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From Tetragermacyclobutene to Tetragermacyclobutadiene Dianion to Tetragermacyclobutadiene Transition Metal Complexes

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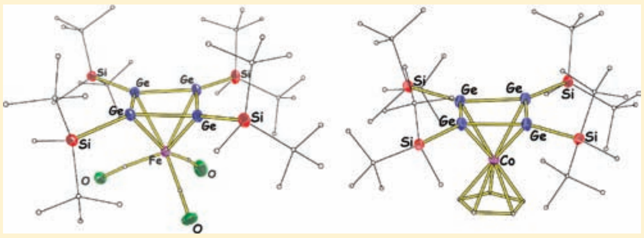
S *Supporting Information*



ABSTRACT: The reaction of 3,4-dichlorotetragermetene derivative **2** with $Na_2[Fe(CO)_4]$ in THF produced a (tetragermacyclobutadiene)tricarbonyliron complex, $[\{\eta^4\text{-}({}^tBu_2MeSi)_4Ge_4\}]Fe(CO)_3$ **4**, which has a slightly folded Ge_4 ring perhaptocoordinated to the Fe center. Structural and spectral characteristics of **4** show a remarkable π-donating ability of the tetragermacyclobutadiene ligand toward the transition metal, surpassing that of tetrasilacyclobutadiene and cyclobutadiene ligands. Reduction of **2** with KC_8 resulted in exclusive formation of the dipotassium salt of the tetragermacyclobutadiene dianion derivative $\mathbf{3}^{2-}\cdot[K^+(thf)_2]_2$, representing a rare example of a 6π-electron compound that, on the basis of its structural and magnetic properties, was recognized as a nonaromatic species. Reaction of $\mathbf{3}^{2-}\cdot[K^+(thf)_2]_2$ with $CpCoI_2(PPh_3)$ produced a (cyclopentadienyl)(tetragermacyclobutadiene)cobalt complex, $[\{\eta^4\text{-}({}^tBu_2MeSi)_4Ge_4\}]CoCp$ **7**, as the first example of a sandwich compound featuring an all-germanium-containing cyclic polyene ligand.

INTRODUCTION

Cyclobutadiene is a highly reactive anti-aromatic four π-electron species that can be effectively stabilized as a ligand in transition metal complexes.[1] It was first proposed theoretically by Longuet-Higgins and Orgel[2] and then verified in a number of experimental observations.[3] The first stable derivative, $(Ph_4C_4)Fe(CO)_3$, was synthesized[4a] and structurally characterized[4b] in 1959−1960, and the remarkable unsubstituted analogue, $(H_4C_4)Fe(CO)_3$, was reported by Pettit and co-workers in 1965.[5] On the other hand, cyclobutadiene dianion, as a doubly reduced analogue of a neutral cyclobutadiene, is a six π-electron species, whose potential aromaticity was debated long ago[6] and was finally acknowledged at first theoretically[7] and then experimentally.[8] The analogues of cyclobutadiene, in which all skeletal carbons are replaced with heavy group 14 elements, have not been reported in the literature,[9] whereas the first analogues of cyclobutadiene dianion derivatives of heavy group 14 elements were communicated by us some years ago.[10] Although several coordination compounds with cyclobutadiene ligands have been synthesized to date, transition metal complexes featuring all-heavy group 14 element-containing cyclobutadiene ligands were virtually unknown until 2005, when we reported the first cobalt complex having a tetrasilacyclobutadiene ligand.[11] Since then, several other representatives of tetrasila- or trisilagermacyclobutadiene transition metal complexes, including the silicon version of Pettit's compound, a (tetrasilacyclobutadiene)tricarbonyliron complex, have been reported.[12] In this contribution, we report the synthesis and structural characterization of the first coordination compounds featuring the "heaviest" group 14 element cyclobutadiene ligand, namely, (tetragermacyclobutadiene)tricarbonyliron half-sandwich and (cyclopentadienyl)(tetragermacyclobutadiene) cobalt sandwich complexes, readily prepared from their precursors, dichlorotetragermetene and tetragermacyclobutadiene dianion derivatives, respectively.

RESULTS AND DISCUSSION

The 3,4-dichloro-$^3\Delta$-1,2,3,4-tetragermetene derivative **2** was readily available from the reaction of the recently prepared trigermirene **1**[13] with a dichlorogermylene dioxane complex (Scheme 1). The proposed mechanism of such unusual ring expansion reaction might involve the multistep reaction sequence that was discussed in our previous report on the generation of the disiladigermetene derivative by the reaction of the 3*H*-disilagermirene with $GeCl_2\cdot$dioxane complex.[14]

Isolated as an orange crystalline material, **2** exhibits simple ^1H and ^{13}C NMR spectra showing only two sets of signals for the substituents, in agreement with its molecular symmetry. Accordingly, two resonances from the ${}^tBu_2MeSi$ groups at 33.6 and 40.2 ppm were observed in the ^{29}Si NMR spectrum of **2**. Representing the first pergermacyclobutene, **2** is remarkably stable, showing no signs of dissociation of the Ge=Ge bond in solution. This is shown by the observation of the longest UV absorption of **2**, corresponding to a Ge=Ge $\pi-\pi^*$ electronic transition occurring at 431 nm (the HOMO−LUMO transition for the Me_3Si-substituted model was calculated as occurring at 424 nm at the TD-DFT B3PW91/6-31G(d) level).[15]

