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# ON THE BEHAVIOUR OF AN OPTICALLY ACTIVE COBALT—SILICON BOND. EVIDENCE FOR THE FORMATION OF ANALOGUES OF SILYL-GRIGNARD REAGENTS *

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## Summary

We describe the behaviour of (*S*)(+)-$(CO)_4CoSiMePh(1\text{-}Np)$, the absolute configuration of which is determined by reference to (S)(+)-$(CO)_4CoGeMePh(1\text{-}Np)$. Electrophiles ($Cl_2$, $Br_2$) cleave the silicon—cobalt bond with retention of configuration at silicon, while nucleophiles ($LiAlH_4$, $H_2O$, MeOH, KOAc, $Hg(OAc)_2$) cleave the bond with inversion. Organolithium and Grignard reagents attack at carbonyl ligands to displace silicon as an anion, yielding $R_3SiLi$ and $R_3SiMgX$. Reactions of $R_3SiLi$ proceed with predominant retention of configuration. The formation of the silyl-Grignard reagent is confirmed by its reactions.

## Introduction

In previous papers [2—4] we described the synthesis and behaviour of compounds containing manganese or iron bound to an optically active silicon atom.

In order to understand better the nature of these bonds, we studied the cleavages of the complexes $(CO)_4CoSiPh_3$ (I) [5] and (+)-$(CO)_4CoSi^*MePh(1\text{-}Np)$ (II) ($[\alpha]_D^{25}$ + 2°). The latter was previously described by Sommer and coworkers [6], who studied its cleavages by triethylsilane and methanol and its behaviour as a catalyst for the $Si^*H—Si^*D$ exchange.

The complexes were prepared by reaction of the corresponding silane with cobalt carbonyl:

$$R_3SiH + Co_2(CO)_8 \rightarrow (CO)_4CoSiR_3 + H_2$$

## Results and discussion

A sample of II was prepared by a slight modification of the method of Sommer [6]. The infrared spectrum and the specific rotation were in agreement with

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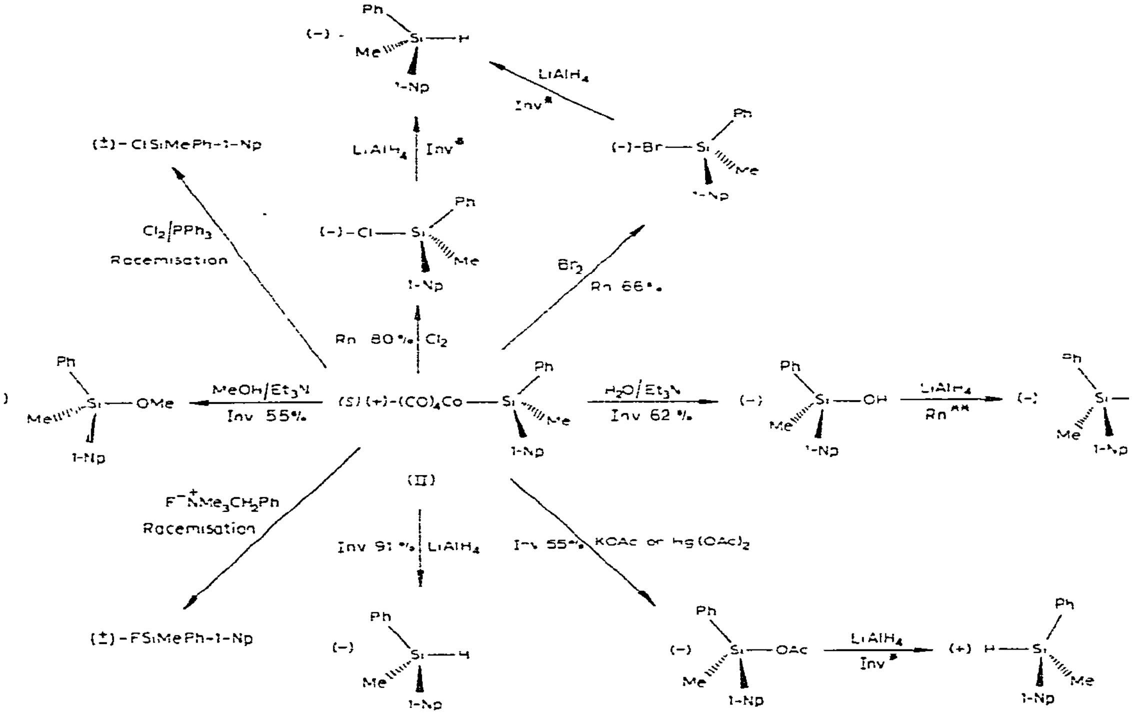
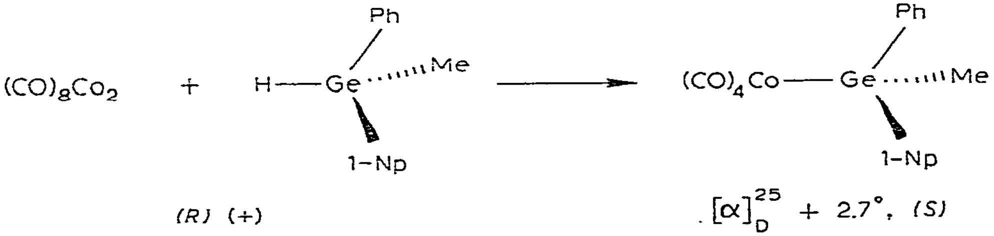
* For a preliminary communication see ref. 1.

