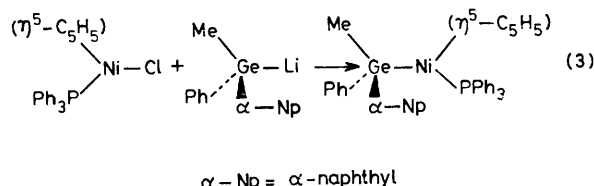


Use of Triorganogermyl-lithium Compounds in Transition Metal Chemistry. Application to the Synthesis of Optically Active Anions containing a Transition Metal–Germanium Bond

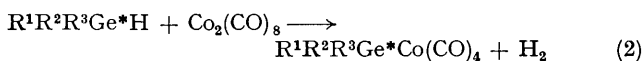
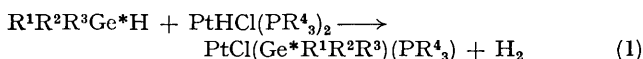
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Summary Optically active germyl-lithium compounds displace carbonyl ligands from transition metal carbonyls providing a convenient synthesis of anionic compounds containing a transition metal bonded to an optically active germanium unit.



THE general method for preparing compounds with a germanium-transition metal bond involves nucleophilic attack of a metallic anion on a halogenogermane. This route cannot be used for optically active germanium since halogenogermanes are easily racemized in solution. The only optically active complexes of this type reported have been synthesized by use of substituted germanes $\text{R}^1\text{R}^2\text{R}^3\text{-Ge*H}$; $1,2$ insertion into the Ge-H bond seems to be difficult³ [reactions (1) and (2)].



$\text{R}^1 = \text{Et}$ or Me , $\text{R}^2 = \text{Ph}$, $\text{R}^3 = \alpha\text{-naphthyl}$.

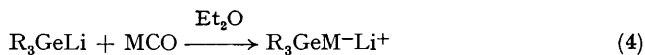
Another possible route to optically active compounds is *via* metal exchange⁴ in a configurationally stable derivative of germanium such as $(S)(+)-(\text{CO})_4\text{CoGeMePh}(\alpha\text{-Np})$.² We have succeeded in replacing the $(\text{CO})_4\text{Co}$ unit in this complex by $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}$, but the reaction yields racemic $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeGeMePh}(\alpha\text{-Np})$.

We describe here the use of an optically stable germyl-lithium compound for this reaction. We have shown⁵ the possibility of nucleophilic attack on a transition metal halide by triphenylgermyl-lithium. Since optically active germyl-lithium compounds are known to conserve the configuration at germanium during substitution,⁶ this reaction should allow the formation of $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-NiGe*MePh}(\alpha\text{-Np})$ without racemization [reaction (3)].

Unfortunately this method is not a general one. The reaction of Ph_3GeLi with $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeX}$ ($\text{X} = \text{Cl}$, Br , or I) or $\text{Mn}(\text{CO})_5\text{Br}$ leads to halogen-metal exchange^{7,8} with formation of Ph_6Ge_2 and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2$ or $\text{Mn}_2(\text{CO})_{10}$, respectively.

The most general method involves direct displacement of a carbonyl ligand by the germyl-lithium compound, and provides a convenient synthesis of transition metal anions. Several conditions have been reported for this reaction, especially in the case of Ph_3SiLi and Ph_3SnLi .⁹⁻¹¹ Surprisingly, attack of simple metal carbonyls by germyl-lithium compounds is not known, although it provides an easy synthesis of anionic transition metal complexes containing bonds to chiral and non-chiral germanium.

Reaction of triphenylgermyl-lithium and the optically active methyl(α -naphthyl)germylphenyl-lithium with $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn}(\text{CO})_3$ leads to anionic complexes, isolated as Et_4N^+ salts [reaction (4)]. The complexes prepared and their properties are in the Table.



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

Germyl-lithium compounds always react with retention of configuration at germanium.⁷ As the starting material was $(R)(+)$ -methyl(α -naphthyl)phenylgermane ($[\alpha]_D^{25} +$

TABLE. Physical properties of germyl-transition metal compounds

Formula	M.p./°C	Colour	$\nu_{\text{CO}}/\text{cm}^{-1}$	$[\alpha]_D^{25}$	% Yield
$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeGePh}_3^a$	157—158	Yellow	2002—1952 ^b		36
$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeGeMePh}(\alpha\text{-Np})$	125—127	"	1995—1948 ^b	Racemic	65
$(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{NiGeMePh}(\alpha\text{-Np})$	102—104 (decomp.)	Green		"	25
$(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{NiGeMePh}(\alpha\text{-Np})$	51—55	Green		+89 ^b	20
$[(\text{CO})_5\text{MoGePh}_3]^- \text{Et}_4\text{N}^{+a}$	197—199	White	2040—1890 ^c		76
$[(\text{CO})_5\text{WGePh}_3]^- \text{Et}_4\text{N}^{+a}$	182—184	"	2040—1890 ^c		75
$[(\text{CO})_5\text{MoGeMePh}(\alpha\text{-Np})]^- \text{Et}_4\text{N}^+$	96—97	Tan	2040—1900 ^c	Racemic	66
$[(\text{CO})_5\text{MoGeMePh}(\alpha\text{-Np})]^- \text{Et}_4\text{N}^+$	114—115	"	2040—1900 ^c	-135 ^b	64
$[(\text{CO})_5\text{WGeMePh}(\alpha\text{-Np})]^- \text{Et}_4\text{N}^+$	94—95.5	Cream	2040—1885 ^c	Racemic	41
$[(\text{CO})_5\text{WGeMePh}(\alpha\text{-Np})]^- \text{Et}_4\text{N}^+$	116—117	"	2040—1885 ^c	-103 ^b	51
$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{MnGePh}_3]^- \text{Et}_4\text{N}^+$	174—175	Yellow	1855—1775 ^c		66
$[(\text{CO})_4\text{FeGePh}_3]^- \text{Et}_4\text{N}^{+a}$	247—249	White	1995—1907 ^c		33

* These compounds have already been prepared by other methods; see refs. 3 and 11; E. E. Isaacs and W. A. G. Graham, *Canad. J. Chem.*, 1975, **53**, 467; D. Seyferth, H. P. Hoffmann, R. Burton, and J. F. Helling, *Inorg. Chem.*, 1962, **1**, 227. All compounds gave satisfactory elemental analyses and i.r. and n.m.r. spectra. Ni-Ge compounds crystallize with one molecule of solvent (benzene or toluene). ^b In cyclohexane. ^c In dichloromethane.

25°),¹² the products should all have the same absolute configuration (S).

Anions from germynl-lithium compounds are the only ones to allow the formation of optically active compounds, since

optically active silyl- or stannyl-lithium compounds are not yet known.

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