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Oligomers with Silicon, Germanium, and Transition Metal Groups: Synthesis and Characterization of Metal-Containing Poly[(silylene)diacetylenes] and Poly[(germylene)diacetylenes]

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In order to prepare polycarbosilanes containing organometallic moieties which could be precursors of transition metal-containing ceramics, poly[(silylene)diacetylenes] (silylene: $SiMe_2$, SiMePh, $SiPh_2$) and poly[(methylphenylgermylene)diacetylene] have been reacted with dicobalt octacarbonyl to give the corresponding polymers with approximately half of the acetylene groups complexed with $Co_2(CO)_6$ moieties. The introduction of a ferrocenyl group into the main chain of poly[(silylene)diacetylenes] has been achieved by the reaction of the di-Grignard reagent of diacetylene, $C_4(MgBr_2)$, with various 1,1′-bis(chlorodiorganosilyl)ferrocene and led to the synthesis of $[-R_2Si-Fc-SiR_2-C\equiv C-C\equiv C-]_n$ (SiR_2: $SiMe_2$, SiMePh, $SiPh_2$) (Fc: 1,1′-ferrocene). $[-R_2Si-Fc-SiR_2-C\equiv C-C\equiv C-SiR'_2-C\equiv C-C\equiv C-]_n$ was obtained in the same way by polycondensation of $1,1'\text{-}(LiC\equiv C-C\equiv C-SiR_2)_2Fc$ with $Cl_2SiR'_2$ (R = Me, R′ = Me, Ph; R = R′ = Ph). The reaction of poly[(2,5-diphenyl-1-silacyclopentadiene-1,1-diyl)diacetylene] with $Fe_2(CO)_9$ and $Mo(CO)_4(COD)$ (COD:cyclooctadiene) gave only the complexation of some of the diene units.

Introduction

Organosilicon polymers in which silicon atoms are joined by organic groups with delocalized π-systems have been investigated extensively over the last several years.[1-5] Such species attract interest either as polymers which can be used as functional materials[6] or for their usefulness in the area of electronics and material science.[1c,7,4b]

From this respect, coupling reactions involving the dilithiobutadiyne (or the corresponding di-Grignard reagent) and dihalosilanes (or -germanes) afforded a convenient route to a large variety of poly[(silylene)diacetylenes] and poly[(germylene)diacetylenes] **1**.[8] Interest in such molecules stems from (i) the high reactivity of the 1,3-butadiyne-1,4-diyl unit which should provide the basis for a large number of useful chemical

1: $[-ER_2-C\equiv C-C\equiv C-]_n$ E = Si,Ge

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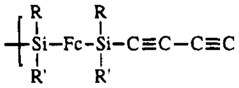
transformations,[9,6a] (ii) the evidence of conducting properties upon treatment with an oxidizing agent such as $FeCl_3$ (indeed, conductivity values in the range 10^{-3}–10^{-5} S cm^{-1}, characteristic of a semiconductive state, have been measured);[8b,c] furthermore, data suggest the possibility of long-range conjugation in polymer chains containing silicon moieties),[1c] and (iii) the potential as precursors of SiC-containing ceramics.[8c,10] Ceramic yields are high, and the total amount of silicon present in **1a** (E = Si, R = Me) remains in the final residue. As outlined previously,[8b,d] the easy thermally induced polymerization of the diacetylene units[11] allows low-temperature cross-linking through the triple bonds to give a C sp^2 network. On further pyrolysis, the mineralization of **1a** (E = Si, R = Me) takes place in the temperature range 450–800 °C and provides nanoscale SiC crystallites, homogeneously dispersed in the whole mass of the amorphous carbon matrix.[12]

Taking advantage of the above observations, we decided to extend our previous works to poly[(silylene)diacetylenes] containing organometallic moieties in their structure. Juxtaposition of a transition metal complex and the diyne entity in one molecule should confer unusual features to such a compound.[13] Furthermore, organometallic polymers of this type would be suitable precursors to transition metal-containing ceramics.[14] Such materials also may possess a wide range of interesting electrical, magnetic, and optical properties;[15] as an example, Manners et al.[15k] have recently reported the pyrolysis of poly(ferrocenylsilanes) to yield FeSiC ceramics. Therefore, we report here two different routes for the synthesis of the poly[(silylene)diacetylenes] and poly[(methylphenylgermylene)diacetylene]-containing inorganic elements. The first approach involves the incorporation of an organometallic fragment, such as 1,1′-bis(diorganosilyl)ferrocene or (η^4-silacyclopentadiene)iron tricarbonyl or -molybdenum tetracarbonyl units into the polymer backbone. A second route consists of the complexation of the triple bonds with dicobalt octacarbonyl.

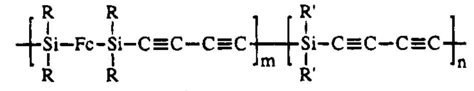
Results and Discussion

I. Polydiacetylenes with an Organometallic Unit. 1. Synthesis of 1,1′-Bis(diorganosilyl)ferrocenyl Derivatives of Diacetylene. In previous work, Pannell et al. reported polysilanes with ferrocenyl side groups.[16] More recently, the use of [1](dimethylsilyl)ferrocenophanes as precursors for poly[ferrocenylsilanes] via thermal ring opening polymerization was investigated by Manners and co-workers and by Pannell et al.[17]

We prepared two types of ferrocenyl oligomers, **2a–c** and **3a–c**, containing diacetylene units and organosilyl groups in the main chain. Oligomers **2a–c** correspond to poly[{1,1′-bis(diorganosilyl)ferrocenyl}diacetylenes], and **3a–c** show a regular alternating arrangement of [(diorganosilyl)diacetylene] and [{1,1′-bis(diorganosilyl)ferrocenyl}diacetylene] units.



$$-\left[\mathrm{Si}(\mathrm{R})(\mathrm{R'})-\mathrm{Fc}-\mathrm{Si}(\mathrm{R})(\mathrm{R'})-\mathrm{C{\equiv}C-C{\equiv}C}\right]_m- \qquad \mathbf{2}$$



$$-\left[\mathrm{Si}(\mathrm{R})_2-\mathrm{Fc}-\mathrm{Si}(\mathrm{R})_2-\mathrm{C{\equiv}C-C{\equiv}C}\right]_m-\left[\mathrm{Si}(\mathrm{R'})_2-\mathrm{C{\equiv}C-C{\equiv}C}\right]_n- \qquad \mathbf{3}$$

Fc = 1,1′-ferrocene

The oligomers **2a–c** were prepared by polycondensation between the di-Grignard reagent of diacetylene, **4**,

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Table 1. Typical Features of Oligomers 2: [$-$RR′Si$-$Fc$-$SiRR′$-$C$\equiv$C$-$C$\equiv$C$-$]$_n$

	R	R′	$\overline{M}_n$[a]	I	$\overline{DP}_n$	yield (%)
2a	Me	Me	2885	1.58	8	92
2b	Me	Ph	1500	1.21	3	87
2c	Ph	Ph	1560	1.3	2–3	90

[a] Determined by GPC using polystyrene standards.

and 1,1′-bis(chlorodiorganosilyl)ferrocene **5a**–**c** (eq 1 and Table 1). The oligomers thus produced were terminated by treatment of the reaction mixture with MeOH. The 1,1′-bis(chlorodiorganosilyl)ferrocenes **5a**–**c**

$$\underset{\mathbf{5}}{\mathrm{ClRR'Si{-}Fc{-}SiRR'Cl}} +$$

a: R = R′ = Me
b: R = Me, R′ = Ph
c: R = R′ = Ph

$$\underset{\mathbf{4}}{\mathrm{BrMg{-}C{\equiv}C{-}C{\equiv}C{-}MgBr}} \xrightarrow{\mathrm{THF}}$$

$$\underset{\mathbf{2}}{[\mathrm{-SiRR'{-}Fc{-}SiRR'C{\equiv}C{-}C{\equiv}C-}]_n} \qquad (1)$$

were obtained by condensation of 1,1′-dilithioferrocene[18] with chlorodiorganosilanes which gave 1,1′-bis(diorganosilyl)ferrocene and subsequent chlorination of the latter using palladium chloride[19] (eq 2).

