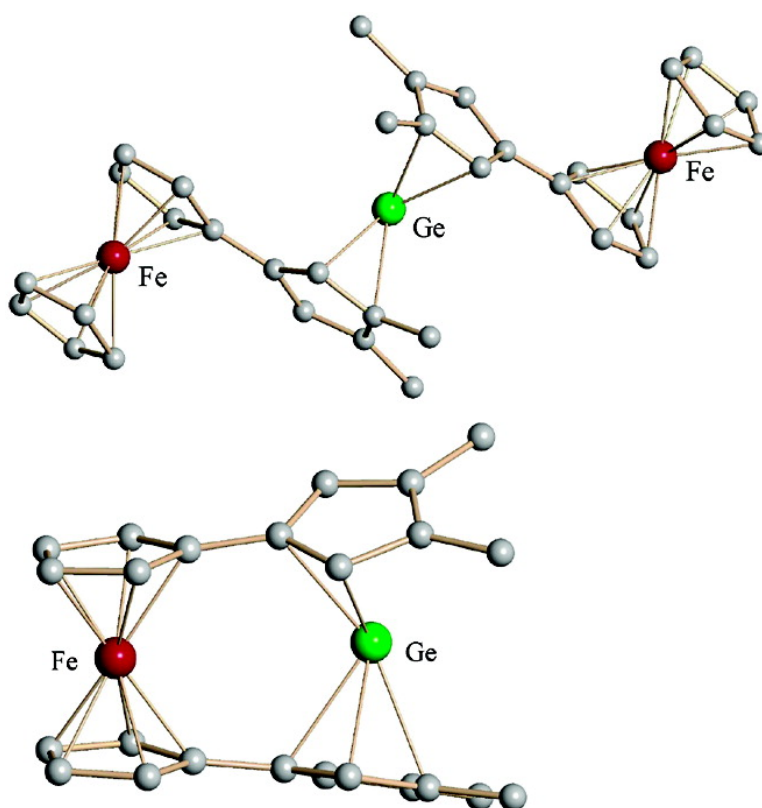


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Synthesis, Structures, and Reactivity of Mono- and Bis(ferrocenyl)-Substituted Group 14 Metallocenes

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New mono- and bis(ferrocenyl)-substituted germanocenes and stannocenes have been synthesized in good yield by the reaction between group 14 dichlorides (Cl₂Ge-dioxane, Cl₂-Sn) and the lithium salts of the corresponding mono- and bis(cyclopentadienyl)-substituted ferrocenes. The X-ray crystal structure analyses of germanocenes **3a** and **4a** reveal a bent sandwich structure with an angle between the cyclopentadienyl planes of 45.4° and 40.9° for **3a** and **4a**, respectively. Mass spectrometry and electrochemical studies show the stabilization of the generated transient cations by ferrocenyl groups, particularly in the germanium series. Their reactions with electrophilic reagents such as catechol and cycloaddition with *o*-quinone also are reported and show, in the latter case, an increase of the specific reactivity of the dimethylcyclopentadienyl moiety.

Introduction

Bimetallic and polymetallic complexes featuring unsaturated bridging ligands between the metal centers have been extensively investigated over the past decade.¹ This interest arises from the possible existence of interactions between the metal centers allowing potential modification of the properties of one metal center by the intrinsic properties of the second inorganic moiety. Indeed, such a cooperative effect is expected to induce at times dramatic changes in structural, spectroscopic, chemical, and physical properties compared to their monometallic counterparts. For example, in stoichiometric and catalytic processes, bimetallic complexes may have higher reaction rates and could lead to transformations that do not occur with mononuclear species.² Their potential use as models of molecular electronic devices has also focused much attention. Featuring a highly delocalized π system that links the metal fragments, they can exhibit a variety of finely tunable behavior according mainly to the size, nature,

and redox ability of transition metals. The first investigations of such interactions have been concentrated on homobimetallic compounds and especially on linked ferrocenes.^{1a,c} The chemistry of heterobimetallic complexes with a fused ring system has been developed rather late because of the difficulty in synthesizing such derivatives. Indeed, the introduction of two different metals into connected cyclopentadienyl rings, for example, implies two selective and successive metalations of the ligands, which are possible only in a few cases with appropriate substituents.

