

Recent Developments in Heterocyclic Systems with a Si-M'-Ge or Ge-M'-Ge Linkage (M' = Fe, Ru, or Co)

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ABSTRACT

The present review describes recent work on the synthesis, spectroscopic analysis, and investigation of the chemical behaviors of new polynuclear heterocyclic complexes **1-7** having M-M'-M catenation. Various CO substitution, cleavage, expansion, and adducts decomposition reactions are described.

INTRODUCTION

The interaction of transition-metal complexes with atoms M of group 14 elements has long been an area of interest involving both stoichiometric and catalytic transformations of the M atom compounds, and many M-M'_n compounds (M' = transition metal) are now well known [1-19].

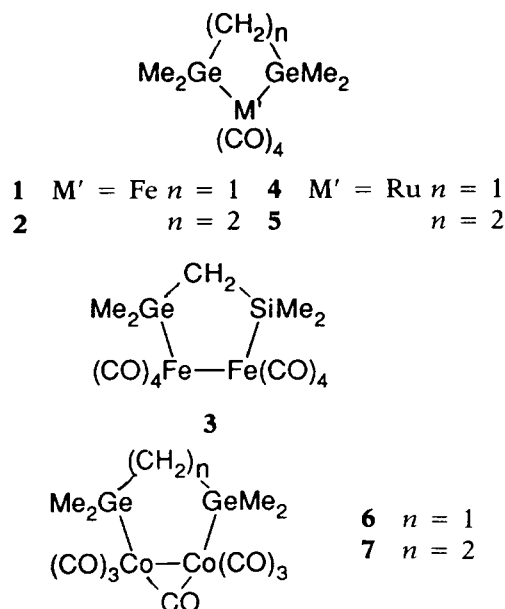
The group of M-Fe compounds is one of the most studied, and since the first example (π^5 -C₅H₅)Fe(CO)₂SiMe₃ reported in 1956 [20], derivatives having one, two, or more iron atoms that are linear or cyclic or involving the M atom in the form of an R₂M group have been reported [19-21]. However, to my knowledge, no four- or five-ring heterocycles having C-Fe-Ge linkages have been described.

Likewise, few cyclic complexes having X-M-Ru or X-M-Co linkages have been reported. The clusters with structures Me₂Si-X-Si(Me₂)Ru(CO)₄ (X = C₂H₄, C₆H₄, C₆H₂X₂, C₆H₄(Me₂Si)₂Pt-P(C₆H₅)₂CH₂CH₂P(C₆H₅)₂) [22, 23] and Me₂M-X-M(Me₂)Ru(CO)₄-Ru(CO)₄ (M = Si and X = O, CH₂; M = Ge and X = O) [24] have been

prepared only in the ruthenium series. While in the cobalt series, the linear structures (CO)₄CoM(Me₂)-X-M(Me₂)Co(CO)₄ (M = Si; Ge and X = O; M = Si and X = CH₂ or C₂H₄) and the

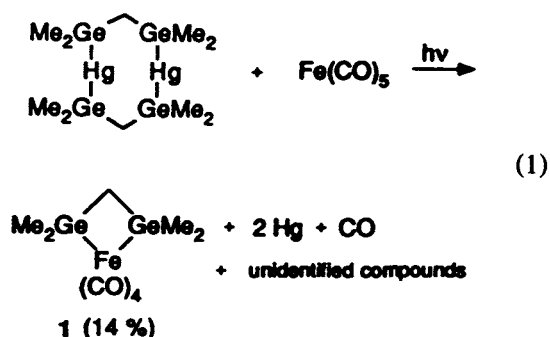
silicones [(CO)₄Co-Si-O]_n are the only known structures.

This article presents synthetic and spectroscopic results on bis(dimethylgermyl) or (dimethylgermyl)(dimethylsilyl) alkane iron **1-3** [25-27] or ruthenium tetracarbonyls **4, 5** [28] and dicobalt heptacarbonyls **6, 7** [29] and reports some of the more interesting properties of these new complexes.



SYNTHESIS

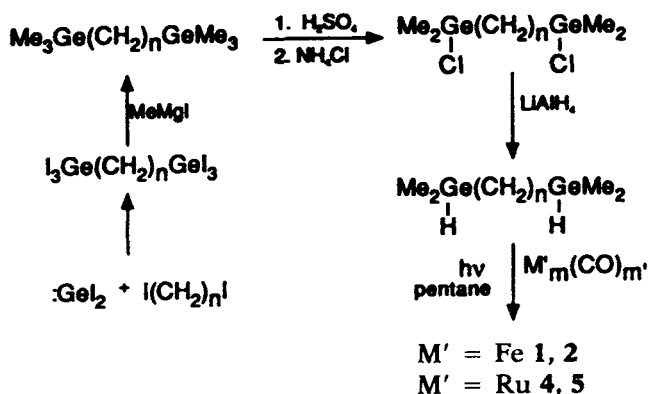
The bisdimethyl(germyl)methane iron tetracarbonyl **1** was first obtained by a mercury route involving the elimination of Hg during UV irradiation of a mixture of tetragermadimercurocane and iron pentacarbonyl (Equation 1).



This reaction afforded a low yield, with the formation of by-products that were difficult to separate; by contrast, reactions starting from M hydrides and $M'_m(\text{CO})_m$ produced high yields of Ge- M' compounds, [19], suggesting the use of this latter method with bis(dimethylgermyl)alkanes and $\text{Fe}(\text{CO})_5$, $\text{Ru}_3(\text{CO})_{12}$, or $\text{Co}_2(\text{CO})_8$.

The $\text{Me}_2(\text{H})\text{Ge}(\text{CH}_2)_n\text{Ge}(\text{H})\text{Me}_2$ hydrides [30] were obtained by insertion of diiodogermylene into diiodoalkanes, methylation, monochlorination at each germanium atom, and reduction. The cyclization reactions are nearly ended after several hours of UV irradiation at room temperature, and the resulting compounds are purified by distillation (for iron and ruthenium) or by crystallization (for cobalt).