$$(\eta^5\text{-}\mathrm{LiC_5H_4})_2\mathrm{Fe} + \mathrm{RR'SiHCl} \xrightarrow{\text{hexane}}$$

$$[\eta^5\text{-}(\mathrm{RR'HSi})\mathrm{C_5H_4}]_2\mathrm{Fe} \xrightarrow{\mathrm{PdCl_2}}$$

$$\underset{\mathbf{5}}{[\eta^5\text{-}(\mathrm{RR'ClSi})\mathrm{C_5H_4}]_2\mathrm{Fe}} \qquad (2)$$

a: R = R′ = Me
b: R = Me; R′ = Ph
c: R = R′ = Ph

Table 1 shows that **2a**–**c** were obtained as oligomers in high yield (87–92%). They are soluble in the usual organic solvents. The polydispersity values are between 1.2 and 1.58 and the average molecular weight corresponds to a number of links between 3 and 8. The number of chain units is smaller than those observed in the case of the polycondensation of dichlorodiorganosilanes and dilithiodiacetylene,[8b] i.e., n = 38 ($SiMe_2$), n = 18 (SiMePh), and n = 8 ($SiPh_2$). This may be due to a decrease of the reactivity of the Grignard (or lithium) derivative when the chain is growing. The physical properties of **2a**–**c** are summarized in Table 2.

The infrared absorption band $\nu_{C\equiv C}$ characteristic of the triple bond of poly[{(diorganosilyl)ferrocenyl}-diacetylene] **2a**–**c** appeared at 2070 and 2050 (sh) cm^{-1}. The small number of units in the polymer chain makes possible the observation of the $-$OMe and $\equiv$C$-$H end units at 2850 and 3300 cm^{-1}, respectively. In ^{13}C NMR, these $\equiv$CH end units are easily identified due to their greater intensity compared to substituted acetylene carbon. Moreover, the ^{13}C NMR spectra of **2a**–**c** showed sharp lines, as exemplified by **2b** (Figure 1, assignment in Table 2), which implied that all units of the oligomer chain are identical. This structural regularity is confirmed by ^{29}Si NMR which gave one single line for each oligomer **2a**–**c** at $-$19.54 (**2a**), $-$23.24 (**2b**), and $-$25.68 ppm (**2c**).

The oligomers **3a**–**c** were prepared by polycondensation of the dilithio derivatives **6a,c** with dichlorosilanes. (Scheme 1). The synthesis of the dilithio derivatives **6a,c** is described in Scheme 2. The condensation of (1-methoxy-1-buten-3-ynyl)lithium[20] with 1,1′-bis(chlorodiorganosilyl)ferrocenes **5a,c** gave derivatives **7a,c**. Reaction of the latter with 4 equiv of n-BuLi led to the dilithio derivatives **6a,c** in moderate yield, as shown by the hydrolysis reaction which gave **8a,c** in only 65% (**8a**) and 40% (**8c**) yields. The best preparation of clean dilithio derivatives **6a,c** in quantitative yield is by metalation of the terminal acetylene compound **8a,c**. This was proved by the reaction of the obtained dilithio derivatives **6a,c** with an excess of Me_3SiCl which gave compounds **9a** and **9c** in 98% yield.

The high purity of the dilithio derivatives **6a,c** makes possible the reaction with dichlorosilanes to give the oligomers **3a**–**c** (Scheme 2). Table 3 summarizes the results obtained in the condensation reactions of the dilithio derivatives **6a** with dimethyl- and diphenyldichlorosilanes and **6c** with dimethyldichlorosilane. Oligomers **3a**–**c** were terminated by treatment of the reaction mixture with MeOH. Products **3a**–**c** were obtained as oligomers in quantitative yield. As observed in the case of **2**, the average number of units in the chain is low, i.e., between 3 and 6. Table 4 gives the physical properties of **3a**–**c**. The infrared and ^{1}H, ^{29}Si, and ^{13}C NMR spectra are in good accordance with the expected structure. The infrared spectra showed a strong band at 2070 cm^{-1} corresponding to the diacetylene unit. The ^{1}H NMR spectra of **3a**–**c** showed sharp bands characteristic of a regular structure; this was confirmed by ^{29}Si NMR.

The solutions of the oligomers **2a**–**c** and a doping agent ($FeCl_3$) have been cast as thin films on a glass substrate from their methylene chloride solutions and the conductivities determined by the four-probe method.[21] The values obtained, 5 × 10^{-10} S cm^{-1} in the case of the dimethylsilyl derivative **2a**, 1 × 10^{-9} S cm^{-1} with the methylphenylsilyl **2b** and 1 × 10^{-8} S cm^{-1} with the diphenylsilyl **2c** are quite low[22] compared to those measured in the case of analogous poly[(silylene)diacetylenes].[8] The ferrocenyl unit seems to prevent charge transport along the main chain of the oligomers. Nevertheless, the conductivity values depend on the substituents on silicon (Ph_2Si > PhMeSi > Me_2Si); the aryl groups, which are able to stabilize a positive charge, led to relatively higher values.

2. Poly[(η^4-2,5-diphenyl-1-silacyclopentadiene-1,1-diyl)diacetylene] Transition Metal Complexes. The chemistry of silacyclopentadiene derivatives has been studied and it was shown that these derivatives

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(19) (a) Sommer, L. H.; Lyons, J. E. *J. Am. Chem. Soc.* **1969**, *91*, 7061. (b) Corriu, R. J. P.; Larcher, F.; Royo, G. *J. Organomet. Chem.* **1975**, *102*, C25.

(20) Zweifel, G.; Rajagopalan, S. *J. Am. Chem. Soc.* **1985**, *107*, 700.

(21) Sze, M. E. *Physics of semiconductive Devices*, 2nd ed; Wiley: New York, 1981; p 31.

(22) The conductivities were measured by F. Garnier and A. Yassar, Laboratoire des Matériaux Moléculaires, CNRS ER 241, 2, rue H. Dunant, F-94320 Thiais, France.

Table 2. Physical Properties of the Oligomers 2 [$-RR'Si-Fc-SiRR'C\equiv C-C\equiv C-]_n$

	R	R′	mp (°C)	IR $\nu_{C\equiv C}$, cm^{-1} (CCl_4)	^1H NMR δ, ppm (CCl_4)	^{29}Si NMR δ, ppm ($CDCl_3$)	^{13}C NMR δ, ppm ($CDCl_3$)
2a	Me	Me	130	2070 2049 (sh) 2850 (OCH_3 ending) 3300 ($\equiv CH$ ending)	0.35 (s, 12H, $SiCH_3$) 4.12 (s, 4H, Fc) 4.35 (s, 4H, Fc)	−19.54	−0.10 ($SiCH_3$); 67.83, 72.80, 73.95 (Fc); 85.62 (Si*C*≡C); 89.02 (SiC≡*C*); 67.61 (C≡*C*H, ending); 68.75 (*C*≡CH, ending)
2b	Me	Ph	110	2068 2047 (sh) 2854 (OCH_3 ending) 3300 ($\equiv CH$ ending)	0.43 (s, 6H, $SiCH_3$) 4.07 (s, 4H, Fc) 4.29 (s, 4H, Fc) 7−8(m, 10H, Ph) 2.0 (s, ≡CH ending)	−23.24	−1.23 (CH_3); 69.72, 73.45, 74.77 (Fc); 84.39 (Si*C*≡); 90.48 (≡*C*-); 128.39, 130.22, 134.43 (Ph) 66.40 (C≡*C*H, ending); 68.75 (*C*≡CH ending)
2c[a]	Ph	Ph	170	2069 2050 (sh) 2850 (OCH_3 ending) 3300 ($\equiv CH$ ending)	4.07 (s, 4H, Fc) 4.27 (s, 4H, Fc) 7−8 (m, 10H, Ph)	−25.50	69.68, 74.24, 75.82 (Fc); 84.19 (Si*C*≡); 92.37 (≡*C*−); 130.56; 134.25; 135.71 (Ph); 64.91 (C≡*C*H, ending), 65.94 (*C*≡CH, ending)

[a] ^{13}C and ^{29}Si NMR in C_6D_6.