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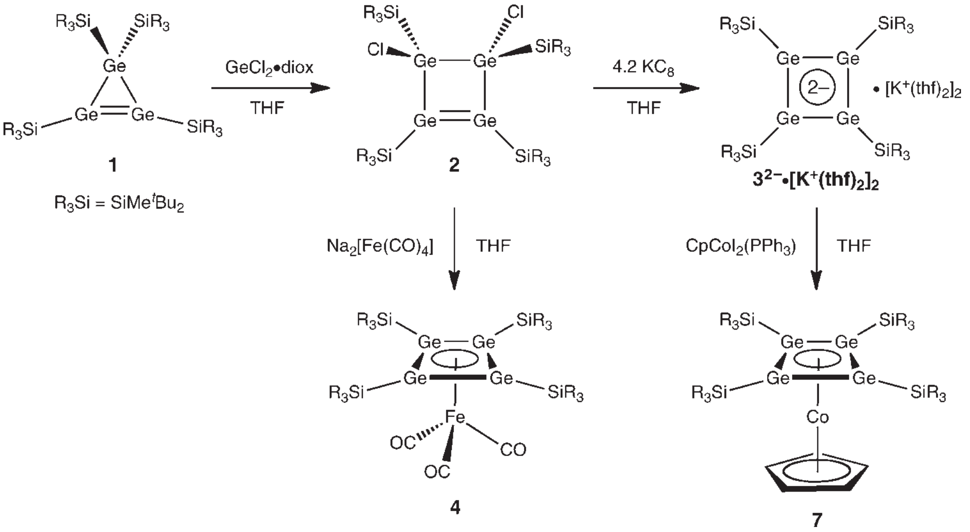
Scheme 1. Syntheses of the Tetragermetene 2, Dipotassium Salt of the Tetragermacyclobutadiene Dianion $3^{2-}\cdot[K^+(thf)_2]_2$, ($\eta^4$-Tetragermacyclobutadiene)tricarbonyliron Complex 4, and (η^5-Cyclopentadienyl)(η^4-tetragermacyclobutadiene)cobalt Complex 7



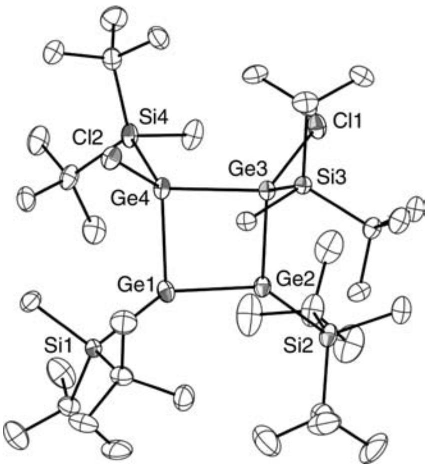


Figure 1. ORTEP drawing of **2** (30% probability level, hydrogen atoms are omitted). The ^{t}Bu$_2$MeSi group on the Ge1 atom is orientationally disordered, and the major configuration (55% occupancy) is shown. Selected bond lengths (Å): Ge1–Ge2 = 2.2993(5), Ge2–Ge3 = 2.4154(5), Ge3–Ge4 = 2.4773(4), Ge1–Ge4 = 2.4165(5), Ge3–Cl1 = 2.2479(8), Ge4–Cl2 = 2.2481(8). Selected bond angles (deg): Ge1–Ge2–Ge3 = 91.274(17), Ge2–Ge3–Ge4 = 86.151(15), Ge3–Ge4–Ge1 = 87.086(16), Ge4–Ge1–Ge2 = 90.214(17).

The molecular structure of **2** was determined by X-ray crystallography, and an ORTEP drawing is shown in Figure 1. Similar to the previously reported hybrid $^3\Delta$-1,2,3,4-disiladigermetene,[14a] the structural features of **2** are indicative of a substantial deviation of the Ge$_4$ skeletal bonds from standard values. Thus, the endocyclic Ge1=Ge2 bond of 2.2993(5) Å is elongated compared with the bond lengths of other known three- and four-membered ring cyclic digermenes (2.239–2.291 Å)[16] and is marginally longer than the Ge=Ge bond of the structurally similar $^3\Delta$-1,2,3,4-disiladigermetene of 2.2911(4) Å.[14a] In contrast, both the Ge1–Ge4 and the Ge2–Ge3 bonds in **2** (2.4165(5) and 2.4154(5) Å, respectively) were markedly shorter than the Ge3–Ge4 bond of 2.4773(4) Å, even considering the different hybridization occurring in the skeletal Ge1/Ge2 and Ge3/Ge4 atoms. Moreover, the Ge–Cl bond lengths of 2.2479(8) and 2.2481(8) Å in **2** were elongated compared with the typical range expected for (skeletal Ge)–Cl bond lengths of 2.192–2.238 Å.[17] Overall, the specific structural features of **2**, namely, the stretching of the endocyclic Ge=Ge and exocyclic Ge–Cl bonds and the shortening of the endocyclic Ge1–Ge4/Ge2–Ge3 bonds, can be explained by taking into account the contribution of a hyperconjugative π(Ge=Ge)–σ^*(Ge–Cl) interaction, lowering the HOMO energy level and thus stabilizing the entire π-system. The Ge=Ge bond in **2** is remarkably twisted: the torsional angle Si1–Ge1–Ge2–Si2 amounts to 69.77°, which exceeds the value of 55.22° previously reported for the disiladigermetene.[14a]

