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Solid State Multinuclear NMR Studies on $M_4(CO)_{12}$ (M=Co, Rh) and $(NMe_3Bz)_2[Rh_6(CO)_{15}C]$

Brian T. HEATON,* Javad SABOUNCHEI, Stuart KERNAGHAN, Hirokazu NAKAYAMA,† Taro EGUCHI,*,† Sadamu TAKEDA,†† Nobuo NAKAMURA,†† and Hideaki CHIHARA††
Department of Chemistry, University of Liverpool, Liverpool L69 3BX, United Kingdom
†College of General Education, Osaka University, Toyonaka, Osaka 560
††Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
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Synopsis. Variable Temperature ^{13}C MAS and ^{59}Co NMR data on solid $Co_4(CO)_{12}$ show that there is a symmetry conserved reorientation of the Co_4-tetrahedron which is more restricted than has been reported previously whereas the room temperature ^{13}C MAS NMR spectra of $Rh_4(CO)_{12}$ and $(NMe_3Bz)_2[Rh_6(CO)_{15}C]$ are consistent with their solid state static structure.

$Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ undergo fast carbonyl exchange in solution.[1,2] In the solid state, the reported ^{13}C MAS NMR spectra of $Co_4(CO)_{12}$ are surprisingly different[3,4] and, although variable temperature measurements indicated some fluxionality, the exact mechanism of CO and/or Co motion is still confused.[3–5] In order to gain further insight into this problem, we report variable temperature ^{13}C and ^{59}Co NMR data for solid $Co_4(CO)_{12}$ which show that there is restricted motion of the Co_4-tetrahedron. These data are more consistent with reorientation of the Co_4-tetrahedron about the C_3-axis incorporating the apical Co rather than the interconversions proposed previously.[3–5] We also report room temperature ^{13}C MAS NMR spectra of the related cluster $Rh_4(CO)_{12}$, and for comparison, because there are presently no reports of ^{13}C NMR spectra in the solid state of tetra- and higher-nuclearity carbonyl clusters which do not exhibit fluxionality in solution, $(NMe_3Bz)_2[Rh_6(CO)_{15}C]$; both spectra are consistent with their solid state structures and their static ^{13}C NMR spectra in solution. Unfortunately, it was impossible to measure the ^{13}C MAS NMR spectra of $Rh_4(CO)_{12}$ at higher temperature because of the extremely long collection times (T_1>3000 s at room temperature) with associated decomposition to $Rh_6(CO)_{16}$.

In solution, $[Rh_6(CO)_{15}C]^{2-}$ is static at all temperatures and the ^{13}C NMR spectrum contains 2 bridging CO resonances in the ratio 3 : 6 due to inter- and intra-triangular bridging CO's respectively and a terminal resonance with relative intensity 6 consistent with the D_{3d} symmetry (Table 1).[6] In the solid state,[7] this symmetry is reduced to C_2 giving rise to the following

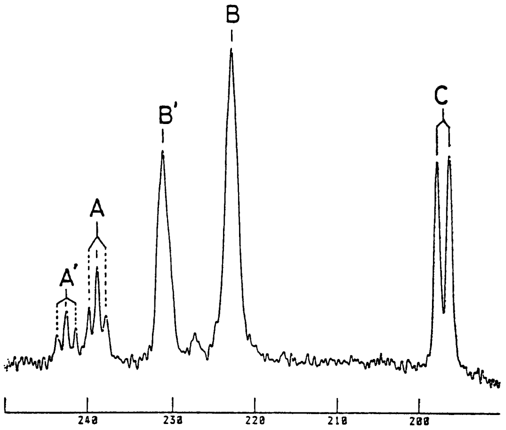
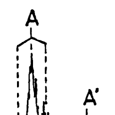


Fig. 1. The ^{13}C MAS NMR spectrum of solid $(NMe_3Bz)_2[Rh_6(CO)_{15}C]$ at room temperature at 50.3 MHz. All the measurements in this study have been carried out by using a Bruker MSL-200 pulsed spectrometer.

Table 1. Comparison of Solution and Solid State ^{13}CO NMR Data

Cluster	Assignment[6,9]	δ(CO)/ppm (^1J(Rh-CO)/Hz)	
		Solution[6,9]	Solid
$(NMe_3Bz)_2[Rh_6(CO)_{15}C]$	Bridge (A,A′)[a]	235.4 (51.4)	242.7 (45.0)
			239.1 (45.0)
	Bridge (B,B′)[b]	224.0 (30.5)	231.4
			223.0
	Terminal (C)	196.9 (79.3)	197.7 (75.5)
$Rh_4(CO)_{12}$	Bridge (A,A′)	228.8 (35)	228 (ca. 31)
			226 (ca. 41)
	Apical (B,B′)	181.8 (64)	183.4 (62.6)
			179.2 (62.8)
	Radical (C,C′)	183.4 (75)	184 (ca. 85)
			182.6 (ca. 75)
	Axial (D.D′)	175.5 (62)	175.4 (62.7)
			173.3 (62.7)

[a] Inter-Rh_3-triangular. [b] Intra-Rh_3-triangular.