those reported. Its optical purity was over 95% and was determined by the calorimetric method of Jacques and Fouquey [7].

The absolute configuration of II is *S* as shown in Scheme 1. This configuration is deduced from the absolute configuration of (+)-$(CO)_4CoGeMePh(1\text{-}Np)$, prepared by the same reaction, which was established by X-ray diffraction [8]:

SCHEME 1. Rn = retention, Inv = inversion, 1-Np = 1-naphthyl. Percentages after Rn or Inv are stereoselectivities. * reduction of halogeno and acetoxysilanes is known to take place with inversion [20 and 21]. ** Reduction of the Si—O bond is known to take place with retention [21]).





The absolute configuration of (*R*)(+)-(1-Np)PhMeGeH was previously shown to be the same as the absolute configuration of (*R*)(+)-(1-Np)PhMeSiH, which was established by X-ray diffraction [9].

This configuration corresponds to retention at silicon for the formation of II, as is the general rule for the substition of the Si—H bond [10] and for the insertion of a metal into this bond [11].

II was treated with a wide variety of reagents. The cleavage reactions are shown in Scheme 1. The stereochemistries were determined by Walden cycles and calculated as defined in ref. 12; the $[\alpha]_D$ of the optically pure compounds were all known.

Treatment with electrophiles ($Cl_2$ or $Br_2$) led to a cleavage of the silicon—cobalt bond with predominant retention of configuration. The measured stereoselectivity was higher with chlorine (80%) than with bromine (66%), but this is probably due to the slower rate of racemisation of the chlorosilane in solution [13]. Cleavage with chlorine in the presence of triphenylphosphine led to complete racemisation instead of the inversion observed with the Fe—Si bond [3].

On the other hand, treatment of II with nucleophiles (the reactions with Grignard and organolithium compounds will be discussed below) led to predominant inversion of configuration: $LiAlH_4$ led to a good stereoselectivity (91%) whereas with water, methanol, potassium or mercuric acetates inversion was less dominant (54—62%). Fluoride causes racemisation.

Comparison of the behaviour of Fe—Si, Mn—Si and Co—Si is particularly interesting. Fe—Si compounds are stable to most nucleophiles and, when cleaved, the predominant stereochemistry is retention, whereas Mn—Si [4] and Co—Si compounds are cleaved with inversion. This is probably due to the fact that the groups ($\pi$-Cp)$Fe(CO)_2$ and ($\pi$-Cp)$Fe(CO)(PPh_3)$ are good nucleophiles [14] and poor leaving groups in contrast with $(CO)_4Co$ which is known to be a poor nucleophile. As a confirmation of this fact, it was not possible to synthesize cobalt—silicon complexes by reaction of $(CO)_4Co$ with chlorosilanes [15]. ($\pi$-Cp)$Mn(CO)_2H$ behaves as a good leaving group, although the literature does not provide any data on its nucleophilicity.

