AN NMR STUDY OF CARBIDE CLUSTERS

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Summary

^{13}C and ^{13}C-$\{^{103}Rh\}$ data on $[Rh_6(CO)_{15}C]^{2-}$ and $[Rh_6(CO)_{13}C]^{2-}$ are reported and compared. $[Rh_6(CO)_{13}C]^{2-}$ undergoes a unique facile intramolecular CO migration around the equator of the Rh_6 octahedron; at 25°C, $[Rh_6(CO)_{15}C]^{2-}$ undergoes preferential intermolecular CO exchange at sites which have the longest Rh—CO bonds and direct exchange of terminal carbonyls is easier than edge-bridging carbonyls with approximately similar Rh—CO bond lengths.

Introduction

Since the first X-ray structural characterisation of a carbide cluster, $[Fe_5(CO)_{15}C]$ [1], many other homo-metallic carbide clusters based on:
five metal atoms, $Os_5(CO)_{15}C$ [2], $[Os_5(CO)_{15}IC]^-$ [2], $HOs_5(CO)_{13}\{OP(OMe)-OP(OMe)_2\}C$ [3], $HOs_5(CO)_{14}\{OP(OMe)_2\}C$ [4];
six metal atoms, $[Fe_6(CO)_{16}C]^{2-}$ [5], $[Ru_6(CO)_{16}C]^{2-}$ [6,7], $Ru_6(CO)_{17}C$ [8], $Ru_6(CO)_{14}(C_9H_{12})C$ [9], $Ru_6(CO)_{14}(C_{14}H_{14})C$ [10], $Os_6(CO)_{16}(MeC \equiv CMe)C$ [11], $[M_6(CO)_{15}C]^{2-}$ (M = Co, Rh) [12], $[Co_6(CO)_{14}C]^-$ [13], $Co_6(CO)_{12}(S)_2C$ [14], $[Rh_6(CO)_{13}C]^{2-}$ [15];
eight metal atoms, $[Co_8(CO)_{18}C]^{2-}$ [16], $Rh_8(CO)_{19}C$ [17];
ten metal atoms, $[Os_{10}(CO)_{24}C]^{2-}$ [18];
twelve metal atoms, $Rh_{12}(CO)_{25}(C_2)$ [19], $[Rh_{12}(CO)_{24}(CO)_2]^{2-}$ [20];
thirteen metal atoms, $[Co_{13}(CO)_{24}H(C)_2]^{4-}$ [21]; and
fifteen metal atoms, $[Rh_{15}(CO)_{28}(C)_2]^-$ [22]
have been structurally characterised as well as the following mixed metal carbide clusters: $[RhFe_4(CO)_{14}C]^-$ [23], $[MoFe_5(CO)_{17}C]^{2-}$ [23] and $(MeCN)_2Cu_2$-

$Rh_6(CO)_{15}C$ [24]. The related, but presently unique, interstitial nitrides, $[M_6(CO)_{15}N]^-$ (M = Co, Rh), have recently also been reported [25].

The position of the interstitial atom resonance in the NMR spectrum of closely related clusters could provide significant information about the charge on the interstitial atom [26] but, apart from our own work in this area [16,27,28], carbide NMR data on the above clusters have not been reported *.

We now describe a variable temperature ^{13}C and ^{13}C-$\{^{103}Rh\}$ NMR study of the octahedral cluster $[Rh_6(CO)_{13}C]^{2-}$, which results on heating the trigonal prismatic cluster $[Rh_6(CO)_{15}C]^{2-}$. This allows NMR data for these two related carbide clusters and for $[Rh_6(CO)_{15}N]^-$ to be compared. Additionally, $[Rh_6(CO)_{13}C]^{2-}$ provides a unique example of carbonyl migration around the equator of a Rh_6-octahedron and evidence is presented for preferential intermolecular CO exchange in $[Rh_6(CO)_{15}C]^{2-}$ at sites involving the longest Rh—CO bond.

Results and discussion

The structure of $[Rh_6(CO)_{13}C]^{2-}$ is rather asymmetric with idealised C_s-m molecular symmetry; it consists of a distorted octahedral metal skeleton containing the interstitial carbide with 7 terminal and 6 edge-bridging carbonyls (see Fig. 1) [15]. However, the ^{13}C NMR spectrum of $[Rh_6(CO)_{13}C]^{2-}$ (ca. 20% ^{13}CO) at —96°C is much simpler than expected for the instantaneous structure and consists of a triplet, quintet, and doublet of relative intensities 4/7/2, respectively (see Fig. 2(3)). This spectrum can be rationalised by the CO-migration shown schematically in Fig. 1. It involves a pairwise CO exchange of 5 terminal with 2 edge-bridging CO's around the $(Rh_B)_4$-equatorial plane and leaves the terminal CO on each Rh_A and the 4 bridging CO's between Rh_A and Rh_B unchanged. It should be noted that this facile CO-migration is related to that found in $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n = 1, 2, 3 and 4) [29], since each step of the cyclic migration regenerates a structure identical to the original.