Surprisingly, despite the abundant literature on this topic, there is, to the best of our knowledge, no report of mixed main group metal/transition metal bridged bimetallic complexes. Indeed, examples of heterobimetallic complexes in which the two metals are directly linked are quite common, but the main group element may be best considered as a ligand.³ Interestingly, main group metallocenes present a formal analogy with their transition metal counterparts. This offers a unique opportunity to switch from ferrocene as end group to its main group element analogue and to study the influence of such a modification. Among main group metallocenes, group 14 species have been widely studied⁴ since the synthesis of the first group 14 sandwich compound [Cp₂Pb]⁵ was described. In contrast to transition metal metallocenes of type (η^5 -C₅H₅)₂M, which involve parallel and symmetrically bound cyclopenta-

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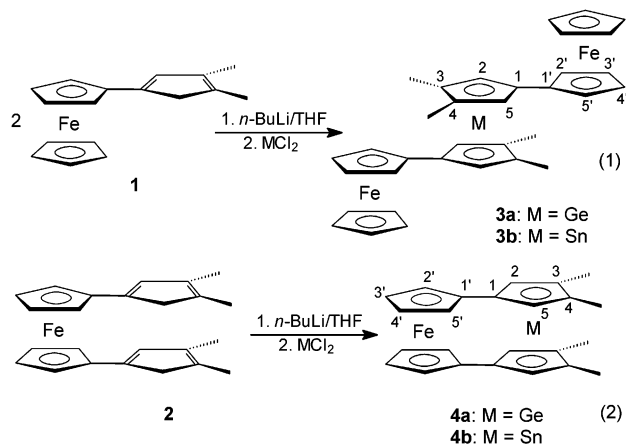
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dienyl ligands, the main group analogues show a bewildering variety of bonding arrangements. Their typical bent structure and the structural role of their metal valence electrons are still subjects of controversy.⁶ Their chemical and electrochemical properties also have been shown to be totally different, as evidenced by an irreversible one-electron oxidation process for group 14 metallocenes. We have recently extended this analogy between the two families of metallocenes with the preparation of the *p*-phenylene- and *p*-biphenylene-bridged germanocenes and stannocenes,⁷ which are the group 14 analogues of dimetallocenes.

As a part of our continuing attempts to expand the chemistry of group 14 polymetallic complexes, we have initiated a study on a series of ferrocenyl-substituted germanocenes and stannocenes, anticipating that such association will result in unusual structural and chemical properties. Indeed, ferrocene, which is well-known for its electron-donor character,⁸ possibly would provide additional stabilization to the germanocenyl or stannocenyl moiety for both the neutral form and the oxidized state. Additionally, its presence might improve the electronic interaction particularly since the bridging ligand (fulvalene) was chosen taking into account that it allows strong coupling between metal centers. This work describes the preparation, the full characterization including crystal structure determinations, and the voltammetric study of the first mixed (group 14-transition group elements) heterodimetallocenes. Some reactivity tests will be presented in order to provide insights of the chemical behavior of these species.

Results and Discussion

Syntheses and Structures. Compounds **3** and **4** were formed as red or orange solids in good yield (68–86%) by nucleophilic substitution reactions on Cl_2Ge -dioxane or Cl_2Sn by the corresponding lithiated ligands in THF at low temperature (eq 1 and 2).



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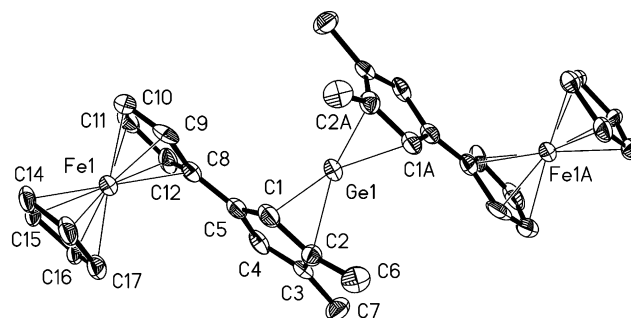


Figure 1. Crystal structure of **3a** at the 50% probability level for the thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ge(1)–C(1) 2.343(9), Ge(1)–C(2) 2.399(8), C(5)–C(8) 1.443(10), C(1)–C(5)–C(8) 126.2(8), C(5)–C(8)–C(12) 124.9(8).

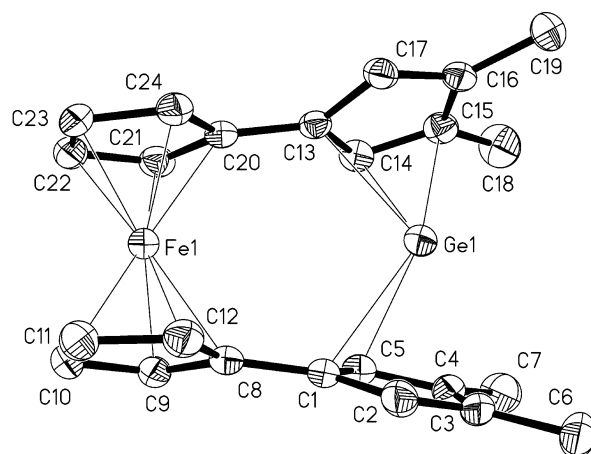


Figure 2. Crystal structure of **4a** at the 50% probability level for the thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ge(1)–C(1) 2.458(2), Ge(1)–C(5) 2.382(2), Ge(1)–C(13) 2.420(2), Ge(1)–C(14) 2.355(2), C(1)–C(8) 1.464(3), C(2)–C(1)–C(8) 126.5(2), C(17)–C(13)–C(20) 126.1(2).