The cobalt—silicon bond appeared to be unreactive towards alkyl, aryl and acyl halides, diisobutylaluminium hydride, $KHF_2$, and $BF_3$.

In contrast, organomagnesium and organolithium compounds did not lead to alkylation of the silicon atom. Treatment of I with a tenfold excess of a Grignard or organolithium reagent led to the formation of the corresponding anionic reagent

$$(CO)_4CoSiPh_3 \xrightarrow{RM} MSiPh_3$$

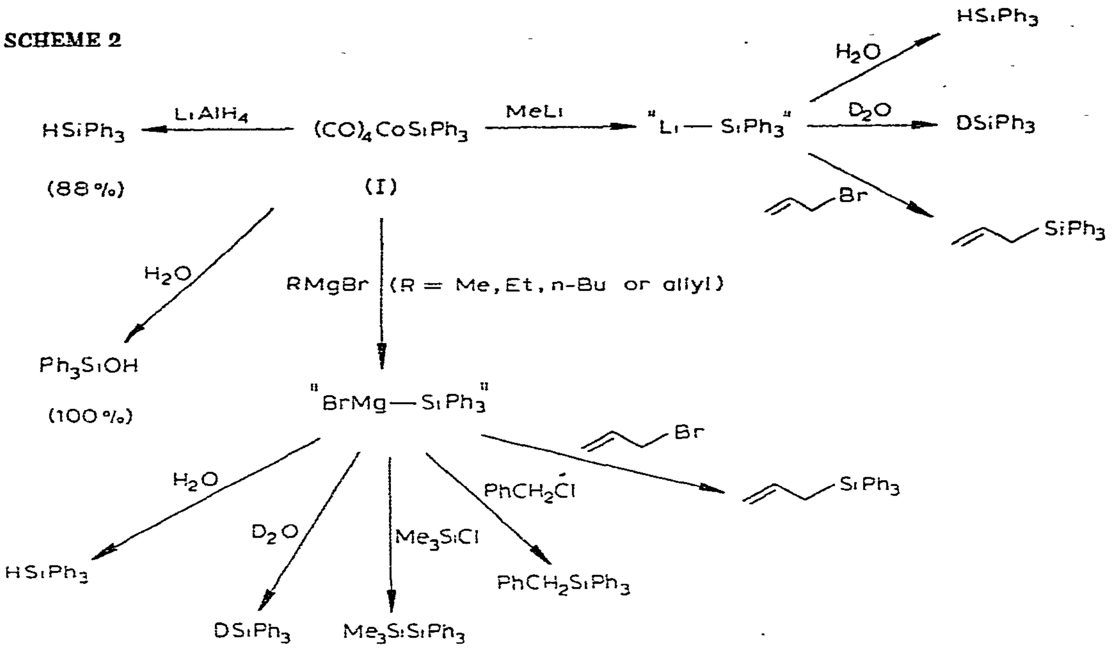
(M = MgBr, R = Me, Et or allyl; M = Li, R = Me, Bu)

The reactions of these derivatives are shown in Scheme 2. Hydrolysis with $D_2O$ yielded only the deuterated silane, identified in IR spectroscopy by the absence of the SiH absorption at $\sim 2100$ cm$^{-1}$ and the appearence of the new SiD band at $\sim 1550$ cm$^{-1}$. This is the first time that $R_3SiD$, free from $R_3SiH$, has been obtained in an attempt to prepare a silyl Grignard. Further evidence for formation of the Grignard reagent is that hydrolysis of I itself yielded triphenylsilanol quantitatively.