The migration illustrated in Fig. 1 is substantiated by specific ^{103}Rh spin-decoupling of the ^{13}C NMR spectrum, (Fig. 2(1) and 2(2)). Thus, decoupling Rh_A collapses the doublet due to CO_a (Fig. 3) and the triplet due to CO_c becomes a doublet due to $^1J(Rh_B$—$CO_c)$; similarly decoupling Rh_B causes the quintet due to CO_b to collapse to a singlet and the triplet due to CO_c again becomes a doublet.

At room temperature all the carbonyls become equivalent, $\delta(^{13}CO)$ 217.7, calc. 218.5 ppm, but this process, which probably involves migration around the two square-planes incorporating $(Rh_A)_2(Rh_B)_2$, is considerably less favourable because it does not regenerate intermediates with structures identical to the original.

The ^{13}C NMR spectrum of an all ^{13}C-enriched sample of $[Rh_6(CO)_{13}C]^{2-}$ (^{13}CO ca. 20%, carbide 90% ^{13}C) at —80°C is essentially the same as shown in Fig. 2(3) except for the appearance of a multiplet due to the carbide at 335.8 ppm and a further doublet splitting of both the quintet and high field doublet is observed due to $^2J(^{13}C_{carbide}$—$^{13}CO)$, 6.5 and 11 Hz, respectively. The carbide resonance is complex because of coupling to 2 Rh_A's, 4 Rh_B's, to the carbonyls involved in exchange (CO_b) and to 2 CO_a's, (see Fig. 3). The large value

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* Note added in proof. $\delta(^{13}C_{carbide})$ = 288 ppm in $[Ru_6(CO)_{16}C]^{2-}$ has recently been reported [34].

= μ-CO

= terminal CO
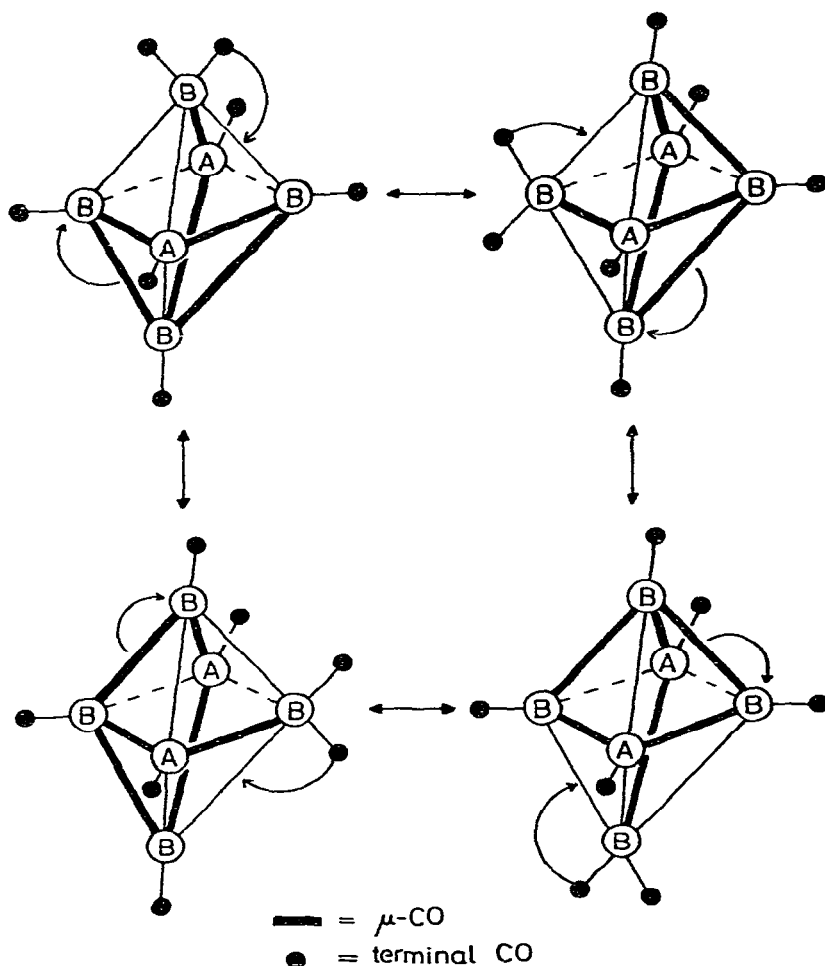
Fig. 1. Schematic representation of the lowest energy terminal/bridging carbonyl exchange in [Rh$_6$(CO)$_{13}$C]$^{2-}$. The interstitial carbide has been omitted for clarity.