Having two chlorine substituents, tetragermetene **2** can be readily reduced with KC$_8$ in THF to form the dipotassium salt of the tetragermacyclobutadiene dianion derivative $\mathbf{3^{2-}\cdot[K^+(thf)_2]_2}$, isolated in 53% yield as emerald-green crystals (Scheme 1). In accord with its molecular composition, $\mathbf{3^{2-}\cdot[K^+(thf)_2]_2}$ exhibited only one set of NMR resonances for the ^{t}Bu$_2$MeSi substituents. The solid state structure of $\mathbf{3^{2-}\cdot[K^+(thf)_2]_2}$, representing an all-Ge analogue of the previously reported tetrasila- and disiladigermacyclobutadiene dianion derivatives,[10a,b] was unequivocally confirmed by X-ray diffraction analysis.[18] Most remarkably, both potassium cations (each coordinated with the two THF molecules) are bound in η^2-fashion to the highly folded Ge$_4$ ring, being situated above and below the ring (for the ORTEP view, see Supporting Information). Moreover, all Ge atoms featured markedly pyramidal geometry and there is significant alternation in the lengths of the skeletal Ge–Ge bonds with one long (2.4955(16) Å), one short (2.4017(16) Å), and two intermediate (2.4625(15) Å and 2.4650(15) Å) bonds, depending on the orientation and degree of steric interaction between the bulky substituents. Such structural features of the tetragermacyclobutadiene dianion derivative $\mathbf{3^{2-}\cdot[K^+(thf)_2]_2}$ are reminiscent of those of its lighter analogues, tetrasilacyclobutadiene and 1,2-disila-3,4-digermacyclobutadiene dianion derivatives, which were classified as nonaromatic compounds.[10a,b] Accordingly, the heaviest all-group 14 element-containing cyclobutadiene dianion derivative $\mathbf{3}^{2-}\cdot[\mathrm{K}^+(\mathbf{thf})_2]_2$ should also be recognized as a 6π-electron nonaromatic organometallic, a conclusion that was further corroborated by the calculation of its NICS(1) = +2.9,[19] pointing to the absence of diatropic ring current effects. It is well-known that, in contrast to other 6π-electron systems, cyclic π-delocalization within the cyclobutadiene dianion molecule has a strongly unfavorable effect, caused by the severe Coulomb repulsion of the two extra electrons and resulting in a remarkable distortion of the four-membered ring from square-planar regularity and its departure from aromaticity.[6] However, lithium ions bound to a cyclobutadiene ring in an η^4 fashion may counteract this unfavorable tendency, resulting in a much greater extent of π-delocalization and, in effect, overall aromatic stabilization of the dianionic system.[7,8] By contrast, in the case of the tetragermacyclobutadiene dianion derivative $\mathbf{3}^{2-}\cdot[\mathrm{K}^+(\mathbf{thf})_2]_2$, spatially remote potassium ions are unable to overcome the influence of the repulsive Coulomb interaction, thus leaving the system as nonaromatic.

Both tetragermetene **2** and tetragermacyclobutadiene dianion derivative $\mathbf{3}^{2-}\cdot[\mathrm{K}^+(\mathbf{thf})_2]_2$ serve as very effective precursors for transition metal complexes featuring tetragermacyclobutadiene ligand. Thus, **2** smoothly reacted with $\mathrm{Na_2[Fe(CO)_4]}$ in THF at room temperature, forming the desired [tetrakis(di-*tert*-butylmethylsilyl)tetragermacyclobutadiene]tricarbonyliron complex, $[\eta^4\text{-}\{(^t\mathrm{Bu_2MeSi})_4\mathrm{Ge_4}\}]\mathrm{Fe(CO)_3}$ **4**, which was isolated in the form of yellow crystals in 26% yield (Scheme 1). The low-energy barrier to rotation about the $\mathrm{Ge_4}$ ring center−Fe axis was manifested in the magnetic equivalence of all four $^t\mathrm{Bu_2MeSi}$ substituents, as seen in the NMR spectra of **4**, showing only a single set of signals for the silyl groups.[20] As is typical for carbonyl complexes, the carbonyl groups resonated in the diagnostic low-field region at 222.2 ppm.

