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SYNTHESIS, CHEMICAL BEHAVIOUR AND CRYSTAL STRUCTURE OF COBALT-STABILIZED CARBENES, $(Ph_3Ge)(CO)_3CoC(OEt)R$

FRANCIS CARRE, GENEVIEVE CERVEAU, ERNESTO COLOMER, ROBERT J.P. CORRIU*, J. COLIN YOUNG

Laboratoire des Organométalliques, Equipe de Recherche Associée au C.N.R.S. No. 554, Université des Sciences et Techniques du Languedoc, 34060 Montpellier-cédex (France).

LOUIS RICARD and RAYMOND WEISS

Institut Le Bel, Laboratoire de Cristallochimie et de Chimie Structurale Associé au C.N.R.S., Université Louis Pasteur, 67070 Strasbourg-cédex (France)

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Summary

Cobalt stabilized carbenes are readily synthesized by reaction of organolithium compounds with $(CO)_4CoGePh_3$. The neutral carbenes are formed from the anion thus obtained by treatment with an ethylating reagent. Anions α to the carbene atom can be generated by treatment with a strong base (NaH, RLi) and trapped with Et_3OBF_4. However attempts to trap both types of anions with chlorosilanes failed, and instead the compound $(CO)_4CoGePh_3$ was recovered in good yield.

An X-ray structural determination of one of these complexes, $(Ph_3Ge)(CO)_3Co(OEt)Et$, shows unusually short bond lengths in the carbene moiety and the linkage *trans* to the triphenylgermyl group. The unusual chemical behaviour can be related to special features of the structure of the complex.

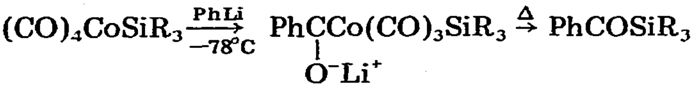
Introduction

We recently reported the formation of benzoylsilanes by the reaction of $(CO)_4CoSiR_3$ with phenyllithium [1].

$$(CO)_4CoSiR_3 \xrightarrow{PhLi} PhCOSiR_3$$

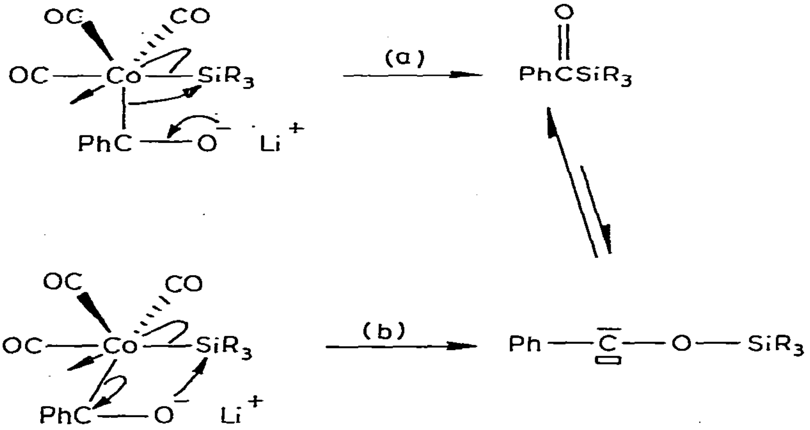
(R = Ph or R_3 = CH_3, Ph and 1-Np (optically active))

The reaction appears to proceed by nucleophilic attack of phenyllithium on a carbonyl ligand of $(CO)_4CoSiR_3$, giving at low temperature a benzoylcobalt anion, which subsequently decomposes on warming to room temperature.


$$(CO)_4CoSiR_3 \xrightarrow[-78^\circ C]{PhLi} Ph\underset{O^-Li^+}{\underset{|}{C}}Co(CO)_3SiR_3 \xrightarrow{\Delta} PhCOSiR_3$$

These reactions did not occur with any other organolithium compound investigated; for instance stoichiometric amounts of butyl- or methyl-lithium give no reaction.

The intermediate anion was isolated as the tetraethylammonium salt and its configuration assigned as *trans* by IR spectrometry. However a *cis* elimination would more easily explain the formation of benzoylsilane, either by (a) direct formation of the carbon—silicon bond, or (b) formation of an oxygen—silicon bond giving a silyloxy carbene, since the latter have been shown to rearrange to silylketones [2].



The literature contains descriptions of the structures of a number of salts and carbene complexes containing MR_3 ligands [3—7]: thus carbenes of the type $R_3MM'(CO)_4C(OR')R$ (where M = P, As, Sb, Ge and M' = Cr, Mo, W, Mn) are *cis* whereas $R_3MM'(CO)_3C(OR')R$ (where M = P, Sn, Pb and M' = Fe, Co) are *trans*.

In this paper we describe the syntheses, chemical behaviour, and structures of carbene complexes with a triphenyl-germyl rather than a -silyl ligand, since those containing silicon are too unstable to be isolated.

