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**Preliminary communication**

# PRESENCE OF A METAL-BONDED HYDROGEN ATOM IN UNSATURATED TRINUCLEAR COBALT CLUSTERS. CRYSTAL STRUCTURE OF $HCo_3(CO)_6(PPh_3)_3$

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## Summary

On the basis of new experimental evidences the cobalt clusters $Co_3(CO)_6(PR_3)_3$ are reformulated as $HCo_3(CO)_6(PR_3)_3$.

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Some years ago an interesting new class of paramagnetic cobalt complexes was prepared by reaction of $(\pi\text{-}C_4H_7)Co(CO)_2PR_3$ (I) (R = n-$C_4H_9$ or $C_6H_5$) with hydrogen, and some aspects of their catalytic activity were investigated. The formula $Co_3(CO)_6(PR_3)_3$ was tentatively attributed to these complexes [1]. More recently the paramagnetic complex $HCo_3(CO)_9$ was prepared and fully characterized [2]. As its catalytic reactivity resembled that of the above mentioned phosphine-containing clusters, we re-examined the complex obtained from I (R = $C_6H_5$) and $H_2$ (II) or $D_2$ (III).

Dark green crystals, slightly soluble in aromatic solvents, were obtained as described in the literature. The IR spectrum in the carbonyl stretching region and the catalytic behaviour of II and III were in agreement with the previous reports [1]; crystals of II suitable for X-ray diffraction investigation were obtained by recrystallization from toluene/n-pentane mixtures. A schematic view of the molecule is shown in Fig. 1 and confirms the analogy between II and $HCo_3(CO)_9$: the molecule is formed by a basal $Co_3$ group bonded to three phosphine groups, three terminal CO, and three bridging carbonyl groups. Two phosphines are located on one side of the $Co_3$ plane and the third on the other

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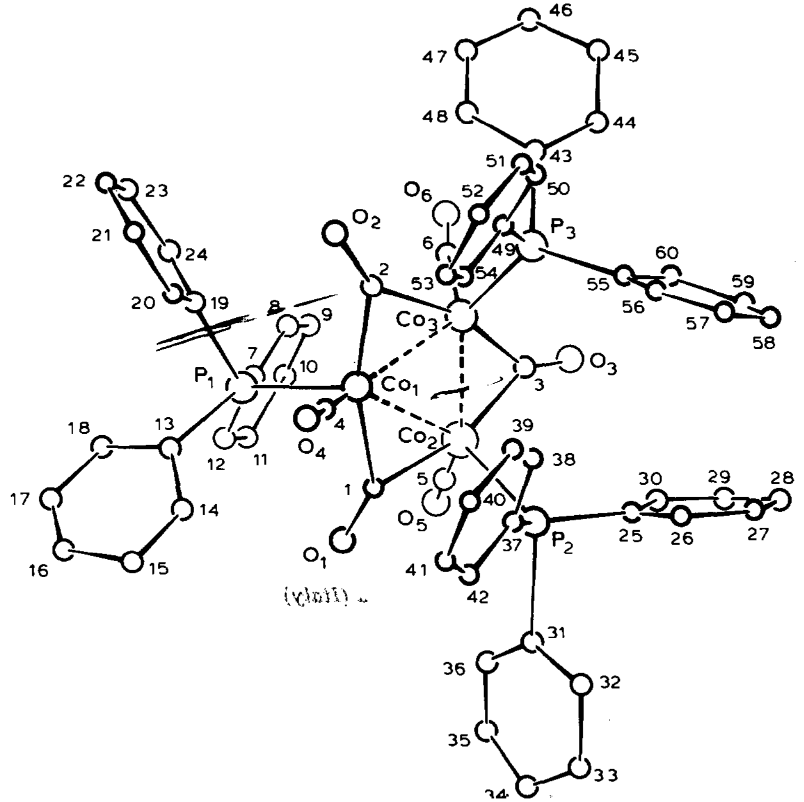

