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Preliminary communication

REACTIONS OF COBALT CARBONYL SPECIES WITH CHLOROSILANES IN ETHER SOLVENTS

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Recent recognition has been given to a mode of reaction of metal carbonyl compounds involving electrophilic attack at the carbonyl oxygen atoms [1, 2]. Such a process is presumably active in the reaction of $Na_2Fe(CO)_4$ with Me_3SiI in THF to give $(Me_3SiOC)_4Fe_2(CO)_6$ [3] and in the formation of $(Me_3SiOC)_4$-$Co_2(CO)_4$ from the thermal decomposition of $Me_3SiCo(CO)_4$ [4]. During an investigation of the reactions of dicobalt octacarbonyl and sodium cobalt tetracarbonyl with chlorosilanes in ether solvents we have observed that the reaction course depends on several factors including solvent basicity, the nature of the chlorosilane, and the cobalt carbonyl species; these features may also be rationalised in terms of electrophilic attack at a carbonyl oxygen.

The most common products of cobalt carbonyl-chlorosilane reactions are methinyltricobalt enneacarbonyls, $YCCo_3(CO)_9$, the apical substituent, Y, being derived either from the R_3Si fragment ($R_3 = Cl_3$, $MeCl_2$) or from cleavage of the solvent THF (Table 1). Although the yields obtained are not high (10 - 20 %),

TABLE 1

REACTIONS OF COBALT CARBONYL SPECIES WITH CHLOROSILANES

Cobalt carbonyl	Chlorosilane	Solvent	Products[a]
$Co_2(CO)_8$	$MeSiCl_3$	THF	$RCCo_3(CO)_9$ [b] ($R = C_4H_9, HO(CH_2)_4$)
$Co_2(CO)_8$	$SiCl_4$	THF	$Cl_3SiOCCo_3(CO)_9$
$NaCo(CO)_4$	$MeSiCl_3$	THF	$HO(CH_2)_4CCo_3(CO)_9$ [b]
$NaCo(CO)_4$	$SiCl_4$	THF	$Co_4(CO)_{10}$
$Co_2(CO)_8$	Me_xSiCl_{4-x} ($x = 0,1$)	Et_2O	no reaction
$NaCo(CO)_4$	$MeSiCl_3$	Et_2O	$MeCl_2SiOCCo_3(CO)_9$
$NaCo(CO)_4$	$SiCl_4$	Et_2O	$Cl_3SiOCCo_3(CO)_9$

[a] Identified by infrared and mass spectrometry, yields ~5 - 20 %.
[b] Via an acyl intermediate.

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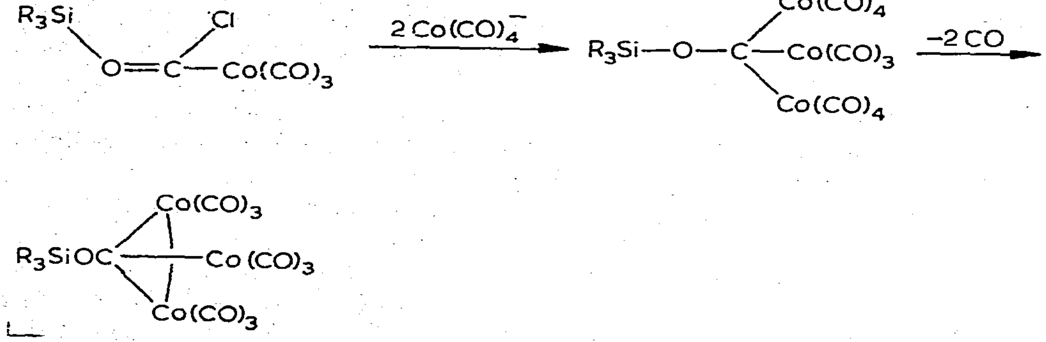
these reactions could be developed as a route to hitherto unaccessible tricobalt carbon derivatives.

No reaction was observed between $Co_2(CO)_8$ and either $MeSiCl_3$ or $SiCl_4$ in diethyl ether while reaction with $Co(CO)_4^-$ in this solvent at room temperature produced the corresponding siloxy cluster $R_3SiOCCo_3(CO)_9$.

