Journal of Organometallic Chemistry, 205 (1981) 31—45
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CHEMICAL BEHAVIOUR OF COBALT-STABILIZED CARBENES HAVING A TRISUBSTITUTED SILYL OR GERMYL LIGAND. STEREOSPECIFIC FORMATION OF BENZOYLSILANES FROM THE REACTION OF ORGANOSILYL-COBALT TETRACARBONYL DERIVATIVES WITH PHENYLLITHIUM *

GENEVIÉVE CERVEAU, ERNESTO COLOMER, ROBERT J.P. CORRIU * and J. COLIN YOUNG

Université des Sciences et Techniques du Languedoc, Laboratoire des Organométalliques, Equipe de recherche associée au C.N.R.S. No. 554, Place Eugène Bataillon, 34060 Montpellier-cédex (France)

(Received July 21st, 1980)

Summary

We report the chemical behaviour of cobalt-stabilized carbenes, $R_3M(CO)_3CoC(OEt)R'$, and their parent anions, $R_3M(CO)_3CoC(O^-)R'$, where M = Si or Ge. The anions where M = Si, R′ = Ph decompose thermally into the corresponding benzoylsilanes; when the silicon atom is chiral (R_3 = MePh-1-Np) optically active $R_3SiCOPh$ is obtained with complete retention of configuration.

Introduction

In previous papers [2] we have reported some reactions of complexes of the type $(CO)_4CoMR_3$ (M = Si, Ge; $R_3 = Ph_3$, MePh-1-Np). Cleavage of the optically active silicon compound by electrophiles (Cl_2, Br_2) takes place with retention of configuration at silicon, but the attack of nucleophiles ($LiAlH_4$, H_2O, MeOH, KOAc, $Hg(OAc)_2$) results in inversion of configuration.

There is a notable difference between the behaviour of the silyl- and germyl-cobalt complexes towards Grignard reagents. An excess of organomagnesium compound generally displaces the organo-silicon or -germanium group as the anion, detected by further reaction of that species. However, in the germanium series the reaction takes this course only when R′ = allyl; substitution at

---

* For a preliminary communication, see ref. 1.

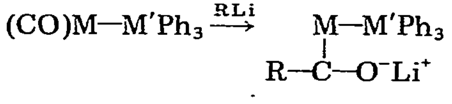
germanium occurs when R′ = Me or Ph, as summarized below:

$$(CO)_4CoSiR_3 \xrightarrow{R'MgX} \text{“}XMgSiR_3\text{”} \qquad (R' = Me, Et, Ph, allyl)$$

$$(CO)_4CoGeR_3 \xrightarrow{R'MgX} \text{“}XMgGeR_3\text{”} \qquad (R' = allyl)$$

$$(CO)_4CoGeR_3 \xrightarrow{R'MgX} R'GeR_3 \qquad (R' = Me, Ph)$$

Reaction with a stoichiometric quantity of an organolithium reagent results in attack at a carbonyl carbon atom and the formation of an acyl metal anion, as reported also for $(CO)_4CoMPh_3$ (M = Ge, Sn, Pb) [3,4], $(CO)_5MnGePh_3$ [5] and $(\eta^5\text{-}C_5H_5)M(CO)_3GePh_3$ (M = Mo, W) [6].



$$(CO)M{-}M'Ph_3 \xrightarrow{RLi} \underset{\displaystyle R{-}C{-}O^-Li^+}{\overset{}{M{-}M'Ph_3}}$$

($M = (CO)_3Co$, M′ = Ge, Sn, Pb;
$M = (CO)_4Mn$, $(\eta^5\text{-}C_5H_5)(CO)_2Mo$, $(\eta^5\text{-}C_5H_5)(CO)_2W$; M′ = Ge)

These anions can subsequently be alkylated to give complexes with carbene ligands.

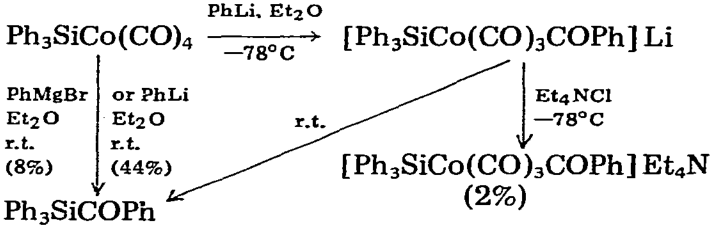
In this paper we describe the chemical behaviour of some cobalt carbene complexes having a triarylgermyl ligand. We also report that the cobalt-silicon complexes $R_3SiCo(CO)_4$ appear to undergo an addition reaction at the carbonyl carbon atom only with aryllithium compounds. The benzoylcobalt anions formed can be isolated with difficulty as the tetraethylammonium or PPN$^+$ salts, but they are otherwise rather unstable, decomposing readily into benzoylsilanes.

Results and discussion

A. Acylcobalt complexes having a silyl ligand

Treatment of triphenylsilyltetracarbonylcobalt in ether solution with the stoichiometric amount of phenyllithium at —78° C gives a yellow precipitate, apparently of lithium triphenylsilyltricarbonylbenzoylcobaltate, from which it is possible to isolate the tetraethylammonium salt in low yield (2%). If the lithium salt is allowed to warm to room temperature, benzoyltriphenylsilane is obtained. The latter compound is also produced directly when $(CO)_4CoSiPh_3$ is treated with the stoichiometric quantity of phenyllithium or phenylmagnesium bromide at room temperature, in yields of 44% and 8%, respectively (Scheme 1).

SCHEME 1



Since silylcobalt complexes are readily obtained from the corresponding silanes [7], this reaction provides a useful preparative route to benzoylsilanes, especially since isolation of the silyltetracarbonylcobalt complex is unnecessary. For example, reaction of diphenylmethylsilane with dicobalt octacarbonyl gives an oily product which, on further treatment with phenyllithium, produces diphenylmethylbenzoylsilane in moderate yield (38% from the starting silane).

