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INTRODUCTION OF OPTICALLY ACTIVE TRIORGANOGERMYL LIGANDS INTO TRANSITION METAL COMPLEXES. SYNTHESIS OF CARBENE COMPLEXES, CRYSTAL STRUCTURE AND ABSOLUTE CONFIGURATION OF *cis-S*(—)(METHYLPHENYL-1-NAPHTHYLGERMYL)-(METHYLETHOXYCARBENE) TETRACARBONYLMANGANESE *

FRANCIS CARRÉ, GENEVIÈVE CERVEAU, ERNESTO COLOMER and ROBERT J.P. CORRIU *

Laboratoire des Organométalliques, Equipe de recherche associée au CNRS No. 554, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 - Montpellier-Cedex (France)

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Summary

The attachment of triorganogermyl ligands to transition metals by displacement of a CO ligand is described. The optical stability of the germyl anions has been used to prepare a nickel-germanium complex by displacement of chloride (this reaction representing a limiting case) and more generally in the synthesis of germanium—transition metal bonds by displacement of CO (the transition metal being Cr, Mo, W, Mn, Fe, or Co). Optically active germyl anions are used in the synthesis of carbene complexes by insertion of CO ligands into a carbon—transition metal sigma bond. A crystallographic study of the complex MePh(1-Np)Ge$(CO)_4$MnC(OEt)Me reveals that the carbene unit is *cis* to the germanium and that the germyllithium has reacted with retention of configuration.

Introduction

The usual method for preparing compounds with a germanium—transition metal bond involves nucleophilic attack of a metallic anion on a halogermane [2]. However, this route cannot be used for optically active germanium since halogermanes rapidly racemize in solution [3] and the introduction of an optically active triorganogermyl ligand into transition metal complexes is a difficult problem. Furthermore, the insertion of metals into the Ge—H bond seems to be more difficult than that into the Si—H bond [4].

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* For a preliminary communication see ref. 1.

The only optically active complexes having a transition metal—germanium bond have been synthesized from germyl hydrides in reactions involving elimination of H_2 [5,6] (eqs. 1 and 2).

$$R^1R^2R^3GeH + Pt(H)Cl(PR^4_3)_2 \rightarrow PtCl(R^1R^2R^3Ge)(PR^4_3)_2 + H_2 \qquad (1)$$

$$R^1R^2R^3GeH + (CO)_8Co_2 \rightarrow R^1R^2R^3GeCo(CO)_4 + H_2 \qquad (2)$$

R^1 = Et or Me; R^2 = Ph; R^3 = 1-Np (1-naphthyl)

Two other routes to optically active complexes of germanium seem possible. One is the metal exchange already used with tin compounds [7] (eq. 3).

$$Ph_3SnCo(CO)_4 + NaY \rightarrow Ph_3SnY + NaCo(CO)_4 \qquad (3)$$

$Y = Mn(CO)_5, Re(CO)_5, (\eta^5\text{-}C_5H_5)Fe(CO)_2$

The other is the use of germyllithiums [8] in the nucleophilic displacement of halogen [9] (eq. 4) or carbonyl ligands [10—12] (eq. 5).

$$(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl + Ph_3GeLi \rightarrow (\eta^5\text{-}C_5H_5)Ni(PPh_3)GePh_3 + LiCl \qquad (4)$$

$$Mo(CO)_6 + GeCl_3AsPh_4 \rightarrow [(CO)_5MoGeCl_3]AsPh_4 + CO \qquad (5)$$

The triorganogermyl anion is of special interest for several reasons: i) it is isoelectronic with phosphines, ii) it is optically stable and iii) its use can lead to anionic species, which should show marked differences in reactivity compared with neutral complexes.

In this paper we describe the introduction of optically active germyl anions in transition metal complexes and the application of this reaction to the synthesis of carbenic complexes. The X-ray structure of a manganese-stabilized carbene is also reported.

Results and discussion

a) Synthesis of germanium-iron complexes via metal exchange

The reaction of the optically stable (*S*)(+)$(CO)_4$CoGeMePh-1-Np with the sodium salt of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ leads to the formation of a germanium—iron bond by nucleophilic displacement of the $(CO)_4Co$ moiety. However, the compound obtained is racemic (Scheme 1).

SCHEME 1

$$(S)(+)(CO)_4CoGeMePh\text{-}1\text{-}Np + [(\eta^5\text{-}C_5H_5)Fe(CO)_2]Na$$

$$\downarrow$$

$$(\pm)(\eta^5\text{-}C_5H_5)Fe(CO)_2GeMePh\text{-}1\text{-}Np + NaCo(CO)_4$$

This racemization is surprising, since the analogous silicon complex can be obtained optically active from the reaction of the iron anion on the chlorosilane [13].

(continued on p. 261)

TABLE 1

PHYSICAL PROPERTIES OF GERMYL- (OR SILYL-) -TRANSITION METAL COMPOUNDS

Formula	No.	M.p. (°C) [a]	Colour	ν(CO) (cm^{-1})	Yield (%)
$(\eta^5\text{-}C_5H_5)(CO)_2FeGePh_3$	1	157—158	Yellow	2002, 1952 [b]	36
$(\eta^5\text{-}C_5H_5)(CO)_2FeGeMePh\text{-}1\text{-}Np$	2	(126—127)	Yellow	1995, 1948 [b]	65
$(\eta^5\text{-}C_5H_5)(PPh_3)NiGeMePh\text{-}1\text{-}Np$	3	51—55 (102—104d)	Green		20—25
$[(CO)_5CrGePh_3]Et_4N$	4	228—230	White	2030, 1875 [c]	32
$[(CO)_5MoGePh_3]Et_4N$	5	197—199	White	2040, 1890 [c]	76
$[(CO)_5WGePh_3]Et_4N$	6	182—184	White	2040, 1890 [c]	75
$[(CO)_5MoSiPh_3]Et_4N$	7	188—190	Pale yellow	2040, 1890 [c]	67
$[(CO)_5CrGeMePh\text{-}1\text{-}Np]Et_4N$	8	124—125 (120—122)	Pale yellow	2020, 1880 [c]	13—14
$[(CO)_5MoGeMePh\text{-}1\text{-}Np]Et_4N$	9	114—115 (96—97)	Tan	2040, 1900 [c]	64—66
$[(CO)_5WGeMePh\text{-}1\text{-}Np]Et_4N$	10	116—117 (94—95.5)	Cream	2040, 1885 [c]	41—51
$[(\eta^5\text{-}CH_3C_5H_4)(CO)_2MnGeMePh\text{-}1\text{-}Np]Et_4N$	11	59—60 (53—55)	Yellow	1850, 1775 [c]	25—33
$[(CO)_4FeGePh_3]Et_4N$	12	247—249	White	1995, 1907, 1879 [c]	33
$[(Ph_3Ge)_2Co(CO)_3]Et_4N$	13	>260	Pale yellow	1880 [c]	28
$[Ph_3GeMn(CO)_4C(O)Me]Et_4N$	14	166—167	Yellow	2030, 1920, 1565 [d, c]	57
$Ph_3GeMn(CO)_4C(OEt)Me$	15	108—109	Yellow	2060, 1980, 1960 [e]	63
$[Ph_3GeRe(CO)_4C(O)Me]Et_4N$	16	170—172	Yellow	2060, 1965, 1950, 1920, 1560 [d, c]	34
$Ph_3GeRe(CO)_4C(OEt)Me$	17	108—109	Pale yellow	2090, 2000, 1980 [e]	60
$MePh\text{-}1\text{-}NpGeMn(CO)_4C(OEt)Me$	18	88 (108—109)	Yellow	2060, 1975, 1955 [e]	57
$MePh\text{-}1\text{-}NpGeRe(CO)_4C(OEt)Me$	19	75—76 (94—96)	Yellow	2060, 2000, 1980 [e]	48—53

