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CLEAVAGE OF SILICON- AND GERMANIUM-TRANSITION METAL BONDS. DEPENDENCE OF THE STEREOCHEMISTRY ON THE NATURE OF THE LIGANDS AND THE GEOMETRY OF COMPLEXES *

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Summary

The cleavages of some new optically active complexes containing Co—Si (or —Ge), Mn—Si (or —Ge), Re—Ge and W—Ge bonds are described. Electrophiles cleave the Co—Si bond with good retention of configuration at silicon, while the Mn—Si bond is not cleaved under the same conditions. The M'—Si and M'—Ge bonds (where M' = transition metal) are cleaved by nucleophiles with retention or inversion of configuration. In the case of trigonal bipyramidal geometry (cobalt complexes) the stereochemical outcome of the reaction is strongly dependent upon electronic effects, the size of the ligand trans to the Co—Si (or —Ge) bond, and the nature of the nucleophilic reagent, in accord with the general rules for nucleophilic substitution at silicon. In contrast the transition metal—silicon or —germanium bonds in the octahedral complexes of manganese, rhenium and tungsten are always cleaved with poor retention of configuration regardless of the nature of the ligands or the nucleophilic reagent. The results provide the first cases in which the stereochemistry of nucleophilic displacement at silicon is independent of the electronic features of both the leaving group and the nucleophile.

Introduction

In previous papers [2—4] we have reported results of cleavage reactions of transition metal—silicon bonds in optically active complexes. Compounds of the type M—SiR_3 were cleaved by electrophilic and nucleophilic reagents.

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* For preliminary communications see ref. 1.

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$$\begin{tikzcd}
 & \text{hal—SiR}_3 \\
\text{M—SiR}_3 \arrow[ur, "\text{hal}_2"] \arrow[dr, "\text{Nu}^-"'] & \\
 & \text{Nu—SiR}_3
\end{tikzcd}$$

retention or inversion of configuration

(M = (η^5-C_5H_5)(CO)(L)Fe; $(CO)_4Co$; (η^5-$CH_3C_5H_4$)(CO_2)(H)Mn;
L = phosphines, phosphites, CO;
R_3 = MePh(1-$C_{10}H_7$) optically active; 1-$C_{10}H_7$ = 1-naphthyl)

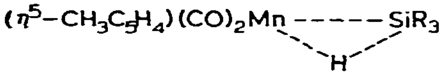
Electrophiles cleave the transition metal—silicon (or —germanium) bonds with either retention or inversion of configuration at silicon depending on the nature of the reagent and the substrate, while nucleophiles cleave Fe—Si bond with retention and Co—Si or Mn—Si bonds with inversion.

The results obtained for nucleophilic cleavage of the iron and cobalt complexes seem to be in agreement with the general rules governing the stereochemistry of nucleophilic displacements at silicon [5]. One factor which determines the stereochemistry at silicon is the nature of the leaving group X. When X is a polarizable substituent it behaves as a good leaving group and nucleophilic substitution reactions occur with inversion of configuration. A nonpolarizable group is replaced with retention [5]. The trends are summarized as follows:

predominant stereochemistry	Inversion $\longrightarrow$ Retention	
	Cl, Br $\gg$ SR $>$ F $>$ OR $\gg$ H	
tendency of the leaving group to be replaced	good leaving group	poor leaving group

To a first approximation, we can apply these concepts to the nucleophilic cleavage of silicon—transition metal bonds. In the iron complexes, (η^5-C_5H_5)-(CO)LFe is a good nucleophile and thus a poor leaving group, whereas for cobalt complexes, $(CO)_4Co$ which is a poor nucleophile should be a good leaving group [6,7], in agreement with the observed results.

Due to the electronic and geometric similarities between the iron and the manganese complexes, retention of configuration should be expected for the latter, but instead good inversion is observed. However these complexes may not be comparable, since there is known to be a highly specific hydrogen—silicon interaction in the manganese complex as shown [8].



It is thus unlikely that the stereochemical behaviour of silicon— or germanium—transition metal bonds can be compared to that of the previously studied Si—X groups and so we have studied the effect of the variation of the ligands at the transition metal center on the stereochemical outcome of the cleavage reaction. The electronic character of the transition metal centre varies, of course, with changes of the nature of the ligands.

The complexes studied have the general formula $(CO)_nLM'$—MR_3 and exhibit trigonal bipyramidal geometry when M' = Co and octahedral geometry when M' = Mn, Re, W. The systems examined are listed in Table 1.

TABLE 1

$(CO)_nLM'$—MR_3 [a]

M'	n	L	M
Co	3	CO, phosphine, phosphite	Si, Ge
Co	3	carbene	Ge
Mn	4	CO, phosphine	Si
Mn	4	CO, carbene	Ge
Re	4	carbene	Ge
W	4	NO	Ge

[a] R_3 = $MePh(1\text{-}C_{10}H_7)$ optically active.

Results and discussion

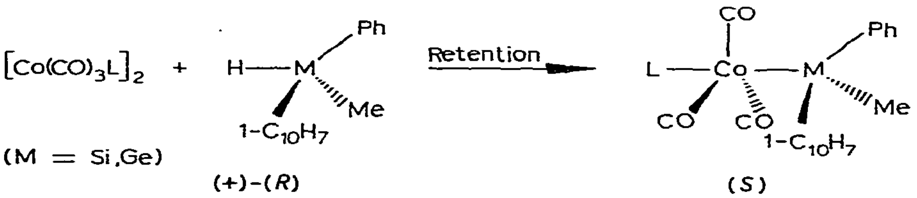
Synthesis of the complexes

Cobalt complexes. The cobalt complexes $(CO)_3LCoMR'_3$ (L = PR_3: R = Ph, OPh, OEt, Cy, n-Bu, t-Bu; M = Si, Ge; R'_3 = Ph_3, $MePh(1\text{-}C_{10}H_7)$ optically active) were prepared by reaction of $[(CO)_3(PR_3)Co]_2$ with the hydrogeno-silane or -germane in refluxing benzene or toluene [9] (reaction 1). Nucleophilic attack of the corresponding sodium cobaltate on the halogeno-silane or -germane [10] cannot be employed due to the much faster racemization of halogeno-silanes [11] and -germanes [12] compared to the rate of substitution of halide.

$$[(CO)_3(PR_3)Co]_2 + 2\,R'_3MH \rightarrow 2\,(CO)_3(PR_3)CoMR'_3 + H_2 \qquad (1)$$

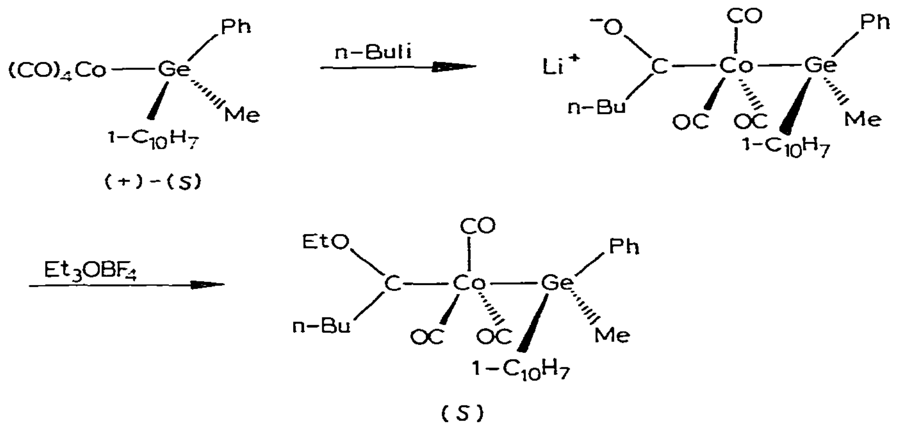
Reaction 1 involves insertion of the transition metal into the Si—H or Ge—H bond with elimination of hydrogen. The absolute configurations of (+)-MePh-$(1\text{-}C_{10}H_7)$GeH and (+)-MePh$(1\text{-}C_{10}H_7)$SiH are known to be *R* [13,14]. Moreover, the absolute configurations of (+)-(*S*)-$(CO)_4$CoGeMePh$(1\text{-}C_{10}H_7)$ [15] and (+)-(*S*)-$(CO)_4$CoSiMePh$(1\text{-}C_{10}H_7)$ [16] have been determined by X-ray diffraction, showing that in the case of L = CO, reaction 1 takes place with retention of configuration. The same stereochemistry is expected in the other cases (Scheme 1). For L = PR_3, the ligand L is *trans* to the silyl or germyl group, as shown by the IR spectra [10a].