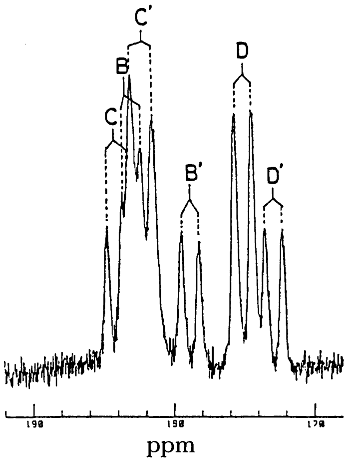


Fig. 2. The ^{13}C MAS NMR spectrum of solid $Rh_4(CO)_{12}$ (ca. 20% ^{13}CO) at room temperature.

inequivalent CO's: intra-triangular 1 : 2, inter-triangular 2 : 2 : 2, terminal 2 : 2 : 2. Figure 1 shows that the observed low field resonance is clearly as expected with some coincidence in the inter-triangular resonances and the terminal CO's give only one sharp doublet. Nevertheless, it is possible to rationalize the solid state spectrum of $[Rh_6(CO)_{15}C]^{2-}$ by consideration of just a single molecule in the unit cell, together with the local symmetry, and the values of both δ(^{13}CO) and *J*(Rh-CO) are similar in solution and the solid state (Table 1).

For $Rh_4(CO)_{12}$, the low temperature spectrum in solution consists of 4 equally intense resonances due to the bridge, apical, radial and axial CO's which have been assigned by comparison with the ^{13}C-{^{103}Rh} decoupled spectra of phosphite substituted derivatives of $Rh_4(CO)_{12}$ (Table 1).[9] Although the X-ray structural determination of $Rh_4(CO)_{12}$ was complicated by twinning,[10] consideration of a single Rh_4-tetrahedron within the unit cell shows that there is a pseudo-plane of symmetry (incorporating the edge M_1M_3 and mid-point of M_2-M_4 in Fig. 3 of Ref. 10). As a result, each of the 4 sets of CO resonances observed in solution could reasonably be expected to be duplicated in the solid state in the ratio 1 : 2. Inspection of Fig. 2 ar

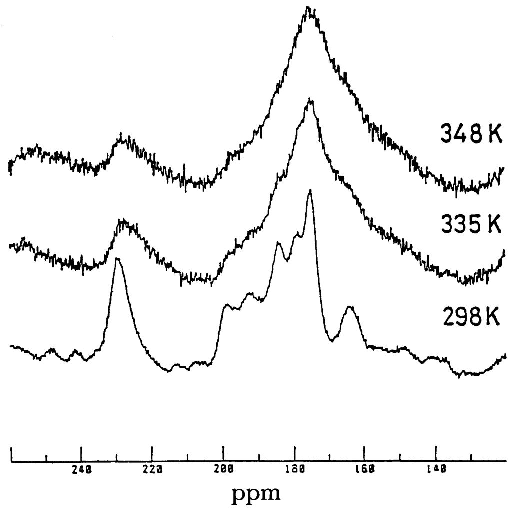


Fig. 3. The ^{13}C MAS NMR spectra of solid $Co_4(CO)_{12}$ (ca. 20.2% ^{13}CO) as a function of temperature.

Table 1 is consistent with such an explanation and clearly show that, at room temperature, $Rh_4(CO)_{12}$ is not fluxional.

The temperature dependent ^{13}C MAS NMR spectra (50.3 MHz) of solid $Co_4(CO)_{12}$ are shown in Fig. 3 and Table 2 lists the peak positions, we find at low temperature which are compared with data previously reported.[3,4] We have no explanation for the widely different values of δ(^{13}CO) in Table 2, but in view of the data in Table 1, we are confident of our data on $Co_4(CO)_{12}$. However, unlike the spectra of the rhodium clusters, it is impossible to make precise assignments for $Co_4(CO)_{12}$ because the resonances are broad due to ^{59}Co-^{13}C dipolar coupling. Nevertheless, the bridging CO resonance (225 ppm) is clearly visible even at 348 K which suggests that there is no exchange of bridge/terminal CO's at this temperature; the broadening of the ^{13}CO resonances with increasing temperature can be attributed solely to the motion of the Co_4-tetrahedron (vide infra) which is better determined through ^{59}Co NMR measurements.