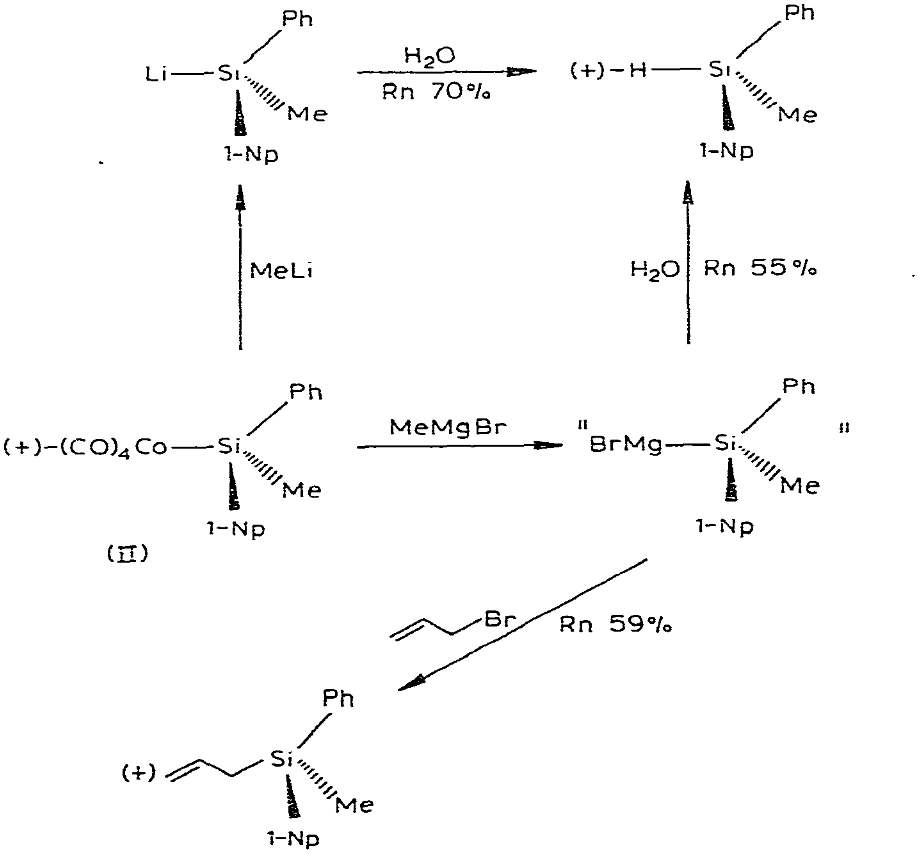
The reactions with alkyl halides proved that couplings proceeded through a silylanion, since they are unreactive towards Co—Si bonds. Thus allyl bromide, benzyl chloride and $Me_3SiCl$ gave the allyl, benzyl and trimethylsilyl derivatives, respectively.

Treatment of the optically active compound II with a Grignard reagent yielded a silyl-Grignard of low optical activity (see Scheme 3). Reaction with MeLi gave, after hydrolysis, a silane with 70% retention of configuration. These results can be compared to those obtained by Sommer and Mason [16] for the