SCHEME 1



The carbene complex (M = Ge, L = C(OEt)-n-Bu) was prepared by nucleophilic attack of n-BuLi at a carbonyl ligand of $(CO)_4CoGeR_3$ followed by ethylation with Et_3OBF_4 [17]. The configuration at germanium is not altered during the course of the reactions. A crystallographic study of $(CO)_3[C(OEt)Et]CoGePh_3$ [17], has confirmed the *trans* structure for the complex (Scheme 2) which was predicted from the IR spectrum [9].

SCHEME 2



The spectroscopic properties of the new compounds are reported in Table 2.

Manganese and rhenium complexes. The complexes $(CO)_4LMnMR_3$ (L = CO, PPh_3, M = Si; L = CO, M = Ge; R_3 = Ph_3, $MePh(1\text{-}C_{10}H_7)$ optically active) were prepared by reaction 2 [18,19].

$$[Mn(CO)_4L]_2 + 2\,R_3MH \rightarrow 2\,(CO)_4LMnMR_3 + H_2 \qquad (2)$$

By analogy with the cobalt complexes and since the Si—H and Ge—H bonds react mainly with retention of configuration, retention is assumed for this reaction. The carbene complexes $(CO)_4[C(OEt)CH_3]M'\text{—}GeR_3$ (M' = Mn, Re) were prepared from $(CO)_5M'CH_3$ and optically active germyllithium [20—22] (Scheme 3), and so the absolute configuration of these complexes is easily determined: starting from (*R*)-germane, the (*S*)-complex is obtained. The structure determined by X-ray diffraction shows a *cis* configuration for $(CO)_4[C(OEt)$-

TABLE 2

IR AND NMR DATA FOR NEW COBALT COMPLEXES

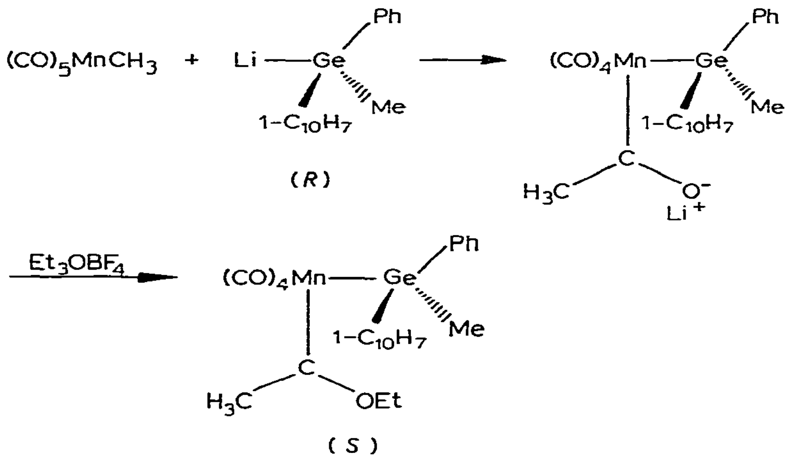
Compound		ν(CO) in benzene (cm^{-1})	δ(CH$_3$—Si) or δ(CH$_3$—Ge) in C$_6$D$_6$
$(CO)_4CoSiMePh(1\text{-}C_{10}H_7)$	(1)	Ref. 3	1.33
$(CO)_3P(OPh)_3CoSiMePh(1\text{-}C_{10}H_7)$	(2)	2050w, 1965s	1.33
$(CO)_3PPh_3CoSiMePh(1\text{-}C_{10}H_7)$	(3)	2030w, 1945s	1.53
$(CO)_3Pcy_3CoSiMePh(1\text{-}C_{10}H_7)$	(4)	2020w, 1935s	*b*
$(CO)_4CoGeMePh(1\text{-}C_{10}H_7)$	(5)	Ref. 3	1.46
$(CO)_3P(OPh)_3CoGeMePh(1\text{-}C_{10}H_7)$	(6)	2060w, 1965s	1.46
$(CO)_3P(OEt)_3CoGeMePh(1\text{-}C_{10}H_7)$	(7)	2050w, 1960s	1.60
$(CO)_3PPh_3CoGeMePh(1\text{-}C_{10}H_7)$	(8)	2040w, 1945s	1.73
$(CO)_3Pcy_3CoGeMePh(1\text{-}C_{10}H_7)$	(9)	2020w, 1945s	*b*
$(CO)_3P(n\text{-}Bu)_3CoGeMePh(1\text{-}C_{10}H_7)$	(10)	2030w, 1930s	*c*
$(CO)_3P(t\text{-}Bu)_3CoGeMePh(1\text{-}C_{10}H_7)$	(11)	2020w, 1935s	1.70
$(CO)_3[C(OEt)n\text{-}Bu]CoGeMePh(1\text{-}C_{10}H_7)$	(12)	2040w, 1947s [a]	1.20 [d]

[a] $CHCl_3$. [b] Overlap with the signals of cy. [c] Overlap with the signals of n-Bu. [d] $CDCl_3$.

CH_3]$MnGeR_3$ [20] as predicted from the infrared spectrum [23].

These compounds can be obtained in the same way as the cobalt carbene complexes [23].

SCHEME 3



The spectroscopic data for the complexes are given in Table 3.

Tungsten complex. Complex $(CO)_4NOWGeR_3$ (18) (R_3 = $MePh(1\text{-}C_{10}H_7)$ is prepared by nitrosylation of the optically active anion $[(CO)_5WGeR_3]Et_4N$ [20,24,25] (reaction 3).

$$(-)\text{-}(S)\text{-}[(CO)_5WGeR_3]^- NEt_4^+ \xrightarrow{NOBF_4} (-)\text{-}(S)\text{-}(CO)_4NOWGeR_3 \qquad (3)$$

Since this reaction does not involve the chiral center, the configuration at germanium is not altered. This complex exists as the *trans*-isomer, as deduced from the IR spectrum [25].

Cleavage reactions

We have studied the cleavage of these complexes with electrophiles and nucleophiles.