[a] In brackets m.p. of the racemic compound. [b] In cyclohexane. [c] In CH_2Cl_2. [d] The last value corresponds to the acyl CO. [e] In $CHCl_3$.

TABLE 2

NMR DATA OF GERMYL-TRANSITION METAL COMPOUNDS δ (ppm) RELATIVE TO $(CH_3)_4Si$

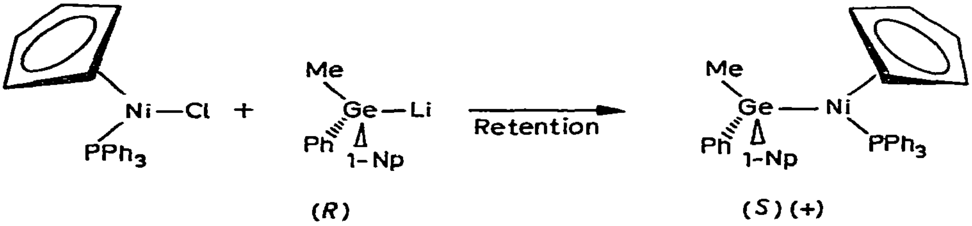
Compound No.	δ(Ar)	δ(Cp)	δ(CH_3Cp)	δ(CH_3—C)	δ(CH_2—O)	δ(CH_2—N)	δ(CH_3—Ge)	δ(CH_3—CH_2)
3 [a]	8.3—7.1(m)	4.80(s)					—0.02(s)	
8 [a]	8.2—7.1(m)					2.66(q)	0.86(s)	0.90(t) [b]
9 [a]	8.5—6.9(m)					2.48(q)	0.83(s)	0.98(t) [b]
10 [a]	8.4—6.9(m)					2.75(q)	0.88(s)	1.03(t) [b]
11 [a]	8.7—6.8(m)	3.96(m) and 3.79(m)	1.69(s)			2.60(m) [d]	0.67(s)	1.03(m) [d]
12 [a]	7.7—7.2(m)					2.80(q)		1.04(t) [b]
13 [a]	7.8—7.1(m)					2.50(q)		0.83(t) [b]
14 [a]	7.9—7.1(m)			2.13(s)		3.00(m) [d]		1.16(m) [d]
15 [c]	7.8—7.1(m)			2.47(s)	3.76(q)			1.33(t)
16 [a]	7.9—7.1(m)			2.07(s)		3.00(q)		1.17(m) [d]
17 [c]	7.7—7.0(m)			2.43(s)	3.96(q)			1.36(t)
18 [c]	8.1—7.1(m)			2.10(s)	3.15(q)		1.01(s)	1.00(t)
19 [c]	8.1—7.1(m)			2.00(s)	3.33(q) [e]		1.03(s)	1.10(t)

[a] In CD_2Cl_2. [b] Triplet of triplets: $^3J(H,H) \sim 8$ Hz, $^3J(H,N) \sim 2$ Hz. [c] In $CDCl_3$. [d] Very broad signal. [e] Broadened. s = singlet, t = triplet, q = quadruplet, m = multiplet.

b) Nucleophilic displacement of halogen in transition metal complexes by R_3GeLi

Treatment of $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$ with optically active R_3GeLi leads to the displacement of chloride ion with formation of the optically active nickel-germanium complex (Scheme 2) (Tables 1 and 2).

SCHEME 2



Since optically active germyllithium is known to retain the configuration at germanium [8,14] we attribute the *S* configuration to the new complex, when starting from the *R* germane.

Unfortunately, this method is not a general one because of the halogen-metal exchange reaction [15]. For instance, the reaction of germyllithium with $Mn(CO)_5Br$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ leads to the formation of Ge—Ge and metal—metal bonds (Scheme 3).

SCHEME 3

$$Ph_3GeLi + MX \rightarrow Ph_3GeX + MLi$$

$$Ph_3GeLi + Ph_3GeX \rightarrow Ph_6Ge_2 + LiX$$

$$MLi + MX \rightarrow M_2 + LiX$$

$M = Mn(CO)_5, (\eta^5\text{-}C_5H_5)Fe(CO)_2$

$X = Cl, Br, I$

c) Displacement of carbonyl ligands by R_3GeLi

Germyllithium compounds easily displace CO ligands of metal carbonyls, giving the corresponding anionic complexes, isolated as tetraethylammonium salts (Scheme 4).

SCHEME 4

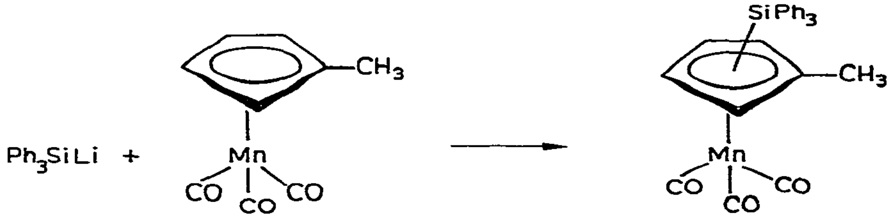
$$\begin{tikzcd} R_3GeLi + MCO \arrow[r, "Et_2O"'] & {[R_3GeM]Li + CO} \arrow[d, "Et_4NCl"] \\ & {[R_3GeM]Et_4N + LiCl} \end{tikzcd}$$

$M = Cr(CO)_5, Mo(CO)_5, W(CO)_5, (\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2, Fe(CO)_4$

$R_3 = Ph_3$ or MePh-1-Np (optically active germanium).