No trace of polymeric products was observed. The ligand **2**, as might be expected, acts as a chelate, leading to the more stable form **4**. Compounds **3** and **4** are stable under an inert atmosphere at room temperature but may be stored at low temperature (–30 °C). They are soluble in common organic solvents such as THF, toluene, diethyl ether, and dichloromethane. The ferrocenyl germanocenes **3a** and especially **4a** are the most stable in solution, and crystals suitable for single-crystal analysis were obtained from a toluene solution at –30 °C within several days. The structures, determined by single-crystal X-ray diffraction, are shown in Figures 1 and 2 with selected bond lengths and angles. The two germanocenes have the typical bent structure^{4a,d} of group 14 metallocenes with angles between the dimethylcyclopentadienyl planes of 45.4° for **3a** and 40.9° for **4a**. These values are comparable to those observed in bridged digermanocenes^{7a} (40°) and in germanocene⁹ itself (50.4°). Moreover, these deviations are similar whatever the geometry of the complexes is, i.e., trans conformation in **3a** or chelated form in **4a**. The germanium atoms do not reside between the dimethylcyclopentadienyl ring centers but are slightly displaced toward the carbon atoms C(1) and C(2) (for **3a**) and C(1)

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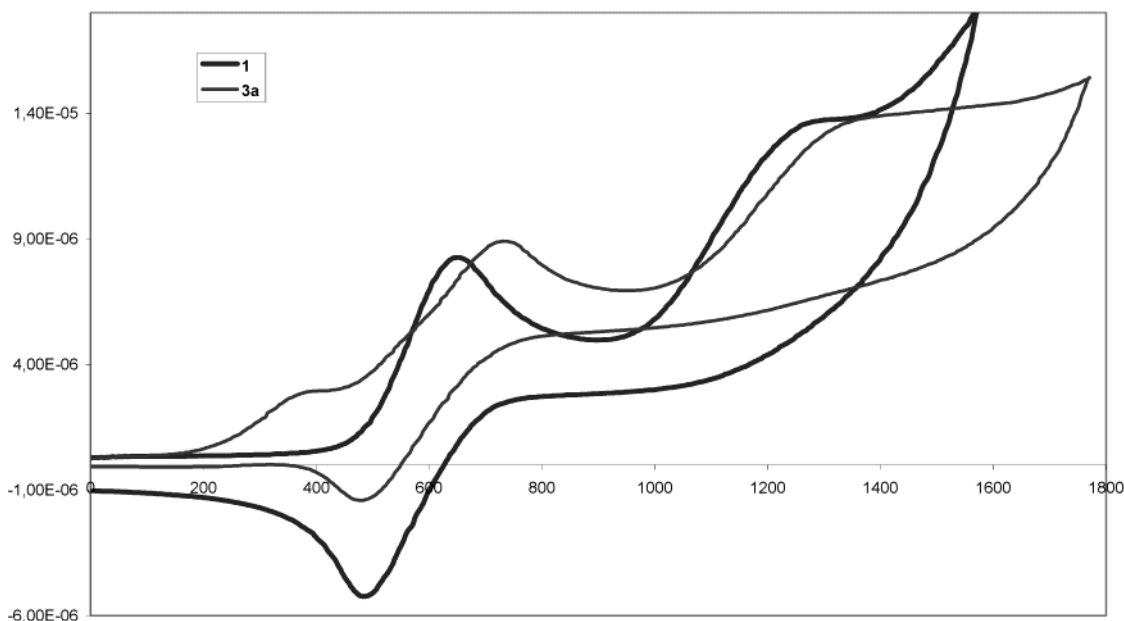


Figure 3. Cyclic voltammograms of compounds **3a** and **1** (bold) (10^{-3} M) in THF under argon atmosphere measured at platinum disk ($r = 0.5$ mm) at room temperature. Scan rate 0.1 V/s, supporting electrolyte NBu_4NBF_4 (0.1 M). Potentials referenced to ECS electrode.

and C(5) (for **4a**). Another interesting structural feature is the torsion angle between adjacent cyclopentadienyl and dimethylcyclopentadienyl rings. For **3a**, which exists in a transoid conformation, a quasi coplanar system is observed for the fulvalenide moiety with dihedral angles C(9)–C(8)–C(5)–C(1) of -1.1° and C(12)–C(8)–C(5)–C(4) of -9.1° . In contrast, **4a** exhibits a clear deviation with dihedral angles C(2)–C(1)–C(8)–C(12) of 21.9° and C(5)–C(1)–C(8)–C(9) of 21.7° . These values are similar to those reported for the ligand **2**¹⁰ (23.5° and 26.1°) and for $\text{Fc}(\eta^5\text{-C}_5\text{Me}_4)_2\text{Fe}^{\text{II}}$ (20°), showing that this deviation probably results from the steric hindrance of the methyl groups rather than from structural deformation induced by the germanium atom.