The $\mathrm{Ge_4}$ ring in **4** is perhaptocoordinated to the transition metal center, as shown in Figure 2, being slightly more distorted from planarity than its silicon analogue $[\eta^4\text{-}\{(^t\mathrm{Bu_2MeSi})_4\mathrm{Si_4}\}]\mathrm{Fe(CO)_3}$ **5**;[12a] the folding angles are 6.1/6.2° vs 1.8°, respectively.[21] The bulky silyl substituents occupy alternating up-and-down positions relative to the mean plane of the $\mathrm{Ge_4}$ ring to minimize mutual steric repulsion, and the conformation of the Me and ^{t}Bu groups is dictated by the degree of their steric interactions with the CO groups, with the smaller Me groups uniformly directed toward the carbonyl ligands. The Ge−Fe bond lengths range from 2.5390(10) to 2.6427(11) Å, being longer than those of other reported complexes (2.240−2.496 Å).[22] The bond lengths of the skeletal Ge−Ge bonds in **4** fit within the narrow range of 2.3541(8)−2.3743(8) Å, being in between those typical for cyclic Ge−Ge single bonds (2.440−2.563 Å)[17] and cyclic Ge═Ge double bonds (2.239−2.298 Å).[16] Moreover, the lengths of the germanium−germanium bonds in **4** are intermediate between those of the Ge−Ge and Ge═Ge bonds of its precursor **2**. Similar to the case of its silicon analogue **5**,[12a] **4** showed a slight distortion of the $\mathrm{Ge_4}$ ring from the ideal square shape; namely, the Ge2−Ge3 bond was the shortest bond (2.3541(8) Å) and the Ge1−Ge4 bond was the longest bond (2.3743(8) Å), whereas the other two bonds, Ge3−Ge4 and Ge1−Ge2, had intermediate values (2.3614(8) and 2.3709(8) Å, respectively). Such a trend in the lengths of the skeletal Ge−Ge bonds within the $\mathrm{Ge_4}$ ring apparently results from the staggered conformation of the $\mathrm{Fe(CO)_3}$ fragment relative to the $\mathrm{Ge_4}$ ring, in which the longest Ge1−Ge4 bond is superimposed onto one of the carbonyl groups, the shortest Ge2−Ge3 bond does not eclipse any of the CO ligands, and the two intermediate Ge3−Ge4 and Ge1−Ge2 bonds are partially superimposed on the carbonyl groups.[23]

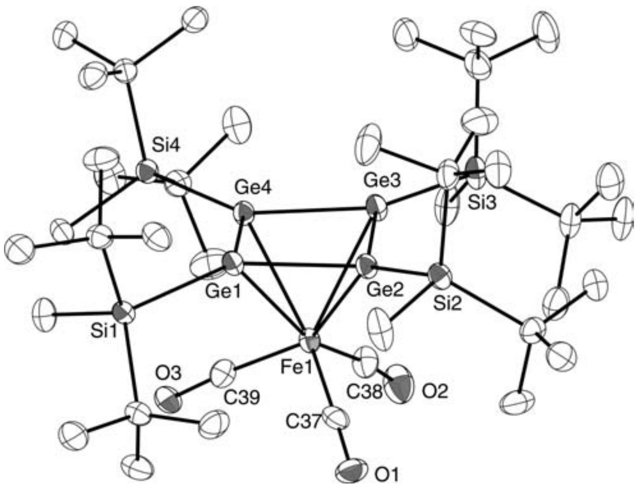


Figure 2. ORTEP drawing of **4** (30% probability level, hydrogen atoms are omitted). Selected bond lengths (Å): Ge1−Ge2 = 2.3709(8), Ge2−Ge3 = 2.3541(8), Ge3−Ge4 = 2.3614(8), Ge1−Ge4 = 2.3743(8), Ge1−Fe1 = 2.6247(10), Ge2−Fe1 = 2.5390(10), Ge3−Fe1 = 2.6427(11), Ge4−Fe1 = 2.5703(10), Fe1−C37 = 1.777(7), Fe1−C38 = 1.740(6), Fe1−C39 = 1.770(6), C37−O1 = 1.166(7), C38−O2 = 1.184(7), C39−O3 = 1.157(7). Selected bond angles (deg): Ge1−Ge2−Ge3 = 90.62(3), Ge2−Ge3−Ge4 = 89.70(3), Ge3−Ge4−Ge1 = 90.36(3), Ge4−Ge1−Ge2 = 88.99(3).

