Contribution from the Laboratoire de Chimie des Organominéraux,
UA 477 du CNRS, Université Paul Sabatier, 31062 Toulouse Cedex, France

Reactivity of [Bis(dimethylgermyl)alkane]iron Tetracarbonyls with Carbonyl Compounds

Jacques Barrau,* Najib Ben Hamida, Hamid Agrebi, and Jacques Satgé*

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[Bis(dimethylgermyl)alkane]iron tetracarbonyls, $\overline{Me_2Ge(CH_2)_nGeMe_2Fe}(CO)_4$ (n = 1, 2), react with chloral, propionaldehyde, and benzaldehyde to give heterocyclic expansion reactions. Thermal decompositions of the adducts produce germylated heterocycles, $\overline{Me_2Ge(CH_2)_nGeMe_2O}$, and alkylidene intermediates, which were isolated as the ylides $(CO)_4Fe^-CH(R)PPh_3^+$. The reaction of [bis(dimethylgermyl)alkane]iron tetracarbonyls with quinones involves an electron-transfer process that results in the nearly quantitative formation of new digermylated dioxepane and dioxocane that are formally the adducts of biradicals $Me_2\dot{G}e(CH_2)_n\dot{G}eMe_2$ (n = 1, 2) with quinones.

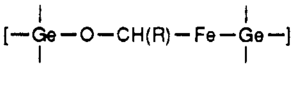
Introduction

We have recently reported the syntheses and different aspects of the reactivity of [bis(dimethylgermyl)alkane]iron tetracarbonyls, $\overline{Me_2Ge(CH_2)_nGeMe_2Fe}(CO)_4$ (n = 1, 2; compounds **1** and **2**).[1] These polymetallic heterocyclic compounds have a high potential in organometallic syntheses. They can lead to organogermanium heterocycles as well as to polynuclear clusters with M_{14}–Fe bonds (M_{14} = group 14 metal). We report here their reactivity with some organic carbonyl compounds.

Results

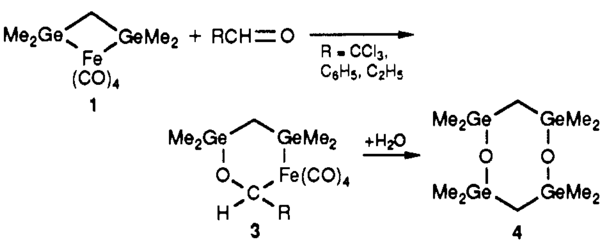
1. Reactions of 1 and 2 with Aldehydes. Numerous reactions of ring expansion by insertion of carbonyl derivatives into Ge–X bonds (where X = O, S, P, or N) have been described,[2,3] but to our knowledge no insertion of carbonyl compounds into germanium–transition metal bonds has been observed. We have studied the reaction of benzaldehyde, propionaldehyde, and chloral with compounds **1** and **2**.

Compound **1** reacts rapidly with these aldehydes in C_6H_6 at 5 °C to give almost quantitatively the 1,2-insertion products **3**, which are stable at ambient temperature (eq 1). These adducts with the structure



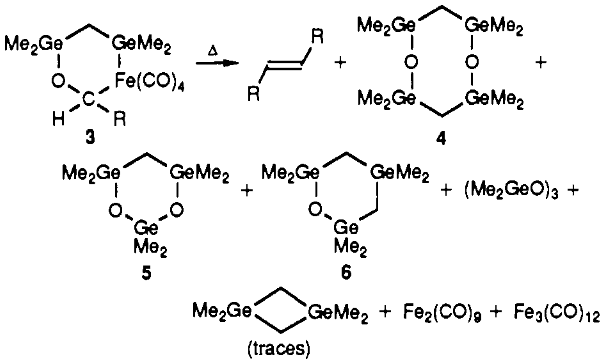
$$[-\overset{|}{\underset{|}{Ge}}-O-CH(R)-Fe-\overset{|}{\underset{|}{Ge}}-]$$

are too unstable to be isolated by distillation and were characterized by NMR analysis and hydrolysis.



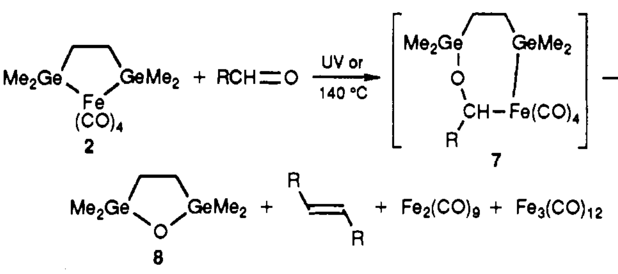
(1)

The new metalla heterocycles **3** decompose thermally to form alkenes and the previously reported[4] germanium oxides **4–6** and $(Me_2GeO)_3$ (eq 2).