Results and discussion

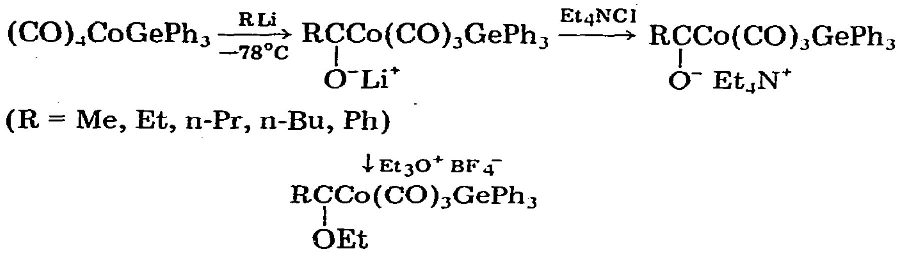
(a) Synthesis of carbene complexes

Treatment of $(CO)_4CoGePh_3$ with organolithium compounds leads to acyl anions which can be isolated as tetraethylammonium salts. The lithium salts give carbene complexes on reaction with Et_3OBF_4 (Scheme 1).

The salts and the carbene complexes show a single strong IR absorption band at ~1900 cm^{-1} and so a *trans* configuration can be assigned to them.

The tetraethylammonium salts appear to be stable in solution at room temperature, but reflux in xylene of the tetraethylammonium salt where R = Ph, gives tetraphenylgermane, rather than the benzoylgermane which might be

SCHEME 1

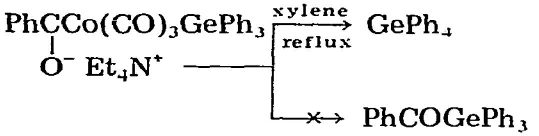


$$(CO)_4CoGePh_3 \xrightarrow[-78^\circ C]{RLi} R\underset{\substack{|\\ O^-Li^+}}{C}Co(CO)_3GePh_3 \xrightarrow{Et_4NCl} R\underset{\substack{|\\ O^-\ Et_4N^+}}{C}Co(CO)_3GePh_3$$

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

$$\downarrow Et_3O^+\ BF_4^- \qquad R\underset{\substack{|\\ OEt}}{C}Co(CO)_3GePh_3$$

expected by analogy with the behaviour of the silyl complex.



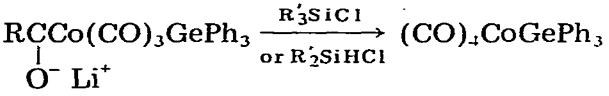
$$Ph\underset{\substack{|\\ O^-\ Et_4N^+}}{C}Co(CO)_3GePh_3 \xrightarrow[reflux]{xylene} GePh_4 \qquad \not\rightarrow PhCOGePh_3$$

(b) Reactivity

Moser and Fischer isolated a chromium stabilized carbene by treatment of the adduct of methyllithium and chromium hexacarbonyl with trimethylchlorosilane [8].

$$(CO)_6Cr \xrightarrow{MeLi} (CO)_5CrC(OLi)Me \xrightarrow{Me_3SiCl} (CO)_5CrC(OSiMe_3)Me$$

Treatment of $(CO)_4CoGePh_3$ with RLi (R = Me, n-Bu) and further reaction with Me_3SiCl, Me_2SiHCl or Ph_2SiHCl leads to decomposition of the lithium salt, which can be shown by IR spectroscopy to have been formed. The starting material $(CO)_4CoGePh_3$ is recovered in yields varying from 32 to 70% and is the only isolable product.



$$R\underset{\substack{|\\ O^-\ Li^+}}{C}Co(CO)_3GePh_3 \xrightarrow[or\ R'_2SiHCl]{R'_3SiCl} (CO)_4CoGePh_3 \qquad (1)$$

(R = Me, n-Bu; R′ = Me, Ph)

It has been shown that α-carbene anions can be generated with n-butyllithium and trapped with a wide variety of electrophiles [9]. Cobalt-stabilized carbenes undergo proton abstraction with n-butyllithium or sodium hydride (Scheme 2), and the resulting anions can be trapped by reaction with an alkylating agent.