A comparison of structurally similar tricarbonyliron complexes $[\eta^4\text{-}\{(\mathrm{Me_3Si})_4\mathrm{C_4}\}]\mathrm{Fe(CO)_3}$ **6**, $[\eta^4\text{-}\{(^t\mathrm{Bu_2MeSi})_4\mathrm{Si_4}\}]\mathrm{Fe(CO)_3}$ **5**[12a] and $[\eta^4\text{-}\{(^t\mathrm{Bu_2MeSi})_4\mathrm{Ge_4}\}]\mathrm{Fe(CO)_3}$ **4** is instructive. Thus, on going from the carbon **6** to the silicon **5** and the germanium **4** versions of the cyclobutadiene ligand, the Fe−C bonds become progressively shorter (average value =1.789 Å in **6** vs 1.775 Å in **5** vs 1.762 Å in **4**), whereas the C−O bonds become longer (average value =1.142 Å in **6** vs 1.144 Å in **5** vs 1.169 Å in **4**), indicative of the increase in the Fe−C bond order and the decrease in the C−O bond order. This corroborates well with the decrease in the carbonyl IR frequency values on going from **6** to **4** (stretching vibration =1965/2035 cm^{-1} in **6** vs 1922/1973 cm^{-1} in **5** vs 1910/1962 cm^{-1} in **4**). The change in the ^{13}C NMR resonance is also in line with the above trend (carbonyl group chemical shift = 216.2 ppm in **6** vs 221.1 ppm in **5** vs 222.2 ppm in **4**). All of these structural and spectral features of tricarbonyliron complexes **4**−**6** point to a remarkable increase in the power of the $\mathrm{R_4E_4}$ cyclobutadiene ligand's π-donating ability toward the transition metal on going from C to Ge versions, resulting in the shift in the formulation of the CO coordination to iron center from one resonance form, $\mathrm{Fe^-{—}C{\equiv}O^+}$ (in **6**), to another resonance extreme, $\mathrm{Fe{=}C{=}O}$ (in **4**), in accordance with the increase in the same direction of the transition metal π-basicity. The appreciable increase in the π-donating strength of the $\mathrm{R_4E_4}$ ligand can be attributed to the rise of its occupied π-orbitals' energy levels seen in the elevation of the HOMOs of iron complexes (HOMO energy level): −6.30 eV (in **6**) vs −5.59 eV (in **5′**) vs −5.36 eV (in **4′**).[15] The stronger π-donation of the tetragermacyclobutadiene ligand is reflected in the NPA charge distribution of the iron

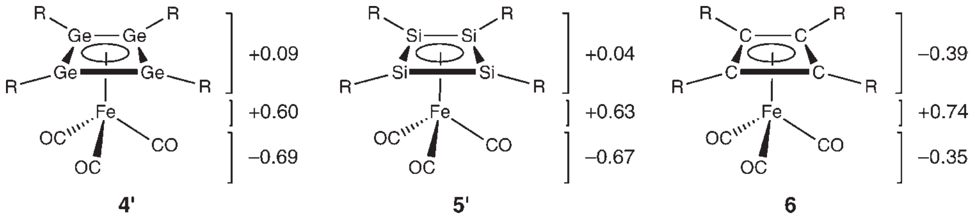


Figure 3. NPA charge distribution in the iron complexes **4′**−**6** (R = $SiMe_3$).

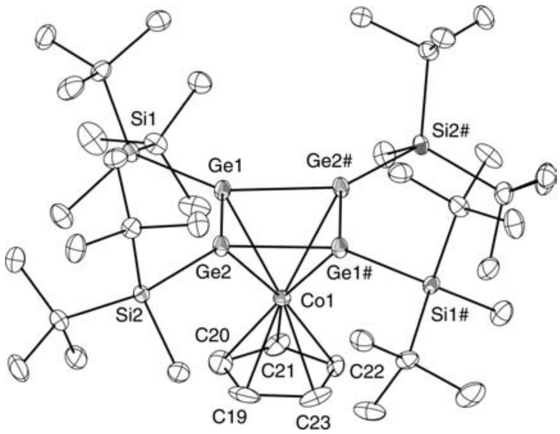


Figure 4. ORTEP drawing of 7 (30% probability level, hydrogen atoms are omitted). The Cp ring is rotationally disordered between the two positions (50%:50% occupancy); one of them is shown. Selected bond lengths (Å): Ge1−Ge2 = 2.3627(3), Ge1−Ge2# = 2.3634(3), Ge1−Co1 = 2.4616(3), Ge2−Co1 = 2.5036(3), Ge1−Si1 = 2.4018(5), Ge2−Si2 = 2.4073(5). Selected bond angles (deg): Ge1−Ge2−Ge1# = 89.859(9), Ge2−Ge1−Ge2# = 90.081(9).

complex fragments (NBO calculation), which showed the most positive $[(Me_3Si)_4E_4]$ fragment and the most negative CO groups in the germanium version **4′** compared with those of its silicon and carbon analogues **5′** and **6**, respectively (Figure 3).

