

## Preliminary communication

### Fluxional behaviour of $\pi$ -bonded acetylenes

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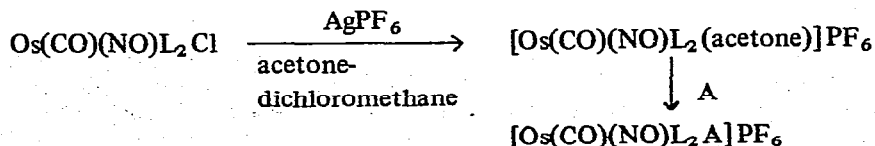
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#### SUMMARY

Some cationic five coordinate complexes of formula  $[\text{Os}(\text{CO})(\text{NO})\text{L}_2\text{A}]\text{PF}_6$  (L = tertiary phosphine, A = an acetylene) have been prepared by reaction of the appropriate acetylene with  $[\text{Os}(\text{CO})(\text{NO})\text{L}_2(\text{acetone})]\text{PF}_6$ ; the variable temperature  $^1\text{H}$  NMR spectra of some of these indicate that the coordinated  $\pi$ -acetylene undergoes fluxional behaviour.

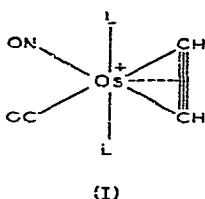
We have previously reported<sup>1</sup> that cationic ethylene complexes of the type  $[\text{Os}(\text{CO})(\text{NO})\text{L}_2\text{C}_2\text{H}_4]\text{PF}_6$  may be prepared from the reaction of  $\text{Os}(\text{CO})(\text{NO})\text{L}_2\text{Cl}$  with  $\text{AgPF}_6$  in the presence of ethylene. A major feature of interest in these complexes is the fluxional behaviour which they exhibit; behaviour which may be interpreted in terms of ethylene rotation about the osmium–ethylene bond. This paper reports a series of cationic acetylene complexes  $[\text{Os}(\text{CO})(\text{NO})\text{L}_2\text{A}]\text{PF}_6$  (L =  $\text{Ph}_3\text{P}$ , A =  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{Ph}_2$ ,  $\text{C}_2\text{HPh}$ ,  $\text{C}_2(\text{COOMe})_2$  and L =  $\text{Cy}_3\text{P}$ , A =  $\text{C}_2\text{H}_2$ ) which also display fluxional properties consistent with rotation about the osmium–acetylene axis. Rather little information is available on such behaviour, and only one previous example has been reported<sup>2</sup>.

An acetone/dichloromethane solution of  $\text{Os}(\text{CO})(\text{NO})\text{L}_2\text{Cl}$  reacts with  $\text{AgPF}_6$  and a range of acetylenes to give products containing the complex acetylene cation  $[\text{Os}(\text{CO})(\text{NO})\text{L}_2\text{A}]^+$  according to the scheme



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The stereochemistry of these complex cations is expected to be closely related to that of  $[\text{Ir}(\text{CO})_2 \text{L}_2 \{ \text{C}_2(\text{CO}_2 \text{Me})_2 \}]^+$ ; that is, to possess approximately trigonal bipyramidal geometry with apical phosphine ligands and one of the three equatorial sites occupied by the coordinated acetylene ligand<sup>4</sup> as in (I). The low-temperature limiting  $^1\text{H}$  NMR spectra are consistent with this stereochemistry. For example, the complex  $\text{L} = \text{Cy}_3\text{P}$ ,  $\text{A} = \text{C}_2\text{H}_2$  exhibited two "acetylenic" peaks at  $\tau$  1.62 and 4.25 (at  $-30^\circ$ ) in a 1/1 ratio. The higher field resonance appeared as a triplet ( $J(\text{P}-\text{H})$  2.5 Hz) indicating that the two phosphines are in identical environments. In the  $^1\text{H}$  NMR spectrum of the complex  $\text{L} = \text{Ph}_3\text{P}$ ,  $\text{A} = \text{C}_2\text{HPh}$  at  $0^\circ$  two resonances of approximately equal intensity were observed at  $\tau$  1.70 (singlet) and  $\tau$  4.44 (triplet,  $J(\text{P}-\text{H})$  2 Hz). The ability to see two signals is consistent with the presence of the two possible ground-state isomers ( $\text{H}$  *trans* to CO and  $\text{H}$  *trans* to NO) and provides further evidence to support the assigned stereochemistry.



Variable temperature  $^1\text{H}$  NMR of certain of the complexes ( $\text{CD}_2\text{Cl}_2$ ) exhibit interesting features. The spectrum of  $[\text{Os}(\text{CO})(\text{NO})(\text{Cy}_3\text{P})_2\text{C}_2\text{H}_2]\text{PF}_6$  is temperature dependent and on raising the temperature ( $-30^\circ \rightarrow +70^\circ$ ) the two peaks initially observed at  $\tau$  1.62 and 4.25 broaden and eventually collapse until at  $+70^\circ$  a broad peak centred at  $\tau$  2.15 is seen. Above this temperature decomposition is rapid. However, the high temperature limit is observed for the complex  $\text{L} = \text{Ph}_3\text{P}$ ,  $\text{A} = \text{C}_2\text{H}_2$  when a sharp singlet at  $\tau$  3.52 is apparent. On cooling this collapses and at  $-75^\circ$  a resonance at  $\tau$  5.11 is observed (the expected lower field resonance is not observed since its predicted position falls under the phenyl resonance of the phosphine ligand.)

The rate of the exchange process is apparently susceptible to changes in the substituents on the acetylene. Thus the bulky electronegative ester groups in the  $\text{C}_2(\text{COOMe})_2$  complex decrease the rate of site exchange and even at  $+35^\circ$  two methyl resonances are seen at  $\tau$  6.50 and 6.69. Values for  $\Delta G_{\text{TC}}^\ddagger$  ( $11.5 \pm 0.2$  for  $\text{L} = \text{Ph}_3\text{P}$ ,  $\text{A} = \text{C}_2\text{H}_2$  and  $14.4 \pm 0.5$  kcal/mole for  $\text{L} = \text{Cy}_3\text{P}$ ,  $\text{A} = \text{C}_2\text{H}_2$ ), calculated using an approximate coalescence formula<sup>3</sup>, also show a dependence on the nature of the other ligands.

Although these data are consistent with the proposed rotation mechanism absolute proof must await the results of further studies currently in progress, e.g. the observation of spin-spin coupling between acetylene and other ligands at the high temperature limit. However, it would appear that the process is almost certainly intramolecular, since the acetylenes are not readily displaced by CO nor has it been possible to detect even traces of free acetylene in the low temperature spectra.

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