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Nuclear Magnetic Resonance Studies in Cluster Chemistry [and Discussion]

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Nuclear magnetic resonance studies in cluster chemistry

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Multinuclear n.m.r. studies on transition metal carbonyl clusters are providing important information about (*a*) mechanisms of ligand inter- and intra-exchange, (*b*) metal polyhedral rearrangements, (*c*) the controlled capping of Rh_3-triangular and Rh_4-square faces, which often provides a convenient route for the synthesis of higher nuclearity carbonyl clusters, and (*d*) bonding within the cluster. Recent ^{13}C and ^{31}P n.m.r. measurements under high pressures of gas promise *in situ* mechanistic information and structural identification of intermediates present under industrially forcing conditions that are usually necessary for catalysis.

INTRODUCTION

The development of X-ray structural analysis over the last few years, coupled with the preparative expertise of cluster chemists in Milan, Cambridge and Union Carbide, has allowed the characterization of increasingly bigger homometallic transition metal carbonyl clusters, which now start to resemble small metallic crystallites. Similar advances are being made with alloy-like, heterometallic clusters. The advent of Fourier transform multi-n.m.r. spectrometers enabled the improved structural characterization in the solid state to be paralleled in solution; additionally, n.m.r. measurements on rhodium carbonyl clusters have allowed important information to be obtained about (*a*) ligand and metal inter- and intra-exchange processes, (*b*) reactivity and capping of particular metal polyhedral faces, which resemble surface reconstruction on metals, and (*c*) bonding within the cluster. Recently it has been possible to carry out n.m.r. measurements under high pressures of gas, which allows mechanistic information to be obtained *in situ* under the industrially forcing conditions that are usually necessary for catalysis. Coincidentally, rhodium carbonyl clusters, which appear to be most active catalytically, are best suited for n.m.r. studies because rhodium exists totally as ^{103}Rh with $I = \frac{1}{2}$, and allows this allows spin–spin coupling information, which assists with structural assignments and mechanistic information relating to inter- or intra-ligand exchange processes to be obtained. Additionally, it is now possible to obtain direct ^{103}Rh n.m.r. spectra on high-field spectrometers and these, together with ^{13}C–$\{^{103}Rh\}$ and ^{1}H–$\{^{103}Rh\}$ measurements, usually allow unambiguous spectroscopic assignments.

MECHANISMS OF LIGAND–METAL EXCHANGE FROM N.M.R. STUDIES

(*a*) *Carbonyl inter-exchange*

It has recently been shown (Heaton *et al.* 1981*b*) that preferential CO inter-exchange in $[Rh_6(CO)_{15}C]^{2-}$ occurs at sites that have the longest Rh–CO bonds, and inter-exchange of terminal carbonyls is easier than edge-bridging carbonyls with approximately similar Rh–CO bond lengths; this provides the first evidence for carbonyl exchange in carbonyl clusters occurring by a dissociative mechanism. Stereospecific CO-exchange in other carbonyl clusters has previously been observed, but these cases involve either the conversion of three-electron donor ligands to one-electron donor ligands (Bhaduri *et al.* 1979; Bryan *et al.* 1977) or the formation of multiply metal–metal bonded species (Johnson *et al.* 1978) with concomitant CO substitution by associative mechanism. Thus mechanisms of carbonyl inter-exchange can range from dissociative to associative and become further complicated if carbonyl intra-exchange (fluxionality) occurs.

(*b*) *Carbonyl intra-exchange*

This is extremely dependent on the geometry of the cluster and, for heterometallic clusters, the nature of the metals. Carbonyl migrations, which are still difficult to predict in advance, occur by either (*a*) the interconversion of terminal and bridging carbonyls, or (*b*) localized rocking or rotations of particular groups on a metal atom.

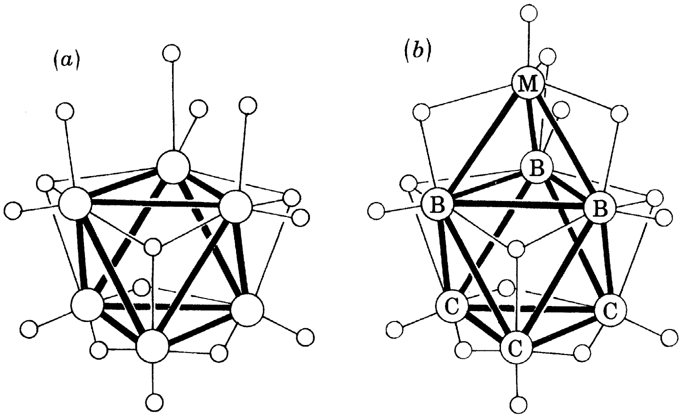

FIGURE 1. Schematic representation of the structures of (*a*) $[Rh_6(CO)_{15}]^{2-}$ and (*b*) $[MRh_6(CO)_{16}]^{n-}$ (M = Rh, n = 3; M = Ni, n = 2), which shows how little reorganization of the carbonyl skeleton occurs on capping a Rh_3-face.

