Journal of Organometallic Chemistry, 88 (1975) 363–365

^{13}C NMR STUDIES OF SOME MIXED METAL POLYNUCLEAR CARBONYL COMPLEXES RELATED TO $Fe_3(CO)_{12}$

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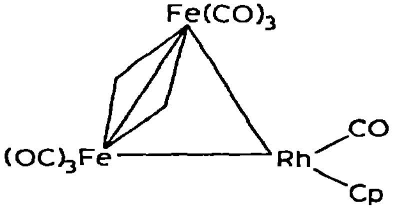
(Received November 1st, 1974)

Summary

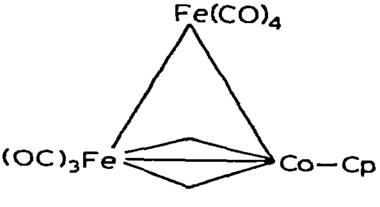
^{13}C NMR data for the complexes $CpMFe_2(CO)_9$ (M = Co or Rh) and Cp_2-$Rh_2Fe(CO)_6$ are reported and discussed.

The advent of Fourier transform ^{13}C NMR has stimulated a great deal of research in the field of fluxional polynuclear transition metal carbonyls. A prime candidate for study using this technique is $Fe_3(CO)_{12}$, the solution structure of which remains unclear even though its molecular structure in the crystal has now been accurately determined [1]. There appears, however, to be little, if any, likelihood of establishing the predominant structure of this complex in solution by recording its ^{13}C spectrum in the slow exchange limit. The reason is that the scrambling process in solution possesses such a low activation energy (<5 kcal mol^{-1}) that the coalescence temperature may be below $-160°$ [1].

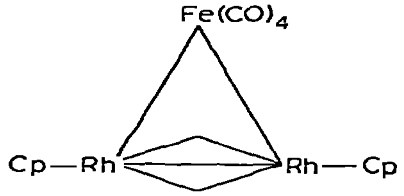
We have previously attempted to throw light on this problem by comparing the solution infrared spectrum of $Fe_3(CO)_{12}$ with the infrared spectra of related trimetallic carbonyls [2]. The ^{13}C NMR spectra of such related molecules are also clearly of interest and we now report ^{13}C NMR data for $CpMFe_2(CO)_9$ (I, M = Rh; II, M = Co) and for $Cp_2Rh_2Fe(CO)_6$ (III). We find that all these species retain to a large extent the fluxional properties in solution of $Fe_3(CO)_{12}$ itself.



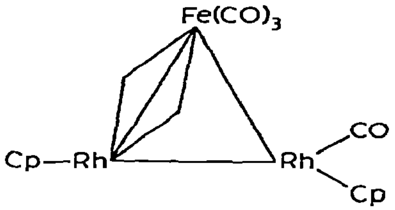
(I)



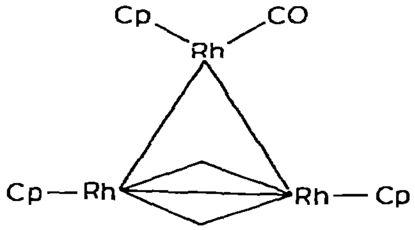
(II)



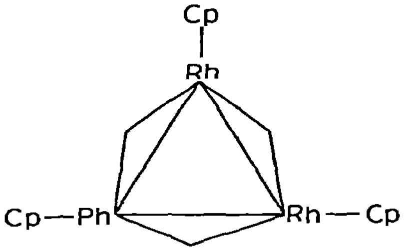
(III)



(IIIa)



(IV)



(V)

Experimental

The complexes were prepared as previously described in the literature [3] and were labelled by stirring under an atmosphere of ^{13}CO in dichloromethane for 24 h. Complex III decomposed at room temperature under these conditions, and so the enrichment was performed at 0°. Enrichment levels of 15-25% (determined by mass spectroscopy) were obtained.

Spectra were obtained of dichloromethane/freon solutions containing 0.05 *M* $Cr(acac)_3$, on a Varian XL-100-15 spectrometer operating at 25.2 MHz in the FT mode. Chemical shifts quoted are relative to TMS.

Results and discussion

The room temperature spectrum of $Fe_3(CO)_{12}$ shows a singlet at 212.5 ppm [4], while the carbonyl absorptions of $CpCo(CO)_2$ and $CpRh(CO)_2$ have been observed at 206.1 and 193.2 ppm [J(Rh—C) = 83 Hz] respectively [5], all in dichloromethane solution.

The room temperature spectrum of I consists of a doublet [J(Rh—C) = 9 Hz] with a chemical shift of 218.8 ppm, consistent with a molecule in which total scrambling of the carbonyl ligand is occurring. On cooling to −115°, line broadening and loss of coupling is observed, indicating a slowing of the exchange rate, although a limiting low temperature spectrum could not be obtained. Similarly the room temperature spectrum of II consists of a singlet at 216.6 ppm which shows only slight line broadening on cooling to −115°, and again, a limiting low temperature spectrum could not be obtained. Structures I and II for these compounds have, however, been inferred from Mössbauer and solution infrared studies as being present both in the solid state and in solution [3].

The ^{13}C spectrum of III at room temperature shows a triplet [J(Rh—C) = 41 Hz] with a chemical shift of 209.2 ppm, again indicating total carbonyl scrambling. A low temperature limiting spectrum may be obtained at −70°, and consists of a triplet [J(Rh—C) = 50 Hz] at 234.5 ppm and two equal intensity singlets in the terminal region at 190.0 and 193.3 ppm. This spectrum is consistent only with structure III. The triplet is assigned to the two bridging carbonyl ligands; the chemical shift and coupling constant are very similar to those observed for the bridging carbonyl group in $Cp_2Rh_2(CO)_3$ [6]. The two singlets are assigned to the axial and equatorial carbonyls of the $Fe(CO)_4$ group. Axial and equatorial carbonyl groups have previously been resolved in the cases of several polynuclear metal carbonyls, and have chemical shift differences of approximately 1 to 15 ppm [5,7-9].

The calculated average chemical shift is in agreement with that observed, while the calculated average coupling constant is smaller than the observed value. The coalescence temperature is estimated to be around −20 to −30°.

This structure differs from the structure IIIa which has been inferred from Mössbauer data [3] as being present in the solid state. Differences between solid state and solution structures are, however, well established for polynuclear transition metal carbonyls.

The low activation energy for carbonyl scrambling in these complexes suggests a mechanism similar to that proposed for $Fe_3(CO)_{12}$ [1] and verified for several binuclear species involving facile bridge—terminal interchange via pairwise opening and closing of bridges. This averages all carbonyl groups over the three metal atoms and over both axial and equatorial coordination positions about the iron atoms. Although limiting spectra could not be obtained for the first two complexes, there does exist the clear trend of a decrease in rate of carbonyl site exchange with increasing substitution of $Fe_3(CO)_{12}$ by the CpM(CO) moiety.

The last complex in this series, $Cp_3Rh_3(CO)_3$, obtained from prolonged irradiation of $CpRh(CO)_2$, is known to exist as the two isomers IV and V in the solid state [14,15]. It would thus have been of interest to determine (a) whether an equilibrium exists between the two isomeric structures in solution, and (b) the relative rates of carbonyl scrambling in the two isomers, since isomer IV possesses a structure for which a scrambling mechanism of the type under discussion may be operative, while isomer V does not. Unfortunately, the limited solubility of this complex precluded its ^{13}C NMR spectrum being obtained.

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