Fig. 1. Molecular structure of $HCo_3(CO)_4(PPh_3)_3$; hydrogen atoms have been omitted for clarity. Selected distances: Co(1)—Co(2), 2.473(3); Co(1)—Co(3), 2.490(3); Co(2)—Co(3), 2.453(3) Å.
*Crystal data*: $C_{60}H_{46}Co_3O_4P_3$, $M$ = 1132.75, orthorombic, space group $P2_12_12_1$, $a$ 23.574(4), $b$ 20.697(4), $c$ 10.779(3) Å, $Z$ = 4, $D_c$ 1.428 g cm³, $\mu$ 10.4 cm⁻¹ (Mo-$K_\alpha$), transmission factors 0.73—0.87. 2814 reflections ($2 \leqslant \theta \leqslant 40$) were scanned in the $\omega$-$2\theta$ mode. 1975 reflections [$I \geqslant 3\sigma(I)$] were used to solve the structure by means of direct methods. Refinement converged to $R$ = 0.0565 ($R_w$ = 0.0561).

side. A maximum of residual electronic density (~0.3 e Å⁻³) at a distance of about 1.7 Å from the Co atoms can be taken as an indication of the possible existence of a hydrogen atom capping the $Co_3$ triangle; further refinements indicate that the hydrogen should lie 0.99 Å out of the plane, on the side bearing two phosphine groups*.

In view of the difficulties of identifying a single hydrogen atom in these strongly paramagnetic clusters by the usual spectroscopic methods, the following series of experiments was deviced to prove the presence of a metal bonded hydrogen, or deuterium, in the complex II, or III.

*(i) Mass spectrometric analysis of the products from the pyrolysis of II and III*

A sample of II was heated under vacuum in the sample container of the mass

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*The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this Communication.

spectrometer, and the volatile products collected in the reservoir of the inlet system were directly analyzed. Upon heating at 80°C only toluene, used to recrystallize the complex, was evolved. Prolonged heating at higher temperature, up to 150°C, gave additional volatile products: the mass spectrum of the mixture showed, as the most significant fragments, peaks at $m/e$ 2, 28, 78, 154, and 262, which can be reasonably attributed to hydrogen, carbon monoxide, benzene, biphenyl, and triphenylphosphine, respectively.

An analogous experiment performed with III gave a mass spectrum in which only the peaks attributed to hydrogen and benzene were shifted to $m/e$ 3 and 4, and $m/e$ 79 respectively. No evidence for the presence of deuterium in the triphenylphosphine fragment was found.

### *(ii) Reaction of II with carbon monoxide*

The reaction of II with carbon monoxide [1], in less than stoichiometric amount, was carried out in a Schlenk tube at room temperature and atmospheric pressure, with toluene as the solvent. After 24 h a partial vacuum had been generated in the tube. The mass spectrometric analysis of the gaseous phase revealed the presence of hydrogen, in amount far exceeding any possible experimental error. In the solid product $[Co(CO)_3P(C_6H_5)_3]_2$ was identified by IR analysis. This is the only experiment in which there was disagreement with the published data.

### *(iii) Reaction between II and deuterium*

After shaking a toluene solution of 0.128 mmol of II under deuterium (1 atm) at 60°C for 6 h, the gaseous phase contained 0.121 mmol HD, as determined by mass spectral analysis.

### *(iv) Isomerization of 4-phenyl-1-butene by III*

The olefin heated at 65°C in toluene under nitrogen in the presence of a stoichiometric amount of III, was completely transformed after 5 h. All the various phenylbutenes obtained, contained in the average between 0.3 and 0.45 deuterium atoms per molecule, as determined by mass spectrometric measurements on the olefins separated by GLC. The total amount of deuterium incorporated in the hydrocarbons was 0.37 equivalents.

The results show beyond any doubt the existence of metal-bonded hydrogen, or deuterium, in the complex II, or III respectively. The presence of only one H, or D, atom is indicated by experiment (iii) and by the magnetic moment measurements [1] which gave values (2.9—3.1 B.M.) far exceeding the 1.8 B.M. expected for a complex containing two metal-bonded hydrogen atoms although somewhat higher than the 2.8 B.M. expected for a high spin complex with 46 electrons as $HCo_3(CO)_6(PPh_3)_3$. The position of the maximum of electronic excess in the X-ray diffraction pattern is also in better agreement with the presence of one triply bridging hydrogen atom.

The structure of the clusters II and III, analogous to that found for $HCo_3(CO)_9$ [2], confirms the existence of a class of trinuclear cobalt carbonyl monohydrides with 46 electrons, which are very close precursors of the catalytic species responsible for the isomerization, the hydrogenation, and the hydroformylation of olefins at low temperature.

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