Hexanuclear Rhodium Hydrido-carbonyl Clusters

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Multinuclear n.m.r. studies (^{1}H, ^{1}H-{^{103}Rh}, ^{13}C, ^{13}C-{^{103}Rh}, and ^{103}Rh) show that protonation of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}C]^{2-}$ at low temperatures gives $[Rh_6H(CO)_{15}]^-$ and $[Rh_6H(CO)_{15}C]^-$ which contain terminal and triangular face-bridging hydrides respectively; warming these solutions to room temperature results in loss of hydrogen and formation of $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_{12}(CO)_{24}(C)_2]^{2-}$ respectively.

THE hydride ligand in transition-metal hydrido-carbonyl clusters can be found (*a*) in a terminal site bonded to one metal, (*b*) in a bridging site bonded to either two metals or a metal and a ligand, (*c*) bridging a M_3 triangular face, or (*d*) in an interstitial site which is usually octahedral or pseudo-octahedral.[1] The difference in energy between different sites is often not very great and this results in facile H migration. Because neutron diffraction studies on $[Co_6H(CO)_{15}]^-$ showed the hydride to be in the centre of the Co_6 octahedron,[2] it was of interest to establish the structure of the analogous rhodium derivative and we now report n.m.r. studies at low temperature which show that $[Rh_6H(CO)_{15}]^-$ is isostructural with $[Rh_6X(CO)_{15}]^-$ (X = I,[3] COEt,[4] or O_2CMe [4]) with the hydride ligand occupying a terminal site whereas the related cluster, $[Rh_6H(CO)_{15}C]^-$, which adopts a trigonal-prismatic metal skeleton, contains a triangular face-bridging hydride.

RESULTS AND DISCUSSION

N.M.R. Studies on $[Rh_6H(CO)_{15}]^-$.—It has previously been reported that $[Rh_{12}(CO)_{30}]^{2-}$ reacts with hydrogen to give $[Rh_{13}H_3(CO)_{24}]^{2-}$ through the intermediate formation of the unstable $[Rh_6H(CO)_{15}]^-$, which can be better prepared by addition of acid to $[Rh_6(CO)_{15}]^{2-}$ at low temperatures.[5,6] In the latter reaction a high-field ^{1}H n.m.r. resonance was observed but, because the product is unstable and difficult to obtain pure by crystallisation, we have now made multinuclear n.m.r. measurements in order to make a complete structural characterisation of this compound, which is shown to be isostructural with $[Rh_6X(CO)_{15}]^-$ (X = I,[3] COEt,[4] or O_2CMe [4]) (Figure 1) and thus different to the structure adopted by the analogous complex, $[Co_6H(CO)_{15}]^-$.[2] There was no evidence for the formation of $[Rh_6H_2(CO)_{15}]$ on addition of excess of CF_3CO_2H to either an acetone or dichloromethane solution of $[Rh_6(CO)_{15}]^{2-}$.

Consistent with the structure shown in Figure 1, the ^{103}Rh-{^{1}H} n.m.r. spectrum shows four resonances at −374, −475, −478, and −538 p.p.m. in the intensity ratio 2 : 2 : 1 : 1 with the last resonance (Rh_A) appearing as a doublet without ^{1}H decoupling; the other resonance of intensity 1 can be assigned to Rh_D (Table). Although the ^{1}H resonance (δ −12.2 p.p.m.) is basically a doublet, [^1J(^{1}H-^{103}Rh) 22.9 Hz], with further long-range coupling, ^{1}H-{^{103}Rh} INDOR measurements could only establish δ($^{103}Rh_A$) −540 p.p.m., which is in close agreement with that obtained by direct ^{103}Rh n.m.r. measurements.