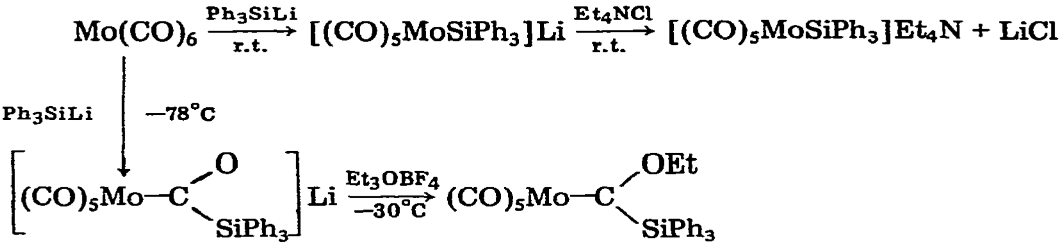
Silyllithium compounds usually react in a different way [16] (Scheme 5).

SCHEME 5



However, displacement of CO is possible, but the reaction does not proceed directly, since Fischer and coworkers have isolated the carbene complex at low temperature [17] (Scheme 6).

SCHEME 6

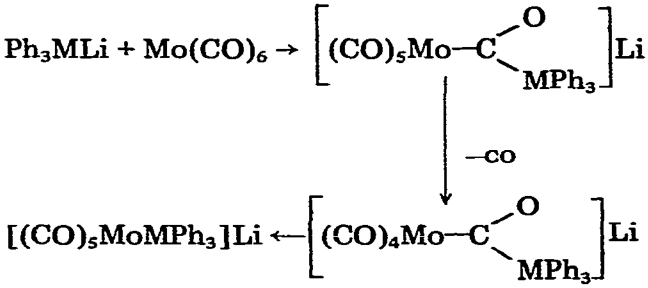


$$Mo(CO)_6 \xrightarrow[r.t.]{Ph_3SiLi} [(CO)_5MoSiPh_3]Li \xrightarrow[r.t.]{Et_4NCl} [(CO)_5MoSiPh_3]Et_4N + LiCl$$

$$Mo(CO)_6 \xrightarrow[-78°C]{Ph_3SiLi} \left[(CO)_5Mo{-}C\begin{matrix}\diagup O \\ \diagdown SiPh_3\end{matrix}\right]Li \xrightarrow[-30°C]{Et_3OBF_4} (CO)_5Mo{-}C\begin{matrix}\diagup OEt \\ \diagdown SiPh_3\end{matrix}$$

The first step in the replacement of CO is nucleophilic attack at a carbonyl ligand, and this is followed by dissociation of CO and migration of the silyl or germyl ligand (Scheme 7).

SCHEME 7

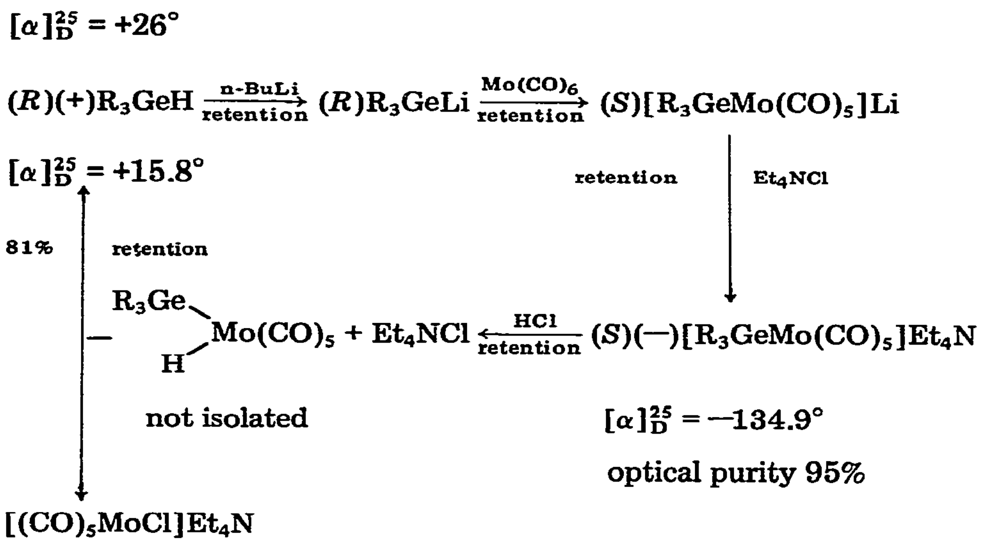


$$Ph_3MLi + Mo(CO)_6 \rightarrow \left[(CO)_5Mo{-}C\begin{matrix}\diagup O \\ \diagdown MPh_3\end{matrix}\right]Li \xrightarrow{-CO} \left[(CO)_4Mo{-}C\begin{matrix}\diagup O \\ \diagdown MPh_3\end{matrix}\right]Li \rightarrow [(CO)_5MoMPh_3]Li$$

M = Si, Ge

Because of the optical stability of the germyl anion [14] the reactions take place with retention of configuration at germanium. Moreover, treatment of the salt with HCl [18] gives the optically active germane with a high degree of retention, as shown in the following Walden cycle (Scheme 8).

SCHEME 8



The formation of the ammonium salt is assumed to take place with retention of configuration since the asymmetric center is not involved in this process. The probable effect of HCl is protonation at molybdenum; here again the asymmetric center retains its configuration. The hydride undergoes reductive elimination of germane, and Mo(CO)$_5$ reacts with Et$_4$NCl to give the well known salt [(CO)$_5$MoCl]Et$_4$N [19]. The elimination of germane is assumed to take place with retention of configuration since homogeneous hydrogermylation of alkenes and alkynes (a catalytic reaction which involves oxidative addition and reductive elimination processes) takes place with full retention of configuration [20].

The physical properties of the new complexes are shown in Tables 1, 2 and 3.

Treatment of Ph$_3$GeLi with a dinuclear metal carbonyl (Co$_2$(CO)$_8$) gives a complex with two germyl ligands bonded to cobalt (Scheme 9).