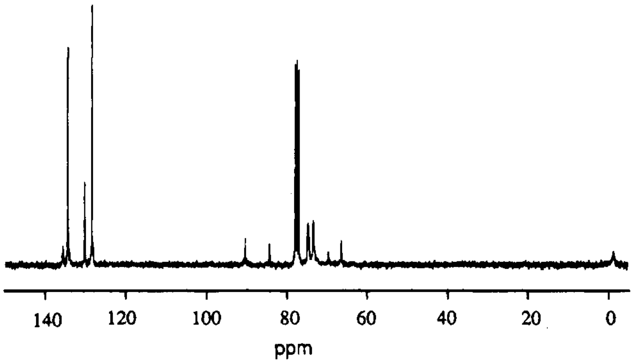
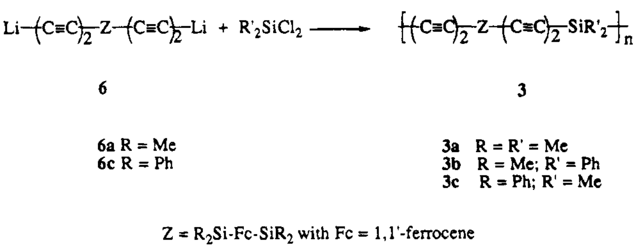


Figure 1. ^{13}C NMR spectrum of **2b**. (See Table 2 for the peak assignments.)

Scheme 1



are good η^4-ligands toward transition metals.[23,24] Thus incorporation of a silacyclopentadiene group between two diacetylene units should give new polymers able to be easily η^4-complexed and converted into metal-containing derivatives.

The oligomer **10** was obtained, as published previously,[8b] by the coupling reaction between 1,4-dilithio-1,3-butadiyne with 1-chloro-2,5-diphenylsilacyclopentadiene, which resulted in the nucleophilic displacement of both Si−Cl and Si−H bonds (eq 3).

Termination of the polymer chain was performed by treatment of the reaction mixture with Me_3SiCl followed by methanolysis to replace unreacted SiCl bonds. Oligomer **10** was obtained as a solid in 50% yield. Gel permeation chromatography (GPC) gave an average weight molecular weight of 1800 (using polystyrene standards) and a polydispersity of 1.47. These results indicated an average number of 6 units in the oligomer.

Scheme 2

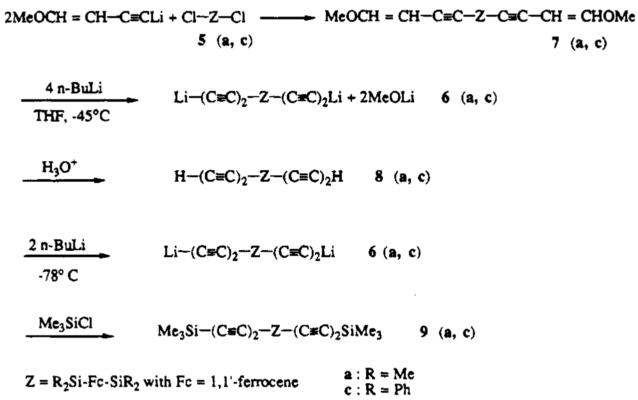


Table 3. Typical Features of Oligomers 3:[a] [$(-C\equiv C-)_2SiR_2-Fc-SiR_2(-C\equiv C-)_2SiR'_2-]_n$

	R	R′	$\overline{M}_n$[b]	I	$\overline{DP}_n$	yield (%)
3a	Me	Me	2920	1.23	6	97
3b	Me	Ph	2461	1.56	4	100
3c	Ph	Me	1630	1.60	3	98

[a] Fc = 1,1′-ferrocene. [b] Determinated by GPC using polystyrene standards.

The η^4-complexation of various silacyclopentadiene derivatives has been performed with different transition metal complexes such as $Co_2(CO)_8$, $Fe_2(CO)_9$, $Cr(CO)_5$-THF, and $Mo(CO)_4(COD)$.[23b,c,24] Analogous reactions were performed with **10** (eq 4). The reactions were performed with $Fe_2(CO)_9$ and $Mo(CO)_4(COD)$ (COD: cyclooctadiene) and were followed by infrared spectroscopy. Table 5 summarizes the results obtained. The infrared bands observed for the carbonyls indicated the η^4-complexation of the silacyclopentadiene with $Fe(CO)_3$ (**11a**) and $Mo(CO)_4$ (**11b**). These new oligomers were obtained in good yields; they are solid, decompose without melting, and are poorly soluble in organic solvents (toluene, THF, CH_2Cl_2, ...). Elemental analysis indicated that all the cyclopentadiene groups were not complexed. This was confirmed by SEM (scanning electron microscopy) using EDX (energy dispersive X-ray) analysis which indicated 1 Fe for 2 Si in the case of **11a**. This ratio value is certainly due to steric factors induced by the polymeric network.

II. Complexation of the Triple Bonds of the Diacetylene Oligomers with Dicobalt Octacarbo-

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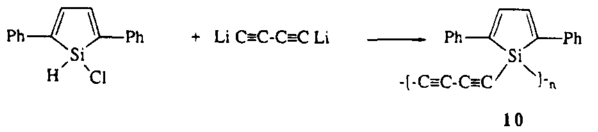
[23] See for instance: (a) Corey, J.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Kolani, B.; Wong Chi Man, W. W. C. *C. R. Acad. Sci. Paris* **1985**, *300*, 331. (b) Corriu, R. J. P.; Carré, F.; Colomer, E.; Corey, J. Y.; Guérin, C.; Henner, B.; Kolani, B.; Wong Chi Man, W. W. C. *Organometallics* **1986**, *5*, 910. (c) Carré, F.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Wong Chi Man, W. W. C. *Organometallics* **1989**, *8*, 313.

[24] Reviews: (a) McMahon, R. J. *Coord. Chem. Rev.* **1982**, *47*, 1. (b) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265.

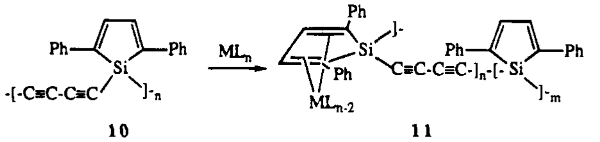
Table 4. Physical Properties of Oligomers 3: $[(-C\equiv C-)_2-SiR_2-Fc-SiR_2C\equiv C-C\equiv C-SiR'_2-]_n$

