

Preliminary communication

CATALYSIS BY PHOSPHINE- OR PHOSPHITE-SUBSTITUTED RHODIUM CLUSTER CARBONYLS

II*. A ^{13}C AND ^{31}P NMR STUDY OF $\text{Rh}_6(\text{CO})_{12}(\text{P}(\text{OPh})_3)_4$

W. ABOUD**, Y. BEN TAARIT, R. MUTIN and J.M. BASSET

*Institut de Recherches sur la Catalyse, C.N.R.S., 2, avenue Albert Einstein,
69626 Villeurbanne Cedex (France)*

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Summary

Variable temperature ^{13}C and ^{31}P NMR studies on $\text{Rh}_6(\text{CO})_{12}[\text{P}(\text{OPh})_3]_4$ show that the solid state structure is maintained in solution from -80 to 60°C . Above 60°C there is a fluxional motion of some of the carbonyls between triply-bridging and edge-bridging positions. The onset of this fluxionality parallels the appearance of catalytic activity in hydrogenation of cyclohexene.

As a part of our study of the mechanism of hydrogenation of olefins or arenes with phosphine- or phosphite-substituted rhodium clusters such as $\text{Rh}_6(\text{CO})_{16-x}\text{L}_x$ [1], ($x = 4,5,6$) we report on the infrared, ^{31}P and ^{13}C NMR spectra of $\text{Rh}_6(\text{CO})_{12}(\text{P}(\text{OPh})_3)_4$ (I), the X-ray structure of which was recently described by Ciani and coworkers [2,3]. The choice of this cluster for ^{13}C and ^{31}P characterisation stems from the fact that it has a very low activity in hydrogenation of cyclohexene and arenes at room temperature, whereas the parent clusters $\text{Rh}_6(\text{CO})_{10}(\text{P}(\text{OMe})_3)_6$ or $\text{Rh}_6(\text{CO})_{10}(\text{PPh}_3)_6$ [1,4] exhibit a significant activity, which may be related to the stereolability of the carbonyl ligands [5] in the metal cluster frame [6]. Complex I becomes catalytically active for cyclohexene hydrogenation only above 70°C .

Complex I, prepared as described by Ciani et al. [2], was enriched in labeled ^{13}C by exchange for 48 h with gaseous ^{13}C in toluene at room temperature. The original cluster exhibits $\nu(\text{CO})$ bands at 2052s, 2027s and 1765m cm^{-1} in chloroform (Fig. 1), in agreement with the X-ray structure which shows linear and triply bridging carbonyl ligands [2,3].

*For Part I see ref. 1.

