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Bis(silylenyl)- and Bis(germylenyl)-Substituted Ferrocenes: Synthesis, Structure, and Catalytic Applications of Bidentate Silicon(II)–Cobalt Complexes**

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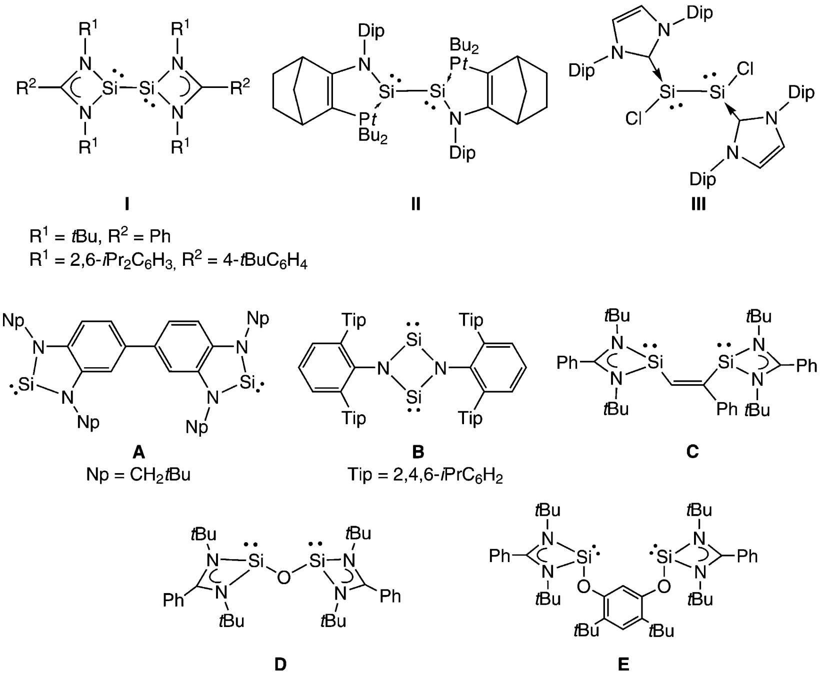
Dedicated to Professor Guy Bertrand on the occasion of his 60th birthday



Scheme 1. Bis(silylenes) **I**–**III** and spacer-separated bis(silylenes) **A**–**E**.

The chemistry of stable silylenes has received wide interest since the first isolation of N-heterocyclic silylenes (NHSis) by Denk and West et al.[1] While stable silylenes have received a lot of attention,[2] the chemistry of bis(silylenes), compounds with two divalent silicon sites in a single molecule, is much less developed.[3] To date, bis(silylenes) have been limited to two types of compounds, which can be defined as follows: 1) "interconnected bis(silylenes)" in which the two divalent silicon atoms are adjacent to each other and connected by a central single bond (**I**–**III**),[4–6] and 2) "spacer-separated bis(silylenes)" in which the divalent silicon atoms are separated by a spacer (**A**–**E**; Scheme 1).[7–11] Recently, interconnected bis(silylenes) **I**–**III** have been the subject of active research because of their distinct reactivity in comparison to isoelectronic disilynes. For example, compounds **I**, which bear amidinate ligands, were independently synthesized by Roesky and co-workers,[4a] and Jones et al.[4b] Furthermore, bis(silylenes) of type **II** and **III**, which are stabilized by an intramolecular phosphine donor and an N-heterocyclic carbene (NHC), respectively, were also reported.[5,6] On the other hand, spacer-separated bis(silylenes) are intriguing as novel bidentate σ-donor ligands for transition metals because of their unique structure and their coordination ability. The first spacer-separated bis(silylene) **A** was reported by Lappert and co-workers in 2005.[7] Bis(silylene) **B** was synthesized by the reduction of dichlorosilaimine NHC·Cl$_2$Si=NR (NHC = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene, R = 2,6-bis(2,4,6-triisopropylphenyl)-phenyl) through initial formation of the elusive silaisocyanide intermediate.[8] In addition, compound **C** was prepared by the reaction of bis(silylene) **I** (R^1 = tBu, R^2 = Ph) with phenylacetylene PhC≡CH.[9] Very recently, we described the synthesis of the first isolatable oxygen-bridged bis(silylene) **D** and pincer-type bis(silylene) **E**.[10,11] This development underlines that silylenes are no longer laboratory curiosities and may provide access to new silicon(II)-based functional groups in coordination chemistry toward transition metals. In general, complexes of silylenes and transition metals have received much attention because they can play a key role as intermediates in transition-metal-catalyzed transformation of silicon compounds.[12] Very recently, bis(silylenes) **D** and **E** have been employed as new silicon(II)-based donor ligands to stabilize unusually electron-rich complexes of silylenes and Group 10 metals. In order to gain access to other new bis(silylenes) as potential bidentate σ-donor ligands,[13] we set out to investigate a novel