We have found no evidence for the proposal that carbonyl fluxionality can be accounted for by the migration of a metal polyhedron within a fixed carbonyl polyhedron (Benfield & Johnson 1978).

The predictive difficulties in this area are illustrated by the gross change in carbonyl fluxionality found recently for the two iso-electronic, iso-structural clusters, $[Rh_7(CO)_{16}]^{3-}$ and $[NiRh_6(CO)_{16}]^{2-}$ (figure 1*b*).

Variable-temperature $^{13}C-\{^{103}Rh\}$ n.m.r. studies show that the only carbonyl migration in $[Rh_7(CO)_{16}]^{3-}$ involves the interchange of terminal and edge-bridging carbonyls around the Rh_3-triangular face remote from the capping atom (Brown *et al.* 1979*a*). However, $[NiRh_6(CO)_{16}]^{2-}$ exhibits three distinct carbonyl migrations; the lowest-energy migration involves a localized interchange of terminal and bridging carbonyls on Rh_B, followed by the same migration that was found in $[Rh_7(CO)_{16}]^{3-}$, followed by a complete carbonyl scrambling over the intact Ni-capped Rh_6-octahedron. It should be noted that the n.m.r. parameters ($\delta(^{13}CO)$, $\delta(^{103}Rh)$, $^1J(^{103}Rh-^{13}CO)$) for these two compounds are very similar except that the chemical shifts of the bridging carbonyls in $[NiRh_6(CO)_{16}]^{2-}$ occur at significantly higher field than in $[Rh_7(CO)_{16}]^{3-}$, which is consistent with the increased charge, on going from the dianion to the trianion, being mainly dissipated onto the bridging carbonyls (Heaton *et al.* 1982*a*).

It should also be noted that CO migrations can occur by the pairwise interconversion of terminal and bridging carbonyls, and this is facilitated if each step of the cyclic migration regenerates a structure identical to the original, as found in $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 1, 2, 3, 4$) (Martinengo *et al.* 1977) and $[Rh_6(CO)_{13}C]^{2-}$ (Heaton *et al.* 1981*b*).

Isoelectronic clusters do not always adopt identical structures, as exemplified by the different structures of $[Rh_5(CO)_{15}]^-$ (Fumagalli *et al.* 1980) and $[FeRh_4(CO)_{15}]^{2-}$, which has been shown by n.m.r. measurements to be similar to $[RuIr_4(CO)_{15}]^-$ (Fumagalli *et al.* 1981). The subtle interplay of steric and electronic effects, which are currently not well understood, are responsible for the different structures of $[Rh_5(CO)_{15}]^-$ and $[FeRh_4(CO)_{15}]^{2-}$, and this in turn leads to different carbonyl migrational behaviour in solution (Ceriotti *et al.* 1982). Direct ^{103}Rh n.m.r. measurements provide no evidence for rearrangement of the apical iron in the $FeRh_4$-trigonal bipyramidal metal skeleton, whereas platinum is found to occupy both equatorial and apical positions in $[PtRh_4(CO)_{14}]^{2-}$ and $[PtRh_4(CO)_{12}]^{2-}$ respectively (Fumagalli *et al.* 1980*a*).

(*c*) *Intramolecular metal polyhedral rearrangements*

These were not found in the above experiments but there is an increasing number of examples of such rearrangements. The first example involved rotation of intact $Pt_3(CO)_6$ groups with respect to each other in the Pt_3-triangular stacked clusters, $[Pt_{3n}(CO)_{6n}]^{2-}$ ($n = 2, 3, 4$) (Brown *et al.* 1979*b*) and further examples involving the mono- and bi-capped square antiprismatic clusters $[Rh_9E(CO)_{21}]^{2-}$ (E = P, As), and $[Rh_{10}E(CO)_{22}]^{n-}$ (E = P, As, $n = 3$; E = S, $n = 2$) have now been found (Gansow *et al.* 1980; Garlaschelli *et al.* 1982).

