Journal of Organometallic Chemistry, 427 (1992) 91–99
Elsevier Sequoia S.A., Lausanne
JOM 22382

Synthesis and reactivity of germyliron complexes $[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2]$ and $[RH_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2]$ $(R = Ph \text{ or } 2,4,6\text{-}Me_3C_6H_2)$

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(Received July 12, 1991)

Abstract

The new complexes $[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2]$ (**1**) and $[RH_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2]$ (R = Ph or Mes, **2a** or **2b**) were prepared by a substitution reaction, from the corresponding arylhalohydrogermanes and the iron salt. Their characterization by IR, ^1H and ^{13}C NMR and mass spectroscopy is reported. They are easily transformed into the mono- or di-halogermyl compounds by action of *N*-chlorosuccinimide. Treatment of **1** with lithium reagents (LDA or ^tBuLi) leads to an initial deprotonation of the cyclopentadienyl ring with migration of the germyl group. The intermediate iron salt was quenched by MeI producing $MeFe(\eta^5\text{-}C_5H_4GeHPh_2)(CO)_2$. Hydrogermylation reactions with phenylacetylene or methylethynylketone were performed in the presence of chloroplatinic acid and yielded mainly the α-isomer of the adduct.

Introduction

Complexes of the general molecular formula $(\eta^5\text{-}C_5R_5)Mn(CO)(L)HER'_3$ (R = H or Me; L = CO or PMe_3; E = Si, Ge, or Sn; R′ = Ph or Cl) have been studied extensively [1–4]. According to the literature, these compounds have structures of which **A** and **B** represent the limiting forms.

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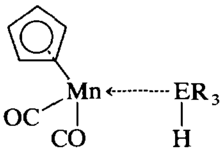
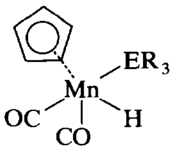
0022-328X/92/$05.00



(A)



(B)

E = Si or Ge

In **A**, the silane or the germane acts as a neutral two-electron donor. In **B**, MnH and Mn–Si bonds are formed. For $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HGePh_3)]$ chemical reactivity suggests that **A** is the best representation [2].

The purpose of this paper is to report a new class of transition metal complex containing a germanium–hydrogen bond, $[R_{3-n}H_nGeFe(\eta^5\text{-}C_5H_5)(CO)_2]$ (R = Ph or Mes; $n = 2$ or 3) and to compare the reactivities of the compounds prepared towards substitution and hydrogermylation reactions.

Results

The hydrogermyl complexes were prepared by substitution reactions from the corresponding organohalogermanes according to eq. 1.

$$R_{3-n}H_nGeCl + Na\left[(\eta^5\text{-}C_5H_5)Fe(CO)_2\right] \xrightarrow{-NaCl} \left[R_{3-n}H_nGeFe(\eta^5\text{-}C_5H_5)(CO)_2\right] \quad (1)$$

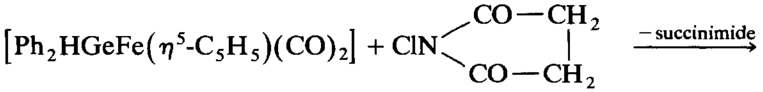
(**1**: R = Ph, $n = 1$;
2a: R = Ph, $n = 2$;
2b: R = Mes, $n = 2$)

These yellow complexes may be readily handled in air, and purified by column chromatography and recrystallization. In the crystalline state complexes **2a** and **2b** are stable, but they slowly decompose in chlorinated solvents.

Spectral data of these new complexes are summarized in Table 1.

The chemical shifts of Ge–*H* in **1**, **2a** and **2b**, are slightly to lower field ($\Delta\delta \sim 0.3$ ppm) compared to those of the corresponding arylgermanes (Ph_3GeH, δ 5.66 ppm; Ph_2GeH_2, δ 5.16 ppm; Mes_2GeH_2, δ 5.05 ppm [5]). These shifts correlate with a negative charge at the germanium atom, as reported for lithium diarylgermyls. The ^{13}C shifts confirm this. The ipso ^{13}C resonance is also slightly shifted to lower field. This effect is less important, and indicates less polarization of the phenyl ring than in (diarylgermyl)lithium [6].

For these compounds, the more effective halogenating reagent is *N*-chlorosuccinimide. Other chlorinating reagents (*e.g.* CCl_4, $HgCl_2$) often used with organogermanes [7,8] are less selective. With this reagent, **1** is easily transformed into the corresponding halogermyl compound.