TABLE 3

OPTICAL ROTATIONS OF NEW COMPLEXES

Compound No.	Configuration	Optical purity [c]	$[\alpha]_D^{25}$ (°)	$[\alpha]_{578}^{25}$ (°)	$[\alpha]_{546}^{25}$ (°)	$[\alpha]_{436}^{25}$ (°)	Concentration (g/l)	Solvent
3	S [a]	d	+101	+79	+32	—	0.56	C_6H_{12}
8	R [b]	~96%	+149	+155	+183	—	3.12	CH_2Cl_2
9	S [a]	~95%	—135	—143	—169	—397	3.90	CH_2Cl_2
10	S [a]	~97%	—103	—108	—129	—301	3.54	CH_2Cl_2
11	R [b]	d	+3.4 [e]	+1.1 [e]	+0.3 [e]	—	6.40	CH_2Cl_2
18	S [a]	d	~~—369~~	~~—394~~	~~—485~~	~~—1722~~	~~3.982~~	~~C_5H_6~~
19	S [a]	d	—239	—255	—310	—903	3.474	C_6H_6

[a] From (R)(+)MePh-1-NpGeH. [b] From (S)(—)MePh-1-NpGeH. [c] Determined by the method of Fouquey and Jacques, [47]. [d] Not determined, complex crystallized until constant rotation. [e] Taking into account that this compound crystallizes with 1 molecule of CH_2Cl_2, optical rotations are: +3.9°, +1.2° and +0.4°, respectively.

SCHEME 9

$$\begin{tikzcd}
Ph_3GeLi + \frac{1}{2}Co_2(CO)_8 \arrow[r, "-CO"] & {[(Ph_3Ge)_2Co(CO)_3]Li} \arrow[d, "Et_4NCl"] \\
 & {[(Ph_3Ge)_2Co(CO)_3]Et_4N + LiCl}
\end{tikzcd}$$

This reaction may follow two different routes: route (a) involves initial elimination of CO followed by nucleophilic displacement of $(CO)_4Co^-$, while route (b) involves initial nucleophilic displacement of $(CO)_4Co^-$ (Scheme 10).

SCHEME 10

$$\begin{tikzcd}
Ph_3GeLi + Co_2(CO)_8 \arrow[r, "-CO", "(a)"'] \arrow[d, "-LiCo(CO)_4"', "(b)"] & {[Ph_3GeCo(CO)_3Co(CO)_4]Li} \arrow[d, "Ph_3GeLi"', "-LiCo(CO)_4"] \\
Ph_3GeCo(CO)_4 \arrow[r, "Ph_3GeLi", "-CO"'] & {[(Ph_3Ge)_2Co(CO)_3]Li}
\end{tikzcd}$$

Path (a) seems more likely. When the addition of Ph_3GeLi is carefully controlled the following features are observed: i) gas evolution occurs during the addition of the first equimolar amount of Ph_3GeLi, ii) this evolution does not take place when the second equimolar amount is added. Moreover, $Ph_3GeCo(CO)_4$, prepared independently, reacts with Ph_3GeLi giving $(Ph_3Ge)_2O$ as the major product [21] (eq. 6).

$$Ph_3GeCo(CO)_4 \xrightarrow{Ph_3GeLi} (Ph_3Ge)_2O \qquad (6)$$

The product complex seems to have the *trans* configuration as inferred from the IR spectrum, $\nu(CO)$ 1880 cm^{-1} (single strong band).

Surprisingly, treatment of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with Ph_3GeLi leads, in low yield, to the same anionic complex (eq. 7), while $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ is completely inert.

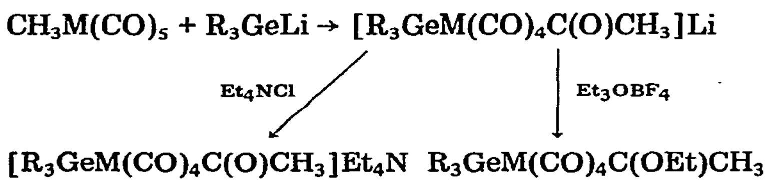
$$(\eta^5\text{-}C_5H_5)Co(CO)_2 + Ph_3GeLi \rightarrow [(Ph_3Ge)_2Co(CO)_3]Li \qquad (7)$$

d) Synthesis of carbene complexes

The reported syntheses of carbene complexes with germanium ligands start with compounds in which the germanium—transition metal bond is already present [22—25], and only in the case of cobalt is the optically active starting material available.

Methylpentacarbonylmanganese (and -rhenium) reacts with germyllithium compounds giving the anionic acyl complexes which can be isolated as tetraethylammonium salts or alkylated to give carbene complexes (Scheme 11) (Tables 1, 2 and 3).

SCHEME 11



$$\begin{tikzcd}
CH_3M(CO)_5 + R_3GeLi \arrow[r] & {[R_3GeM(CO)_4C(O)CH_3]Li} \arrow[dl, "Et_4NCl"'] \arrow[d, "Et_3OBF_4"] \\
{[R_3GeM(CO)_4C(O)CH_3]Et_4N} & R_3GeM(CO)_4C(OEt)CH_3
\end{tikzcd}$$

M = Mn, Re; $R_3 = Ph_3$ or MePh-1-Np (optically active germanium)

In this case the germyl anion reacts in the same way as a phosphine, leading to migration of a methyl group to a carbonyl ligand [26] (eq. 8) ($L = PR_3$).

$$RMn(CO)_5 + L \rightarrow RCOMn(CO)_4L \quad (8)$$

This type of reaction has also been reported with charged nucleophiles ($L = I^-$, $GeCl_3^-$) [27,28].

Similar carbenic complexes containing optically inactive germyl ligands were previously prepared by nucleophilic attack on a carbonyl ligand with CH_3Li, and are reported to have a *cis* octahedral structure as indicated by infra-red spectroscopy [22]. This *cis* structure contrasts with the *trans* configuration observed for cobalt analogues [24].

e) Crystallographic study and absolute configuration of the compound cis(S)-(—)MePh-1-NpGe(CO)$_4$MnC(OEt)Me

The computer-drawn model displayed in Fig. 1 shows the essential features of the germylmethylethoxycarbenemanganese complex. It confirms the *cis* octahedral geometry around the manganese atom and the assumed retention of configuration at germanium. The manganese—germanium distance is 2.524(4) Å, comparable with bond lengths of 2.53 and 2.54(2) Å for the compound Ph_3Ge—$Mn(CO)_5$ [29]. The manganese—carbonyl bond length *trans* to the germyl moiety, 1.72(2) Å, is significantly shorter than the average of 1.77 Å for the three *cis* Mn—CO distances. These *cis*-carbonyl groups are tilted toward the MePh(1-Np)Ge group, with a mean Ge—Mn—CO angle of 84.4° (Table 7). This is a general feature which has been noted also for germylcobalt tetracarbonyls [30,31], the germyltricarbonylcarbenecobalt complex $Ph_3Ge(CO)_3CoC(Et)(OEt)$ [24], and even for silyliron [32] and silylmolybdenum complexes [33].