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

The optically active silicon-cobalt compound $S(+)$-$\mathrm{(CO)_4CoSiMePh}$-1-Np, $|\alpha|_{\mathrm{D}}^{25}$ + 2°, gives the optically active benzoylsilane $S(-)$-MePh-1-NpSiCOPh, $|\alpha|_{\mathrm{D}}^{25}$ —6.25° (in benzene), [8] in 47% yield with complete retention of configuration (Scheme 2). (It is interesting to note that the optical rotation of this compound exhibits a marked dependence on the solvent employed: in cyclohexane $|\alpha|_{\mathrm{D}}^{25} = -35.6°$.)

SCHEME 2

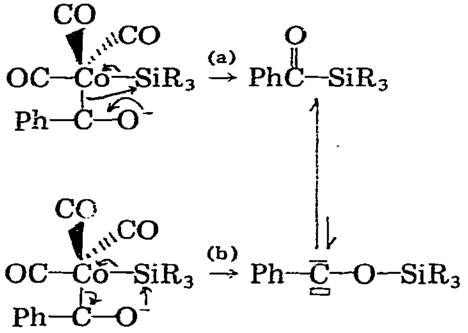
$$\begin{tikzcd}
\text{1-NpPhMeSiCo(CO)}_4 \arrow[r, "\mathrm{PhLi}", "-78^\circ\mathrm{C}"'] & {[\text{1-NpPhMeSiCo(CO)}_3\text{COPh}]^-\mathrm{Li}^+} \arrow[d, "\mathrm{(PPh_3)_2NCl}"] \arrow[dl, "\mathrm{r.t.}"'] \\
\text{1-NpPhMeSiCOPh} \\ (|\alpha|_{\mathrm{D}}^{25} - 6.25^\circ) & {[\text{1-NpPhMeSiCo(CO)}_3\text{COPh}]^-\mathrm{(PPh_3)_2N}^+} \\ (|\alpha|_{\mathrm{D}}^{25} + 1.3^\circ)
\end{tikzcd}$$

No crystalline derivative could be obtained from treatment of the lithium salt with tetraethylammonium chloride, but pale olive-green crystals of [MePh-1-NpSiCo$\mathrm{(CO)_3}$COPh] $\mathrm{(PPh_3)_2N}$ were isolated from the exchange reaction with $\mathrm{(PPh_3)_2NCl}$.

The benzoylcobaltate salt shows a single broad carbonyl absorption in the infrared at 1880 $\mathrm{cm^{-1}}$, a similar value to that observed for the $\mathrm{(CO)_4Co^-}$ salt of the same counter-ion [9], and suggests that the complex has the *trans* configuration. This stereochemistry was also observed in the analogous reaction of phenyllithium with the compounds $\mathrm{(CO)_4CoMPh_3}$ (M = Sn, Pb); the attack takes place at the carbonyl group *trans* to the Group IV ligand [4]. The germylcobaltate salt $\mathrm{[Ph_3GeCo(CO)_3C(O^-)Bu]Et_4N^+}$ displays a similar carbonyl absorption at 1890 $\mathrm{cm^{-1}}$, and the carbene complexes $\mathrm{Ph_3GeCo(CO)_3C(OEt)R}$, like the analogous tin and lead compounds, absorb in the region of 1950 $\mathrm{cm^{-1}}$. The *trans* structure is supported by the X-ray diffraction study of $\mathrm{Ph_3GeCo(CO)_3C(OEt)Et}$ [3].

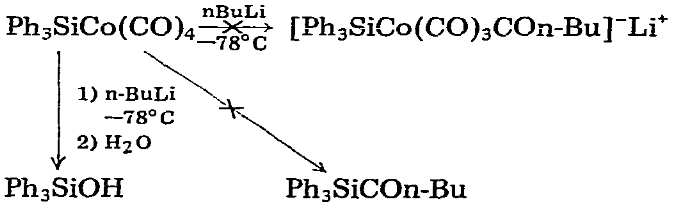
Attempts to convert the silylbenzoylcobalt salts into the corresponding carbene derivatives were unsuccessful, the decomposition into the benzoylsilane occurring even in the presence of alkylating agents such as $\mathrm{Et_3OBF_4}$.

The mechanism of formation of the benzoylsilanes has not been elucidated. Assuming an intramolecular reaction, a *cis* elimination would allow the production of the acylsilane either by direct formation of a carbon—silicon bond (a), or through the initial formation of a siloxycarbene (b). The latter species are known to rearrange to give acylsilanes [10].



Whereas addition to a carbonyl carbon atom takes place with both alkyl- and aryllithium compounds in the germylcobalt carbonyls, the silyl compounds apparently react in this way only with aryllithium reagents. Treatment of $(CO)_4CoSiPh_3$ with an equimolar quantity of n-butyllithium at —78° C, followed by hydrolysis after allowing the reaction mixture to reach room temperature does not give the expected pentanoylsilane. Instead, triphenylsilanol is obtained in good yield, arising as reported earlier from the cleavage of the cobalt—silicon bond by water. We recall that the formation of "$LiSiPh_3$" occurs with a tenfold excess of organolithium reagent [2].

SCHEME 3



This set of reactions provides a new simple synthetic route to benzoylsilanes, which is stereospecific in the case of an optically active compound.

B. Acyl- and carbenecobalt complexes having a germyl ligand

The acylcobalt anions resulting from the addition reaction of both alkyl- and aryllithium reagents to the coordinated carbonyl group of $(CO)_4CoGePh_3$ can be alkylated by Et_3OBF_4 to yield the corresponding carbene complexes [3] (Scheme 4).

However, the reaction with triphenylgermyllithium takes quite a different course. After attempted alkylation, the oxide $(Ph_3Ge)_2O$ was isolated in good yield.

