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(η^5-Cyclopentadienyl)(η^4-tetrasila- and η^4-trisilagermacyclobutadiene)cobalt: Sandwich Complexes Featuring Heavy Cyclobutadiene Ligands

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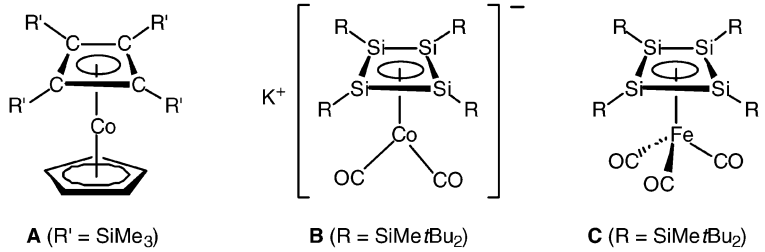
(η^5-Cyclopentadienyl)(η^4-tetrasilacyclobutadiene)cobalt {[(η^4-R_4Si_4)CoCp], **2**} and (η^5-cyclopentadienyl)(η^4-trisilagermacyclobutadiene)cobalt {[(η^4-R_4Si_3Ge)CoCp], **4**} (R = SiMe*t*Bu$_2$) were synthesized by reaction of the dipotassium salts of tetrasilacyclobutadiene dianion K^+_2·$[R_4Si_4]^{2-}$ (**1**) and trisilagermacyclobutadiene dianion K^+_2·$[R_4Si_3Ge]^{2-}$ (**3**) with $[CpCoI_2(PPh_3)]$. Alternatively, **4** was prepared by the reaction of **3** with $[Cp_2Co]^+$·$[PF_6]^-$. X-ray crystallographic analysis of **2** confirmed its sandwich-type structure, manifesting a nearly square-planar Si_4 ring and diagnostic perhaptocoordination of both ligands, η^4-tetrasilacyclobutadiene and η^5-cyclopentadienyl, to the Co atom.

Introduction

Sandwich complexes, known since the revolutionary discovery of ferrocene in 1951[1a,1b] and the determination of its novel structure in 1952,[1c,1d] constitute one of the most important classes of organotransition metal complexes. Accordingly, such sandwich complexes, particularly those featuring cyclopentadienyl and cyclobutadiene ligands, attracted a great deal of interest from both the fundamental and industrial organometallic chemistry communities.[2] For example, (η^5-cyclopentadienyl)[η^4-tetrakis(trimethylsilyl)cyclobutadiene]cobalt [η^4-$(Me_3Si)_4C_4$]CoCp (**A**)[3] represents such an important sandwich complex that found an interesting synthetic application as a convenient precursor for the 6π-electron aromatic derivative of the dilithium salt of the cyclobutadiene dianion.[3c,3d] The novel field of transition metal complexes with cyclic polyene ligands incorporating the heavier Group 14 elements represents another organometallic challenge that is very attractive from the viewpoint of their unique electronic structures and possible practical applications.[4] Thus, a series of transition metal complexes with heavy cyclopentadienyl ligands has been synthesized by Tilley,[4a–4g] whereas Kira recently reported the preparation of a (silacyclobutadiene)Co complex[4m] and Tokitoh reported the synthesis of sila-, germa- and stannaarene complexes of Cr, Mo and Ru.[4h–4l] We have also contributed to the field, utilizing tetrasilacyclobutadiene[4n,4o] and heavy cyclopentadienyl[4h] as a novel ligand for transition metal complexes. Thus, we succeeded in the synthesis of two types of carbonyl(tetrasilacyclobutadiene) transition metal complexes, K^+·[(η^4-R_4Si_4)$Co(CO)_2]^-$ (**B**)[4n] and [(η^4-R_4Si_4)$Fe(CO)_3$] (**C**)[4o] (R = SiMe*t*Bu$_2$) (Scheme 1), which show a stronger π-donating ability of the tetrasilacyclobutadiene ligand compared with that of its carbon counterpart. However, to the best of our knowledge, sandwich complexes in which the ring of one of the ligands entirely consists of heavier Group 14 elements are still unknown. In this paper, we report the synthesis and structural characterization of the first sandwich cyclopentadienyl complexes, featuring η^4-tetrasilacyclobutadiene and η^4-trisilagermacyclobutadiene ligands.



A (R' = $SiMe_3$) **B** (R = SiMe*t*Bu$_2$) **C** (R = SiMe*t*Bu$_2$)

Scheme 1. Cyclobutadiene complex **A** and tetrasilacyclobutadiene complexes **B** and **C**.

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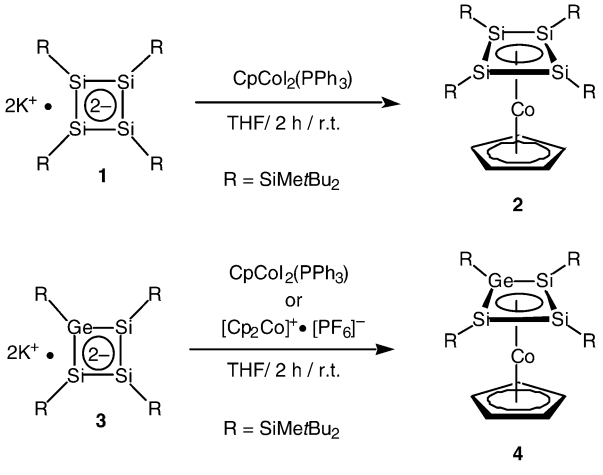
Results and Discussion