	R	R′	mp (°C)	IR cm^{-1} (CCl$_4$)	^{1}H NMR δ, ppm (CCl$_4$)	^{29}Si NMR δ, ppm (CDCl$_3$)	^{13}C NMR δ, ppm (CDCl$_3$)	analysis
3a	Me	Me	80–100	$\nu_{C\equiv C}$: 2070, 2050 (sh) δ_{SiCH_3}: 1250 δ_{SiFc}: 1165	0.35 (s, 18H, SiCH$_3$) 4.00 (s, 4H, Fc) 4.21 (s, 4H, Fc)	−19.50 (Fc SiMe$_2$) −37.18 (SiMe$_2$) −15.7 (SiOMe ending)	−0.12 (Si*C*H$_3$); 0.04 (FcSi*C*H$_3$); 69.72, 72.82, 73.81 (Fc); 85.72, 87.0, 89.11 (−*C*≡)	calcd for $(C_{24}H_{26}Si_3Fe)_n$: C, 63.43; H, 5.72; Si, 18.50 found: C, 61.71; H, 6.27; Si, 17.0; O, 2.07
3b	Me	Ph	70–80	$\nu_{C\equiv C}$: 2070, 2050 (sh) δ_{SiCH_3}: 1250 δ_{SiPh}: 1460, 1120 δ_{SiFc}: 1165	0.35 (s, 12H, SiCH$_3$) 4.00 (s, 4H, Fc) 4.22 (s, 4H, Fc) 7.0–8.0 (m, 10H, Ph)	−19.0, −19.5	−0.17 (Si*C*H$_3$); 67.82, 72.81, 73.97 (Fc); 85.72, 87.0, 89.11, 92.5 (−Si*C*≡); 128.22, 131.20, 135.32 (Ph) (main peaks)	calcd. for $(C_{44}H_{30}Si_3Fe)_n$: C, 70.58; H, 5.19; Si, 14.53. found: C, 70.04; H, 5.15; Si, 15.00; O, 2.87
3c[b]	Ph	Me	220 dec	$\nu_{C\equiv C}$: 2072 ν_{OCH_3} ending: 2850 δ_{SiCH_3}: 1256 δ_{SiPh}: 1429, 1114 δ_{SiFc}: 1167	0.25 (s, 6H, SiCH$_3$) 3.95 (s, 4H, Fc) 4.15 (s, 4H, Fc) 7.0–8.0 (m, 20H, Ph)	−25.64 (FcSiPh$_2$) −36.57 (SiMe$_2$)	−0.54 (Si*C*H$_3$); 65.92, 74.10, 75.76 (Fc); 82.8, 84.1, 90.03, 93.5 (−*C*≡); 130.54, 134.30, 135.66 (Ph) (main peaks)	calcd for $(C_{44}H_{34}Si_3Fe)_n$: C, 75.21; H, 4.84; Si, 11.96 found: C, 67.88; H, 4.63; Si, 9.88

[a] Fc = 1,1′-ferrocene. [b] ^{29}Si, ^{13}C NMR in C_6D_6.

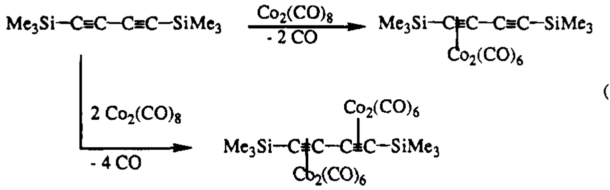


(3)



(4)

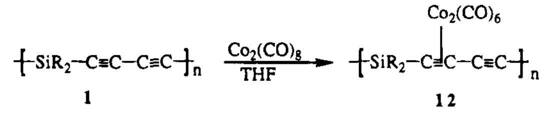
nyl. Acetylene groups are good ligands in coordination chemistry and the complexation of a triple bond using dicobalt octacarbonyl is a well-known reaction.[9b,25–28] For instance, Pannell et al. have complexed the triple bonds of 1,4-bis(trimethylsilyl)-1,3-butadiyne[26] (eq 5).



(5)

Complexation of a triple bond with $Co_2(CO)_8$ has been also performed with 1-alkynyl-1-silacyclopentadienes,[27] functional ethynylsilanes,[28] and recently, poly(alkynylsilanes) having aromatic groups in the polymer backbone.[6c]

1. Reaction of Poly[(silylene)diacetylenes] with $Co_2(CO)_8$. Poly[(silylene)diacetylenes] were prepared by polycondensation reactions of dilithiodiacetylene with the corresponding dichlorosilane[8a,b] (**1a**, M_w = 4060; **1b**, M_w = 3070; **1c**, M_w = 1830). The complexation of polymers **1** (E = Si) was performed with $Co_2(CO)_8$ at room temperature in THF as solvent (eq 6).



1 **12** (6)

a : R_2 = Me_2; b : R_2 = MePh; c : R_2 = Ph_2

Table 6 gives the physical properties of the oligomers **12a–c**.

The oligomers **12a–c** were obtained in high yields. Elemental analysis indicated the complexation of approximately one of the triple bonds in the case of the dimethylsilyl **12a** and methylphenylsilyl **12b** derivatives. In the case of the more hindered diphenylsilyl oligomers, analysis indicated 1.3 cobalts per silicon. Complex **12a** had no detectable melting point and decomposed around 150 °C with evolution of carbon monoxide.[29]

The infrared spectra showed three bands at 2092, 2060, and 2029 cm^{-1} assigned to the carbonyls of $Co_2(CO)_6$ and one band at 2079 attributed to the free triple

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(25) See for instance: (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980. (b) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

(26) Pannell, K. H.; Crawford, G. M. *J. Coord. Chem.* **1973**, *2*, 251.

(27) Carré, F.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Kolani, B.; Wong Chi Man, W. W. C. *J. Organomet. Chem.* **1987**, *328*, 15.

(28) Corriu, R. J. P.; Moreau, J. J. E.; Praet, H. *Organometallics* **1989**, *8*, 2779.

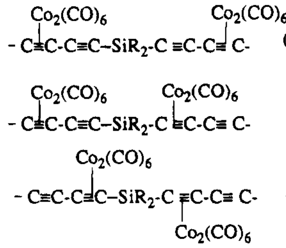
(29) Corriu, R. J. P.; Devylder, N.; Guérin, C.; Henner, B.; Jean, A. To be published.

Table 5. Infrared Spectra and Composition of the Complexed Polymers 11

polymer	ML_{n-2}	yield (%)	IR cm^{-1} (solvent)	analysis
11a	$Fe(CO)_3$	70	$\nu_{C\equiv O}$: 1987, 2045 $\nu_{C\equiv C}$: 2067 (sh) (methylcyclohexane)[b]	calcd for $C_{23}H_{12}FeO_3Si$: C, 65.72; H, 2.88; O, 11.42; Fe, 13.32; Si, 6.66 found:[a] C, 54.36; H, 4.66; O, 14.79; Fe, 7.44; Si, 10.30
11b	$Mo(CO)_4$	70	$\nu_{C\equiv O}$: 2033, 1980, 1940, and 1887 $\nu_{C\equiv C}$: 2072 (THF)	calcd for $C_{24}H_{12}MoO_4Si$: C, 59.03; H, 2.48; Mo, 19.65; O, 13.11; Si, 5.73 found:[a] C, 59.84; H, 5.36; Si, 8.80; Mo, 8.93

[a] The sum of the individual percentages accounts for 91.55% (**11a**) and 82.93% (**11b**) of the expected values. [b] The intensities of the carbonyl bands made possible the use of a hydrocarbon as solvent.

bond. ^{13}C NMR spectroscopy confirmed the complexation of one of the triple bonds of the diacetylene unit. More interesting was the ^{29}Si NMR spectrum of **12a–c**. The latter showed three signals (**12a**, **12b**) or two (**12c**) (see Table 6) which can be assigned to the three different possible environments of the silicon atom (A, B, and C); indeed, in the case of the diphenylsilyl oligomer **12c**, the most crowded environment (C) must be very minor and, therefore, not observable. Displacement of chemical shifts toward low field compared to **1** (**1a**, −38.89 ppm; **1b**, −42.14 ppm; **1c**, −47.37 ppm)[8b] was observed for the silicon adjacent to the complexed triple bond (see Table 6).

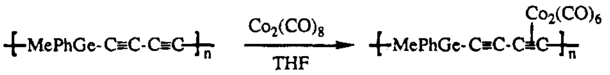


(A)

(B)

(C) (minor)

2. Reaction of Poly[(methylphenylgermylene)diacetylene] with $Co_2(CO)_8$. The complexation of poly[(methylphenylgermylene)diacetylene] with $Co_2(CO)_8$ was performed at room temperature in THF (eq 7). The result corresponded to the complexation of approximately one of the triple bonds of the diacetylene unit (see the Experimental Section), as observed in the case of the silylated analogs **1**.