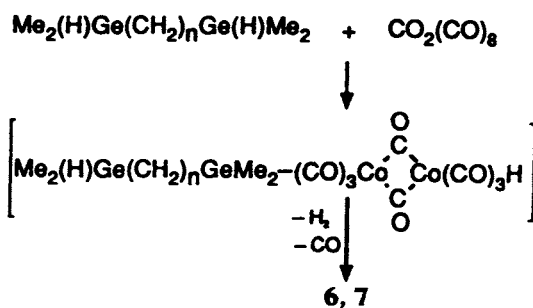
Starting from bis(dimethylgermyl)alkanes, mono-metallated tetracarbonyl compounds are isolated for iron and ruthenium (Scheme 1).



SCHEME 1

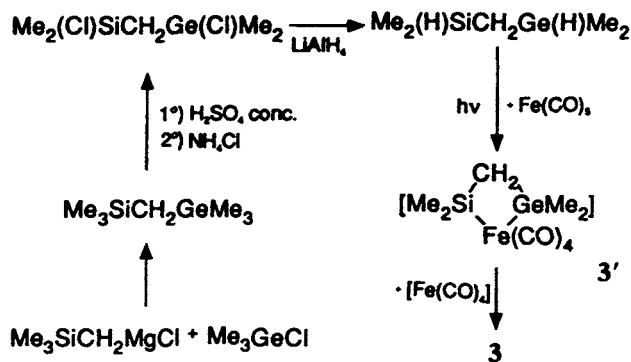
Bimetalated heptacarbonyl clusters are obtained for cobalt (Scheme 2). This reaction, irrespective of the stoichiometry and comparable with

the reaction of Ph_2GeH_2 with $\text{Co}_2(\text{CO})_8$ [31, 32], can be rationalized by (i) cleavage of the cobalt-cobalt bond of $\text{Co}_2(\text{CO})_8$ by a Ge-H bond of the digermene with formation of a hydridocarbonyl group; (ii) intramolecular elimination of H_2 and elimination of carbon monoxide (Scheme 2). There is no evidence for preliminary formation of intermediate $\text{Me}_2\text{Ge}[\text{Co}(\text{CO})_4](\text{CH}_2)_n\text{Ge}[\text{Co}(\text{CO})_4]\text{Me}_2$, which could spontaneously lose one carbonyl group. Complexes such as $\text{Me}_2\text{M}[\text{Co}(\text{CO})_4]-\text{X}-\text{M}[\text{Co}(\text{CO})_4]\text{Me}_2$ ($X = \text{O}$, $M = \text{Si}$ or Ge ; $X = \text{C}_2\text{H}_4$, $M = \text{Si}$) [22, 24] are known, and they are thermally labile, giving $\text{Co}_4(\text{CO})_{12}$.



SCHEME 2

Starting from (dimethylgermyl)(dimethylsilyl)methane, the expected four-membered heterocycle **3'** is not obtained. Distillation of the reaction mixture allows only the isolation of **3**, resulting from the formal insertion of irontetracarbonyl into **3'** (Scheme 3).



SCHEME 3

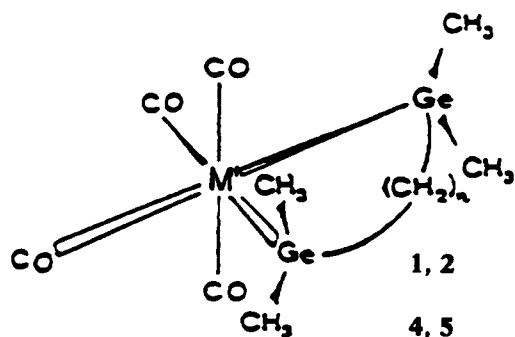
PHYSIOCOCHEMICAL PROPERTIES

All these compounds were characterized by Mass, IR, and ^1H and ^{13}C NMR spectroscopies.

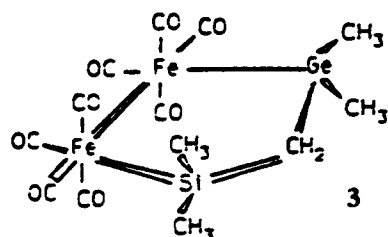
For **1**, **2** and **4**, **5**, the appearance of four carbonyl bands with the usual intensity pattern for $\text{M}-\text{M}'(\text{CO})_4-\text{M}$ species in the IR spectra and of sharp proton NMR singlets for methyl and methylenic or ethylenic protons of the germyl ligands are characteristic of C_{2v} local symmetry at iron and ruth-

enium in these compounds. Their ^{13}C NMR spectra show high stereochemical rigidity, because even at 150°C coalescence of signals due to axial-equatorial exchange of carbonyl is not observed.

All mass spectra have peaks corresponding to molecular ions M^+ (of weak relative intensity in the case of **1**) and to fragmentations characteristic of such heterocyclic structures (loss of carbonyl groups and substituents on the germanium atoms). For the five-membered ring compound **2**, the most intense peak corresponds to $[\text{M}-140]^+$, due to loss of all CO groups and C_2H_4 , which suggests the formation of a germanium species of type $[\text{Me}_2\text{Ge}-\text{Fe}-\text{GeMe}_2]^+$. By comparison, in the case of the four-membered ring compound **1**, the peak that corresponds to the loss of all carbonyls and CH_2 is much less intense. The most intense peak in this case is $[\text{M}-4\text{CO}]^+$, corresponding to usual behavior.

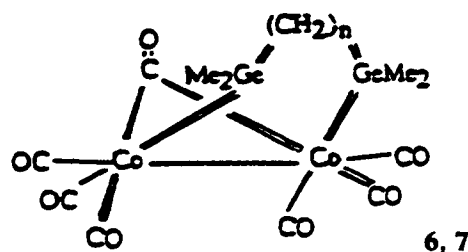


According to the analysis of ^1H , ^{13}C NMR and IR spectra of **3**, the structure of this cluster is compatible with a molecular model with a C_s symmetry.



The cobalt complexes **6** and **7** undoubtedly have the structure in which the germylated group replaces a bridging carbonyl in dicobaltocarbonyl. This structure is indicated in the IR spectra by the band at 1850 cm^{-1} showing the presence of the bridging carbonyl, and by the pattern of four strong bands in the terminal carbonyl region.