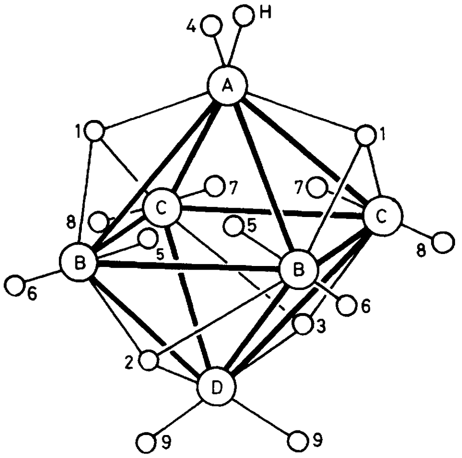

FIGURE 1 Schematic representation of the structure of $[Rh_6H(CO)_{15}]^-$; large spheres = Rh, small spheres = CO

The structure in Figure 1 contains four face-bridging carbonyls and 11 terminal carbonyls. Consideration of the symmetry shows there to be three types of face-bridging carbonyls in the ratio 2 : 1 : 1 (C^1O, C^2O, and C^3O respectively) and six types of terminal carbonyls in the ratio 1 : 2 : 2 : 2 : 2 : 2 (C^4O—C^9O respectively). The ^{13}C n.m.r. spectrum is thus quite complicated [Figure 2(*e*)] but, through ^{13}C-{^{103}Rh} measurements, can be assigned.

The ^{13}C n.m.r. spectrum resulting from broad-band ^{103}Rh decoupling is shown in Figure 2(*d*). It clearly shows the correct number of face-bridging carbonyl resonances with the correct intensities but there are fewer peaks than might have been expected in the terminal region. Thus, there are only four resonances at 191.8, 187.1, 184.6, and 183.6 p.p.m. with relative intensities 1 : 4 : 2 : 4 respectively. Decoupling Rh_A collapses the doublet of intensity 1 at 191.8 p.p.m. which can be thus assigned to C^4O, while leaving the remaining terminal carbonyl resonances essentially unchanged [Figure 2(*b*)]. Decoupling at 3.158 818 MHz [δ(^{103}Rh) −374 p.p.m.], which could be due to Rh_B or Rh_C, collapses the doublet of intensity 4 at 187.1 p.p.m. [Figure 2(*c*)]; this resonance must be due to either C^5O and C^6O or C^7O and C^8O being coincident. Figure 2(*c*) also clearly shows the doublet of intensity 2 at 184.6 p.p.m. due to C^9O and a doublet of intensity 4 at 183.6 p.p.m., which is again due to coincidences of either C^5O and C^6O or C^7O and C^8O; both these doublets collapse on irradiation at 3.158 495 MHz [$\delta(^{103}Rh)$ −476 p.p.m.] which simultaneously decouples Rh_D and Rh_B or Rh_C [Figure 2(*a*)]. Unfortunately, since it is not possible to differentiate Rh_B from Rh_C, it is not possible to assign unambiguously which of the resonances of intensity 4 is due to C^5O/C^6O and C^7O/C^8O. Nevertheless, the structure of $[Rh_6H(CO)_{15}]^-$ is clearly consistent with that shown in Figure 1 and all the n.m.r. data on this compound are summarised in the Table.