**Fellow of the Lebanese C.N.R.S., P.O. Box 11-8281, Beirut, Lebanon.

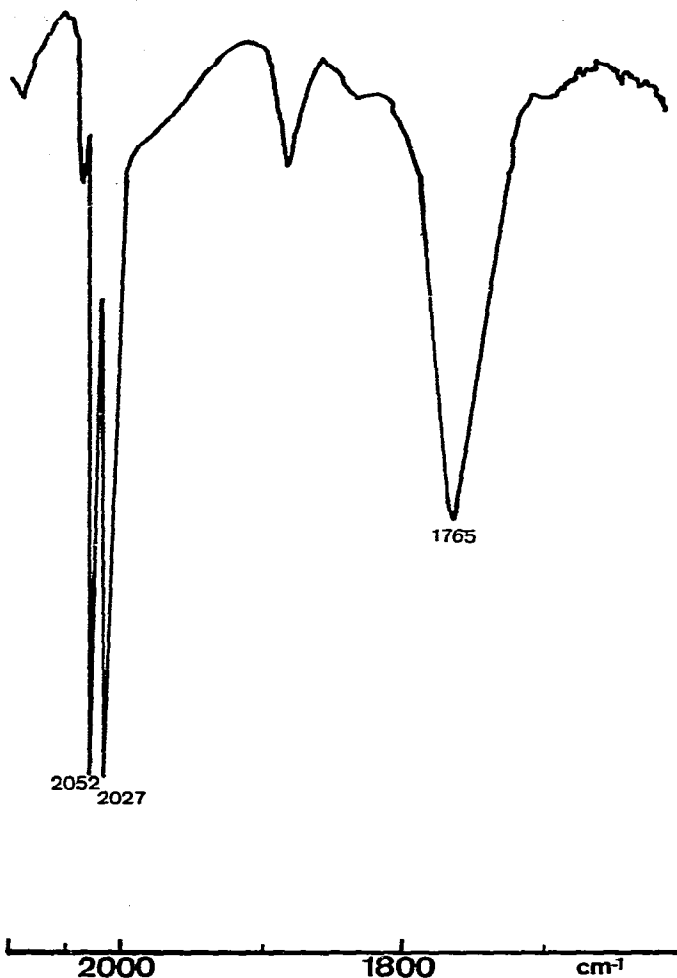


Fig. 1. Infrared spectrum in the $\nu(\text{CO})$ region of $\text{Rh}_6(\text{CO})_{12}(\text{P}(\text{OPh})_3)_4$ (I) in CHCl_3 .

From -80°C up to room temperature the ^{31}P spectrum of I exhibits a doublet centered at -34.4 ppm with respect to H_3PO_4 ($J(^{103}\text{Rh}-^{31}\text{P})$ 250 Hz). The X-ray structure of I shows that all the phosphite ligands are equivalent, since they occupy the square plane of the slightly distorted octahedron structure and a doublet corresponding to the single coupling $^{103}\text{Rh}-^{31}\text{P}$ (Fig. 2) would thus be expected.

The ^{13}C spectrum was recorded at various temperatures between -80 up to 80°C . If the resonances due to the phosphite phenyl groups are disregarded, there are two sets of resonances, with a 2/1 intensity ratio at room temperature, at 188 and 243 ppm, respectively.

At -80°C the low field resonance appears as a quartet 1/3/3/1 with a separation of 23 Hz centered at 244.2 ppm (Fig. 4). The high field resonance consists of two doublets of different intensity situated at 187.2 ppm (low intensity) and 186 ppm (high intensity). The coupling constants are 68.3 Hz and 69.4 Hz, respectively (Fig. 3).

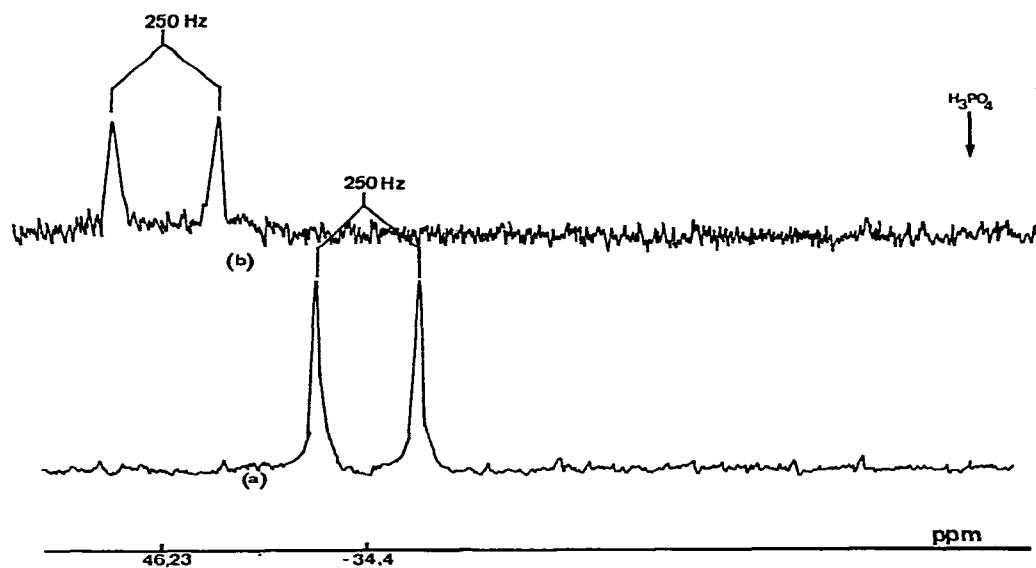


Fig. 2. (a) ^1H decoupled ^{31}P spectrum of I in deuterated toluene at 25°C . (b) Same as (a) at 80°C .

