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Formation of Benzoylsilanes from the Reaction of Organosilylcobalt Tetracarbonyl Derivatives with Phenyl-lithium

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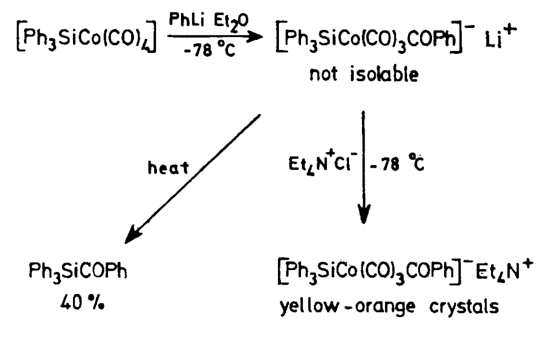
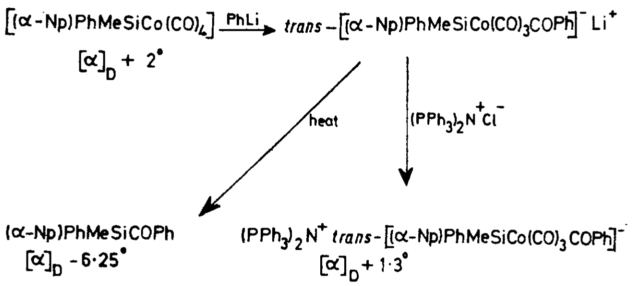
Summary Treatment of organosilylcobaltcarbonyl complexes $[R_3SiCo(CO)_4]$ with phenyl-lithium gives benzoylsilanes $R_3SiCOPh$, with retention of configuration at silicon; an intermediate adduct $[R_3SiCo(CO)_3COPh]^- Li^+$ is probably formed and the salt $[(\alpha\text{-Np})PhMeSi^*Co(CO)_3COPh]^- N^+(PPh_3)_2$ (where α-Np = α-naphthyl) has been isolated.

CONTINUING our studies of the reactions of complexes in which a transition metal is bound to a Group IVa element, we have found that compounds of the type $[R_3SiCo(CO)_4]$, which give silyl metallic compounds with excess of alkyl-lithium reagents,[1] react quite differently with an equimolar amount of phenyl-lithium (Scheme 1). Since the silylcobalt derivatives are obtainable from the corresponding silane,[2] this reaction provides a simple preparative route from the silane to the acylsilane. Indeed it is not necessary to isolate the cobalt complex; thus reaction of diphenylmethylsilane with dicobalt octacarbonyl gave an oily product which, on treatment with phenyl-lithium at −78 °C and subsequent decomposition, produced diphenylmethylbenzoylsilane in 39% yield [reaction (1)]. The optically active cobalt compound $(+)$-$[(\alpha\text{-Np})PhMeSiCo(CO)_4]$, $[\alpha]^{25}$ + 2°,[3] gave the optically active benzoyl derivative $(\alpha\text{-Np})PhMeSiCOPh$, $[\alpha]^{25}_{D}$ −6·25°,[4] in 47% yield with complete retention of stereochemistry (Scheme 2) (the optical rotation of this compound exhibits a marked dependence on the solvent employed; in cyclohexane $[\alpha]^{25}_{D} = -35{\cdot}6°$).

$$MePh_2SiH \xrightarrow{[Co_2(CO)_8]} [MePh_2SiCo(CO)_4] \xrightarrow{PhLi} \xrightarrow{heat} MePh_2SiCOPh \quad (1)$$



SCHEME 1



SCHEME 2

The compounds $[Ph_3MCo(CO)_4]$ (M = Sn or Pb) are attacked by phenyl-lithium at the carbon atom of the carbonyl group *trans* to the ligand containing a Group IVa element.[5] We have confirmed that this behaviour is shown also by the compounds in which M = Si or Ge. In particular we have prepared the salt $[(\alpha\text{-Np})PhMeSiCo(CO)_3\text{-}COPh]^- \, {}^+N(PPh_3)_2$, m.p. 172—175 °C, which shows a single broad carbonyl i.r. absorption band at 1880 cm^{-1}, a similar value to that observed for the $[Co(CO)_4]^-$ salt of the same counter-ion.[6]

The mechanism of formation of the acylsilane has not yet been elucidated. However, *cis*-elimination of the silyl and benzoyl groups would appear not to be favoured by the *trans* configuration of the intermediate.

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