As expected, the atom C(5) has the trigonal geometry, but an interesting feature is that the plane of the carbene atom, (Mn, C(5), O(5), C(6)) is roughly parallel to the mean plane of the naphthyl group. This feature brings to mind charge-transfer complexes between anthracene (or naphthalene) and electron-deficient aromatic compounds. However, we do not think such charge-transfer can take place in our complex since the carbene atom is not above the plane of the naphthyl rings but on its side (see Fig. 2).

The aim of the present crystallographic study was mainly the determination of the absolute configuration of complex 21. Figure 2 shows clearly that when the methyl group lies away from the observer, the manganese moiety, the naphthyl and the phenyl groups are encountered anti clockwise, thus defining an *S* configuration. Examination of Figs. 2 and 3 shows that the germanium

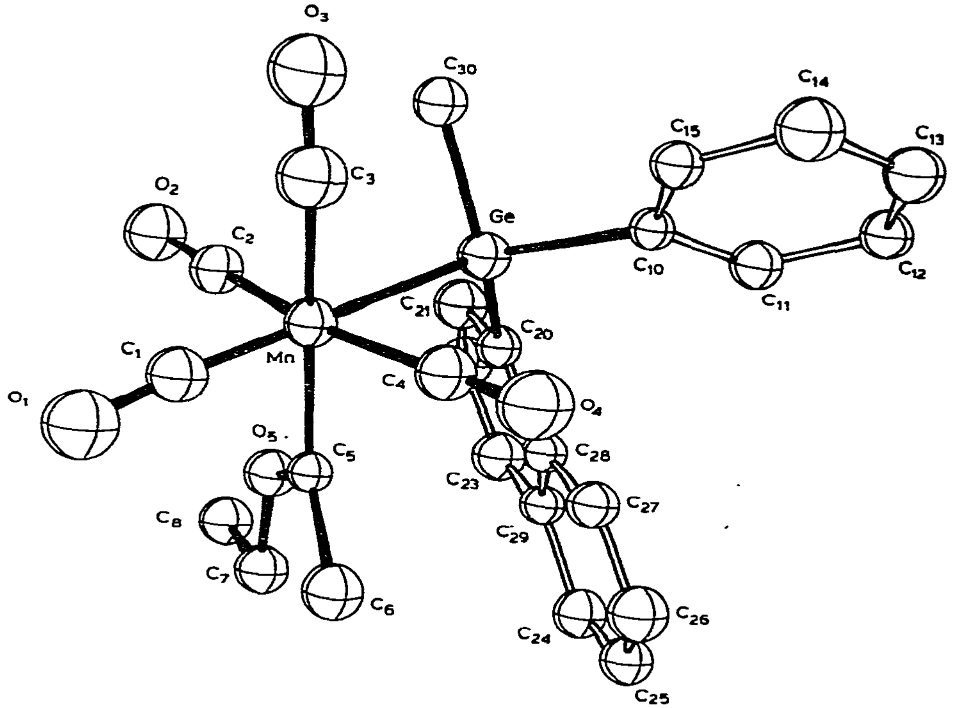


Fig. 1. ORTEP representation of (*S*)(—)MePh-1-NpGe(CO)$_4$MnC(Me(OEt) with 30% probability ellipsoids.

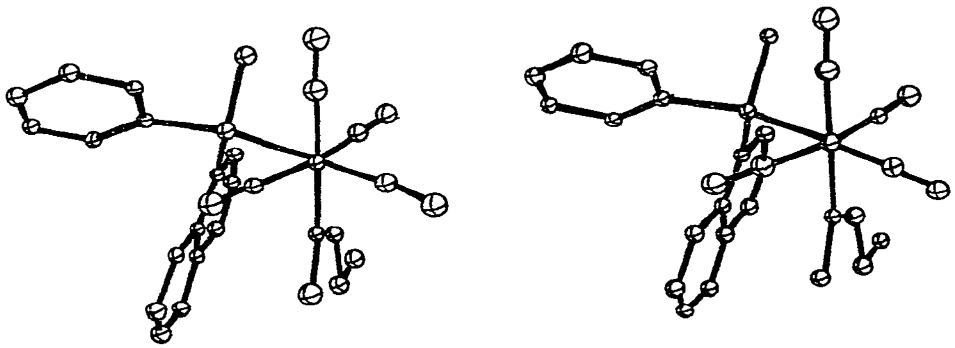
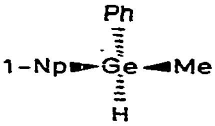


Fig. 2. Stereoscopic view of complex **18**. Thermal ellipsoids enclose 10% of the electron density.



$$\text{1-Np}\blacktriangleright\overset{\text{Ph}}{\underset{\text{H}}{\text{Ge}}}\blacktriangleleft\text{Me}$$

Fig. 3. The absolute configuration of (*R*)(+)methylphenyl-1-naphthylgermane [34].

atom in the complex and the germane (*R*)(+)MePh(1-Np)GeH [34] have the same relative configuration.

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 standard methods.

Melting points of transition metal complexes were taken under vacuum in a Tottoli apparatus and are uncorrected. IR spectra were recorded with a Perkin-