SCHEME 2

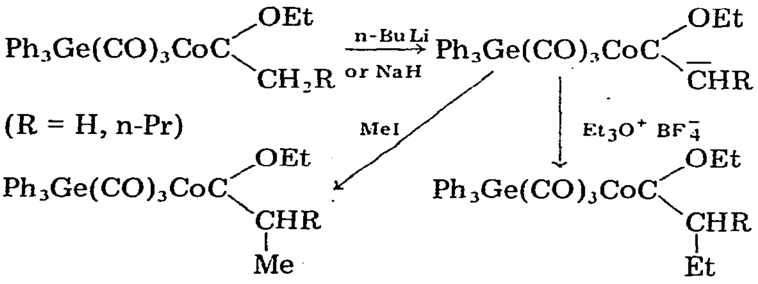


TABLE 1

REACTIONS INVOLVING CARBENE ANIONS GENERATED FROM $Ph_3Ge(CO)_3CoC(OEt)R$

Starting material R=	Base	Trapping agent	Product R=	yield [a] (%)
Me	n-BuLi	$Et_3O^+BF_4^-$	Me	13
			n-Pr	12
Me	n-BuLi	CH_3I	Me	22
			Et	27
Me	NaH	$Et_3O^+BF_4^-$	Me	48
			n-Pr	12
n-Bu	n-BuLi	$Et_3O^+BF_4^-$	CH(Et)Pr	21
n-Bu	MeLi	$Et_3O^+BF_4^-$	CH(Et)Pr	<5

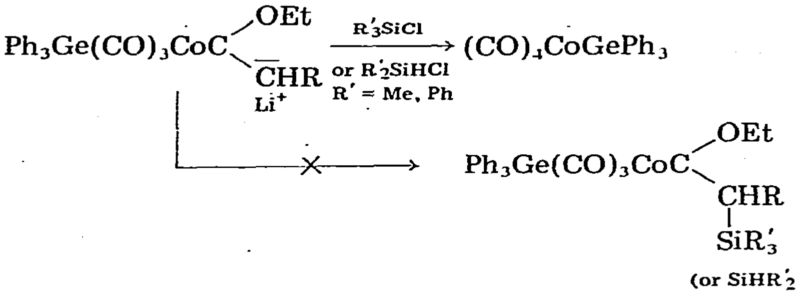
[a] Chemical yield of isolated product.

The products are identified by comparison with authentic samples prepared by direct attack of the appropriate organolithium reagent on $(CO)_4CoGePh_3$, and subsequent O-ethylation. In some cases a mixture of starting material and final product is obtained. Their respective amounts have been determined by NMR spectroscopy and the results are summarized in Table 1.

When R = Ph, no reaction takes place with n-BuLi or PhLi, and 90% of the starting material is recovered after the usual work-up. This confirms that a dicarbene complex cannot be obtained by successive attack of organolithiums on $(CO)_4CoGePh_3$.

Attempts to trap these anions with chlorosilanes revealed an unexpected reaction. $Ph_3Ge(CO)_3CoC(OEt)CH(SiR'_3)R$ was not obtained and $(CO)_4CoGePh_3$ was formed instead, in yields varying from 66 to 90% (Scheme 3).

SCHEME 3



(2)

At the moment it is difficult to explain the chemical behaviour of these species, since chlorosilanes are normally good trapping agents for anions, although difficulties in alkylating iron acylates have been reported (10).

(c) Crystallographic study of the ethylethoxycarbene derivative

The computer-drawn model displayed in Fig. 1 shows the essential features of the ethylethoxycarbenecobalt complex. The geometry of the molecule is approximately trigonal bipyramidal, with the three carbonyls in the equatorial

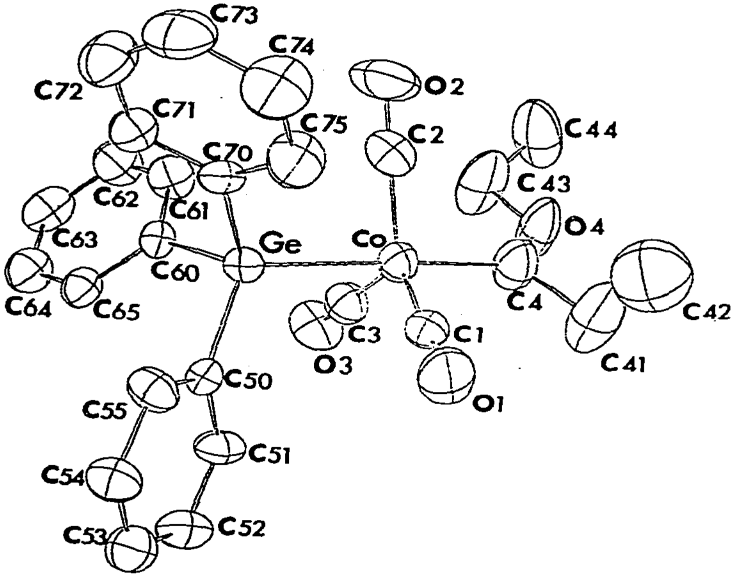


Fig. 1. ORTEP drawing of triphenylgermyl(ethylethoxycarbene) tricarbonylcobalt with the numbering of the atoms.

plane. The triphenylgermyl group is thus linked *trans* to the carbene atom. The carbon cobalt—germanium distance is 2.419 Å, longer than the value of 2.34(2) Å reported for the compound $Co(GePh_3)(CO)_3PPh_3$ [11] and comparable with a bond length of 2.458 Å for the compound $Me(1\text{-}Np)PhGeCo(CO)_4$ [12]. The equatorial carbonyl groups are tilted toward the triphenylgermyl group, with a mean C—Co—Ge angle of 84.1°. Similar values have been reported for germylcobalt tetracarbonyls $H_3GeCo(CO)_4$ [13] and $MePh(1\text{-}Np)GeCo(CO)_4$ [12].