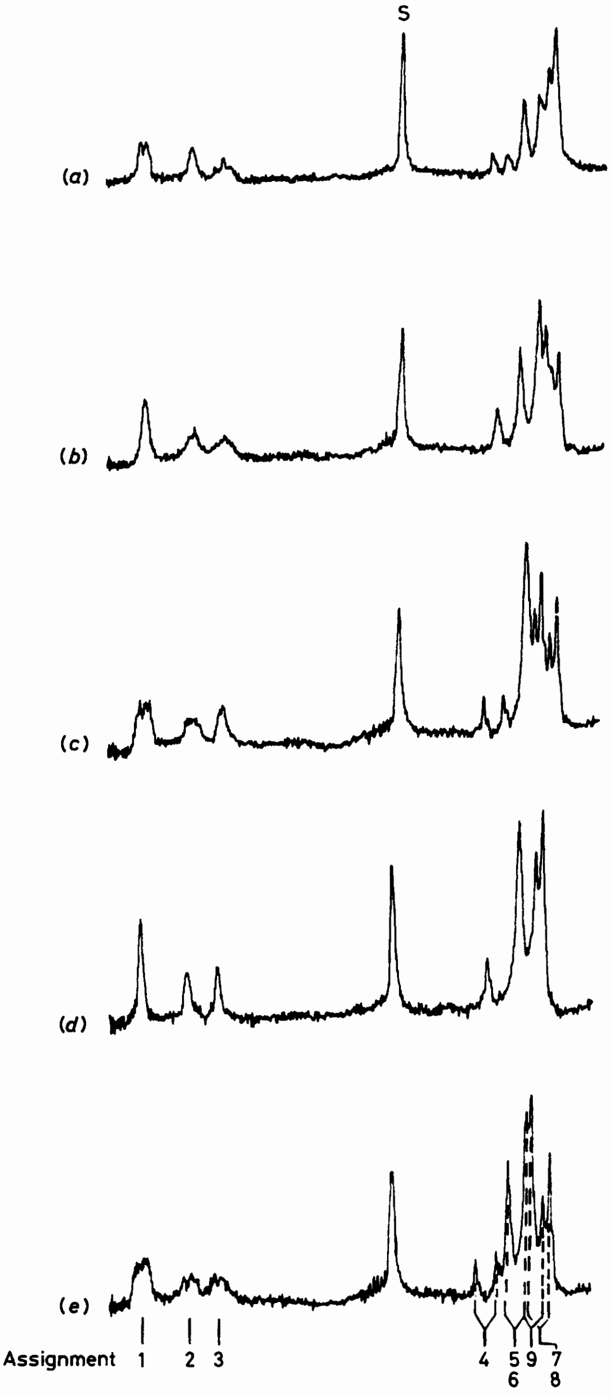

FIGURE 2 Carbon-13 n.m.r. spectra (25.15 MHz) of $[NBu_4][Rh_6H(CO)_{15}]$ in $(CH_3)_2CO$ at −70 °C. (*a*) Decoupling at 3.158 495 MHz [$\delta(^{103}Rh)$ = −476 p.p.m.], (*b*) decoupling at 3.158 300 MHz [$\delta(^{103}Rh)$ = −538 p.p.m.], (*c*) decoupling at 3.158 818 MHz [$\delta(^{103}Rh)$ = −374 p.p.m.], (*d*) broad-band Rh decoupling at 3.158 547 MHz, (*e*) non-decoupled spectrum. S = solvent

Since there are probably small energetic differences between different sites occupied by hydrogen, it is unwise to speculate too much on the different structures adopted by $[M_6H(CO)_{15}]^-$ (M = Co or Rh). Nevertheless, it could be associated with the increasing M–H bond strength found with the heavier metals. Thus the rhodium cluster is stabilised by a single terminal Rh–H bond, whereas a multicentre Co_6–H bond is required to stabilise the cobalt cluster.

N.M.R. Studies on $[Rh_6H(CO)_{15}C]^-$.—The ^{13}C n.m.r. spectrum of $[Rh_6(CO)_{15}C]^{2-}$ has been previously shown [7] to be entirely consistent with the solid-state structure.[8] Addition of excess CF_3CO_2H to a dichloromethane solution of $[Rh_6(CO)_{15}C]^{2-}$ at low temperature results in the appearance of (*a*) two new rhodium resonances [$\delta(^{103}Rh_A)$ = −144.5 and $\delta(^{103}Rh_B)$ = −412.5 p.p.m.] with the latter occurring as a doublet [$^1J(^1H-^{103}Rh_B)$ 15 Hz] in the non-^1H-decoupled ^{103}Rh spectrum,* and (*b*) a high-field quartet of quartets in the ^1H n.m.r. spectrum [$\delta(^1H)$ = −15.6 p.p.m., $^1J(^1H-^{103}Rh_B)$ 15, $^2J(^1H-^{103}Rh_A)$ 1.5 Hz].

