Complexes Containing Cobalt–Silicon Metal–Metal Bonds

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Summary The complexes $(Ph_3P)_3CoH_2(SiR_3)$ (R = F, OEt) are formed by an oxidative-elimination reaction between R_3SiH and $(Ph_3P)_3Co(N_2)H$; the reaction is reversible when R = OEt, and this complex functions as an efficient catalyst for *O*-silylation and hydrosilylation reactions.
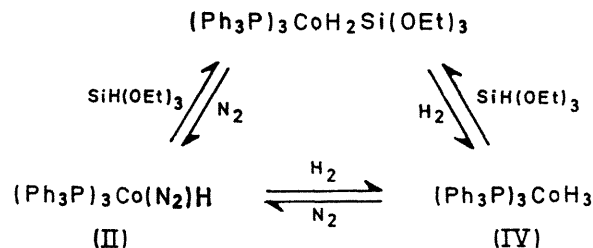
THE only known silyl complexes of the first-row transition metals involve low oxidation states of the metals, which are stabilized by carbonyl or cyclopentadienyl ligands.[1] There appear to be no silyl complexes of these metals which contain only tertiary phosphines as the neutral ligand, nor are there any in which the metal is in a high formal oxidation state.†

We now report the first complexes of this type, the cobalt(III) complexes $(Ph_3P)_3CoH_2(SiR_3)$ (I; R = F, OEt), obtained as yellow solids by the oxidative-elimination reaction of the silane R_3SiH with the dinitrogen complex (II),[2] suspended in hexane. Reaction proceeds smoothly at room temperature with loss of one molar equivalent of nitrogen. Similar preparative routes have been used to

$$(Ph_3P)_3Co(N_2)H + R_3SiH \rightarrow (Ph_3P)_3CoH_2(SiR_3) + N_2$$
$$\quad\quad\text{(II)} \quad\quad\quad\quad\quad\quad\quad\quad\text{(I)}$$
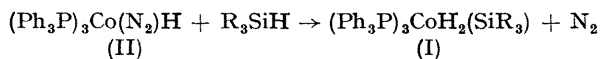
make silyl derivatives of the heavier metals.[3] Under similar conditions no reaction occurs when R = Et, and when R = Cl chlorination of cobalt occurs to give the known[4] complex $(Ph_3P)_3CoCl$ (III).

The silyl complexes (I; R = F or OEt) decompose rapidly in air, but are stable *in vacuo* or under argon. Under nitrogen, however, (I; R = OEt) loses the R_3SiH and reforms (II). (I; R = F) is stable to dissociation in benzene–hexane, from which solvent it may be recrystallised; (I; R = OEt) dissociates in this solvent system.

$$(Ph_3P)_3CoH_2Si(OEt)_3$$

$$(Ph_3P)_3Co(N_2)H \underset{N_2}{\overset{H_2}{\rightleftharpoons}} (Ph_3P)_3CoH_3$$
$$\quad\quad\text{(II)} \quad\quad\quad\quad\quad\quad\quad\quad\text{(IV)}$$

(I; R = OEt) can also be obtained by the reaction of the cobalt compound $(Ph_3P)_3CoH_3$ (IV)[4] with the silane in an atmosphere of argon. This reaction is related to that of (IV) with nitrogen to give (II),[5] and all three complexes can be interconverted reversibly: (I; R = F) can be prepared from (IV), but is unaffected by nitrogen or hydrogen.

In addition to bands characteristic of Ph_3P and $-SiR_3$, the i.r. spectra of (I) show weak absorptions at *ca.* 1945 cm^{-1} which are probably due to Co–H stretching vibrations. The 100 MHz ^1H n.m.r. spectra (benzene) show single, broad (*ca.* 40 Hz halfwidth) signals at τ 24·9 (R = F) and 25·1

† Cyclopentadienyl derivatives of some of these metals in high formal oxidation states have been reported since the submission of this communication (W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 4).
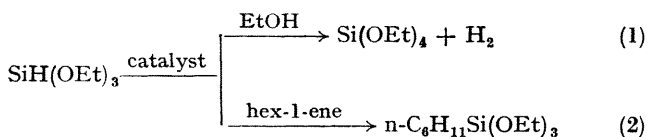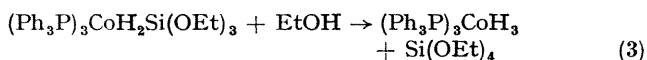
(R = OEt), which compare with a resolved quartet (J_{P-H} ca. 50 Hz) at τ 29 for (II).[6] The lack of fine structure for the silyl complexes suggests a rapid exchange process, although no dissociation was detected in a molecular weight determination on (I; R = F) in the same solvent.

The complexes (I; R = F, OEt) react with carbon tetrachloride to give the silane R_3SiH, chloroform, and (III); as previously reported,[5] (III) reacts further with carbon tetrachloride to form $(Ph_3P)_2CoCl_2$.

(I; R = OEt) and its precursors (II) and (IV) are useful homogeneous catalysts for O-silylation and for hydrosilylation reactions, e.g. reactions (1) and (2). Reaction (1)

$$SiH(OEt)_3 \xrightarrow{\text{catalyst}} \begin{cases} \xrightarrow{\text{EtOH}} Si(OEt)_4 + H_2 & (1) \\[2mm] \xrightarrow{\text{hex-1-ene}} n\text{-}C_6H_{11}Si(OEt)_3 & (2) \end{cases}$$

proceeds via (IV), since the rapid occurrence of reaction (3)

$$(Ph_3P)_3CoH_2Si(OEt)_3 + EtOH \rightarrow (Ph_3P)_3CoH_3 + Si(OEt)_4 \quad (3)$$

probably has been demonstrated independently. The complex (IV) then reacts with triethoxysilane to regenerate (I; R = OEt). Reaction (1) is quite rapid, being 80% complete in 2·5 h with a 2:1:2 × 10^{-4} molar ratio of ethanol : silane : catalyst. O-Silylation has recently been shown to be similarly catalysed by dicobalt octacarbonyl.[7]

Reaction (2) is very vigorous and strongly exothermic. With 2:1:2 × 10^{-4} and 1:1:2 × 10^{-4} molar ratios of hex-1-ene : silane : catalyst the temperature of the mixture rises from 25 °C to ca. 65 °C in 4 min and the reaction is 75% and 40% complete, respectively, in 10 min. If the mixture is deliberately kept at 25—30 °C (2:1:2 × 10^{-4} ratio), ca. 40% reaction occurs in 20 min. In all cases, some isomerisation of the olefin also occurs; at 25—30 °C the rate of isomerisation is about half that of hydrosilylation. Unlike the cobalt carbonyl catalysed hydrosilylation reaction,[8] it seems probable that reaction (2) proceeds via a silyl-complex, presumably (I; R = OEt). The more stable complex (I; R = F) does not react with hex-1-ene, and attempts to catalyse the reaction of this olefin with trifluorosilane, using (II), resulted only in the formation of (I; R = F).

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