Dicarbonyl-π-Allylrhodium

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THE number of simple π-allylic metal carbonyls known at the present time is limited to $(C_3H_5)Mn(CO)_4$,[1,2] $(C_3H_5)Co(CO)_3$[2,3] and $(C_3H_5)_2Fe(CO)_2$.[4] In addition, the metal–metal bonded binuclear complex $[(C_3H_5)Fe(CO)_3]_2$ is known and this in solution exists in equilibrium with a paramganetic monomer.[5] In the present communication a square-planar complex of this type prepared from a second-row transition metal is described, $(C_3H_5)Rh(CO)_2$ (I). In solution (I) exists as a monomer, a carbonyl bridged binuclear species or as an equilibrium mixture of both depending on the temperature.

The complex (I) is prepared by the action of allylmagnesium chloride on rhodium carbonyl chloride dimer. The product is obtained as yellow sublimable crystals, susceptible to atmospheric oxidation, m.p. 55—60° with decomposition. When the crystals are cooled below −78° in liquid nitrogen

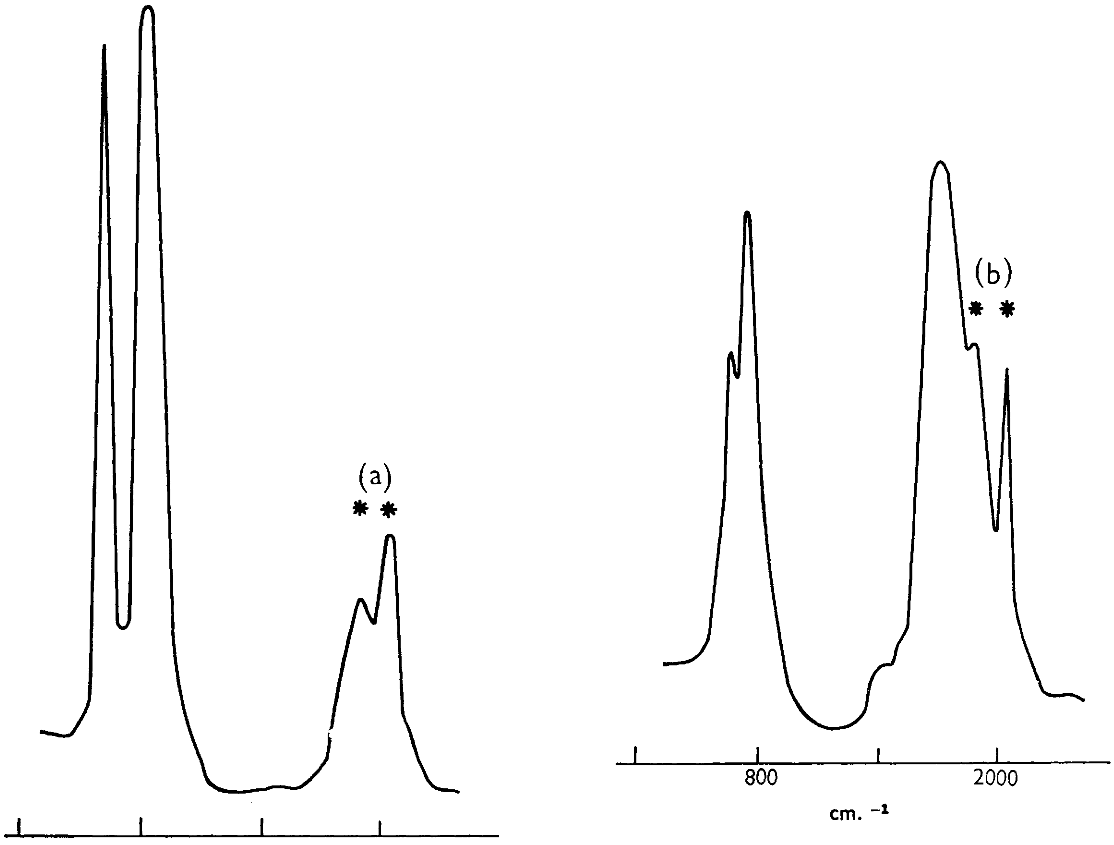


FIGURE *I.r. spectrum of* $(C_3H_5)Rh(CO)_2$ *in* $CDCl_3$ *at* (a) 0° *and* (b) −60°. *Peaks indicated with an asterisk are overtone bands of the solvent.*

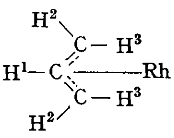
reversible colour changes are observed, the crystals going blue and finally dark red.