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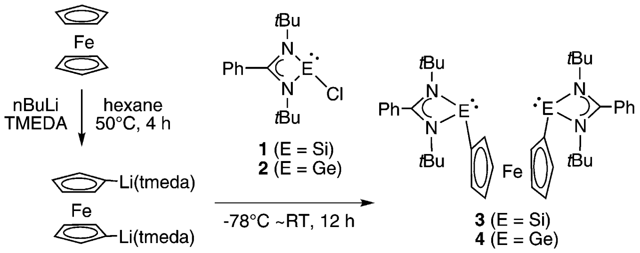
type of bis(silylene) with a ferrocenyl spacer, which could result in unique properties. Herein, we present the facile synthesis and characterization of the first bis(silylenyl)- and bis(germylenyl)-substituted ferrocenes LSi-Fc-SiL **3** (Fc = ferrocendiyl, $\mathrm{L = PhC(N}t\mathrm{Bu)_2}$) and LGe-Fc-GeL **4**, respectively, as well as their corresponding CpCo (Cp = η^5-cyclopentadienyl) complexes **5** and **6**. Additionally, **5** and **6** were probed as catalysts for [2+2+2] cycloaddition reactions of phenylacetylene and acetonitrile to give substituted benzenes and pyridines, respectively.

Recently, we reported the reaction of chlorosilylene LSiCl **1**[14] with dilithium resorcinolate to afford the pincer-type bis(silylene) **E** in high yield.[11] We anticipated that chlorosilylene **1** and chlorogermylene LGeCl **2**[15] could be suitable precursors for the synthesis of the desired bismetallene-functionalized ferrocenes **3** and **4**. In fact, treatment of **1** with 1,1′-dilithioferrocene led to the formation of bis(silylene) **3** in 70 % yield (Scheme 2). Similarly, the Ge analogue **4** could be isolated in 77 % yield by salt metathesis reaction of 1,1′-dilithioferrocene with **2**. Compounds **3** and **4** represent the first examples of isolatable silylene- and germylene-substituted ferrocenes, respectively. Recently, disilene-functionalized ferrocene was reported by Tokitoh and co-workers.[16] The structures of **3** and **4** were determined by multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallographic analysis (only for compound **4**). Accordingly, the ^{13}C NMR spectra of **3** and **4** each exhibit three resonances for the ferrocendiyl moieties ($\delta = 70.9$, 72.7, and 84.6 ppm for **3**; $\delta = 70.1$, 72.3, and 92.0 ppm for **4**). Furthermore, bis(silylene) **3** shows a singlet at $\delta = 43.3$ ppm in the ^{29}Si NMR spectrum.



Scheme 2. Synthesis of bis(silylene)–ferrocene ligand **3** and its Ge analogue **4**.

