Long-range Phosphorus–Hydrogen Interactions in Bis(dimethylglyoximato)cobalt(III) Complexes

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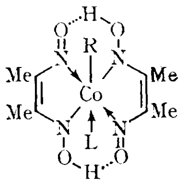
A SERIES of compounds of the type *trans*-$(dmg)_2CoLR$ (I), where dmg represents the dimethylglyoximate mono-anion, L is a neutral ligand with nitrogen or phosphorus donor atom, and R is an alkyl or aralkyl group, has been studied by Schrauzer and Kohnle.[1]



(I)

In order to obtain an order of stabilities for complexes with different ligands L, and to study the effect on this order of varying the group R, we have been obtaining equilibrium constants for the reactions

$$trans\text{-}(dmg)_2CoLR + L' \rightleftharpoons trans\text{-}(dmg)_2CoL'R + L$$

in deuterochloroform at 33°, by observing the changes in the proton magnetic resonance (p.m.r.) spectra of the solutions during the reactions.* Tetramethylsilane was used as an internal standard.

Details of the p.m.r. spectrum of the complex (I; L = triphenylphosphine, R = benzyl) are given in the Table. Of particular interest were the doublets at τ 6·92 (J = 7 c./sec.) and at τ 8·36 (J = 3 c./sec.), which can be assigned to the benzyl $>CH_2$ group and the methyl groups of the dmg anions, respectively. For similar complexes with R = benzyl but L = ligand with nitrogen donor atom, singlets were always observed for these two resonances. Thus for L = 2,4-dimethylaniline, singlets were observed, at τ 7·17 and 8·18, for the benzyl $>CH_2$ group and the dmg methyl groups, respectively. We therefore conclude that the appearance of doublets in the spectrum of the triphenylphosphine complex is due to interactions between the appropriate protons and the phosphorus atom. Such a coupling would certainly be expected for the benzyl $>CH_2$ group, but that for the protons of the dmg methyl groups is most unusual, in view of the distance between these protons and the phosphorus atom.

Schrauzer and Windgassen[2] have recently reported, without practical details, the p.m.r. spectrum of the complex (I; L = triphenylphosphine, R = methyl). They mention that a doublet is observed at τ 8·81 (J = 4 c./sec.) for the methyl group bonded to cobalt, due to the interaction with the phosphorus atom, but do not record the resonance due to the dmg methyl groups. We have now recorded the spectrum of this complex (*cf.* the Table). Our findings for the methyl group bonded to cobalt are in agreement with those of Schrauzer, but we also find that a doublet, at τ 8·17 (J = 3 c./sec.) is observed for the dmg methyl groups. As in the case of the benzyl compound, there appears to be a long-range

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* Equilibrium constants for a wide range of ligands L and L′ will be reported in a forthcoming paper.

TABLE

Compound	τ-value	Multiplicity	J (c./sec.)	Assignment
(I) L = PPh_3 R = CH_2Ph	2·63	doublet	5	P*Ph*$_3$
	3·00	singlet	—	CH_2*Ph*
	6·92	doublet	7	*CH*$_2$Ph
	8·36	doublet	3	Me (on dmg)
(I) L = PPh_3 R = Me	2·63	doublet	5	P*Ph*$_3$
	8·17	doublet	3	Me (on dmg)
	8·81	doublet	4	*Me*-Co

interaction between the phosphorus atom and the protons of these methyl groups.

Since the distance between the phosphorus atom and the protons concerned seems to be too great to allow the possibility of a "through-space" interaction, we conclude that the interaction is probably *via* the bond system P–Co–N–C–C–H. A similar mechanism has recently been postulated for a long-range phosphorus–hydrogen interaction in *p*-methylbenzyltriphenylphosphonium bromide,[3] although the interaction in this case is through carbon atoms only.

Proton magnetic resonance spectra were recorded on a Perkin-Elmer R10 spectrophotometer by Mrs. M. S. Sutherland of this department. In every case assignments have been checked by integration of the spectra.

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[1] G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 1964, **97**, 3056.
[2] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1966, **88**, 3738.
[3] K. Khaleeluddin and J. M. W. Scott, *Chem. and Ind.*, 1966, 1034.