Structure and Dynamical Properties of $Rh_4(CO)_{12}$ in Solution: ^{13}C Nuclear Magnetic Resonance Study

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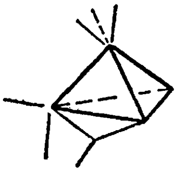
Summary $Rh_4(CO)_{12}$ has been shown by ^{13}C n.m.r. to have the same structure in solution as in the crystal, and the changes in line shape as a function of temperature are consistent with a CO scrambling mechanism which has the fully symmetric (T_d) structure as an intermediate.

THE structure of $Rh_4(CO)_{12}$ in the crystal has been demonstrated to possess idealised C_{3v} symmetry (**1**).[1] While the i.r. spectrum[2] of $Rh_4(CO)_{12}$ when compared with that of $Co_4(CO)_{12}$ strongly suggests that the C_{3v} structure persists in solution, conclusive evidence has been lacking. A carbon-13 n.m.r. study from about 0° to +60° showed that rapid intramolecular equilibration of the carbonyl groups occurs,[3] as previously postulated,[4] but fell short of affording either structure proof or direct evidence for the mechanism of the scrambling of CO groups. We now report a low temperature carbon-13 n.m.r. investigation yielding direct information on both points.

Spectra of 30 mg of a 70% ^{13}C enriched sample of the cluster were obtained in CD_2Cl_2 solution, with the addition of 0·04 M $Cr(acac)_3$ as a relaxation reagent.[5] The limiting low temperature spectrum was observed at — 65°, exhibiting four resonances of equal intensity: (downfield of Me_4Si) −228·8 (d, $^{1}J_{Rh-C}$ 35 Hz, $\nu_{\frac{1}{2}}$ 21 Hz), −183·4 (d, $^{1}J_{Rh-C}$ 75 Hz, $\nu_{\frac{1}{2}}$ 14 Hz), −181·8 (d, $^{1}J_{Rh-C}$ 64 Hz, $\nu_{\frac{1}{2}}$ 24 Hz), and −175·5 (d, $^{1}J_{Rh-C}$ 62 Hz, $\nu_{\frac{1}{2}}$ 22 Hz). Since these intensities should reflect the relative abundances of the carbon environments, this spectrum is entirely compatible with structure (**1**). As observed for $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ (**2**),[6] the lowest field signal is due to the bridging carbonyl groups. In that study it was found that, since $^{2}J_{Rh-Rh-C}$ and $^{1}J_{Rh-Rh}$ are small, at high enrichement levels the linewidths of the carbonyl signals are governed by $^{2}J_{C-Rh-C}$. The apical carbonyl groups in (**1**) participate in a simpler local spin system (AA′A″X) than either of the two basal terminal environments (ABMM′X). They should, therefore, possess a smaller linewidth. On this basis we conclude that the signal at −183·4 results from the carbonyl groups attached to the unique rhodium atom.



(**1**)

Spectra were recorded at temperature intervals up to and above the coalescence temperature of −5 ± 5°. The coalesced signal appears at −190·7. The weighted average coupling constants (J_{Rh-C}) and chemical shifts agree satisfactorily with those observed in the high temperature limit.[3]

The collapse of the slow exchange spectrum is substantially uniform. Within the limitations imposed by the signal to noise level and the closeness of all the terminal CO resonances, there is no indication of any site-selectivity in the scrambling process. The results are therefore consistent with the mechanism previously suggested.[3]

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