TABLE 3

IR AND NMR DATA FOR NEW MANGANESE COMPLEXES

Compound		ν(CO) (cm^{-1})	$\delta(CH_3\text{—}Si)$ or $\delta(CH_3\text{—}Ge)$ in C_6D_6
$(CO)_5MnSiMePh(1\text{-}C_{10}H_7)$	(13)	2100sh, 2040sh 2000s, 1960w [a]	
$(CO)_4PPh_3MnSiMePh(1\text{-}C_{10}H_7)$	(14)	1940s [b]	2.13
$(CO)_5MnGeMePh(1\text{-}C_{10}H_7)$	(15)	2105sh, 2042sh 1990s, 1960w [a]	1.17

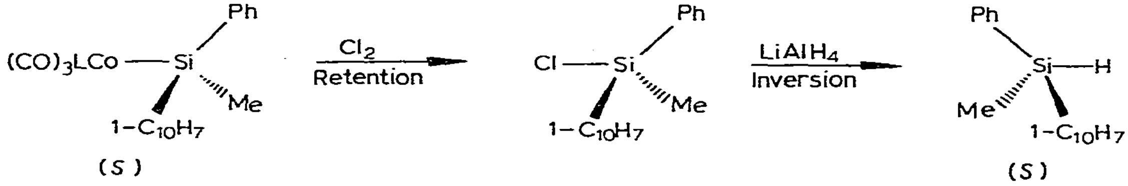
[a] Cyclohexane. [b] Toluene.

Electrophilic cleavage with halogens. The experimental results are shown in Table 4.

The stereochemistries were determined by Walden cycles. The percentages of stereochemistry shown represent minimum values since we assumed that the starting complexes were optically pure.

Chlorosilanes are known to be racemized by the solvents [11], so they were not isolated, but converted in situ into the optically stable hydrogenosilanes (Scheme 4). The reduction reaction is known to take place with inversion of configuration [26].

SCHEME 4

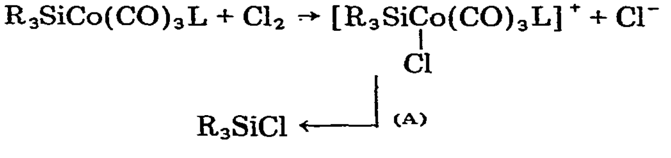


The cleavage of germanium compounds was not studied since chlorogermanes are racemized too rapidly in solution [12].

Electrophiles such as chlorine (Table 3) and bromine [3] cleave the cobalt—silicon bond with good retention of configuration. In all cases, the stereoselectivities are almost the same, and the influence of the phosphorus ligand, L, and of electrophile on the stereochemistry is relatively small. The manganese complexes are not cleaved by halogens under the same conditions.

We consider the following possibilities for the mechanism of the electrophilic cleavage reaction: (i) Direct displacement on R_3Si by the electrophile Cl^+; (ii) Electrophilic attack of Cl^+ on the cobalt atom, giving the intermediate A (Scheme 5) which subsequently undergoes reductive elimination of R_3SiCl with retention of configuration. An alternative possibility involves a nucleophilic attack of Cl^- on A [2].

SCHEME 5



$$R_3SiCo(CO)_3L + Cl_2 \rightarrow [R_3Si\underset{\underset{\displaystyle Cl}{|}}{Co}(CO)_3L]^+ + Cl^-$$

$$R_3SiCl \longleftarrow (A)$$

(iii) Electron transfer from the complex to Cl^+ followed by substitution with $Cl^\bullet$.

Our results are in good agreement with direct displacement (i), since the same stereoselectivities are obtained with Cl_2 and $Cl_2/AlCl_3$ which probably generates the electrophile Cl^+ [27]. The second mechanism proposed, (ii), is likely to operate only if a reductive elimination is assumed. A nucleophilic attack of Cl^- on A should give inversion of configuration since $[(CO)_3LCoCl]^+$ is expected to be a good leaving group.

Nucleophilic cleavage. We have studied the cleavage of these complexes with various types of nucleophiles. The observed stereochemistry can be either retention or inversion of configuration, as determined by Walden cycles and

TABLE 4

STEREOCHEMISTRIES OF ELECTROPHILIC CLEAVAGE OF TRANSITION METAL—SILICON BONDS

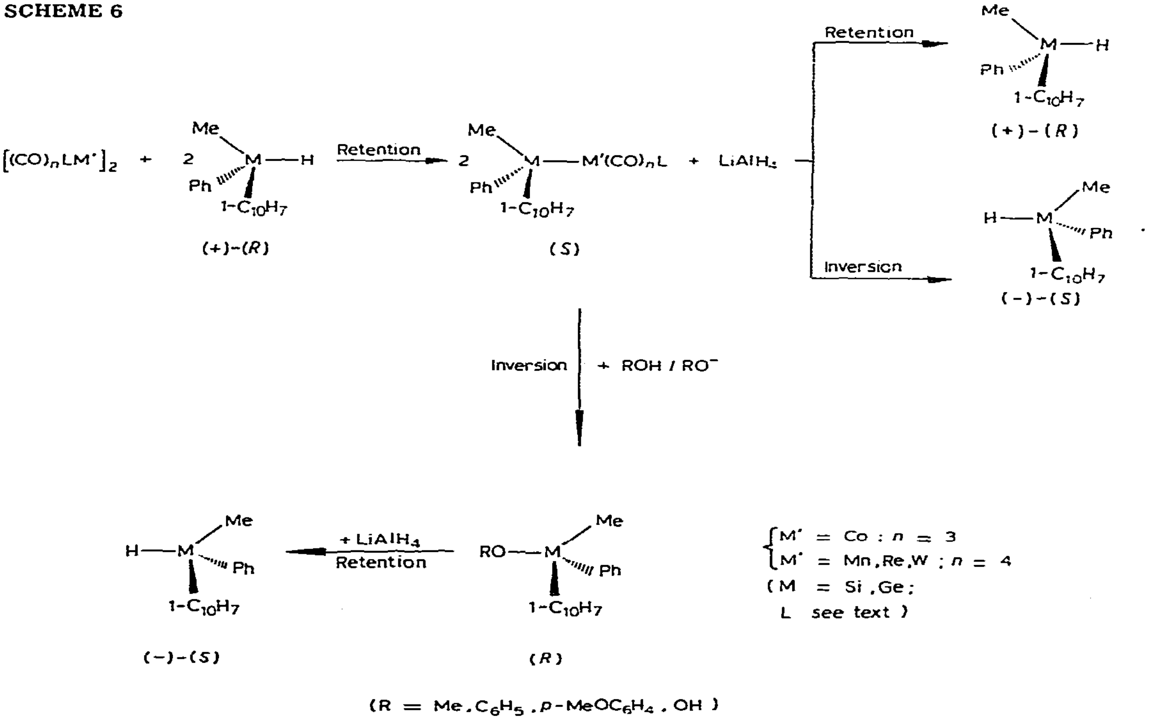
Compound [a]		Reagent	Stereochemistry (%)
$(CO)_4CoSiR_3$	(1)	Cl_2	80 RN [b]
$(CO)_4CoSiR_3$	(1)	$Cl_2/AlCl_3$ [c]	80 RN
$(CO)_3P(OPh)_3CoSiR_3$	(2)	Cl_2	84 RN
$(CO)_3P(OPh)_3CoSiR_3$	(2)	$Cl_2/AlCl_3$ [c]	75 RN
$(CO)_3PPh_3CoSiR_3$	(3)	Cl_2	75 RN
$(CO)_3Pcy_3CoSiR_3$	(4)	Cl_2	78 RN
$(CO)_5MnSiR_3$	(13)	Cl_2	no reaction

[a] R_3 = MePh(1-$C_{10}H_7$). [b] RN = retention. [c] 2 mol of $AlCl_3$ per mol of complex.

calculated as defined in ref. 28. An example is shown in Scheme 6.

The experimental results are reported in Table 5. $LiAlH_4$ cleaved the M′—M bond to give the hydrogeno-silane or -germane. Other nucleophiles (MeO^-/MeOH, sodium phenoxides or water) cleaved the M′—Si bond and gave the alkoxysilane, phenoxysilane or silanol, which was not isolated, but converted in situ into the hydrogenosilane by $LiAlH_4$ reduction, with complete retention of configuration [5c] (Scheme 6).