Possible routes to the phosphorus-substituted complexes $R_3P(Ph_3Ge)Co$-

SCHEME 4

$$\begin{tikzcd}
\mathrm{(CO)_4CoGePh_3} \arrow[r, "\mathrm{RLi}", "\mathrm{Et_2O}"'] & \mathrm{[RC(O)(CO)_3CoGePh_3]\,Li} \arrow[dl, "\mathrm{Et_4NCl}"'] \arrow[d, "\mathrm{Et_3OBF_4}"] \\
\mathrm{[RC(O)(CO)_3CoGePh_3]\,Et_4N} & \mathrm{RC(OEt)(CO)_3CoGePh_3}
\end{tikzcd}$$

(R = Me, Et, n-Pr, n-Bu, Ph)

$(CO)_2C(OEt)R$ were also explored. However no product of this type was obtained, either by the attempted substitution of a carbonyl group in $Ph_3GeCo(CO)_3C(OEt)R$ by a phosphine ligand, or from the addition of an organolithium reagent to the phosphorus-substituted carbonyls $PPh_3(Ph_3Ge)$-$Co(CO)_3$ and $P(OPh)_3(Ph_3Ge)Co(CO)_3$.

$$\mathrm{PR_3(CO)_3CoGePh_3} \xrightarrow{\mathrm{R'Li}} \text{no reaction}$$

(R = Ph, OPh; R' = Me, n-Bu, Ph)

$$\mathrm{RC(OEt)(CO)_3CoGePh_3} \xrightarrow{\mathrm{PR'_3}} \text{no reaction}$$

(R = Me, Et, n-Pr, n-Bu, Ph; R' = Ph, OPh)

These compounds were obtained by reaction of $[PPh_3(CO)_3Co]_2$ or $[P(OPh)_3(CO)_3Co]_2$ with triphenylgermane in refluxing benzene or toluene, rather than by nucleophilic attack of the corresponding sodium cobaltate on triphenylbromogermane [11].

$$\mathrm{[PR_3(CO)_3Co]_2 + 2\ Ph_3GeH \rightarrow 2\ PR_3(CO)_3CoGePh_3 + H_2}$$

(R = Ph, OPh)

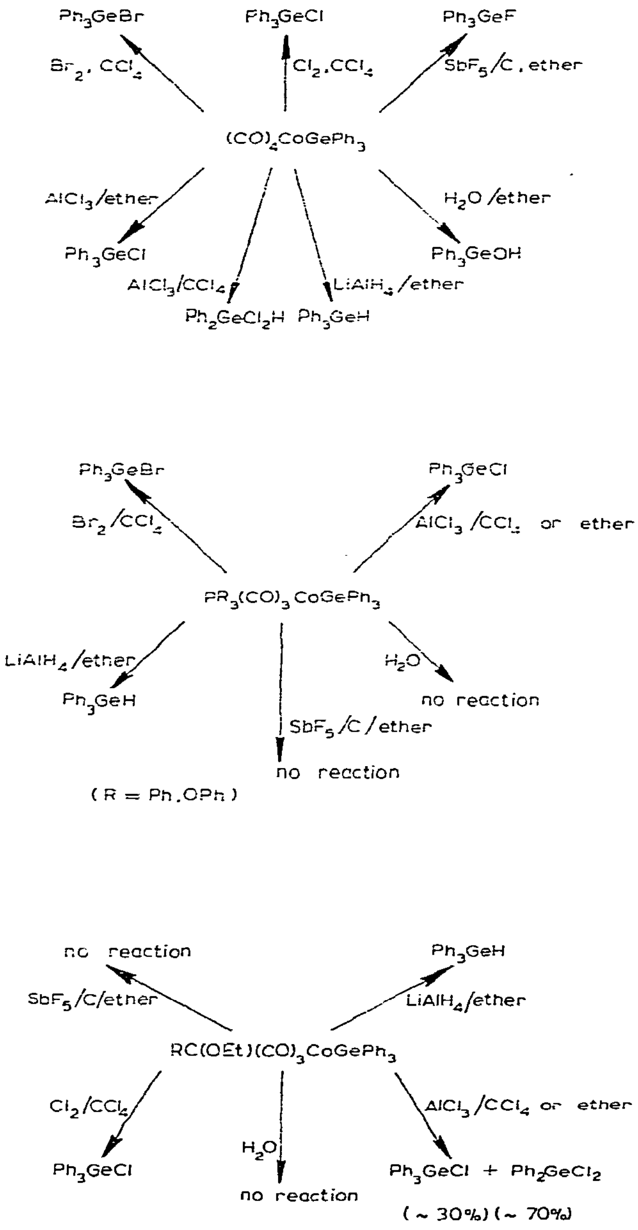
The lack of reactivity would appear to result from the fact that both phosphorus and germyl ligands are good sigma donors. The increased electron density at the metal in its turn increases the back-donation to the carbonyl ligands, which are thus more strongly bound to the metal and rendered less susceptible to nucleophilic attack at the carbon atom. Lack of reaction with organolithium compounds has already been noted in bis- or tris-phosphine metal complexes [4], but substitution of carbon monoxide by a phosphine has been reported in carbene complexes having carbon monoxide as the only other ligands [12,13].

The cobalt—germanium bond is cleaved by both electrophiles and nucleophiles (Scheme V and Table 1). Halogens cleave the cobalt-germanium bond, affording in the first place the halogenogermane and cobalt(II) chloride. If an excess of halogen is used, the phenyl groups will also be cleaved.

$$\begin{tikzcd}
\mathrm{(CO)_4CoGePh_3} \arrow[r, "\mathrm{X_2}"] \arrow[dr, "\mathrm{X_2\ excess}"] & \mathrm{Ph_3GeX} \\
& \mathrm{Ph_2GeX_2}
\end{tikzcd}$$

(X = Cl, Br)

SCHEME 5



Aluminium chloride may also cleave both the germanium—cobalt and germanium—phenyl bonds. The ease of reaction is strongly dependent on the solvent and on the nature of the starting material.