of $^2J(^{13}C_{carbide}$—$^{13}CO_a)$ undoubtedly arises because of the 180° bond angle between these two carbons. Assuming that $^2J(^{13}C$—$^{13}C)$ is only significant when the angle $C_{carbide}$—Rh—CO is ca. 180°, then the smaller value of $^2J(^{13}C_{carbide}$—CO$_b$) 6.5 Hz is exactly that predicted ($\frac{3}{5} \times$ 11 Hz) when there is fast CO exchange around the (Rh$_B$)$_4$ square-plane.

Consistent with the solid state structure of [Rh$_6$(CO)$_{15}$C]$^{2-}$ [12], previous ^{13}C NMR spectra contained three carbonyl resonances of intensities 3/6/6 [27]. These measurements were carried out on samples prepared via: (a) ^{13}C-enriched [Rh(CO)$_4$]$^-$ and (b) direct exchange of ^{13}CO with [Rh$_6$(CO)$_{15}$C]$^{2-}$ at 80°C. It is now known that, at 80°C, [Rh$_6$(CO)$_{15}$C]$^{2-}$ is converted to [Rh$_6$(CO)$_{13}$C]$^{2-}$ which is transformed back to [Rh$_6$(CO)$_{15}$C]$^{2-}$ on cooling under a CO atmosphere. As a result, no specific site ^{13}C-enrichment would be expected from either of these preparations. However, the ^{13}C NMR spectrum (Fig. 4(2)) of a sample prepared by direct exchange with ^{13}CO at 25°C clearly shows that reso-

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Assignment   c   b   a

Fig. 2. Specific ^{103}Rh spin-decoupling of the ^{13}C NMR spectrum of $[Rh_6(CO)_{13}C]^{2-}$ at $-96°$C in THF-d_8. Decoupling at: (1) 3.156842 MHz ($\delta(Rh_A)$ —1003 ppm); (2) 3.158067 MHz ($\delta(Rh_B)$ —615.3 ppm); (3) no decoupling. (For assignments see Figs. 1 and 3.)

Fig. 3. Schematic representation of the structure of $[Rh_6(CO)_{13}C]^{2-}$. The interstitial carbide has been omitted for clarity.

Intensity		x		y		z
	calculated	3	:	6	:	6
	found	3	:	33	:	10

Fig. 4. ^{13}C (2) and ^{13}C-$\{^{103}$Rh$\}$ (1) NMR spectrum of [Rh$_6$(CO)$_{15}$C]$^{2-}$ (ca. 25% ^{13}CO) prepared by direct exchange with ^{13}CO at 25°C; S = solvent resonance.

nance y is more intense than expected due to specific site enrichment at the edge-bridging site within a Rh$_3$-triangle *. The ratio of observed intensities for the two edge-bridging carbonyl resonances x/y (Fig. 4) is 3/33, which should be compared with the expected ratio of 3/6. This suggests that CO exchange occurs via a dissociative mechanism since the intra-triangular carbonyls, which have the longer Rh—CO bond (2.12 Å), exchange faster than the inter-triangular carbonyls (d(Rh—CO) 2.04 Å). Because of the different number of Rh—CO bonds involved, it is difficult to use similar arguments when comparing terminal and edge-bridging carbonyls. Nevertheless, direct exchange at a terminal site appears easier than at a bridging site since, despite the Rh—CO$_{terminal}$ bond (1.89 Å) being shorter than the intertriangular Rh—CO bond (2.04 Å), there is

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* ^{13}C NMR measurements were carried out on deuterioacetone solutions (ca. 0.1 mol dm^{-3}), doped with [Cr(acac)$_3$] (acac = acetylacetonate) at a level of 1 mg per 400 mg of sample (ca. 30—40% ^{13}CO enriched). The relative intensities of the carbonyl peaks were unchanged on varying the repetition time (T_R) between pulses from 1 to 5 s. Previous measurements [27], which resulted in the correct ratio of relative intensities, used T_R 1 s.