In this structure, the two methyl groups are nonequivalent; thus, the observation of a single sharp methyl resonance in the NMR spectrum at room temperature indicates that this molecule is fluxional. Several rearrangement pathways might explain this observation. Adams and Cotton have shown that the bis(germylene)dicobalt complex

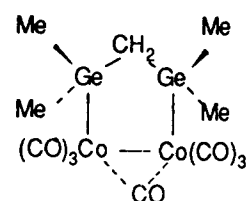
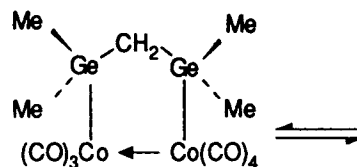
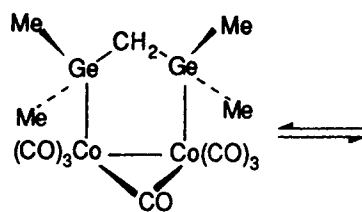


$(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ has a temperature-dependent NMR spectrum and have postulated a pseudorotation mechanism, but they have not excluded one involving terminal germylene exchange [33]. In addition to these two mechanisms, Job and Curtis have postulated, but not demonstrated, a rapid bridged/nonbridged/bridged interconversion for the germylated compound $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ [34].

To evaluate the mechanism, I have examined the ^{13}C NMR spectrum of **6** as a function of temperature.

The single peak observed at 35°C collapses and separates at 0°C into two peaks of equal intensities. At -50°C four other methyl resonances appear, and in the meantime carbonyl resonances collapse. Then the bridged carbonyl peak decreases and two carbonyl resonances remain.

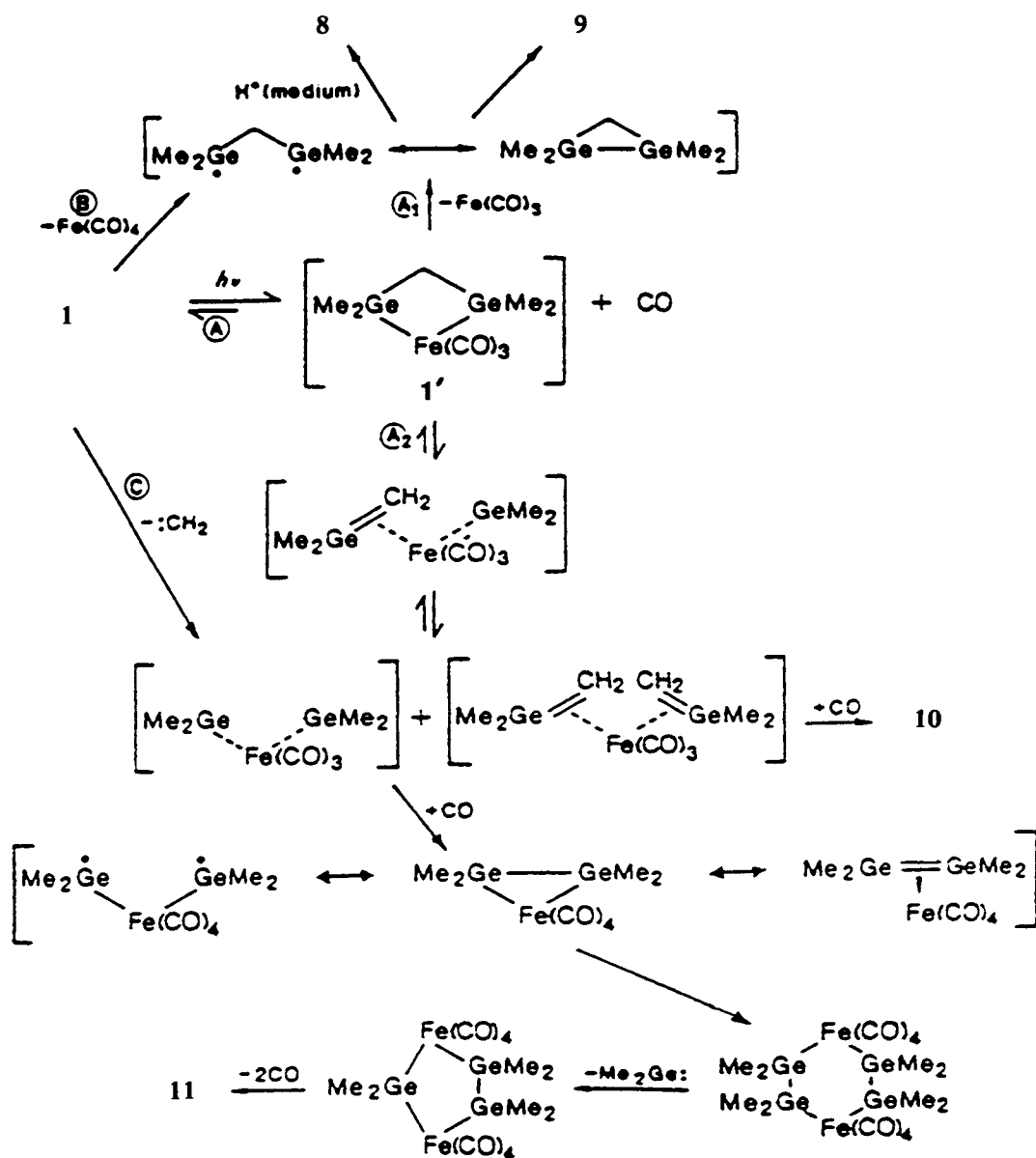
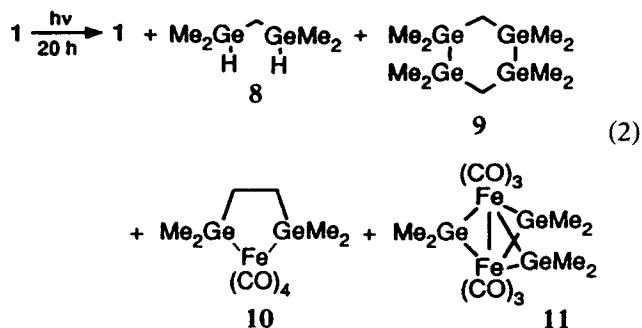
These results seem to provide proof that bridged/nonbridged interconversion occurs. Thus, the complexes **6**, **7** may average the environment of the methyl groups via a terminal/bridged carbonyl exchange in which the new cobalt-carbonyl-cobalt bridge is formed on the opposite side of the $\text{Ge}-\text{Co}-\text{Co}-\text{Ge}$ plane.



PHOTOLYSIS

All these heterocycles 1–7 are stable at room temperature, but the heterocycles with $n = 1$ decompose under prolonged UV irradiation; the photochemical decomposition of 1 has been particularly studied. These reactions produce a complex mixture of germanium derivatives 8–11 besides $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ (Equation 2).