Tetragermacyclobutadiene dianion derivative $\mathbf{3^{2-}}\cdot[\mathbf{K^+(thf)_2}]_2$ readily reacts with transition metal complexes, providing easy access to novel coordination compounds featuring the tetragermacyclobutadiene ligand. Thus, reaction of $\mathbf{3^{2-}}\cdot[\mathbf{K^+(thf)_2}]_2$ with $CpCoI_2(PPh_3)$ in THF resulted in the formation of the (η^5-cyclopentadienyl)(η^4-tetragermacyclobutadiene)cobalt sandwich $[\eta^4\text{-}\{(^t\text{Bu}_2\text{MeSi})_4\text{Ge}_4\}]\text{CoCp}$ **7**, which was isolated as bright-orange crystals in 30% yield (Scheme 1). As in the case of the iron tricarbonyl half-sandwich **4** (see above), only one set of resonances for the silyl substituents was observed in the NMR spectra of sandwich **7**, whereas the signals of the Cp group were found at 5.33 ppm (^{1}H NMR) and 78.2 ppm (^{13}C NMR), which are in the regions characteristic of the Cp ligands in (η^5-cyclopentadienyl)(η^4-cyclobutadiene)transition metal sandwich complexes.[24]

In accord with its sandwich composition, the tetragermacyclobutadiene ring in **7** is tetrahaptocoordinated to the Co center and showed a rather insignificant departure from planarity, being only marginally more folded than that of its Si analogue $[\eta^4\text{-}\{(^t\text{Bu}_2\text{MeSi})_4\text{Si}_4\}]\text{CoCp}$[12b] but less folded than that in the half-sandwich **4**: 3.7° vs 1.1° and 6.1/6.2° (Figure 4).

Furthermore, similar to the silicon analogue $[\eta^4\text{-}\{(^t\text{Bu}_2\text{MeSi})_4\text{Si}_4\}]\text{CoCp}$[12b] and in contrast to the half-sandwich **4**, the silyl substituents in **7** are nearly coplanar with the mean plane of the Ge_4 ring and are arranged in a clockwise manner to minimize their repulsive interactions. The Co complexes with all-germanium-containing ligands are unprecedented; therefore, direct comparison of the Ge−Co bonds was not possible. However, these bonds in **7** of 2.4616(3) and 2.5036(3) Å are stretched, being at the upper limit of the 2.262−2.529 Å range reported for germanium−cobalt carbonyl complexes,[22] evidently because of the increased hapticity of coordination of the η^4-bound tetragermacyclobutadiene ligand. The skeletal Ge−Ge bonds in **7** of 2.3627(3) and 2.3634(3) Å are intermediate between the typical Ge−Ge single and Ge=Ge double bond lengths (see above), testifying to the cyclic electron delocalization within the four-membered ring. This was also supported by the magnetic properties calculation for the model cobalt sandwich **7′**, giving a negative NICS(1)[19] value of −12.9, which was more negative than that for the iron half-sandwich model **4′** (−9.94).[15] Compared with the iron complex **4′**, cobalt complex **7′** showed a Ge_4 ring that is more planar (folding angles: 3.7° vs 6.2°) and more regularly square-shaped ($\Delta_{\text{Ge−Ge}}$: 0.0007 Å vs 0.0202 Å) because of the differing extent of the steric interaction between the silyl substituents of the Ge_4 ring and Cp vs CO ligands.

CONCLUSIONS

In the present study, four novel all-germanium-containing cyclic derivatives, namely, 2π-electron tetragermetene **2**, 6π-electron tetragermacyclobutadiene dianion $\mathbf{3^{2-}}\cdot[\mathbf{K^+(thf)_2}]_2$, and 18-electron tetragermacyclobutadiene transition metal complexes, half-sandwich (tricarbonyl)iron **4** and sandwich (cyclopentadienyl)cobalt **7**, were prepared and fully characterized as the first examples of compounds of such types. Tetragermacyclobutadiene dianion derivative $\mathbf{3^{2-}}\cdot[\mathbf{K^+(thf)_2}]_2$ was classified as a nonaromatic species based on its structural and magnetic properties, whereas in both tetragermacyclobutadiene complexes **4** and **7** a substantial cyclic electron delocalization within the Ge_4 ring, taking place upon its complexation to the transition metal center, was established. Moreover, structural (X-ray) and spectroscopic (IR, ^{13}C NMR) data of the (tetragermacyclobutadiene)tricarbonyliron complex **4** are indicative of the remarkable π-donating power of the tetragermacyclobutadiene ligand toward the transition metal, surpassing that of its carbon and even silicon analogues.

EXPERIMENTAL SECTION

General Procedures. All experiments involving air-sensitive compounds were performed using high-vacuum line techniques or in an argon atmosphere using MBRAUN MB 150B-G glovebox. All solvents were dried and degassed over potassium mirror in vacuum prior to use. NMR spectra were recorded on Bruker AC-300FT NMR (^{1}H NMR at 300.1 MHz; ^{13}C NMR at 75.5 MHz; ^{29}Si NMR at 59.6 MHz), AV-400FT NMR (^{1}H NMR at 400 MHz; ^{13}C NMR at 100.6 MHz; ^{29}Si

NMR at 79.5 MHz) spectrometers. UV/vis spectra were recorded on a Shimadzu UV-3150 UV/vis spectrophotometer in hexane or THF. IR spectra were recorded on a Shimadzu IRPrestige-21 FT/IR spectrophotometer. GPC separation was performed using a recycling preparative LC-908W instrument. Tetrakis(di-*tert*-butylmethylsilyl) trigermirene **2**[13] and tetrakis(trimethylsilyl)cyclobutadiene[25] were prepared according to the published procedures.