$$L(CO)_3CoGePh_3 \xrightarrow{AlCl_3} Ph_3GeCl \text{ and/or } Ph_2GeCl_2$$

$(L = CO, PPh_3, P(OPh)_3, MeCOEt)$

TABLE 1

CLEAVAGE REACTIONS OF COBALT-GERMANIUM COMPLEXES

Starting material	Reagent	Time	Product	Yield (%)
$(CO)_4CoGePh_3$	Cl_2/CCl_4 [a]	15 min	Ph_3GeCl	80 [b]
$(CO)_4CoGePh_3$	Br_2/CCl_4 [a]	10 min	Ph_3GeBr	83 [b]
$(CO)_4CoGePh_3$	$AlCl_3/CCl_4$ [c]	24 h	Ph_2GeCl_2	75 [b]
$(CO)_4CoGePh_3$	$AlCl_3$/ether [c]	8 d	Ph_3GeCl	99 [b]
$(CO)_4CoGePh_3$	SbF_5/C/ether [d]	6 d	Ph_3GeF	100
$(CO)_4CoGePh_3$	H_2O/ether	3 d	Ph_3GeOH	60
$(CO)_4CoGePh_3$	$LiAlH_4$/ether	2 d	Ph_3GeH	74
$(CO)_4CoGePh_3$	$SnCl_3^-$/THF	3 d	Ph_3GeCl	82
$PPh_3(CO)_3CoGePh_3$	Br_2/CCl_4 [a]	2 h	Ph_3GeBr	95 [b]
$PPh_3(CO)_3CoGePh_3$	$AlCl_3/CCl_4$ [c]	6 d	Ph_3GeCl + traces Ph_2GeCl_2	94 [b]
$PPh_3(CO)_3CoGePh_3$	$AlCl_3$/ether	5 d	Ph_3GeCl + traces Ph_2GeCl_2	72 [b]
$PPh_3(CO)_3CoGePh_3$	$LiAlH_4$/ether	2 d	Ph_3GeH	93
$P(OPh)_3(CO)_3CoGePh_3$	Br_2/CCl_4 [a]	2 h	Ph_3GeBr	79 [b]
$P(OPh)_3(CO)_3CoGePh_3$	$AlCl_3/CCl_4$ [c]	7 d	Ph_3GeCl + traces Ph_2GeCl_2	99 [b]
$P(OPh)_3(CO)_3CoGePh_3$	$AlCl_3$/ether [c]	8 d	Ph_3GeCl + traces Ph_2GeCl_2	91 [b]
$P(OPh)_3(CO)_3CoGePh_3$	$LiAlH_4$/ether	2 d	Ph_3GeH	92
$MeC(OEt)(CO)_3CoGePh_3$	$AlCl_3/CCl_4$ [c]	6 d	Ph_3GeCl + Ph_2GeCl_2	68 [b] 30 [b]
$MeC(OEt)(CO)_3CoGePh_3$	$AlCl_3$/ether [c]	6 d	Ph_3GeCl + Ph_2GeCl_2	63 [b] 33 [b]
n-$PrC(OEt)(CO)_3CoGePh_3$	SbF_5/C/ether [c]	6 d	no reaction	
n-$BuC(OEt)(CO)_3CoGePh_3$	Cl_2/CCl_4 [d]	15 min	Ph_3GeCl	93 [b]
n-$BuC(OEt)(CO)_3CoGePh_3$	$LiAlH_4$/ether	3 d	Ph_3GeH	64

[a] 1.5 mol of Cl_2 or Br_2/mol of complex. [b] After $LiAlH_4$ reduction to hydrogermane. [c] 1 mol reagent/mol of complex. [d] 4 mol Cl_2/mol of complex.

When L = CO, only the cobalt—germanium bond is cleaved in ether, whilst in carbon tetrachloride both the cobalt—germanium and one of the germanium—phenyl bonds are broken. When L = PPh_3 and $P(OPh)_3$ only the cobalt—germanium bond is cleaved in both solvents. The carbene complex gives a mixture of both chlorogermanes in either carbon tetrachloride or ether (Scheme 5).

These reactions were followed by infrared spectroscopy, monitoring the disappearance of the carbonyl absorption bands. The halogenogermanes were then reduced with lithium aluminium hydride, and the products identified by comparison with authentic samples of the organogermanium hydrides.

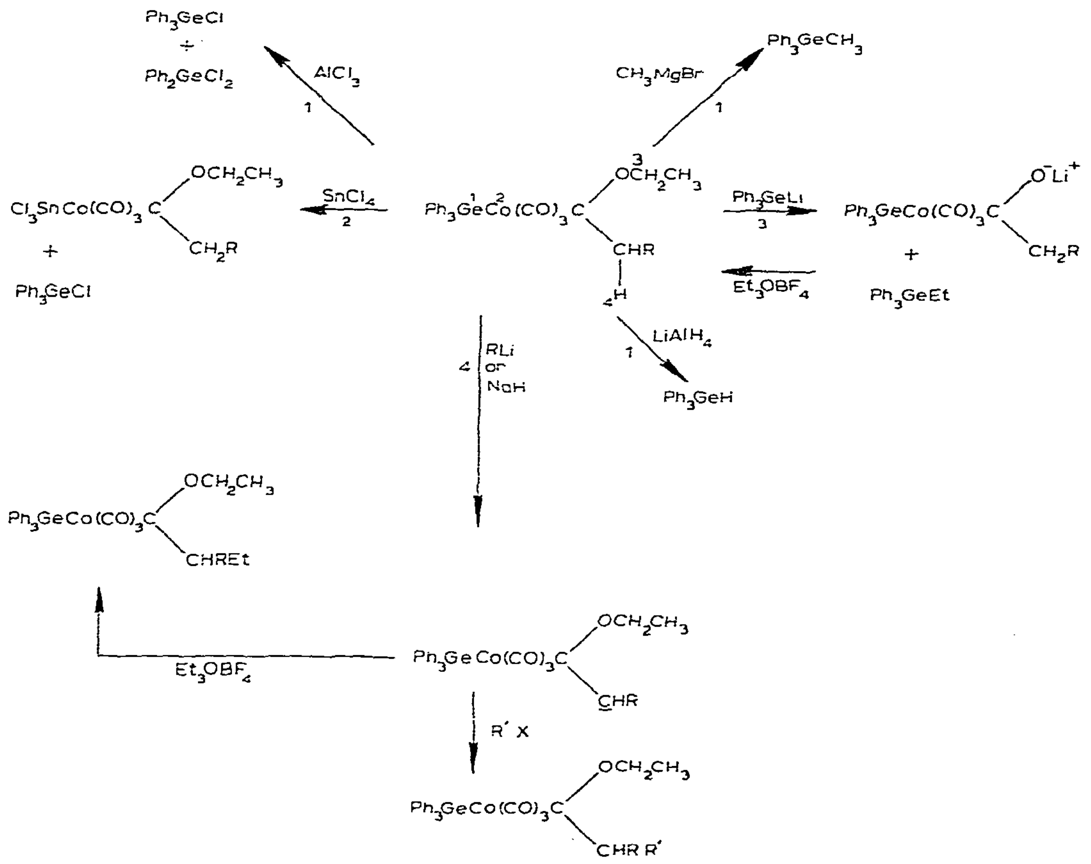
Antimony pentafluoride cleaves the cobalt—germanium bond in $(CO)_4CoGePh_3$ to give the fluorogermane in quantitative yield, but the carbene complexes do not react under these conditions.

