The Mode of Olefin Rotation in $[Os(CO)NO(C_2H_4)(PPh_3)_2]PF_6$

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Summary The first direct experimental evidence that indicates the axis and mode of rotation of co-ordinated olefin molecules has been obtained from variable temperature ^1H and ^{13}C n.m.r. studies on the complex $[Os(CO)NO(C_2H_4)(PPh_3)_2]PF_6$.

THE phenomenon of olefin rotation was first suggested by Cramer[1] who demonstrated that the temperature dependent ^1H n.m.r. spectrum of $(C_2H_4)_2RhCp$ could best be interpreted on the basis of such behaviour. By a process of elimination and as a result of further experiments he was able to show that all other conceivable mechanisms for the observed proton equilibration could be disregarded. Two possible modes of rotation [Figure 1(i) and (ii)] satisfy the variable temperature n.m.r. data obtained on all olefin complexes that have so far been reported and Cramer[1] and

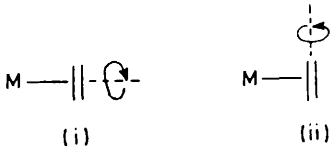

FIGURE 1

others[2] have only been able to eliminate the rotational mode shown in Figure 1(ii) by invoking intuitive arguments based on bonding models derived from the Dewar–Chatt MO description.

We report the preparation (see Scheme) and study of an ethylene complex in which it has been possible to produce a ground state configuration where each *end* of the co-ordinated olefin is in a different chemical environment† (Figure 2). From such a ground-state geometry clear distinction between the two rotational modes may be made.

$$\mathrm{Os(CO)NO(PPh_3)_2Cl} \xrightarrow[\mathrm{CH_2Cl_2/acetone}]{\mathrm{AgPF_6}} \text{intermediate } \{[\mathrm{Os(CO)NO(acetone)(PPh_3)_2}]\mathrm{PF_6}\,?\}$$

$$\xrightarrow{\mathrm{C_2H_4}} [\mathrm{Os(CO)NO(C_2H_4)(PPh_3)_2}]\mathrm{PF_6}$$

SCHEME

The ^{13}C n.m.r. spectrum of $[\mathrm{Os(CO)NO(C_2H_4)(PPh_3)_2}]\mathrm{PF_6}$ in $\mathrm{CD_2Cl_2}$ or $\mathrm{(CD_3)_2CO}$ at +20 °C shows a single resonance at 49·3 p.p.m.‡ in which ^{31}P coupling has not been resolved. On cooling to −80 °C two resonances of equal intensity are seen in $\mathrm{(CD_3)_2CO}$ at 54·4 p.p.m. and 43·6 p.p.m. the former being masked by solvent absorptions in $\mathrm{CD_2Cl_2}$ solution. These results are taken to indicate that the ethylene molecule does occupy an *in plane* orientation in the *pseudo* octahedral ground state geometry (as drawn). At −90 °C the ^{1}H n.m.r. spectrum of this complex in $\mathrm{CD_2Cl_2}$ + 10% $\mathrm{CF_2Cl_2}$ also shows two resonances of equal intensity (4H) and these are centred at τ 6·51 and 8·77 (taking the $\mathrm{CH_2Cl_2}$ resonance position as τ 4·65); the fully resolved low temperature limiting spectrum has not been attained. On warming coalescence occurs at −65 °C and at the high temperature limit a single 1:2:1 triplet is resolved at τ 7·38 with J_{PH} 5·3 Hz. Based on the ground state configuration in Figure 2 coalescence by rotation can only occur in the ^{13}C and ^{1}H spectra if the metal–olefin bond *is* the rotational axis [Figure 1 (i)]. Since ^{31}P coupling is maintained in the proton spectrum at the high temperature limit an exchange mechanism cannot be regarded as playing a significant part in the proton equilibration.

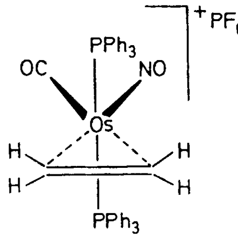

FIGURE 2

The value of $\Delta G^{\ddagger}_{T_c}$ (9·5 kcal mol^{-1}) obtained[4] for the rotational process is lower than that found for square planar platinum(II) complexes[2] and the factors responsible for this difference will be discussed in a more detailed report.

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† It has been assumed that the basic structure of this molecule is a trigonal bipyramid with axial phosphine ligands. The recently reported crystal structure of $[\mathrm{Os(CO)_2NO(PPh_3)_2}]^+$ would support this view.[3] Use of alternative structures however, which satisfy both the i.r. and n.m.r. data, also enables elucidation of the rotational mode.

‡ Measured as p.p.m. downfield from external TMS relative to a solvent deuterium lock. A triplet resonance at 182·9 p.p.m. with J_{PC} 8 Hz has been attributed to the carbon monoxide group.

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