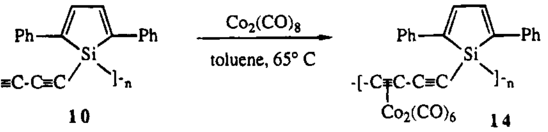
$$\left[\text{MePhGe-C}\equiv\text{C-C}\equiv\text{C}\right]_n \xrightarrow[\text{THF}]{Co_2(CO)_8} \left[\text{MePhGe-C}\equiv\text{C-}\overset{Co_2(CO)_6}{\text{C}\equiv\text{C}}\right]_n \quad (7)$$

13

Poly[(methylphenylgermylene)diacetylene] was prepared by polycondensation of dilithio-1,4-butadiyne with $MePhGeCl_2$ as published previously (79% yield, $M_w = 3093$, $n_w = 15$).[8b]

3. Complexation of Poly[(2,5-diphenyl-1-silacyclopentadiene-1,1-diyl)diacetylene], 10. As noted previously (vide supra), silacyclopentadiene groups are good η^4-ligands toward transition metals.[23,24,27] In the case of **10**, there are three possible complexation modes with $Co_2(CO)_8$: (i) η^4-complexation of the diene, (ii) complexation of the triple bonds, and (iii) both types of complexation. Indeed, we observed previously all these complexation reactions in the case of 1-methyl-1-propynyl-2,5-diphenylsilacyclopentadiene and dicobalt octacarbonyl, depending on the silacyclopentadiene/$Co_2(CO)_8$ ratio.[27]

The reaction of oligomer **10** was performed in toluene at 65 °C (eq 8) and led, in 45% yield after purification, to the oligomer **14** with only one of the triple bonds complexed with $Co_2(CO)_6$. Indeed, the infrared spectrum of **14** gave a $\nu_{C\equiv C}$ absorption at 2076 cm^{-1} corresponding to a noncomplexed triple bond and the carbonyl bands characteristic of $Co_2(CO)_6$ at 2097, 2057, 2028, and 2019 (sh) cm^{-1}. Small amounts of $SiCo(CO)_4$ groups may be present, due to the reaction of $Co_2(CO)_8$ and the SiH bonds[30] of the starting oligomer **10** end groups. Due to the low solubility of **14** in the usual organic solvents, ^{13}C NMR (CD_2Cl_2, 25 000 scans) showed, along with a large peak corresponding to the solvent, a broad peak at 128 ppm for the carbons of the phenyl and vinylic groups and a peak at 200.5 ppm attributed to the carbonyl ligands. The terminal Me_3Si groups were also visible at 1.45 ppm. Oligomer **14** was the only compound characterized from the reaction mixture.



10 **14** (8)

Conclusion

In conclusion, we have shown that poly[(silylene)diacetylenes] can be suitable precursors to organosilicon oligomers containing transition metal elements. Three approaches have been successful: (i) direct complexation of the triple bonds of the 1,3-butadiyne-1,4-diyl unit using an organometallic molecule, as illustrated with $Co_2(CO)_8$ (this complexation was extended to poly[(methylphenylgermylene)diacetylene]); (ii) complexation of a suitable group bonded to silicon, exemplified by the reaction of metal carbonyls [$Fe_2(CO)_9$, $Mo(CO)_4(COD)$] with a silacyclopentadiene moiety present in the polymeric backbone; (iii) polycondensation of the dilithiobutadiyne (or the corresponding di-Grignard reagent) with a dichlorosilane, affording the organometallic group. The latter can be provided by the diacetylide itself, as shown in the case of the ferrocenyl oligomers. However, this approach involving dilithio derivatives was limited by a significant decrease in the reactivity of the intermediate anionic species formed during the initial stages of the polycondensation reaction. Thus, molecules of low molecular weights were obtained.

In any case, due to the high reactivity of the 1,3-butadiyne-1,4-diyl group and the variety of substituents which can be attached to silicon, these routes can be extended to the incorporation of a large number of transition metal moieties. Further work directed to-

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(30) See for instance: (a) Colomer, E.; Corriu, R. J. P. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1981; Vol. 96, p 27. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Pataï, S., Rappoport, Z., Eds.; John Wiley: Chichester, U.K., 1989; Chapter 24, p 1415.

Table 6. Physical Properties of Poly[(silylene)diacetylenes] Complexed with $Co_2(CO)_6$ (12)

	yield (%)	IR cm^{-1} (THF)	^1H NMR δ, ppm ($CDCl_3$)	^{29}Si NMR δ, ppm ($CDCl_3$)	^{13}C NMR δ, ppm ($CDCl_3$)	analysis	x = Co/Si
12a	98	$\nu_{C\equiv O}$: 2092, 2060, 2029 $\nu_{C\equiv C}$: 2079	0.07 (s, $^1/_3$ H, $SiMe_2$) 0.41, 0.5, and 0.61 (3s, $^2/_3$ H, $SiMe_2$)	−18.29 (A) −3.83 (B) 1.05 (C)	0.9, 1.3, 2.3 (Si*C*H_3); 79.3 (Si*C*≡C); 82.74 (Si*C*Co_2); 102.2 and 102.4 (SiC≡*C*); 103.6 and 103.9 (C—*C*Co_2); 199 and 199.6 (CO)	calcd for $C_{12}H_6SiO_6Co_2$: C, 36.73; H, 1.53; Si, 7.14; O, 24.49; Co, 30.10 found: C, 34.05; H, 1.95; Si, 6.56; O, 25.85; Co, 28.91	2.1
12b	98	$\nu_{C\equiv O}$: 2092, 2060, 2029 $\nu_{C\equiv C}$: 2079	0.12 (p, 0.5H, SiMe) 0.81 (m, 2.5H, SiMe) 7.5 (m, 5H, SiPh)	−24.85 (A) −22.33 (B) −11.52 (C)	0.2, 1.4 (Si*C*H_3); 81 (Si*C*Co_2); 99 and 100 (SiC≡*C*); 103 and 105 (C—*C*Co_2); 198.8 and 199.3 (CO)	calcd for $C_{17}H_8SiO_6Co_2$: C, 44.93; H, 1.76; Si, 6.17; O, 21.15; Co, 25.99 found: C, 41.27; H, 1.88; Si, 5.83; O, 23.01; Co, 26.30	2.1
12c[a]	82	$\nu_{C\equiv O}$: 2092, 2060, 2029 $\nu_{C\equiv C}$: 2079	7.5 (m, SiPh)	−25.2 (A) −21.25 (B)	80 (Si*C*Co_2); 97.1 and 102.9 (SiC≡*C*); 108.2 (C—*C*Co_2); 126.5, 130.5, 134.5, 135.5 (Ph); 198 and 199 (CO)	calcd for $C_{22}H_{10}SiO_6Co_2$: C, 51.16; H, 1.94; Si, 5.43; O, 18.6; Co, 22.87 found:[b] C, 47.13; H, 2.84; Si, 7.51; O, 21.14; Co, 20.48	1.4

[a] C_6D_6 in the case of ^{29}Si NMR. [b] The sum of the individual percentages accounts for 99.1%.

ward the thermal behavior of the prepared oligomers is under progress and will be published soon.

Experimental Section

General Comments. All reactions were carried out under nitrogen using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. Tetrahydrofuran (THF) was first distilled over calcium hydride and then over sodium benzophenone.

The mono- and dichlorosilanes used were purchased from Janssen, Aldrich, or Lancaster and distilled over magnesium before use. Methyllithium–lithium bromide in diethyl ether was purchased from Aldrich; *n*-BuLi in hexane, from Janssen. 1-Methoxy-1-buten-3-yne from Aldrich was purified according to the literature.[31] Cobalt carbonyl and iron pentacarbonyl were purchased from Strem Chemicals; molybdenum hexacarbonyl and palladium dichloride, from Janssen. Diiron nonacarbonyl,[32] (cyclooctadiene)tetracarbonylmolybdenum,[33] 1,1′-dilithioferrocene,[18] 1,4-dilithio-1,3-butadiyne,[20] 1,4-bis(bromomagnesio)-1,3-butadiyne,[8b] and 4-lithio-1-methoxy-1-buten-3-yne[20] were prepared according to the literature. The syntheses of poly[(dimethylsilylene)diacetylene], poly[(methylphenylsilylene)diacetylene], and poly[(diphenylsilylene)diacetylene] were published previously.[8]

All NMR spectra were obtained at ambient temperature. ^1H spectra were acquired by using a Bruker AW 80 instrument, and ^{13}C and ^{29}Si solution spectra, with a Bruker WP 200 SY or WP 250 AC spectrometer. Chemical shift data were referenced to tetramethylsilane (TMS). Very often, ^{13}C and ^{29}Si NMR spectra needed long accumulation times to give observable peaks. IR specta were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer operating at 4-cm^{-1} resolution. Elemental analyses were performed by the "Centre de Microanalyse du CNRS".