As found in solution,[11] the ^{59}Co NMR spectrum consists of 2 resonances in the ratio 1 : 3 due to the apical and basal Co's respectively. With increasing

Table 2. Solution and Solid State δ (^{13}CO) NMR Data on $Co_4(CO)_{12}$ Attributed to the Static Structure

	Solution	Solid		
	Ref. 11[a)]	Ref. 3[b)]	Ref. 4[c)]	This work[d)]
Bridge	243.1		244.9	229.3
			236.1	
Terminal	ca. 200—205	213.2	206.2	198.4
	195.6	189.8	199.3	192.4
	191.7	170.8	184.9	183.7
		158.2		178.9
				175.0
				163.8

Measurements at: a) 100.6 MHz, b) 22.6 MHz, c) 68 MHz, d) 50.3 MHz.

Table 3. Solution and Solid State δ (^{59}Co) NMR Data on $Co_4(CO)_{12}$[a)]

T/K	Solution[b)]	Solid[c)]		
	298	106	295	351
Apical	−715	−766	−715	−671
Basal	−2065	−1500	−1125	−973

a) The shifts are relative to the ^{59}Co resonance of aqueous $K_3[Co(CN)_6]$. b) Ref. 11. c) This work.

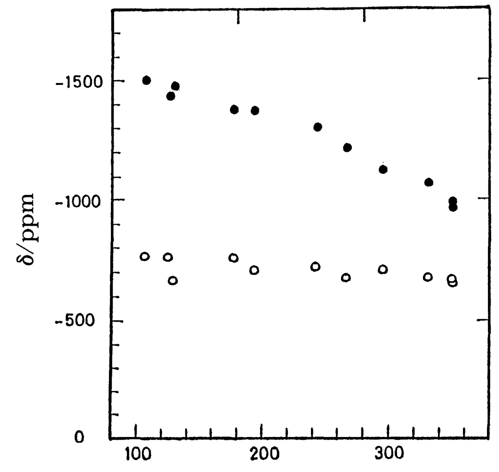


Fig. 4. Temperature dependence of δ (^{59}Co) for solid $Co_4(CO)_{12}$ with respect to $K_3[Co(CN)_6]$ at 47.2 MHz; (positive values of δ are to high frequency) ● basal Co; ○ apical Co.

temperature, there is a dramatic shift in $\delta(Co_{basal})$ whereas $\delta(Co_{apical})$ effectively remains unchanged (Table 3 and Fig. 4). Because of this coalescence, it is almost impossible to obtain separate relaxation times for the apical and basal Co atoms at different temperatures. However, it was found that the apparent width of a $\pi/2$ pulse for Co_{apical} is much shorter than that for the Co_{basal}. This leads to that the quadrupole coupling constant (e^2Qq/h) of Co_{apical} should be larger than e^2Qq/h of Co_{basal}.[12)] In addition, for nuclei with I=7/2, the recovery of magnetization always consists of at least two components. It is clear from the measured ^{59}Co spin-lattice relaxation time, which must be dominated by the basal Co's, that there are two components and both show a sharp decrease above 250 K (Fig. 5) due to fluctuations in electric field gradient induced by some reorientation. This motion (activation energy 40±5 kJ mol^{-1}) with $\tau_c \simeq 0.1$—10 ms is comparable to the ^{13}CO linewidths and is sufficient to account for the line-broadening in Fig. 3. Since coalescence of bridge/terminal carbonyl resonances has not been observed and because of the dependence of δ(^{59}Co) with temperature, these data are more consistent with only a symmetry conserved reorientation of the Co_4-tetrahedron about the C_3-axis incorporating Co_{apical}.

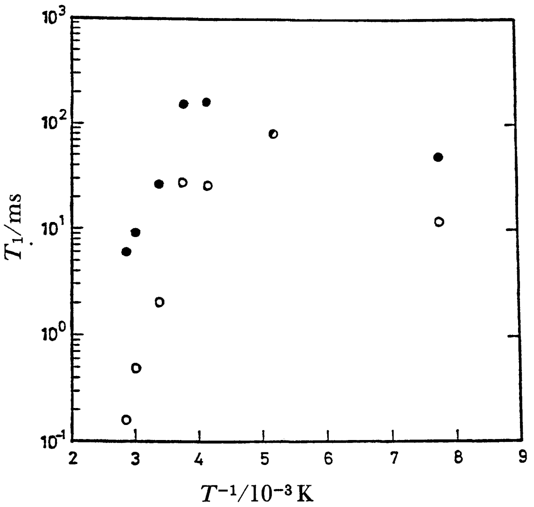


Fig. 5. ^{59}Co T_1 vs. $1/T$; ○ short component, ● long component. T_1 was determined by the inversion recovery method.

The above data does not support any of the previous proposals based on complete CO-exchange, rotation about four three-fold axes of the Co_4-tetrahedron or rotation about the C_2-axis associated with the disorder in the crystal.

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