(*d*) H *migration*

This can occur either around the periphery of the metallic skeleton as found for $[Ru_4(CO)_{11}\{P(OMe)_3\}H_4]$ (Knox *et al.* 1975) or within the metallic skeleton as found for $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 1, 2, 3, 4$) (Martinengo *et al.* 1977) and $[Rh_{14}(CO)_{25}H]^{3-}$ (Heaton *et al.* 1980). The latter two examples resemble H diffusion in metals. At low temperatures, (−90 °C), it is possible to stop H migration in $[Rh_{13}(CO)_{24}H_3]^{2-}$ and ^{1}H–{^{103}Rh} n.m.r. measurements show that the hydrides occupy the pseudo-octahedral holes that contain one and two edge-bridging carbonyls on the Rh_4-square faces of the hexagonal close-packed metal skeleton (figure 2*a*).

CLUSTER AGGLOMERATION BY CAPPING TRIANGULAR SQUARE FACES OF METAL POLYHEDRA

Capping of triangular or square-faces of metal polyhedra provides a controlled method for cluster growth and somewhat resembles surface reconstruction on metals.

The triangular faces of the trigonal prismatic cluster $[Rh_6(CO)_{15}C]^{2-}$ (Albano *et al.* 1973) can be capped, and n.m.r. measurements show that successive additions of $Ag[BF_4]$ to this cluster result in the progressive formation of

$$[\{Rh_6(CO)_{15}C\}Ag\{Rh_6(CO)_{15}C\}]^{3-},\ [\{Rh_6(CO)_{15}C\}Ag\{Rh_6(CO)_{15}C\}Ag\{Rh_6(CO)_{15}C\}]^{4-},$$
$$[\{Rh_6(CO)_{15}C\}Ag]_n^{n-},\ [Ag\{Rh_6(CO)_{15}C\}Ag\{Rh_6(CO)_{15}C\}Ag\{Rh_6(CO)_{15}C\}Ag]^{2-},$$
$$[Ag\{Rh_6(CO)_{15}C\}Ag\{Rh_6(CO)_{15}C\}Ag]^-,\text{ and }[Ag\{Rh_6(CO)_{15}C\}Ag].$$

The first-formed double-decker sandwich compound has been isolated and shown by X-ray crystallography to have staggered Rh_6-trigonal prismatic units bridged by Ag^I (V. G. Albano, personal communication 1982). It seems as though there is a pair of electrons located on the Rh_3-face in $[Rh_6(CO)_{15}C]^{2-}$, which is thus acting as a sophisticated ligand to Ag^I. Protonation of this face also occurs on the formation of $[HRh_6(CO)_{15}C]^-$ (Heaton *et al.* 1982*c*), but in this case there is no evidence for H-bridged oligomers.

Related reactions on Rh_3-faces can also occur with nucleophilic reagents:

$$[Rh_6(CO)_{15}]^{2-} + [Rh(CO)_4]^- \underset{-70\ °C}{\overset{+25\ °C}{\rightleftharpoons}} [Rh_7(CO)_{16}]^{3-} + 3CO. \qquad (1)$$

This reaction has been shown by ^{13}C n.m.r. to be completely reversible in MeOH under 1 atm CO, with higher temperatures favouring the larger cluster. This result appears to be quite general and there is obviously a delicate balance between cluster fragmentation and agglomeration on varying the temperature and pressure of CO.

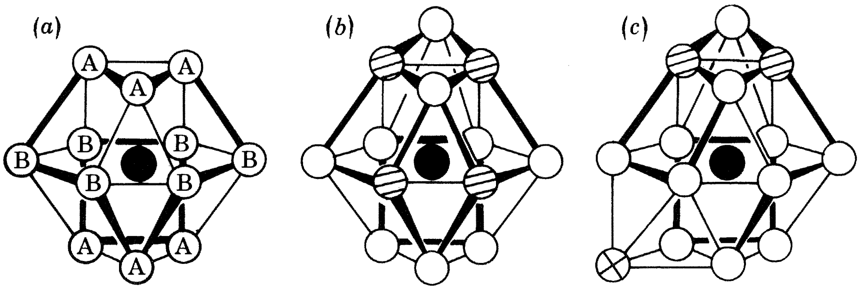

FIGURE 2. Schematic representation of the structures of (*a*) $[Rh_{13}(CO_{24}H_{5-n}]^{n-}$ ($n = 2,3,4$), (*b*) $[Rh_{14}(CO)_{25}H_{4-n}]^{n-}$ ($n = 3,4$) and (*c*) $[Rh_{15}(CO)_{27}]^{3-}$, which shows how little reorganization of the carbonyl skeleton occurs on capping a Rh_4-square-face. ●, Interstitial Rh_C; ○, rhodium with one terminal CO; ⊕, rhodium with two terminal CO's; ⊜, rhodium with no terminal CO's.