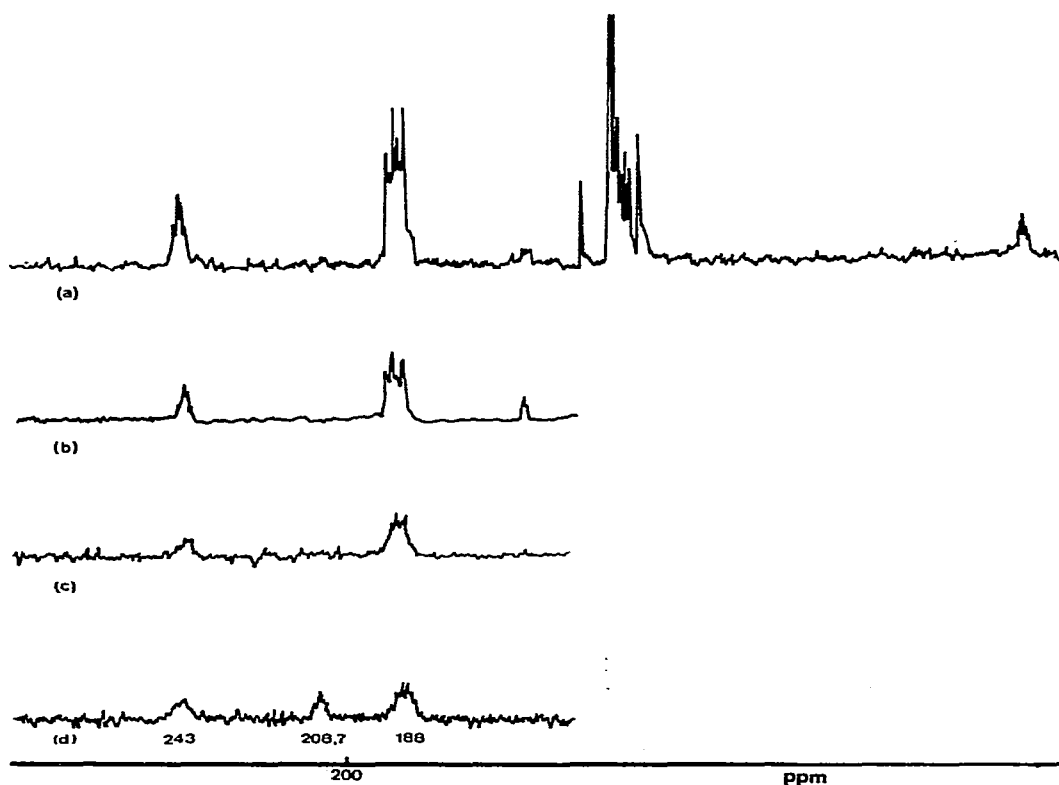


Fig. 3. ^{13}C spectrum of ^{13}C enriched I at -80°C (a), 25°C (b), 60°C (c) and 80°C (d).