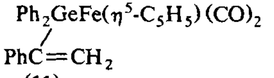


$$\left[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2\right] + ClN\begin{matrix} CO-CH_2 \\ | \\ CO-CH_2 \end{matrix} \xrightarrow{-\text{succinimide}} \left[Ph_2ClGeFe(\eta^5\text{-}C_5H_5)(CO)_2\right] \quad (2)$$

(**3**)

Table 1

Spectral data of complexes

Products	^1H or ^{19}F NMR (solvent)	^{13}C NMR (solvent)	IR [a]
$Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(1)**	4.71 (C_5H_5), 5.36 (GeH), 7.10–7.80 (C_6H_5) ($CDCl_3$)	84.32 (C_5H_5), 128.42, 134.69, 144.39 (C_6H_5), 215.52 (CO) (CD_2Cl_2)	ν(GeH), ν(CO) 1994, 1956, 1932
$PhH_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(2a)**	3.98 (C_5H_5), 4.81 (GeH), 7.00–7.75 (C_6H_5) (C_6D_6)	84.73 (C_5H_5), 128.58, 134.99, 143.27 (C_6H_5), 215.76 (CO) (THF-d_8)	ν(GeH), ν(CO) 2014, 1956
$MesH_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(2b)**	2.16, 2.51 (CH_3), 4.03 (C_5H_5), 4.69 (GeH_2), 6.82 (C_6H_2) (C_6D_6)	21.22 (p-CH_3), 24.15 (o-CH_3), 84.77 (C_5H_5), 128.72, 137.84, 139.00, 143.25 (C_6H_2), 216.20 (CO) (THF-d_8)	ν(GeH), ν(CO) 2015, 1956
$Ph_2ClGeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(3)**	4.87 (C_5H_5), 7.20–7.80 (C_6H_5) ($CDCl_3$)	84.87 (C_5H_5), 128.22, 128.99, 132.50, 146.00 (C_6H_5), 213.09 ($CDCl_3$)	ν(CO) 2009, 1945
$PhCl_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(4a)**	4.06 (C_5H_5), 7.00–8.05 (C_6H_5) (C_6D_6)	86.56 (C_5H_5), 129.18, 130.77, 131.67, 149.99 (C_6H_5), 212.44 (CO) (THF-d_8)	ν(CO) 2022, 1959
$MesCl_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(4b)**	2.25, 2.65 (CH_3), 5.03 (C_5H_5), 6.81 (C_6H_2) ($CDCl_3$)	21.00 (o-CH_3), 24.86 (p-CH_3), 85.85 (C_5H_5), 129.98, 139.96, 141.08, 142.95 (C_6H_2), 211.33 (CO) ($CDCl_3$)	ν(CO) 2036, 2018, 1990, 1971
$PhHClGeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(5)**	4.01 (C_5H_5), 6.82 (GeH), 7.05–7.90 (C_6H_5) (C_6D_6)	85.83 (C_5H_5), 128.98, 132.96, 146.19 (C_6H_5), 213.92 (CO) (THF-d_8)	ν(GeH), ν(CO) 2012, 1955
$PhMe_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(6)**	0.70 (CH_3), 4.57 (C_5H_5), 7.20–7.70 (C_6H_5) ($CDCl_3$)	4.32 (CH_3), 83.34 (C_5H_5), 127.55, 127.82, 132.38, 149.53 (C_6H_5), 215.67 (CO) ($CDCl_3$)	ν(CO) 1995, 1945
$PhF_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(7)**	5.08 (C_5H_5), 7.20–7.70 (C_6H_5) ($CDCl_3$) ^{19}F −133.50 ($CDCl_3$)	83.64 (C_5H_5), 128.69, 130.77, 131.13 (C_6H_5), 210.50 (CO) ($CDCl_3$)	ν(CO) 2021, 1969
$(Ph_2HGeC_5H_4)FeMe(CO)_2$ **(8)**	0.13 (CH_3), 4.80 (m, C_5H_4), 5.64 (s, GeH), 7.20–7.70 (C_6H_5) ($CDCl_3$)	−22.68 (CH_3), 82.99, 87.37, 93.52 (C_5H_5), 128.53, 129.56, 133.69, 134.89 (C_6H_5), 217.11 (CO) ($CDCl_3$)	ν(GeH), ν(CO) 2049, 2003, 1942 (pure)
$Ph_2MeGeFe(\eta^5\text{-}C_5H_5)(CO)_2$ **(9)**	0.93 (CH_3), 4.65 (C_5H_5), 7.20–7.70 (C_6H_5) ($CDCl_3$)	04.00 (CH_3), 83.73 (C_5H_5), 127.92, 133.67, 146.55 (C_6H_5), 215.51 (CO) ($CDCl_3$)	ν(CO) 1988, 1980, 1949, 1926
$(Ph_2MeGeC_5H_4)FeMe(CO)_2$ **(10)**	0.12 (CH_3), 0.99 (CH_3Ge), 4.83 (m, C_5H_4), 7.10–7.70 (C_6H_5) ($CDCl_3$)	−22.92 (CH_3), −3.56 (CH_3Ge), 86.43, 87.73, 93.11 (C_5H_4), 128.42, 129.34, 134.28, 137.39 (C_6H_5), 217.46 (CO) ($CDCl_3$)	ν(CO) 2007, 1954
 $Ph_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2$ / $PhC{=}CH_2$ **(11)**	4.44 (C_5H_5), 5.53 (d, J = 3 Hz, CH_2), 6.03 (d, J = 3 Hz, CH_2), 7.20–7.70 (C_6H_5) ($CDCl_3$)	83.74 (C_5H_5), 126.45, 127.04, 127.57, 127.89, 128.06, 134.56, 144.91, 155.21 (C_6H_5, CH_2), 215.30 (CO) ($CDCl_3$)	ν(CO) 1990, 1923

