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Recent developments in arylgermyl and arylhydridogermanium-metal compounds *

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Abstract

Recent work on the synthesis, stabilization, spectroscopic analysis and chemical reactivity of new organogermyl and organohydridogermanium-metal compounds is reviewed. Various transmetallation reactions are described; these allow the formation of organogermyl-magnesium, -mercury and Main Group 14 metal derivatives from organogermylalkali metal compounds. The synthesis of organogermyltransition-metal complexes is also reviewed. Since these compounds have two reactive sites, the germanium–metal and the germanium–hydrogen bonds, a major study of their reactivity has developed, including nucleophilic substitutions and additions, transmetallation reactions, oxidations and SET reactions.

1. Introduction

The organogermylalkali metal compounds R_3GeM ($M = Li$, Na, or K) have been very useful reagents in organometallic synthesis for many years [1,2]. They germylate organic halides, metal halides, and carbonyl compounds. However, only a few reports concern organogermylalkali metal compounds [1]. In the case of the lithium series, only organohydridogermanium lithium compounds have been postulated in the reactions of organodihydrogermanes with RLi compounds ($R = Me$, Bu, or Ph) [1]; however, in these reactions competition between metallation and alkylation reactions has always been observed. Starting with organogermylalkali-metal compounds, various other organogermyl metal compounds have been obtained [1–3].

2. Organogermylalkali metal compounds

2.1. Synthesis

The hydrogermolysis procedure has been modified to permit a more specific synthesis of arylgermyllithium compounds stabilized by steric effects and nucleophilic solvents (eqn. (1)) [4–7].

$$R_nGeH_{4-n} \xrightarrow[\text{2-MeC}_3H_7]{{}^tBuLi/THF} RnH_{3-n}GeLi \qquad (1)$$

$R = Ph$ or Mes; $n = 1, 2, 3$

These metallation reactions require a slight excess of ${}^tBuLi$ (20–40%) and low temperatures to avoid competitive alkylation reactions. The stability of these compounds depends on the R group and the solvent. Thus, the very bulky Mes_3GeLi has been isolated as a solid 1 : 2 THF complex. A similar complex, $(Me_3Si)_3GeLi$ with THF, was described recently [8]. Other less bulky organogermyllithiums are less stable and must be stored in solution at low temperature. In the case of $R = Ph$ and $n = 2$ and in the presence of an amine (Et_3N or Et_2NMe) reaction (1) leads to polygermanes, via transient germylene insertions into the germanium–metal bond (Scheme 1) [4].

If a large excess of ${}^tBuLi$ (> 100%) is used, the corresponding diaryldilithiogermane is obtained in good yield (eqn. (2)).

$$R_2GeH_2 + {}^tBuLi \xrightarrow[-\text{2-MeC}_3H_7]{THF} R_2HGeLi + R_2GeLi_2 \qquad (2)$$

$R = Ph$ 41% 59%
$R = Mes$ 28% 72%

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* Dedicated to Professor M.F. Lappert with respect and admiration. We are grateful to him for his considerable contribution and our collaboration in organometallic chemistry.

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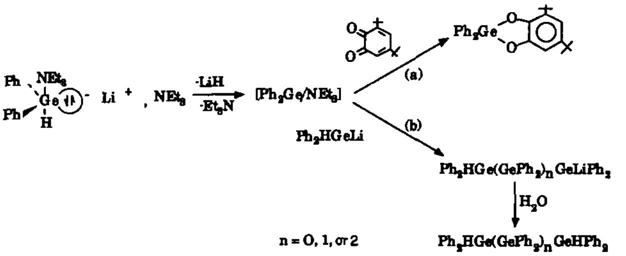


Scheme 1.

For R = Mes, hexamethylphosphoramide was used as solvent in addition to THF to optimize reaction (2).

In the case of asymmetrical aryldigermanes, one equivalent of ${}^tBuLi$ gave the monolithiated compound

$$Mes_2HGeGeHPh_2 + {}^tBuLi \xrightarrow{-2\text{-}MeC_3H_7} Mes_2LiGeGeHPh_2 \quad (3)$$

With the less sterically hindered tetraphenyldigermane, a decomposition reaction occurred with formation of polygermanes (eqn. (4a)).

$$\begin{tikzcd}
 & {[Ph_2HGeGeLiPh_2]} \arrow[r, "-LiH"] & 1/n\,(Ph_2Ge)_n \\
Ph_2HGeGeHPh_2 \arrow[ur, "1\,{}^tBuLi", "a"'] \arrow[dr, "2\,{}^tBuLi"', "b"] & & \\
 & Ph_2LiGeGeLiPh_2 &
\end{tikzcd}$$