SCHEME 2



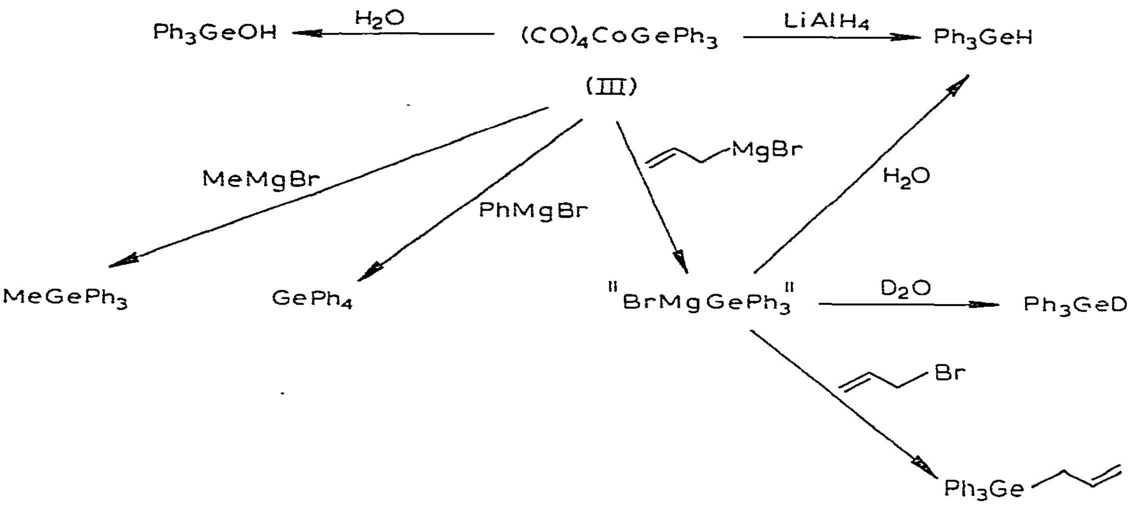
SCHEME 3



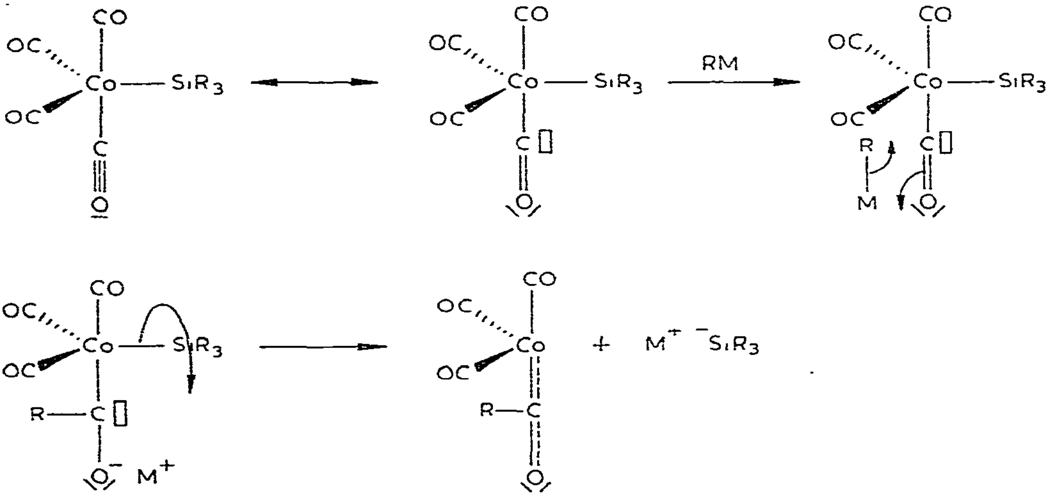
preparation of an optically active silyllithium.

Surprisingly, treatment of $(CO)_4CoGePh_3$ (III) [17] with MeMgBr led to alkylation of Ge, while allylmagnesium bromide led to the germyl-Grignard (see Scheme 4). Hydrolysis of the latter with $D_2O$ led to $Ph_3GeD$ identified by the GeD vibration at ~1470 $cm^{-1}$. Reduction with $LiAlH_4$ and hydrolysis of III yielded $Ph_3GeH$ and $Ph_3GeOH$ respectively. Treatment with $LiAlH_4$ was carried

SCHEME 4



SCHEME 5



out in refluxing tetrahydrofuran for 6 hours and only 48% of III was reduced, showing the greater stability of the Co—Ge bond than of the Co—Si bond.

The behaviour of these compounds is surprising since we had expected, in all cases, nucleophilic attack at silicon or germanium to occur. We think instead, that Grignard and lithium reagents attack the carbonyl ligands [18,19], the silicon moiety being displaced as a silyl anion (Scheme 5).

It seems appropriate to emphasize on the great variation in the behaviour of silicon—transition metal bonds towards organometallic reagents. $(CO)_4CoSiR_3$ gave silyl anions, Fe—Si compounds were stable to such reagents, whereas $\pi$-$MeCpMn(CO)_2(H)SiR_3$ gave $R_3SiH$ [4].

## Experimental section

All experiments were carried out under nitrogen, using a vacuum line, in Schlenk tubes. All solvents were dry, distilled and deoxygenated. Starting materials were purchased from Strem Chemicals ($Co_2(CO)_8$) or prepared by literature methods (triphenylsilane [22] (+)-methylphenyl-1-naphthylsilane [23] triphenylgermane [24] (+)-methylphenyl-1-naphthylgermane [25]. Grignard and organolithium reagents were prepared using ether as solvent and kept under nitrogen in a deep freeze.