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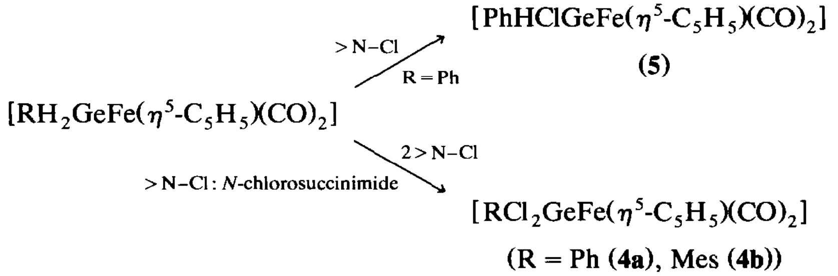
[a] IR spectra recorded in Nujol mull unless otherwise noted

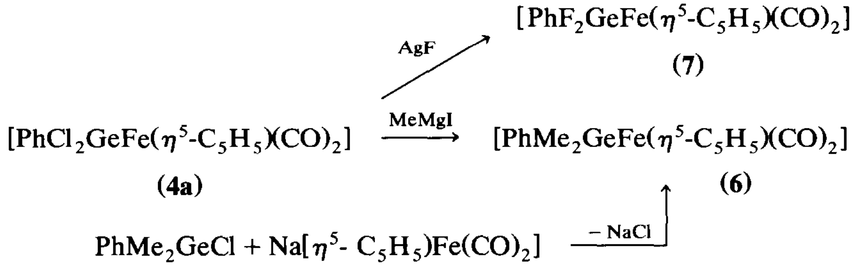
When one equivalent of *N*-chlorosuccinimide reacted with complex **2a**, the transient formation of the chlorogermyl compound **5** was observed. It could not be isolated pure, but it was completely characterized by ^1H and ^{13}C NMR spectroscopy. We never observed such a selective reaction with diphenylgermane [7,8] and *N*-chlorosuccinimide. Complex **5** is relatively unstable and decomposes quite rapidly in halogenated solvents.



$$\begin{tikzcd}
 & {[PhHClGeFe(\eta^5\text{-}C_5H_5)(CO)_2]}\ \mathbf{(5)} \\
{[RH_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2]} \arrow[ur, ">N\text{-}Cl", "R=Ph"'] \arrow[dr, "2>N\text{-}Cl", ">N\text{-}Cl:\ N\text{-chlorosuccinimide}"'] & \\
 & {[RCl_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2]}
\end{tikzcd} \qquad (3)$$

(R = Ph (**4a**), Mes (**4b**))

The use of an excess of *N*-chlorosuccinimide leads to the formation of the isolable complexes **4a** and **4b**, which are also characterized by their alkylation reactions.