SCHEME 6



The main experimental facts may be summarized as follows:

(i) The results obtained for the cleavage of the silicon—transition metal and germanium—transition metal bonds are similar as has been observed previously [29].

TABLE 5

STEREOCHEMISTRIES OF NUCLEOPHILIC CLEAVAGES OF TRANSITION METAL—SILICON (OR —GERMANIUM) BONDS

The percentages of stereochemistry are calculated as defined in ref. 28, assuming that all complexes are optically pure and using the maximum rotations for MePh(1-$C_{10}H_7$)SiH $[\alpha]_D^{25}$ ± 36° and MePh(1-$C_{10}H_7$)GeH $[\alpha]_D^{25}$ ± 26.7° (cyclohexane). R_3 = MePh(1-$C_{10}H_7$). RN = retention, INV = inversion of configuration.

Compounds		Nucleophiles						
		$LiAlH_4/Et_2O$	$LiAlH_4$/DME	MeONa/MeOH	MeOH	p-RC_6H_4ONa	H_2O	F^-
$(CO)_4CoSiR_3$	(1)	91 INV	94 INV	63 INV [a] rac [b]	55 INV	86 INV (R = H) 85 INV (R = Me)	62 INV	Rac [c]
$(CO)_3P(OPh)_3CoSiR_3$	(2)	91 INV		no reaction				
$(CO)_3PPh_3CoSiR_3$	(3)	68 INV				no reaction		
$(CO)_3Pcy_3CoSiR_3$	(4)	58 RN	80 INV	no reaction				
$(CO)_4CoGeR_3$	(5)	87 INV				racemization		
$(CO)_3P(OPh)_3CoGeR_3$	(6)	87 INV	89 INV					
$(CO)_3P(OEt)_3CoGeR_3$	(7)	65 INV [e]						
$(CO)_3P(t\text{-}Bu)_3CoGeR_3$	(11)	63 INV [e]						
$(CO)_3PPh_3CoGeR_3$	(8)	60 INV						
$(CO)_3Pcy_3CoGeR_3$	(9)	rac	81 INV					
$(CO)_3[C(OEt)n\text{-}Bu]CoGeR_3$	(12)	55 RN				no reaction		
$(CO)_3P(n\text{-}Bu)_3CoGeR_3$	(10)	58 RN	82 INV					
$(CO)_5MnSiR_3$	(13)	68 RN	69 RN	53 RN	57 RN		66 RN	Rac [d]
$(CO)_4PPh_3MnSiR_3$	(14)	66 RN						
$(CO)_5MnGeR_3$	(15)	57 RN						
$(CO)_4[C(OEt)Me]MnGeR_3$	(16)	57 RN	62 RN					
$(CO)_4[C(OEt)Me]ReGeR_3$	(17)	53 RN						
$(CO)_4NOWGeR_3$	(18)	67 RN						

[a] MeOH/MeONa = 4.3 molar ratio. [b] MeOH/MeONa = 82 molar ratio. [c] F^- from CsF or $FNMe_3CH_2Ph$ (ref. 3). [d] F^- from CsF. [e] Complexes **7** and **11** were oils and could not be crystallized until constant optical rotation.

(ii) For a given nucleophile the stereochemical behaviour depends on the geometry and is quite different for trigonal bipyramidal and octahedral complexes.

The stereochemistry of cleavage of the Si—Co and Ge—Co bonds in trigonal bipyramidal complexes, *trans*-L$(CO)_3CoMR_3$ (M = Si, Ge), by $LiAlH_4$ in ether is strongly dependent on the nature of the ligand L (*trans* to the Co—Si (or Ge) bond. It seems to be in accord with the general rules for nucleophilic displacement at silicon [5]. In contrast, for octahedral complexes of Mn, Re and W the same stereochemistry (poor retention) is observed whatever the ligand L, and irrespective of whether it is in a *cis* or *trans* position.

This differing behaviour of pentacoordinated and hexacoordinated complexes is also shown by comparison of the results for the related complexes $(CO)_4CoSiR_3$, **1** and $(CO)_5MnSiR_3$, **13**: $(CO)_4CoSiR_3$ is always cleaved with a good inversion of configuration whatever the nature of the nucleophile, while $(CO)_5MnSiR_3$ is always cleaved with retention under the same conditions.

(iii) For cobalt complexes, the stereochemistry of cleavage by $LiAlH_4$ is strongly dependent upon the solvent. When the reaction is performed in DME, good inversion of configuration is always observed whatever the ligand L, while in ether both inversion and retention are observed depending on the nature of L.

(iv) The reported complexes show unexpected behaviour towards methoxide, phenoxide and fluoride ions, only the complexes $(CO)_4CoMR_3$, **1** and **5**, and $(CO)_5MnSiR_3$ (**13**) being cleaved by these reagents.

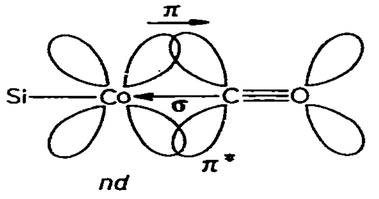
Surprisingly, when one CO ligand is replaced by a phosphorus or a carbene ligand, no cleavage occurs with phenoxides and methoxides.

Trigonal bipyramidal cobalt complexes: $(CO)_3LCoMR_3$ (M = Si, Ge)

Cleavage with $LiAlH_4$. To a first approximation, the Co—SiR_3 and Co—GeR_3 complexes appear to be similar to the R_3Si—X derivatives: the stereochemistry observed for the bond cleavage reaction in these compounds depends upon both the nature of the nucleophile and the leaving group X.

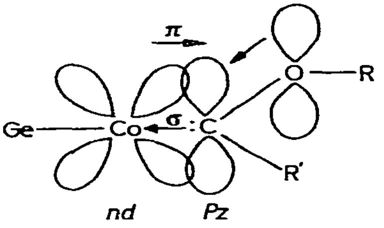
The cleavage reactions in ether solution can be rationalized by taking into account the changes of electronic properties of the silicon— or germanium—transition metal bond when the ligand *trans* (apical) to the Si—Co or Ge—Co bond is varied. These changes in electronic properties must influence the ability of the Si—M′ or Ge—M′ bond to stretch when the nucleophile approaches.

In the case of $(CO)_4CoMR_3$, **1** and **5**, good inversion is observed. The CO ligand *trans* (apical) to the Si—Co (or Ge—Co) bond increases the ease of stretching the Si—Co or Ge—Co bond when the nucleophile attacks.



The charge on the transition metal is delocalized into the carbonyl ligand and the nucleophilic cleavage takes place with good inversion of configuration. This result is in good agreement with the well known reactions of Si—Cl [30] or Si—Br [31] bonds with inversion: such bonds are easily stretched if a charged nucleophile approaches [32] and they are always displaced with inversion of configuration.

If the carbonyl ligand *trans* to the Si—Co (or Ge—Co) bond is replaced by another ligand, L, the electronic properties of the Si—Co (or Ge—Co) bond are changed, and the stereochemistry changes from good inversion to poor retention of configuration. For example, in the carbene complex **12**, the ligand, L = C(OEt)-n-Bu, is a good σ-donor and a poor π-acceptor ligand [33,34] as shown.



Since the electron density on the cobalt atom is increased, the Ge—Co bond is less able to stretch when the nucleophile attacks, and so retention of configuration is observed.