It should be noted that there is minimum reorganization of the carbonyl polyhedron on going from $[Rh_6(CO)_{15}]^{2-}$ to $[Rh_7(CO)_{16}]^{3-}$ (figure 1).

Electrophilic additions to square-faces occur in (2) and (3):

$$[Rh_{13}(CO)_{24}H]^{4-} + [Rh(CO)_2(CH_3CN)_2]^+ \longrightarrow [Rh_{14}(CO)_{25}H]^{3-} + CO; \qquad (2)$$

$$[Rh_{14}(CO)_{25}]^{4-} + [Rh(CO)_2(CH_3CN)_2]^+ \longrightarrow [Rh_{15}(CO)_{27}]^{3-}. \qquad (3)$$

Again it should be noted that minimum reorganization of the carbonyl polyhedron occurs (figure 2). The two square-faces that are capped are the same as two of the three faces that are occupied by hydrogen at low temperature in $[Rh_{13}(CO)_{24}H_3]^{2-}$, and this probably results because these faces are situated beneath large pentagonal holes on the periphery of the carbonyl polyhedron in $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 1,2,3$) (Ciani *et al.* 1981; Albano *et al.* 1975, 1979).

BONDING WITHIN THE CLUSTER

(*a*) *Carbonyls*

Charge delocalization is most effectively accomplished by bridging carbonyls, and for isoelectronic clusters there is a significant shift of $\delta(^{13}CO)_{mean}$ to lower field with increasing charge on the anion. Recent CNDO calculations (Freund & Hohlneicher 1979) on $[Co_4(CO)_{12}]$ showed that the axial carbonyl carbon is most positive and thus involved in the least metal→carbonyl back-bonding. This is also consistent with the axial carbonyl ^{13}C resonance in $[Rh_4(CO)_{12}]$ derivatives always occurring at highest field (Heaton *et al.* 1982*b*) and with their patterns of substitution. The first ligand always occupies an axial site in $[M_4(CO)_{12}]$ (M = Co, Rh, Ir) and then depending on steric effects as to whether the next ligand also goes into the electronically preferred but now sterically hindered axial site or into a radial site.

TABLE 1. ROOM-TEMPERATURE N.M.R. DATA† (SEE FIGURE 2) FOR $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n = 1, 2, 3, 4)

n =	4	3	2	1
$10^6\delta(^{103}Rh_A)$‡	−340	−403	−532	−527
$10^6\delta(^{103}Rh_B)$‡	−240	−522	−600	−536
$10^6\delta(^{103}Rh_C)$‡	+6370	+4554	+3547	+2917
$10^6\delta(^1H)$‡	−25.5	−26.7	−29.3	−31.2
$J(Rh_A\text{–}H)$/Hz	5.2	4.4	4.8	4.9
$J(Rh_B\text{–}H)$/Hz	5.2	5.8	5.7	4.9
$J(Rh_C\text{–}H)$/Hz	17.1	22.3	23.2	18.6

† $\delta(^{103}Rh)\ 0 \times 10^{-6}$ = 3.16 MHz at such a magnetic field that the protons in TMS resonate at exactly 100 MHz.
‡ The factor 10^{-6} is used to denote the notion of parts per million.

(*b*) *Metals*

Interstitial rhodium atom resonances are always at high frequency in a region normally associated with positive oxidation states. For $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n = 1, 2, 3, 4), increasing the number of hydrides migrating interstitially around the interstitial rhodium atom, Rh_C, results in a dramatic shift of $\delta(^{103}Rh_C)$ to lower frequency while the peripheral rhodium atoms, Rh_A and Rh_B, vary very little (table 1). This is consistent with increased diamagnetic shielding of Rh_C and suggests that interstitial metal atoms are more positive than surface metal atoms, which is in keeping with bulk metallic properties. It seems probable that the large variation in $\delta(^{103}Rh)$ that alternates along the C_3-axis in $[Rh_7(CO)_{16}]^{3-}$ and along the C_4-axis is $[Rh_{14}(CO)_{25}H_{4-x}]^{x-}$ (x = 3, 4) (Brown *et al.* 1979*a*; Heaton *et al.* 1980) could also be ascribed to alternation of charge along the principal axis of the metallic skeleton, with capping atoms exhibiting electropositive character similar to kink and step sites on metallic surfaces.