(4)

Aryldigermyl dilithium compounds were also synthesized using the same hydrogermolysis reaction (eqns. (4b) and (5)) [7].

$$MesH_2GeGeH_2Mes \xrightarrow{{}^tBuLi} MesHLiGeGeLiHMes \quad (75\%) \quad (5)$$

2.2. Physicochemical properties

Several germylalkali metal compounds were examined by IR, UV, ${}^1H$, ${}^{13}C$ and ${}^7Li$ NMR spectroscopies to clarify the nature of the germanium–alkali metal bond and possible interactions between the germyl anion centre and the substituent linked to germanium [5–7,9–11]. Conversion of an organogermane to the corresponding organogermylalkali metal is accompanied by a bathochromic shift of the UV absorption maximum band, an upfield shift of the ${}^1H$ NMR signals, a downfield shift of the ${}^{13}C$ NMR signals and a 10% elongation of the Ge–C bond lengths when the germylalkali metals are compared with the corresponding neutral species. In addition, arylhydrogermyllithiums show a displacement of ν(GeH) to high frequency due to the inductive effect (+I) of the alkali metal.

The spectroscopic data in the aryl series can be rationalized by a polarization of the phenyl ring resulting in decreased electron density at the aromatic *ipso* carbon. Such polarization could be caused by a localized negative charge residing on the germanium, which is consistent with a predominant inductive effect and the absence of a mesomeric effect in the germyl anion. An additional feature is the effect of solvent on the ${}^1H$ and ${}^{13}C$ NMR chemical shifts. The *ipso* carbon is the most sensitive to interaction with solvent (*e.g.* THF, $N(CH_2CH_2OCH_2CH_2OCH_3)_3$, 12-crown-4) because dissociation of ion pairs occurs more readily in polar solvents and so the negative charge at germanium is increased.

Organogermyl lithium compounds have also been chemically characterized by deuterolysis and alkylation with methyl iodide, which is a very efficient reagent for these organometallic compounds (eqn. (6)).

$$\begin{tikzcd}
 & R_2HGeMe \quad R = Ph\ 68\%,\ R = Mes\ 78\% \\
R_2GeHLi \arrow[ur, "MeI", "-LiI"'] \arrow[dr, "D_2O"'] & \\
 & R_2HGeD
\end{tikzcd}$$

(6)

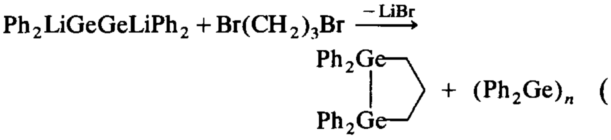
2.3. Chemical properties

2.3.1. Reaction with organic halides

The reaction of organohydridogermanium lithium compounds with organic halides is an effective way to form Ge–C bonds [5,7].

$$PhH_2GeLi + ClCH_2OCH_3 \xrightarrow{-LiCl} PhH_2GeCH_2OCH_3 \quad (73\%) \quad (7)$$

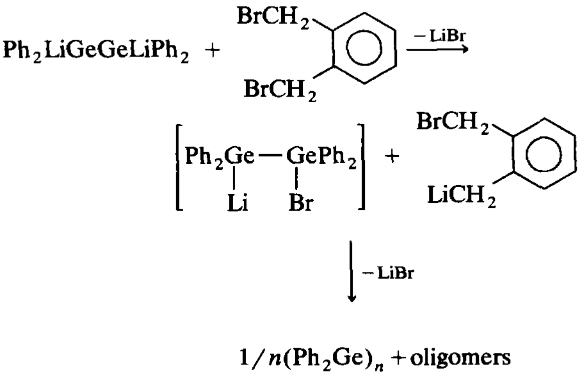
Cyclization results from the reaction of a dilithiodigermane with a dihaloalkane.



$$Ph_2LiGeGeLiPh_2 + Br(CH_2)_3Br \xrightarrow{-LiBr} \text{cyclo-}[Ph_2Ge(CH_2)_3GePh_2] + (Ph_2Ge)_n \quad (8)$$

(26%)

However, in the case of 1,2-di(bromomethyl)benzene, halogen–metal exchange is preponderant (eqn. (9)).