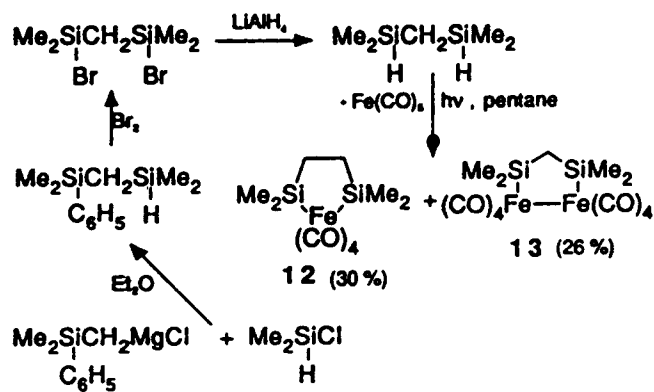
This decomposition can be explained by an initial loss of CO, under photochemical activation, and formation of the intermediate 1', which can lead to 8 or 9 by reductive elimination (Scheme 4, path A₁)



SCHEME 4

and to **10** or **11** by retro [2 + 2] cleavage (Scheme 4, path A₂). This last cycloreversion could involve formation and symmetrization of an intermediate germaethylene-germylene complex of iron that strongly resembles a key step in the olefin metathesis reaction catalyzed by transition-metal complexes [35]. However, it is not possible to exclude the intervention of radical processes involving homolytic scission (i) of Ge–Fe bonds (Scheme 4, path B), probably leading directly to the digermyl biradical and (ii) of Ge–C bonds (Scheme 4, path C), resulting in the formation of carbene CH₂ (which can react with **1** or with an intermediate derived from **1** to give **10**), and in the direct formation of the biradical that, by dimerization, loss of germylene, loss of CO, and rearrangement of Ge–Ge bonds, leads to **11** as proposed in ref. [36].

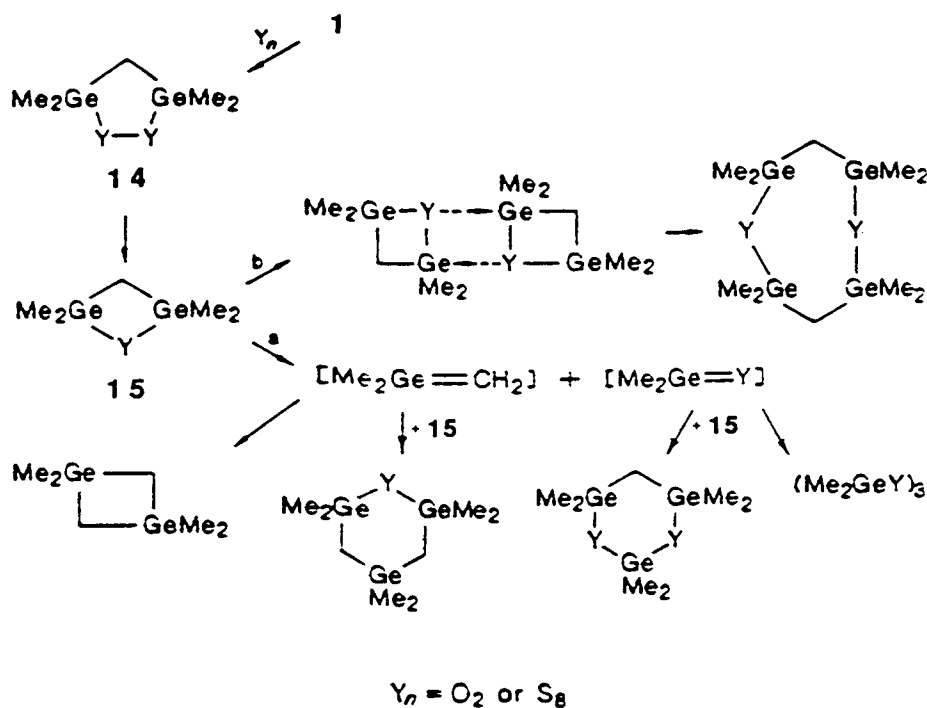
Such a decomposition involving formal carbene addition has been found again during the attempted synthesis of Me₂SiCH₂Si(Me₂)Fe(CO)₄, the silicon analogue of **1**, from bis(dimethylsilyl)methane and iron pentacarbonyl, in which distillation of the reaction mixture gave only the adduct bis(dimethylsilyl)ethane-irontetracarbonyl **12** [22]. Chromatography on a silica column of the same reaction mixture allowed the isolation only of bis(dimethylsilyl) methane diiron octacarbonyl **13**, as has already been observed [24], according to Scheme 5. It seems that **12** and **13** are both directly formed during this reaction as **12** is stable on the chromatography column.