A notable feature of the molecule is the planarity of the carbene moiety. The small displacements of the carbene atoms out of the plane (Co, C(4), O(4), C(41)) are illustrated in Fig. 2. Identical computations with the atomic coordinates given in the literature for manganese and rhenium derivatives [14,15] show displacements of the same magnitude.

Since the chemical behaviour of the triphenylgermylcobalt carbene complex is significantly different from that of other carbene complexes, precise details of its geometry have been carefully determined. Another interesting feature, for instance, is a small dihedral angle between the carbene plane and one of the carbonyl groups of the metal, which may be indicative of some overlap between the molecular orbital of the cobalt tricarbonyl moiety and the empty *p* orbital of the carbene atom, thus stabilising the carbene complex.

The angle between the carbonyl group CO and the carbene plane is 3.9° and

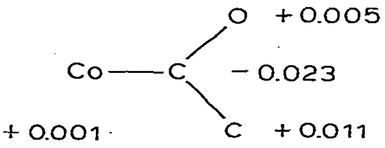


Fig. 2. Diagram showing the departure of each atom from the C(4) plane. Values are in Å.

is similar to that observed for the manganese and rhenium complexes [14,15]. It is noteworthy that much larger angles (34 to 45°) have been reported for chromium carbene complexes [16,17], so we do not think this feature of the geometry is essential to the stabilisation of the carbene ligand by the transition metal.

The main evidence for strong interaction between the metal and the carbene atoms is usually to be found the bond lengths. The Co—C distance, 1.91 Å, is short compared with other metal—carbene bond lengths, which range from 1.95 to 2.06 Å for manganese, chromium and molybdenum complexes [14,16—19]. The value of 1.289 Å for the carbene—oxygen bond also seems to be the shortest yet observed for such compounds: the C—O distances in other series of complexes range from 1.299 to 1.376 Å [14,16—19].

The metal—carbene and carbene—oxygen bond lengths are both significantly greater than the corresponding distances for a carbonyl group (mean Co—C: 1.77 Å; mean C—O: 1.13 Å). However, it seems that in this cobalt complex the carbene moiety has a greater resemblance (both chemically and physically) to the original carbonyl group than is the case for any carbene complex hitherto described. This could account for the unusual reactions of the cobalt complex, for instance the cleavage of the ethyl group with recovery of triphenylgermylcobalt tetracarbonyl in reactions 1 and 2.

Another unusual feature of the cobalt complex is the location of the carbene moiety *trans* to the triphenylgermyl group. When a ligand other than carbonyl is present the transition metal carbene complexes usually have *cis*-configurations [3,14—16]. However, *trans*-configurations have been reported for a triphenylgermylmolybdenum carbene, $Ph_3GeMo(C_5H_5)(CO)_2C(Ph)(OEt)$ [18], and for an iron derivative $Ph_3PFe(CO)_3C(OEt)Ph$ [3], the latter complex being isoelectronic at the transition metal with the former.

Experimental

Experiments were carried out under nitrogen in Schlenk tubes, using a vacuum line. All solvents were dry, distilled and deoxygenated. $(CO)_4CoGePh_3$ was prepared as described previously [19]. Organolithium reagents were prepared using ether as solvent and kept under nitrogen at —20°C. They were titrated by use of iodine and $Na_2S_2O_3$.

Melting points of organometallics were measured under vacuum with a Tottoli apparatus and are uncorrected. IR spectra were recorded in a Perkin—Elmer 257 spectrophotometer and NMR spectra on a Varian EM 390, or a Bruker FT Wp 80 spectrograph.

(1) Representative reactions. Preparation of n-butylalkoxycarbenes $[Ph_3GeCo(CO)_3C(O)\text{-}n\text{-}C_4H_9]^-Et_4N^+$

To 475 mg of $Ph_3GeCo(CO)_4$ (1 mmol) in 10 ml ether at —78°C was added 1 mmol of n-butyllithium. The mixture was well stirred and allowed to warm to —20°C; the solvent was pumped off and the white gum obtained was dissolved in CH_2Cl_2 (10 ml). To this solution, 170 mg (1 mmol) of Et_4NCl in 10 ml of CH_2Cl_2 were added. After a few minutes this solution was filtered through a short Celite column using CH_2Cl_2 as eluant. The clear yellowish solution obtained was concentrated to 10—15 ml, and hexane was carefully added to form two layers. Standing at —20°C afforded 390 mg (yield 60%) of white crystals.