Experimental Procedure and Spectral and Crystallographic Data for Compound 2. Trigermirene **1** (50 mg, 0.06 mmol) and a dichlorogermylene dioxane complex (14 mg, 0.06 mmol) were placed in a reaction tube with a magnetic stirring bar. Dry, oxygen-free THF was introduced into the tube by vacuum transfer, and the reaction mixture was stirred for 10 min at room temperature. After evaporation of the solvent, the residue was recrystallized from hexane at −30 °C to give **2** as orange crystals (39 mg, 65%). Mp 163−164 °C. ^{1}H NMR (C_6D_6, δ, ppm) 0.51 (s, 6 H, Me), 0.56 (s, 6 H, Me), 1.15 (s, 18 H, ^{t}Bu), 1.18 (s, 18 H, ^{t}Bu), 1.32 (s, 18 H, ^{t}Bu), 1.36 (s, 18 H, ^{t}Bu); ^{13}C NMR (C_6D_6, δ, ppm) −4.8 (Me), −3.8 (Me), 22.0 (Me_3C), 22.4 (Me_3C), 22.6 (Me_3C), 22.8 (Me_3C), 29.7 (Me_3C), 29.8 (Me_3C), 30.2 (2 C, Me_3C); ^{29}Si NMR (C_6D_6, δ, ppm) 33.6 (silyl substituents), 40.2 (silyl substituents); UV/vis (hexane) λ_{max}/nm (ε) 335 (6400), 390 (4950), 431 (6700); HRMS (APCI) *m*/*z* calcd for $C_{36}H_{84}Cl_2Ge_4Si_4$ $[M]^+$ 990.1857, found 990.1903.

The single crystals of **2** for X-ray diffraction analysis were grown from a hexane solution. Diffraction data were collected at 150 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo Kα radiation (λ = 0.71070 Å). The structure was solved by the direct method, using the SIR-92[26] program, and refined by the full-matrix least-squares method by the SHELXL-97 program.[27] Crystal data for **2** at 150 K: MF = $C_{36}H_{84}Cl_2Ge_4Si_4$, MW = 990.65, monoclinic, $C2/c$, a = 41.2970(9), b = 15.6660(7), c = 17.2710(7) Å, β = 112.773(2)°, V = 10302.6(7) Å^3, Z = 8, D_{calcd} = 1.277 g cm^{-3}. The final R factor was 0.0432 for 8979 reflections with $I_0 > 2\sigma(I_0)$ (R_w = 0.1203 for all data, 11764 reflections), GOF = 0.997.

Experimental Procedure and Spectral Data for Compound $3^{2-}\cdot[K^+(thf)_2]_2$. Tetragermetene **2** (116 mg, 0.12 mmol) and KC_8 (72 mg, 0.53 mmol) were placed in a reaction tube with a magnetic stirring bar. Dry oxygen-free THF was introduced into this tube by vacuum transfer, and the reaction mixture was stirred for 30 min at room temperature. After removal of graphite and inorganic salts, the residue was recrystallized from hexane/THF (ca. 95:5) mixed solvent at −30 °C to give $\mathbf{3}^{2-}\cdot[K^+(\mathbf{thf})_2]_2$ as emerald-green crystals (31 mg, 53%). Mp 114−116 °C (dec.). ^{1}H NMR (THF-d_8, δ, ppm) 0.41 (s, 12 H, Me), 1.21 (s, 72 H, ^{t}Bu); ^{13}C NMR (THF-d_8, δ, ppm) −2.3 (Me), 20.7 (Me_3C), 29.3 (Me_3C); ^{29}Si NMR (THF-d_8, δ, ppm) 20.7 (silyl substituents); UV/vis (THF) λ_{max}/nm (ε) 424 (2200), 628 (200). The structure was unambiguously characterized by X-ray diffraction analysis; however, the crystal structure data of $\mathbf{3}^{2-}\cdot[K^+(\mathbf{thf})_2]_2$ are not discussed in the paper because they are not sufficiently good due to the poor completeness.

Experimental Procedure and Spectral and Crystallographic Data for Compound 4. Tetragermetene **2** (79 mg, 0.08 mmol) and $Na_2[Fe(CO)_4]$ (22 mg, 0.09 mmol) were placed in a reaction tube with a magnetic stirring bar. Dry, oxygen-free THF was introduced into the tube by vacuum transfer, and the reaction mixture was stirred for 30 min at room temperature. After evaporation of the solvent and filtration of the inorganic salts, the residue was recrystallized from toluene at −30 °C to give **4** as yellow crystals (22 mg, 26%). Mp > 151 °C (dec.). ^{1}H NMR (C_6D_6, δ, ppm) 0.42 (s, 12 H, Me), 1.20 (s, 72 H, ^{t}Bu); ^{13}C NMR (C_6D_6, δ, ppm) −3.6 (Me), 22.8 (Me_3C), 30.2 (Me_3C), 222.2 (CO); ^{29}Si NMR (C_6D_6, δ, ppm) 38.8 (silyl substituents); IR (KBr tablet, ν, cm^{-1}) 1911, 1963 (CO). Anal. Calcd for $C_{39}H_{84}FeGe_4O_3Si_4$: C, 44.19; H, 7.99. Found: C, 44.02; H, 7.95.