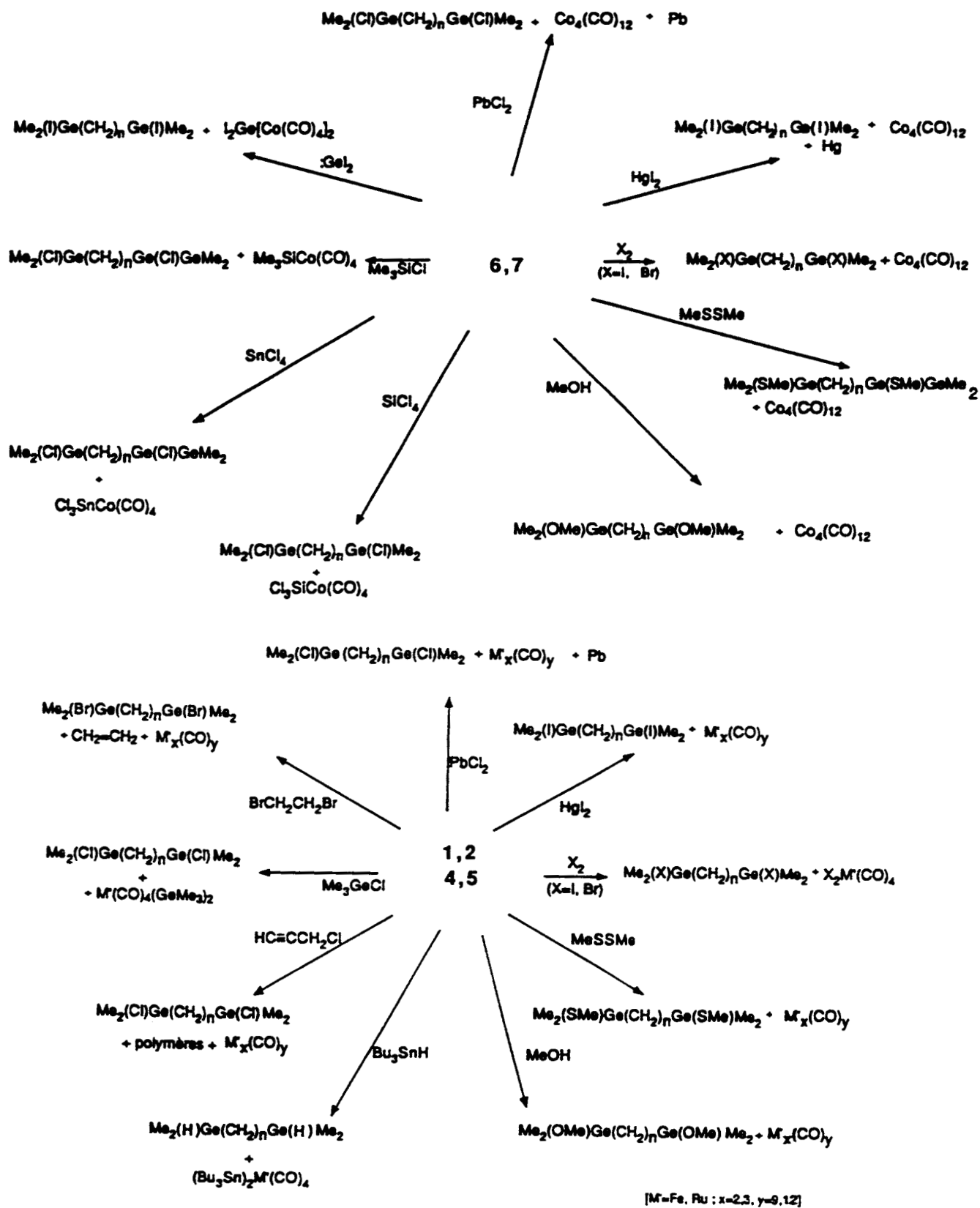
CHEMICAL REACTIVITY

Reactions with Oxygen, Elemental Sulfur, and Oxides

All these new metalla heterocycles **1–7** exhibit high reactivity and are very sensitive to oxygen and sulfur giving rise to various germylated oxides or sulfides. For example, the behavior of bis(dimethylgermyl) methane–iron or ruthenium tetracarbonyls **1** or **4**, with respect to O₂ and S₈, implies the formation of the unstable dioxo- and dithia-digermolanes **14**, the decomposition of which by loss of an oxygen or a sulfur atom and decomposition of the corresponding digermaoxetane and thietane **15**



SCHEME 6



SCHEME 7

probably involve the tricoordinated species $[\text{Me}_2\text{Ge}=\text{CH}_2]$ and $[\text{Me}_2\text{Ge}=\text{Y}]$ ($\text{Y} = \text{O}, \text{S}$); this has been observed in analogous reactions of tetra-germadimercurocane [37] and can be summarized by the same reaction sequence (Scheme 6).

In contrast, reactions of **2**, **5**, **7** with O_2 and S_8 lead to formation of the corresponding stable oxo- and thiadigermolanes $\text{Me}_2\text{Ge}(\text{CH}_2)_2\text{GeMe}_2\text{Y}$ ($\text{Y} = \text{O}$ or S).

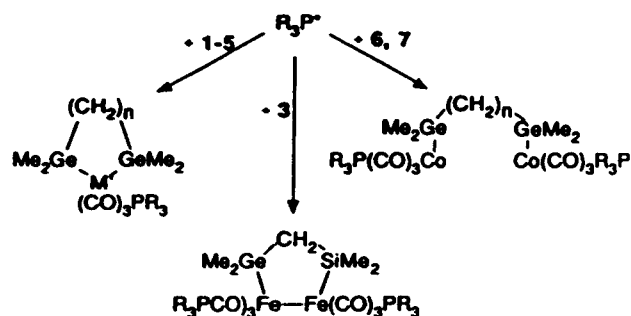
Z^+-O^- oxides ($\text{Z} = \text{Hg}, \text{C}_5\text{H}_5\text{N}, \text{C}_6\text{H}_5\text{N}, \text{Me}_2\text{S}$) are deoxidized by all these complexes **1–7** and lead to the same heterocycles $\text{Me}_2\text{M}(\text{CH}_2)_n\text{GeMe}_2\text{O}$ ($\text{M} = \text{Ge}, n = 1$ or 2 ; $\text{M} = \text{Si}, n = 1$), which are stable or unstable at room temperature depending on the size of the heterocycle.

Reactions with Halogen and Organic or Organometallic Halides

$\text{Ge}-\text{M}'$ bond cleavage reactions are observed with various halogens, alcohols, organic halides, and, more interestingly, with organometallic halides leading to polynuclear clusters have $\text{M}-\text{M}'$ bonds (Scheme 7).

Ligand-Exchange Reactions

Because ligands having a lone pair are able to substitute one or more CO groups of metal carbonyls, various CO substitution reactions with phosphines, with or without heating, have been observed (Scheme 8).



*Experimental conditions:

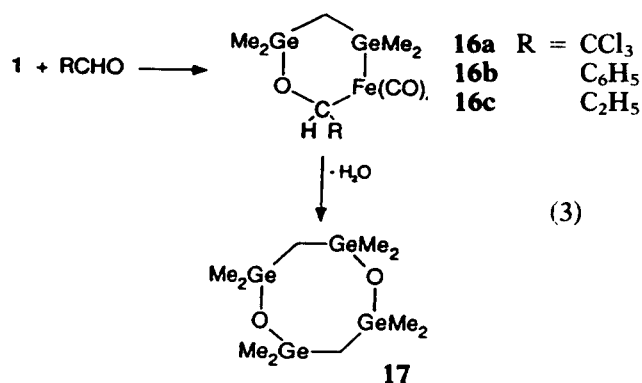
R = Ph	$h\nu, 20^\circ\text{C}$ or 100°C	
	20°C 3	
	100°C 4, 5	
	20°C 6, 7	
1 or 2	R = nBu	20°C 1, 2
		20°C 3
		100°C 4, 5
		20°C 6, 7

SCHEME 8

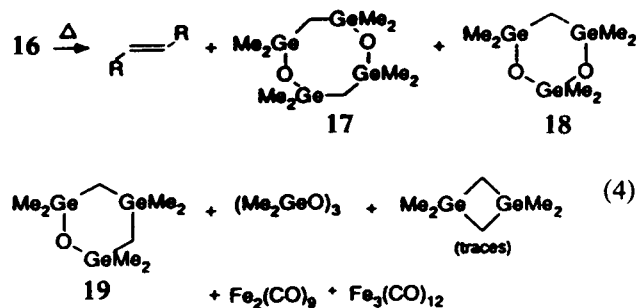
Reactions with Carbonyl Compounds

These polynuclear heterocycles are also very reactive toward organic carbonyl compounds. These kinds of reaction have been particularly studied in the case of iron compounds.