Melting points of cobalt compounds were taken under vacuum with a Dr. Tottoli's apparatus and are uncorrected. IR spectra were recorded with a Perkin—Elmer 257 spectrophotometer. Optical rotations were measured with a Perkin—Elmer 141 polarimeter.

### *(+)-Methylphenyl-1-naphthylsilylcobalt tetracarbonyl (II)*

A solution of 6.7 g of $Co_2(CO)_8$ (19.6 mmol) in 200 ml of pentane was filtered and added to a well stirred solution of 9.72 g of (+)-MePh(1-Np)SiH, $[\alpha]_D$ + 35° (39.2 mmol). The mixture was heated at 30—40°C for 1 week. [The solution was dark-brown and hydrogen was slowly evolved. It was possible to follow the disappearance of the Si—H band at 2040 $cm^{-1}$ and the bridging carbonyls of $Co_2(CO)_8$ at 1860 $cm^{-1}$; new bands appeared at 2073, 2053, 2013, 1988 and 1953 $cm^{-1}$ characteristic of the silylcobalt tetracarbonyl.] After this time, the solution was concentrated to 100 ml and left at —20°C overnight. This solution was filtered, leaving a black residue, concentrated to 60 ml, and left at —78°C for 6 hours. The crystals that formed were filtered, dissolved in 60 ml of pentane, and crystallized at —20°C. This recrystallization was repeated 2 or 3 times until the crystals were colourless. 5.1 g of (+)-MePh(1-Np)$SiCo(CO)_4$, $[\alpha]_D^{25}$ + 2° (*c* 13.3 pentane) m.p. 93°C (uncorrected, reported 102—104.5°C) were obtained. Other preparations afforded the compound with a lower optical purity $[\alpha]_D^{25}$ + 1.5° (*c* 14.8 pentane) Racemic MePh(1-Np)$SiCo(CO)_4$ m.p. 100°C was obtained in a similar way.

### *(+)-Methylphenyl-1-naphthylgermylcobalt tetracarbonyl*

Reaction of $Co_2(CO)_8$ (1.3 g, 3.8 mmol) and (+)-MePh(1-Np)GeH $[\alpha]_D$ + 25° (2.23 g, 7.6 mmol) as described above yielded 3.1 g of (+)-$(CO)_4CoGeMePh$(1-Np) (yield 86%), $[\alpha]_D^{25}$ + 2.7° (*c* 10.0 pentane) m.p. 92.5—93°C. $\nu$(CO) 2073, 2053, 2013, 1988 and 1953 $cm^{-1}$. Anal. Found: C, 54.53; H, 3.32; Co, 12.87.

$C_{21}H_{15}CoGeO_4$ calcd.: C, 54.43; H, 3.24; Co. 12.74%.

Racemic $(CO)_4CoGeMePh(1\text{-}Np)$ m.p. 96.5—97.5°C was obtained similarly.

*Cleavage of II with chlorine*

To 320 mg of II $[\alpha]_D + 2°$, (0.77 mmol) in 15 ml $CCl_4$ were added 3.08 ml of a 0.5 *M* solution of $Cl_2$ in $CCl_4$ (1.54 mmol). The solution was stirred for 1 night at room temperature. A gas was evolved and a blue-green precipitate formed. The solvent was pumped off and the residue was extracted with pentane. The solution was filtered and the solvent pumped off again. The residue was dissolved in ether and slowly added to a suspension of an excess $LiAlH_4$ in ether at 0°C. After hydrolysis, the crude silane was extracted with ether and chromatographed on silica gel using hexane as eluant. The solvent was evaporated leaving the oily (—)-silane (yield 150 mg, 70%), $[\alpha]_D^{25} - 20.2°$ (*c* 3.5 cyclohexane). The rotation was taken before the silane crystallized. $CoCl_2$ was also formed.

*Cleavage of II with bromine*

320 mg of II $[\alpha]_D + 1.5$ (0.77 mmol) were treated analogously with 2.8 ml of a 0.55 *M* solution of $Br_2$ in $CCl_4$ (1.54 mmol). Chromatography gave 172 ml (yield 90%) of (—)-silane $[\alpha]_D - 8.3°$ (*c* 7.4 cyclohexane). In this case cobalt was oxidized to $CoBr_2$.