$$(CO)_4CoGePh_3 \xrightarrow[\text{ether}]{SbF_5/C} Ph_3GeF$$

We reported earlier [2] that the compound $(CO)_4CoGePh_3$ was cleaved by lithium aluminium hydride only with difficulty. After two days at room temperature, however, triphenylgermane is obtained in 74% yield.

$$(CO)_4CoGePh_3 \xrightarrow[\text{ether, 2 days}]{LiAlH_4} Ph_3GeH$$

SCHEME 6 *



* The different sites of attack by these reagents are marked by numbers.

The related complexes containing a carbene, phosphine or phosphite ligand also afford a good yield of triphenylgermane under similar conditions after 3 days.

As other workers have found [14], transition metal carbene complexes are generally reluctant to release the carbene ligand, and do not furnish a source of the free carbene. However, a number of reagents do react in specific ways with these complexes. The reactions we have investigated are summarized in Scheme 6. It is, however, difficult to rationalize the differences in reactivity which are apparent. The comparison of the behaviour of the organometallic reagents is particularly interesting. The basic properties of organolithium reagents are evident in the proton abstraction from the carbon atom adjacent to the carbenoid carbon; methylmagnesium bromide alkylates at germanium, whereas triphenylgermyllithium displaces the ethyl group from the ethoxycarbene, generating triphenylethylgermane and a salt which can be re-alkylated by Et_3OBF_4 to reform the starting carbene complex.

The germanium—cobalt bond is cleaved by both aluminium chloride and tin(IV) chloride. From the reaction with the latter reagent, a compound which appears to be the trichlorostannylcobalt derivative can be isolated, but

TABLE 2

ELEMENTAL ANALYSES

Compound	Formula	Analysis Found(calcd.)(%)			
		C	H	N	P [a]
I	$C_{36}H_{40}CoNO_4Si$	67.66 (67.79)	6.45 (6.32)	2.10 (2.20)	
II	$C_{63}H_{50}CoNO_4P_2Si$	72.86 (73.18)	4.79 (4.84)	1.85 (1.36)	
III [b]	$C_{39}H_{30}CoGeO_3P.C_6H_6$	68.17 (68.65)	4.57 (4.23)		5.01 (3.94)
IV	$C_{39}H_{30}CoGeO_6P$	61.88 (61.86)	4.04 (3.79)		5.39 (4.10)
V	$C_{30}H_{33}CoGeO_4$	61.08 (61.17)	5.43 (5.61)		

[a] Low precision due to the presence of germanium. [b] Crystallized with one molecule of benzene.

attempts at purification by recrystallisation result in decomposition. An alternative synthesis of this compound was sought, to provide an authentic sample for comparison, but without success.

Cleavage of the germanium—cobalt bond occurs less readily than silicon—cobalt fission, with both electrophiles and nucleophiles. Substitution of a carbonyl group by a good sigma donor enhances this stability. The action of aluminium chloride can cause cleavage of only the cobalt—germanium bond, or of this bond and carbon—germanium bonds, depending on the solvent. The formation of triphenylchlorogermane only, in the reaction of the compound $R_3P(CO)_3CoGePh_3$ (R = Ph, OPh) with aluminium chloride indicates that in $(CO)_4CoGePh_3$ the carbon—germanium bond is attacked prior to that between cobalt and germanium.

Experimental section

All experiments were carried out under nitrogen, using standard vacuum line techniques. All solvents were dried, distilled and deoxygenated. Starting materials were commercial products or prepared by literature methods: $(CO)_4CoSiPh_3$ [7], $MePh_2SiH$ [15], *S*(+)-$(CO)_4CoSiMePh$-1-Np [2], $(PPh_3)_2NCl$ [9], acylcobalt complexes [3], $[PPh_3(CO)_3Co]_2$ [16], $[P(OPh)_3(CO)_3Co]_2$ [17], Ph_3GeH [18].

Melting points of cobalt compounds were taken under vacuum in a Tottoli apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer and NMR spectra with a Bruker WP-80 FT spectrometer. Chemical shifts are relative to TMS. Optical rotations were measured with a Perkin—Elmer 141 polarimeter.

Elemental analyses for new compounds are reported in Table 2.

Tetraethylammonium benzoyl(tricarbonyl)(triphenylsilyl)cobaltate, I

To $(CO)_4CoSiPh_3$ (430 mg, 1 mmol) in 20 ml ether was added PhLi (1 mmol; 1.4 ml of a 0.75 *M* solution) at —78°C. A yellow precipitate was formed. The solvent was pumped off, CH_2Cl_2 (10 ml) was added and the solution treated with Et_4NCl (200 mg, 1.25 mmol) in 10 ml CH_2Cl_2. The solution darkened as a white precipitate appeared. The solution was filtered, concentrated to ca. 5 ml and hexane was added. Dirty yellow crystals formed. Three further crystallisations afforded analytically pure $[PhCO(CO)_3Ph_3SiCo]Et_4N$ (12 mg, 1.9%) orange-yellow crystals, mp. 131—134°C, ν(CO) 1890 vs cm^{-1}.