The ^1H and ^{13}C NMR spectra of **3** and **4** are consistent with a dimetalloocene structure. The equivalence of CH_3 and CH groups of the dimethylcyclopentadienyl groups indicates π -linked structures. As expected, the two proton pairs H(2'), H(5') and H(3'), H(4') of the ferrocenyl moiety are nonequivalent, and a complete assignment was obtained from homonuclear (COSY) and heteronuclear experiments (HSQC and HMBC). In addition, the ^{119}Sn NMR spectra exhibit a high-field resonance ($\delta = -2071$ ppm for **3b** and $\delta = 2017$ ppm for **4b**) in the typical region for stannocenes,^{4a} confirming their π -linked structures. Interestingly, in contrast to group 14 metallocenes and dimetalloccenes, molecular ions with the expected isotopic pattern were observed for **3a**, **4a**, and **4b**, respectively, at m/z 628, 442, and 488, respectively, suggesting a stabilization of the cationic forms by the ferrocenyl groups. The $[\text{FcC}_5\text{H}_2\text{Me}_2\text{M}]^+$ fragments ($\text{M} = \text{Ge}$, m/z 351; $\text{M} = \text{Sn}$, m/z 397) characteristic of the group 14 metallocenes^{4b} also were observed.

Electrochemical Study of Complexes 3a,b and 4a. Cyclic voltammetry is a useful tool to investigate metal–metal interactions. In homobimetallic systems

that contain two equivalent redox centers, the ΔE separation between the two redox events is indicative of the degree of interaction. In the case of heterobimetallic complexes, the ΔE value that is of importance to evaluate interaction is the difference between the redox potential of one metal of the heterobimetallic species and the redox potential of the corresponding monometallic compound.¹² Cyclic voltammetry (in THF with $[\text{Bu}_4\text{N}]\text{BF}_4$ as supporting electrolyte) of **3a** (Figure 3) reveals an irreversible oxidation peak at 406 mV (vs SCE) similar to that obtained for decamethylgermanocenes under the same experimental conditions.¹³ The second quasi reversible anodic process was attributed to the concomitant oxidation of the two ferrocenyl groups. Linear voltammetry confirms this assignment: the Fe(III)/Fe(II) wave is about twice as large as the one-electron oxidation wave of the germanocene group. The difference between this last oxidation peak (740 mV) and that obtained for the ligand **1** (646 mV) seems to indicate some degree of interaction between the ferrocenyl groups and the germanocene moiety. Comparable results were obtained for the stannocene **3b** (425 and 724 mV for the oxidation peaks), but some decomposition appeared after 20 min. Surprisingly, **4a** presents a completely different behavior. Although the first oxidation peak of the germanocene group is observed at 303 mV, we have an irreversible redox event at 530 mV from the ferrocenyl group. Even if the origin of this phenomenon still remains uncertain, such irreversibility for a ferrocenyl moiety is not unprecedented and has already been observed for a diferrocenyltitanium complex.¹⁴ Interestingly, the oxidation potential of germanocene occurs at lower potential than that of **3a** ($\Delta E = 103$ mV). Such lowering of the first

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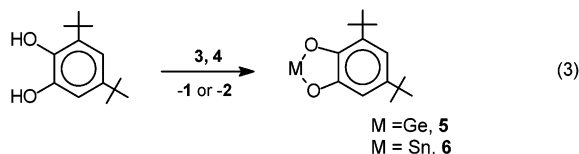
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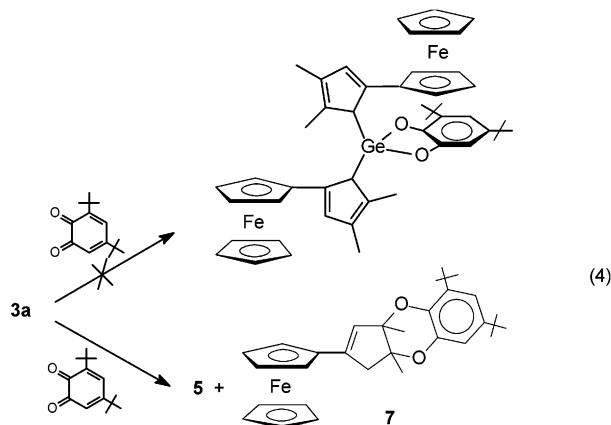
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oxidation potential is comparable to that observed in the iron series with bis(fulvalene)diiron and biferrocene.^{1a,15} This indicates, in agreement with the mass spectral results, a greater stabilization of the cation in the di(fulvanide) structure and also provides evidence for a significant interaction between the two metal centers. Thus, although the redox event is irreversible for the germanocene moiety, the presence of the ferrocenyl group induces significant changes in the redox properties of the germanium fragment.