The single crystals of **4** for X-ray diffraction analysis were grown from a toluene solution. Diffraction data were collected at 150 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo Kα radiation (λ = 0.71070 Å). The structure was solved by the direct method, using the SIR-92[26] program, and refined by the full-matrix least-squares method by the SHELXL-97 program.[27] Crystal data for **4** at 150 K: MF = $C_{39}H_{84}FeGe_4O_3Si_4$, MW = 1059.63, triclinic, $P\bar{1}$, a = 8.9900(8), b = 15.4640(15), c = 19.0130(15) Å, α = 89.362(5)°, β = 87.150(5)°, γ = 84.547(5)°, V = 2627.9(4) Å^3, Z = 2, D_{calcd} = 1.339 g cm^{-3}. The final R factor was 0.0586 for 6917 reflections with $I_0 > 2\sigma(I_0)$ (R_w = 0.1666 for all data, 11526 reflections), GOF = 0.954.

Experimental Procedure and Spectral Data for Compound 6. $Fe(CO)_5$ (300 mg, 1.531 mmol) was added to a solution of tetrakis(trimethylsilyl)cyclobutadiene (200 mg, 0.587 mmol) in dry oxygen-free THF (2 mL) in a reaction tube with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 6 h under UV irradiation (λ > 320 nm) to give an orange solution. After evaporation of the solvent and excess $Fe(CO)_5$, the residue was purified using GPC followed by recrystallization from hexane giving **6** as pale yellow crystals (92 mg, 33%). Mp 103 °C (sublimation). ^{1}H NMR (C_6D_6, δ, ppm) 0.20 (s, $SiMe_3$); ^{13}C NMR (C_6D_6, δ, ppm) 2.5 ($SiMe_3$), 90.3 (skeletal C), 216.2 (CO); ^{29}Si NMR (C_6D_6, δ, ppm) −7.4 (silyl substituents); UV/vis (THF) λ_{max}/nm (ε) 249 (8400), 299 (2500); IR (KBr tablet, ν, cm^{-1}) 1965, 2035 (CO). Anal. Calcd for $C_{19}H_{36}FeO_3Si_4$: C, 47.48; H, 7.55. Found: C, 47.47; H, 7.69.

Experimental Procedure and Spectral and Crystallographic Data for Compound 7. Tetragermacyclobutadiene dianion derivative $\mathbf{3}^{2-}\cdot[K^+(\mathbf{thf})_2]_2$ (76 mg, 0.06 mmol) and $CpCoI_2(PPh_3)$ (38 mg, 0.06 mmol) were placed in a reaction tube with a magnetic stirring bar. Dry oxygen-free THF was introduced into this tube by vacuum transfer, and the reaction mixture was stirred for 30 min at room temperature. After evaporation of the solvents and filtration of inorganic salts; the residue was recrystallized from toluene at −30 °C to give **7** as bright-orange crystals (19 mg, 30%). Mp 234−236 °C. ^{1}H NMR (C_6D_6, δ, ppm) 0.35 (s, 12 H, Me), 1.23 (s, 72 H, ^{t}Bu), 5.33 (s, 5 H, C_5H_5); ^{13}C NMR (C_6D_6, δ, ppm) −3.2 (Me), 22.3 (Me_3C), 30.3 (Me_3C), 78.2 (C_5H_5); ^{29}Si NMR (C_6D_6, δ, ppm) 34.8 (silyl substituents); UV/vis (THF) λ_{max}/nm(ε) 319 (8800), 395 (3800), the longest wavelength absorption (>460 nm) tails to 650 nm. Anal. Calcd for $C_{41}H_{89}CoGe_4Si_4$: C, 47.17; H, 8.59. Found: C, 47.29; H, 8.55.

The single crystals of **7** for X-ray diffraction analysis were grown from a toluene solution. Diffraction data were collected at 150 K on a Bruker AXS APEX II CCD X-ray diffractometer (Mo Kα radiation, λ = 0.71073 Å, 50 kV/30 mA). The structure was solved by the direct method with the SHELXS-97 program,[28] and refined by the full-matrix least-squares method with the SHELXL-97 program.[27] Crystal data for **7** at 150 K: MF = $C_{41}H_{89}CoGe_4Si_4$, MW = 1043.77, orthorhombic, $Pccn$, a = 19.3738(8), b = 15.9280(6), c = 17.0381(7) Å, V = 5257.7(4) Å^3, Z = 4, D_{calcd} = 1.319 g cm^{-3}. The final R factor was 0.0223 for 4346 reflections with $I_0 > 2\sigma(I_0)$ (R_w = 0.0548 for all data, 5410 reflections), GOF = 1.042.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Tables of crystallographic data, including atomic positional and thermal parameters, for compounds **2**, **4**, and **7**; energies, atomic coordinates, and geometries of the optimized structures for the model complexes **4′**, **5′**, **6**, and **7′** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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