TABLE 4

ELEMENTAL ANALYSES OF NEW COMPOUNDS

Compound No.	Formula	Found (calcd.) (%)				
		C	H	N	P	Cl
1	$C_{25}H_{20}FeGeO_2$	62.40	4.15			
		(62.46)	(4.16)			
2	$C_{24}H_{20}FeGeO_2$	61.21	4.32			
		(61.49)	(4.26)			
3	$C_{40}H_{35}GeNiP$ [a]	73.30	5.60		7.63	
		(73.34)	(5.59)		(7.58)	
4	$C_{31}H_{35}CrGeNO_5$	59.76	5.50	2.11		
		(59.46)	(5.59)	(2.24)		
5	$C_{31}H_{35}GeMoNO_5$	55.15	5.24	2.09		
		(55.56)	(5.23)	(2.09)		
6	$C_{31}H_{35}GeNO_5W$	49.04	4.74	1.69		
		(49.11)	(4.62)	(1.85)		
7	$C_{31}H_{35}MoNO_5Si$	59.19	5.65	2.47		
		(59.52)	(5.60)	(2.24)		
8	$C_{30}H_{35}CrGeNO_5$	58.50	5.88	2.33		
		(58.67)	(5.70)	(2.28)		
9	$C_{30}H_{35}GeMoNO_5$	53.99	5.36	2.04		
		(54.74)	(5.32)	(2.13)		
10	$C_{30}H_{35}GeNO_5W$	47.30	4.57	1.89		
		(48.30)	(4.70)	(1.88)		
11	$C_{33}H_{42}GeMnNO_2$ [b]	58.59	6.51	2.16		9.96
		(58.57)	(6.32)	(2.01)		(10.19)
12	$C_{30}H_{35}FeGeNO_4$	58.89	5.84	2.34		
		(58.84)	(5.82)	(2.33)		
13	$C_{47}H_{50}CoGeNO_3$	63.78	4.53	1.61		
		(64.08)	(4.39)	(1.59)		
14	$C_{32}H_{38}GeMnNO_5$	59.04	5.92	2.21		
		(59.67)	(5.91)	(2.18)		
15	$C_{26}H_{23}GeMnO_5$	57.68	4.41			
		(57.50)	(4.24)			
16	$C_{32}H_{38}GeNO_5Re$	48.99	5.00	1.76		
		(49.56)	(4.90)	(1.81)		
17	$C_{26}H_{23}GeO_5Re$	46.96	3.48			
		(46.30)	(3.41)			
18	$C_{25}H_{23}GeMnO_5$	56.39	4.49			
		(56.55)	(4.36)			
19	$C_{25}H_{23}GeO_5Re$	45.36	3.58			
		(45.33)	(3.48)			

[a] Crystallizes with 1 molecule of toluene; [b] Crystallizes with 1 molecule of CH_2Cl_2.

Elmer 257 spectrophotometer and NMR spectra with a Varian EM 360 or a Bruker WP 80 FT spectrometer. Optical rotations were measured with a Perkin-Elmer 141 polarimeter.

Elemental analyses are reported in Table 4.

(η^5-Cyclopentadienyl)(methylphenyl-1-naphthylgermyl)dicarbonyliron 2 and (η^5-cyclopentadienyl)(triphenylgermyl)dicarbonyliron, 1

A solution of Na[(η^5-C_5H_5)Fe(CO)$_2$] [15], prepared from 1.2 g (3.3 mmol) of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ and 6 ml of a 1% sodium amalgam in THF (60 ml) was evaporated to dryness and the solid salt was suspended in 20 ml ether. To this suspension a solution of (*S*)(+)(CO)$_4$CoGeMePh-1-Np [6] ($[\alpha]^{25}_D$ + 2.7°, 926 mg, 2 mmol) in 20 ml ether was added at room temperature. The mixture was stirred overnight, solvent was pumped off and the residue chromatographed on acid alumina (20/80 CH_2Cl_2/hexane as eluant). The yellow band was collected, the solvent pumped off and the residue crystallized from ether/hexane at —20° C; 610 mg of racemic 2 were obtained.

Compound 1 was obtained similarly starting from (CO)$_4$CoGePh$_3$ [6].

(η^5-Cyclopentadienyl)(methylphenyl-1-napthylgermyl)(triphenylphosphine)-nickel, 3

Optically active MePh-1-NpGeLi was prepared by mixing (*R*)MePh-1-NpGeH [35] ($[\alpha]^{25}_D$ + 25°, 2.93 g, 10 mmol) in 20 ml ether with 10 mmol n-BuLi (13.3 ml of a 0.75 *M* solution in ether) and keeping the mixture for 1 hour. The solution was then added dropwise to (η^5-C_5H_5)(PPh$_3$)NiCl [36] (4.22 g, 10 mmol) in 100 ml benzene at 0°C. After stirring for 2 h, 2 ml EtOH were added and solvent was pumped off. The residue was taken up with benzene and chromatographed on acid alumina (hexane/benzene: 1/1). The deep green band was collected, the volume was reduced to ca. 25 ml and 25 ml of hexane were added. On standing at 0°C deep green crystals were obtained. The product was recrystallized twice from toluene/hexane at —20°C; 1.3 g of 3 were obtained.

Racemic 3 was obtained similarly.

Attempted reaction of Ph$_3$GeLi with Mn(CO)$_5$Br and with (η^5-C_5H_5)(CO)$_2$FeX

To 1.06 g (5 mmol) of (η^5-C_5H_5)(CO)$_2$FeCl [37] in 20 ml ether at —78°C a solution of Ph$_3$GeLi (from 1.5 g, 5 mmol, Ph$_3$GeH and 5 mmol n-BuLi) in 20 ml ether was added dropwise. The red solution turned brick red; it was allowed to warm to room temperature and the solvent was pumped off. Chromatography of the residue on acid alumina gave 1.1 g of Ph$_6$Ge$_2$ [38] (CH_2Cl_2/hexane: 50/50) and 700 mg of [(η^5-C_5H_5)(CO)$_2$Fe]$_2$(CH_2Cl_2).

The same procedure was used with Mn(CO)$_5$Br [39], (η^5-C_5H_5)(CO)$_2$FeBr [37] and (η^5-C_5H_5)(CO)$_2$FeI [40].

Syntheses of compounds 4—12

All these complexes were prepared by the same method. The synthesis of tetraethylammonium (methylphenyl-1-naphthylgermyl)pentacarbonylmolybdate 9 is given as an example.

A solution of 10 mmol of MePh-1-NpGeLi in 20 ml ether was added dropwise at room temperature to a suspension of 2.64 g (10 mmol) Mo(CO)$_6$ in 100 ml ether. The mixture turned red-orange and a vigorous evolution of gas was observed during the addition. After stirring for 2 h the solvent was pumped off and the residue taken up in CH_2Cl_2. To this solution was added 1.64 g (10 mmol (Et_4NCl in CH_2Cl_2; after 15 min the solution was filtered through a sintered disc (G4). The clear solution was evaporated and the residue taken up in THF and filtered. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (ca. 30 ml) and hexane (ca. 40 ml) was carefully added to form two layers. Standing at —20°C gave tan crystals. Two further crystallizations yielded 4.35 g of 9.

For the synthesis of compound 7, Ph_3SiLi was prepared in THF as described in ref. 41.

For chromium anions, chromium carbonyl was dissolved in THF and the ethereal solution of germyllithium was added.