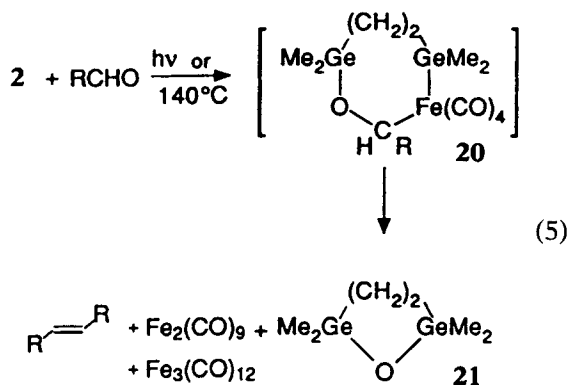
Reactions with Aldehydes. For example, compound **1** reacts rapidly with benzaldehyde, propionaldehyde, and chloral in C_6H_6 at 5°C to give almost quantitatively the 1,2-adducts **16**, which are stable at ambient temperature (Equation 3).



These adducts with structure $\text{Ge}-\text{O}-\text{t}-\text{Fe}-\text{Ge}$ were characterized by NMR analysis and hydrolysis. They decompose thermally to form alkenes and the previously reported germanium oxides **17**, **18**, **19** (Equation 4).



The bis(dimethylgermyl)ethane iron tetracarbonyl **2** is much less reactive than bis(dimethylgermyl) methane iron tetracarbonyl. Compound **2** reacts with aldehydes only on irradiation or at 140°C (Equation 5). This is also unlike its silicon homolog, studied by Gladysz, which reacts at low temperatures with aldehydes [38–39]. The reaction gives the oxadigermolane **21** in high yield. Although no intermediate could be detected in this reaction, initial formation of the 1,2-adduct **20** could be postulated by analogy to the precedent reaction.

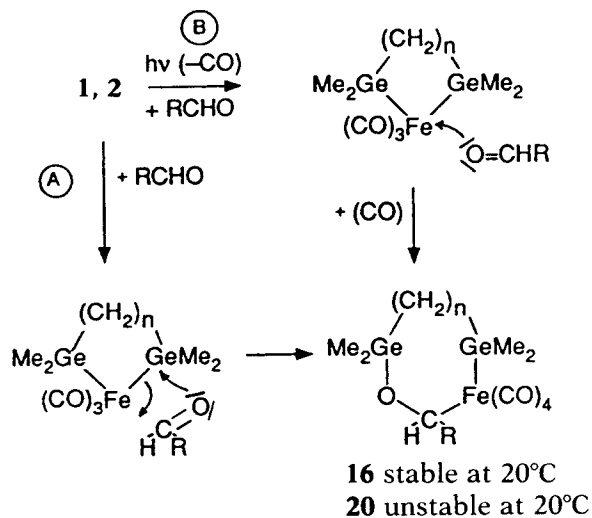


These reactions are faster when carried out under UV irradiation. Because UV irradiation results in easy displacement of carbon monoxide ligands in this kind of heterocycle, I propose for these reactions a mechanism involving, in the first step, coordination of the carbonyl compound to the iron atom. Then the carbonyl, which is activated by its coordination, inserts into the germanium–iron bond. The high oxygen affinity of the germyl group favors bond formation between oxygen and germanium leading to the 1,2-adduct, the stability of which depends on the size of the heterocycle (Scheme 9-A). The six-membered heterocycles are stable at room temperature.

Without irradiation, the rate of these insertion reactions depends on the nature of the aldehyde and follows the order $\text{CCl}_3\text{CHO} > \text{CH}_3\text{CH}_2\text{CHO} > \text{C}_6\text{H}_5\text{CHO}$.

These reactions are slightly faster when carried out in acetonitrile rather than in benzene and are slower in THF or ether solution. Lewis acids (such as H_2PtCl_6 or ZnI_2) have no effect on the rates of addition of aldehydes to **1** or **2**.

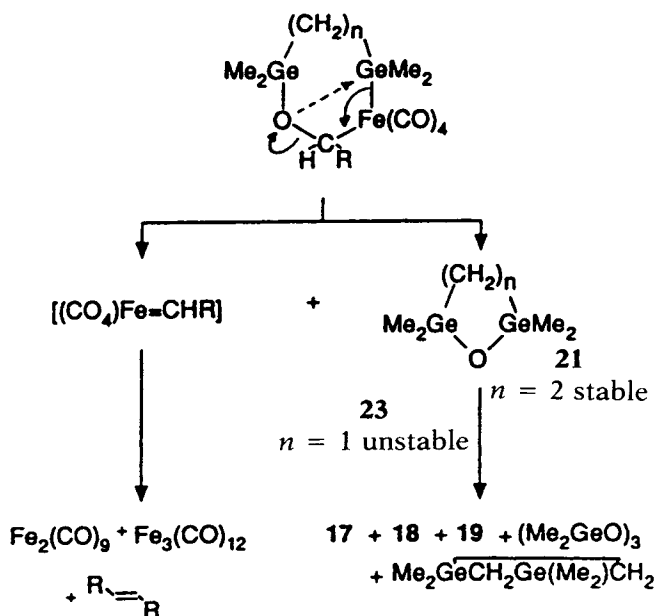
Thus, although high reactivity seems to depend on the carbon atom of the organic carbonyl group