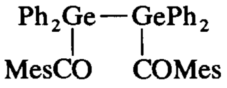
(9)

Reactions with carboxylic acid chlorides have been used to prepare acylgermanes [4,12]

$$Mes_2HGeLi + PhCOCl \xrightarrow{-LiCl} Mes_2HGeCOPh \quad (10)$$

Previously unknown digermyldiketones have been synthesized in the same way [7].

$$Ph_2LiGeGeLiPh_2 + 2MesCOCl \xrightarrow{-LiCl}$$



$$\begin{matrix} Ph_2Ge & - & GePh_2 \\ | & & | \\ MesCO & & COMes \end{matrix} \quad (11)$$

(45%)

2.3.2. Transmetallation reactions

Organogermyllithium compounds have also been used to prepare hitherto unknown hydridogermanium-magnesium compounds which could not be isolated, but their presence as intermediates was confirmed by selective germylation reactions (eqn. (12)) [13].

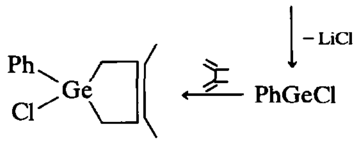
$$R_2HGeLi + MgBr_2 \xrightarrow[-LiBr]{-10°C} [R_2HGeMgBr] \quad (12)$$

$$\xrightarrow{PhClGeH_2} R_2HGeGeH_2Ph$$

R = Ph 56%
R = Mes 67%

In contrast, when the same digermanes are prepared from the organohydrogermyl lithium compounds, a competitive Li-chlorine exchange leading to a germylene was observed (eqn. (13)) [4].

$$Ph_2HGeLi + PhCl_2GeH \longrightarrow Ph_2GeH_2 + [PhCl_2GeLi]$$



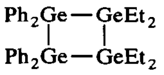
(13)

Thus, to avoid a competitive exchange reaction, lithiogermolysis of the Ge–O bond is often preferred (eqns. (14), (15)) [5,7].

$$MesH_2GeLi + MesH_2GeOMe \xrightarrow{-LiOMe} MesH_2GeGeH_2Mes \quad (14)$$

(48%)

$$Ph_2LiGeGeLiPh_2 + Et_2(MeO)Ge—Ge(OMe)Et_2 \xrightarrow{-2LiOMe}$$



$$\begin{matrix} Ph_2Ge & - & GeEt_2 \\ | & & | \\ Ph_2Ge & - & GeEt_2 \end{matrix} \quad (15)$$

(49%)

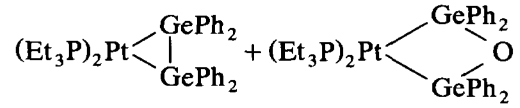
The organogermyllithiums are also efficient in the synthesis of mixed silicon-germanium compounds (eqn. (16)) [14]

$$Ar_2HGeLi + Mes_2SiCl_2 \longrightarrow Ar_2HGeSiClMes_2$$

Ar = Mes; 2,4,6-triisopropylphenyl (16)

With *trans*-dichlorobis(triethylphosphine)platinum (II), new cyclic germyltransition-metal complexes were obtained (eqn. (17)) [7].

$$Ph_2LiGeGeLiPh_2 + trans[PtCl_2(PEt_3)_2] \xrightarrow[-40°C]{-LiCl}$$



(17)

Organogermyl cuprates, which can be synthesized from germyllithium (eqn. (18)), are of particular interest in organometallic chemistry, being used, for example, in the regioselective germylation of acetylenic compounds [15].

$$2R_3GeLi + CuX \xrightarrow{THF} (R_3Ge)_2CuXLi \quad (18)$$

R = alkyl, aryl X = LiCN, SMe_2 *etc.*

A similar reaction with copper(II) chloride leads mainly to digermanes (eqn. (19)) [16].

$$R'R_2GeLi \xrightarrow[t°C]{CuCl_2} 1/2\ R_2R'GeGeR'R_2 \quad (19)$$

R′ = Mes, R = H $t = -60°C$
R′ = H, R = Mes $t = -40°C$
R = R′ = Ph $t = 20°C$

Various organogermyl-, organohalogermyl- and organopolygermyl-mercury compounds have been prepared by hydrogermolysis of dialkyl mercury (eqns. (20), (21)) [17–19]. Tetragermadimercurocane (eqn. (22)) [20] has been obtained similarly.