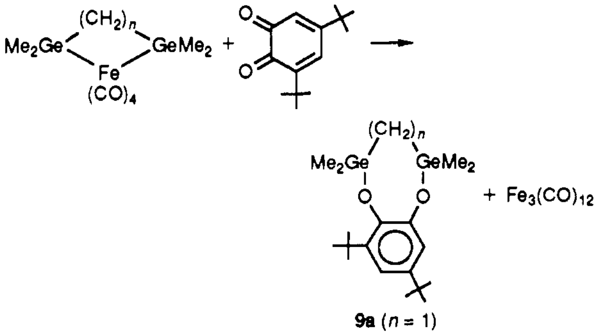
(2)

[1,2-Bis(dimethylgermyl)ethane]iron tetracarbonyl (**2**) is much less reactive than [bis(dimethylgermyl)methane]iron tetracarbonyl (**1**). **2** reacts with aldehydes RCHO (where R = C_6H_5, CH_3CH_2, and CCl_3) only upon irradiation or at 140 °C. This low reactivity is also unlike that of its silicon homologue, studied by Gladysz, which reacts at low temperature with aldehydes.[5,6] The reaction gives the oxadigermolane **8** in high yield. Although no intermediate could be detected in this reaction, initial formation of the 1,2-insertion product **7** could be postulated by analogy to eq 1.



(3)

2. Reaction with Quinones. While 1,4-benzoquinones bond to transition metals through the diene linkage, 1,2-benzoquinones appear to bond exclusively through their oxygen atoms.[7,8] Thus compounds **1** and **2** both react exothermally with 1,2-quinones, producing new digermanium heterocycles **9** (n = 1 (**9a**), 2 (**9b**)) in high yields (eq 4).



(4)

9a (n = 1)
b (n = 2)

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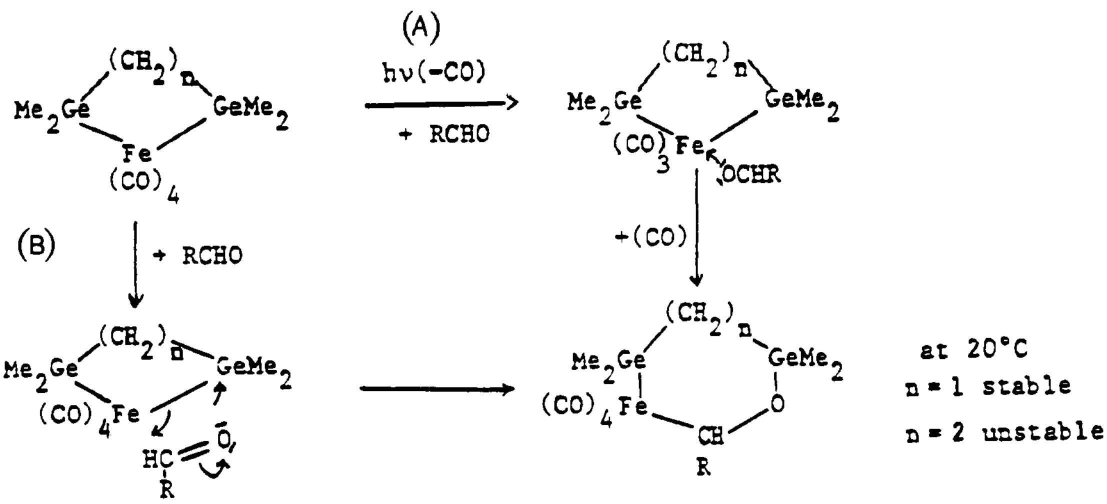
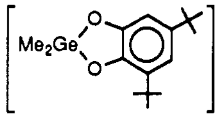
Scheme I



Heterocycles **9**, that are formally the adducts of biradicals $Me_2\dot{G}e(CH_2)_n\dot{G}eMe_2$ ($n = 1, 2$) with 3,5-di(*tert*-butyl)-*o*-quinone, were characterized by NMR, MS, and elemental analyses. The mass spectrum obtained by electron impact (70 eV) revealed, in addition to the $[M]^+$ peak, a strong peak corresponding to the loss of $Me_2Ge(CH_2)_n$, which therefore suggests the formation of **10**.



