Carbonyl Intra-exchange in Hexa- and Hepta-rhodium Carbonyl Clusters

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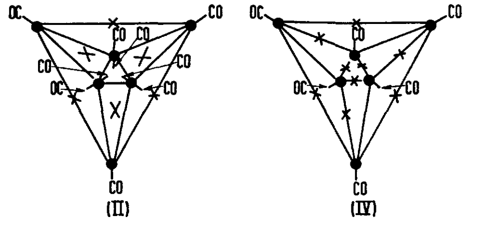
Summary ^{13}C n.m.r. studies on the three structurally related carbonyl clusters $[Rh_6(CO)_{16}]$, $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$ show that $[Rh_6(CO)_{16}]$ is not fluxional at +70°, $[Rh_6(CO)_{15}]^{2-}$ readily undergoes intra-carbonyl exchange at −70° and $[Rh_7(CO)_{16}]^{3-}$ is not fluxional at −70° but undergoes partial intra-exchange at +25°.

^{13}C N.M.R. MEASUREMENTS on rhodium carbonyl clusters have recently shown that carbonyl scrambling can occur *via* interconversions of terminal and edge-bridging carbonyl groups.[1] We now report on the fluxionality, from ^{13}C n.m.r. studies, of three structurally related carbonyl clusters $[Rh_6(CO)_{16}]$ (I), $[Rh_6(CO)_{15}]^{2-}$ (II) and $[Rh_7(CO)_{16}]^{3-}$ (III), (Scheme).

The structure of $[Rh_6(CO)_{16}]$, (I), is based on an octahedron containing 6 equivalent rhodium atoms and to each rhodium atom is bonded two equivalent terminal carbonyls and two equivalent face-bridging carbonyls.[2] Despite its low solubility, the ^{13}C n.m.r. spectrum of $[Rh_6(CO)_{16}]$ (33·6% ^{13}CO) has been obtained at +70° in $CDCl_3$ solution and is entirely consistent with the solid-state structure. The 12 equivalent terminal carbonyls appear as a doublet (180·1 p.p.m., J 70·2 ± 6 Hz) and the 4 equivalent face-bridging carbonyls as a quartet, (231·5 p.p.m., J 24·4 ± 6 Hz).

The structure of $[Rh_6(CO)_{15}]^{2-}$† is derived from $[Rh_6(CO)_{16}]$ by removal of one face-bridging carbonyl, which allows one terminal carbonyl group per rhodium atom on that unoccupied face to occupy each edge of that face (Scheme). An increase in non-terminal carbonyls with increasing negative charge on the cluster is general and, for structures based on Rh_6 octahedra,[2,3] the 'average charge'



SCHEME. Schematic representation (down a 3-fold axis) of the structures of $[Rh_6(CO)_{16}]$ (I), $[Rh_6(CO)_{15}]^{2-}$ (II) and $[Rh_7(CO)_{16}]^{3-}$ (III). ● = Rh, $\overset{\vee}{\underset{\wedge}{-}}$ = edge-bridging CO; × = face-bridging CO.

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† In view of the i.r. spectral similarity,[4] $[Rh_6(CO)_{15}]^{2-}$ is assumed to be isostructural with $Cs_2[Co_6(CO)_{15}]$, which has been determined by X-ray crystal structure analysis.[5] However, because we have been unable to obtain good crystals of $Cs_2[Rh_6(CO)_{15}]$ and because both $(PPh_4)_2[Rh_6(CO)_{15}]$ and $(PPh_4)_2[Co_6(CO)_{15}]$ give triclinic crystals, it has not yet been possible to prove that the cobalt and rhodium analogues are isomorphous.[6]

per carbonyl group (i.e. the total charge on the cluster/number of carbonyls), Δ, and the % terminal carbonyls, TCO, are related linearly by TCO = $(-111{\cdot}5 \pm 2{\cdot}3)\Delta + (74{\cdot}66 \pm 0{\cdot}37)$. The ^{13}C n.m.r. spectrum of $(PPh_4)_2[Rh_6(CO)_{15}]$ (*ca.* 50% ^{13}CO) in perdeuterio-acetone at −70° is a symmetrical septet (209·2 p.p.m.) due to rapid carbonyl intra-exchange. The spacing between the lines is 13·9 ±0·5 Hz which is, as expected, approximately one sixth the value found for terminal rhodium-carbonyl coupling constants.[7] $W_{\frac{1}{2}}$ for the 5 most intense lines is 1·2 Hz which is the same as the natural line-width for $[Rh(^{12}CO)_3(^{13}CO)]^-$ at −70°.[8]

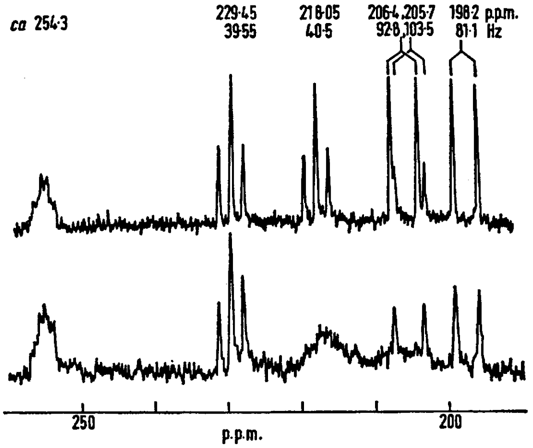

FIGURE 1. ^{13}C n.m.r. spectrum of $(NEt_4)_3[Rh_7(CO)_{16}]$ (*ca.* 47% ^{13}CO) in CD_3CN solution containing 0·01M $Cr(acac)_3$, (a) −70°, (b) +25°.