Triphenylbenzoylsilane

To $(CO)_4CoSiPh_3$ (430 mg, 1 mmol) in 20 ml ether was added PhLi (1 mmol; 0.83 ml of a 1.2 *M* solution) at room temperature. The solution turned orange-yellow. After 1 h it was hydrolyzed with 4 *N* acetic acid. The organic layer was separated and dried over Na_2SO_4. The solvent was pumped off and the oily residue was chromatographed on silica gel (hexane/benzene: 1/1). Crude $Ph_3SiCOPh$ 160 mg (yield 44%) mp. 88—92°C was obtained and compared to an authentic sample [19]. Crystallization from hexane afforded the pure compound mp. 99—102°C.

The same product was obtained by addition of PhLi at —78°C and then warming to room temperature or by addition of PhMgBr at r.t. (in the latter case the yield was only 8%).

Methyldiphenylbenzoylsilane

A solution of $Co_2(CO)_8$ (750 mg, 2.2 mmol) in 20 ml hexane was slowly added to $MePh_2SiH$ (875 mg, 4.4 mmol). The reaction mixture was stirred overnight, the solvent pumped off and the residue dissolved in ether. PhLi (4.4 mmol; 4.4 ml of a 1 *M* solution) was added at —78°C. After warming to r.t., the mixture was hydrolyzed with 4 *N* acetic acid, the organic layer separated and dried over Na_2SO_4. The solvent was pumped off and the dark residue chromatographed on silica gel (hexane); $MePh_2SiCOPh$ (510 mg, yield 38%) was compared to an authentic sample [20].

S(—)-Methylphenyl-1-naphthylbenzoylsilane

A similar procedure to the one described for triphenylbenzoylsilane was used. Starting with *S*(+)-$(CO)_4$CoSiMePh-1-Np, $[\alpha]_D^{25}$ +2°, (429 mg, 1 mmol) in 20 ml ether, MePh-1-NpSiCOPh (167 mg; yield 47%), $[\alpha]_D^{25}$ —6.25° (*c* 3.42 in benzene), mp. 82—85°C, was obtained and compared to an authentic sample [8].

μ-nitridobis(triphenylphosphorus)benzoyl(tricarbonyl)(methylphenyl-1-naphthylsilyl)cobaltate, II

To $(CO)_4$CoSiMePh-1-Np (420 mg, 1 mmol) ($[\alpha]_D^{25}$ +2°) in 15 ml ether was added PhLi (1 mmol; 1.5 ml of a 0.7 *M* solution) at —78°C. A yellow colouration developed immediately but no precipitate formed. $(PPh_3)_2NCl$ (500 mg, 0.87 mmol) dissolved in CH_2Cl_2 (10 ml) was added with stirring. The solvent was then removed in vacuo to give a dark oil containing some solid. This residue was redissolved in CH_2Cl_2 to give a brown solution over a white solid (LiCl). The solution was then filtered through a short column of celite, the filtrate was concentrated to ~10 ml and hexane (10 ml) was added. Standing at —20°C precipitated a solid which was redissolved in CH_2Cl_2. THF was added until cloudiness, and the solution cooled at —20°C. The crystals which formed (unreacted $(PPh_3)_2NCl$) were filtered off, the filtrate was evaporated to dryness in vacuo and the residue crystallized from CH_2Cl_2 by addition of hexane at —20°C. Another crystallization afforded olive crystals of $[PhCO(CO)_3(MePh\text{-}1\text{-}NpSi)Co](PPh_3)_2N$ (200 mg, yield 19.4%) mp. 172—175°C, $\nu(CO)$ 1880 vs cm^{-1}, $|\alpha|_D^{25}$ +1.3° (*c* 2.5 CH_2Cl_2).

Reaction of $(CO)_4CoSiPh_3$ with n-BuLi

A similar procedure was used to the one described for the reaction with PhLi which gave $PhCOSiPh_3$. $(CO)_4CoSiPh_3$ (430 mg, 1 mmol) and n-BuLi (1 mmol) gave traces of Ph_3SiH and Ph_3SiOH (250 mg, yield 90%) mp. 150—152°C, compared to an authentic sample [15].

Reaction of $(CO)_4CoGePh_3$ with Ph_3GeLi

To $(CO)_4CoGePh_3$ (475 mg, 1 mmol) in 20 ml ether at —78°C was added a solution of Ph_3GeLi (from 305 mg (1 mmol) Ph_3GeH in 10 ml ether and 1 mmol of n-BuLi). The solution turned orange. After 16 h the solvent was pumped off, water was added to the orange residue and the suspension treated with Et_3OBF_4 (200 mg, 1.04 mmol). The reaction mixture was extracted with ether several times and the combined organic layers were dried over Na_2SO_4. Column chromatography on silica gel (toluene) afforded a solid which was crystallized from benzene/hexane. $(Ph_3Ge)_2O$ (450 mg, yield 72%) mp. 180—182°C were obtained and compared to an authentic sample [21].

(Triphenylphosphine)(triphenylgermyl)tricarbonylcobalt, III

A mixture of $[PPh_3(CO)_3Co]_2$ (1 g, 1.23 mmol) and triphenylgermane (753 mg, (2.46 mmol) were refluxed in 60 ml benzene for 72 h, during which time a black powder appeared. The mixture was freed from this powder by filtration through a fritted funnel (G 4) to afford a clear yellow solution. This solution was concentrated to ca. 10 ml and 20 ml of n-pentane were added. After standing at —20°C pale yellow crystals were obtained. Two further crystallizations afforded the analytical pure sample, white crystals, 760 mg (yield 44%) mp. 229—231°C, $\nu(CO)$ 2040w, 1945vs cm^{-1}. The elemental analysis showed an excess of carbon; this was due to the presence of one molecule of benzene as solvent of crystallization, confirmed by the NMR spectrum of a sample crystallized from toluene/n-pentane: NMR (δ ppm) 2.40 (3 H, singlet methyl group); 7.44 (35 H, multiplet, aromatic) ($CDCl_3$).

(Triphenylphosphite)(triphenylgermyl)tricarbonylcobalt, IV

A similar procedure to that above employing $[P(OPh)_3 (CO)_3Co]_2$ (1.8 g, 2 mmol) and Ph_3GeH (1.22 g, 4 mmol) in 60 ml toluene afforded 1.9 g (yield 63%) of the title compound, white crystals, mp. 145—146.5°C, $\nu(CO)$ 2010w, 1955vs cm^{-1}.