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Discussion

1. Reactions with Aldehydes. These reactions are faster when carried out upon UV irradiation. The mechanism of such reactions clearly differs from the insertions of activated carbonyl compounds into Ge–X bonds (X = O, S, PR, NR), which involve four-centered-type transition species.[3,9,10] Since UV irradiation results in easy displacement of carbon monoxide ligands in this kind of heterocycle,[11] we propose for these reactions a mechanism involving, in the first step, coordination of the carbonyl compound to the iron atom. Then the carbonyl that 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-insertion product, the stability of which depends on the size of the heterocycle (Scheme IA). 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 $CCl_3CHO > CH_3CH_2CHO > C_6H_5CHO$. These reactions are slightly faster when carried out in acetonitrile solution rather than in THF or ether solution. Lewis acids such as H_2PtCl_6 or ZnI_2 have no effect on the rate of addition of aldehydes to **1** and **2**. They slowly react with **1** and **2**, giving the unstable side products $(CO)_4FeX_2$ and $(CO)_3FeX_2$ and germylated halides $Me_2XGe(CH_2)_nGeXMe_2$ (X = Cl, I). A strongly oxophilic group (germyl or silyl) must be present on iron in order for an aldehyde adduct to be formed. So, although high reactivity seems to depend on the carbon atom of the organic carbonyl group being positive, the effect of solvent suggests a nucleophilic attack of the carbonyl oxygen of the aldehyde on the germanium in the first step of this mechanism (Scheme IB). THF and ether may, by complexation with germanium, disturb this nucleophilic attack on the group 14 metal.

Note that the reactivity of [1,2-bis(dimethylgermyl)ethane]iron tetracarbonyl (**2**) is lower than that of its silylated homologue $\overline{Me_2Si(CH_2)_2SiMe_2Fe}(CO)_4$ toward benzaldehyde[5,6] and deserves discussion. The small difference ($\Delta\nu(CO) = 10\ cm^{-1}$) between the average $\nu(CO)$ for the germylated complex **2** and that for its silylated homologue ($\overline{Me_2GeCH_2CH_2GeMe_2Fe}(CO)_4$: $\nu(CO) = 2060, 2000, 1980, 1970\ cm^{-1}$; average $\nu(CO) = 2002\ cm^{-1}$. $\overline{Me_2SiCH_2CH_2SiMe_2Fe}(CO)_4$: $\nu(CO) = 2068, 2003, 2000, 1978\ cm^{-1}$; average $\nu(CO) = 2012\ cm^{-1}$) shows a small increase of the charge transfer in the direction of the iron atom when the silicon is replaced by a germanium atom (in a series of iron carbonyl complexes with the same symmetry, the average $\nu(CO)$ stretching frequency depends on the force constant, which is a decreasing function of the electron transfer to the transition metal[12]). On account of the small difference in electronegativity between the two group 14 metal atoms [Ge (2.05) > Si (1.90)],[13] a possible explanation for these increasing charge transfers between the iron silane and germane may be found in a diminution of π transfer between the filled d orbitals of the transition metal to the empty d orbitals of the group 14 metal when silicon is replaced by germanium. In these complexes the differences of electron transfer to the iron atom are not important enough to explain the high difference in reactivity observed between the silylated and the germylated compounds. The basis for this reactivity difference toward benzaldehyde of the silicon and germanium complexes can be explained in terms of the oxophilic character of silicon being higher than that of germanium. The relative group 14 metal–transition metal bond energies must be involved, considering that an Fe–Ge(Si) bond cleavage might be involved in the initial step of the reaction. This might explain the difference in reactivity of **1** and **2** (ring strain in **1**) and between **2** and its silylated analogue.

The formation of the decomposition products (alkenes and various germoxanes depending on the size of the heterocycle) can be explained by a mechanism of intramolecular decomposition of the heterocycles **3** and **7** occurring by nucleophilic attack of the oxygen atom bonded to a germanium atom on the other germanium atom, thereby forming the unstable species $[(CO)_4Fe{=}CHR]$ and $\overline{Me_2Ge(CH_2)_nGeMe_2O}$, as represented by Scheme II.

As shown by Gladysz,[6] the alkylidene intermediates can be stabilized by complexation with triphenylphosphine when the decomposition of **3** is done in the presence of equimolar amounts of PPh_3 (Scheme II). The zwitterions $(CO)_4Fe^-CHRPPh_3^+$ (R = CCl_3 (**11a**), CH_3CH_2 (**11b**), C_6H_5 (**11c**)) were isolated and

