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XVI*. THE REACTIONS OF HYDRIDOBIS[BIS(DIPHENYLPHOSPHINO)-ETHANE]COBALT(I) WITH CHLOROSILANES

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Summary

The complex $(diphos)_2CoH$ (diphos = $Ph_2PCH_2CH_2PPh_2$) reacts with chlorosilanes, $ClSiR_3$ ($R_3 = HCl_2$, HMeCl, Ph_3, Cl_3) to give $(diphos)_2CoCl$ and $HSiR_3$. In the presence of hydrogen chloride this complex reacts further to form the new complex $[(diphos)_2CoHCl]Cl$.

Introduction

Silyl derivatives of transition metals can be readily prepared by the reaction of low-valent metal complexes with silanes, $HSiR_3$ [2]. In particular, d^8-complexes have been widely studied. Four-coordinate complexes usually react by oxidative-addition, e.g. $(Ph_3P)_2Ir(CO)Cl$ [3], although oxidative-elimination may also occur, as with $(Ph_3P)_3RhCl$ [4] or $(Ph_3P)_2Ir(N_2)Cl$ [5]. Five-coordinate complexes normally react by oxidative-elimination, e.g. $(Ph_3P)_3Co(N_2)H$ [6] or $Fe(CO)_5$ [7].

$$(Ph_3P)_2Ir(CO)Cl + HSiCl_3 \rightarrow (Ph_3P)_2Ir(CO)Cl(SiCl_3)H$$

$$(Ph_3P)_3RhCl + HSi(OEt)_3 \rightarrow (Ph_3P)_2RhCl[Si(OEt)_3]H + Ph_3P$$

$$(Ph_3P)_2Ir(N_2)Cl + HSiEt_3 \rightarrow (Ph_3P)_2IrCl(SiEt_3)H + N_2$$

$$(Ph_3P)_3Co(N_2)H + HSiF_3 \rightarrow (Ph_3P)_3CoH_2(SiF_3) + N_2$$

$$Fe(CO)_5 + HSiCl_3 \rightarrow Fe(CO)_4(SiCl_3)H + CO$$

It was therefore of interest to examine the reactions of silanes with $(diphos)_2$-CoH (diphos = $Ph_2PCH_2CH_2PPh_2$), for which oxidative-elimination is less likely, there being no suitable leaving group. Elimination of hydrogen is an alternative possible reaction, which could give a product analogous to $R_3SiCo(CO)_4$ [8]. During the course of our investigation Lappert and Speier reported [9] the reac-

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* For part XV see ref. 1.

tion of $(diphos)_2CoH$ with various chlorosilanes, $HSiR_2Cl$, which they formulated as protonation reactions giving the complexes $[(diphos)_2CoH_2][SiR_2Cl]$. The occurrence of anions of this type seems unlikely. The only other example to have been reported previously, $SiCl_3^-$, has been detected only in the presence of strongly basic tertiary amines and in one solid salt, $[Me_3NH][SiCl_3]$ [10]. We have observed reactions similar to those described by Lappert and Speier, but we formulate the products differently since they appear not to contain silicon.

Results and discussion

Suspensions of the complex $(diphos)_2CoH$ in normal laboratory samples of either trichlorosilane or methyldichlorosilane react rapidly to give pale green compounds which appear to be identical (IR analysis). The implication that these products do not contain the silyl groups is confirmed by the isolation of the same product from the reaction of $(diphos)_2CoH$ (suspended in hexane) with gaseous hydrogen chloride. These products contain two chlorine atoms per cobalt atom, one of which can be replaced by the tetraphenylborate anion. The tetraphenylborate thus obtained behaves as a 1/1-electrolyte in nitromethane solution. The conductivities of the chloro-complexes are initially similar to that of the tetraphenylborate, but decrease rapidly (1-2 min) to about half this value. The concomitant colour changes (light green to brown to dark green) suggest the formation of $(diphos)_2CoCl_2$, which also has a low molar conductivity in nitromethane. The IR spectra of the chloro-complexes and of the tetraphenylborate show weak bands at 1960 cm^{-1}, assigned as Co—H stretching modes. The spectra differ from that of $(diphos)_2CoCl_2$, and the compounds are therefore formulated as $[(diphos)_2CoHCl]X$ ($X = Cl, BPh_4$).

