^{13}C-{^{103}Rh} Nuclear Magnetic Resonance Studies and Fluxional Behaviour of the Nickel Capped Rhodium Cluster $[NiRh_6(CO)_{16}]^{2-}$

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Rhodium-103 decoupled ^{13}C n.m.r. measurements have been used to assign the ^{13}C n.m.r of $[NiRh_6(CO)_{16}]^{2-}$ and variable-temperature measurements establish a completely different fluxional behaviour to that found for the isostructural cluster, $[Rh_7(CO)_{16}]^{3-}$.

It has been postulated that carbonyl fluxionality in transition-metal carbonyl clusters can be rationalised by movements of the metal skeleton *within* a fixed carbonyl polyhedron.[1] In all our work, we find no evidence for this and there is often definite evidence against this occurring.[2-10] Instead, we have only evidence for either concerted terminal-bridge carbonyl exchange processes or rocking movements (or a rotation) of carbonyl groups localised on a particular metal atom. Both these migrations are extremely dependent on (*i*) the geometry of the carbonyl polyhedron around the metal skeleton, which is unfortunately not easy to predict, and (*ii*) the various M–C bond strengths, which are also usually not available but can be significantly different, especially in heterometallic clusters.

As part of a continuing programme of work in this area we now report variable-temperature ^{13}C-{^{103}Rh} n.m.r. measurements on $[NiRh_6(CO)_{16}]^{2-}$, which is found to undergo a completely different low-energy carbonyl migration to that found in the isostructural cluster, $[Rh_7(CO)_{16}]^{3-}$,[6] and emphasises the present difficulties associated with attempts to invoke general migrational pathways for carbonyls even in closely related clusters.

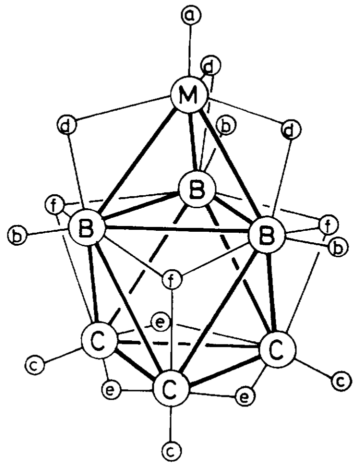

Figure 1. Schematic structure of $[MRh_6(CO)_{16}]^{n-}$ (M = Ni, n = 2;[11] M = Rh^A, n = 3 [12]). Large spheres are Rh or M, small spheres are CO

Results and Discussion

The schematic structure of $[MRh_6(CO)_{16}]^{n-}$ (M = Ni, n = 2; M = Rh, n = 3), which has a C_3 axis incorporating M and the centre of the Rh_3 triangle remote from M, is shown in Figure 1.[11,12] At low temperature, the ^{13}C n.m.r. spectrum [Figure 2(*c*)] of $[NiRh_6(CO)_{16}]^{2-}$ is entirely consistent with this structure and ^{13}C-{^{103}Rh} n.m.r. measurements [Figure 2(*a*) and (*b*)] allow a complete assignment. The n.m.r. data for $[NiRh_6(CO)_{16}]^{2-}$, together with that found previously for $[Rh_7(CO)_{16}]^{3-}$ are summarised in the Table where it can be seen that the corresponding values of $\delta(^{13}CO)_{mean}$, $\delta(^{103}Rh)$, and $^1J(^{103}Rh-^{13}CO)$ for both compounds are very similar whereas $\delta(^{13}CO)$ for the bridging carbonyls are at significantly higher field (*ca.* 10 p.p.m.) for $[NiRh_6(CO)_{16}]^{2-}$. This is consistent with the increased charge, for the trianion compared to the dianion, being mostly dissipated onto the bridging carbonyls.

It should also be noted that at high resolution the resonance due to the terminal carbonyl on nickel is a quartet (3.8 ± 2 Hz) and this has been shown to arise from $^2J(^{103}Rh-^{13}C^aO)$ by specific decoupling measurements. In keeping with the wide variation in the bond length d(Rh–CO) found in $[NiRh_6(CO)_{16}]^{2-}$,[11] there is a smooth increase in $^1J(^{103}Rh-^{13}CO)$ with decreasing metal-carbon distance (Figure 3); unfortunately, the refinement of the structure of $[Rh_7(CO)_{16}]^{3-}$ was not so complete and data of comparable accuracy are not available.[12]

Variable-temperature ^{13}C n.m.r. measurements on $[NiRh_6(CO)_{16}]^{2-}$ (Figure 4) show that two independent carbonyl migrations occur. The lowest energy process (at −40 °C) involves concomitant exchange of C^bO, C^dO, and C^fO. This exchange involves a localised, concerted exchange, which resembles a rotation on Rh^B, and is facile because both the bridging carbonyls (C^dO and C^fO) are most strongly bonded to Rh^B, which thus allows their ready conversion to a terminal carbonyl. This migration was *not* found in $[Rh_7(CO)_{16}]^{3-}$. In this case, C^dO is more strongly bonded to the capping metal and thus less able to swing into a terminal position on Rh^B.