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Scheme II

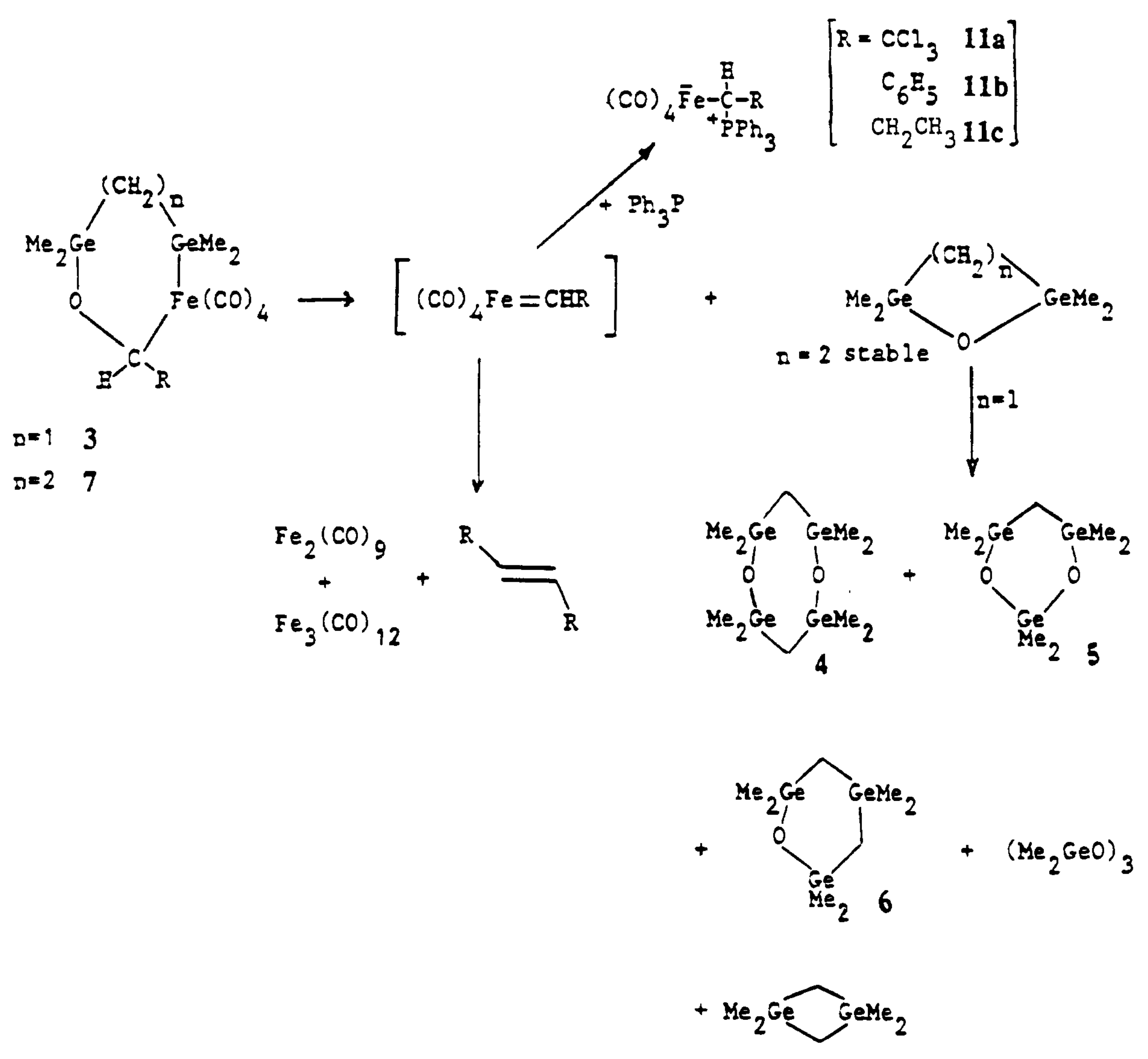
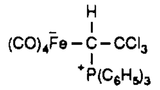
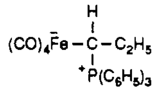
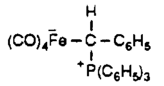


Table I. Spectroscopic Characterization of Ylide Complexes $(CO)_4Fe^-CHRPPh_3^+$ Prepared from $Me_2Ge(CH_2)_nGeMe_2Fe(CO)_4$ (n = 1, 2), Aldehydes, and PPh_3