These results are consistent with protonation of a Rh_3 triangular face (Figure 3), which is confirmed by $^{13}C-\{^{103}Rh\}$ measurements. The data resulting from these experiments, together with the corresponding data for $[Rh_6(CO)_{15}C]^{2-}$ are summarised in Figure 3. It should be noted that Rh_B occurs at lower frequency than Rh_A and this is in keeping with similar shifts to lower frequency observed for the interstitial rhodium atom in $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 1—4) on increasing protonation; thus, the interstitial rhodium chemical shifts in $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ are +6 370, +4 554, +3 547, and +2 917 p.p.m. for n = 4, 3, 2, and 1 respectively.[9] $^1J(^{103}Rh-^{103}Rh)$ has yet to be observed in direct ^{103}Rh n.m.r. measurements and appears to be immeasurably small in rhodium carbonyl clusters. The values of $J(^{103}Rh-^{13}CO)$ remain essentially the same on protonation whereas there are significant variations in ^{13}C chemical shifts with the average value of $\delta(^{13}CO)$ in $[Rh_6H(CO)_{15}C]^-$ (209.5 p.p.m.) being, as expected, lower than in $[Rh_6(CO)_{15}C]^{2-}$ (215.4 p.p.m.) Without the benefit of spin-decoupling experiments, it is necessary to be extremely careful when assigning $\delta(^{13}CO)$. Thus, although

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* The ^{103}Rh chemical shifts were initially obtained by INDOR measurements. Thus Rh_B was readily located by $^1H-\{^{103}Rh\}$ INDOR and a triple-resonance $^1H-\{^{103}Rh, ^{103}Rh\}$ experiment located Rh_A. The rhodium chemical shifts of Rh_A and Rh_B obtained in this way are −143 and −412 p.p.m. respectively.

N.m.r. data for $[NBu_4][Rh_6H(CO)_{15}]$ in $(CD_3)_2CO$ at −70 °C [a,b]

δ(^{103}Rh) [c]				δ(^{13}CO) [d]						
Rh_A	Rh_B	Rh_C	Rh_D	C^1O	C^2O	C^3O	C^4O	C^5O C^6O	C^7O C^8O	C^9O
−538	−374 [e]	−475 [e]	−478	244.6	237.5 [e]	232.9 [e]	191.8 (77.1)	187.1 [e] (70.3)	183.6 [e] (72.3)	184.6 (68.4)

[a] In CD_2Cl_2 at −75 °C, δ(^{1}H) = −12.2 p.p.m. ($SiMe_4$ as standard), ^1J(H − Rh_A = 22.9 Hz. [b] For numbering see Figure 1. [c] 11.376 MHz = 0 p.p.m. at such a magnetic field that the protons in $SiMe_4$ resonate at exactly 360 MHz; negative chemical shifts are to low frequency of 11.376 MHz. [d] Values in p.p.m. with $SiMe_4$ as standard; figures in parentheses indicate ^1J(^{103}Rh–^{13}CO) values in Hz (±2). [e] Assignments could be reversed.

one terminal carbonyl and one inter-triangular bridging carbonyl resonance in $[Rh_6H(CO)_{15}C]^-$ have similar chemical shifts (193.3 and 223.5 p.p.m.) to those found in $[Rh_6(CO)_{15}C]^{2-}$ (196.9 and 224.0 p.p.m.), specific Rh-decoupling measurements show them to be on different planes, see Figure 3. It should also be noted that the original, somewhat contentious, assignment of ^2J(Rh–CO) for the terminal carbonyls in $[Rh_6(CO)_{15}C]^{2-}$ to *inter-triangular* coupling [7] has been substantiated by the present measurements. Thus, for $[Rh_6H(CO)_{15}C]^-$ there are two resonances due to the terminal carbonyls which both appear as doublets of doublets. Decoupling Rh_A causes the resonances at 193.3 p.p.m. to become a doublet [^2J(Rh_B–CO) 3.9 Hz] while the resonance at 189.6 p.p.m. also becomes a doublet [^1J(Rh_B–CO) 78.1 Hz]; related results are obtained on decoupling Rh_B (Figure 3). However, similar long-range coupling is not found in $[Rh_6H(CO)_{15}]^-$. The carbide resonance in $[Rh_6H(CO)_{15}C]^-$ is complicated (quartet of quartets) but becomes a simple quartet on decoupling either Rh_A or Rh_B. In keeping with previous findings,[10] the reduced negative charge on $[Rh_6H(CO)_{15}C]^-$ results in the carbide resonance occurring at higher frequency than in $[Rh_6(CO)_{15}C]^{2-}$.