Reactions with 3,5-Di-*tert*-butylcatechol and 3,5-Di-*tert*-butyl-*ortho*-quinone. As shown in the electrochemical study, modifications of the typical reducing or nucleophilic properties (for example, enhanced for **4a**) compared to those of the corresponding group **14** metallocenes may be expected. Therefore, we decided to carry out some typical reactivity tests in order to obtain some insight into the potential changes in the chemical reactivity. We first tried a typical electrophilic attack¹⁶ by a protic reagent. Treatment of **3** and **4** with 3,5-di-*tert*-butylcatechol effectively gave the ligand **1** or **2** and the corresponding cyclic divalent species **5**¹⁷ and **6**^{7b} (eq 3). However for **4a**, the cleavage is more difficult, only a 50% conversion was obtained after 12 h at room temperature, while, under the same conditions, complete reaction occurred with the other complexes. This result probably is due to the chelating structure, which hinders the cleavage of the germanium–(dimethylcyclopentadienyl) π -bonds.

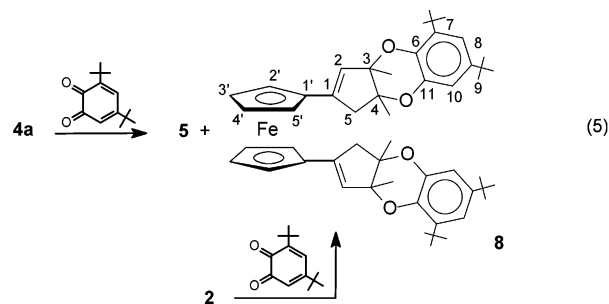


To verify the presence of divalent germanium sites in these complexes, we performed an oxidative cycloaddition reaction with 3,5-di-*tert*-butyl-*ortho*-quinone¹⁷ (eq 4). Treatment of **3a** or **4a** with an excess of *ortho*-quinone at room temperature in THF led to immediate disappearance of the green color of *ortho*-quinone. Instead of the expected germanium(IV) cycloadduct, we observed the formation of **5**, suggesting a cycloaddition with elemental germanium. Concurrent competitive heterocycloaddition with ligands **1** and **2** occurred, giving, respectively, **7** and **8**.



This result may be interpreted as an increase of the dienic reactivity of the C₅H₃Me₂ system by an electron-

donating group such as ferrocene, favoring Diels–Alder heterocyclization¹⁸ and consequently the formation of **7** and **8**. Recently, we have performed the direct cycloaddition reaction of ligands **1** with the same *ortho*-quinone, thus providing evidence for its feasibility.¹⁹ These reactions occur on the more substituted double bond of the dimethylcyclopentadienyl group, leading to the exclusive formation of one isomeric form, the endo-product on the basis of an X-ray diffraction study. Ligand **2** similarly reacted with *ortho*-quinone in THF solution at room temperature, giving selectively cycloadduct **8**, which was identified as the endo-isomer on the basis of the ¹H and ¹³C spectra (eq 5).



Experimental Section

General Procedures. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques and dry solvents. 1D NMR spectra were recorded on Bruker AC 80 (80.13 MHz) and ARX 400 (400.13 MHz) (¹H), AC 200 (50.32 MHz) and ARX (100.62 MHz) (¹³C), and ARX 400 (111.93 MHz) (¹¹⁹Sn). All 2D NMR spectra (COSY, correlation spectroscopy; HSQC, heteronuclear single quantum correlation; HMBC, heteronuclear multiple bond correlation) were acquired at 298 K on a Bruker ARX-400 spectrometer equipped with an inverse 1H/broadband z gradient probe. To perform these experiments, standard pulse sequences of the Bruker library were used. Data were processed on a SGI O2 workstation using Bruker Xwinnmr 2.1 software. Mass spectra were measured with a Hewlett-Packard HP 5989A in the electron impact mode (70 eV) or a Rybermag R10-10 spectrometer operating in the electron impact mode or by chemical desorption (DCI, CH₄). Voltammetric measurements were carried out with a homemade potentiostat²⁰ using the interrupt method to minimize the uncompensated resistance (*iR*) drop. Experiments were performed at room temperature in an airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm³ apparent surface. The working electrode was a Pt electrode (diameter = 1 mm). The supporting electrolyte [*n*-Bu₄N]BF₄ (Fluka, electrochemical grade) was dried under vacuum for 1 h. THF was distilled over sodium prior use. The