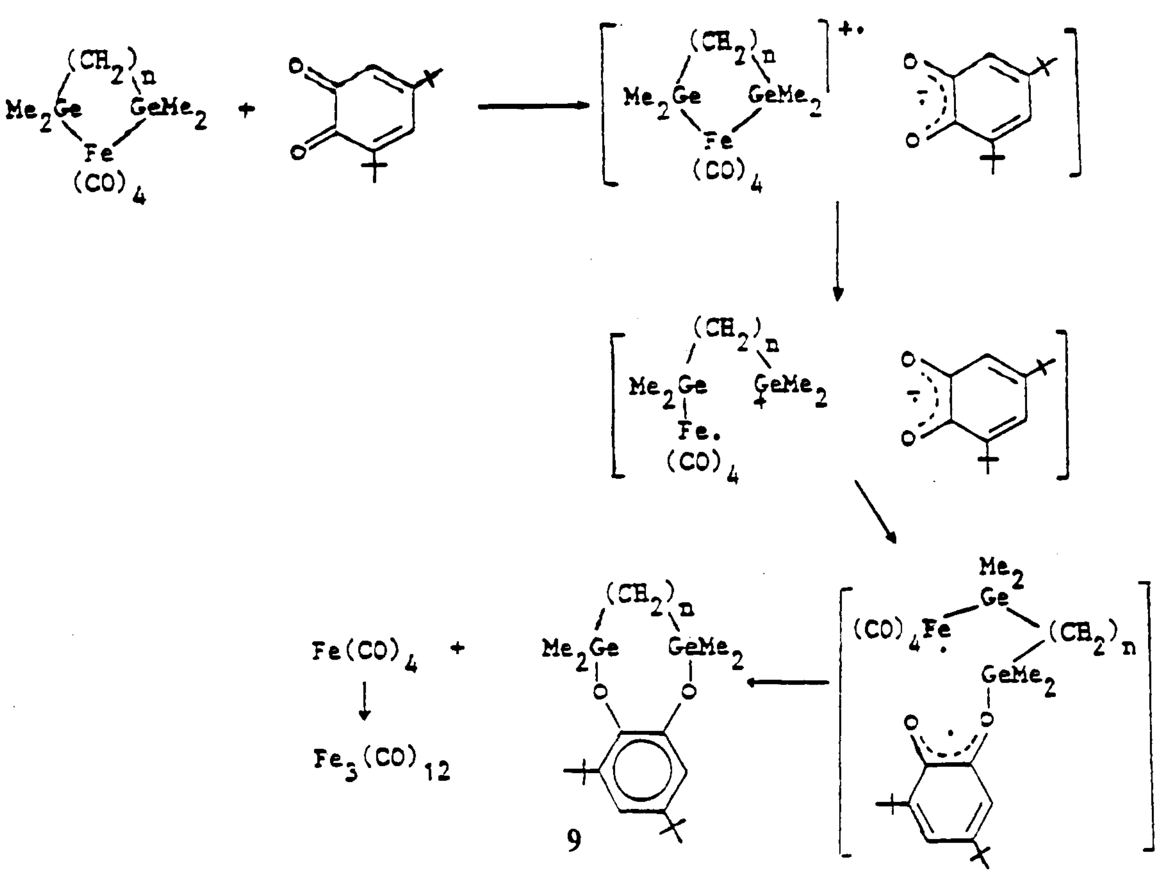
aldehyde	zwitterion (yield)	mp, °C	IR,[a] cm^{-1}	^1H NMR,[b] ppm	^{31}P NMR,[b] ppm
CCl_3CHO	 $(CO)_4\bar{F}e-\overset{H}{\underset{+P(C_6H_5)_3}{C}}-CCl_3$ (53%)	135–140	1910 vs 1995 m 2045 m	8.2–7.15 (m, 15 H) 5.18 (d, J_{P-H} = 13.1 Hz, 1 H)	32.09[c]
C_2H_5CHO	 $(CO)_4\bar{F}e-\overset{H}{\underset{+P(C_6H_5)_3}{C}}-C_2H_5$ (46%)[d]	130	1901 vs 1923 m 2023 m	7.97–7.08 (m, 15 H) 2.5–1.4 (m, 6 H)	34.47
C_6H_5CHO	 $(CO)_4\bar{F}e-\overset{H}{\underset{+P(C_6H_5)_3}{C}}-C_6H_5$ (12%)	115–120 dec	1905 s 1930 m 2020 m	7.63–6.90 (m, 20 H) 4.02 (d, J_{P-H} = 12.7 Hz, 1 H)	30.05[c]

[a] In THF. [b] In C_6D_6, TMS unless noted. [c] In $CDCl_3$. [d] In agreement with literature values (cf. ref 6).

characterized by IR and NMR (^1H and ^{31}P) spectroscopy (Table I) and were in agreement with literature values; they are stable at room temperature but decompose rapidly under thermal effects to give $Fe(CO)_4PPh_3$, $Fe(CO)_3(PPh_3)_2$, and the trans isomers RCH=CHR.

2. Reactions with Quinones. Galvinoxyl, a highly effective inhibitor of free radical chain processes has no effect on the rate of these reactions between quinones and **1** or **2** (galvinoxyl does not react with complexes **1** or **2** or quinones). Moreover, it can be shown that these reactions are photochemically induced by carrying out the photolysis of a mixture of quinone and **2** at −40 °C under very dilute conditions with parallel control experiments (the thermal process is slow at this temperature). So these additions, which are very similar to the reaction of quinones or tetracyanoethylene with group 14 metal-hydride, M–H (M = Si, Ge, Sn),[14-18] or group 14 metal-nitrogen compounds[19] proceed

Scheme III



probably through a one-electron-transfer mechanism. The transient semiquinone radical involved can be detected by ESR spectroscopy, as either the anion radical or the ion paired with the metal. The deep green solution obtained upon mixing 3,5-di-*tert*-butyl-*o*-quinone 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 ESR spectra of *o*-semiquinone species obtained by different means.[19-21] The Ge–Fe bond in **1** or **2** can act as an electron donor to the quinone and the reaction sequence in Scheme III is therefore postulated to account for the formation of the adduct **9**.

Novel reactions of **1** and **2** complexes with organic molecules, especially nitriles and organometallic species like [>Ge=X] (X = O, S, P–R), will be the subject of future reports.