For the ligands of the type L = PR_3, the order observed for nucleophilic cleavage is:

Ligand	$P(OPh)_3 > P(OEt)_3 \simeq P(t\text{-}Bu)_3 \simeq PPh_3 > Pcy_3 > P(n\text{-}Bu)_3$	
Stereo-chemistry	Inversion	Retention

This sequence from inversion to retention reflects an increase in the σ-donor and a decrease in the π-acceptor effects of the ligands [35] with one exception, the inversion of configuration observed for the best σ-donor, $P(t\text{-}Bu)_3$. This exception may be attributed to steric factors: $P(t\text{-}Bu)_3$ is very bulky and the three CO ligands are certainly markedly bent over towards the germyl ligand, hindering the frontal attack of the hydride for retention of configuration.

As for solvent effects, inversion of configuration is observed regardless of the nature of the ligand L, when the reaction is performed in DME. This observation is in agreement with results obtained for the reduction of Si—X bonds by metal hydrides [5a,b]. A change in stereochemistry from retention to inversion is observed with increasing solvating power (Et_2O < THF < DME).

Cleavage with other nucleophiles. The results obtained for the cleavage reactions with methoxide, phenoxide and fluoride ions may be summarized as follows:

(i) Only complexes **1** and **5** (CO ligands) undergo cleavage and the reaction occurs with inversion of configuration for **1** and with racemization for **5**.

(ii) If a CO ligand is replaced by another ligand, L, no reaction occurs.

These results show the large influence of a ligand L *trans* (apical) to the Co—Si or Co—Ge bond, on the reactivity of the complexes. Thus, $LiAlH_4$, a strong nucleophile, cleaves the Si—Co or Ge—Co bond in all cases. In contrast, weaker nucleophiles (methoxide, phenoxide, fluoride ions) do not react with *trans*-$(CO)_3LCoMR_3$ (M = Si, Ge). To a first approximation the leaving group $Co(CO)_4$ can be compared with chloride [5] which is a very good leaving group, easily replaced in all cases with inversion of configuration. When the CO group *trans* (apical) to the Si—Co or Ge—Co bond is replaced by another ligand the reactivity decreases, and in the case of $L = PR_3$ or carbene the leaving group $Co(CO)_3L$ might be comparable to methoxide [36].

It is difficult to account for all the detailed features revealed by this study. The most recent explanations of nucleophilic substitution at silicon consider the reaction as a frontier orbital process between the HOMO of the nucleophile and the σ^* Si—X antibonding orbital as LUMO [5b,37]. No molecular orbital calculations have yet been performed for the Si—M′ or Ge—M′ complexes, but we expect not only the energy of the LUMO but the distribution between the σ and σ^* Si—M′ or Ge—M′ orbitals to vary with the nature of ligand L.

We also consider the possibility that the cleavage of Si—M′ or Ge—M′ bonds could involve electron transfer from the nucleophile to the complex as shown in Scheme 7.

SCHEME 7

$$Nu^- + R_3Si{-}M' \rightarrow Nu^{\bullet} + R_3Si^{\bullet}{-}M'^- \rightarrow R_3SiNu + M'^-$$

Electrochemical determinations [38] show reduction potentials for Si—M′ or Ge—M′ bonds lower than those observed for Si—Cl. These facts could be in agreement with a one electron-transfer process (Scheme 7). Further studies of this possibility are in progress.

Octahedral manganese, rhenium and tungsten complexes $(CO)_4LM'MR_3$

For these complexes, the stereochemistry is quite different: it depends neither upon the nature of the nucleophile nor upon the ease of stretching the Si—Co or Ge—Co bond. Poor retention is always observed whatever the nucleophile or the ligands. This is the first case reported in which the stereochemistry of nucleophilic displacement at silicon is independent of both the nature of the leaving group and of the nucleophile. This result is not in agreement with the general rules concerning nucleophilic substitution at silicon [5].

The complexes $(CO)_4CoSiR_3$, **1** and $(CO)_5MnSiR_3$, **13** should have comparable stereochemical behaviour to a first approximation, since the leaving groups, $(CO)_4Co$ and $(CO)_5Mn$, are both poor nucleophiles [6]. However, inversion is observed for the cobalt complex and retention for the manganese one. Furthermore, the group $(CO)_4NOW$, should behave as a good leaving group because of the presence of the stronger π-acceptor nitrosyl ligand; $(NO > CO)$ [39], and should be replaced with inversion [5b]. In fact it is replaced with retention of configuration at germanium (in $(CO)_4NOWGeR_3$ **18**) (Table 5).

These results demonstrate that the stereochemistry of cleavage depends upon the geometry of the complexes, and for octahedral ones, in particular does not seem to be in agreement with the rules of nucleophilic substitution at silicon or germanium. This could reflect differences in the distribution of energy levels in octahedral versus trigonal bipyramidal geometry.

Conclusion

Nucleophilic cleavage of octahedral complexes provides a notable exception to the leaving group rules governing nucleophilic displacement at silicon. For hexacoordinated complexes (irrespective of whether the ligand L is *cis* or *trans* to the silyl or germyl group), the stereochemistry is always poor retention of configuration whatever the metal.

In contrast, for trigonal bipyramidal cobalt complexes, the stereochemistry and reactivity depend closely on the electronic effects of the ligand L, *trans* to Co—Si or Co—Ge bond: the $Co(CO)_4$ group behaves as a good leaving group very similar to chloride, and is replaced with inversion of configuration. Replacement of a CO ligand by a phosphorus or carbene group decreases the reactivity of the complexes, and the $Co(CO)_3L$ group might be compared to methoxide.

Experimental section

All experiments were carried out in Schlenk tubes under nitrogen on a vacuum line. All solvents were dried, distilled and deoxygenated. Starting materials were purchased from Strem Chemicals ($Co_2(CO)_8$, $Mn_2(CO)_{10}$) or prepared by literature methods (triphenylsilane [40], (+)-methylphenyl-1-naphthylsilane [41], triphenylgermane [42], (+)-methylphenyl-1-naphthylgermane [13b], (+)-(*S*)-$(CO)_4CoSiMePh(1\text{-}C_{10}H_7)$ [3,43], (+)-(*S*)-$(CO)_4CoGeMePh(1\text{-}C_{10}H_7)$ [3], (—)-(*S*)-$(CO)_4[C(OEt)Me]MnGeMePh(1\text{-}C_{10}H_7)$ and (—)-(*S*)-$(CO)_4[C(OEt)Me]ReGeMePh(1\text{-}C_{10}H_7)$ [19]).

Melting points were taken under vacuum with a Dr Tottoli apparatus and are uncorrected. IR spectra were recorded with a Perkin—Elmer 257 or 298 spectrophotometer, and NMR spectra on a Varian EM 360 or 390 spectrograph using TMS as internal standard. Optical rotations were measured with a Perkin—Elmer 141 or 241 polarimeter.

Elemental analyses are listed in Table 6 and optical rotations of new compounds in Table 7.

Preparation of cobalt complexes $(CO)_3(PR_3)CoMR'_3$ **2, 3, 4, 6—11**

These compounds were prepared by the procedure described previously for (triphenylphosphine)(triphenylgermyl)tricarbonylcobalt and (triphenylphosphite)(triphenylgermyl)tricarbonylcobalt [9].

The preparation of racemic **3** is described as an example. 4.05 g of $[(CO)_3PPh_3Co]_2$ [44] (5 mmol) and 2.48 g of racemic $MePh(1\text{-}C_{10}H_7)SiH$ (10 mmol) were refluxed in 60 ml of benzene or toluene for 72 h. A black residue was formed and was removed by filtration through a fritted funnel (G4). The filtrate was concentrated to ca. 30 ml and 30 ml of hexane were added. After standing at —20°C off-white crystals were obtained. Ten or fifteen further crystallizations gave the analytical pure sample, 1.93 g (yield 30%).