TABLE 2

YIELDS, MELTING POINTS, IR SPECTRA AND ANALYTICAL DATA OF CARBENE COMPLEXES

Complex	Colour	Yield (%)	m.p. (°C)	IR data, ν(CO) (cm^{-1})	Analysis (Found (calcd) (%))			
					C	H	N	Co
[$Ph_3GeCo(CO)_3C(O)$-n-Bu]Et_4N	White	60	142–146	1800vs (br) [a]	61.55 (61.67)	6.68 (6.65)	2.27 (2.12)	8,89 (8,92)
[$Ph_3GeCo(CO)_3C(O)Ph$]Et_4N	Orange	57	133–134	1890vs (br) [a]	63.17 (63.37)	5.91 (5.91)	2.06 (2.06)	
$Ph_3GeCo(CO)_3C(OEt)Me$	Yellow	58	109	2040w (sh) 1950s (br) [b]	57.57 (57.86)	4.62 (4.44)		
$Ph_3GeCo(CO)_3C(OEt)Et$	Yellow	65	109–112	2040w (sh) 1950s (br) [b]	58.59 (58.57)	4.69 (4.71)		
$Ph_3GeCo(CO)_3C(OEt)$-n-Pr	Yellow	84	103–104	2040w (sh) 1950s (br) [b]	59.05 (59.29)	4.95 (4.94)		
$Ph_3GeCo(CO)_3C(OEt)$-n-Bu	Yellow	74	93–94	2040w (sh) 1945s (br) [b]	60.04 (59.95)	5.31 (5.17)		
$Ph_3GeCo(CO)_3C(OEt)Ph$	Orange	57	128–130	2040w (sh) 1950s (br) [b]	62.08 (62.00)	4.35 (4.33)		

[a] CH_2Cl_2. [b] $CHCl_3$ solution.

TABLE 3

NMR SPECTRA OF CARBENE COMPLEXES (τ, ppm) IN $CDCl_3$

	Aromatic	$O{-}CH_2$	CH_3	α-Carbene protons
$Ph_3GeCo(CO)_3C(OEt)Me$	~2.55	4.95	8.36	6.90
$Ph_3GeCo(CO)_3C(OEt)Et$	~2.65	4.97	8.37	6.59
$Ph_3GeCo(CO)_3C(OEt)$-n-Pr	~2.70	4.97	8.38	6.63
$Ph_3GeCo(CO)_3C(OEt)$-n-Bu	~2.55	4.92	8.38	6.63
$Ph_3GeCo(CO)_3C(OEt)Ph$	~2.50	4.80	8.30	

(2) $Ph_3GeCo(CO)_3C(OEt)$-n-C_4H_9

To 475 mg of $Ph_3GeCo(CO)_4$ (1 mmol) in 30 ml of ether at −78°C 1 mmol of n-butyllithium was added. The solvent was pumped off as before. The white gum was treated with water and 200 mg (1.04 mmol) of Et_3OBF_4. After 1 h the orange-yellow solution was extracted with ether and dried over Na_2SO_4. The solvent was pumped off and the oily residue chromatographed on silica gel (toluene/hexane: 1/9). The yellow band was collected, the solvent pumped off and the oil crystallized from pentane at −20°C. 414 mg (yield 74%) of yellow crystals were obtained.

Tables 2 and 3 summarize IR spectra, analytical data and NMR spectra of the alkoxycarbene complexes.

The ^{13}C NMR spectrum (in C_6D_6) of $Ph_3GeCo(CO)_3C(OEt)Ph$ showed resonances (relative to TMS) at −324 ppm (□C<), −201 ppm (C≡O), −150 to −130 ppm (aromatic), −79 ppm ($O{-}CH_2$) and −14 ppm (CH_3)

(3) Reaction of $[Ph_3GeCo(CO)_3C(O)Ph]Et_4N$ in xylene

The Et_4N salt was prepared as usual from 1 mmol of $Ph_3GeCo(CO)_4$. After the solvent was pumped off, the remaining gum was dissolved in xylene and refluxed for 1 h. The solvent was pumped off the residue extracted with ether and the extract filtered; ether was pumped off and the residual solid crystallized from toluene. 279 mg of Ph_4Ge (yield 73%) were obtained.

(4) Reaction of $[Ph_3GeCo(CO)_3C(O)$-n-$Bu]Li$ with Ph_2SiHCl

The lithium salt was prepared from 270 mg (0.57 mmol) of $Ph_3GeCo(CO)_4$ and n-BuLi as described previously. To the ether solution was added 1 g (excess) of Ph_2SiHCl. The solution was stirred overnight and filtered. The solvent was

TABLE 4

REACTIONS OF $[Ph_3GeCo(CO)_3C(O)R]Li$ WITH CHLOROSILANES

R	chlorosilane	yield (%) of $Ph_3GeCo(CO)_4$
Me	Me_2SiHCl	50
Me	Me_3SiCl	40
Me	Ph_2SiHCl	32
n-Bu	Me_2SiHCl	63
n-Bu	Ph_2SiHCl	70

pumped off and the residue crystallized from pentane. 190 mg of $Ph_3GeCo(CO)_4$ (yield 70%) were isolated.