Experimental Section

All reactions were done under an atmosphere of dry argon with use of standard Schlenk and high-vacuum-line techniques. ^1H NMR spectra were recorded on a Varian 360 A spectrometer operating at 60 MHz; chemical shifts are reported in parts per million relative to internal Me_4Si as reference. ^{31}P NMR spectra were measured at 36.4 MHz by using a Bruker WP 90 spectrometer and 85% H_3PO_4 as an external reference. Gas-phase chromatography was carried out on an Intersmat IGC apparatus using helium as the carrier gas, a thermistor detector, and an SE 30 chromosorb column. ESR measurements were made at room or low temperatures on solution samples by using a Bruker ER 200 spectrometer. Mass spectra were recorded on a Ribermag R 1010 or a Varian Mat 311 A spectrometer operating in the electron-impact mode at 70 eV. In all cases the complex envelope of peaks obtained for polygermanes agreed with the expected isotopic distribution based on the number of isotopes of germanium.[22] Microanalyses were performed by the Microanalytical Laboratory of the CNRS or ENSCT, Toulouse, France.

Reaction of Chloral with [Bis(dimethylgermyl)methane]iron Tetracarbonyl. To **1** (1.00 g, 2.58 mmol) in anhydrous C_6H_6 (5 mL) was added dropwise Cl_3CCHO (0.35 g, 2.58 mmol). An exothermic reaction occurred, and the mixture was stirred for 2 h at 5 °C. The course of the reaction was monitored by GC (disappearance of **1** and CCl_3CHO), by IR spectroscopy of aliquots, and by ^1H NMR analysis, which showed the formation of **3a** (64%): ^1H NMR (C_6H_6) 0.65 (s, 6 H, CH_3GeFe), 0.70 (s, 6 H, CH_3GeO), 5.25 (s, 1 H), 0.25 (s, 2 H). The attempt of distillation at 140 °C under 10 mmHg produced the appearance of iron carbonyls ($Fe_3(CO)_{12}$ and $Fe_2(CO)_9$), which were recovered by filtration. *trans*-1,1,1,4,4,4-Hexachloro-2-butene[23] (mp 81 °C) was extracted by crystallization in pentane. GC (comparison with authentic samples described in ref 4), ^1H NMR spectroscopy, and GC-MS of the supernatant solution revealed that known compounds **4** and **5** had been formed in relative amounts of 60% and 25%, respectively, in addition to traces of known compounds **6**, $(Me_2GeO)_3$, and $\overline{Me_2GeCH_2GeMe_2CH_2}$.

Hydrolysis of 3a. To **1** (0.88 g, 2.27 mmol) was added a benzene solution of CCl_3CHO (0.31 g, 2.27 mmol) under argon at 5 °C. After the reaction was complete, the resulting mixture was warmed to room temperature. After hydrolysis with deoxygenated water and filtration of iron products, GC and NMR analysis showed the formation of the known compound **4**[4] (87%).

Reaction of Benzaldehyde with [Bis(dimethylgermyl)methane]iron Tetracarbonyl. Under the same experimental conditions as in the preceding preparation, **1** (0.75 g, 1.93 mmol) mixed with C_6H_5CHO (0.20 g, 1.93 mmol) in anhydrous C_6H_6 (5 mL) gave **3b** after concentration of the organic phase (57%): ^1H NMR (C_6D_6) 0.33 (s, 6 H, CH_3Ge), 0.35 (s, 6 H, CH_3GeO), 7.10–7.30 (m, 5 H), 4.55 (s, 1 H), 0.17 (s, 2 H). Distillation under reduced pressure (1 mmHg) resulted in the isolation

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of **4** and **5**[4] in relative amounts of 65% and 25%, respectively, in addition to traces of **6**, $(Me_2GeO)_3$, and $Me_2GeCH_2GeMe_2CH_2$. White crystals of *trans*-stilbene were extracted with a few milliliters of pentane and dried under 10 mmHg.

Reaction of Propionaldehyde with [Bis(dimethylgermyl)methane]iron Tetracarbonyl. As just described, **1** (0.90 g, 2.32 mmol) mixed with CH_3CH_2CHO (0.13 g, 2.32 mmol) in C_6H_6 (5 mL) gave **3c** after concentration of the organic phase (0.55 g, 50% yield): ^1H NMR (C_6D_6) 0.16 (s, 6 H, CH_3Ge), 0.20 (s, 6 H, CH_3GeO), 0.8 (t, 3 H), 1.4 (m, 2 H), 0.10 (s, 2 H), 3.4 (t, 1 H).

Reaction of Chloral with [1,2-Bis(dimethylgermyl)ethane]iron Tetracarbonyl. A benzene solution of **2** (1.20 g, 3.0 mmol) and CCl_3CHO (0.41 g, 3.0 mmol) in C_6H_6 (5 mL) was heated at 140 °C for 2 h in a sealed tube. After elimination of iron products by filtration, *trans*-1,1,1,4,4,4-hexachloro-2-butene[23] (0.60 g, 76% yield) was extracted by crystallization in pentane. ^1H NMR spectroscopy and GC of the supernatant solution revealed that **8** had been formed (86% yield, identified by GC and NMR comparison with an authentic sample[1]).