*Cleavage of II with chlorine and triphenylphosphine*

320 mg of II $[\alpha]_D + 2°$ (0.77 mmol) in 10 ml $CCl_4$ were treated with various quantities of $Cl_2$ (1.05 to 1.55 mmol) and $PPh_3$ (1.54 to 3.08 mmol). After work-up as before, yields varying from 53 to 84% of racemic methylphenyl-1-naphtylsilane were obtained.

*Cleavage of II with $LiAlH_4$*

320 mg of II, $[\alpha]_D + 2°$ (0.77 mmol) in 15 ml ether were added to a suspension of an excess of $LiAlH_4$ in ether at 0°C. After 1 night the reaction mixture was hydrolyzed and chromatographed as before. 180 mg of (—)-silane (yield 95%), $[\alpha]_D - 28.3°$ (*c* 6 cyclohexane) were obtained.

*Cleavage of II with water*

320 mg of II, $[\alpha]_D + 2°$ (0.77 mmol) in 15 ml ether were added to 10 ml water containing 5 ml triethylamine (to trap $HCo(CO)_4$, a strong acid * which would racemize the silanol). After 24 h the mixture was extracted with ether, the ether was pumped off. The residue was dissolved in di-n-butyl ether and gently refluxed for 2 h. After hydrolysis and extraction with ether, the solvent was pumped off. Chromatography afforded 180 mg of (—)-silane (yield 94%) $[\alpha]_D - 8.4°$ (*c* 14.4 cyclohexane).

*Cleavage of II with methanol*

320 mg of II, $[\alpha]_D + 2°$ (0.77 mmol) in 10 ml benzene were added to 10 ml methanol containing 5 ml triethylamine. After 2 h the solvent was pumped off

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* $HCo(CO)_4$ is an acid of approximately the same strength as HCl [26].

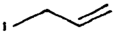
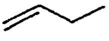
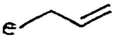
and the residue extracted with pentane. The solution was filtered and evaporation of the pentane afforded 214 mg of (—)-methoxysilane (yield 100%) $[\alpha]_D$ — 1.8° (*c* 10, pentane).

*Cleavage of II with potassium acetate and mercuric acetate*

320 mg of II, $[\alpha]_D$ + 1.5° (0.77 mmol) in 20 ml benzene were added to an excess of KOAc. After 24 h the solution was filtered, the solvent pumped off and the residue treated with $LiAlH_4$ in ether. Chromatography on silica gel afforded 100 mg of (+)-silane (yield 50%) $[\alpha]_D$ + 2° (*c* 4, cyclohexane). Further elution with benzene yielded 100 mg of (±)-silanol (silanol racemized on hydrolysis with diluted HCl).

Similar treatment of II with excess $Hg(OAc)_2$ at reflux temperature for 3 h gave 90 mg of (+)-silane (yield 45%), $[\alpha]_D$ + 1.5° (*c* 4.6 cyclohexane). Again

TABLE 1

| Starting material | Organometallic reagent | Reagent | Product | Yield (%) |
|---|---|---|---|---|
| $(CO)_4CoSiPh_3$ | $CH_3Li$ | $H_2O$ | $Ph_3SiH$ | 46 |
| $(CO)_4CoSiPh_3$ | $CH_3Li$ | $D_2O$ | $Ph_3SiD$ | 50 |
| $(CO)_4CoSiPh_3$ | $CH_3Li$ |  Br | $Ph_3Si$  | 41 |
| $(CO)_4CoSiPh_3$ | $CH_3CH_2MgBr$ | $H_2O$ | $Ph_3SiH$ | 50 |
| $(CO)_4CoSiPh_3$ |  MgBr | $H_2O$ | $Ph_3SiH$ | 63 |
| $(CO)_4CoSiPh_3$ | $CH_3MgBr$ | $D_2O$ | $Ph_3SiD$ | 38 |
| $(CO)_4CoSiPh_3$ | $CH_3MgBr$ | $(CH_3)_3SiCl$ | $Ph_3SiSi(CH_3)_3$ | 42 |
| $(CO)_4CoSiPh_3$ | $CH_3MgBr$ | $PhCH_2Cl$ | $Ph_3SiCH_2Ph$ | 40 |
| $(CO)_4CoSiPh_3$ | $CH_3MgBr$ |  Br | $Ph_3Si$  | 37 |
| $(CO)_4CoGePh_3$ | $CH_3MgBr$ | $H_2O$ | $Ph_3GeCH_3$ | 63 |
| $(CO)_4CoGePh_3$ |  MgBr | $H_2O$ | $Ph_3GeH$ | 52 |
| $(CO)_4CoGePh_3$ | $PhMgBr$ | $H_2O$ | $Ph_4Ge$ | 34 |
| $(CO)_4CoGePh_3$ |  MgBr | $D_2O$ | $Ph_3GeD$ | 42 |
| $(CO)_4CoGePh_3$ |  MgBr |  Br | $Ph_3Ge$  | 35 |

