Variable Temperature ^{13}C Nuclear Magnetic Resonance of Dicyclopentadienyltricarbonyldirhodium

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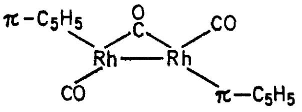
Summary The ^{13}C n.m.r. chemical shifts of bridging and terminal carbonyl carbons in $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ have been established from $^{103}Rh\text{–}^{13}C$ coupling data at −80°; at 20° the spectrum shows rapid intramolecular interconversion of all carbonyl groups.

We have examined the variable temperature ^{13}C n.m.r. spectra of $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$, a complex with rhodium nuclear spin to allow unequivocal assignment of bridging and terminal carbonyl ^{13}C n.m.r. resonances. The structure of this compound has been shown by *X*-ray analysis[1] to be (**1**). Thus we have been able to investigate the possibility of exchange of a single carbonyl bridge with a terminal carbonyl group in a cyclopentadienyl metal carbonyl dimer. Such a process, rather than the previously assumed[2] intermediacy of a nonbridged form, would be necessary if the suggestion[3] that $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ exchanges bridging and terminal carbonyls without *trans-cis* isomerization were correct.

The bright red rhodium dimer, (**1**), previously reported only as the single crystal used for crystallographic analysis can be prepared in 5% yield by photolysis of $(\pi\text{-}C_5H_5)Rh(CO)_2$ in hexane solution for 15 h. The product was shown to be identical with that examined by Mills and Nice[1] by analysis and mass spectroscopy; in hexane its i.r. spectrum has ν(CO) at 1989 cm^{-1} (terminal) and 1841 cm^{-1} (bridging). Stirring a toluene solution for one day under excess 88% ^{13}C-enriched carbon monoxide gave (**1**) with its carbonyl ligands 80% labelled, measured by ν(CO) at 1951 cm^{-1} (terminal) and 1798 cm^{-1} (bridging).

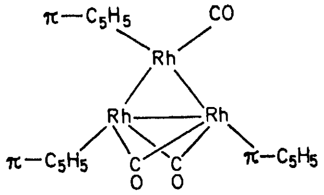


(1)

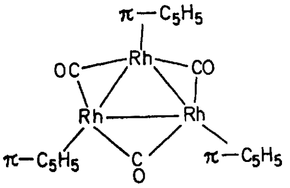
Proton-decoupled ^{13}C n.m.r. spectra of the enriched complex were obtained in CD_2Cl_2 with the addition of 0·04M $Cr(acac)_3$ as a relaxation reagent.[4] At 20° the carbonyl region ^{13}C n.m.r. spectrum shows only a sharp triplet at 203·8 (downfield from $SiMe_4$) with J_{Rh-C} 43 Hz, reflecting the rapid intramolecular interconversion of the two types of carbonyl groups. At −60° broad separate peaks begin to appear; at −80° they sharpen to a triplet at δ 231·8 (J_{Rh-C} 45 Hz) and a doublet at 191·8 (J_{Rh-C} 83 Hz). The relative intensities are 1 : 2; to the extent that $Cr(acac)_3$ lacks relaxational specificity and quenches any small Overhauser effects present[4] these numbers should reflect relative abundances. Clearly the downfield triplet is the resonance of the bridging carbonyl group and the upfield doublet that of the terminal carbonyl groups. The weighted average coupling constants and chemical shifts agree satisfactorily with those observed in the high-temperature limit at 20°.

The terminal carbonyl chemical shift (δ 191·8) for (**1**) is very close to the fast-interconversion-limit average chemical shift recently reported for $Rh_4(CO)_{12}$ (δ 190·3).[5] The observation of a bridging carbonyl signal, from (**1**), at δ 40·0 downfield from the terminal one corroborates the assignment[3] of a signal at about 264 to a bridging carbonyl in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. The change in the bridge-terminal chemical shift difference from δ 64·2 in (**2**) to 40·0 in (**1**) is surprising in view of the similar solid-state geometries observed for (**1**)[1] and both isomers of (**2**).[6,7]

The consistency of low- and high-temperature apparent coupling constants for $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$, and the absence of observable second-order effects in the terminal resonances at the low-temperature limit, show that the observed splittings have been correctly attributed to $^1J_{Rh-C}$ and that $^2J_{Rh-Rh-C}$ and $^1J_{Rh-Rh}$ are negligible in comparison. It is notable that J_{Rh-C} varies from 83 Hz in (**1**) to 69 Hz in $[Rh(CO)_2Cl]_2$,[5] reflecting the variation in the carbonyl J_{Rh-C} with the remaining ligands in the co-ordination sphere. At high enrichment levels such as those employed here, ^{13}C–^{13}C coupling ought to affect spectra involving nonequivalent carbonyl groups. The broad ($\Delta\nu_{\frac{1}{2}}$ about 10 Hz) linewidths remaining in both carbonyl multiplets at −80° may be so caused. It does appear, however, that the effects arising from $^2J_{C-C}$ are sufficiently small that they need not be allowed to determine the extent of ^{13}C enrichment into nonequivalent metal carbonyl sites in studies of this sort.



(3)



(4)

Thus the type of interconversion proposed[3] for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ has been unequivocally shown to occur intramolecularly at a rate of at least $10^3\ s^{-1}$ at 20° in the compound $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$. This result, and the recent demonstration[5] that at 50° all the carbonyl groups in $Rh_4(CO)_{12}$ are equivalent, in ^{13}C n.m.r., have shown that such interconverisons can even occur with second-row transition metals. However, they are not necessarily ubiquitous. A probable exception occurs with the isomers from prolonged $(\pi\text{-}C_5H_5)Rh(CO)_2$ photolysis known crystallographically[8,9] to have structures (**3**) and (**4**). The most plausible paths for carbonyl site exchanges would also have led to isomerization and precluded separation.

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