The i.r. spectrum in $CDCl_3$ at 0° showed two strong absorption bands at 2060 and 1995 cm.$^{-1}$ (see Figure a) which can be attributed to the symmetrical and antisymmetrical stretchings of the two *cis*-CO ligands. On lowering the temperature below −20° a new band appeared at 1845 cm.$^{-1}$ and the intensity of this band increased with decreasing temperature; concurrently the bands in the 2000 cm.$^{-1}$ region start to change until at −60° there is one strong and one weak band at 2009 and 2040 cm.$^{-1}$, respectively (see Figure b). The new low-frequency band is in the position where bridging carbon monoxide ligands absorb and would indicate that a bi- or poly-meric species must be present. As the above changes are reversible loss of CO cannot occur, in contrast to the formation of the binuclear complex from $(C_5H_5)Rh(CO)_2$.[6] The Nujol mull spectrum at room tepmerature contained a number of bands in this region (2060 s, 2012 wsh, 2000 s, 1975 w, 1860 s, +3 weak bands 1820—1850 cm.$^{-1}$) and therefore in the solid state the compound exists, at least partially, in the oligomeric form.

Evidence for a monomeric–dimeric equilibrium is gained by cryoscopic molecular-weight determinations in CCl_4 and $CHCl_3$. In CCl_4 the molecular weight was 201 (the i.r. spectrum showed no change over the temperature range +25 to −20° in this solvent). In $CHCl_3$ the molecular weight for three determinations was 364, 369, 373 [calc. for (C_3H_5)-$Rh(CO)_2$, 200]. The electron-impact mass spectrum showed peaks only consistent with a monomeric species [the most intense metal-containing ion peaks present were due to Rh^+, $Rh(C_3H_5)^+$, $Rh(CO)(C_3H_5)^+$, and $Rh(CO)_2(C_3H_5)^+$]. The metal–metal bonded dimeric chromium complex, $[(C_5H_5)$-$Cr(CO)_3]_2$, similarly shows no ions in the electron-impact mass spectrum containing two metal atoms.[7]

The ^1H n.m.r. spectrum in $CDCl_3$ at room temperature was of the AM_2X_2 type expected for a symmetrically bonded π-allyl group. All the protons showed evidence of coupling to the rhodium atom and this was greatest for H^1. On

τ_1	4·72 (multiplet)
τ_2	5·98 (doublet)
τ_3	7·60 (doublet)
J_{12}	7·2 c./sec.
J_{13}	13·3 c./sec.



lowering the temperature, new broad resonances appeared in the region τ5—9 and the intensities of the new resonances increased with decreasing temperature; simultaneously the intensity of the AM_2X_2 spectrum decreased, with the doublets remaining sharp, until at approximately −50 to −60° they have entirely disappeared.

As the changes observed in the n.m.r. and i.r. spectra occur over the same temperature range we suggest that the AM_2X_2 spectrum is due to the monomeric compound and the broad resonances are due to the dimeric species. The reason for the broadness of the new low-temperature resonances is not clear; it cannot be due to a further equilibration giving rise to a time-averaged spectrum as only the intensity and not the shape of the peaks alter in the temperature range studied. One possible explanation is that the dimeric species has a weak metal–metal interaction and this gives rise to a small degree of paramagnetism (magnetic susceptibility measurements on the solid in the range +20° to −160° gave μ_{eff} 0·6 B.M.).

Triphenylphosphine reacts with (I) to give $(C_3H_5)Rh(CO)(PPh_3)_2$. The rhodium atom is this complex can be either four- or five-co-ordinated depending on whether the allyl is σ- or π-bonded to the metal.

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