Table 4 summarizes these reactions.

(5) α-Carbene anions. Reaction of $Ph_3GeCo(CO)_3C(OEt)$-n-Bu with n-BuLi

To 560 mg (1 mmol) of the carbene in 30 ml of ether at —78°C was added 1 mmol of n-BuLi. The solution decolorized, and after 1 h 198 mg (1.04 mmol) Et_3OBF_4 were added. Ether was pumped off at —78°C, water was added at room temperature and the suspension was extracted with ether and dried over Na_2SO_4. The solvent was then pumped off and the residue chromatographed on silica gel (hexane/benzene 1/1). The yellow-brown solution was evaporated and crystallization from pentane gave 120 mg (yield 20%) of pure $Ph_3GeCo(CO)_3C(OEt)CH(Et)$-n-Pr, yellow-crystals. Anal. Found: C, 61.08; H, 5.43. $C_{30}H_{33}CoGeO_4$ calcd.: C, 61.17; H, 5.61%. M.p. 124—125°C, NMR spectrum (τ, ppm). ~2.58 (aromatic), 4.90 (OCH_2), 6.03 (C—H, tertiary). 8.1—9.2 all other protons.

(6) Reactions of α-carbene anions with chlorosilanes

The α-carbene anion of $Ph_3GeCo(CO)_3C(OEt)$-n-Bu, 220 mg (0.35 mmol), was generated as before. To the solution an excess of Me_2SiHCl (1 g) was added. After 15 min the solvent was pumped off and the residue extracted with pentane. The solution was concentrated and allowed to stand at —20°C. 150 mg (yield 90%) of $Ph_3GeCo(CO)_4$ were obtained.

In some cases a proportion of the starting material was also recovered. In these cases the yield was calculated by means of the NMR spectrum of the mixture.

(7) Structure determination of the triphenylgermyltricarbonylethylethoxycarbene cobalt $Ph_3Ge(CO)_3CoC(Et)(OEt)$

Crystal data. Crystals of the product were grown by slow cooling of pentane solutions. The air sensitive crystals were cut under Nujol and encapsulated in epoxy cement for data collection. The space group and unit cell parameters were obtained from a peak hunting procedure using a Philips PW 1100 diffractometer. The crystals are triclinic, space group $P\bar{1}$, with *a* 9.928(4), *b* 13.357(5), *c* 10.066(5) Å and α 92.62(6)°, β 95.56(5)°, γ 109.41(4)°. The sensitivity of the crystal prevented any accurate density measurement. However, an approximate value of 1.42(5) was obtained. A unit cell containing two molecules of complex ($C_{26}H_{25}CoGeO_4$, mol. wt. 533) gives a calculated density of 1.418 g cm^{-3}.

TABLE 5

REACTIONS OF α-CARBENE ANIONS GENERATED FROM $Ph_3GeCo(CO)_3C(OEt)R$ WITH CHLOROSILANES

Starting material R=	Base	Chlorosilane	Yield (%) of $Ph_3GeCo(CO)_4$
Me	NaH	Me_2SiHCl	21
n-Bu	n-BuLi	Me_3SiCl	60
n-Bu	n-BuLi	Me_2SiHCl	90
n-Bu	n-BuLi	Ph_2SiHCl	66

Data collection and solution of the structure

A total of 5814 reflections were measured in the range $4° < 2\theta < 45°$. Individual reflections were step-scanned over a θ range of 0.6° with a step width of 0.03 degree. The scanspeed was $0.032° \text{ sec}^{-1}$, and monochromated Mo-K_α radiation was employed. Data reduction was accomplished using the procedure described by Coppens et al. [20].

Because the σ's are underestimated in this procedure, a $\sigma(I)/I$ limit of 0.20 was used. The 1721 reflections meeting this criterion were used to solve the structure by conventional Patterson and Fourier techniques. The structure was refined by least-squares to $R = 0.060$. At this point unsatisfactory geometrical features in the alkyl chain of the carbene ligand led us to introduce two disordered positions for the methyl group C(42). These were arbitrarily given occupancies of 0.75 and 0.25 and no attempt was made to refine these parameters. The final R factor is 0.046; $R_W = 0.051$.