At higher temperatures (+25 °C) there is also localised exchange of the terminal (C^cO) and edge-bridging (C^eO) carbonyls around the $Rh^C{}_3$ face. The ^{13}C n.m.r. spectrum at this temperature consists of a sharp resonance at 203.3 p.p.m. due to C^aO and two broad resonances at 218.9 and 207.3 p.p.m. due to the two groups of exchanging carbonyls C^bO, C^dO, C^fO, and C^cO, C^eO [calc. $\delta(^{13}CO)_{mean}$ 219.2 and 206.6 p.p.m., respectively]. On increasing the temperature to +90 °C (in EtCN) *all* the carbonyls become fluxional as evidenced by the disappearance of all three resonances in Figure 4(*a*) and the appearance of a new resonance at 214.7

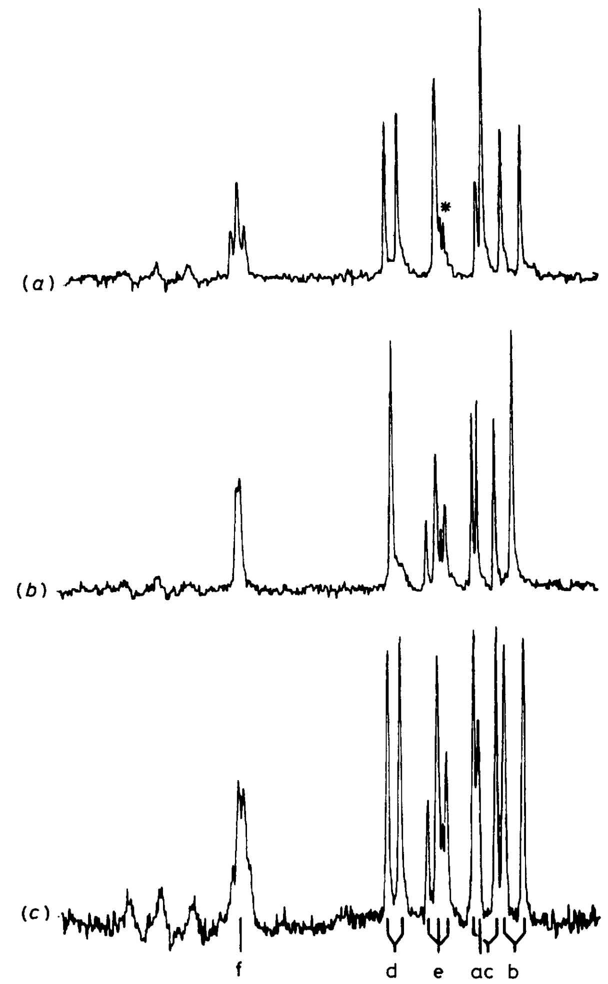

Figure 2. Carbon-13 and $^{13}C-\{^{103}Rh\}$ n.m.r. spectra of $[N(PPh_3)_2]_2[NiRh_6(CO)_{16}]$ in thf at −77 °C: (*a*) decoupling Rh^C, (*b*) decoupling Rh^B (see Figure 1), and (*c*) non-decoupled. The impurity $[Rh_6(CO)_{15}]^{2-}$ is marked with an asterisk

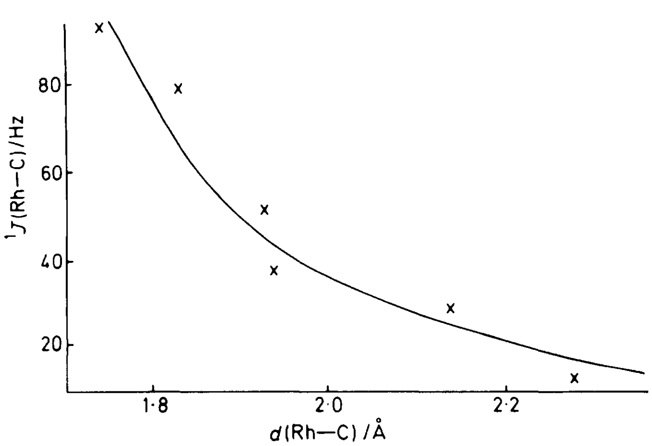

Figure 3. Variation of *d*(Rh-C)/Å with $^1J(^{103}Rh-^{13}CO)$/Hz in $[NiRh_6(CO)_{16}]^{2-}$