~100 mg of (±)-silanol were obtained. The formation of silanol is probably due to moisture in potassium and mercuric acetates. Silanol is not reduced by $LiAlH_4$ in ether.

*Cleavage of II with $F^{-+}NMe_3CH_2Ph$*

320 mg of II (0.77 mmol), $[\alpha]_D$ + 1.5° in 20 ml of ether were added to 200 mg of trimethylbenzylammonium fluoride in 20 ml of ether at −80°C. After 2 hours solvent was pumped off and the residue was extracted with pentane. The solution was filtered, and the solvent evaporated to give 95 mg of racemic fluorosilane (yield 46%).

*Preparation of triphenylgermylcobalt tetracarbonyl*

2.9 g of $Co_2(CO)_8$ (8.5 mmol) were dissolved in 20 ml hexane. This solution was filtered and slowly added to a well stirred solution of 5.2 g $Ph_3GeH$ (17 mmol) in 100 ml hexane. A fast evolution of hydrogen occurred during the addition as on off-white precipitate appeared. The solution was stirred for 2 h, and the precipitate was filtered off and recrystallized from toluene/hexane. $(CO)_4$-$CoGePh_3$ is an air-stable crystalline solid (m.p. 158—160°C). The IR spectrum shows carbonyl absorptions at 2100s(sh) 2040s(sh) 2005vs and 1960w $cm^{-1}$. The mass spectrum is in agreement with the structure. Anal. Found: C, 55.67; H, 3.22; Co, 11.68. $C_{22}H_{15}CoGeO_4$ calcd.: C, 55.63; H, 3.16; Co, 12.41%.

*Reactions of cobalt—silicon and cobalt—germanium complexes with Grignard and organolithium compounds*

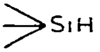
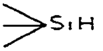
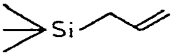
All reactions were carried out in the same way. We describe only one example. The products were always isolated by chromatography on silica gel using hexane to elute hydrogeno- and deuterio-silanes or -germanes, and 9/1 hexane/benzene to elute the tetrasubstituted silanes or germanes. In all cases yields of about 40% of silanol or germanol were obtained by elution with benzene, showing that the formation of silyl or germyl Grignard or lithium compound is not quantitative.

Tables 1 and 2 show the yields and optical rotations in every case.

To 430 g of I (1 mmol) in 25 ml ether 5 ml of 2 *N* $CH_3MgBr$ (10 mmol) were added with stirring. 2.5 g of allyl bromide (~20 mmol) were added after 24 h.

TABLE 2

REACTIONS OF (+)-$(CO)_4CoSiMePh$-1-Np WITH GRIGNARD AND LITHIUM REAGENTS

| Organometallic reagent | Reagent | Product | Stereoselectivity (%) | Yield (%) |
|---|---|---|---|---|
| $CH_3Li$ | $H_2O$ |  | Rn 70 | 58 |
| $CH_3MgBr$ | $H_2O$ |  | Rn 55 | 72 |
| $CH_3MgBr$ |  |  | Rn 59 | 39 |
| n-BuLi | $H_2O$ |  | Racemisation | 63 |

The mixture was stirred for a further 24 h, then hydrolyzed and extracted with ether. The residue was chromatographed on silica gel to give 112 mg of allyltriphenylsilane (yield 37%), which was identical with an authentic sample.

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