Compounds **2** and **6**, **4** and **9**, **7**, **10**, **11** were obtained in the same manner starting respectively from $[(CO)_3P(OPh)_3Co]_2$ [44], $[(CO)_3Pcy_3Co]_2$ [45], $[(CO)_3P(OEt)_3Co]_2$ [44], $[(CO)_3P(n\text{-}Bu)_3Co]_2$ [46] and $[(CO)_3P(t\text{-}Bu)_3Co]_2$ [47] and the corresponding silane or germane.

Yields, melting points and colour of new compounds are given in Table 8.

TABLE 6

ELEMENTAL ANALYSES FOR NEW COMPOUNDS

Compound	Formula	Analyses (Found (calcd. (%))			
		C	H	Mn	N
$(CO)_3P(OPh)_3CoSiPh_3$	$C_{39}H_{30}CoO_6PSi$	65.21 (65.73)	4.37 (4.21)		
2 [a]	$C_{38}H_{30}CoO_6PSi$	65.12 (65.15)	4.43 (4.29)		
3 [a]	$C_{38}H_{30}CoO_3PSi$	69.73 (69.94)	4.94 (4.60)		
$(CO)_3Pcy_3CoSiPh_3$	$C_{39}H_{48}CoO_3PSi$	69.03 (68.62)	7.21 (7.04)		
4 [a]	$C_{38}H_{48}CoO_3PSi$	68.51 (68.06)	7.25 (7.16)		
6 [a]	$C_{38}H_{30}CoGeO_6P$	62.09 (61.24)	4.76 (4.03)		
$(CO)_3P(OEt)_3CoGePh_3$	$C_{27}H_{30}CoGeO_6P$	52.73 (52.89)	5.08 (4.90)		
8 [a]	$C_{38}H_{30}CoGeO_3P$	65.90 (65.46)	4.53 (4.31)		
$(CO)_3Pcy_3CoGePh_3$	$C_{39}H_{48}CoGeO_3P$	64.79 (64.41)	6.68 (6.61)		
9 [a]	$C_{38}H_{48}CoGeO_3P$	64.09 (63.81)	6.94 (6.72)		
$(CO)_3P(n\text{-}Bu)_3CoGePh_3$	$C_{33}H_{42}CoGeO_3P$	60.99 (61.05)	6.48 (6.48)		
10 [a]	$C_{32}H_{42}CoGeO_3P$	60.26 (60.32)	6.64 (6.60)		
$(CO)_3P(t\text{-}Bu)_3CoGePh_3$	$C_{33}H_{42}CoGeO_3P$	61.07 (61.05)	6.47 (6.48)		
14 [a]	$C_{39}H_{30}MnO_4PSi$	68.90 (69.23)	4.52 (4.44)	8.32 (8.14)	
15 [a]	$C_{22}H_{15}GeMnO_5$	54.36 (54.25)	3.20 (3.08)		
18 [a]	$C_{21}H_{15}GeNO_5W$	40.12 (40.82)	2.55 (2.43)		2.31 (2.27)

[a] $R_3 = MePh(1\text{-}C_{10}H_7)$.

(S)-(Ethoxy-1-n-butylcarbene)(methylphenyl-1-naphthylgermyl)tricarbonylcobalt 12

The procedure is described in ref. 17.

To 231 mg of (*S*)-$(CO)_4CoGeMePh(1\text{-}C_{10}H_7)$ [3] $[\alpha]_D^{25}$ + 2.7° (0.5 mmol) in 20 ml ether at −78°C, 0.67 ml of a 0.75 *M* solution of n-BuLi in ether (0.5 mmol) was added with stirring. The mixture turned yellow. It was allowed to warm to room temperature, the solvent was pumped off, and the yellow residue was treated with water and 100 mg (0.52 mmol) of Et_3OBF_4. After one hour, the mixture was extracted with ether and dried over Na_2SO_4. Ether

TABLE 7

OPTICAL ROTATIONS OF NEW COMPLEXES

Compound	Configuration	$[\alpha]_D^{25}$ (°)	$[\alpha]_{578}^{25}$ (°)	$[\alpha]_{546}^{25}$ (°)	$[\alpha]_{436}^{25}$ (°)	Concentration (g/l)	Solvent
2	*S*	−6,4	−7,9	−11,3	−39,1	6,576	benzene
3	*S*	−6,5	−8,1	−13,2		4,026	benzene
4	*S*	−5,7	−6,2	−6,7	−39,2	5,664	benzene
6	*S*	−3,5	−4,4	−5,8	−24,3	5,19	benzene
8	*S*	−5,4	−5,7	−8,4	−35,2	3,692	benzene
9	*S*	+4,6 [a]				3,942	benzene
10	*R*	+5,4	+6,0	+9,5	+35,2	3,354	benzene
13	*S*	−107,1	−113,1	−133,6	−289,8	10,040	pentane
14	*S*	−150	−158	−187	−416	2,6	benzene
15	*R*	+60,5				2,2	hexane
18	*S*	−85	−91,4	−110,8		2,528	pentane

[a] Surprisingly compound *S* **9** shows a positive $[\alpha]_D$. A negative sign should be expected by analogy to the other *S* compounds, mainly *S* **4**.

TABLE 8

YIELDS AND COLOURS OF NEW COMPOUNDS

Compound	Yield (%)	m.p. (°C) [a]	Colour
$(CO)_3P(OPh)_3CoSiPh_3$	45	146—148 dec	white
2	17—18	124—125 dec (86 dec)	white
3	14—30	186 dec (161 dec)	white
$(CO)_3Pcy_3CoSiPh_3$	40	228 dec	off white
4	25—62	218 dec (185 dec)	light brown
6	52—63	123—124 dec (74—76 dec)	white
$(CO)_3P(OEt)_3CoGePh_3$	50	150—152 dec	off white
7	25—45	gum	brown
8	20—44	198—199 dec (210—211.5 dec)	tan
$(CO)_3Pcy_3CoGePh_3$	63	260 dec	white
9	30—53	234 dec (206 dec)	white
$(CO)_3P(n\text{-}Bu)_3CoGePh_3$	69	127—128 dec	white
10	43—71	118—119 dec (85 dec)	off white
$(CO)_3P(t\text{-}Bu)_3CoGePh_3$	42	234—235 dec	light green
11	45	oily	tan gum
12		oily	orange
13	13	oily	colourless
14	20	201—203	yellow
15	20—43	oily (124.5—125.5)	pale yellow
18	38—40	120—121 (102—104)	orange

[a] In brackets m.p. of the racemic compound.

was pumped off and the oily residue chromatographed on silica gel using toluene/hexane (1/9) as eluant. The pale yellow fraction was collected. The solvent was pumped off. The oily residue was dissolved in pentane and kept at —20°C. Yellow crystals were obtained, but they melted at room temperature. No further purification was attempted, and the oil was used directly for cleavage reactions.

The NMR spectrum (in $CDCl_3$) showed signals at (δ ppm) 7.50 (12H, multiplet, aromatic); 4.98 (2H, quartet, OCH_2); 3.33 (2H, triplet, $-\overset{O}{\overset{\|}{C}}-CH_2$); 2.00—0.38 (13H with low resolution, (1.55, triplet, OCH_2CH_3; 1.20, singlet, CH_3Ge; 0.90 triplet, $CH_2CH_2CH_3$)).