$$\begin{tikzcd}
 & {[PhF_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2]}\ \mathbf{(7)} \\
{[PhCl_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2]}\ \mathbf{(4a)} \arrow[ur, "AgF"] \arrow[r, "MeMgI"] & {[PhMe_2GeFe(\eta^5\text{-}C_5H_5)(CO)_2]}\ \mathbf{(6)} \\
PhMe_2GeCl + Na[\eta^5\text{-}C_5H_5)Fe(CO)_2] \arrow[ur, "-NaCl"'] &
\end{tikzcd} \qquad (4)$$

We could not obtain the halogermyl complexes **4a** and **4b** by direct synthesis from the corresponding aryltrichlorogermanes and the iron salt because the reactions were not selective and led to a mixture of several products. All these halogermyl complexes have low stability in solution and decompose during successive recrystallizations. Alkylation reactions were performed in ether or THF solution. Compound **6** can be easily prepared via the standard salt elimination reaction (eq. 4).

Complex **4a** was also treated with silver fluoride at room temperature, giving the corresponding fluorogermyl complex in moderate yield.

Some metalation reactions with lithium alkyls were attempted. Treatment of **1** with lithium diisopropylamide (LDA) led to an initial deprotonation of the cyclopentadienyl ring and migration of the germyl group. Such phenomena were previously observed with triorganogermyl complexes [9–11] or silyl complexes [12,13]. In our case, the functional germylated group was transferred to the cyclopentadienyl ring without any metalation reaction of the germanium–hydrogen bond. The iron intermediate salt was trapped by reaction with methyl iodide producing complex **8**.

$$[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2] \xrightarrow{LDA,\ MeI} \underset{\mathbf{(8)}}{[MeFe(\eta^5\text{-}C_5H_4GeHPh_2)(CO)_2]} \qquad (5)$$

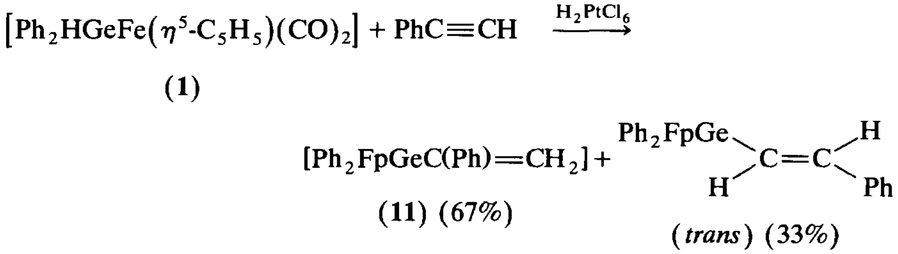
When ^{t}BuLi was used, the reaction was more complex. Metalation reactions of both germanium–hydrogen bond and cyclopentadienyl group were observed as well as partial decomposition of the initial complex.

$$\begin{tikzcd}
{[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2]} \arrow[r, "{^tBuLi,\ THF}", "MeI"'] & {\underset{\mathbf{(9)}}{[Ph_2MeGeFe(\eta^5\text{-}C_5H_5)(CO)_2] + \mathbf{8}}} \\
{Ph_2MeGeCl + Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]} \arrow[ur, "-NaCl"'] &
\end{tikzcd}$$

(6)

Complex **9** was also obtained by reaction of the corresponding sodium salt with the halogermane. The formation of the corresponding germylcyclopentadienyl complex $[MeFe(\eta^5\text{-}C_5H_4GeMePh_2)(CO)_2]$ (**10**), synthesized by other means, was never observed.

Hydrogermylation reactions of **1** with hexyne or several carbonyl compounds (cyclohexanone, benzaldehyde, acrolein) were tried, using various catalysts (azobisisobutyronitrile AIBN, chloroplatinic acid). In contrast with the phenylgermane series [14], only the addition reaction on phenylacetylene was successful. The reaction was performed in refluxing benzene and in the presence of chloroplatinic acid, and resulted in the corresponding germylalkenes.



$$[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2] + PhC{\equiv}CH \xrightarrow{H_2PtCl_6} [Ph_2FpGeC(Ph){=}CH_2] + (Ph_2FpGe)HC{=}CH(Ph) \tag{7}$$

(1)