Gel permeation chromatography (GPC) was performed using a Waters 410 instrument with UV and refractive index detection. The solvent used was THF, and the porosities of the columns used were 100, 500, 10^3, and 10^4 Å (elution rate 0.9 mL min^{-1}). The molecular weight distributions were determined using polystyrene standards (162, 1200, 3100, 9000, ...).

Melting points were taken using a Gallenkamp melting point apparatus and are uncorrected.

Synthesis of 1,1′-Bis(dimethylsilyl)ferrocene. A solution of 1,1′-dilithioferrocene[19] prepared from 10 g (0.053 mol) of ferrocene in hexane (350 mL) was added dropwise to a solution of dimethylchlorosilane (0.15 mol, 16.5 mL) in hexane (60 mL) maintained at 0 °C, and the mixture was stirred at room temperature for 12 h. After hydrolysis (acidic), extraction with pentane, and drying of the organic phase, the volatiles were evaporated under vacuum and the residue was chromatographed over silica gel using a mixture of pentane/dichloromethane (50/50). The title compound was obtained as a red liquid (14 g, 90% yield). The physical properties are identical with those reported in the literature.[34]

Synthesis of 1,1′-Bis(methylphenylsilyl)ferrocene. The same procedure as for 1,1′-bis(dimethylsilyl)ferrocene was used. A red liquid was obtained in 72% yield. IR (CCl_4, cm^{-1}): ν(CH) 3070, 2962; ν(Si–H) 2120; δ(SiPh) 1428, 1114; δ(SiFc) 1166; δ($SiCH_3$) 1250. ^1H NMR (CCl_4, δ, ppm): 0.27 (d, 3.5 Hz, 6H, $SiCH_3$), 3.95 (s, 4H Fc), 4.15 (s, 4H, Fc), 4.80 (q, 3.5 Hz, 2H, SiH), 7.0–8.0 (m, 10H, Ph). Anal. Calcd for $C_{24}H_{26}FeSi_2$: C, 67.60; H, 6.10. Found: C, 67.55; H, 6.29.

Synthesis of 1,1′-Bis(diphenylsilyl)ferrocene. The same procedure as for 1,1′-bis(dimethylsilyl)ferrocene was used. An orange solid was obtained in 53% yield. Mp: 126 °C. IR (CCl_4,

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cm^{-1}: ν(CH) 3070, 3030; ν(SiH) 2125; δ(SiPh) 1429, 1115; δ(SiFc) 1166. ^{1}H NMR (CCl_4, δ, TMS): 4.00 (s, 4H, Fc), 4.18 (s, 4H, Fc), 5.3 (s, 2H, SiH), 7.0–8.0 (m, 20H, Ph). Mass spectrum, *m/e* (assignment, relative intensity): 550 (M$^+$, 100). Anal. Calcd for $C_{34}H_{30}FeSi_2$: C, 74.18; H, 5.45. Found: C, 74.20; H, 5.49.

Synthesis of 1,1′-Bis(chlorodimethylsilyl)ferrocene, 5a. A solution of 1,1′-bis(dimethysilyl)ferrocene (4 g, 0.013 mol) in hexane (30 mL) was added to a suspension of $PdCl_2$ (4.8 g, 0.027 mol) in hexane (10 mL) and stirred at room temperature for 2 h. Filtration on Celite and concentration under vacuum gave 4.4 g (89% yield) of the title compound. The physical properties are identical with those reported in the literature.[35] Mp: 46–49 °C. ^{1}H NMR (CCl_4, δ, ppm): 0.47 (s, 6H, $SiCH_3$), 4.01 (s, 4H, Fc), 4.19 (s, 4H, Fc).

Synthesis of 1,1-Bis(chloromethylphenylsilyl)ferrocene, 5b. The same procedure as for **5a** was used, giving the title compound as an orange solid in 95% yield. IR (CCl_4, cm^{-1}): ν(CH) 3073, 2965; δ(SiPh) 1429, 1114; δ(SiFc) 1166; δ($SiCH_3$) 1256. ^{1}H NMR (CCl_4, δ, ppm): 0.31 (s, 6H, $SiCH_3$), 4.05 (s, 4H, Fc), 4.25 (s, 4H, Fc), 7.0–8.0 (m, 10H, Ph). Anal. Calcd for $C_{24}H_{24}Cl_2FeSi_2$: C, 58.18; H, 4.84. Found: C, 58.44; H, 4.92.

Synthesis of 1,1′-Bis(chlorodiphenylsilyl)ferrocene, 5c. The same procedure as for **5a** was used, giving the title compound as an orange solid in 97% yield. Mp: 137 °C. IR (CCl_4, cm^{-1}): ν(CH) 3070; δ(SiPh) 1429, 1114; δ(SiFc) 1166. ^{1}H NMR (CCl_4, δ, ppm): 4.10 (s, 4H, Fc), 4.35 (s, 4H, Fc), 7.0–8.0 (m, 20H, Ph). Anal. Calcd for $C_{34}H_{28}Cl_2FeSi_2$: C, 65.91; H, 4.52; Cl, 11.47. Found: C, 65.30; H, 4.68; Cl, 11.47.

Synthesis of [$-SiMe_2-Fc-SiMe_2-C\equiv C-C\equiv C-$]$_n$, 2a. A solution of 1,1′-bis(chlorodimethylsilyl)ferrocene (**5a**) (1.92 g, 0.0052 mol) in THF (18 mL) was added over 1.5 h, using an automatic syringe, to a slurry of 1,4-bis(bromomagnesio)-1,3-butadiyne (0.0051 mol) in THF (10 mL), and the mixture was stirred for 12 h. A 0.5-mL portion of methanol was then added to substitute the residual Si–Cl terminations, and the reaction mixture was stirred for 2 h. After hydrolysis at 0 °C, the mixture was extracted several times with pentane. The organic phase was then dried over $MgSO_4$ and concentrated under vacuum to give an orange solid which was washed with hexane to give the title compound **2a** (1.65 g, 92% yield). Anal. Calcd for $C_{18}H_{20}FeSi_2$: C, 62.06; H, 5.74; Si, 16.05. Found: C, 62.41; H, 5.82; Si, 14.70; O, 0.55. The physical properties of **2a** are summarized in Tables 1 and 2.

Synthesis of [$-SiMePh-Fc-SiMePh-C\equiv C-C\equiv C-$]$_n$, 2b. The same procedure as for **2a** was used with poly[1,1′-bis(chloromethylphenylsilyl)ferrocene (**5b**) (2.6 g, 0.0052 mol) and 1,4-bis(bromomagnesio)-1,3-butadiyne (0.0051 mol). The title compound was obtained as an orange powder (2.13 g, 87% yield). Anal. Calcd for $C_{28}H_{24}FeSi_2$: C, 71.18; H, 5.08; Fe, 11.86; Si, 11.86. Found: C, 70.38; H, 5.27; Fe, 12.00; Si, 9.70; O, 0.69. The physical properties of **2b** are summarized in Tables 1 and 2.

Synthesis of [$-SiPh_2-Fc-SiPh_2-C\equiv C-C\equiv C-$]$_n$, 2c. The same procedure as for **2a** was used, with 1,1′-bis(chlorodiphenylsilyl)ferrocene (**5c**) (3.2 g, 0.0052 mol) and 1,4-bis(bromomagnesio)-1,3-butadiyne (0.0051 mol). The precipitation of the title compound occurred when the reaction mixture was hydrolyzed (2.81 g, 90% yield). Anal. Calcd for $C_{38}H_{28}FeSi_2$: C, 76.51; H, 4.70; Fe, 9.39; Si, 9.39. Found: C, 74.32; H, 4.64; Fe, 9.30; Si, 8.70; O, 1.07. The physical properties of **2c** are summarized in Tables 1 and 2.