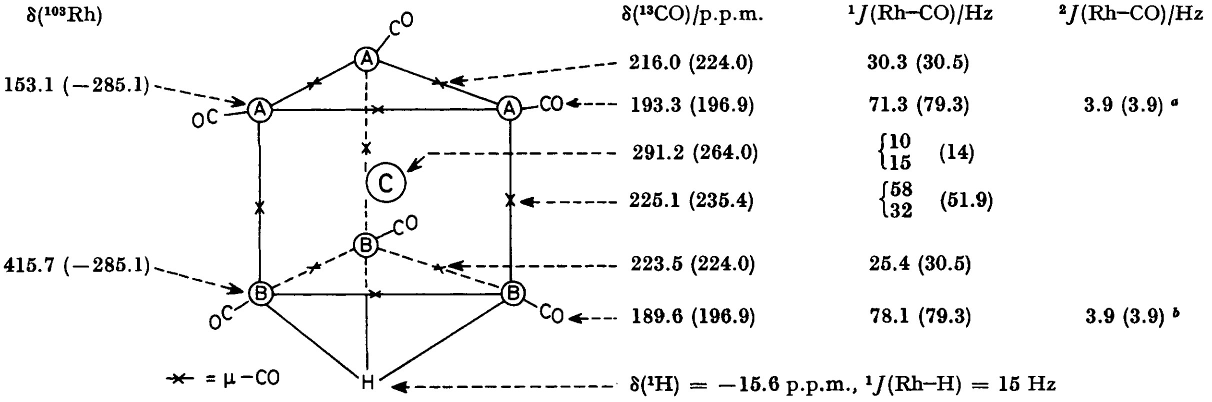

FIGURE 3 Schematic representation of the structure of $[Rh_6H(CO)_{15}C]^-$ together with ^{1}H, ^{13}C, and ^{103}Rh n.m.r. data at −25 °C. The values shown in parentheses are data for $[Rh_6(CO)_{15}C]^{2-}$. Values of *J* are ±1 Hz; superscript *a* denotes ^2J(Rh_B–CO), and *b*, ^2J(Rh_A–CO)

It has previously been shown that successive addition of up to two $[Cu(NCMe)]^+$ groups occurs on the triangular faces of $[Rh_6(CO)_{15}C]^{2-}$,[11] whereas we find no evidence for formation of $[Rh_6H_2(CO)_{15}C]$, even with excess CF_3SO_3H. However, the similar addition of both H^+ and $[Cu(NCMe)]^+$ to the triangular face suggests that this plane is highly susceptible to electrophilic attack. We have also found a similar addition with Ag^+ to give $[Ag\{Rh_6(CO)_{15}C\}_2]^{3-}$,[12] but we have, as yet, no evidence for exposing the carbide by opening the metallic skeleton through oxidation as was recently observed by Bradley *et al.*[13]

Finally, it should be noted that warming either $[Rh_6H(CO)_{15}]^-$ or $[Rh_6H(CO)_{15}C]^-$ to room temperature results in loss of hydrogen with concomitant dimerisation to $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_{12}(CO)_{24}(C)_2]^{2-}$ respectively.