SCHEME 9

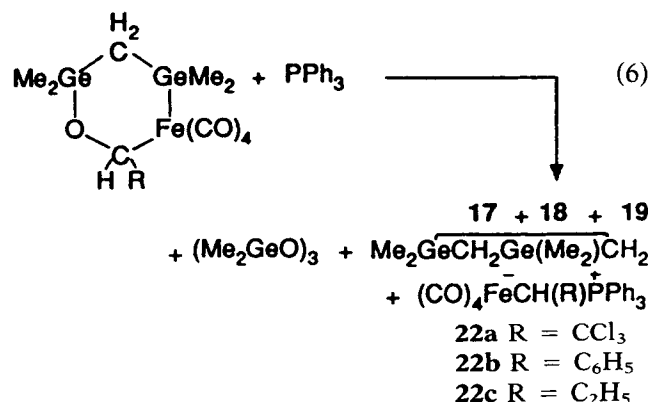
being positive, the effects of solvents suggest a nucleophilic attack of the carbonyl oxygen of the aldehyde on the germanium in the first step of this mechanism (Scheme 9-B). THF and ether may, by complexation with germanium, disturb this nucleophilic attack on the group 14 metal.

The formation of the decomposition products (alkenes and various germoxanes) can be explained by a mechanism of intramolecular decomposition of the heterocycles **16** and **20** occurring by nucleophilic attack of the oxygen atom bonded to a germanium atom on the other germanium atom, thereby forming the unstable species $[(\text{CO}_4\text{Fe}=\text{CHR})]$ and $\text{Me}_2\text{Ge}(\text{CH}_2)_n\text{Ge}(\text{Me}_2)\text{O}$ (Scheme 10).



SCHEME 10

As shown by Gladysz [39], the alkylidene intermediates can be stabilized by complexation with triphenylphosphine when the decomposition of **16** is carried out in the presence of equimolar amounts of PPh_3 (Equation 6).



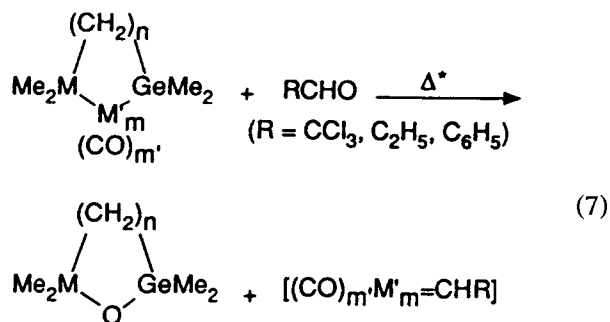
The zwitterions (**22a**, **22b**, and **22c**) were isolated and characterized by IR and NMR spectroscopy (**22b** and **22c** are in agreement with literature values); they were stable at room temperature but decomposed on heating.

Although the reactivity of **1** is lower than that of the silylated homologue [39] and lower also than

that of **3** and near that of **6** or **7**, the compounds **2**, **4**, and **5**, unlike their iron homologues, react with aldehydes only when heated. In all these cases, the intermediate adduct cannot be isolated, and the reactions lead directly to the germylated oxides **21**, **23**, or **24** (Equation 7).

Reactions with Quinones. Although 1,4-benzoquinones bond to transition metals through the diene linkage, 1,2-benzoquinones appear to bond exclusively through their oxygen atoms [40, 41].

Thus, compounds **1** and **2** both react exothermally with 1,2-quinones producing new digermanium heterocycles **25** in high yields (Equation 8).

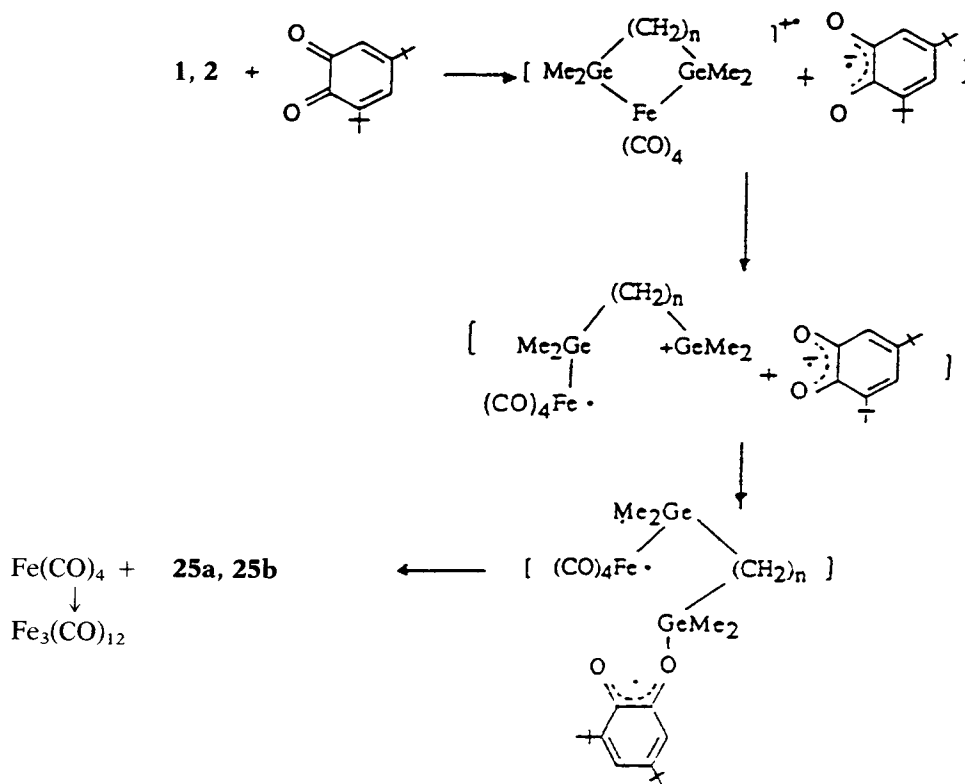
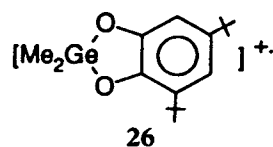
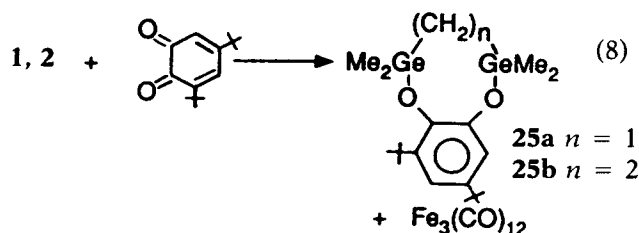