$$RnX_{3-n}Ge—H \xrightarrow[-2BuH]{Bu_2Hg} (R_nX_{3-n}Ge)_2Hg \quad (20)$$

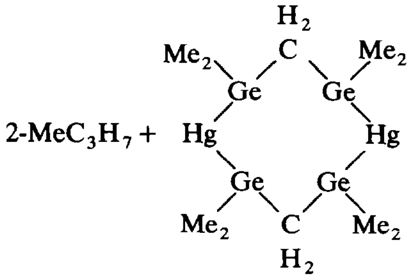
R = aryl, alkyl, CF_3, or Me_3Si (symmetrical or asymmetrical); X = halogen

$$R_nGeH_{4-n} \xrightarrow[-2BuH]{Bu_2Hg} (R_nGe)_2Hg_{4-n} \quad (21)$$

$n = 1, 2$ or 3

R = aryl or halogen

$$2Me_2HGeGeHMe_2 \xrightarrow{{}^tBu_2Hg}$$



(22)

(74%)

Germyl mercury compounds have also been prepared from germyl lithium compounds (eqn. (23)) [6].

$$\mathrm{Mes_3GeLi} \xrightarrow[-\mathrm{LiCl}]{\mathrm{HgCl_2}} \mathrm{Mes_3GeHgCl} \xrightarrow[-\mathrm{LiCl}]{\mathrm{HgCl_2}} (\mathrm{Mes_3Ge})_2\mathrm{Hg} \quad (23)$$

2.3.3. Addition reactions

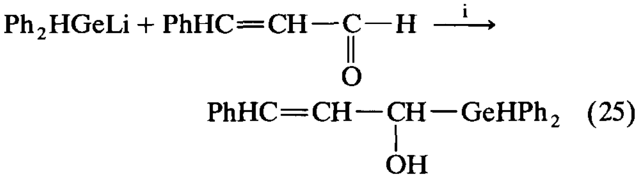
Organogermyllithiums add to the carbonyl group of aromatic ketones or aldehydes leading to the corresponding germylated alcohols in the usual way (eqn. (24)) [4] after hydrolysis.

$$\mathrm{R_2HGeLi + PhCHO \xrightarrow{i} R_2HGeCHOHPh} \quad (24)$$

R = Ph or Mes

i – after hydrolysis

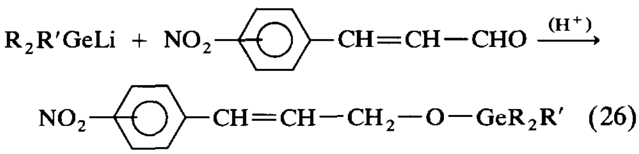
With conjugated systems, germylation of only the carbonyl group was observed (eqn. (25)). There was no evidence of a reaction with the ethylenic groups or of a 1–4 addition. The latter has been observed in the case of α-ethylenic amides [21].



$$\mathrm{Ph_2HGeLi + PhHC{=}CH{-}\underset{\underset{O}{\|}}{C}{-}H \xrightarrow{i} PhHC{=}CH{-}\underset{\underset{OH}{|}}{CH}{-}GeHPh_2} \quad (25)$$

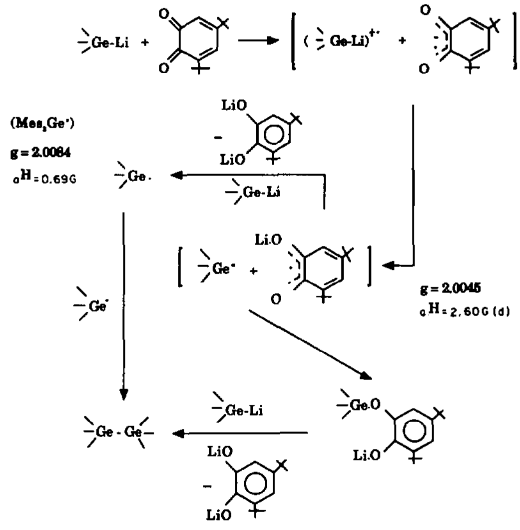
i – after hydrolysis

When the α-ethylenic carbonyl compound has a low energy LUMO, as in nitrocinnamaldehyde, the reverse addition occurs (eqn. (26)), which corresponds to a change from the classic nucleophilic addition to a SET reaction.



An ESR study of reaction (26) revealed a transient nitrocinnamyl ion radical. 1,2-$NO_2C_6H_4$-CH=CH-CHO$^{-\cdot}$ (g = 2.0046, a^N = 11.2 G (t), a^{CH} = 4,5 G (d), $a^{Ca\text{-}H}$ = 1,5 G (quint).

