Hydrogen and Carbonyl Scrambling in $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 2$ and 3); A Unique Example of Hydrogen Tunnelling

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Summary ^{1}H, $^{1}H-\{^{103}Rh\}$ INDOR, and ^{13}C n.m.r. spectroscopy has been used to show that the hydrogens in $[Rh_{13}(CO_{24}H_{5-n}]^{n-}$ ($n = 2$ or 3) migrate rapidly around the inside of the hexagonal close-packed cluster; ^{13}C n.m.r. spectroscopy also shows that at room temperature all the edge-bridging carbonyl groups, except for the 3 carbonyl groups which bridge the rhodium atoms in the hexagonal plane, undergo exchange with the 12 terminal carbonyl groups on the outside of the cluster.

THE carbonyl cluster anions $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 2$ or 3), which are isolated from the reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with hydrogen, have been shown by *X*-ray analysis ($n = 2,3$) to adopt a hexagonal close packing of rhodium atoms; each of the 12 surface metal atoms has one terminal carbonyl ligand and 12 carbonyl groups occupy edge-bridging positions (Figure 1).[1]

The high-field ^{1}H n.m.r. spectra of both these anions ($n = 2,3$) at ambient temperatures are, as reported previously,[1] complex multiplets (Figure 2),† which we have now been able to show, using ^{1}H, $^{1}H-\{^{103}Rh\}$ INDOR, and ^{13}C n.m.r. spectroscopy, are due both to rapid H-migration around the inside of the hexagonal close-packed cluster and to the exchange of 9 of the edge-bridging carbonyl groups with the 12 terminal carbonyl groups.

At room temperature, the ^{13}C n.m.r. spectra‡ of $[Rh_{13}(CO)_{24}H_{2}]^{3-}$§ consist of a triplet due to 3 edge-bridging carbonyl groups, $Rh_{B}(\mu\text{-}CO)Rh_{B}$ (Figure 1) *vide infra*, and a broad resonance due to exchange of the remaining carbonyl groups (Table); at 193 K, edge-terminal interchange still occurs. The ^{13}C n.m.r. spectrum of $[Rh_{13}(CO)_{24}H_{3}]^{2-}$ at

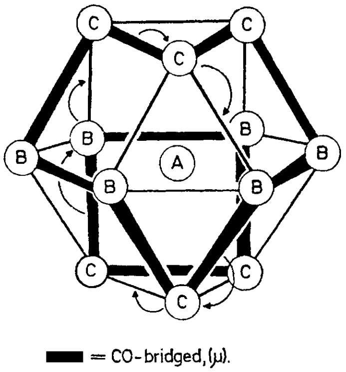

FIGURE 1. Schematic structure of $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 2,3$), (see ref. 1). The arrows show one of the three pathways which may be used for edge–terminal carbonyl-exchange. There is also a second equivalent pathway which is related to the first by the plane of symmetry, while a third pathway becomes equivalent only after migration *via* the first or second pathway; for simplicity these are not shown in this Figure. A fourth pathway in the equatorial hexagonal plane, which involves only Rh_{B} atoms, does not preserve the original distribution of ligands.

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† The spacings within each of the multiplets are unchanged at 60, 100, and 220 MHz.

‡ With or without [^{1}H]-decoupling.

§ Prepared from directly enriched $[Rh_{13}(CO)_{24}H_{3}]^{2-}$ (^{13}CO = *ca.* 30%).

193 K, however, is well resolved but complicated owing to the many inequivalent carbonyl groups in the instantaneous structure; at higher temperatures, similar spectra to the room temperature spectrum of the dihydride are obtained (Table) showing that CO-exchange is similar to that when $n = 3$ but occurs with a higher activation energy owing to the decreased negative charge on the anion.[2,3] These spectra can be explained assuming: (a) conservation of the original distribution of the carbonyl ligands, and (b) a concerted pseudo-circular pattern of terminal–bridge shifts. This concerted exchange, which is shown schematically in Figure 1, results in all the hexagonal rhodium atoms (Rh_B) becoming equivalent and all the triangular rhodium atoms (Rh_C) becoming equivalent at room temperature.