The dichloro-complex, $[(diphos)_2CoHCl]Cl$, is presumably formed by initial chlorination of $(diphos)_2CoH$ to give $(diphos)_2CoCl$ which then reacts with hydrogen chloride. Hydrogen chloride is a normal contaminant of chlorosilanes and sufficient would be present, in the relatively large amounts of silane employed, to give the observed reaction. Similar oxidation reactions of $(diphos)_2CoBr$ have been reported previously [11]. In the reaction between $(diphos)_2CoH$ and trichlorosilane, no hydrogen was detected but the volatile products contained dichlorosilane, H_2SiCl_2, indicating that the chlorosilane is a more effective chlorinating agent than hydrogen chloride.

When a completely pure chlorosilane reacts with $(diphos)_2CoH$, only $(diphos)_2CoCl$ is formed. This was demonstrated by using the cobalt complexes to remove hydrogen chloride from the silane by passing a small amount of a chlorosilane down a column of $(diphos)_2CoH$. As the chlorosilane moves down the column the red colour of the hydrido-complex changes to brown and, as the brown region extends, the top of the column becomes green. As more of the chlorosilane passes down the column the brown region extends further, but the green band ceases to grow when all the hydrogen chloride has been consumed. If hydrogen chloride is now deliberately introduced, the green band becomes extended. The green and brown compounds were isolated and identified as $[(diphos)_2CoHCl]Cl$ and $(diphos)_2CoCl$ respectively. Precisely similar effects are found using trichlorosilane, dichloromethylsilane, chlorotriphenylsilane or tetrachlorosilane. Since the last two of these do not contain hydrogen, protonation reactions of the type proposed by Lappert and Speier [9] cannot be occurring. It is significant that these workers found that only chlorosilanes were effective; a range of other silanes which do not contain chlorine did not react. We have also found that $(diphos)_2CoH$ and triethoxysilane do not react, even after several weeks.

The brown complex $(diphos)_2CoCl$ was obtained independently by careful reduction of $(diphos)_2CoCl_2$ with sodium borohydride, and was found to react with hydrogen chloride to give the green complex $[(diphos)_2CoHCl]Cl$. These products were identical to those described above. The IR spectra of $[(diphos)_2CoHCl]X$ (X = Cl, BPh_4) show very weak absorptions at 1960 cm^{-1} which are presumably due to the Co—H bond, although overtone bands of the phosphine also occur in this region. The characteristically sharp bands of $[(diphos)_2CoH_2]^+$, observed [12] at 1980 and 1930 cm^{-1}, are definitely absent. Surprisingly, no absorption is found in the far IR region which can be attributed to Co—Cl stretching, although the same is also true of $(diphos)_2CoCl$.

Further support for the identity of $[(diphos)_2CoHCl]Cl$ was obtained from its reaction with ethanolic sodium hydroxide. The complex dissolves rapidly to give a brown solution from which the red complex $(diphos)_2CoH$ crystallises after several hours. Back titration with hydrochloric acid shows that two molar equivalents of base have been consumed; the same result is obtained for the products from all three routes: $(diphos)_2CoH$/chlorosilanes, $(diphos)_2CoH/HCl$, or $(diphos)_2CoCl/HCl$. Presumably, one mole of base is consumed in removing the elements of hydrogen chloride giving $(diphos)_2CoCl$ which then reacts with a second molar equivalent of the base to form $(diphos)_2CoH$ and acetaldehyde; the presence of the latter was demonstrated by the formation of a yellow precipitate on addition of 2,4-dinitrophenylhydrazine. The second step of this process was confirmed independently, starting with $(diphos)_2CoCl$. The use of