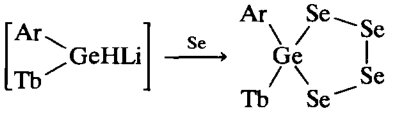
The SET mechanism predominates in the case of various highly conjugated derivatives (fluorenone, quinones, tetracyanoquinodimethane, 2,4,6 tritert-butylnitrosobenzene, and galvinoxyl), as has been demonstrated by the ESR signal of the transient radical species (organic radical anions and germanium-centred radicals $R_3Ge\cdot$) and by quantitative diamagnetization of paramagnetic galvinoxyl. Digermanes are the main products of these reactions, being formed by direct Ge–Ge bond formation as well as lithiogermolysis of reaction adducts (Scheme 2) [22,23].



Scheme 2.

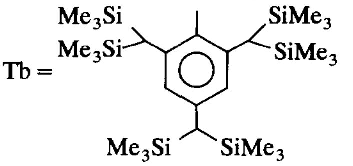
2.3.4. Reaction with elemental selenium

The treatment of arylhydridogermanium lithium intermediates with elemental selenium produced the first hindered tetraselenagermolanes (eqn. (27)) [24].



(27)

Ar = Mes or 2,4,6-triisopropylphenyl



3. Organohydridogermanium-transition metal compounds

3.1. Preparations

Although some preparations of organohydrogermyl transition-metal compounds have been described in the literature, their reactivities have not been developed [25–28]. We synthesized a new class of such complexes by substitution reactions of organohalogermanes according to eqns. (28) and (29) [29,30].

$$\mathrm{R_{3-\mathit{n}}H_\mathit{n}GeCl + Na[Fe(\eta^5C_5H_5)(CO)_2] \xrightarrow{-NaCl} [R_{3-\mathit{n}}H_\mathit{n}GeFe(\eta^5\text{-}C_5H_5)(CO)_2]} \quad (28)$$

R = Et, Ph or Mes; n = 1 or 2

$$\mathrm{R_2HGeGeClR_2 + NaML_\mathit{n} \xrightarrow[-NaCl]{THF} [R_2HGeGeR_2ML_\mathit{n}]} \quad (29)$$

R = Et, Ph; ML_n = $Fe(\eta^5\text{-}C_5H_5)(CO)_2$ or $W(\eta^5\text{-}C_5H_5)(CO)_3$

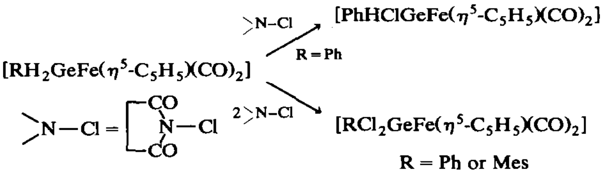
3.2. Physicochemical properties

In the crystalline state, these complexes are stable and they may be readily handled in air, but they slowly decompose in chlorinated solvents. As reported for diarylgermyllithiums (see 2.1.2), the spectroscopic data (IR, ^1H and ^{13}C NMR) correlate with a negative charge at the germanium atom, but the charge separation is small, indicating less polarization of the phenyl ring than in organogermyllithium compounds.

3.3. Chemical properties

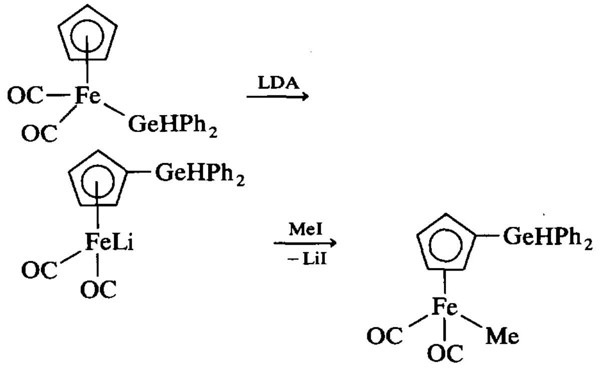
3.3.1. Nucleophilic substitution

The most effective halogenating reagent for germyl-transition metal compounds is *N*-chlorosuccinimide (eqn. (30)). Other chlorinating reagents such as CCl_4 and $HgCl_2$, often used with organogermanes [1], are less selective.



(30)

Some metallation reactions with lithium alkyls have been reported [27,31,32]. Treatment of hydridogermaniumtransition metal complexes with lithium diisopropylamide (LDA) led initially to deprotonation of the cyclopentadienyl ring and migration of the organohydrogermyl group without metallation of the germanium–hydrogen bond (eqn. (31)) [30].



