Electron Spin Resonance Study of Transition-metal Complexes. Detection of a Paramagnetic Cobalt(II) Hydrido-complex

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Summary A cobalt(II) hydrido-complex, which shows an e.s.r. signal, has been shown to be formed when $CoCl_2$,-$2R_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR_2$ complexes react with Grignard reagents.

PARAMAGNETIC transition-metal hydrides are uncommon.[1] Even more scarce are paramagnetic hydrides giving an e.s.r. signal, and thus making possible the determination of the unpaired spin density at the hydrogen nucleus.[2,3] We report evidence for a Co^{II} hydrido-species, showing a strong e.s.r. signal, produced by Co–H interaction.

The compounds $CoCl_2$, $2R_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR_2$, with R = Ph (I) and R = Et (II) have been described.[4] When these complexes react with methylmagnesium chloride (Mg/Co $\leqslant 8$) in 1,2-dichloroethane, essentially no reduction of cobalt takes place, but the reaction solution gives a strong e.s.r. signal which accounts for some 40—50% of the cobalt present (assuming a low-spin Co^{II} species).

At higher Mg/Co ratio, reduction to a diamagnetic Co^{I} species occurs, but after some time the e.s.r. signal reappears, indicating reoxidation, $Co^{I} \rightarrow Co^{II}$, by the solvent.

The e.s.r. signal shows hyperfine structure due to the interaction of the unpaired electron of the Co^{II} with one nucleus of spin $I = 1/2$ (see Figure). Interaction with only one phosphorus atom appears unlikely, there being four equivalent phosphorus atoms in the complex; also, the unpaired spin density at the magnetic nucleus is greater in the case of (II), which would be contrary to expectation because of the electron-donating ethyl substituents on the phosphorus (see Table; coupling constants and line-width data are obtained by comparison with computer-simulated spectra [5]). Thus we suggest that the splitting is due to cobalt–hydrogen interaction, indicating the formation of a cobalt hydrido-species. The very high hyperfine coupling constants a_H mean that 15—19% of the unpaired spin resides at the hydrogen nucleus.

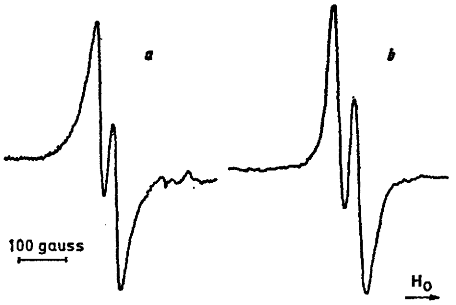


FIGURE. *E.s.r. signals of the reaction solutions of complex* (I) (a) *and complex* (II) (b) *with methylmagnesium chloride* (20°).

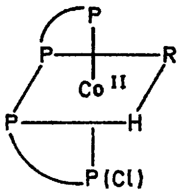
E.s.r. data for the reaction products of complexes (I) *and* (II) *with Grignard reagent*

No.	Complex	Grignard reagent	*g*-value	a_H (MHz)	T_2^{-1} (MHz)
1	(I)	MeMgCl	2·15	220	148
2	(II)	MeMgCl	2·12	270	151
3	(I)	EtMgCl	2·13	220	167

If EtMgCl is used, a doublet is also observed, with essentially the same hyperfine coupling constant a_H, but with a somewhat different *g*-value and with a significantly greater line-width (compare Nos. 1 and 3). These differences point to the presence of the alkyl group of the Grignard reagent in the e.s.r.-active Co^{II} species; presumably it has replaced a chlorine ligand of the cobalt. Particularly the greater line-width points to a somewhat bulkier molecule, since for compounds with anisotropic *g*-value the line-width is, to a first approximation, proportional to the rotational correlation time, and thus to the cube of the molecular radius.[6]

The use of CD_3MgCl leads to the same signal; thus the hydrogen does not come from the alkyl group. Since the signal may also be observed in toluene it does not appear likely that the hydrogen comes from the solvent. The ligands of the phosphorus remain as the most probable hydrogen donors.

Hydrogen transfer from alkyl and phenyl substituents of phosphine ligands to the central metal ion has often been reported.[7] In all cases, a valency change of 2 in the metal was assumed, due to σ-bonding of the metal to the hydrogen as well as to the carbon residue. In the present case, however, the presence of the alkyl group in the complex, as well as the paramagnetism of the compound (indicating Co^{II}) point to an exchange of the remaining chlorine ligand of the cobalt and a hydrogen of the phosphine substituents:



[P–P = bidentate phosphine ligands in (I) and (II); P(Cl) means that one of the hydrogens is substituted by Cl.]

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