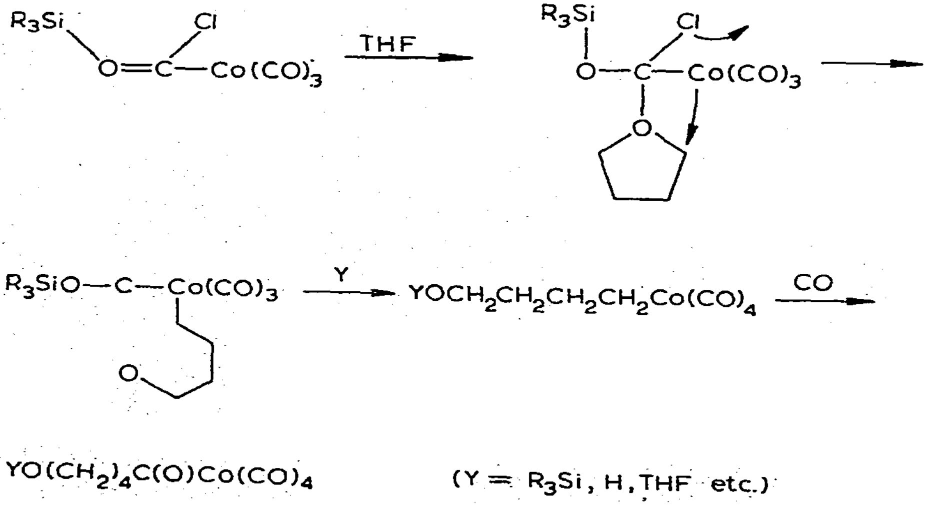
For all the systems examined here in which reaction occurred, $Co(CO)_4^-$ is undoubtedly the active species [5] and the lack of reaction of $Co_2(CO)_8$ in diethyl ether can be attributed to the lower basicity of this solvent. The initial formation of a silicon—cobalt bonded compound, $R_3SiCo(CO)_4$ can be discounted as no reaction was observed between $Cl_3SiCo(CO)_4$ and THF even at reflux. This is in contrast to $Me_3SiCo(CO)_4$ which is reported [4] to give good yields of $Me_3SiOCCo_3(CO)_9$ with THF at room temperature.

The formation of tricobalt carbon derivatives can be explained in terms of electrophilic attack by the chlorosilane on $Co(CO)_4^-$. The resulting intermediate could then undergo nucleophilic attack either by $Co(CO)_4^-$ to produce siloxy clusters (Scheme 1), or by the solvent THF to give alkyl or alcohol clusters (Scheme 2).

Scheme 1



Scheme 2



In reactions leading to solvent cleavage, infrared examination of the reaction mixtures suggested the intermediacy of acyl complexes, $RCOCo(CO)_4$. We have subsequently shown that the thermal decomposition of $RCOCo(CO)_4$ in THF to tricobalt carbon derivatives is a general reaction:

$$3RCOCo(CO)_4 \rightarrow RCCo_3(CO)_9 + 4CO + RCOR$$

(R = Et, n-Pr, Ph, etc.)

Yields in these reactions vary from 5 - 15 % and minor products such as $Co_4(CO)_{12}$ and diketones are also identifiable. The addition of chlorosilanes during these decomposition reactions has no obvious effect on the yield or nature of the cluster species produced. We have also found that dicobalt octacarbonyl reacts with acyl chlorides in THF at room temperature to give tricobalt carbon derivatives. Thus n-PrCOCl and $Co_2(CO)_8$ gave the novel ether cluster $PrOCCo_3(CO)_9$, characterised by its infrared and mass spectra. In the light of these observations, it is noteworthy that pyrolysis of $RCOCo(CO)_4$ derivatives in the absence of solvent gives $Co_2(CO)_8$, $Co_4(CO)_{12}$ and the appropriate ketone [6, 7]. Further studies are currently in hand to elucidate the scope and mechanism of these reactions.

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