This interpretation is confirmed for both compounds ($n = 2,3$) by $^1H-\{^{103}Rh\}$ INDOR measurements, which show 3 signals due to Rh_A, Rh_B, and Rh_C (Table). The resonance due to Rh_A is at very high frequency compared with the resonance frequencies of Rh_B and Rh_C which, as expected, are quite similar. Specific spin-decoupling of Rh_B, or Rh_C results in simplification of the ^1H n.m.r. spectra which, as a result, can be deconvoluted into a doublet of septets (Figure 2 and Table). For $[Rh_{13}(CO)_{24}H_3]^{2-}$ it has been possible simultaneously to decouple Rh_B and Rh_C which results in the collapse of the multiplet to a doublet $[J(Rh_A-H)]$. The magnitude of $J(Rh_A-H)$ implies a one-bond coupling constant[4] and the spacing within each of the septets is consistent with a time-averaged coupling to each of the 2 sets of 6 rhodium atoms. These observations, together with the much higher τ-values (Table) compared with the face-bridging hydride in $[Rh_3(C_5H_5)_4H]$ [τ_H 22·47, $J(Rh-H)$ 26·5 Hz],[5] are consistent with a rapid migration of the hydrogens on the inside of the hexagonal close-packed cluster. This suggests that the hydrogens are protonic in character since the accepted value for the atomic radius of a hydrogen atom (0·37 Å) is much greater than the hole in a triangular Rh_3-face, (0·22 Å), on the inside of the cluster. It furthermore requires occupancy of both tetrahedral and octahedral holes in order for the hydrogens to 'visit' all the Rh_B and Rh_C atoms, although the relative populations of these sites are unknown.

TABLE. N.m.r. data for $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 2$ and 3) in $(CD_3)_2CO$ at 298 K.

	$n = 3$	$n = 2$
τ_H[a]	36·7	39·3
δ_{Rh}/p.p.m.	+4554, −408, −522	+3547, −532, −600
δ_{CO}/p.p.m.[c]	235·4,t,(3) 209·8,br,(21)	229·6,t,(3) 209·9,br,(21)
$J(Rh-CO)$	38·4 Hz	35·1 Hz

[a] 100 MHz data. [b] 3·16 MHz = 0 p.p.m. with shifts to high frequency being positive. [c] t = triplet, br = broad, figures in parentheses refer to relative intensities.

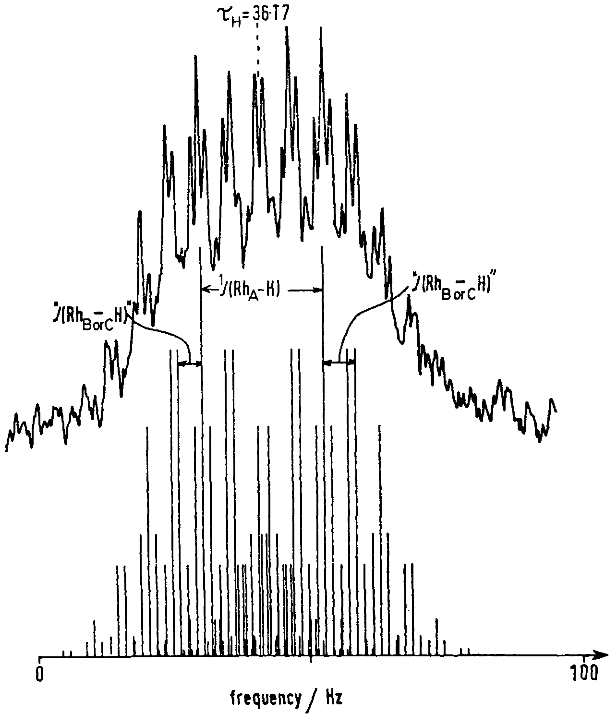

FIGURE 2. High-field ^1H n.m.r. spectrum (60 MHz, 8 mm tube) of $(PPh_3CH_2Ph)_3[Rh_{13}(CO)_{24}H_2]$ in $(CD_3)_2CO$ at 25 °C. $J(Rh-H)$: for $n = 2$, 23·1, 5·5, and 4·2; for $n = 3$, 22·75 6·0, and 4·45 Hz. For calculation of histogram see text and Table.

The simulated spectrum of $[Rh_{13}(CO)_{24}H_2]^{3-}$ using $W_{\frac{1}{2}} = 1{\cdot}2$ Hz gives a good fit with the observed spectrum at 298 K, whereas it is necessary to go to higher temperatures (*ca.* 317 K) to obtain similar values of $W_{\frac{1}{2}}$ for $[Rh_{13}(CO)_{24}H_3]^{2-}$. The activation energy for H-migration is thus higher when $n = 2$ than when $n = 3$ and, although this may be formally related to the similar variation in activation energies for CO-exchange, *vide supra*, it is possibly also a reflection of the increased number of hydrogens.

Although the hydrogen atom in $[Fe_4(CO)_{13}H]^-$[6] and $[FeCo_3(CO)_{12}H]$[7] has been claimed to be inside the metal polyhedron, subsequent work,[8] which has recently been summarised,[3] casts serious doubts on these claims. These Rh_{13} clusters appear to be the first authentic examples in which hydrogen atoms are inside the metal polyhedron of a carbonyl cluster and the observed H-migration may clearly be significant for the problem of H-diffusion in metals.[9]

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