Atomic coordinates and the associated anisotropic thermal parameters are listed in Tables 6 and 7 respectively. The geometry of the complex and the

TABLE 6

ATOMIC COORDINATES IN THE UNIT CELL OF THE CRYSTAL

Atom	x/a	y/b	z/c
Ge	0.10902(9)	0.31929(7)	0.16579(8)
Co	0.19601(12)	0.19438(9)	0.28257(10)
C(1)	0.1709(9)	0.1305(6)	0.1174(8)
C(2)	0.0476(10)	0.1785(7)	0.3725(8)
C(3)	0.3543(9)	0.3050(7)	0.3330(8)
C(4)	0.2661(12)	0.0924(8)	0.3654(9)
O(1)	0.1561(8)	0.0915(5)	0.0139(6)
O(2)	−0.0493(7)	0.1683(6)	0.4313(7)
O(3)	0.4549(6)	0.3755(5)	0.3656(7)
O(4)	0.3028(9)	0.0901(5)	0.4913(6)
C(41)	0.2973(17)	0.0018(10)	0.2901(11)
C(42)	0.1743(25)	−0.0837(18)	0.2719(22)
C(43)	0.3001(16)	0.1682(9)	0.5930(9)
C(44)	0.2931(22)	0.1155(10)	0.7212(11)
C(50)	0.1800(8)	0.3461(5)	−0.0094(7)
C(51)	0.3260(8)	0.3725(6)	−0.0215(8)
C(52)	0.3740(9)	0.3999(7)	−0.1440(8)
C(53)	0.2784(10)	0.3980(7)	−0.2557(8)
C(54)	0.1365(9)	0.3712(7)	−0.2447(8)
C(55)	0.0863(8)	0.3442(6)	−0.1213(7)
C(60)	0.1696(8)	0.4590(6)	0.2665(7)
C(61)	0.1545(10)	0.4691(7)	0.4003(7)
C(62)	0.1980(11)	0.5679(8)	0.4728(9)
C(63)	0.2574(9)	0.6597(7)	0.4077(9)
C(64)	0.2720(10)	0.6516(7)	0.2711(9)
C(65)	0.2271(8)	0.5523(6)	0.2005(8)
C(70)	−0.1022(7)	0.2711(6)	0.1321(7)
C(71)	−0.1715(8)	0.3431(7)	0.1433(8)
C(72)	−0.3205(9)	0.3121(8)	0.1170(9)
C(73)	−0.4008(9)	0.2065(8)	0.0763(9)
C(74)	−0.3305(9)	0.1334(7)	0.0641(11)
C(75)	−0.1813(9)	0.1641(7)	0.0917(10)

TABLE 7

ANISOTROPIC THERMAL PARAMETERS × 10^2

Atom	$\beta_{1,1}$	$\beta_{2,2}$	$\beta_{3,3}$	$\beta_{1,2}$	$\beta_{1,3}$	$\beta_{2,3}$
Ge	0.926(10)	0.572(6)	0.821(9)	0.238(6)	0.142(7)	0.058(6)
Co	1.53(2)	0.69(1)	0.95(1)	0.49(1)	0.22(1)	0.16(1)
C(1)	1.93(15)	0.71(7)	1.05(10)	0.54(9)	0.45(10)	0.19(7)
C(2)	1.72(14)	0.90(8)	1.32(12)	0.31(9)	0.21(10)	0.27(8)
C(3)	1.67(14)	0.88(8)	1.22(11)	0.47(9)	0.07(10)	0.26(8)
C(4)	3.20(22)	1.09(9)	1.20(12)	1.19(12)	0.32(13)	0.22(8)
O(1)	3.40(15)	1.01(6)	1.07(7)	0.82(8)	0.38(9)	−0.05(5)
O(2)	2.25(13)	1.84(9)	1.89(10)	0.59(8)	1.10(9)	0.74(8)
O(3)	1.56(10)	1.17(6)	2.17(11)	0.15(7)	−0.24(8)	0.32(7)
O(4)	4.78(19)	1.44(7)	1.24(8)	2.06(10)	0.12(10)	0.26(6)
C(41)	5.66(38)	1.82(14)	1.59(16)	2.33(20)	−0.22(19)	−0.14(12)
C(42)	13.3(6) [a]					
C(43)	5.27(33)	1.62(13)	0.94(12)	1.96(18)	−0.03(16)	−0.29(10)
C(44)	7.85(54)	1.32(13)	1.59(17)	1.66(23)	1.51(24)	0.49(12)
C(50)	1.08(11)	0.50(6)	0.94(9)	0.34(7)	0.25(8)	0.09(6)
C(51)	0.99(11)	0.77(7)	1.16(10)	0.10(7)	0.45(9)	0.04(7)
C(52)	1.64(14)	1.00(8)	1.05(11)	0.35(9)	0.45(10)	0.03(7)
C(53)	1.82(15)	0.62(7)	1.36(12)	0.28(8)	0.32(11)	0.00(7)
C(54)	1.74(14)	0.93(8)	0.93(10)	0.44(9)	0.33(9)	0.17(7)
C(55)	1.35(12)	0.80(7)	0.82(9)	0.29(8)	0.03(9)	0.19(6)
C(60)	1.04(11)	0.52(6)	0.99(9)	0.30(6)	0.03(8)	0.07(6)
C(61)	2.12(16)	0.78(7)	0.80(10)	0.40(9)	0.10(10)	−0.12(6)
C(62)	2.25(18)	0.92(9)	1.45(13)	0.38(10)	0.30(12)	0.00(8)
C(63)	1.49(14)	0.94(8)	1.59(13)	0.39(9)	−0.11(11)	−0.39(8)
C(64)	1.54(14)	0.69(7)	1.73(13)	0.23(8)	0.12(11)	−0.07(8)
C(65)	1.08(11)	0.53(6)	1.40(11)	0.21(7)	0.08(9)	0.00(6)
C(70)	0.95(10)	0.63(6)	0.87(9)	0.18(7)	0.34(8)	0.03(6)
C(71)	1.20(12)	0.82(7)	1.29(11)	0.41(8)	0.25(9)	0.20(7)
C(72)	1.49(14)	1.06(9)	1.86(14)	0.56(9)	0.03(12)	0.08(9)
C(73)	1.04(13)	1.38(10)	1.82(14)	0.29(9)	0.27(11)	0.21(10)
C(74)	0.95(12)	0.84(9)	2.67(18)	−0.14(8)	−0.19(12)	−0.22(10)
C(75)	1.20(13)	0.66(7)	2.23(15)	0.01(8)	0.05(11)	−0.06(8)