$$[(diphos)_2CoHCl]Cl + EtO^- \rightarrow (diphos)_2CoCl + EtOH + Cl^-$$

$$(diphos)_2CoCl + EtO^- \rightarrow (diphos)_2CoH + CH_3CHO + Cl^-$$

ethoxide ion as a hydride-forming reagent is well-known for other Group VIII transition metals [13, 14] but has not previously been reported for a 3*d*-metal. The reaction of a complex such as $[(diphos)_2CoH_2][SiCl_3]$ with base would require a single molar equivalent for deprotonation of the cation and, presumably, three further molar equivalents to react with the acid produced by solvolysis of the anion.

The reactions of $(diphos)_2CoH$ with silanes thus appears to be confined to chlorosilanes. However, as trifluorosilyl complexes are often of greater stability than other silyl derivatives, we have also examined the reaction of trifluorosilane with an ether suspension of the hydrido-complex. Reaction is very slow (ca. 3 days) giving a white product, $[(diphos)_2CoH_2]_2[SiF_6]$. The IR spectrum of this product clearly shows the two absorptions at 1980 and 1930 cm^{-1}, characteristic of this cation [12], and also those of the anion. The SiF_6^{2-} anion is presumably formed by the slow reaction of the trifluorosilane with traces of moisture, which is consistent with the observed lack of change in the total pressure. The identity of the product was confirmed by independent synthesis from $(diphos)_2CoH$ and $(NH_4)_2SiF_6$ in the presence of an acid. The complex

$$2\,HSiF_3 + 2H_2O \rightarrow H_2SiF_6 + SiO_2 + 2\,H_2$$

$$2\,(diphos)_2CoH + H_2SiF_6 \rightarrow [(diphos)_2CoH_2]_2[SiF_6]$$

$[(diphos)_2CoH_2]_2[SiF_6]$ is deprotonated by ethanolic sodium hydroxide to give $(diphos)_2CoH$.

Conclusion

The complex $(diphos)_2CoH$ reacts with silanes to form neither a cobalt—silicon bond nor the protonated cation, although cationic species can be formed by reaction with adventitious acid. That oxidative-addition of the silanes does not occur is presumably due to the difficulty of dissociation of $(diphos)_2CoH$ to give a four-coordinate intermediate. The complex $[(PhO)_3P]_4CoH$ is similarly unreactive [15], whereas $(Ph_3P)_3Co(N_2)H$ reacts readily [6], presumably by facile loss of the dinitrogen ligand prior to the addition of the silane. The chlorination of $(diphos)_2CoH$ by chlorosilanes is similar to that of many hydrido-complexes with chlorinated solvents [16].

Experimental

Infrared spectra were obtained for Nujol or hexachlorobutadiene mulls using a Perkin—Elmer 621 spectrometer. Conductivities were measured on $10^{-3}M$ nitromethane solutions using a Cambridge Instrument Co. conductivity bridge.

Unless otherwise specified all reactions were carried out in nitrogen or argon atmospheres. The complex $(diphos)_2CoH$ was prepared by the method of Sacco and Ugo [12]. Analytical data for the new compound are presented in Table 1.

Reaction of $(diphos)_2CoH$ with an excess of trichlorosilane

Trichlorosilane (3 ml) and $(diphos)_2CoH$ (0.3 g) were sealed in an evacuated tube which was shaken for 1 h, after which time the excess trichlorosilane was distilled off. The pale green solid product was dried under vacuum.

A precisely similar product was obtained using dichloromethylsilane.

When the reaction with trichlorosilane (2 moles per mole of hydrido-complex) was carried out in a closed system, the IR spectrum of the residual volatiles showed, in addition to the spectrum of $HSiCl_3$, bands at 2200 and 878 cm^{-1} which correspond to the strongest bands in the reported spectrum [17] of H_2SiCl_2.