Treatment of III and IV with organolithium compounds

The general procedure for working up was the following: compounds III or IV were treated with an equimolar amount of MeLi or n-BuLi in ether solution at —78°C. The reaction mixture was allowed to warm to room temperature, the solvent was pumped off and water was added to the gummy residue which was then treated with a small excess of Et_3OBF_4. The mixture was extracted with ether, the organic layer dried over Na_2SO_4, the solvent pumped off and the residue chromatographed on a silica gel column. Starting material was recovered (toluene) in 74—90% yields in all cases.

Treatment of carbene complexes with PPh_3 or $P(OPh)_3$

A sample of the complex in hexane was treated at room temperature or under UV light with the stoichiometric amount of the phosphorus complexes. Evaporation of the solvent and chromatography on silica gel afforded the starting material as the sole isolable compound.

Cleavage reactions with halogens

The general procedure was the following: the complex dissolved in CCl_4 was treated at room temperature with the appropriate amount of chlorine or bromine (0.5 *M* solutions in CCl_4) (Table 1). The reactions were monitored by IR spectroscopy; the disappearance of the CO absorptions indicated total reaction. A blue or green precipitate had formed, indicating the presence of $CoCl_2$ or $CoBr_2$ respectively. The solvent was then pumped off and the residue was extracted with n-pentane (IR spectra were identical to those of authentic samples of Ph_3GeCl [22] and Ph_3GeBr [23]). Pentane was evaporated and the crystalline residues were compared by mixed melting points to authentic samples. The halogermanes were dissolved in ether and treated with an excess of $LiAlH_4$. After hydrolysis the organic layer was dried over Na_2SO_4, the solvent pumped off and the residue chromatographed on silica gel. Elution with benzene/hexane (20/80) afforded the organogermane, Ph_3GeH (Table 1) which was compared to an authentic sample.

Cleavage reactions with $AlCl_3$

The general procedure was the following: the complex in CCl_4 or ether was treated with an equimolar amount of $AlCl_3$. The progress of the reactions was monitored by IR spectroscopy. When reaction was complete as indicated by the disappearance of the CO absorptions, the solution was filtered, the solvent pumped off and the residue treated with $LiAlH_4$ as described above. Usual work up afforded Ph_3GeH and/or Ph_2GeH_2 [18]. When both germanes were obtained, their respective yields were estimated by separation of the two compounds by preparative thin layer chromatography on silica gel (elution with hexane/benzene: 80/20).

Cleavage of $(CO)_4CoGePh_3$ with SbF_5

A solution of $(CO)_4CoGePh_3$ (219 mg, 0.46 mmol) in 20 ml ether was added at room temperature dropwise with stirring to 200 mg of SbF_5/C (53%) suspended in 20 ml ether. After 6 days the reaction was complete (disappearance of CO absorptions in the IR spectrum). The solution was then filtered and the solvent pumped off to leave a pale pink oil. This residue was dissolved in pentane, the solution filtered, concentrated to ca. 5 ml and cooled at —20°C. White crystals of Ph_3GeF, 150 mg (yield 100%) mp. 73°C (compared by mixed melting point to an authentic sample [24]).

The same treatment did not result in cleavage of the Co—Ge bond in carbene derivatives.

Cleavage of $(CO)_4CoGePh_3$ with $LiAlH_4$

$(CO)_4CoGePh_3$ (244 mg, 0.51 mmol) was stirred for 2 days at room temperature in 20 ml of ether with a excess of $LiAlH_4$. Hydrolysis with aqueous HCl and column chromatography on silica gel (hexane/benzene: 80/20) gave Ph_3GeH (115 mg, yield 74%), which was compared to an authentic sample.

$PPh_3(CO)_3CoGePh_3$ and $P(OPh)_3(CO)_3CoGePh_3$ reacted similarly under the same conditions.

Cleavage of (ethoxy-1-butylcarbene)(triphenylgermyl)tricarbonylcobalt with $LiAlH_4$

The title compound (230 mg, 0.41 mmol) [3] in 20 ml ether was stirred at room temperature with an excess of $LiAlH_4$ for 3 days. The same work up as above afforded Ph_3GeH (80 mg, yield 64%), which was compared to an authentic sample.

Reaction of (ethoxy-1-butylcarbene)(triphenylgermyl)tricarbonylcobalt with CH_3MgBr

The title complex (280 mg, 0.5 mmol) in 30 ml ether was treated at room temperature with CH_3MgBr (1 ml of a 2.7 *M* ethereal solution). The solution darkened immediately. Hydrolysis, extration with ether and layer chromatography (SiO_2), using hexane/benzene: 90/10 as eluant, afforded Ph_3GeCH_3 (120 mg, yield 75%) mp. 71°C, compared to an authentic sample [25].

Reaction of (ethoxy-1-butylcarbene)(triphenylgermyl)tricarbonylcobalt with n-C_4H_9Li or NaH

The title complex (560 mg, 1 mmol) in 50 ml ether at —78°C was treated with the stoichiometric amount of n-BuLi. The yellow solution decolourized after the addition of the lithium compound. After a short time Et_3OBF_4 (198 mg, 1.04 mmol) was added and the solvent pumped off. The residue was stirred with water and the mixture extracted with ether at room temperature. The organic layer was separated and evaporated to dryness. The residue was chromatographed on silica gel (toluene/hexane: 50/50). The yellow band was collected, the solvent pumped off and the solid left recrystallized from pentane at —20°C. (ethoxy-3-hexylcarbene)(triphenylgermyl)tricarbonylcobalt, V (120 mg, yield 21%) mp. 124—125°C. dec. was obtained. NMR spectrum (δ, ppm): 7.42 (multiplet, 15 H, aromatics), 5.10 (quartet, 2 H, CH_2O), 3.90 (multiplet, 1 H, CH α to the carbene atom) 2.0 —0.9 (15 H), 1.63 (triplet, CH_3—CH_2O).

The same procedure was used with NaH.