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solutions used during the electrochemical studies were typically 10^{-3} M in the studied compound and 0.1 M in supporting electrolyte. Cyclic voltammetry was performed in the potential range of -2 to 2 versus SCE at 0.1 V/s. Before each measurement, the working electrode was polished with Emery paper (Norton A621). A quasi steady state behavior is obtained by linear voltammetry at 5 mV/s. All reported potentials in the present paper are referred to a SCE electrode. Melting points were measured on a Leitz microscope or Electrothermal apparatus (capillary). Elemental analyses were performed by the Centre de Microanalyse de l'Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques Et Technologiques. The starting materials, the mono- and bis(cyclopentadienyl)-substituted ferrocenes, **1** and **2**,^{10,11} and $\text{Cl}_2\text{Ge}\cdot\text{dioxane}$ ²¹ were prepared according to the previously reported procedure.

Preparation of 3a. *n*-Butyllithium (1.19 mmol) (1.6 M solution in hexane) was added to a stirred solution of **1** (0.30 g, 1.08 mmol) in THF (5 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 30 min. Then, a solution of $\text{Cl}_2\text{Ge}\cdot\text{dioxane}$ (0.13 g, 0.54 mmol) in THF (3 mL) was added at -78 °C. The temperature was slowly raised to room temperature, and the mixture was stirred for 2 h. The solvents were removed under reduced pressure, and the residual solid was extracted with toluene. The extracts were filtered and concentrated, giving an orange powder of **3a** (0.26 g, 78%). Crystallization from toluene at -30 °C gave orange crystals suitable for X-ray analysis: mp 190 °C dec; ^1H NMR (CDCl_3 , 400 MHz) δ 1.98 (s, 12H, $\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 4.05 (s, 10H, C_5H_5), 4.18 (m, 4H, $\text{C}(3')\text{-H}$ and $\text{C}(4')\text{-H}$), 4.30 (m, 4H, $\text{C}(2')\text{-H}$ and $\text{C}(5')\text{-H}$), 5.76 (s, 4H, $\text{C}(2)\text{-H}$ and $\text{C}(5)\text{-H}$); $^{13}\text{C}\{1\}$ NMR (CDCl_3 , 100.6 MHz) δ 12.41 ($\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 66.14 ($\text{C}(3')$ and $\text{C}(4')$), 67.71 ($\text{C}(2')$ and $\text{C}(5')$), 69.65 (C_5H_5), 82.23 ($\text{C}(1)$), 108.35 ($\text{C}(2)$ and $\text{C}(5)$), 122.20 ($\text{C}(1)$), 123.32 ($\text{C}(3)$ and $\text{C}(4)$); MS/EI $[\text{M}]^+ m/z$ 628 (2%). Anal. Calcd for $\text{C}_{34}\text{H}_{34}\text{GeFe}_2$: C, 65.14; H, 5.47. Found: C, 64.72; H, 5.17.

Preparation of 3b. A similar procedure was used. **1** (0.29 g, 1.05 mmol) and Cl_2Sn (0.10 g, 0.53 mmol) gave an orange powder: 0.23 g (68%), mp 150 °C dec; ^1H NMR (CDCl_3 , 400 MHz) δ 2.02 (s, 12H, $\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 4.03 (s, 10H, C_5H_5), 4.16 (m, 4H, $\text{C}(3')\text{-H}$ and $\text{C}(4')\text{-H}$), 4.29 (m, 4H, $\text{C}(2')\text{-H}$ and $\text{C}(5')\text{-H}$), 5.82 (s, 4H, $\text{C}(2)\text{-H}$ and $\text{C}(5)\text{-H}$); $^{13}\text{C}\{1\}$ NMR (CDCl_3 , 100.6 MHz) δ 12.49 ($\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 65.98 ($\text{C}(3')$ and $\text{C}(4')$), 67.55 ($\text{C}(2')$ and $\text{C}(5')$), 69.68 (C_5H_5), 82.80 ($\text{C}(1)$), 106.87 ($\text{C}(2)$ and $\text{C}(5)$), 120.62 ($\text{C}(1)$), 121.97 ($\text{C}(3)$ and $\text{C}(4)$); ^{119}Sn NMR (CDCl_3 , 111.9 MHz) -2071 ppm; MS/EI $[\text{FcC}_5\text{H}_2\text{Me}_2\text{Sn}]^+ m/z$ 397 (6%). Anal. Calcd for $\text{C}_{34}\text{H}_{34}\text{SnFe}_2$: C, 60.68; H, 5.09. Found: C, 60.04; H, 4.65.