23 $n = 1$ $\text{M} = \text{Ge}$

24 $n = 1$ $\text{M} = \text{Si}$

21 $n = 2$ $\text{M} = \text{Ge}$

$\Delta^* \text{ } ^\circ\text{C}$ ($\text{R} = \text{CCl}_3$) = [Fe]: -5° (**1**); 140° (**2**); -20° (**3**)
[Co]: 20° (**6**); 60° (**7**). [Ru]: 70° (**4**); 150° (**5**)



SCHEME 11

Heterocycles **25**, which are formally the adducts of biradicals $\text{Me}_2\text{Ge}(\text{CH}_2)_n\text{GeMe}_2$ ($n = 1, 2$) with 3,5-di-*tert*-butylorthoquinone, were characterized by NMR and MS spectroscopy and by element analysis. The mass spectrum obtained by electron-impact (70 eV) revealed, in addition to the $[\text{M}]^+$ peak, a strong peak corresponding to the loss of $\text{Me}_2\text{Ge}(\text{CH}_2)_n$, which therefore suggests the formation of **26**.

Galvinoxyl, a highly effective inhibitor of free radical processes, has no effect on the rate of these reactions between quinones and compounds **1** or **2** (galvinoxyl does not react with complexes **1** or **2** or quinones). Moreover, it can be shown that these reactions are not photochemically induced by carrying out the photolysis of a mixture of compound **2** and quinone at -40°C under very dilute conditions with parallel control experiments (the thermal process is slow at this temperature).

Thus, these additions, which are very similar to the reaction of quinones or tetracyanoethylene with group 14 metal-hydride [42–46] or with group 14 metal-nitrogen [47] compounds, proceed probably through a one electron transfer mechanism (Scheme 11). The transient semiquinonic radical involved can be detected by ESR spectroscopy, either as the anion radical or ion paired with the metal.

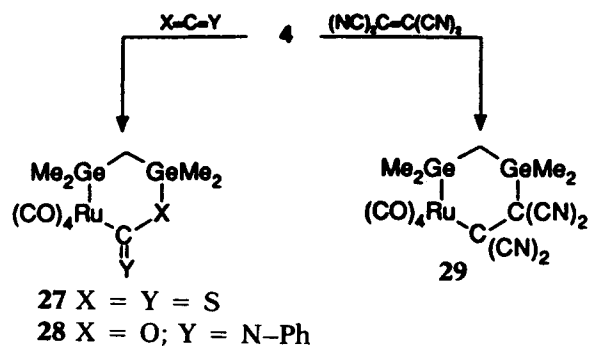
The deep green solution obtained by mixing 3,5-di-*tert*-butylorthoquinone and **1** or **2** in pentane at -40°C exhibits an ESR signal ($g = 2.0018 a^H = 3,5$ G) that shows striking similarity to the ESR spectra of *o*-semiquinonic species obtained by different means [47–49]. The Ge–Fe bond in **1** or **2** can act as an electron donor to the quinone, and Scheme 11 is therefore postulated to account for the formation of the adduct **25**.

As with their iron homologues, compounds **4**, **5** and **6**, **7** react similarly with 1,2-quinones through a one-electron mechanism producing the digermylated dioxepane and dioxocane **25** that are formally the adducts of biradicals $\text{Me}_2\text{Ge}(\text{CH}_2)_n\text{GeMe}_2$ ($n = 1$ or 2) with quinones. The transient semiquinonic radical involved has also been detected, starting from **4** and **5**, by ESR spectroscopy either as the anion radical or ion paired with the metal ($g = 2.0029 a^H = 2.8$ G).

Reactions with Various Unsaturated Compounds

These polymetallic heterocyclic compounds **1–7** are also reactive toward various other unsaturated derivatives.

Thus, for example, compounds **4** and **5** react at room temperature with CS_2 , PhNCO and $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ to give heterocyclic expansion reactions. Adducts **27–29** are stable at ambient temperature and have been characterized by NMR, IR, and mass spectrometry analyses (Scheme 12).



SCHEME 12

The new metalla heterocycles **27**, **28** decompose thermally to form the previously reported heterocycles $(\text{Me}_2\text{GeX})_3$ and $\text{Me}_2\text{GeCH}_2\text{Ge}(\text{Me}_2)\text{CH}_2$ suggestive of $\text{Me}_2\text{GeCH}_2\text{Ge}(\text{Me}_2)\text{X}$ ($X = \text{O}, \text{S}$), and then, as observed, $[\text{Me}_2\text{Ge}=\text{X}]$ and $[\text{Me}_2\text{Ge}=\text{CH}_2]$ intermediates [30, 37].

CONCLUSION

This article illustrates the high potential of these polynuclear clusters in organometallic synthesis. They can lead to new organogermanium heterocycles as well as to new polynuclear clusters having M–M' bonds.

In the series of complexes of Fe (**1–3**), Ru (**4**, **5**), Co (**6**, **7**) there is a decrease of reactivity in the order $\text{Co} > \text{Fe} > \text{Ru}$. The reactions with oxygen and sulfur of the four- or five-membered heterocycles **1**, **3**, **4** proceed via decomposition of unstable thia- or oxagermetanes $[\text{Me}_2\text{Ge}=\text{X}]$ ($X = \text{O}, \text{S}$) and $[\text{Me}_2\text{M}=\text{CH}_2]$ intermediates and lead to various new germylated oxides and sulfides. The first insertion reaction of a carbonyl compound into a germanium–transition metal bond leads to expansion adducts, which then thermally decompose to produce germylated heterocycles and, with $\text{M}' = \text{Fe}$, alkylidene intermediates $[(\text{CO})_4\text{Fe}=\text{CHR}]$.

The effects of having three or more metal atoms in proximity has not been fully examined but potential exists for catalytic activity. Systems of this nature also provide models for the study of catalytic reactions because this kind of complex could be the catalytic species involved, for instance, in many germylation reactions of various unsaturated compounds, redistribution of groups on germanium, and carbonylation of aldehydes.

This work is currently being expanded by the study of synthesis and investigation of the chemical properties of novel polynuclear structures, which are potential precursors of transient divalent, or doubly bonded [50] germanium (or M atom) derivatives stabilized by complexation with transition metals.

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