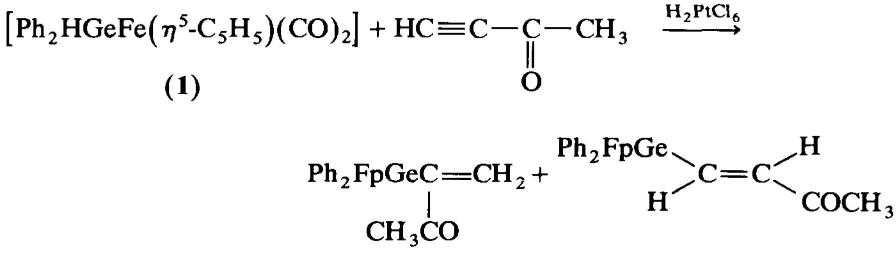
(11) (67%)

(*trans*) (33%)

$(Fp = (\eta^5\text{-}C_5H_5)(CO)_2Fe)$

Spectroscopic analysis (^{1}H NMR) shows the presence of two isomers, the α-germylstyrene (**11**) and the *trans*-β-germylstyrene. The predominant form was **11** which can be isolated by column chromatography and recrystallization.

In the case of methylethynylketone, which has a conjugated structure, only hydrogermylation with the acetylenic function was observed. A reaction with the carbonyl group or a 1–4 addition reaction never occurred. This hydrogermylation reaction also requires chloroplatinic acid and the α-form **12** was preferentially formed.



$$[Ph_2HGeFe(\eta^5\text{-}C_5H_5)(CO)_2] + HC{\equiv}C{-}C({=}O){-}CH_3 \xrightarrow{H_2PtCl_6} Ph_2FpGeC(COCH_3){=}CH_2 + (Ph_2FpGe)HC{=}CH(COCH_3) \tag{8}$$

(1)

(12)

It has been previously shown [14,15] that chloroplatinic acid is more effective in the case of hydride addition (Et_3Ge–H) to alkyne, giving mainly the gem isomer, whereas an acidic hydrogermane such as $PhCl_2Ge$–H yields cis and trans adducts. Our results provide evidence of the hydridic character of hydridogermyliron complexes.

Experimental section

All manipulations were performed under nitrogen or argon with dry, oxygen-free solvents. Organogermanium compounds Ph_2GeHCl [7,8], PhH_2GeCl [7,8], $MesH_2GeCl$ [5] were prepared according to literature procedures. NMR spectra were recorded on Bruker AC 80 (^1H) and AC 200 (^{13}C) spectrometers, IR spectra on a Perkin–Elmer 1600 spectrometer, and mass spectra on a Ribermag R 10-10H spectrometer operating in the electron-impact mode at 70 eV. Elemental analyses were done at the Ecole Nationale Supérieure de Chimie de Toulouse, France.

Synthesis of [$Ph_2HGeFe(\eta^5$-$C_5H_5)(CO)_2$] (1)

To a solution of Na[(η^5-C_5H_5)Fe$(CO)_2$] [16] prepared from 1.00 g (2.8 mmol) of [{(η^5-C_5H_5)Fe$(CO)_2\}_2$] in THF (40 mL), 30 mL of a THF solution of Ph_2GeHCl (1.47 g, 5.6 mmol) were added. The solution was stirred for 2 h. The solvent was removed under vacuum, and the residue extracted with 100 mL of a 40:60 methylene chloride/hexane solution and filtered. The filtrate was reduced to 10 mL and this solution was placed on a silica-gel column (2.5 × 30 cm). A yellow band was eluted with a 40:60 methylene chloride/hexane solution. Concentration and recrystallization from more methylene chloride/hexane solution yielded 1.43 g (63%) of **1**, m.p. 90°C Mass spectrum: [$M-1$] 405. Anal. Found: C, 56.10; H, 3.87. $C_{19}H_{16}FeGeO_2$ calc.: C, 56.37; H, 3.90%.

Synthesis of [$RH_2GeFe(\eta^5$-$C_5H_5)(CO)_2$] (2a, 2b)

The above procedure was used, but pure complexes were only obtained after several recrystallizations from pentane. The yields were variable (40–70%) and depended essentially upon elution conditions on the silica-gel column. For **2b**, a yellow oil was obtained which gave crystals after several days at −30°C.

2a: m.p. 50°C. Mass spectrum: m/z 330 (M^+). Anal. Found: C, 47.72; H, 3.74. $C_{13}H_{12}FeGeO_2$ calc.: C, 47.50; H, 3.65%.