Synthesis of 1,1′-Bis[dimethyl(4-methoxy-3-buten-1-ynyl)silyl]ferrocene, 7a. A solution of *n*-BuLi (0.011 mol) in hexane was added dropwise to a solution of 1-methoxy-1-buten-3-yne (0.011 mol) in 10 mL of THF cooled at −78 °C, and the reaction mixture was stirred at that temperature for 30 min. After heating at room temperature, a solution of 1,1′-bis(chlorodimethylsilyl)ferrocene (2.0 g, 0.0055 mol) in 5 mL of THF was added dropwise and stirred for 3 h. After hydrolysis and extraction from pentane, the organic phase was dried over $MgSO_4$, evaporated under vacuum, and chromatographed using silica gel and a 10/90 mixture of CH_2Cl_2/pentane. An orange solid (1.9 g, 75% yield) was obtained. Mp: 57 °C. IR (CCl_4, cm^{-1}): ν(CH) 3080, 3040, 2965, 2940, 2860; ν($C\equiv C$) 2155; ν(C=C) 1630; δ($SiCH_3$) 1250; δ(SiFc) 1167; δ(C–O) 1110. ^{1}H NMR (CCl_4, δ, ppm): 0.35 (s, 12H, $SiCH_3$), 3.48 (s, 6H, OCH_3), 4.16 (s, 4H, Fc), 4.35 (s, 4H, Fc), 4.40 (d, *J* = 6.6 Hz, 2H, $C\mathit{H}{=}CHOCH_3$), 5.96 (d, *J* = 6.6 Hz, 2H, $CH{=}C\mathit{H}-OCH_3$). Mass spectrum (EI), *m/e* (assignment, relative intensity); 462 (M$^+$, 100). Anal. Calcd for $C_{24}H_{30}FeO_2Si_2$: C, 61.99; H, 7.00. Found: C, 61.46; H, 7.29.

Synthesis of 1,1′-Bis[diphenyl(4-methoxy-3-buten-1-ynyl)silyl]ferrocene, 7c. The same procedure as for the synthesis of **7a** was used. An orange solid (1.83 g, 47% yield) was obtained. Mp: 189 °C. IR (CCl_4, cm^{-1}): ν(CH) 3059, 2933, 2854; ν($C\equiv C$) 2150; ν(C=C) 1621; δ(SiPh) 1429; δ(SiFc) 1166; ν(C–O) 1116. ^{1}H NMR (CCl_4, δ, ppm): 3.78 (s, 6H, OCH_3), 4.16 (s, 4H, Fc), 4.36 (s, 4H, Fc), 4.47 (d, *J* = 6.5 Hz, 2H, $-C\mathit{H}{=}CHOMe$), 6.24 (d, *J* = 6.5 Hz, 2H, $-CH{=}C\mathit{H}OCH_3$), 7–8 (m, 20H, Ph). Mass spectrum (EI), *m/e* (assignment, relative intensity): 710 (M$^+$, 100). Anal. Calcd for $C_{44}H_{38}FeO_2Si_2$: C, 74.36; H, 5.35. Found: C, 74.22; H, 5.31.

Synthesis of 1,1′-Bis[dimethyl(1,3-butadiynyl)silyl]ferrocene, 8a. A solution of 0.015 mol of *n*-BuLi in hexane was added dropwise to a solution of **7a** (1.7 g, 0.0037 mol) in THF (30 mL) at −50 °C. Stirring was maintained at that temperature for 20 min. The mixture was allowed to warm to room temperature, hydrolyzed (HCl 2N), and extracted with pentane, and the organic phase was dried over $MgSO_4$. After removal of the solvent under vacuum, the residue was chromatographed on silica gel using pentane as the eluent. An orange solid (1.35 g, 92% yield) was obtained. Mp: 98–99 °C; IR (CCl_4, cm^{-1}): ν(CH) 3311, 3094, 2959, 2925; ν($C\equiv CH$) 2188; ν($C\equiv C$) 2037; δ($SiCH_3$) 1250; δ(SiFc) 1165, 1037. ^{1}H NMR (CCl_4, δ, ppm): 0.34 (s, 12H, $SiCH_3$), 1.89 (s, 2H, $C\equiv C-H$), 4.08 (s, 4H, Fc), 4.30 (s, 4H, Fc). ^{13}C NMR ($CDCl_3$, δ, ppm): −0.14 ($SiCH_3$); 67.77, 72.82, 73.98 (Fc); 67.60 ($C\equiv \mathit{C}H$); 68.75 ($\mathit{C}\equiv CH$); 83.94 ($Si-C\equiv \mathit{C}$); 88.35 ($Si-\mathit{C}\equiv C$). ^{29}Si NMR ($CDCl_3$, δ, ppm): −19.25. Mass spectrum (EI), *m/e* (assignment, relative intensity): 398 (M$^+$, 100). Anal. Calcd for $C_{22}H_{22}FeSi_2$: C, 66.33; H, 5.52. Found: C, 65.95; H, 5.62.

Synthesis of 1,1′-Bis[diphenyl(1,3-butadiynyl)silyl]ferrocene, 8c. The same procedure as for the synthesis of **8a** was used with *n*-BuLi (0.015 mol) and **7c** (2.6 g, 0.0037 mol). The title compounnd was obtained as an orange solid (0.96 g, 40% yield). Mp: 148 °C dec. IR (CCl_4, cm^{-1}): ν(CH) 3310, 3071, 2927; ν($C\equiv CH$) 2190; ν($C\equiv C$) 2037; δ(SiPh) 1428, 1112; δ(SiFc) 1168, 1036. ^{1}H NMR (CCl_4, δ, ppm): 2.19 (s, 2H, $\equiv CH$); 4.02 (s, 4H, Fc); 4.23 (s, 4H, Fc); 7.2–7.8 (m, 20H, Ph). Anal. Calcd for $C_{42}H_{30}FeSi_2$: C, 78.02; H, 4.64. Found: C, 78.25; H, 4.81.

Synthesis of 1,1′-Bis[dimethyl(4-(trimethylsilyl)-1,3-butadiynyl)silyl]ferrocene, 9a. A solution of *n*-BuLi (0.005 mol in hexane) was added dropwise to a solution of 1,1′-bis[dimethyl(1,3-butadiynyl)silyl]ferrocene (**8a**) (1 g, 0.0025 mol) in THF (30 mL) at −78 °C, and the mixture was stirred at that temperature for 30 min. Pure chlorotrimethylsilane (0.006 mol, 0.76 mL) was added to the lithio derivative, and the reaction mixture was allowed to warm to room temperature and was stirred for 15 min. Evaporation of the volatiles under vacuum followed by extraction with pentane to remove salts, concentration of the medium, and chromatography over silica gel using pentane as the eluent gave the title compound as an orange solid (1.33 g, 98% yield). Mp: 121–122 °C. IR (CCl_4, cm^{-1}): ν(CH) 2960, 2890; ν($C\equiv C$) 2070, 2050; δ(SiFc) 1160; δ($SiCH_3$) 1250. ^{1}H NMR (CCl_4, δ, ppm): 0.17 (s, 18H, $SiMe_3$), 0.38 (s, 12H, $SiMe_2$), 4.03 (s, 4H, Fc), 4.25 (s, 4H, Fc). Mass spectrum (EI), *m/e* (assignment, relative intensity): 542 (M$^+$, 100). Anal. Calcd for $C_{28}H_{38}FeSi_4$: C, 61.69; H, 7.00. Found: C, 61.90; H, 7.29.