Single crystals of **4** suitable for an X-ray analysis were obtained from hexane solution.[17] The crystals of **4** consist of two conformational isomers, and one of them is shown in Figure 1 (see also the Supporting Information). The molecular structure of **4** confirms that the two N-donor-stabilized germylene moieties are bonded to C1 and C8 of the ferrocendiyl spacer. The Ge1–C1 and Ge2–C8 distances are 1.991(2) and 1.9774(19) Å, respectively. The Ge–N bonds (2.0261(16), 2.0247(17), 2.0162(16), and 2.0402(15) Å) of **4** are slightly shorter than those of precursor **2**.[15] The Ge$^{\mathrm{II}}$ centers of **4** adopt a pyramidal geometry with the sums of bond angles of 255.93 and 256.67°, respectively. The structural features of the amidinate ligands in **4** are comparable to those reported for related bis(germylenes), such as $\mathrm{[\{LGeN(Ph)\}_2]}$[18] and L′GeEGeL′ (E = O, S, $\mathrm{L} = t\mathrm{BuC(NAr)_2}$, Ar = 2,6-$i\mathrm{Pr_2C_6H_3}$).[19] In addition, the molecular structure of bis(silylene) **3** could also be unambiguously determined by X-ray diffraction. The structural features of **3** are very similar to those of **4**, however, the X-ray data are not sufficient for discussion (Supporting Information).

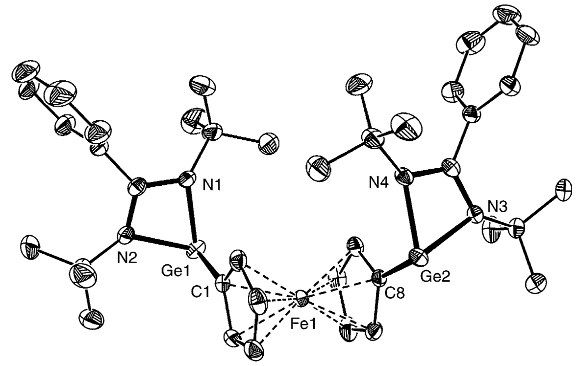
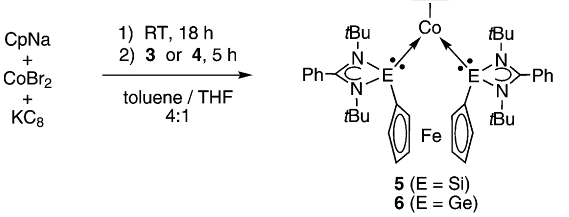


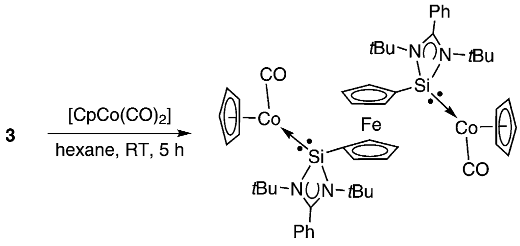
Figure 1. Molecular structure of compound **4**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C1 1.991(2), Ge2–C8 1.9774(19), Ge1–N1 2.0261(16), Ge1–N2 2.0247(17), Ge2–N3 2.0402(15), Ge2–N4 2.0162(16); C1-Ge1-N1 96.62(7), C1-Ge1-N2 94.45(7), N1-Ge1-N2 64.86(7), C8-Ge2-N3 94.92(7), C8-Ge2-N4 97.16(7), N3-Ge2-N4 64.59(6).

A first set of experiments was undertaken to investigate the coordination ability of **3** and **4** toward transition metals. Inspired by the reactivity of the bis(silylenes) **D** and **E** toward Ni^0 and Pd^0 [10,11] and by reports on interconnected bis(germylene) iron $\mathrm{[\{LGeFe(CO)_4\}_2]}$[18] and spacer-separated bis(germylene) molybdenum chelate complexes *cis*-$\mathrm{[Mo(CO)_4\{(CH_2CMe_2CH_2)[NGeN(CH_2}t\mathrm{Bu)\text{-}C_6H_4]_2\}]}$,[20] we explored the coordination behavior of potentially bidentate ligands **3** and **4** toward CpCo complex fragments. In addition, we wanted to test the reactivity of the resulting complexes as precatalysts for Co-mediated [2+2+2] cycloaddition reactions of phenylacetylene and acetonitrile. Suitable CpCo$^{\mathrm{I}}$ sources are accessible through treatment of cobalt(II) dibromide ($\mathrm{CoBr_2}$) with sodium cyclopentadienide (NaCp) and potassium graphite ($\mathrm{KC_8}$) in toluene or THF, resulting in the generation of $\mathrm{[CpCo^IL_\mathit{n}]}$ (L = toluene or THF) in solution. Reactions of CpCo precursors with bis(silylene) **3** afforded the desired bis(silylene) Co$^{\mathrm{I}}$ complex **5** in 30 % yield (Scheme 3).[21] In the ^{29}Si NMR spectrum, the coordination of the bis(silylene) moieties to the Co atom leads to a drastic downfield shift of the resonance of **5** ($\delta = 82.0$ ppm) in