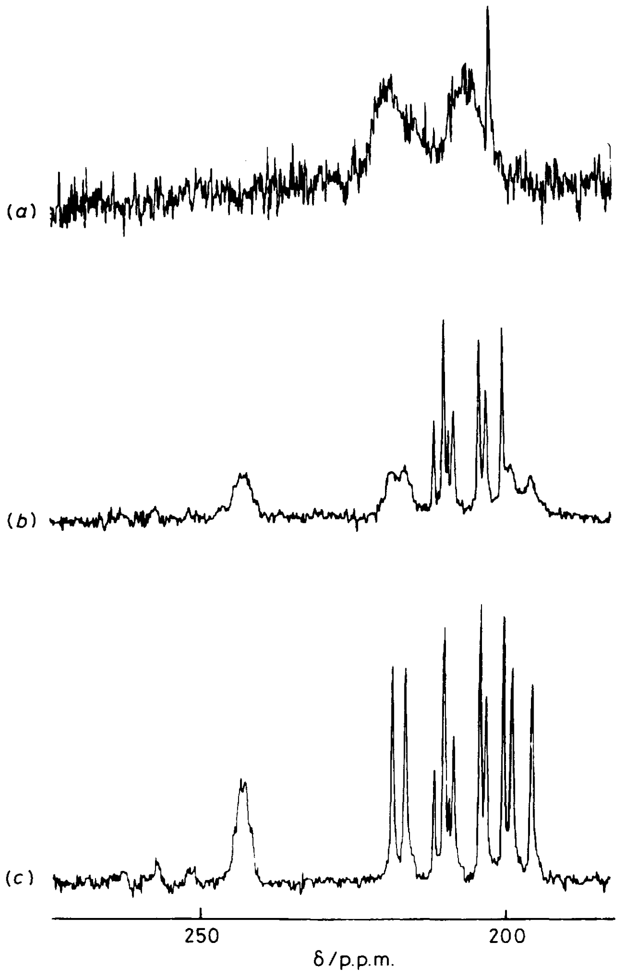

Figure 4. Variable-temperature ^{13}C n.m.r. spectra of $[N(PPh_3)_2]_2[NiRh_6(CO)_{16}]$ in thf: at (*a*) +25, (*b*) −40, and (*c*) −61 °C

Table. N.m.r. data * for $[N(PPh_3)_2]_2[NiRh_6(CO)_{16}]$ in thf at −77 °C and $[NEt_4]_3[Rh_7(CO)_{16}]$ in CD_3CN at −30 °C (see Figure 1)

	$[NiRh_6(CO)_{16}]^{2-}$	$[Rh_7(CO)_{16}]^{3-}$
$\delta(C^aO)$	203.3	205.7
$^1J(Rh^A-C^aO)$		103.5
$\delta(C^bO)$	197.4	198.2
$^1J(Rh^B-C^bO)$	81	81
$\delta(C^cO)$	202.2	206.4
$^1J(Rh^C-C^cO)$	94	93
$\delta(C^dO)$	217.3	229.4
$^1J(Rh^A-C^dO)$		39.5
$^1J(Rh^B-C^dO)$	53	39.5
$\delta(C^eO)$	210.0	218.0
$^1J(Rh^C-C^eO)$	38	40.5
$\delta(C^fO)$	243.1	254.3
$^1J(Rh^B-C^fO)$	30	29
$^1J(Rh^C-C^fO)$	12	13
$\delta(Rh^A)$		+483
$\delta(Rh^B)$	−376	−376
$\delta(Rh^C)$	+692	+690

* $\delta(^{13}CO)$ in p.p.m. relative to $SiMe_4$; $\delta(^{103}Rh)$, 0 p.p.m. = 3.16 MHz at such a magnetic field that the protons of $SiMe_4$ resonate at exactly 100 MHz; high-frequency shifts are positive. ^1J values are ±2 Hz.

p.p.m. [calc. $\delta(^{13}CO)_{mean}$ 213.5 p.p.m.]. Remeasuring the spectrum at low temperature showed that no decomposition had occurred at high temperatures. Thus, in the absence of CO, $[NiRh_6(CO)_{16}]^{2-}$ is thermodynamically quite stable.

It should be noted that only migration of C^cO and C^eO around the Rh^C_3 face was found for $[Rh_7(CO)_{16}]^{3-}$ and the grossly different carbonyl migrational behaviour of $[NiRh_6(CO)_{16}]^{2-}$ illustrates the profound variation which is possible even in such closely related clusters.

Experimental

Carbon-13 and ^{13}C-{^{103}Rh} n.m.r. measurements were carried out as described previously[13,14] on tetrahydrofuran (thf) solutions of $[N(PPh_3)_2]_2[NiRh_6(CO)_{16}]$, which was prepared as described previously.[11] Carbon-13 carbonyl enrichment (*ca.* 30%) was carried out by direct exchange with ^{13}CO using standard vacuum-line techniques but it was important to remove the carbon monoxide from a frozen (−196 °C) solution, because of the equilibrium (i). Allowing the resultant

$$[NiRh_6(CO)_{16}]^{2-} \underset{N_2}{\overset{CO}{\rightleftharpoons}} [Rh_6(CO)_{15}]^{2-} + [Ni(CO)_4] \quad \text{(i)}$$

frozen solution under nitrogen to warm to room temperature produced the ^{13}CO-enriched cluster, $[NiRh_6(CO)_{16}]^{2-}$, with only a trace of $[Rh_6(CO)_{15}]^{2-}$.

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