Synthesis of 1,1′-Bis[diphenyl(4-(trimethylsilyl)-1,3-butadiynyl)silyl]ferrocene, 9c. The same procedure as for

9a was used with 1,1′-bis[diphenyl(1,3-butadiynyl)silyl]ferrocene (**7c**) (0.000 31 mol), *n*-BuLi (0.000 62 mol) and chlorotrimethylsilane (0.0007 mol, 0.1 mL). The title compound was obtained as an orange solid (0.24 g, quantitative yield). Mp: 211 °C dec. IR (CCl_4, cm^{-1}): ν(CH) 3068, 2965; $\nu(C{\equiv}C)$ 2069; δ(SiPh) 1429, 1113; δ(SiFc) 1160, 1036; $\delta(SiCH_3)$ 1252. ^{1}H NMR (CCl_4, δ, ppm): 0.11 (s, 18H, $SiMe_3$), 3.98 (s, 4H, Fc), 4.21 (s, 4H, Fc), 7.0–7.6 (m, 20H, SiPh). Mass spectrum (EI), *m/e* (assignment, relative intensity): 790 (M^+, 100). Anal. Calcd for $C_{48}H_{46}FeSi_4$: C, 72.91; H, 5.82. Found: C, 72.24; H, 5.82.

Synthesis of $[SiMe_2{-}Fc{-}SiMe_2{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_2{-}]_n$, 3a. To a solution of the dilithio derivative **6a** (0.000 75 mol) in THF, prepared as described in the preparation of **9a**, was added neat (0.0008 mol, 0.1 mL) dichlorodimethylsilane, over 40 min using an automatic seringe. The mixture was stirred overnight and 0.1 mL of MeOH was then added to substitute the residual SiCl bonds. The mixture was then hydrolyzed (neutral medium), extracted with pentane, and dried over $MgSO_4$, and the volatiles were removed under vacuum to give an orange solid (0.33 g, 97%). See Table 4 for physical properties.

Synthesis of $[SiMe_2{-}Fc{-}SiMe_2{-}C{\equiv}C{-}C{\equiv}C{-}SiPh_2{-}]_n$, 3b. The same procedure as for **3a** was used with 0.000 75 mol of the dilithio compound **6a** and dichlorodiphenylsilane (0.0008 mol, 0.17 mL). An orange powder of **3b** was obtained quantitatively (0.43 g). See Table 4 for physical properties.

Synthesis of $[SiPh_2{-}Fc{-}SiPh_2{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_2{-}]_n$, 3c. The same procedure as for **3a** was used, but starting from dilithio derivative **6c**, prepared as described in the synthesis of **9c**. Starting with 0.000 75 mol of **6c** and dichlorodimethylsilane (0.0008 mole, 0.1 mL), oligomer **3c** was obtained (0.42 g, 80% yield) by precipitation at the hydrolysis step followed by filtration. See Table 4 for physical properties.

Reaction of Poly[(dimethylsilylene)diacetylene] with Dicobalt Octacarbonyl. A solution of dicobalt octacarbonyl (2.3 g, 0.0068 mol) in THF (20 mL) was added to a solution of poly[(dimethylsilylene)diacetylene] (0.7 g) in the same solvent (30 mL). Gas evolution was observed. The reaction was followed using IR spectroscopy. After stirring at room temperature for 12 h, the volatiles were eliminated under vacuum and the residue was washed with pentane to give **12a** as a brown powder (2.58 g) in quantitative yield. Table 6 summarizes the physical properties of **12a**.

Reaction of Poly[(methylphenylsilylene)diacetylene] with Dicobalt Octacarbonyl. The same procedure as for **12a** was used with dicobalt octacarbonyl (2.8 g, 0.0082 mol) and poly[(methylphenylsilylene)diacetylene] (1.09 g). Polymer **12b** (2.89 g) was obtained as a brown powder. Table 6 summarizes the physical properties of **12b**.

Reaction of Poly[(diphenylsilylene)diacetylene] with Dicobalt Octacarbonyl. The same procedure as for **12a** was used with dicobalt octacarbonyl (1.98 g, 0.0058 mol) and poly[(diphenylsilylene)diacetylene] (1.21 g) which led to **12c** (2.73 g) as a brown powder. Table 6 summarizes the physical properties of **12c**.

Reaction of Poly[((1,4-diphenyl-1,3-butadiene-1,4-diyl)silylene)diacetylene] with Diiron Nonacarbonyl. A solution of silole **10** (0.81 g, 0.0020 mol) in toluene (30 mL) was added to a slurry of $Fe_2(CO)_9$ (1.1 g, 0.003 mole) in the same solvent (40 mL), and the mixture was heated at 60 °C under argon for 52 h. The reaction was followed using IR spectroscopy. Evaporation of the solvent under vacuum led to a residue poorly soluble in organic solvents. See Table 5 for IR and elemental analysis of **11a**.

Reaction of Poly[((1,4-diphenyl-1,3-butadiene-1,4-diyl)silylene)diacetylene] with Molybdenum Cyclooctadiene Tetracarbonyl. A solution of silole **10** (0.66 g, 0.0023 mol) in THF (30 mL) was added to a solution of $Mo(CO)_4(COD)$ (0.75 g, 0.0024 mol) in the same solvent (30 mL), and the mixture was stirred at 40 °C for 19 h. The reaction was followed using IR spectroscopy. Evaporation of the solvent under vacuum led to a residue poorly soluble in organic solvents. See Table 5 for IR and elemental analysis of **11b**.

Reaction of Poly[(methylphenylgermylene)diacetylene] with Dicobalt Octacarbonyl. A solution of dicobalt octacarbonyl (1.8 g, 0.0053 mol) in the minimum of THF was added to a solution of poly[(methylphenylgermylene)diacetylene] (1.1 g, 0.0052 mol) dissolved in 60 mL of the same solvent. The mixture was stirred at room temperature for 12 h, and the volatiles were removed under vacuum. A dark red powder of **13** was obtained in quantitative yield. IR (pentane, cm^{-1}): $\nu C{\equiv}O$ 2094, 2079, 2063, 2030. ^{1}H NMR (CCl_4, δ, ppm): 0.9 (m, 3 H, Me), 7.0–7.8 (m, 5 H, Ph). ^{13}C NMR (CD_2Cl_2, δ, ppm): 1.4 (GeMe); 81.0 ($Ge{-}\mathit{C}{\equiv}C$); 100.6 ($Ge{-}C{\equiv}\mathit{C}$); 104.4 ($Ge{-}C{\equiv}\mathit{C}Co_2$); 86.5 ($Ge{-}\mathit{C}{\equiv}CCo_2$); 199.35 ($C{\equiv}O$); 137.03, 133.9, 133.56, 130.34, 128.8 (GePh). Anal. Calcd for $(C_{17}H_8Co_2GeO_6)_n$: C, 40.93; H, 1.6; Co, 23.63; Ge, 14.56; O, 19.25. Found: C, 42.8; H, 1.56; Co, 20.04; Ge, 14.04; O, 21.5.

Reaction of Poly[((1,4-diphenyl-1,3-butadiene-1,4-diyl)silylene)diacetylene] with Dicobalt Octacarbonyl. A solution of silole **10** (1.4 g, 0.005 mol) in toluene (30 mL) was added to a solution of $Co_2(CO)_8$ (2.6 g, 0.0076 mol) in the same solvent (40 mL), and the mixture was heated at 65 °C under argon for 14 h. The reaction was followed using IR spectroscopy. Evaporation of the solvent under vacuum led to a residue poorly soluble in organic solvents. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2097, 2057, 2028, 2019 (sh); $\nu(C{\equiv}C)$ 2076; ν(CH) 3077, 3022, 2961; $\nu(C{=}C)$ 1598, 1484; $\delta(SiCH_3)$ 1251; δ(SiPh) 1444. ^{13}C NMR (CD_2Cl_2, δ, ppm; 25 000 scans): 1.45 ($SiCH_3$); 88.1 ($C{\equiv}\mathit{C}{-}Si$); 104.5 ($\mathit{C}{\equiv}C{-}Si$); 128.5 (broad, shoulder at 127.5, Ph + diene); 200.5 (CO). Anal. Calcd for $C_{26}H_{12}Co_2O_6Si$: C, 54.88; H, 2.54; Co, 20.00; O, 16.26; Si, 6.32. Found: C, 48.90; H, 4.01; Co, 20.84; O, 18.84; Si, 3.32.

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