Treatment of optically active 9 with HCl

To a solution of (*S*)[$(CO)_5$MoGeMePh-1-Np]Et_4N ($[\alpha]_D^{25} - 135°$, optical purity ~95% (329 mg, 0.5 mmol) in 25 ml THF were added 4 ml of a 0.135 *M* solution of HCl in ether at room temperature. The initially colorless solution turned yellow. The infrared spectrum showed the absence of starting material and new bands at 2060, 2040, 1975, 1915 and 1855 cm^{-1}, which were due to $Et_4N[(CO)_5MoCl]$. The solvent was then pumped off and the residue extracted with pentane. Evaporation of the pentane afforded 98 mg (67%) of pure MePh-1-NpGeH, which was identified by comparison with an authentic sample [35], $[\alpha]_D^{25} + 15.8°$ (cyclohexane). From the maximum rotation of the germane, $[\alpha]_D^{25} + 26.7°$ the deduced stereochemistry is 81% retention (calculated as in ref. 42).

Tetraethylammonium bis(triphenylgermyl)tricarbonylcobaltate, 13

To 3.6 g (10.5 mmol) of $Co_2(CO)_8$ in 50 ml ether, 21 mmol Ph_3GeLi in 50 ml ether was added dropwise at room temperature. During the addition of the first 25 ml vigorous gas evolution occurred. After the addition a fine crystalline precipitate formed. The solid was filtered off and dissolved in CH_2Cl_2, and 3.28 g (20 mmol) Et_4NCl in CH_2Cl_2 were added. Treatment as above and two crystallizations from CH_2Cl_2 at room temperature afforded 2.5 g of pale yellow crystals of the title compound.

Attempted reactions of $PPh_3(CO)_5Mo$ and of (1,1-bipyridyl)$Mo(CO)_4$ with Ph_3GeLi

$PPh_3(CO)_5Mo$ [43] or (1,1-bipyridyl)$Mo(CO)_4$ [44] were treated in ether at room temperature or in refluxing THF with the stoichiometric amount of Ph_3GeLi. Infrared analysis of the mixture showed that in both cases no reaction had occurred.

Syntheses of compounds 14 and 16

To 800 mg (3.8 mmol) $CH_3Mn(CO)_5$ [45] in 20 ml ether 3.8 mmol Ph_3GeLi were added dropwise at room temperature. After the usual work up and three crystallizations from CH_2Cl_2/ether, 1.4 g of tetraethylammonium (triphenylgermyl)(acetyl) tetracarbonylmanganate were obtained as yellow needles.

Compound 16 was obtained similarly from $CH_3Re(CO)_5$ [46].

Syntheses of compounds 15 and 17—19

Synthesis of (*S*)(−)(methylphenyl-1-naphthylgermyl)(methylethoxycarbene) tetracarbonylmanganese 18 is given as an example.

To 400 mg (1.9 mmol) $CH_3Mn(CO)_5$ in 10 ml ether at room temperature were added 2 mmol of (*R*)MePh-1-NpGeLi (from 584 mg of (*R*)MePh-1-NpGeH, $[\alpha]_D^{25}$ + 24.5°, and 2 mmol n-BuLi) in 10 ml ether. After stirring for 2 h, the solvent was pumped off, the residue was taken up in 40 ml CH_2Cl_2, and 1 g (excess) of Et_3OBF_4 in 10 ml CH_2Cl_2 was added. The solvent was pumped off the residue was chromatographed on silica gel with toluene as eluent. A yellow band was collected, the solvent pumped off and the residue crystallized from boiling hexane, affording 590 mg of yellow crystals.

Crystal structure determination of MePh(1-Np)Ge(CO)$_4$MnC(Me)(OEt), 18

Two successive recrystallizations by evaporation of an hexane solution improved the melting point of complex 18 from 88 to 89.5°C. Thin elongated

TABLE 5

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS (Å^2)

Atom	*x/a*	*y/b*	*z/c*	*B*
Ge	0.2341(3)	0.3690(1)	−0.1794(3)	[a]
Mn	0.1398(4)	0.2976(1)	−0.2547(5)	[a]
C(1)	0.0742(25)	0.2488(7)	−0.2987(29)	5.4(6)
O(1)	0.0134(20)	0.2168(6)	−0.3293(23)	8.3(5)
C(2)	0.1715(24)	0.2884(6)	−0.0430(29)	4.7(6)
O(2)	0.1951(17)	0.2805(4)	0.0987(21)	6.4(4)
C(3)	0.3197(33)	0.2839(8)	−0.2947(38)	7.2(8)
O(3)	0.4439(24)	0.2746(6)	−0.3064(26)	8.7(5)
C(4)	0.1243(30)	0.3187(7)	−0.4594(33)	5.8(6)
O(4)	0.1123(22)	0.3326(5)	−0.5914(24)	7.7(5)
C(5)	−0.0575(21)	0.3141(6)	−0.2048(26)	3.5(5)
O(5)	−0.0931(16)	0.3210(4)	−0.0507(18)	4.8(3)
C(6)	−0.1840(24)	0.3141(6)	−0.3233(31)	5.5(6)
C(7)	−0.2388(30)	0.3329(6)	0.0163(27)	5.6(5)
C(8)	−0.2145(25)	0.3392(6)	0.1960(27)	5.5(6)
C(10)	0.3065(20)	0.4040(6)	−0.3577(25)	3.7(5)
C(11)	0.2732(26)	0.4475(6)	−0.3618(23)	4.4(5)
C(12)	0.3400(25)	0.4740(6)	−0.4851(26)	4.2(5)
C(13)	0.4253(26)	0.4559(7)	−0.6027(28)	5.0(6)
C(14)	0.4619(28)	0.4131(8)	−0.5963(30)	5.8(6)
C(15)	0.3956(24)	0.3874(6)	−0.4746(26)	3.9(5)
C(20)	0.0996(22)	0.4030(6)	−0.0480(23)	3.2(4)
C(21)	0.1310(26)	0.4094(7)	0.1204(26)	4.9(5)
C(22)	0.0345(29)	0.4315(7)	0.2233(31)	6.1(6)
C(23)	−0.0932(27)	0.4458(7)	0.1660(31)	5.6(6)
C(24)	−0.2705(31)	0.4553(7)	−0.0687(28)	5.2(5)
C(25)	−0.2916(27)	0.4507(7)	−0.2318(31)	5.8(6)
C(26)	−0.2013(28)	0.4308(8)	−0.3427(32)	6.5(7)
C(27)	−0.0688(23)	0.4147(6)	−0.2850(27)	4.2(5)
C(28)	−0.0328(24)	0.4193(6)	−0.1121(26)	3.5(5)
C(29)	−0.1298(28)	0.4405(7)	−0.0077(29)	4.6(5)
C(30)	0.4135(25)	0.3616(7)	−0.0423(26)	5.0(5)