The structure of $[Rh_7(CO)_{16}]^{3-}$ [9] is derived from $[Rh_6(CO)_{15}]^{2-}$ by capping the face, which contains 3 rhodium atoms each with 2 terminal carbonyls, with a rhodium-terminal carbonyl group and at the same time converting 3 terminal carbonyls on that face into edge-bridging to the added rhodium atom (Scheme). At −70° the ^{13}C n.m.r. spectrum of $[Rh_7(CO)_{16}]^{3-}$ (Figure 1a) is entirely consistent with the solid-state structure;[9] there are 3 types of terminal carbonyls in the ratio 3:3:1, two types of edge-bridging carbonyls in the ratio 3:3 and 3 equivalent face-bridging carbonyls. At +25°, the spectrum (Figure 1b) shows that one set of three terminal carbonyls is undergoing exchange with one set of three edge-bridging carbonyls. Alternative assignments of the spectrum at −70° are possible but, in order not to involve the unique apical terminal carbonyl group in exchange, edge-terminal intra-exchange at 25° probably involves (A) and (B) in (III) (Scheme).

The probability of intra-carbonyl-exchange in clusters should be enhanced if there is an 'intermediate' which involves minimal changes in symmetry, co-ordination numbers of the rhodium atoms, and total back-bonding, compared with the solid-state structure. These requirements cannot easily be met for $[Rh_6(CO)_{16}]$, which is consistent with its non-fluxional behaviour even at +70°, whereas they are all satisfied for $[Rh_6(CO)_{15}]^{2-}$ by a consideration of (IV) (Scheme), which provides a possible pathway for exchange of terminal, edge- and face-bridging carbonyls. These ideas also accord with only A/B exchange in (III).

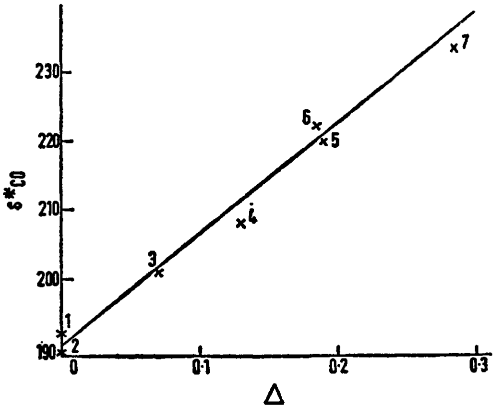

FIGURE 2. Plot of the weighted average of the ^{13}CO chemical shift ($\delta^{\bullet}_{CO}$) versus the 'average charge' per carbonyl group (Δ). 1. $[Rh_6(CO)_{16}]$, 2. $[Rh_4(CO)_{12}]$ (ref. 10), 3. $[Rh_{12}(CO)_{30}]^{2-}$ (ref. 7), 4. $[Rh_6(CO)_{15}]^{2-}$, 5. $[Rh_7(CO)_{16}]^{3-}$, 6. $[Rh_4(CO)_{11}]^{2-}$ (ref. 11); at −72° the ^{13}C n.m.r. spectrum of $[Rh_4(CO)_{11}]^{2-}$ consists of a symmetrical quintet at 222·8 p.p.m. due to rapid carbonyl intra-exchange. 7. $[Rh_6(CO)_{14}]^{4-}$; at −72° the ^{13}C n.m.r. spectrum of $[Rh_6(CO)_{14}]^{4-}$ consists of resonances at 252·9 p.p.m. and 207 p.p.m. due to face-bridging and terminal carbonyls respectively.

For rhodium carbonyl clusters, which contain only carbon monoxide as ligand, there is a good correlation between 'average charge' per carbonyl group (Δ) versus the weighted average of the ^{13}CO chemical shift ($\delta^{\bullet}_{CO}$), (Figure 2). This observation should aid structural assignments of unknown carbonyl clusters and is directly related to the earlier observation[7] of carbonyl ^{13}C chemical shifts; terminal < edge-bridging < face-bridging.

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[1] F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, 1972, **94**, 6191; J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1973, **79**; B. F. G. Johnson, J. Lewis, and T. W. Matheson, *ibid.*, p. 441.

[2] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

[3] V. G. Albano and P. L. Bellon, *J. Organometallic Chem.*, 1969, **19**, 405; P. Chini and S. Martinengo, *Chem. Comm.*, 1969, 1092.

[4] S. Martinengo and P. Chini, *Gazzetta*, 1972, **102**, 344.

[5] V. Albano, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1968, **15**, 423.

[6] V. Albano, personal communication.

[7] P. Chini, S. Martinengo, D. J. A. McCaffrey, and B. T. Heaton, *J.C.S. Chem. Comm.*, 1974, 311.

[8] V. G. Albano, P. Chini, S. Martinengo, D. J. A. McCaffrey, D. Strumolo, and B. T. Heaton, *J. Amer. Chem. Soc.*, 1974, **96**, 8106.

[9] V. G. Albano, P. L. Bellon, and G. Ciani, *Chem. Comm.*, 1969, 1024.

[10] J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J.C.S. Chem. Comm.*, 1973, 807.

[11] V. G. Albano, P. Chini, S. Martinengo, and A. Fumagalli, unpublished results.