(—)-(S)-Methylphenyl-1-naphthylsilylpentacarbonylmanganese 13 *and (+)-(R)-methylphenyl-1-naphthylgermylpentacarbonylmanganese* 15

These compounds were prepared by a modification of the procedure described in ref. 18.

A mixture of 1 g of $Mn_2(CO)_{10}$ (2.6 mmol) and 1.44 g of $MePh(1\text{-}C_{10}H_7)SiH$ (5.8 mmol) $[\alpha]_D^{25}$ +35° was heated in a sealed, evacuated tube at 150°C for 72 h, and the tube was then cooled and opened. The unreacted $Mn_2(CO)_{10}$ was sublimed out at ~65°C under ~0.1 mmHg. The solid residue was taken up with toluene and Florisil. The solvent was removed at reduced pressure on a rotary evaporator. The adsorbed sample was then placed on a Florisil column made up with hexane. Elution with hexane yielded a yellow band of unreacted $Mn_2(CO)_{10}$. A mixture of a small quantity of unreacted silane and $(CO)_5MnSiR_3$ was obtained with hexane/benzene (1/1). Elution was monitored by IR spectroscopy.

Further purification was performed by column chromatography on silica gel. A colourless band was eluted with hexane/benzene (1/1). 400 mg of oily **13** $[\alpha]_D^{25}$ —107° (pentane) were obtained.

Racemic **15** was obtained in the same manner. The product was crystallized from hexane at —20°C.

trans-(—)-(S)-(Triphenylphosphine)(methylphenyl-1-naphthylsilyl)tetracarbonylmanganese **14**

This was made by a procedure described in ref. 19.

A mixture of 858 mg of $[(CO)_4PPh_3Mn]_2$ [48] (1 mmol), 496 mg of (+)-MePh-(1-$C_{10}H_7$)SiH $[\alpha]_D^{25}$ +34° (2 mmol) and 8 ml of benzene was sealed in an evacuated tube and heated at 130°C for 72 h. The tube was then cooled and opened, 30 ml of benzene were added, and the solution was filtered. The solvent was pumped off, and the solid residue was taken up with 20 ml of toluene, 20 ml of pentane were added and the solution was left at —20°C to give a yellow solid $[\alpha]_D^{25}$ —116° (benzene). This solid residue was recrystallized from toluene at —20°C. Crystals were obtained $[\alpha]_D^{25}$ —136° (benzene), m.p. 189—200°C (d) under vacuum. Further purification of the product was performed by chromatography on Florisil, with benzene as eluant. Benzene was pumped off and the yellow residue was recrystallized in toluene at —20°C to give 270 mg of yellow crystals (yield 20%) $[\alpha]_D^{25}$ —150° (benzene).

trans(—)-(S)-(Methylphenyl-1-naphtylgermyl)nitrosyltetracarbonyltungsten **18**

To a stirred suspension of 153 mg of $NOBF_4$ (1.32 mmol) in 10 ml CH_2Cl_2 at —78°C, a solution of 740 mg of (—)-(*S*)-$[(CO)_5WGeMePh(1\text{-}C_{10}\text{-}H_7)]NEt_4$ [20] $[\alpha]_D^{25}$ —103° (1 mmol) in 20 ml CH_2Cl_2 was added dropwise. The solution was left at —20°C overnight. The solvent was pumped off at ~—10°C and the residue extracted several times with pentane. Pentane was removed in vacuo and the residue crystallized several times from hexane at —20°C. Orange crystals of (*S*)-(methylphenyl-1-naphthylgermyl)(nitrosyl)tetracarbonyltungsten **18** (250 mg, 40%) were obtained.

Yields, melting points and colour of new compounds are reported in Table 8.

Cleavage reactions with chlorine

All cleavage reactions were carried out in the same manner, and the cleavage of complex **2** is given as an example. To 350 mg of **2** $[\alpha]_D^{25}$ — 6.4° (0.5 mmol) in 30 ml of CCl_4 at room temperature were added 4.3 ml of a 0.23 *M* solution of Cl_2 in CCl_4 (1 mmol). The solution was stirred overnight. Gas evolution occurred and a blue precipitate separated. The solvent was pumped off and the residue was extracted with pentane. The solution was filtered and the solvent pumped off again. The white residue was dissolved in ether and slowly added to a suspension of $LiAlH_4$ in ether at room temperature. After hydrolysis, the solution was extracted with ether, the solvent pumped off and the pure silane separated by preparative thin-layer chromatography on silica gel (elution with benzene/hexane 1/9). 123 mg of MePh(1-$C_{10}H_7$)SiH $[\alpha]_D^{25}$ —24.1° (cyclohexane) (yield 100%) were obtained and found to be identical with an authentic sample [41].

The results obtained are reported in Table 9.

TABLE 9

CLEAVAGE REACTIONS WITH Cl_2 AND $Cl_2/AlCl_3$

Compound	$[\alpha]_D^{25}$ (°)	Reagent	$[\alpha]_D^{25}$ of recovered silane (°)	Yield (%) (silane) [a]
(*S*)-1	+2	$Cl_2/AlCl_3$	−21.9	98
(*S*)-2	−6.4	Cl_2	−24.1	100
(*S*)-2	−6.4	$Cl_2/AlCl_3$	−18.1	98
(*S*)-3	−6.5	Cl_2	−18.2	93
(*S*)-4	−5.7	Cl_2	−20.1	79
(*S*)-13	−53.4	Cl_2		no reaction

[a] After $LiAlH_4$ reduction.

Cleavage reactions with $Cl_2/AlCl_3$ of compounds **1** *and* **2**

To 210 mg of **2** $[\alpha]_D^{25}$ −6.4° (0.3 mmol) and 81 mg of $AlCl_3$ (0.6 mmol) in 30 ml of CCl_4 were added 2.9 ml of a 0.21 *M* solution of Cl_2 in CCl_4 (0.6 mmol) at room temperature. Work-up as above afforded 73 mg of silane $[\alpha]_D^{25}$ −18.13° (cyclohexane) (yield 98%) which was identical with an authentic sample [41].

The same procedure was used for the cleavage of **1** $[\alpha]_D^{25}$ + 2° affording the silane $[\alpha]_D^{25}$ − 21.9° (cyclohexane) (yield 98%).

Cleavage reactions with $LiAlH_4$ in ether

The cleavage of **2** is given as an example. 350 mg of **2** $[\alpha]_D^{25}$ −6.4° (0.5 mmol) in 30 ml of ether were added to a suspension of an excess of $LiAlH_4$ in 50 ml of Et_2O at room temperature. The mixture was stirred for 2 h, then hydrolyzed with a 4 *N* HCl solution. The solution was extracted with ether, the solvent was pumped off and the silane was isolated by preparative thin-layer chromatography. 111 mg of $MePh(1\text{-}C_{10}H_7)SiH$ $[\alpha]_D^{25}$ −28.5° (cyclohexane) (yield 90%) were obtained and shown to be identical with an authentic sample [41].

The same procedure was used for the other complexes except that the mixture was sometimes refluxed for 8 to 24 h.

Cleavage reactions with $LiAlH_4$ in dimethoxyethane

The same procedure as above was employed using DME as solvent. The results are shown in Table 10.