Scheme 3. Synthesis of bis(silylene)–CpCo complex **5** and its germanium analogue **6**.

comparison to that of **3** ($\delta = 43.3$ ppm). Likewise, the bis(germylene) Co^I complex **6** could be successfully synthesized from **4**, and isolated in 61% yield. When the bis(silylene) **3** was allowed to react with two molar equivalents of [CpCo(CO)$_2$], the bis(silylene)–Co complex [{LSiCo(CO)Cp}$_2$Fc] **7** could be obtained in 87% yield, accompanied by elimination of CO (Scheme 4). The ^{29}Si NMR spectrum of **7** shows a singlet resonance at $\delta = 85.7$ ppm, similar to that of **5**. In the ^{13}C NMR spectrum of **7**, one characteristic signal for the CO ligands appears at $\delta = 207.8$ ppm. Furthermore, the IR spectrum of **7** exhibits a strong stretching band at $\nu = 1888$ cm^{-1} attributed to the carbonyl groups on the Co^I atoms. The observed CO stretching frequency of **7** is much lower than those of [(LSiCl)Co(CO)Cp] ($\nu = 1968$ cm^{-1}),[22] thus indicating that the bis(silylene)-substituted ferrocene **3** is a much stronger σ donor than LSiCl **1**.



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Scheme 4. Synthesis of bis(silylene)–Cp(CO)Co complex **7**.

The molecular structures of the heterobimetallic complexes **5** (Figure 2) and **6** (Figure 3) were determined by single-crystal X-ray diffraction analyses; both structures show similar features. The silicon atoms in **5** and germanium atoms in **6** are four coordinated and show a distorted tetrahedral geometry. The Co–Si bond lengths of **5** (2.1252(14) and 2.1200(14) Å) are similar to that of [(LSiCl)CoCp(CO)] (2.1143(4) Å).[22] Furthermore, the Co–Si bonds of **5** are shorter than those of [{(NHC)SiCl$_2$}CoCp(CO)] (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) (2.1348(5) Å),[23] [{(NHC)Cl$_2$Si}$_2$Co(CO)$_3$]$^+$[CoCl$_3$(thf)]$^-$ (2.228(2) Å),[24] [(LSiCl)$_2$Co(CO)$_3$]$^+$[Co(CO)$_4$]$^-$ (2.2060(6) and 2.2017(6) Å),[22] and [PNP{HSi=Co(H)$_3$(SiH$_2$Ph)$_2$}] (PNP = {Ph$_2$PCH$_2$SiMe$_2$}N$^-$) (2.3990(7) Å), respectively.[25] Moreover, the Co–Ge bonds of **6** (2.1967(6) Å and 2.1979(6) Å) are also shorter than those of [[{(Me$_3$Si)$_2$N}$_2$GeCo(CO)$_3$]$_2$] (2.262(1) Å)[26] and [η^4-{(tBu$_2$MeSi)$_4$Ge$_4$}CoCp] (2.4616(3) Å and 2.5036(3) Å),[27] respectively. To the best of our knowledge, the Co–Ge bonds in **6** are the shortest Co–Ge bonds known to date. The relatively short E^{II}–Co bonds in **5** and **6** indicate that **3** and **4** are two of the strongest σ-donor ligands in the series of divalent silicon and germanium donors, respectively.