[a] The anisotropic thermal parameters (×10^4) for germanium and manganese are: Ge: 94(3), 10.2(2), 182(4), 4(1), −30(4), 2(1) Mn: 128(5), 8.8(4), 172(7), 5(1), −21(5), 1(2). The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

plates developed on the walls of the Schlenk flask. All such plates were twinned as revealed by a systematic examination through a polarizing microscope. Careful cleavage of a twin gave a small needle-like block of approximate dimensions 0.08 × 0.08 × 0.30 mm which was mounted with the *a* axis coincident with the φ axis of the diffractometer. Rotation and Weissenberg photographs showed orthorhombic symmetry with systematic absences ($h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$) uniquely defining space group $P2_12_12_1$.

Crystal data. $C_{25}H_{23}GeMnO_5$, $M = 530.98$, orthorhombic, $a = 9.294(3)$, $b = 32.051(10)$, $c = 8.099(2)$ Å, $V = 2412.6$ Å^3, $d_c = 1.462$, $d_m = 1.44(1)$ g cm^{-3}, $Z = 4$, Mo-K_α radiation, graphite monochromatized, $\lambda = 0.71069$ Å. μ(Mo-K_α) is 17.6 cm^{-1}. The experimental density was obtained by flotation in aqueous potassium iodide solution.

A total of 1354 reflections were measured in the range $4° < 2\theta < 40°$ on an Enraf-Nonius CAD-4 automated diffractometer using the ω—2θ scanning technique. The intensities of three standard reflections were monitored after intervals of 60 min. No significant change in their intensities occurred during data collection. All data were used in solving the structure. Most were weak reflections due to the size of the crystal: on the 588 data kept in the final refinement with $\sigma(I)/I < 0.6$ only 419 were found to have $\sigma(I)/I < 0.35$. Corrections for Lorentz and polarization effects were applied. No correction for absorption was made.

The positions of the manganese and germanium atoms were determined by direct methods, using a 1972 version of the Multan program, and carefully checked in a Patterson calculation. The remaining 30 non-hydrogen atoms were located from three successive difference Fourier syntheses. The atomic scattering factors were taken from ref. 48. Two cycles of full matrix isotropic refinement gave a residual value of $R = 0.050$. At this stage the absolute configu-

TABLE 6

INTERATOMIC DISTANCES WITH e.s.d.'s FOR MePh(1-Np)Ge(CO)$_4$MnC(Me)(OEt)

Atoms	Distance (Å)	Atoms	Distance (Å)
Ge—Mn	2.524(4)	C(10)—C(11)	1.43(3)
Ge—C(10)	1.949(20)	C(11)—C(12)	1.45(3)
Ge—C(20)	1.971(20)	C(12)—C(13)	1.37(3)
Ge—C(30)	2.017(23)	C(13)—C(14)	1.41(3)
Mn—C(1)	1.717(23)	C(14)—C(15)	1.42(3)
Mn—C(2)	1.764(24)	C(15)—C(10)	1.36(3)
Mn—C(3)	1.759(31)		
Mn—C(4)	1.797(26)	C(20)—C(21)	1.41(3)
Mn—C(5)	1.951(20)	C(21)—C(22)	1.42(3)
C(1)—O(1)	1.20(3)	C(22)—C(23)	1.35(4)
C(2)—O(2)	1.20(3)	C(23)—C(29)	1.46(3)
C(3)—O(3)	1.20(4)	C(29)—C(24)	1.48(4)
C(4)—O(4)	1.16(3)	C(24)—C(25)	1.34(3)
		C(25)—C(26)	1.38(4)
C(5)—O(5)	1.31(3)	C(26)—C(27)	1.42(3)
C(5)—C(6)	1.52(3)	C(27)—C(28)	1.45(3)
C(7)—O(5)	1.51(3)	C(28)—C(20)	1.43(3)
C(7)—C(8)	1.49(3)	C(28)—C(29)	1.41(3)

TABLE 7

SELECTED BOND ANGLES (°)

Mn—Ge—C(10)	117.6(6)	C(2)—Mn—C(3)	88.8(12)
Mn—Ge—C(20)	114.3(6)	C(3)—Mn—C(4)	90.0(13)
Mn—Ge—C(30)	108.3(6)	C(4)—Mn—C(5)	90.8(11)
C(10)—Ge—C(20)	107.5(8)	C(5)—Mn—C(2)	90.0(10)
C(10)—Ge—C(30)	101.0(8)	C(2)—Mn—C(4)	166.6(10)
C(20)—Ge—C(30)	107.0(8)	C(3)—Mn—C(5)	178.1(11)
		Mn—C—O(1—4)mean	175.7(22)
Ge—Mn—C(1)	178.0(8)	Mn—C(5)—O(5)	118.7(14)
Ge—Mn—C(2)	81.8(7)	Mn—C(5)—C(6)	126.7(15)
Ge—Mn—C(3)	86.6(9)	O(5)—C(5)—C(6)	114.0(17)
Ge—Mn—C(4)	84.8(8)	C(5)—O(5)—C(7)	127.7(16)
Ge—Mn—C(5)	91.7(6)	O(5)—C(7)—C(8)	104.4(19)

ration was determined. The germanium and manganese atoms were then given anisotropic thermal parameters. The real and imaginary parts of Ge and Mn scattering factors [49] were introduced in calculations. The structure factors were calculated for both enantiomers and the R factors were $R^+ = 0.048$ and $R^- = 0.039$. Their ratio (1.23) indicates the second model is preferred at a significance level of greater than 99.5%, [50]. Thus this model was chosen for the structure of the molecule: the absolute configuration at germanium is *S*. Two further cycles of least-squares refinement gave no changes in the agreement indices ($R_F = 0.039$, $R_{wF} = 0.050$) but reduced the largest shift-to-error ratio to 0.008. In view of the low number of observed reflections compared to the number of variables, no attempt was made to assign anisotropic thermal parameters to carbon and oxygen atoms. The final atomic coordinates with the associated thermal parameters are listed in Table 5. The labeling scheme is given on Fig. 1. Individual bond lengths are listed in Table 6, important bond angles in Table 7. A list of observed and calculated structure factor amplitudes can be obtained from the authors on request.

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