2b: m.p. 52–55°C. Mass spectrum: [$M-1$] 371. Anal. Found: C, 51.74; H, 4.83. $C_{16}H_{18}FeGeO_2$ calc.: C, 51.83; H, 4.86%.

Reaction of 1 with N*-chlorosuccinimide*

N-Chlorosuccinimide (0.10 g, 0.76 mmol) was added to a solution of **1** (0.31 g, 0.76 mmol) in THF (4 mL). The mixture was stirred for 5 h. The solvent was concentrated and the residue extracted successively with 3 × 5 mL of 3:1 hexane/ether mixture. The combined extracts were cooled to −30°C for 12 h. Yellow crystals precipitated, were isolated after decantation and dried in a vacuum giving **3**: 0.30 g (90%). m.p. 80–90°C (dec.). Mass spectrum: m/z 440 (M^+). Anal. Found: C, 51.83; H, 3.37; Cl, 8.28. $C_{19}H_{15}ClFeGeO_2$ calc.: C, 51.95; H, 3.41; Cl, 8.07%.

*Reaction of **2a** and **2b** with* N*-chlorosuccinimide*

With one equivalent of N*-chlorosuccinimide.* A solution of **2a** (0.30 g, 0.90 mmol) and *N*-chlorosuccinimide (0.12 g, 0.90 mmol) in THF (15 mL) was stirred for 12 h. After concentration *in vacuo*, extraction of the residue by 3 × 5 mL of 3:1 hexane/ether mixture, the filtrate was evaporated leading to yellow crystals of **5**. Compound **5** was always obtained with traces of **2a** (< 5%), 0.24 g (73%). Mass spectrum: $[M-1]$ 363.

*Syntheses of **4a** and **4b**.* A mixture of 0.30 g (2.26 mmol) of *N*-chlorosuccinimide (0.30 g, 2.26 mmol) and complexes **2a** or **2b** (1.13 mmol) in THF (10 mL) was stirred for 12 h. The solvent was removed under vacuum. The residue was extracted with 15 mL of a 3:1 hexane/ether mixture and cooled to −30°C for 12 h. After decantation and drying under vacuum, yellow crystals were obtained. **4a**: 0.40 g (67%). m.p. 80–85°C (dec.). Mass spectrum: m/z 398 (M^+). Anal. Found: C, 39.66; H, 2.71; Cl, 17.98. $C_{13}H_{10}Cl_2FeGeO_2$ calc.: C, 39.26; H, 2.52; Cl, 17.84%. **4b**: 0.35 g (70%); m.p. 76–80°C (dec). Mass spectrum: m/z 440 [M^+].

*Reaction of **4a** with MeMgI*

A solution of MeMgI (1.15 mmol) in ether was added dropwise to a solution of **4a** (0.19 g, 0.48 mmol) in ether (10 mL) at −78°C. After 1 h at −78°C, the mixture was warmed to ambient temperature and stirred for 12 h at 20°C. Inorganic salts were removed by centrifugation. After concentration under vacuum, analysis of the residue by ^{1}H NMR spectroscopy showed the formation of **6** (80%), identified by comparison with a pure product obtained as described below.

*Synthesis of **6***

A solution of $PhMe_2GeCl$ (0.60 g, 2.8 mmol) in THF (15 mL) was added to a solution of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (2.8 mmol) in THF (15 mL). Using the same procedures as described for the synthesis of **1**, we obtained 0.50 g (50%) of **6**; m.p. 78–81°C. Mass spectrum: m/z 358 (M^+). Anal. Found: C, 50.37; H, 4.39. $C_{15}H_{16}FeGeO_2$ calc.: C, 50.50; H, 4.49%.

*Reaction of **4a** with AgF*

A mixture of **4a** (0.20 g, 0.5 mmol) and AgF 0.13 g (1 mmol) in THF (10 mL) was stirred at 20°C for 12 h. After concentration *in vacuo*, the residue was extracted with 10 mL of a 1:3 ether/pentane solution and cooled to −30°C for 12 h. After decantation and drying under vacuum, yellow crystals were obtained. **7**: 0.09 g (49%); m.p. 95°C. Mass spectrum: m/z 366 (M^+). Anal. Found: C, 42.18; H, 2.74. $C_{13}H_{10}F_2FeGeO_2$ calc.: C, 42.80; H, 2.74%.