Reaction of Benzaldehyde with [1,2-Bis(dimethylgermyl)ethane]iron Tetracarbonyl. Under the same experimental conditions as in the preceding preparation, a mixture of **2** (1.46 g, 65 mmol) and C_6H_5CHO (0.38 g, 3.65 mmol) in C_6H_6 (5 mL) heated at 140 °C for 8 h gave, after elimination of *trans*-stilbene and iron products ($Fe_2(CO)_9$, $Fe_3(CO)_{12}$), the known[1] oxide **8** (90% yield; identified by GC and NMR analyses).

UV Irradiation of Benzaldehyde with [1,2-Bis(dimethylgermyl)ethane]iron Tetracarbonyl. Under $h\nu$, to **2** (1.15 g, 2.88 mmol) in C_6H_6 (3 mL) was added C_6H_5CHO (0.30 g, 2.88 mmol). The solution was irradiated (λ = 254 nm) in a quartz tube for 2 h at ambient temperature. The progress of the reaction was followed by GC (disappearance of **2** and appearance of **8**). After elimination of iron products and *trans*-stilbene by filtration, analysis by GC and NMR spectroscopy of the supernatant solution revealed the formation of **8**[1] (88% yield).

Reaction of Propanal with [1,2-Bis(dimethylgermyl)ethane]iron Tetracarbonyl. As just described, a mixture of **2** (1.35 g, 3.37 mmol) and CH_3CH_2CHO (0.20 g, 3.37 mmol) in C_6H_6 (5 mL) heated at 140 °C for 5 h gave, after elimination of iron products, the oxide **8**[1] (85% yield) and *trans*-diethylethylene (identified by GC and NMR comparisons with authentic samples).

Reaction of Chloral with [Bis(dimethylgermyl)methane]iron Tetracarbonyl in the Presence of Ph_3P. To a mixture of **1** (0.90 g, 2.32 mmol) and Ph_3P (0.60 g, 2.32 mmol) in C_6H_6 (5 mL) was added at 5 °C, drop by drop, CCl_3CHO (0.31 g, 2.32 mmol) dissolved in C_6H_6 (3 mL). This mixture was stirred magnetically for 2 h at room temperature, and pentane (10 mL) was added, upon which a green precipitate appeared. After filtration under argon, the precipitate was washed with pentane and dried under 30 mmHg, yielding green crystals of **11a** (0.69 g, 53% yield): mp 135–140 °C; ^1H NMR ($CDCl_3$) 7.15–8.2 (m, 15 H), 5.18 (d, J(PH) = 13.1 Hz, 1 H); ^{31}P NMR ($CDCl_3$) 32.09; IR ν(CO) 1995 m, 2045 m, 1910 cm^{-1} vs. Anal. Calcd for $C_{24}H_{16}Cl_3FeO_4P$: C, 51.29; H, 2.85; Cl, 18.97. Found: C, 51.61; H, 2.97; Cl, 18.64.

The filtrate was concentrated under 10 mmHg and analysis by ^1H NMR spectroscopy and GC showed that **4** (83% yield) and traces of **5**, **6**, $Me_2GeCH_2GeMe_2CH_2$, and $(Me_2GeO)_3$ had been formed.[4]

Reaction of Chloral with [1,2-Bis(dimethylgermyl)ethane]iron Tetracarbonyl in the Presence of Ph_3P. A solution of **2** (0.87 g, 2.17 mmol) and Ph_3P (0.57 g, 2.17 mmol) in C_6H_6 (10 mL) was treated at 5 °C with CCl_3CHO (0.29 g, 2.17 mmol), and the mixture was heated at 140 °C for 4 h in a sealed tube. Yellow crystals of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$[24] were recovered by filtration. After elimination of *trans*-1,1,1,4,4,4-hexachloro-2-butene, distillation under reduced pressure (1 mmHg) of the organic phase provided a liquid fraction containing **8** (0.51 g, 95% yield). **8** was identified by GC and ^1H NMR comparison with an authentic sample.[1]

Reaction of Benzaldehyde with [Bis(dimethylgermyl)methane]iron Tetracarbonyl in the Presence of Ph_3P. To **1** (0.73 g, 1.88 mmol) and Ph_3P (0.49 g, 1.88 mmol) in C_6H_6 (5 mL) was added C_6H_5CHO (0.2 g, 1.88 mmol) in C_6H_6 (2 mL). The reaction was slightly exothermic, and the reaction mixture was left for 16 h at 20 °C with magnetic stirring. After concentration of the solvent, the mixture was taken up with a minimum amount of anhydrous C_6H_6 (2 mL). Addition of pentane (20 mL) caused a precipitate, which was filtered out under argon. The precipitate was dried under 30 mmHg, and it proved to be yellow crystalline **11b** (0.12 g, 12% yield), whose properties are in agreement with those in the literature.[6] The filtrate was concentrated under 10 mmHg, and then analysis by GC and ^1H NMR spectroscopy showed that **4** (52%) and **5** (17%) had been produced in addition to traces of **6**, $Me_2GeCH_2GeMe_2CH_2$, and $(Me_2GeO)_3$.[4]