EXPERIMENTAL

^{1}H-{^{103}Rh}, ^{13}C, and ^{13}C-{^{103}Rh} measurements were made as described previously [14–16] and ^{103}Rh n.m.r. spectra were recorded on a Bruker WH 360 MHz spectrometer using 15 mm n.m.r. tubes containing solutions (5 cm^3, 0.5 mmol) doped with $[Cr(acac)_3]$ (acac = acetylacetonate) at a level similar to that used for ^{13}C measurements.[15] Optimum signal to noise was obtained using a pulse angle of 13° and a pulse repetition rate of 0.348 s. Hydrogen-1 n.m.r. spectra were obtained on a JEOL PS-100 spectrometer using 5 mm n.m.r. tubes. It has previously been suggested [17] that $[Rh_6(CO)_{15}C]^{2-}$ should be used as a reference (0 p.p.m.) for ^{103}Rh chemical shifts. This seems to us unwise because of its general unavailability and because δ(^{103}Rh) is significantly affected by both solvent and temperature effects. As a result, we prefer to relate δ(^{103}Rh) = 0 p.p.m. to a standard frequency (3.16 or 11.376 MHz) at such a magnetic field that the protons in $SiMe_4$ resonate at exactly 100 or 360 MHz respectively. Converting the data of Gansow *et al.*[17] on $[Rh_6(CO)_{15}C]^{2-}$ to our scale gives δ(^{103}Rh) = −277.2 p.p.m.

which, although it is not stated at what temperature this measurement was made, is in close agreement with our data, $\delta(^{103}\mathrm{Rh}) = -285$ p.p.m., at -25 °C.

^{13}CO-Enrichments were carried out using standard vacuum line techniques and all preparations were carried out under a nitrogen atmosphere using Schlenk tube techniques.

$[\mathrm{NBu_4}]_2[\mathrm{Rh_6(CO)_{15}}]$ was prepared as described previously [18] and converted to $[\mathrm{NBu_4}][\mathrm{Rh_6H(CO)_{15}}]$ by addition of excess (*ca.* four times the stoicheiometric equivalent) of $\mathrm{CF_3CO_2H}$ to an acetone or dichloromethane solution of $[\mathrm{NBu_4}]_2[\mathrm{Rh_6(CO)_{15}}]$ at low temperature (-76 °C). This resulted in an immediate colour change from deep green to brown. Warming the brown solution to room temperature results in a further colour change to purple due to the formation of $[\mathrm{Rh_{12}(CO)_{30}}]^{2-}$, which shows three ^{103}Rh resonances at $+158$, -332, and -551 p.p.m. of relative intensities 1 : 4 : 1. This supports our earlier ^{13}C-{^{103}Rh} measurements [19] and contradicts recent claims for fluxional behaviour of the metal skeleton.[20]

$[\mathrm{N(PPh_3)_2}][\mathrm{Rh_6(CO)_{15}C}]$ was prepared from $\mathrm{K_2[Rh_6(CO)_{15}C]}$ [8] by adding an excess of $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ in MeOH. The resulting precipitate was filtered off, dried, and recrystallised from acetone–Pr^{i}OH to give the desired product.

$[\mathrm{N(PPh_3)_2}][\mathrm{Rh_6(CO)_{15}{}^{13}C}]$ was prepared by addition of $^{13}\mathrm{CCl_4}$ (6 μl, 92% ^{13}C) to a methanol solution of $[\mathrm{N(PPh_3)_2}][\mathrm{Rh(CO)_4}]$ (0.25 g). There was an immediate reaction to give the crude product which was filtered off and recrystallised from acetone–Pr^{i}OH, yield 80%.

$[\mathrm{N(PPh_3)_2}][\mathrm{Rh_6H(CO)_{15}C}]$ was prepared by addition of excess (*ca.* four times the stoicheiometric equivalent) of $\mathrm{CF_3CO_2H}$ to either an acetone or dichloromethane solution of $[\mathrm{N(PPh_3)_2}][\mathrm{Rh_6(CO)_{15}C}]$ at -30 °C.

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