(*c*) *Main group elements in interstitial sites*

These have already been discussed (Chini 1980) and the recent low-field shift of the carbide resonance on going from the trigonal prismatic cluster, $[Rh_6(CO)_{15}C]^{2-}$, to the octahedral cluster, $[Rh_6(CO)_{13}C]^{2-}$, is in keeping with a contraction of the radius of carbon and an increase in positive charge (Heaton *et al.* 1981).

Recent infrared work on the isostructural, isoelectronic clusters $[M_6(CO)_{15}C]^{2-}$ and $[M_6(CO)_{15}N]^-$ (M = Co and Rh) showed the metal–interstitial atom force constants to be very similar for the M_6–C and M_6–N groups with the values for M = Rh being significantly smaller than when M = Co (Creighton *et al.* 1982).

N.M.R. MEASUREMENTS UNDER HIGH PRESSURES OF GAS

Homogeneous catalytic reactions often require high pressures and elevated temperatures, and until recently high-pressure infrared spectroscopy has been the only spectroscopic technique available to monitor such reactions. However, n.m.r. probes capable of measurements under high pressures of gas (up to 1 kbar (10^5 Pa)) have recently been developed and these will provide more unambiguous spectroscopic evidence about catalytic intermediates and mechanisms than has been available hitherto. The first studies in this area were connected with the catalytic synthesis of ethylene glycol from synthesis gas as it was shown that $[Rh_5(CO)_{15}]^-$ was the only species present under 1 kbar CO–H_2 at 25 °C (Heaton *et al.* 1981*a*).

Further developments are in hand to allow measurements at higher temperatures so that *in situ* measurements under catalytic conditions can be made. This technique promises to be extremely important, especially as it can readily be extended to other nuclei (e.g. ^{1}H, ^{13}C, ^{31}P).

I thank the S.E.R.C. for their financial support of this work, the preparative expertise of Dr L. Strona and Dr R. Della Pergola in Canterbury and the group of cluster chemists in Milan, Dr R. J. Goodfellow for ^{1}H–{^{103}Rh} measurements, Dr I. H. Sadler for ^{103}Rh measurements, and Professor J. Jonas for the use of his spectrometer for the initial high-pressure n.m.r. experiments.

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Discussion

Joan Mason (*Chemistry Department, The Open University, U.K.*). Ed Randall has mentioned the usefulness of the quadrupolar nucleus ^{17}O in n.m.r. studies of metal carbonyl clusters. We found that both ^{14}N and ^{15}N n.m.r. spectroscopy were interesting and informative in the study of interstitial nitrogen in the trigonal prismatic clusters of cobalt and rhodium, $[PPh_4][M_6N(CO)_{15}]$ (Martinengo *et al.* 1979). This is because the quadrupolar ^{14}N nucleus gives relatively sharp lines when the local symmetry is high, as well as the line width containing information on this symmetry. Indeed, the line widths were similar ($W_{\frac{1}{2}} \sim 40$ Hz) in ^{14}N and in ^{15}N resonance (with ^{15}N enrichment) in the cobalt cluster, with line broadening due to the ^{59}Co quadrupole and to unresolved cobalt–nitrogen coupling. The ^{14}N and ^{15}N lines were sharper for the rhodium cluster, because ^{103}Rh has $I = \frac{1}{2}$. The ^{14}N line width was now 20 Hz, no spin–spin coupling being resolved; but ^{15}N resonance, with enrichment, yielded the central five lines of the expected septet, with $J_{Rh^{15}N} = 6$ Hz and $W_{\frac{1}{2}} = 1$ Hz. This coupling constant matches the $J_{Rh^{13}C} = 14$ Hz observed for interstitial carbide in the isostructural complexion $[Rh_6C(CO)_{15}]^{2-}$ (given the different magnetogyric ratios), which suggests that the charge dispositions may be similar for the nitride and carbide.

The rhodium–^{15}N coupling constant of 6 Hz corresponds to a ^{14}N value of 4 Hz, so the ^{14}N line width in the absence of unresolved coupling may be as small as 5–8 Hz. Coupling to interstitial ^{14}N might therefore be measurable for metal nuclei with higher magnetogyric ratios.