*Reaction of **1** with LDA*

An equivalent of LDA in THF (3 mL) was added dropwise to a solution of **1** (1.02 g, 2.52 mmol) in THF (15 mL) at 0°C and the mixture was stirred for 30 min. The iron salt so obtained was treated with an excess of MeI at 0°C. The mixture was heated to ambient temperature. After 2 h at 20°C and concentration under vacuum, the residue was extracted with ether (20 mL) and centrifuged (elimination of LiI). The solvent was removed under vacuum and the residue was extracted with 10 mL of a 50:50 methylene chloride/hexane mixture and purified by chromatography on a silica gel column (2.5 × 30 cm). A yellow band was eluted with the same solvent mixture. Concentration led to a yellow oil identified as **8**, 0.60 g (57%). Mass spectrum: m/z 420 (M^+). Anal. Found: C, 56.62; H, 3.94. $C_{20}H_{18}FeGeO_2$ calc.: C, 57.36; H, 4.30%.

Reaction of 1 with ^{t}BuLi

To a solution of **1** (0.48 g, 1.18 mmol) in THF (10 mL) ^{t}BuLi (1.18 mmol, 1.7 M) in pentane at −78°C was added. After 1 h at −78°C the mixture was treated with an excess of MeI, heated to ambient temperature and stirred for 2 h. A similar procedure but with a 40:60 methylene chloride/hexane mixture led to a yellow oil. Analysis of this oil by ^{1}H and ^{13}C NMR spectroscopy showed the presence of **8** (11%), **9** (19%) and 70% of by-products.

Synthesis of 9

A solution of $Ph_2MeGeCl$ (0.77 g, 2.8 mmol) in THF (15 mL) was added to a solution of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (2.8 mmol) in THF (20 mL). Using the same procedures as described for the synthesis of **1**, we obtained yellow crystals which were recrystallized in pentane, 0.62 g (53%); m.p. 104–110°C. Mass spectrum: m/z 390 (M − CO). Anal. Found: C, 57.95; H, 4.40. $C_{20}H_{18}FeGeO_2$ calc.: C, 57.35; H, 4.30.

Synthesis of $[MeFe(\eta^5\text{-}C_5H_4GeMePh_2)(CO)_2]$ (10)

An equivalent of LDA in THF (5 mL) was added dropwise to a solution of **9** (0.90 g, 2.15 mmol) in THF (15 mL) at 0°C and the mixture was stirred for 40 min. The iron salt was quenched with an excess of MeI. After 2 h at 20°C and concentration under vacuum, the residue was extracted with ether (20 mL) and centrifuged. The solvent was removed under reduced pressure and replaced by 10 mL of a 40:60 methylene chloride/hexane solution. After chromatography on a silica-gel column eluted with the same solvent mixture and concentration *in vacuo*, the residue was dissolved with 10 mL of 3:1 pentane/ether mixture and cooled to −30°C for 12 h. After decantation and drying under vacuum, yellow crystals were obtained (**10**), m.p. 82°C. Mass spectrum: m/z 434 (M^+). Anal. Found: C, 58.08; H, 4.63. $C_{21}H_{20}FeGeO_2$ calc.: C, 58.27; H, 4.62%.

Reaction of 1 with phenylacetylene

A solution of **1** (0.51 g, 1.26 mmol), 0.56 g (excess) of $PhC{\equiv}CH$ and 1–2 mg of H_2PtCl_6 in 10 mL of C_6H_6 was heated under reflux for 1 h. The solvent was removed under reduced pressure and the residue extracted into 10 mL of a 40:60 methylene chloride/hexane solution. This was placed on a silica-gel column (2.5 × 30 cm), and a yellow band was eluted with the same solvent mixture. After concentration, 0.87 g (70%) of a yellow semi-solid was recovered. NMR ^{1}H analysis ($CDCl_3$) showed the formation of $[Ph_2FpGeC(Ph){=}CH_2]$ (**11**) (67%) and $[Ph_2FpGeCH{=}CHPh]$ (trans) (33%).

This semi-solid was dissolved in a 50:50 hexane/pentane solution (10 mL) and was left at −30°C for 3 days, giving yellow crystals which were isolated by decantation and drying; 0.20 g (31%) of **11** were so obtained, m.p. 134–136°C. Mass spectrum: m/z 508 (M^+). Anal. Found: C, 63.75; H, 4.20. $C_{27}H_{22}FeGeO_2$ calc.: C, 63.98; H, 4.34%.