The anion could also be trapped with CH_3I instead of Et_3OBF_4. In this case a mixture of the desired product and starting material was obtained. Their respective amounts were determined by NMR spectroscopy. For instance, starting with (ethoxymethylcarbene)(triphenylgermyl)tricarbonylcobalt, a mixture of the ethoxyethylcarbene complex and starting material was obtained (overall yield 50%, respective amounts 23 and 77%).

Reaction of (ethoxy-1-butylcarbene)(triphenylgermyl)tricarbonylcobalt with Ph_3GeLi

To the title compound (700 mg, 1.25 mmol) in 30 ml ether was added 1.25

mmol of an ethereal solution of Ph_3GeLi (from 382 mg of Ph_3GeH and 1.8 ml of a 0.7 *M* solution of n-BuLi) at room temperature. The initially yellow solution darkened as a brown solid deposited. After 1 day the solvent was pumped off and the residue was taken up with hexane. The solution was filtered and Ph_3GeEt (93 mg, yield 23%) was isolated by layer chromatography on silica gel (benzene/hexane: 10/90) and compared to an authentic sample [25].

The starting material (327 mg, yield 46%) was obtained by treatment of the residue (insoluble in hexane) with Et_3OBF_4 (see Experimental of reference 3).

Reaction of (ethoxyethylcarbene)(triphenylgermyl)tricarbonylcobalt with $SnCl_4$

The title compound (745 mg, 1.4 mmols) in 40 ml of benzene was treated with (164 μl, 1.4 mmols) of $SnCl_4$ at room temperature. The solution became light brown and a purple precipitate formed; after 2 days it was filtered and the solvent pumped off. The residue was taken up with pentane and filtered. The solid residue showed ν(CO) at 2070m and 2000vs cm^{-1}. Crystallization at —20°C from toluene/pentane afforded yellow crystals (258 mg, yield 41%, mp. 66—67°C) of crude $Cl_3SnCo(CO)_3C(OC_2H_5)C_2H_5$. The elemental analysis of this complex could not be performed because of its great instability.

The NMR spectrum (in $CDCl_3$) showed signals at (δ ppm) 5.30 (quartet, 2 H, OCH_2), 3.63 (quartet, 2 H, $-\bar{C}-CH_2$), 1.80 (triplet, 3 H, OCH_2-CH_3) and 1.15 (triplet, 3 H, $-\bar{C}CH_2-CH_3$).

Attempts at further purification resulted in decomposition.

The pentane solution afforded after evaporation Ph_3GeCl (333 mg, yield 70%, mp. 114°C), which was compared to an authentic sample [25].

Cleavage reaction of $(CO)_4CoGePh_3$ with Et_4NSnCl_3

To $(CO)_4$ $CoGePh_3$ (745 mg, 1.57 mmol) in 30 ml THF was added a THF solution of Et_4NSnCl_3 (559 mg, 1.57 mmols) at room temperature. The reaction mixture was stirred for 3 days; after this time the solution was filtered, the solvent pumped off and the residue taken up with pentane. The pentane was pumped off and Ph_3GeCl (434 mg, yield 82%) was identified by comparison with an authentic sample [25], mp. 114°C.

References

1 E. Colomer, R.J.P. Corriu and J.C. Young, J. Chem. Soc. Chem. Commun., (1977) 73.

2 E. Colomer and R. Corriu, J. Chem. Soc. Chem. Commun., (1976) 176; E. Colomer and R.J.P. Corriu, J. Organometal. Chem., 133 (1977) 159.

3 F. Carré, G. Cerveau, E. Colomer, R.J.P. Corriu, J.C. Young, L. Ricard and R. Weiss, J. Organometal. Chem., 179 (1979) 215.

4 D.J. Darensbourg and M.Y. Darensbourg, Inorg. Chem., 9 (1970) 1691.

5 M.J. Webb, R.P. Stewart Jr. and W.A.G. Graham, J. Organometal. Chem., 59 (1973) C21.

6 W.K. Dean and W.A.G. Graham, Inorg. Chem., 16 (1977) 1061.

7 A.J. Chalk and J.F. Harrod, J. Amer. Chem. Soc., 89 (1967) 1640.

8 A.G. Brook, J.M. Duff, P.F. Jones and N.R. Davis, J. Amer. Chem. Soc., 89 (1967) 431, A.G. Brook, personal communication.

9 J.K. Ruff and W.J. Schlientz, Inorg. Synth., 15 (1974) 84.

10 J.M. Duff and A.G. Brook, Can. J. Chem., 51 (1973) 2869.

11 M.D. Curtis, Inorg. Chem., 11 (1972) 802.

12 H. Werner and H. Rascher, Helv. Chim. Acta., 51 (1968) 1765.

13 H. Fischer, E.O. Fischer and F.R. Kreissl, J. Organometal. Chem., 64 (1974) C41.

14 C.P. Casey, Transition Metal Organometallics in Organic Synthesis, Academic Press New York, 1976, p. 189.
15 V. Bazant and V. Chvalovsky, Organosilicon Compounds, Academic Press, New York, 1965.
16 W. Hieber and W. Freyer, Chem. Ber., 91 (1958) 1230.
17 A. Sacco, Ann. Chimica., 43 (1953) 495.
18 O.H. Johnson and D.M. Harris, J. Amer. Chem. Soc., 72 (1950) 5564.
19 A.G. Brook, J. Amer. Chem. Soc., 79 (1957) 4373.
20 A.G. Brook, M.A. Quigley, G.J.D. Peddle, N.W. Schwartz and C.M. Warner, J. Amer. Chem. Soc., 82 (1960) 5102.
21 A.G. Brook, J. Amer. Chem. Soc., 77 (1955) 4827.
22 A.B. Thomas and E.G. Rochow, J. Inorg. Nucl. Chem., 4 (1957) 205.
23 O.H. Johnson and D.M. Harris, J. Amer. Chem. Soc., 72 (1950) 5566.
24 C.A. Kraus and L.S. Foster, J. Amer. Chem. Soc., 49 (1927) 457.
25 M. Lesbre, P. Mazerolles and J. Satgé, The Organic Compounds of Germanium, John Wiley and Sons, London, 1971.