Comparison of the ^{14}N and ^{15}N line widths indicates broadening by quadrupolar relaxation for ^{14}N; the local symmetry is less than spherical, and molecular vibrations and collisions give rise to transient electric field gradients. Smaller line widths, less than 1 Hz, are observed for aqueous $^{14}NH_4^+$ and $^{14}NMe_4^+$, and these are explained in part by shorter correlation times τ_q for the smaller ions, because $W_{\frac{1}{2}}$ is proportional to τ_q. The observed quadrupolar relaxation time $T_q (= 1/\pi W_{\frac{1}{2}} \approx 50$ ms) for nitride in the rhodium cluster, with a correlation time of say, 10^{-10} s, corresponds to a nuclear electric quadrupole coupling constant of about 1 MHz. This is larger than has been observed for NH_4^+ in solids (Wolff *et al.* 1977) and so may correspond to slightly lower symmetry for nitrogen in the cluster.

The nitrogen shifts were unexpected. We observed (Martinengo *et al.* 1979) the customary increase in shielding down the group of the transition metal (from cobalt to rhodium) for the nitrides, as for the isostructural carbides in ^{13}C resonance; but the lines were at relatively high field in nitrogen resonance and at low field in carbon resonance. The radial factor $\langle r^{-3} \rangle_{2p}$ in the paramagnetic shielding term commonly gives nitrogen shifts (measured downfield of NH_4^+) that are roughly double the carbon shifts (measured downfield of CH_4) in isoelectronic molecules, the deshielding circulations of the 2p electrons being closer to the more electronegative nucleus. The reversal that we observe for the isoelectronic carbide and nitride points to the dominant factor being the energy denominator (in the paramagnetic term) which represents the h.o.m.o.–l.u.m.o. gap for the rotation of electronic charge in the magnetic field (Mason 1981). Certainly the range of chemical shifts observed for interstitial atoms in (diamagnetic) metal carbonyl clusters, which is 54×10^{-6} for ^{1}H so far, is larger than could be accounted for by differences in atomic charge (which act upon the radial factor). X-ray crystallographic measurements give the carbon and nitrogen radii within the Co_6 trigonal prism as 74 and 67 pm respectively (Martinengo *et al.* 1979), so perhaps there is greater overlap and splitting of the relevant orbitals in the nitride, increasing the h.o.m.o.–l.u.m.o. gap for charge rotation. (Interestingly,

$[Co_6C(CO)_{15}]^{2-}$ is black and $[Co_6N(CO)_{15}]^{-}$ orange-red!) There is, however, no simple relation between ^{13}C shift and cavity size for the small number of interstitial carbides so far reported; as we might expect, the cluster symmetry is also important.

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B. T. Heaton. The supposition by Dr Mason that comparison of $^1J(^{103}Rh–^{13}C)$ and $^1J(^{103}Rh–^{15}N)$ in $[Rh_6(CO)_{15}E]^{n-}$ ($E = C$, $n = 2$; $E = N$, $n = 1$) provides information on charge disposition on the interstitial atom is erroneous. While agreeing with her final statement on the importance of cluster symmetry in determining the interstitial atom chemical shift, it seems premature to state that 'there is no simple relation between ^{13}C shift and cavity size' because, apart from Bradley's work (see his paper in this symposium), there is only one other report (Heaton *et al.* 1981 *b*) of interstitial atom n.m.r. data on closely related clusters containing the same number of the same metal atoms. Comparisons outside such closely related clusters are positively hazardous at the moment!

E. W. Randall (*Chemistry Department, Queen Mary College, London, U.K.*). Since Dr Heaton used material enriched in ^{13}C for his n.m.r. studies did he consider measuring ^{13}C T_1 values?

B. T. Heaton. Few reports have currently appeared on ^{13}C T_1 values of carbonyl clusters. It would be very interesting to obtain this information but so far we have been prevented from carrying out these experiments by the limited spectrometer time available to me.

E. W. Randall. One advantage that ^{17}O has over ^{13}C is the generally fast relaxation (up to 1000 times faster than for ^{13}C), which allows relatively easy measurement of T_1, $T_{1\rho}$ and T_2. These quantities yield information on the overall dynamics of the cluster, including fluxional processes, and a comparison of these quantities for any one centre enables a separation of the different processes to be made. Additionally, in non-fluxional limits which yield resolved environments it is possible in the relatively isotropic overall tumbling case of large clusters to deduce from differences in T_1 values for different sites quite pronounced differences in the contribution of the term involving the nuclear electric quadropole to the ^{17}O relaxation. Dr G. E. Hawkes and Dr S. Aime have found a factor of about 500 in this (quadrupolar) term for the two CO environments of $Rh_6(CO)_{16}$.