[$Ph_2FpGeCH{=}CHPh$] (trans) NMR ^1H: 4.71 (C_5H_5, 5H, s), 6.65 (CH, 1H, d), 6.90–7.80 (CH, C_6H_5, 11H, m), $J = 18$ Hz (in agreement with [13]), ($CDCl_3$).

Reaction of 1 with methylethynylketone

Using the above procedure, 0.7 g (1.73 mmol) of **1**, 0.23 g (excess) of $HC{\equiv}C{-}COMe$ and 1–2 mg of H_2PtCl_6 in 15 mL of C_6H_6 led, after elution with a 50:50 hexane/ether solution and concentration *in vacuo*, to a yellow oil (0.50 g) which was analysed by NMR ^1H spectroscopy. This showed the formation of [$Ph_2FpGe{-}C(MeCO){=}CH_2$] (**12**) (32%) and [$Ph_2FpGeCH{=}CH(MeCO)$] (trans) (5%) ($CDCl_3$); pure products could not be isolated from this mixture. **12**: ^1H NMR: 2.34 (CH_3CO, 3H, s), 4.72 (C_5H_5, 5H, s), 5.93 (CH_2, 1H, d, $J = 1.5$ Hz), 6.55 (CH_2, 1H, d, $J = 1.5$ Hz), 7.15–7.70 (C_6H_5, 10H, m). [$Ph_2FpGeCH{=}CH(MeCO)$] (trans): 2.28 (CH_3CO, 3H, s), 4.71 (C_5H_5, 5H, s), 6.40 (CH_2, 1H, s), 7.15–7.60 (C_6H_5, CH_2, 11H, m) ($CDCl_3$).

References

1 (a) U. Schubert, Adv. Organomet. Chem., 30 (1990) 151; (b) U. Schubert, G. Schlohz, J. Müller, K. Ackermann and B. Wörle, J. Organomet. Chem., 306 (1986) 303; (c) U. Schubert, E. Kunz, B. Harkers, J. Willnecker and J. Meyer, J. Chem. Soc., 111 (1989) 2572.
2 (a) F. Carré, E. Colomer, R.J.P. Corriu and A. Vioux, Organometallics, 3 (1984) 1272; (b) E. Colomer, R.J.P. Corriu, C. Mazzin and A. Vioux, Inorg. Chem., 21 (1982) 368; (c) E. Colomer, R. Corriu and A. Vioux, Inorg. Chem., 18 (1979) 695; J. Chem. Res., (S) (1977) 168; (M) (1977) 1939.
3 W. Jetz and W.A.G. Graham, Inorg. Chem., 10 (1971) 4.
4 D.L. Lichtenberger and A. Rai-Chaudhurt, J. Chem. Soc., Dalton Trans., (1990) 2161.
5 P. Rivière, M. Rivière-Baudet, A. Castel, J. Satgé and A. Lavabre, Synth. React. Inorg. Met.-Org. Chem., 17 (1987) 539.
6 A. Castel, P. Rivière, J. Satgé and H.Y. Ko, Organometallics, 9 (1990) 205.
7 M. Lesbre, P. Mazerolles and J. Satgé, The Organic Compounds of Germanium, Wiley, London, 1971.
8 P. Rivière, M. Rivière-Baudet and J. Satgé, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 2, Pergamon Press, Oxford, 1982, Chap. 10, p. 399.
9 W.K. Dean and W.A.G. Graham, Inorg. Chem., 16 (1977) 1060.
10 J. Cervantes, S.P. Vincenti, R.N. Kapoor and K.H. Pannell, Organometallics, 8 (1989) 744.
11 E.L. Kenneth, A.M. Arif and J.A. Gladysz, Organometallics, 10 (1991) 751.
12 S.R. Berryhill, G.L. Clevenger and P.Yu. Burdurli, Organometallics, 4 (1988) 1509.
13 K.H. Pannell, J.M. Rozell, J. Lii and S.Y. Tien-Mayr, Organometallics, 7 (1988) 2524.
14 P. Rivière and J. Satgé, Bull. Soc. Chim. Fr., (1967) 4039.
15 J. Satgé and P. Rivière, J. Organomet. Chem., 16 (1969) 71.
16 (a) A. Marinetti-Mignani and R. West, Organometallics, 6 (1987) 141; (b) T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.