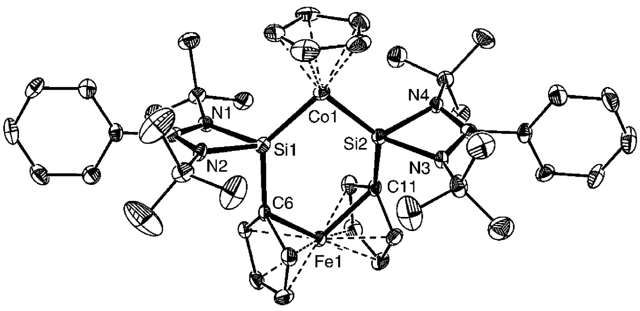


Figure 2. Molecular structure of compound **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–Si1 2.1252(14), Co1–Si2 2.1200(14), Si1–C6 1.894(5), Si2–C11 1.887(5), Si1–N1 1.898(4), Si1–N2 1.907(4), Si2–N3 1.904(4), Si2–N4 1.922(4); N1-Si1-N2 68.47(15), N3-Si2-N4 68.66(16), Si1-Co1-Si2 93.89(5), C6-Si1-Co1 132.54(14).

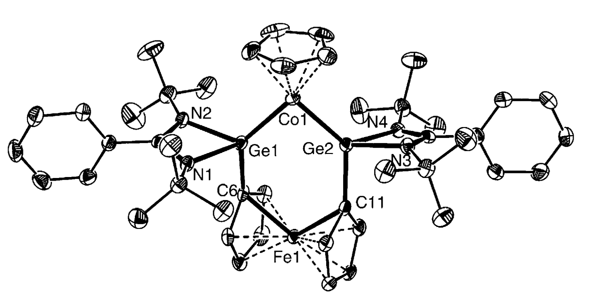
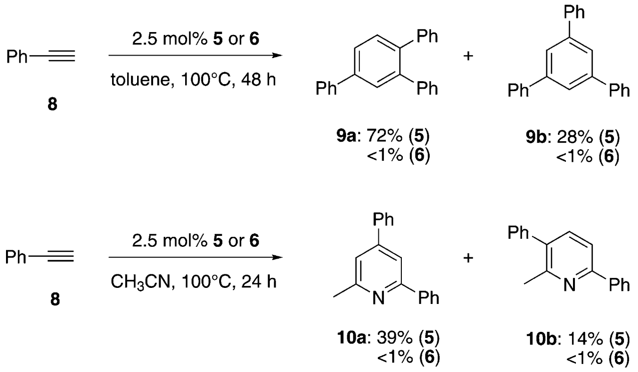


Figure 3. Molecular structure of compound **6**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–Ge1 2.1967(6), Co1–Ge2 2.1979(6), Ge1–C6 1.965(4), Ge2–C11 1.961(4), Ge1–N1 2.020(3), Ge1–N2 2.031(3), Ge2–N3 2.041(3), Ge2–N4 2.029(3); N1-Ge1-N2 64.90(11), N3-Ge2-N4 64.85(11), Ge1-Co1-Ge2 92.79(2), C6-Ge1-Co1 132.80(10), C11-Ge2-Co1 131.40(10).

Numerous Co complexes have been successfully applied as pre-catalysts in [2+2+2] cycloaddition reactions, which are a powerful tool in organic chemistry to form arene and heteroarene moieties.[28,29] Thus, we were interested in the evaluation of the catalytic abilities of complexes **5** and **6** in [2+2+2] cycloaddition reactions (Scheme 5).[28] A first set of experiments was dedicated to the benchmark trimerization of phenyl acetylene **8**, and resulted in the quantitative formation of isomers **9a** and **9b** in the presence of complex **5**. Surprisingly, similar attempts to employ **6** as precatalyst showed no product formation, possibly because of a stronger



Scheme 5. Application of **5** and **6** as precatalysts in [2+2+2] cycloaddition reactions.

coordination of Ge^{II} donor centers to Co, which consequently hampers the formation of an active site for substrate coordination. Moreover, the formation of substituted pyridines by [2+2+2] cycloaddition of phenyl acetylene and an excess of acetonitrile was examined.[30] Again, catalytic activity was exhibited for Si^{II}–Co complex **5**, while no product formation could be observed with Ge^{II}–Co complex **6**. Interestingly, to some extend the application of [CpCo(CO)$_2$] as precatalyst gave substituted pyridines **10a** (3%) and **10b** (11%) in lower yields.

