Carbonyl Site Exchange in the Mixed Metal Carbonyl $RhCo_3(CO)_{12}$

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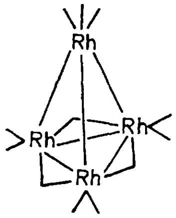
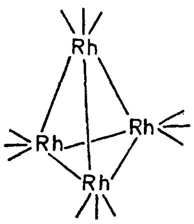
Summary ^{13}C N.m.r. studies confirm the structure of $RhCo_3(CO)_{12}$ and indicate that two types of carbonyl site exchange occur *via* a concerted carbonyl-terminal exchange process.

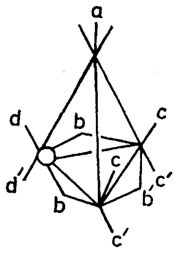
Evidence has been presented that at −85 °C in solution $Rh_4(CO)_{12}$ possesses the C_{3v} structure (**1**) and that at higher temperatures[1] carbonyl site exchange occurs rapidly by a single process. This implies that bridge-terminal carbonyl exchanges occur *via* the intermediacy of the more symmetrical T_d intermediate (**2**) in the manner initially suggested by Cotton.[2] We present here recent observations on the mixed metal carbonyl $RhCo_3(CO)_{12}$ (**3**) which indicate that in this case bridge-terminal site exchange occurs *via* two distinct and independent processes.



(1)

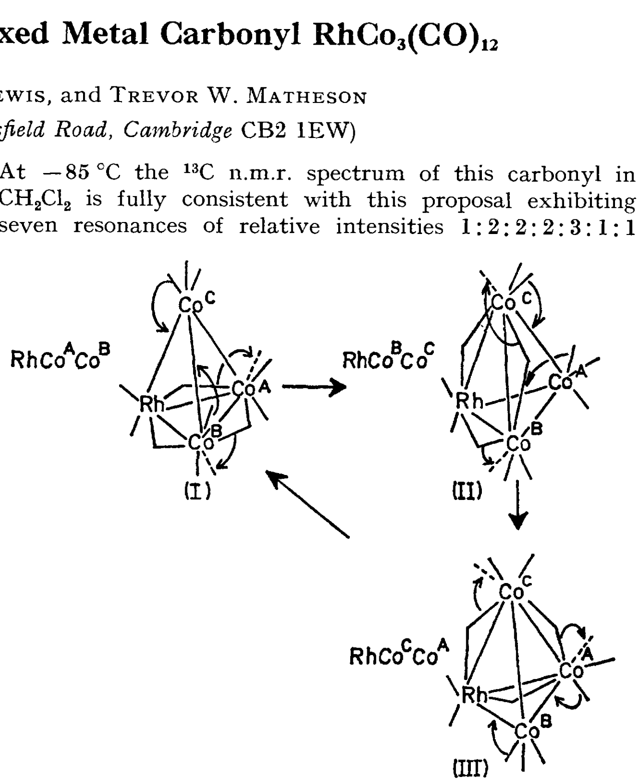


(2)



(3)

The compound $RhCo_3(CO)_{12}$ was first prepared by Chini[3] who proposed structure (**3**) on the basis of its i.r. spectrum. At −85 °C the ^{13}C n.m.r. spectrum of this carbonyl in CH_2Cl_2 is fully consistent with this proposal exhibiting seven resonances of relative intensities 1:2:2:2:3:1:1 (downfield of Me_4Si) at −251·2 (s), −238·3 [d, ^1J (Rh–^{13}C) 38 Hz], −201·1 (s), −200·1 (s), −195·5 (s), −188·2 [d, ^1J (Rh–^{13}C) 78 Hz], and −183·1 p.p.m. [d, ^1J (Rh–^{13}C) 51 Hz].



Scheme

At +30 °C the ^{13}C n.m.r. spectrum of (**3**) shows a single broad resonance at −201·3 p.p.m. Upon cooling this signal broadens and is eventually resolved into two lines at 10 °C. One line, at −208 p.p.m., is broad and the other at −186·2 p.p.m., appears as a well resolved doublet [^1J (Rh–^{13}C) 72 Hz]. As the temperature is lowered further, the broad resonance broadens further until at −85 °C it is replaced by the five new signals associated with the ground-state geometry discussed above. The coalescence point is estimated to be *ca.* −45 °C. In addition at this temperature the doublet centred at −186·2 p.p.m., which is broad at −60 °C, is resolved into two doublets centred at −188·2 p.p.m. [^1J (Rh–^{13}C) 78 Hz] and −183·1 p.p.m. [J (Rh–^{13}C) 51 Hz]. As observed with other cobalt systems[4] the coalesced signal at +30 °C and above remains broad, and probably arises from the high quadruple moment of the cobalt nucleus.

We postulate that two mechanisms of carbonyl site exchange are occurring. In the low temperature region (−60 to −30 °C) re-arrangements (I), (II), and (III) (see Scheme) combined lead to site exchange within the three triangular metal faces $\mathrm{RhCo^ACo^B}$, $\mathrm{RhCo^BCo^C}$, and $\mathrm{RhCo^C}$-$\mathrm{Co^A}$ and imply a *concerted* interchange of bridging and terminal CO groups. These re-arrangements coalesce carbonyl resonances due to groups a, b, b′, c, and c′. Carbonyl groups d and d′ do not participate in this-re-arrangement process; however, since the process causes all cobalt atoms to become equivalent, carbonyl groups d and d′ also become equivalent. At higher temperatures (>−30 °C) interconversion of all carbonyl groups occurs leading to bridge formation in any one of the four triangular metal faces $\mathrm{RhCo^ACo^B}$, $\mathrm{RhCo^BCo^C}$, $\mathrm{RhCo^CCo^A}$, and $\mathrm{Co^ACo^BCo^C}$. These observations clearly indicate that carbonyl site exchange in carbonyl clusters is not necessarily a simple one-stage process and show that such exchanges are very dependent on the disposition of the metal ions within a cluster unit.

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[3] S. Martinengo, P. Chini, V. G. Albano, F. Cariati, and T. Salvatori, *J. Organometallic Chem.*, 1973, **59**, 379.

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