Cleavage reactions with sodium methoxide

A solution of 209 mg of **1** $[\alpha]_D^{25}$ + 1.5° (0.5 mmol) in 10 ml of benzene was added to a solution of sodium methoxide [49] in 15 ml of benzene at room temperature. The mixture was stirred for 2 h, and after this time IR spectroscopy showed the disappearance of carbonyl absorptions due to **1**. The solvent was pumped off and the residue extracted with pentane. The solution was filtered and the pentane evaporated. The solid residue was identical with an authentic sample of methylphenyl-1-naphthylmethoxysilane [5c]. It was dissolved in ether and converted into silane by reduction with $LiAlH_4$ in ether. The usual work up afforded 28 mg of silane $[\alpha]_D^{25}$ −6.8° (cyclohexane) yield 23%), which was identical with an authentic sample [41].

Cleavage of **13** and attempts to cleave **2** and **4** were carried out similarly.

TABLE 10

CLEAVAGE REACTIONS WITH LiAlH$_4$

Compound	$[\alpha]^{25}_D$	Reagent	$[\alpha]^{25}_D$ of recovered silane or germane	Yield (%) (silane or germane)
(*S*)-1	+1.5°	LiAlH$_4$/DME [a]	−23.4°	60
(*S*)-2	−6.4°	LiAlH$_4$/Et$_2$O [a]	−28.4°	90
(*S*)-3	−6.5°	LiAlH$_4$/Et$_2$O [a]	−13.1°	54
(*S*)-4	−5.7°	LiAlH$_4$/Et$_2$O [b]	+5.7°	35
(*S*)-4	−5.7°	LiAlH$_4$/DME [a]	−21.9°	82
(*S*)-5	+2.7°	LiAlH$_4$/Et$_2$O [a]	−19.6°	85
(*S*)-6	−3.5°	LiAlH$_4$/Et$_2$O [a]	−19.6°	55
(*S*)-6	−3.5°	LiAlH$_4$/DME [a]	−20.7°	83
(*S*)-7		LiAlH$_4$/Et$_2$O [b]	−7.5°	54
(*S*)-8	−5.4°	LiAlH$_4$/Et$_2$O [a]	−5.3°	54
(*S*)-9	+4.6°	LiAlH$_4$/Et$_2$O [b]	0°	10
(*S*)-9	+4.6°	LiAlH$_4$/DME [b]	−16.5°	68
(*R*)-10	+5.2°	LiAlH$_4$/Et$_2$O [b]	−4.4°	23
(*R*)-10	+5.4°	LiAlH$_4$/DME [b]	+17.1°	50
(*S*)-11		LiAlH$_4$/Et$_2$O [b]	−6.5°	37
(*S*)-12		LiAlH$_4$/Et$_2$O [a]	+2.5°	40 [c]
(*S*)-13	−107°	LiAlH$_4$/Et$_2$O [a]	+12.9°	32
(*S*)-13	−64°	LiAlH$_4$/DME [a]	+8°	56
(*S*)-14	−150°	LiAlH$_4$/Et$_2$O [a]	+11.5°	68
(*R*)-15	+60.5°	LiAlH$_4$/Et$_2$O [a]	−3.8°	58
(*S*)-16	−369°	LiAlH$_4$/Et$_2$O [a]	+3.8°	71
(*S*)-16	−369°	LiAlH$_4$/DME [a]	+6.1°	52
(*S*)-17	−239°	LiAlH$_4$/Et$_2$O [a]	+1.3°	62
(*S*)-18	−85°	LiAlH$_4$/Et$_2$O [a]	+9.1°	81

[a] Reaction carried out at room temperature. [b] Reaction carried out under reflux. [c] Yield calculated from compound 5.

Cleavage reactions with phenoxides

Cleavage of triphenylgermyltetracarbonylcobalt is given as an example.

A solution of 375 mg of the complex (0.79 mmol) in 20 ml of ether was added to a suspension of 410 mg of sodium *p*-methylphenoxide (obtained by addition of *p*-methylphenol to a suspension of NaH in ether) (3.15 mmol) at room temperature. After 3 h stirring, IR spectroscopy showed that the absorptions due to the starting material had disappeared. The excess of phenoxide was filtered off and ether pumped away. The residue was extracted with hexane, the solution was filtered, and white crystals of *p*-tolyloxytriphenylgermane were obtained, m.p. 88—89°C. Mass spectrum (*m/e* assignment) 412 (molecular peak). Analysis. Found: C, 72.66; H, 5.47. $C_{25}H_{22}GeO$ calcd.: C, 73.07; H, 5.36%. It was converted into triphenylgermane by reduction with LiAlH$_4$. 120 mg (yield 50%) of germane were obtained.

Cleavage reaction with CsF

A solution of 277 mg of **2** (0.66 mmol) in 20 ml of ether was added to 1.5 g of CsF suspended in 20 ml of ether at room temperature. The mixture was stirred for 3 h. After this time **2** had reacted and the product was identified as MePh(1-$C_{10}H_7$)SiF by comparison with an authentic sample [50]. The solvent

TABLE 11

CLEAVAGE REACTIONS WITH OTHER NUCLEOPHILES

Compound	$[\alpha]_D^{25}$	Reagent	$[\alpha]_D^{25}$ of recovered silane (in cyclohexane)	Yield (%) silane [c]
(*S*)-1	+1.5°	$MeO^-/MeOH$ [a]	0°	25
(*S*)-1	+1.5°	$MeO^-/MeOH$ [b]	−6.8°	25
(*S*)-1	+1.5°	PhONa	−19.2°	72
(*S*)-1	+1.5°	*p*-MePhONa	−19°	22
(*S*)-1	+1.5°	CsF	0°	30
(*S*)-5	+2.7°	*p*-MePhONa	+0.2°	83
(*S*)-13	−106°	$MeO^-/MeOH$ [b]	+2.2°	25
(*S*)-13	−51°	MeOH	+2.3°	30
(*S*)-13	−64°	CsF	0°	30
(*S*)-13	−64°	H_2O	+7°	78

[a] MeOH/MeONa 82 molar ratio. [b] MeOH/MeONa 4.3 molar ratio. [c] After $LiAlH_4$ reduction (retention of configuration for Si—O bond and inversion for Si—F bond cleavages [5c]).

was pumped off, the residue extracted with pentane, pentane evaporated and the white residue dissolved in ether and added to a suspension of $LiAlH_4$ in ether. The usual work-up afforded 50 mg of racemic silane (yield 30%).

13 was cleaved in the same manner.

The results obtained for cleavage reactions with methoxide, phenoxide and fluoride ions are reported in Table 11.

Cleavage of **13** *with methanol*

A solution of 90 mg of **13** $[\alpha]_D^{25}$ −51° (0.2 mmol) in 10 ml of benzene was added to 10 ml of methanol at room temperature. After 2 h, IR spectroscopy showed that the absorptions due to **13** had disappeared. The solvent was pumped off and the residue extracted with pentane. The solution was filtered and evaporation of pentane afforded the corresponding methoxysilane which was reduced by $LiAlH_4$ to give 15 mg of $MePh(1\text{-}C_{10}H_7)SiH$ $[\alpha]_D^{25}$ + 2.3° (cyclohexane) (yield 30%), which was identical with an authentic sample [41].

Cleavage of **13** *with water*

A solution of 120 mg of **13** $[\alpha]_D^{25}$ −64° (0.27 mmol) in 15 ml of ether was added to 10 ml of water at room temperature and stirred for 12 h. The mixture turned yellow and the IR absorptions due to **13** disappeared. The mixture was extracted with ether, the ether was pumped off, and the residue was dissolved in di-n-butyl ether and added to a suspension of $LiAlH_4$ in $n\text{-}Bu_2O$. This was refluxed for 2 h. The usual work-up afforded 53 mg of $MePh(1\text{-}C_{10}H_7)SiH$ $[\alpha]_D^{25}$ + 7° (cyclohexane) (yield 78%), which was identical with an authentic sample [41].

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