In conclusion, the synthesis, characterization, and reactivity of bis(silylenyl)- and bis(germylenyl)-substituted ferrocenes **3** and **4** have been reported. These ligands are easily accessible by the reaction of 1,1′-dilithioferrocene with the respective N-donor-stabilized metallene chlorides LECl (E = Si, Ge), and represent two of the strongest bidentate M^{II}-based σ-donor ligands, as shown by coordination of **3** and **4** to CpCo to give the Co complexes **5** and **6**, respectively. In addition, the catalytic abilities of these ligands in Co-mediated [2+2+2] cycloaddition reactions of phenylacetylene and acetonitrile were probed. Unexpectedly, complex **5** is catalytically active, while complex **6** is inactive, possibly because of a stronger coordination of the Ge^{II} donor centers to Co, which hampers the creation of an active site at Co for the substrate coordination.

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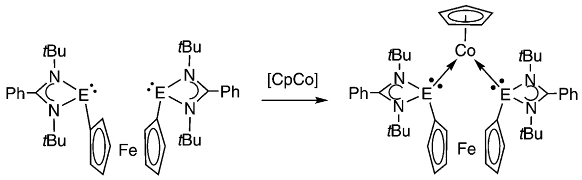
Communications

Chelate Ligands

W. Wang, S. Inoue,* S. Enthaler,*
M. Driess* ________________ ■■■■–■■■■

Bis(silylenyl)- and Bis(germylenyl)-Substituted Ferrocenes: Synthesis, Structure, and Catalytic Applications of Bidentate Silicon(II)–Cobalt Complexes



1 2

Strong bite: The two respective Si^{II} and Ge^{II} centers in ferrocene-containing bis(silylene) and bis(germylene) ligands **1** can serve as excellent σ donors, as shown in the formation of Co complexes **2** (see scheme, Cp = η^5-cyclopentadienyl). Unexpectedly, only the bis(silylene)–Co complex **2** is a precatalyst for the [2+2+2] cycloaddition of phenylacetylene and MeCN, possibly because of a stronger coordination of the Ge^{II} donor centers to Co.

Chelatliganden

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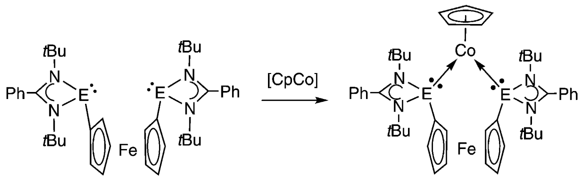

1 2

Starker Biss: Die Si^{II}- bzw. Ge^{II}-Zentren in den Ferrocen-haltigen Bis(silylen)- und Bis(germylen)-Liganden **1** können als exzellente σ-Donoren dienen, wie anhand der Bildung der Co-Komplexe **2** gezeigt wird (siehe Schema). Jedoch kann nur der Bis(silylen)-Co-Komplex **2** als Präkatalysator für die [2+2+2]-Cycloaddition von Phenylacetylen und MeCN fungieren, vermutlich aufgrund der stärkeren Koordination des Ge^{II}-Zentrums an Co.

Chelate Ligands

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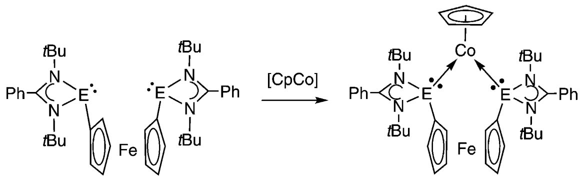

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