Optically Active Silylanions. Evidence for the Formation of Analogues of Silyl Grignard Reagents

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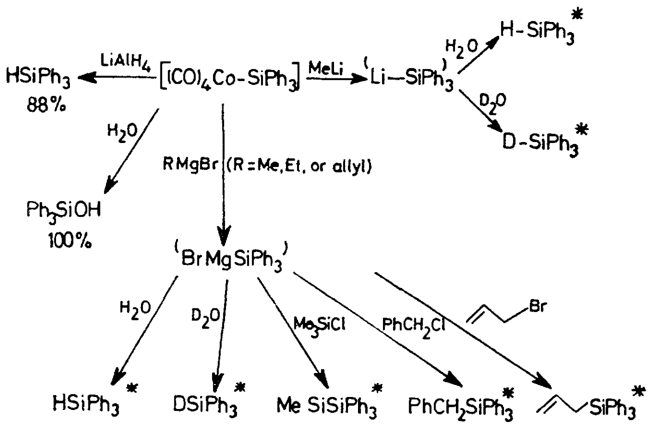
Summary The preparation and reactions of an analogue of R_3SiMgX are reported; its reactions proceed with 55% retention of configuration and those of the analogous R_3SiLi 70%.

Silyl anions offer a versatile synthetic route to organosilanes and have been widely studied[1] *e.g.*, the 'S-system' of Calas and Dunoguès[2] offers a large variety of synthetic possibilities. We describe here a possible new route to silyl anions, and particularly to R_3SiMgX. The formation of this species has never been established but was reasonably invoked by West[3] and Gilman[4] and their co-workers.

Treatment of $[(CO)_4CoSiPh_3]$[5] with a tenfold excess of a Grignard or alkyl-lithium reagent led to the formation of the corresponding anionic reagent (reaction 1). The reactions

$$[(CO)_4CoSiPh_3] \xrightarrow{RM} M\text{–}SiPh_3 \qquad (1)$$

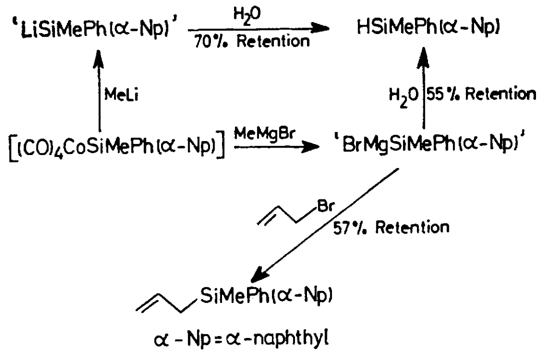
M = MgBr, R = Me, Et, or allyl; M = Li, R = Me of these derivatives are shown in Scheme 1. Hydrolysis with D_2O yields only the deuteriated silane, showing that the silane is formed from an anionic species, since hydrolysis of the cobalt–silicon complex gives the silanol quantitatively. The reactions of the alkyl halides gave further proof that the coupling reactions did proceed through a silyl anion, since they are unreactive towards Co–Si bonds.



Scheme 1†

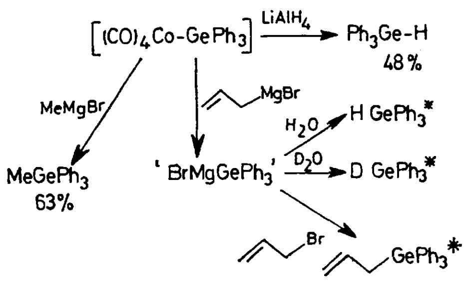
Treatment of the optically active compound [(+)-$(CO)_4$-CoSiMePh(α-Np)], $[\alpha]_D^{25}$ + 2·7°[6] with a Grignard reagent yielded a silyl Grignard reagent of low optical activity (Scheme 2). Treatment with MeLi gave, after hydrolysis, a silane with 70% retention of configuration. These results should be compared with those obtained by Sommer and Mason[7] for the preparation of an optically active silyllithium.

Surprisingly, treatment of $[(CO)_4CoGePh_3]$,[8] m.p. 158—160 °C, with MeMgBr led to substitution on Ge, while allylmagnesium bromide led to the germyl Grignard reagent (Scheme 3).



Scheme 2

The behaviour of these complexes is surprising since we had expected nucleophilic attack on silicon or germanium to occur. In fact treatment of both types of compounds with $LiAlH_4$ led to formation of the corresponding Si–H or Ge–H bond. The reaction takes place[9] with inversion of configuration in the case of the optically active cobalt–silicon compound.



Scheme 3†

The magnesium or lithium alkyl probably attacks the carbonyl ligands,[10] the silicon unit being displaced as a silyl anion.

(*Received*, 18*th December* 1975; *Com.* 1397.)

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† Reactions marked with an asterisk (*) in Schemes 1 and 3 take place in *ca.* 40% yield. We presume that this corresponds to the yield of the silyl or germyl anion formed. After hydrolysis *ca.* 40% yields of the silanol or germanol byproduct are formed. Some tar is formed in all cases.

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