Preparation of 4a. A solution of *n*-butyllithium (1.57 mmol) in hexane (1.6 M) was added to a solution of **2** (0.26 g, 0.70 mmol) in THF (5 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. Then, a solution of $\text{Cl}_2\text{Ge}\cdot\text{dioxane}$ (0.16 g, 0.70 mmol) in THF (6 mL) was added at -78 °C. A procedure similar to the synthesis of **3a** was used, giving a dark red powder, **4a** (0.27 g, 86%). Crystallization from toluene at -30 °C gave dark red crystals; mp 200 °C dec; ^1H NMR (CDCl_3 , 400 MHz) δ 2.12 (s, 12H, $\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 4.08 (m, 4H, $\text{C}(3')\text{-H}$ and $\text{C}(4')\text{-H}$), 4.22 (m, 4H, $\text{C}(2')\text{-H}$ and $\text{C}(5')\text{-H}$), 5.33 (s, 4H, $\text{C}(2)\text{-H}$ and $\text{C}(5)\text{-H}$); $^{13}\text{C}\{1\}$ NMR (CDCl_3 , 100.6 MHz) δ 12.45 ($\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 66.19 ($\text{C}(3')$ and $\text{C}(4')$), 68.05 ($\text{C}(2')$ and $\text{C}(5')$), 82.84 ($\text{C}(1)$), 108.60 ($\text{C}(2)$ and $\text{C}(5)$), 110.98 ($\text{C}(1)$), 125.30 ($\text{C}(3)$ and $\text{C}(4)$); MS/EI $[\text{M}]^+ m/z$ 442 (100%). Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{GeFe}$: C, 65.38; H, 5.49. Found: C, 65.01; H, 5.46.

Preparation of 4b. Stannocene **4b** was synthesized using a similar procedure (0.39 g (1.05 mmol) of **2** and 0.20 g (1.05 mmol) of Cl_2Sn), yielding an orange powder: 0.38 g (75%); mp 180 °C dec; ^1H NMR (CDCl_3) δ 2.09 (s, 12H, $\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 4.01 (m, 4H, $\text{C}(3')\text{-H}$ and $\text{C}(4')\text{-H}$), 4.13 (m, 4H, $\text{C}(2')\text{-H}$ and $\text{C}(5')\text{-H}$), 5.47 (s, 4H, $\text{C}(2)\text{-H}$ and $\text{C}(5)\text{-H}$); $^{13}\text{C}\{1\}$ NMR

(CDCl_3 , 100.6 MHz) δ 12.48 ($\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), $J(\text{C}-^{117/119}\text{Sn}) = 15.5$ Hz), 66.07 ($\text{C}(3')$ and $\text{C}(4')$), 67.79 ($\text{C}(2')$ and $\text{C}(5')$), 83.53 ($\text{C}(1)$), $J(\text{C}-^{117/119}\text{Sn}) = 13.8$ Hz), 108.55 ($\text{C}(1)$), $J(\text{C}-^{117/119}\text{Sn}) = 41.2$ Hz), 109.54 ($\text{C}(2)$ and $\text{C}(5)$), 124.03 ($\text{C}(3)$ and $\text{C}(4)$), $J(\text{C}-^{117/119}\text{Sn}) = 40.2$ Hz); ^{119}Sn NMR (CDCl_3 , 111.9 MHz) -2017 ppm; MS/EI $[\text{M}]^+ m/z$ 488 (100%). Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{SnFe}$: C, 59.19; H, 4.97. Found: C, 58.57; H, 4.51.