TABLE 1

NMR DATA FOR $[Rh_6(CO)_{13}C]^{2-}$, $[Rh_6(CO)_{15}N]^-$ AND $[Rh_6(CO)_{15}C]^{2-}$ IN THF-d_8 OR ACETONE-d_6 SOLUTIONS

Compound	T (°C) (solvent)	δ (interstitial)	δ(^{13}CO) [a]			δ(^{103}Rh) [b]	(^{13}CO)$_{mean}$	(^{103}Rh)$_{mean}$
			μ-CO	CO$_{terminal}$				
$[Rh_6(CO)_{13}C]^{2-}$	−96 (THF-d_8)	324	242.5(38.1) [4]	207.7(22.5) [7]	202.4(91.8) [2]	−1003(Rh$_A$) [c] / −615(Rh$_B$) [c]	217.6	−744.3
$[Rh_6(CO)_{15}N]^-$	−82 (acetone-d_6)	90.7 [d]	226.8(48.3) [3]	217.6(29.8) [6]	191.4(85.9) [6]	−241.8	209.0	−241.8
$[Rh_6(CO)_{15}C]^{2-}$	−79 (acetone-d_6)	264.7	236.3(51.7) [3]	225.2(30.3) [3]	198.1(78.1) [6]	−313.0	216.6	−313

[a] Figures in () are values of $^1J(^{103}$Rh—^{13}CO) and figures in [] indicate relative intensities. [b] 3.16 MHz = 0 ppm at such a magnetic field that protons resonate at exactly 100 MHz, high frequency (downfield) shifts are positive. [c] See Fig. 3 for assignments. [d] With respect to ^{15}NH$_4$NO$_3$.

higher enrichment at the terminal site (this ratio is expected to be 3/6 for x/z, Fig. 4, but the observed ratio is 3/10). Stereospecific CO exchange is now well established in mono- and di-metallic carbonyls and a few examples have recently also been reported in trimetallic clusters [30,31]. However, the latter substitutions involve conversion of 3-electron donor ligands (e.g. NO, Cl) to 1-electron ligands with concommitant CO substitution via an associative route and, to our knowledge, stereospecific site exchange in $[Rh_6(CO)_{15}C]^{2-}$ provides the first conclusive evidence for dissociative exchange in clusters being related to $d(Rh-CO)$ and for terminal CO exchange being easier than bridging CO exchange.

The NMR data of $[Rh_6(CO)_{13}C]^{2-}$ (1), and the isoelectronic, isostructural clusters, $[Rh_6(CO)_{15}N]^-$ (2) and $[Rh_6(CO)_{15}C]^{2-}$ (3), are tabulated in Table 1. The interstitial atom in (1) is located in a smaller cavity (0.60 Å) than in (3) (0.74 Å) and, consistent with this contraction of the radius of carbon and associated increase in positive charge, the interstitial atom resonance in (1) has a much bigger chemical shift than in (3). Comparison of NMR data of isoelectronic/isostructural $^{13}C/^{15}N$ derivatives show that $\delta(^{13}C) \simeq 2\ \delta(^{15}N)$. The ^{15}N chemical shift in (2) is significantly less than would have been expected using this relationship and this suggests that the interstitial carbon in (3) is more positive than the nitrogen in (2) which is consistent with nitrogen donating less electrons to the cluster than carbon because of its higher electronegativity.

The value of $\delta(^{13}CO)_{mean}$ in (3) is higher than in (2), which is consistent with the difference in charge on these two anions, and similarly $\delta(^{13}CO)_{mean}$ in (1) is higher than in (3) because of the smaller number of carbonyls involved in charge dissipation.

In closely related clusters, $\delta(^{103}Rh)$ can provide information on charge distribution within the metallic skeleton [32] with large positive chemical shifts being associated with positive oxidation states. The difference in $\delta(^{103}Rh)_{mean}$ between (2) and (3) is minimal. However, in (1) $\delta(^{103}Rh)_{mean}$ is significantly lower and this could be due to the rhodium atoms being more negative because of the less effective charge dissipation by the reduced number of carbonyls.

Experimental

^{13}C and $^{13}C-\{^{103}Rh\}$ NMR measurements were carried out as described previously [33] and $[Rh_6(CO)_{15}C]^{2-}$ and $[Rh_6(CO)_{13}C]^{2-}$ were prepared using literature methods [12,15].

Acknowledgements

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