TABLE 1

ANALYTICAL DATA (%) FOR $[(diphos)_2CoHCl]Cl$

	C	H	Cl
From $(diphos)_2CoH + HSiCl_3$	67.3	5.8	7.6, 7.9
From $(diphos)_2CoH + HSiCl_2Me$	67.9	5.3	7.7
From $(diphos)_2CoH + HCl$	67.3	5.6	7.9
Calculated	67.5	5.6	7.7

Reaction of (diphos)$_2$CoH with hydrogen chloride

Hydrogen chloride was bubbled for a few minutes into a suspension of (diphos)$_2$CoH (0.3 g) in hexane (15 ml). The pale green product was filtered off, washed with hexane and dried in vacuum. The IR spectrum was identical to those obtained from the products of the reactions with chlorosilanes.

Hydridochlorobis[bis(diphenylphosphino)ethane]cobalt(III) chloride

The complex (diphos)$_2$CoCl$_2$ (2 g) was suspended in ethanol (15 ml) and a dilute solution of sodium borohydride in ethanol was added dropwise. The dark green solid gradually dissolved to a brown solution and eventually traces of a red precipitate of (diphos)$_2$CoH were formed. The reduction was then stopped, the solvent removed under reduced pressure, and the brown residue of (diphos)$_2$-CoCl was washed with ethanol and allowed to dry. [Found: Cl, 4.8%. Calcd.. Cl, 4.0%.] The IR spectrum showed no trace of the band at 310 cm^{-1} which is observed for (diphos)$_2$CoCl$_2$.

The brown solid was suspended in hexane and hydrogen chloride gas passed through the suspension for a few minutes. The pale green solid product was filtered off, dried, and then thoroughly washed with water to remove traces of sodium chloride. Finally the product was dried under vacuum. The IR spectrum was identical to those described above.

Hydridochlorobis[bis(diphenylphosphino)ethane]cobalt(III) tetraphenylborate

The complex [(diphos)$_2$CoHCl]Cl (0.93 g) was added to a stirred solution of sodium tetraphenylborate (0.69 g) in ethanol (20 ml). A yellow precipitate was rapidly formed and was filtered off, washed with ethanol, recrystallised from hot ethanol and dried under vacuum.

Reaction of [(diphos)$_2$CoHCl]Cl with ethanolic sodium hydroxide

(i) The complex [(diphos)$_2$CoHCl]Cl (0.093 g), was stirred with ethanolic sodium hydroxide (10 ml, 0.1 *M*). A brown solution was formed quickly and, after several hours, a red precipitate began to form. After 16 h the precipitate was filtered off, dried, and identified as (diphos)$_2$CoH by its IR spectrum [ν(Co—H) 1890 cm^{-1}]. Addition of a solution of 2,4-dinitrophenylhydrazine to the filtrate and acidification gave a yellow precipitate.

(ii) The complex [(diphos)$_2$CoHCl]Cl (0.03 g) was stirred with ethanolic sodium hydroxide (10 ml, 0.1 *M*) for 30 min. The solution was then diluted with water (20 ml) and titrated potentiometrically with hydrochloric acid (0.05 *M*).

The following results were obtained on samples from the three different routes:

Preparative route	Moles of base consumed per mole of [(diphos)$_2$CoHCl]Cl	
(diphos)$_2$CoH + HSiCl$_3$	2.2,	2.4
(diphos)$_2$CoH + HCl	1.6,	1.6
(diphos)$_2$CoCl + HCl	2.0,	1.9

Reaction of (diphos)$_2$CoCl with ethanolic sodium hydroxide

The complex (diphos)$_2$CoCl (0.089 g) was stirred with ethanolic sodium hydroxide (10 ml, 0.1 *M*). The brown suspension slowly became red and after six hours the solid product was filtered off, washed with ethanol, dried, and identified as $(\mathrm{diphos})_2\mathrm{CoH}$ by its IR spectrum [ν(Co—H) 1890 cm^{-1}].

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