(31)

When ^tBuLi was used, the reaction was more complex. Metallation reactions of both the germanium–hydrogen bond and the cyclopentadienyl group were observed, as well as partial decomposition of the initial complex (eqn. (32)) [30].

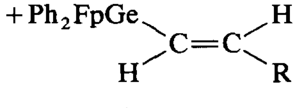
$$[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2] \xrightarrow[MeI]{^tBuLi,\ THF} [MeFe(\eta^5\text{-}C_5H_4GeHPh_2)(CO)_2] + [Ph_2MeGeFe(\eta^5\text{-}C_5H_5)(CO)_2] \quad (32)$$

3.3.2. Addition to unsaturated compounds

Hydrogermylation reactions of phenylacetylene or methylethynylketone done in the presence of chloroplatinic acid led preferentially to the α-form of the vinylic adduct (eqn. (33)) [30].

$$[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2] + RC{\equiv}CH \xrightarrow{H_2PtCl_6} [Ph_2FpGeCR{=}CH_2]$$

(predominant form)



(33)

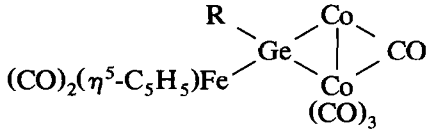
(*trans*)

R = Ph, CH_3CO
Fp = $Fe(\eta^5\text{-}C_5H_5)(CO)_2$

3.3.3. Dehydrogenation reactions

With dicobaltoctacarbonyl, organohydridogermanium-transition metal complexes easily gave the corresponding clusters (eqn. (34)).

$$[RH_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2] \xrightarrow[-[HCo(CO)_4]]{[Co_2(CO)_8]}$$



(34)

With Wilkinson's reagent, an interesting dehydrocoupling reaction was observed which led to the corresponding digermane (eqn. (35)) [16].

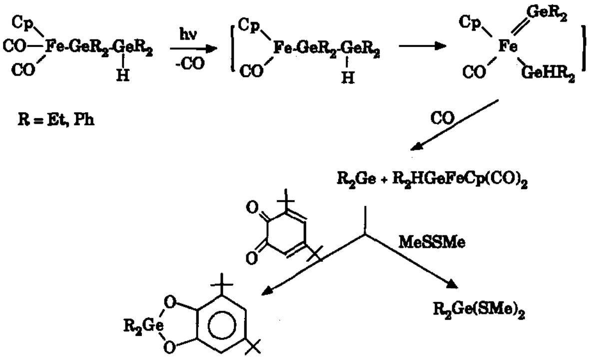
$$[PhH_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2] \xrightarrow[40\text{–}60°C]{[(Ph_3P)_3RhCl]} [PhFpHGeGeHFpPh] + H_2 \quad (35)$$

Fp = $Fe(\eta^5\text{-}C_5H_5)(CO)_2$

3.3.4. Photolysis

UV photolysis of organo- and organomethoxygermanyliron complexes, $[(\eta^5\text{-}C_5H_5)(CO)_2FeGeMe_2\text{-}GeMe_2R]$, has been recently reported [33]. When R is a methoxy group, a methoxy-bridged bis(germylene)iron complex was obtained. When R is alkyl [33] or hydrogen [30], a germylene is ejected to yield a germyliron complex (Scheme 3).

The first step is a photolytic ejection of a carbonyl group to give a 16-electron intermediate which rearranges to form a germyl(germylene)iron complex. The last is unstable and decomposes with release of germylene and formation of an organohydrogermyl complex. The diorganogermylenes were trapped almost quantitatively by 3,5-di-tert-butylorthoquinone or dimethyldisulfide.



Scheme 3.

4. Conclusion

The synthesis of organogermanium metal compounds has undergone continuous and major development over the last decade and the literature now offers a wide range of preparative methods for these compounds. This paper shows that hydridogermylmetals constitute a new class of compound whose novelty arises from the presence of two reactive sites at the germanium atom: the Ge–H and the Ge–metal bonds. Apparently in organohydridogermyl alkali metal compounds the activity of the germyl anion predominates, giving principally nucleophilic or SET-type reactions. In the case of organohydridogermyltransition metal complexes, it was possible to demonstrate the activity of the Ge–H bond. These two reaction tendencies may be exploited in heterocyclization reactions, in the synthesis of cross-linked germylated polymers, and in studies of organohydridogermyl radicals resulting from SET reactions.

Acknowledgments

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