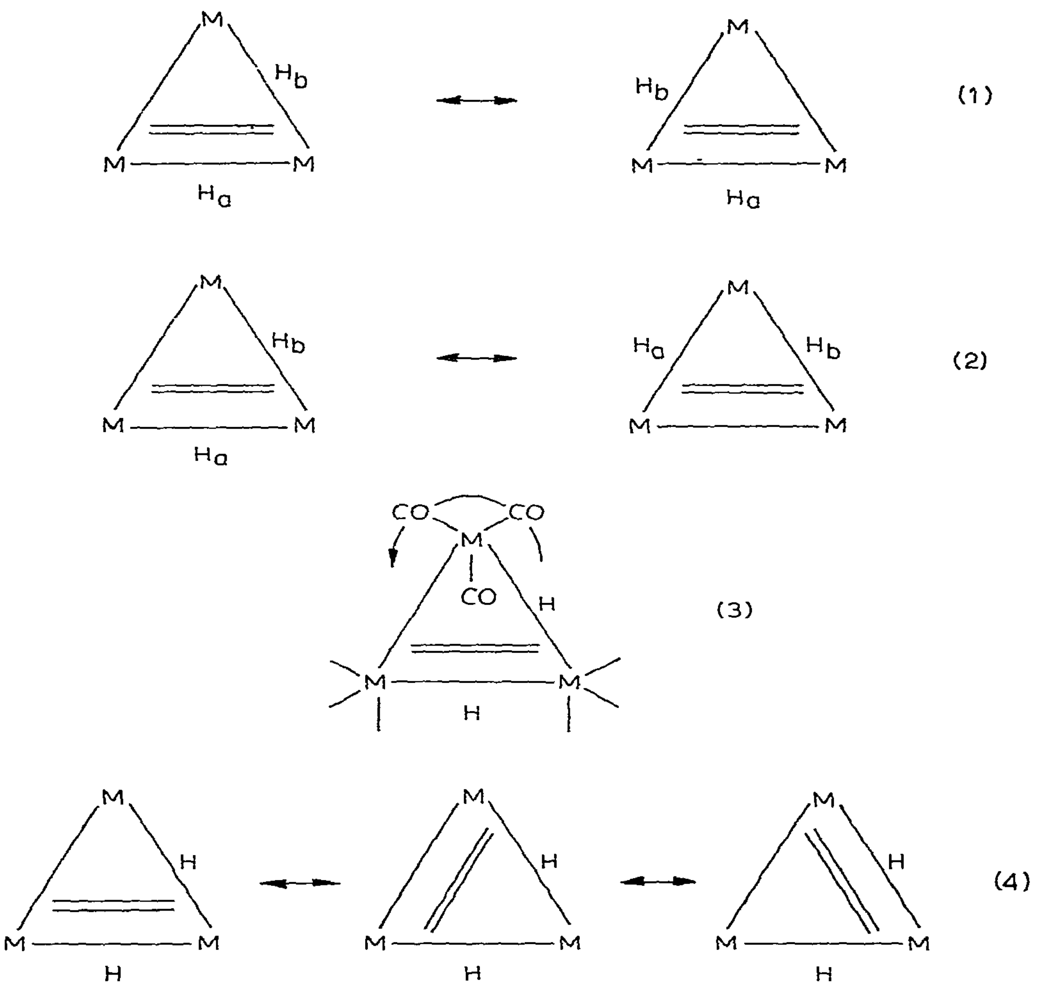

Fig.2.

olefin rotation, must be considered in B. Processes of this sort have previously been suggested for $H_2Ru_3(CO)_9(C_8H_{12})$ [1] and $Os_3(C_6H_4)(AsMe_2)_2$-$(CO)_7$ [5].

Complexes of type A (M = Os, C=C(R)(R′) = C=C(H)(H), $C=C(CH_3)$-$[CH_2CH(CH_3)_2]$) and B (M = Ru, RC=CR = cyclooctene, M = Os, RC=CR = cyclooctene, $CH_3C=CH_3$) were prepared from $M_3(CO)_{12}$ (enriched with ^{13}CO to ~50%) and the appropriate olefin. Slow exchange ^{13}C NMR spectra of the carbonyl region were obtained for all samples other than H_2Ru_3-$(CO)_9(C_8H_{12})$ and showed the required nine different carbonyl environments (confirming the asymmetric hydride assignment as in Fig. 1) except for $H_2Os_3(CO)_9\{C=C(CH_3)[CH_2CH(CH_3)_2]\}$ when sixteen lines due to the presence of geometric isomers occur. On warming the solutions a marked difference was observed in the exchange processes operating in the two different structural forms A and B.

On warming $H_2Os_3(CO)_9[C=C(H)(H)]$ to +100 °C all but one of the carbonyl resonances observed in the slow exchange limit broadened. This is consistent with mechanism 1 (Fig. 2). A similar mechanism would account for the observed collapse for $H_2Os_3(CO)_9\{C{=}C(CH_3)[CH_2CH(CH_3)_2]\}$ at —40 °C of the 16 resonance lines to nine on warming from the "frozen" limit. Higher temperatures resulted in coalescence of some of the remaining signals, presumably through "localized" exchange as previously observed [6,7]. In neither of these compounds was the fast exchange limit reached.

Scrambling by mechanism 1 (Fig. 2) was the initial step in the carbonyl exchange observed for $H_2Os_3(CO)_9(C_8H_{12})$ and $H_2Os_3(CO)_9(CH_3C_2CH_3)$ and, by analogy, $H_2Ru_3(CO)_9(C_8H_{12})$ (although a slow exchange spectrum could not be obtained for this last named complex) as this resulted in a collapse of the nine line spectrum to five resonances. Further warming led to a four line spectrum (intensity ratio 2/2/2/3) for both of the cyclooctene complexes; these results can be accommodated by mechanism 3 (Fig. 2) in which localized scrambling occurs at one osmium, the unique $Os(CO)_3$. For $H_2Os_3(CO)_9(CH_3C_2CH_3)$ a two line spectrum (ratio 3/6) was obtained. This can be explained in terms of mechanism 3, with localized carbonyl scrambling at all osmiums or by olefin rotation above the metal triangle (mechanism 4). Finally, the fast exchange limit, giving one resonance, was reached for the three complexes; as a result of "total" carbonyl exchange as found for many other complexes and/or localized scrambling accompanied by olefin rotation. Olefin rotation will also lead to the observed $H_A \leftrightarrow H_B$ interconversion as shown in mechanism 2. Indeed, by comparing the values of the free energies calculated from the ^{13}C data with those from the ^1H NMR data we have shown that in the osmium complexes of type B the highest energy carbonyl exchange process and the intramolecular hydride exchange have similar energies*.

Therefore, in the temperature range studied, it is apparent that while a bond-breaking olefin rotation mechanism must be considered for complexes B it does not occur in the alternative bonding arrangement A and in both forms a number of exchange mechanisms are operating simultaneoulsy.

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*For $H_2Os_3(CO)_9(CH_3C_2CH_3)$: ^{13}C NMR $\Delta G^{\neq} = 13$ kcal/mole; ^1H NMR $\Delta G^{\neq} = 12.3$ kcal/mole.
For $H_2Os_3(CO)_9(C_8H_{12})$: ^{13}C NMR $\Delta G^{\neq} = 17$ kcal/mole; ^1H NMR $\Delta G^{\neq} = 16.9$ kcal/mole.