Reaction of Benzaldehyde with [1,2-Bis(dimethylgermyl)ethane]iron Tetracarbonyl in the Presence of Ph_3P. A mixture of **2** (0.96 g, 2.39 mmol) in C_6H_6 (10 mL), C_6H_5CHO (0.25 g, 2.39 mmol), and Ph_3P (0.63 g, 2.39 mmol) was kept in a sealed tube for 12 h at 140 °C. After elimination of the iron products $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$[24] by filtration, the *trans*-stilbene was extracted by crystallization in pentane. ^1H NMR and GC analyses of the liquid phase confirmed that only **8**[1] had been formed (0.55 g, 93% yield).

Reaction of Propanal with [Bis(dimethylgermyl)methane]iron Tetracarbonyl in the Presence of PPh_3. To **1** (1.10 g, 2.84 mmol) and Ph_3P (0.74 g, 2.84 mmol) in C_6H_6 (5 mL) was added CH_3CH_2CHO (0.16 g, 2.84 mmol) in C_6H_6 (5 mL), and the reaction was left for 6 h at 20 °C with magnetic stirring. After concentration of the solvent, addition of pentane (10 mL) caused a precipitate, which was filtered out and dried under reduced pressure (30 mmHg); it proved to be yellow crystalline **11c** (0.61 g, 46% yield), whose properties are in agreement with those in the literature:[6] mp 130 °C; IR (THF) ν(CO) 2023 m, 1923 m, 1901 cm^{-1} vs; ^1H NMR (C_6D_6) 7.97–7.08 (m, 15 H), 2.50–1.40 (m, 6 H); ^{31}P NMR (C_6D_6) 34.47.

Reaction of 3,5-Di-*tert*-butyl-*o*-quinone with [Bis(dimethylgermyl)methane]iron Tetracarbonyl. [Bis(dimethylgermyl)methane]iron tetracarbonyl (0.82 g, 2.11 mmol) in C_6H_6 (3 mL) was added dropwise to 3,5-di-*tert*-butyl-*o*-quinone (0.46 g, 2.11 mmol) dissolved in C_6H_6 (2 mL). The reaction was slightly exothermic, and CO was released rapidly. After elimination of iron products ($Fe_2(CO)_9$ and $Fe_3(CO)_{12}$) by filtration and concentration of the solvent under reduced pressure (10 mmHg), pentane (10 mL) was added, upon which the product **9a** (0.70 g, 75% yield) precipitated as dark green crystals, which were decanted and dried in vacuo: mp 115 °C; ^1H NMR (C_6D_6) 7.0–7.25 (m, 2 H), 1.65 (s, 9 H), 1.40 (s, 9 H), 0.60 (s, 2 H), 0.50 (s, 6 H), 0.40 (s, 6 H); MS *m/e* 440 ($[M]^+$), 425 ($[M - CH_3]^+$), 324 ($[M - Me_2CH_2]^+$). Anal. Calcd for $C_{19}H_{34}Ge_2O_2$: C, 51.91; H, 7.74. Found: C, 52.02; H, 7.76.

Reaction of 3,5-Di-*tert*-butyl-*o*-quinone with [1,2-Bis(dimethylgermyl)ethane]iron Tetracarbonyl. Under the same experimental conditions as in the preceding preparation, **2** (1.04 g, 2.60 mmol) reacted with the quinone (0.57 g, 2.60 mmol) to give the dark green crystalline product **9b** (0.75 g, 82% yield): mp 185 °C dec; ^1H NMR (C_6D_6) 7.25–6.9 (m, 2 H), 1.64 (s, 9 H), 1.38 (s, 9 H), 1.18 (s, 2 H), 0.42 (s, 6 H), 0.22 (s, 6 H); MS *m/e* 454 ($[M]^+$), 439 ($[M - CH_3]^+$), 324 ($[M - Me_2Ge(CH_2)_2]^+$). Anal. Calcd for $C_{20}H_{36}Ge_2O_2$: C, 52.96; H, 7.94. Found: C, 53.01; H, 8.06.

ESR Spectrum. A solution of quinone (0.40 g, 2 mmol) in deoxygenated pentane (10 mL) was slowly added at −40 °C to **2** (0.80 g, 2 mmol) in deoxygenated pentane (10 mL). The ESR spectrum of the green solution at −40 °C shows a doublet for which a^H = 3.5 G and g = 2.0018.

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[24] Cotton, F. A.; Parish, R. V. *J. Chem. Soc.* **1960**, 1440.