Crystal Data for 3a and 4a. **3a:** $\text{C}_{34}\text{H}_{34}\text{Fe}_2\text{Ge}$, $M = 626.90$, monoclinic, $C2$, $a = 21.280(4)$ Å, $b = 6.167(1)$ Å, $c = 12.005(3)$ Å, $\beta = 120.017(4)^\circ$, $V = 1364.0(5)$ Å³, $Z = 2$, $T = 193(2)$ K. 3219 reflections (2058 independent, $R_{\text{int}} = 0.0459$) were collected. Largest electron density residue: $0.758 \text{ e } \text{Å}^{-3}$, R_1 (for $I > 2\sigma(I)$) = 0.0539 and $wR_2 = 0.1156$ (all data) with $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{0.5}$. **4a:** $\text{C}_{24}\text{H}_{24}\text{FeGe}$, $M = 440.87$, monoclinic, $C2/c$, $a = 20.119(1)$ Å, $b = 21.3232(1)$ Å, $c = 18.009(1)$ Å, $\beta = 90.338(1)^\circ$, $V = 7725.8(9)$ Å³, $Z = 16$, $T = 193(2)$ K. 23 319 reflections (8429 independent, $R_{\text{int}} = 0.0251$) were collected. Largest electron density residue: $0.364 \text{ e } \text{Å}^{-3}$, R_1 (for $I > 2\sigma(I)$) = 0.0286 and $wR_2 = 0.0747$ (all data). All data for both structures were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The structure was resolved by direct methods (SHELXS-97),²² and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2 .²³ The files CCDC 238502 (**3a**) and CCDC 238503 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Reaction of 3 and 4 with 3,5-Di-*tert*-butylcatechol. A solution of the catechol (0.06 g, 0.27 mmol) in 2 mL of THF was added to **3a** (0.17 g, 0.27 mmol) in 5 mL of THF. The solution was stirred for 12 h at room temperature, and the volatile solvents were removed in vacuo. Analysis of the residue by ^1H NMR spectroscopy showed the formation of **5** (28%) and **1** (72%), confirmed by mass spectrometry (**5**, m/z 294; **1**, m/z 278). A similar procedure was used for the other complexes, and the results are as follows: **3b**: **6** (37%), **1** (63%); **4a**: **4a** residual (52%), **5** (24%), **2** (24%); **4b**: **6** (53%), **2** (47%).

Reaction of 3a and 4a with 3,5-Di-*tert*-butyl-ortho-quinone. A solution of the *ortho*-quinone (0.05 g, 0.25 mmol) in 2 mL of THF was added to **3a** (0.06 g, 0.10 mmol) in 3 mL of THF. The solution was stirred for 6 h at room temperature, and the volatile solvents were removed in vacuo. Analysis of the residue by ^1H NMR spectroscopy showed the formation of **5** (15%) and cycloadduct **7** (60%), confirmed by mass spectrometry (**5**, m/z 294). A similar procedure was used for **4a**, and the result is as follows: **5** (52%), cycloadduct **8** (24%).

Preparation of 8. To a solution of **2** (0.20 g, 0.54 mmol) in 4 mL of THF was added a solution of *ortho*-quinone (0.24 g, 1.08 mmol) in 5 mL of THF. The mixture was stirred at 20 °C overnight. The solvent was evaporated and the residue washed with pentane. After filtration and drying, 0.15 g (34%) of **8** was obtained as an orange powder: mp 233 °C; ^1H NMR (CDCl_3 , 200 MHz) δ 1.21 (s, 18H, *t*-Bu), 1.44 (s, 18H, *t*-Bu), 1.41 (s, 12H, $\text{CH}_3\text{-C}(3)$ and $\text{CH}_3\text{-C}(4)$), 2.32 (dd, $^2J = 15.7$ Hz, $^4J = 2.0$ Hz, 2H, $\text{C}(5)\text{-H}$), 2.72 (dd, $^2J = 15.7$ Hz, $^4J = 1.2$ Hz, 2H, $\text{C}(5)\text{-H}$), 4.10 (m, 8H, C_5H_5), 5.66 (sl, 2H, $\text{C}(2)\text{-H}$), 6.72 (d, $^4J = 2.3$ Hz, 2H, $\text{C}(10)\text{-H}$), 6.82 (d, $^4J = 2.3$ Hz, 2H, $\text{C}(8)\text{-H}$); $^{13}\text{C}\{1\}$ NMR (CDCl_3 , 100.6 MHz) δ 20.34 ($\text{CH}_3\text{-C}(3)$), 23.05 ($\text{CH}_3\text{-C}(4)$), 30.02, ((CH_3)₃ $\text{C-C}(7)$), 31.68 ((CH_3)₃ $\text{C-C}(9)$), 34.40 ((CH_3)₃ $\text{C-C}(9)$), 35.04 ((CH_3)₃ $\text{C-C}(7)$), 45.58 ($\text{C}(5)$), 66.87, 69.37 ($\text{C}(3')$ and $\text{C}(4')$), 69.88, 70.47 ($\text{C}(2')$ and $\text{C}(5')$), 80.69 ($\text{C}(1)$), 84.48 ($\text{C}(4)$), 86.51 ($\text{C}(3)$), 111.78 ($\text{C}(10)$), 114.76 ($\text{C}(8)$), 126.54 ($\text{C}(2)$), 137.55 ($\text{C}(7)$), 140.90 ($\text{C}(1)$ and $\text{C}(6)$), 142.86 ($\text{C}(9)$), 144.40 ($\text{C}(11)$); MS/EI

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[M]⁺ *m/z* 810 (6%). Anal. Calcd for C₅₂H₆₆FeO₄: C, 77.02; H, 8.20. Found: C, 76.44; H, 8.03.

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Supporting Information Available: Tables and figures giving details of the electrochemical study and of the X-ray structure determination, atomic coordinates, and bond distances and angles for **3a** and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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