[a] This value is the isotropic *B* for this atom. Only the atomic position having the occupancy of 0.75 was retained (see text)

numbering system used in Tables 6—9 for the atoms in the asymmetric unit are displayed in Fig. 1. Individual bond angles and bond lengths in the carbon moiety are listed in Table 8; bond parameters for the remaining part of the molecule are given in table 9. Tables of structure factors can be obtained from the authors on request.

TABLE 8

BOND LENGTHS AND BOND ANGLES IN THE CARBENE MOIETY. ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond lengths (Å)		Bond angles (deg)	
Co—C(4)	1.913(11)	Co—C(4)—C(41)	124.9(0.6)
C(4)—O(4)	1.289(10)	Co—C(4)—O(4)	127.1(0.5)
C(4)—C(41)	1.531(19)	C(41)—C(4)—O(4)	107.9(0.9)
C(41)—C(42)	1.357(24)	C(4)—O(4)—C(43)	124.1(1.1)
C(43)—O(4)	1.438(14)	O(4)—C(43)—C(44)	105.9(0.9)
C(43)—C(44)	1.494(16)	C(4)—C(41)—C(42)	107.8(1.3)

TABLE 9

BOND LENGTHS AND BOND ANGLES IN THE TRIPHENYLGERMYL GROUP AND THE COBALT TRICARBONYL MOIETY

Bond lengths (Å)		Selected bond angles (deg)	
Ge—Co	2.419(1)	Ge—Co—C(1)	82.7(3)
Ge—C(50)	1.966(7)	Ge—Co—C(2)	84.1(3)
Ge—C(60)	1.958(7)	Ge—Co—C(3)	85.6(3)
Ge—C(70)	1.967(7)	Ge—Co—C(4)	176.8(3)
Co—C(1)	1.790(7)	Co—Ge—C(50)	113.0(2)
Co—C(2)	1.762(10)	Co—Ge—C(60)	112.1(2)
Co—C(3)	1.773(7)	Co—Ge—C(70)	112.7(2)
C(1)—O(1)	1.118(9)	Co—C(1)—O(1)	179.3(5)
C(2)—O(2)	1.151(12)	Co—C(2)—O(2)	179.9(5)
C(3)—O(3)	1.129(9)	Co—C(3)—O(3)	179.6(5)
C(50)—C(51)	1.393(10)	Ge—C(50)—C(51)	120.7(4)
C(51)—C(52)	1.386(11)	Ge—C(50)—C(55)	120.3(4)
C(52)—C(53)	1.393(12)	Ge—C(60)—C(61)	121.6(4)
C(53)—C(54)	1.351(13)	Ge—C(60)—C(65)	119.8(4)
C(54)—C(55)	1.402(11)	Ge—C(70)—C(71)	119.6(4)
C(55)—C(50)	1.383(10)	Ge—C(70)—C(75)	120.5(5)
C(60)—C(61)	1.375(10)	C(51)—C(50)—C(55)	119.0(7)
C(61)—C(62)	1.390(12)	C(61)—C(60)—C(65)	118.6(8)
C(62)—C(63)	1.396(13)	C(71)—C(70)—C(75)	119.8(8)
C(63)—C(64)	1.400(13)		
C(64)—C(65)	1.387(11)		
C(65)—C(60)	1.414(10)		
C(70)—C(71)	1.364(13)		
C(71)—C(72)	1.392(12)		
C(72)—C(73)	1.390(12)		
C(73)—C(74)	1.383(16)		
C(74)—C(75)	1.395(12)		
C(75)—C(70)	1.402(10)		

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