Group IV–Cobalt Complexes as Catalysts for Silylation and Cyclic Ether Polymerization

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Summary Dicobalt octacarbonyl was found to catalyse the reaction:

$$\mathrm{R^2_3SiH + XH \xrightarrow{25^\circ} XSiR^2_3 + H_2} \tag{1}$$

where $\mathrm{X = R^1O,\ R^1CO_2,\ R^1CONH + R^1_3SiO}$ but not when X = ArO (R = alkyl, Ar = aryl), while tetrahydrofuran was polymerized to poly-(1,4-butylene oxide) (*ca.* 50,000 molecular weight) in the presence of dicobalt octacarbonyl and a silane.

GROUP IV–transition metal chemistry is currently the subject of extensive investigation.[1] However, the only homogeneous catalyses related to this chemistry are hydrosilylation[2] and hydrogen–deuterium exchange.[3] We now report two new catalytic applications.

The study of dicobalt octacarbonyl as a silylation catalyst followed from a consideration of reactions (2) and (3),[2] together with some recently reported reactions of silylcobalt carbonyls (4),[4] (5),[5] and (6).[3a,5]

$$\mathrm{Co_2(CO)_8 + 2R_3SiH \rightarrow 2R_3SiCo(CO)_4 + H_2} \tag{2}$$

$$\mathrm{HCo(CO)_4 + R_3SiH \rightarrow R_3SiCo(CO)_4 + H_2} \tag{3}$$

$$H_3SiCo(CO)_4 + HCl \rightarrow H_3SiCl + HCo(CO)_4 \quad (4)$$

$$Me_3SiCo(CO)_4 + Me_2NH \rightarrow Me_2NSiMe_3 + HCo(CO)_4 \quad (5)$$

$$R_3SiCo(CO)_4 + MeOH \rightarrow MeOSiR_3 + HCo(CO)_4 \quad (6)$$

A combination of reactions (2) and (3) with any of the remainder could represent examples of the homogeneous catalysis of reaction (1) in the absence of side reactions such as cobalt hydrocarbonyl reacting with amines.[6] Sommer *et al.* recently reported heterogeneous catalysts for reaction (1) where XH included phenols and amines.[7,8] The present homogeneous system shows greater differentiation, making it possible to silylate alcohols and acids selectively as in reactions (7) and (8).

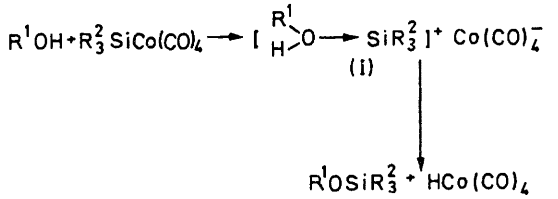
$$p\text{-}OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H + Et_3SiH \rightarrow p\text{-}OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2SiEt_3 + H_2 \quad (7)$$

$$o\text{-}OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH + Et_3SiH \rightarrow o\text{-}OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}OSiEt_3 + H_2 \quad (8)$$

Silylation is a very effective method of blocking reactive groups[9] so that the ability to do this selectively should have considerable application in synthetic organic chemistry.

Reactions were carried out under nitrogen with a catalyst concentration of *ca.* 0·1% w/w. Under these conditions, triethylsilane reacted vigorously with ethanol, benzyl alcohol, acetic acid, and acetamide and cooling was required to offset the considerable heat produced. After a few hours at 25°, yields of 90% or better were thus obtained for $EtOSiEt_3$, $MeCO_2SiEt_3$, and $PhCH_2OSiEt_3$. Using a 5% excess of triethylsilane, reaction (7) required 2 days at 25° in ether to give a 90% yield. Reaction (8) required 4 days at 25° in benzene to give an 88% yield. In both cases the solid reactants went into solution during the reaction.

Catalyst was removed by refluxing the mixtures under dry nitrogen or oxygen in benzene and centrifuging the precipitate. The products were then obtained by removal of solvent followed by distillation [except for reactions (7) and (8)]. Products were identified by comparison (n.m.r., i.r.) with authentic samples ($EtOSiEt_3$, $MeCO_2SiEt_3$) or by a combination of n.m.r., i.r., m.s., and elemental analysis (C, H, Si, N).

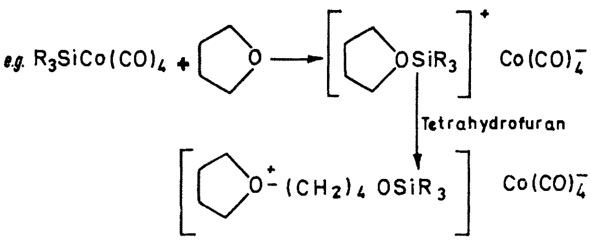


(9)

No catalytic reaction was found for triethylsilane with phenol, diethylamine, butyl chloride, or 2-amino-2-methylbutan-1-ol.

The absence of any reaction with phenols suggests a change in mechanism in going from basic to acidic reagent with a minimum reactivity for phenols. Basic reagents presumably attack silicon nucleophilically as in reaction (9). A possible intermediate is (I), since similar complexes with aprotic bases such as dimethylformamide,[10] pyridine,[6] and trimethylamine[11] are formed readily. Attack on the silylcobalt carbonyl by acidic reagents must involve a more important role for the proton such as electrophilic attack on cobalt or an attack on silicon by the anion.

Tetrahydrofuran is an unsuitable solvent for these reactions. Dicobalt octacarbonyl in the presence of a twofold or greater excess of a silicon hydride was found to polymerize tetrahydrofuran within 20 min at 25—40° to *ca.* 50,000 molecular weight (estimate from gel permeation chromatography). Formation of such high molecular weight polymer from tetrahydrofuran is unusual and has only been achieved by a cationic mechanism.[12] The present catalysis could be related. Thus the solvation of a silylcobalt carbonyl as in reaction (10) would facilitate ring opening and could lead to a polymerization as in (11). Silylcobalt carbonyls were found to react with tetrahydrofuran but did not lead to high molecular weight polymer unless a silicon hydride was also present.



(10)

(11)

A similar catalytic activity was found for $Co_2(CO)_8$ in the presence of an excess of GeI_2 which also gives rise to a Group IV–Co bond.[13] These catalytic systems were also found to catalyse the polymerization of other cyclic oxides such as 3-n-butoxy-2,2-dimethyloxetan and propylene oxide.

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