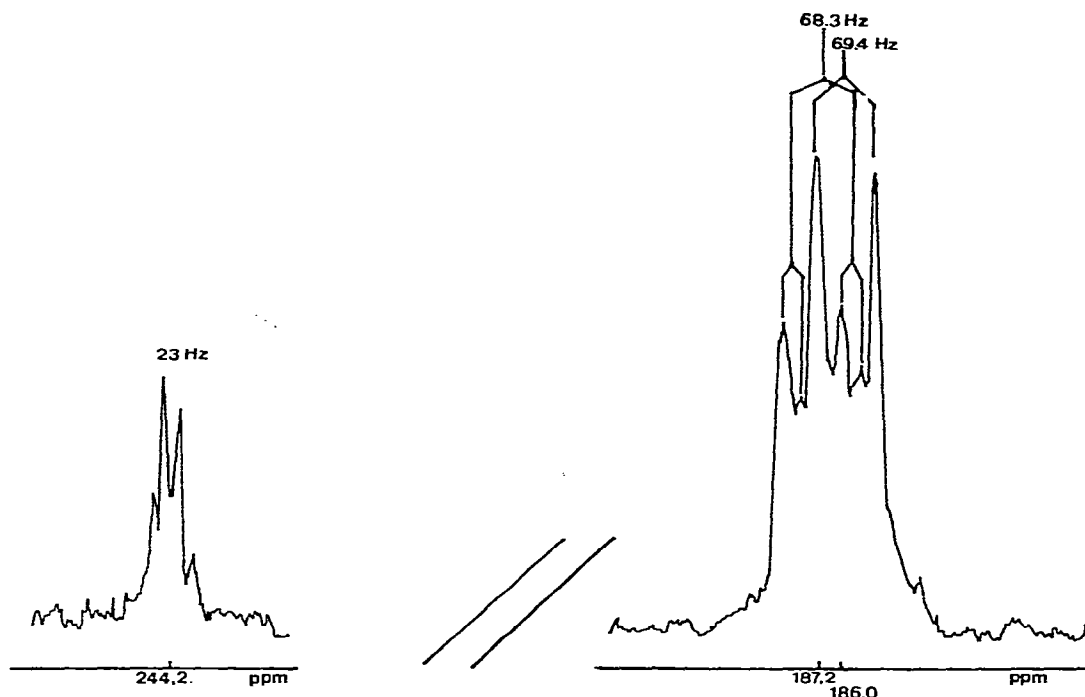


Fig. 4. Enlarged ^{13}C spectrum of I taken at -80°C .

A more careful examination of the low intensity doublet reveals that each peak is, in fact, a doublet of doublets with a coupling constant of 21 Hz. The quartet at low fields indicates that each bridging carbonyl ligand interacts with three equivalent rhodium nuclei ($I = \frac{1}{2}$). The corresponding coupling constant is consistent with such a triply bridging ligand ($J = 23 \text{ Hz} = \frac{69}{3}$). The low field resonance is due to triply bridging carbonyls, whereas the high field resonance belongs to linear carbonyls [7–10]. The two high field doublets are different; the simple doublet arises from the carbonyl ligands bound to the apical rhodium atoms which have no adjacent phosphite ligands. The doublet of doublets must be due to the four equivalent linear carbonyls which are bound to the four equatorial rhodium atoms alternately above and below the same Rh_4 plane. In this situation those carbonyls are coupled to the rhodium and to the adjacent ^{31}P nuclei. The coupling constant corresponds to a $J(^{13}\text{C}-\text{Rh}-^{31}\text{P})$ via a rhodium atom ($\text{C}-\text{Rh}-\text{P}$) (21 Hz).

At ca. 60°C the ^{13}C NMR spectrum begins to broaden. At 80°C , a new peak appears at 208.7 ppm while the intensity of the linear and triply bridging carbonyls decreases, but the three signals are present simultaneously. This behaviour is reversed when the temperature is lowered. At the same time, the ^{31}P spectrum shows a downfield shift of about 13 ppm, while the ($\text{P}-\text{Rh}$) coupling remains unchanged indicating the equivalence and significant deshielding of the phosphorus nuclei (Fig. 2b), which can be related to the concomitant shielding of some of the triply bridging carbonyl carbons.

In conclusion, the ^{31}P and ^{13}C NMR spectrum of I in deuterated toluene are consistent with the X-ray structure in the solid state [2,3]. No carbonyl migration seems to occur below 60°C . Above this temperature there is fluxional motion of some carbonyls between triply bridging and edge bridging positions. Interestingly, it is only above this temperature that this complex catalyses the hydrogenation of cyclohexene to cyclohexane. The lack of catalytic activity at lower temperatures may be associated with the rigidity of the carbonyl ligands.

References

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- 6 The molecule consists of a slightly distorted octahedral cluster of metal atoms bearing 12 carbonyl groups and four $\text{P}(\text{OPh})_3$ ligands. The ligand arrangement is derived from that of the parent $\text{Rh}_6(\text{CO})_{16}$ by the substitution of four terminal CO groups by triphenyl phosphite ligands, which are bound to the four equatorial rhodium atoms alternately above and below the same Rh_4 plane (see ref. 3).
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