

^{13}C Nuclear Magnetic Resonance of Triacontacarbonyldodecarhodate(2—):
 $[\text{Rh}_{12}(\text{CO})_{20}(\mu_2\text{-CO})_2(\mu_3\text{-CO})_8]^{2-}$

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Summary The ^{13}C n.m.r. spectrum of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ is shown to be fully consistent with X-ray structural data and provides the first example of a triply bridging carbonyl resonance.

METAL carbonyl cluster chemistry is rapidly expanding mainly because of the ease of obtaining X-ray structural data.¹ Useful structural information on such species can now also be obtained from n.m.r. measurements,^{2,3} which

also provide a reliable comparison of solid and solution structures. Carbonyl metallate cluster derivatives, with suitable cations, have high solubility at low temperatures and are thus particularly amenable to n.m.r. measurements. We are currently investigating the relationship between solid and solution structures of such species and we are also using n.m.r. spectroscopy to characterise less stable species which cannot be isolated as crystalline solids.

This paper reports the ^{13}C n.m.r. spectrum of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$, (ca. 60% ^{13}C) in perdeuterioacetone solution containing $\text{Cr}(\text{acac})_3$ as relaxing agent.⁴ At -70° , the ^{13}C n.m.r. spectrum (Figure 1) is entirely consistent with the X-ray structural determination⁵ (Figure 2) and shows the presence of 3 inequivalent groups of terminal carbonyls (A, B, and C), one type of doubly bridging carbonyl group (D), and a complex pattern at low field due to the two

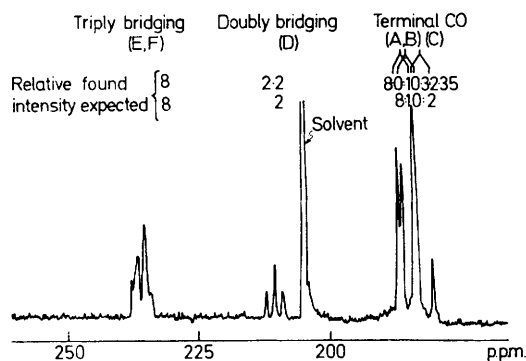


FIGURE 1. ^{13}C n.m.r. spectrum of $(\text{NMe}_4)_3[\text{Rh}_{12}(\text{CO})_{30}]$ at -70° perdeuterioacetone solution.

Identical values of $^1J(\text{Rh}-\text{C})$ are found for inequivalent carbonyls (A, B) attached to the same rhodium atom; this is similar to the results obtained for $\text{Rh}_4(\text{CO})_{12}$.² Moreover, for $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$, increasing Rh-C bond length due to increasing bridging character results in a decrease in Rh-C coupling constant and a lower-field resonance. Furthermore, the same trend is found for the different terminal carbonyl groups, (for A and B, 1.88 Å; for C = 1.82 Å⁵). On increasing the temperature from -70° to $+52^\circ$ the spectrum remains essentially unchanged except for a slight broadening of the triply bridging carbonyl resonance. Thus, unlike $[\text{Rh}_4(\text{CO})_{12}]^6$ and $[\text{Rh}_2(\text{C}_6\text{H}_5)_2(\text{CO})_3]^3$, the ^{13}C n.m.r. spectrum of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ provides no evidence for intra-exchange, whereas at 25° this species undergoes carbonyl inter-exchange, which was the method used for the ^{13}C -enrichment.

Added in proof: A recent paper⁷ on the ^{13}C n.m.r. spectrum of $[\text{Rh}_3(\text{C}_6\text{H}_5)_3(\mu_3\text{-CO})\{\text{C}_2(\text{C}_6\text{H}_5)_2\}]$ has come to our at-

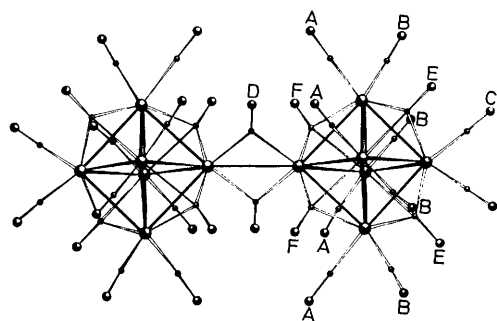


FIGURE 2. X-Ray structure of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$.⁵

TABLE

Chemical shift (p.p.m. relative to Me_4Si) and, in parentheses, $^1J(\text{Rh}-\text{C})/\text{Hz}$ of rhodium carbonyl compounds

Compound	Terminal	Bridging
$[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$	A,B 186.3 (73)	D 211.5 (36.6) ^a
	A,B 186.1 (73)	E,F ca. 237.4 (ca. 27.5) ^b
	C 183.4 (87.7)	
$\text{Rh}_4(\text{CO})_{12}$	183.4 (75)	228.8 (35) ^a
	181.8 (64)	
	175.5 (62)	
	151.8 (83)	231.8 (45) ^a
$\text{Rh}_2(\text{C}_6\text{H}_5)_2(\text{CO})_3$ ³	180.4 (76.4, c 68.8) ⁶	

^a Doubly bridging. ^b Triply bridging. ^c ± 0.5 Hz.

types of inequivalent triply bridging carbonyl groups (E, F). The experimentally observed intensities (A, B, C:D:E, F = 20.65:2.02:8.0) show good agreement with those expected (A, B, C:D:E, F = 20:2:8) and the values of $^1J(\text{Rh}-\text{C})$ and chemical shift for the terminal carbonyl and doubly bridging carbonyl groups are similar to those recently found for related compounds,^{2,3} (see Table). The most intense peak in the terminal carbonyl region has been resolved (Du Pont curve resolver) in order to obtain accurate values of $^1J(\text{Rh}-\text{C})$ and δ for the terminal carbonyls.

tention. The ^{13}C n.m.r. spectrum of this compound at -90° shows the presence of a triply bridging carbonyl group, which is bridging the three rhodium atoms unsymmetrically (δ 241.6 $^1J(\text{Rh}-\text{C})_{\text{triplet}}$ 43.7, $^1J(\text{Rh}-\text{C})_{\text{doublet}}$ 28.4 Hz).

We thank The Royal Society for a post-doctoral fellowship (D.J.A.McC.), N.A.T.O. for a grant, and D. O. Smith for recording the ^{13}C n.m.r. spectra.

(Received, 5th February 1974; Com. 165.)

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