Reaction of the dipotassium salt of tetrasilacyclobutadiene dianion derivative $K^+_2{\cdot}[R_4Si_4]^{2-}$ (R = SiMe*t*Bu$_2$) (**1**)[5] with [CpCoI$_2$(PPh$_3$)] in THF produced the corresponding sandwich complex, (η^5-cyclopentadienyl)[η^4-tetrakis(di-*tert*-butylmethylsilyl)tetrasilacyclobutadiene]cobalt {[(η^4-R_4Si_4)CoCp], **2**}, accompanied by elimination of PPh$_3$ (Scheme 2). Complex **2** was isolated as air- and moisture-sensitive orange crystals in 36% yield by recrystallization from hexane. Both the ^{1}H and ^{13}C NMR spectra of **2** display only one set of signals for the Me and *t*Bu groups of the *t*Bu$_2$MeSi substituents because of the free rotation about the vertical axis passing through the Si$_4$ ring center and the Co atom. The cyclopentadienyl carbon signals are observed in the normal region at δ = 80.3 ppm. The endocyclic silicon atoms of the Si$_4$ ring resonate at δ = 0.4 ppm; this value being shifted upfield compared with typical values of sp^2-Si atoms.[6] Our GIAO computations well reproduced such chemical shift, giving a value of δ = –4.7 ppm for the model complex [(η^4-R′$_4$Si$_4$)CoCp] (**2′**) (R′ = SiMe$_3$).[7] Such general tendency of the great shielding of skeletal Si atoms of the tetrasilacyclobutadiene ligand upon its complexation to transition metal atoms, previously observed by us for other transition metal complexes, could be most reasonably achieved in terms of the strong 3d(Co)→π*(Si$_4$) π back donation. Utilizing the same synthetic procedure, we also prepared the Si$_3$Ge hybrid heavy cyclobutadiene complex (η^5-cyclopentadienyl)[η^4-tetrakis(di-*tert*-butylmethylsilyl)trisilagermacyclobutadiene]cobalt {[η^4-R_4Si_3Ge]CoCp, **4**} (yield 41%) by reaction of the dipotassium salt of the trisilagermacyclobutadiene dianion derivative $K^+_2{\cdot}[R_4Si_3Ge]^{2-}$ (R = SiMe*t*Bu$_2$) (**3**)[8] with [CpCoI$_2$(PPh$_3$)] in THF. Alternatively, **4** was synthesized (yield 62%) by the reaction of **3** with $[Cp_2Co]^+{\cdot}[PF_6]^-$, accompanied by the elimination of CpK, similar to the case of complex **B**.[4n] Although highly air- and moisture-sensitive, **4** is thermally very stable up to 287 °C. The structure of **4** was established by NMR spectral and X-ray diffraction data. Thus, **4** exhibits three sets of signals for the Me and *t*Bu groups in both ^{1}H and ^{13}C NMR spectra, as expected. The ^{29}Si NMR spectrum of **4** shows a total of five signals (δ = –13.7, 22.0, 24.1, 32.1 and 43.5 ppm), of which the most upfield (δ = –13.7 ppm) and the most downfield (δ = 43.5 ppm) signals were attributed to the endocyclic Si atoms with the latter signal corresponding to Si atoms bound to the Ge atom.

The X-ray crystal structure of **2** is represented in Figure 1. The bond lengths between the skeletal silicon and cobalt atoms in **2** range from 2.3862(7) to 2.3990(7) Å, which is in the range reasonably expected for a tetrahaptocoordinated tetrasilacyclobutadiene ligand, being similar to those in the previously reported complex $K^+{\cdot}[(\eta^4\text{-}R_4Si_4)Co(CO)_2]^-$ (**B**) [2.3935(7)–2.4225(7) Å].[4n] The endocyclic silicon–silicon bond lengths in **2** spread over the narrow range of 2.2718(10)–2.2725(9) Å, which is just in between the typical values of an Si–Si single (2.34 Å) and an Si=Si double (2.15 Å) bond.[9] The difference between the longest and shortest endocyclic silicon–silicon bond in **2** (Δ = 0.0007 Å) is smaller than that in (η^4-R_4Si_4)Fe(CO)$_3$ (**C**) (Δ = 0.0192 Å),[4o] primarily because of the different degree of steric interaction between the bulky *t*Bu$_2$MeSi substituents on the tetrasilacyclobutadiene ring and cyclopentadienyl (in **2**) or carbonyl (in **C**) ligands. The latter reason affects also the orientation of the *t*Bu$_2$MeSi groups in **2** to minimize their mutual steric interaction: they are arranged in a clockwise manner with the silyl substituents' Si atoms being nearly coplanar with the Si$_4$ ring plane [the up and down deviations of the Si atoms from the Si$_4$ mean plane are 0.0198(7) and 0.0043(7) Å, respectively]. On the other hand, the small Me groups of the *t*Bu$_2$MeSi substituents in **C**[4o] are uniformly directed toward the carbonyl ligands. Remarkably, the tetrasilacyclobutadiene ligand in **2** possesses an almost regular square-planar geometry, with the sum of the interior bond angles being 360.0°, which corresponds to a negligible folding of 1.1°. The crystal structure of **4** was also unambiguously determined by X-ray crystallography to confirm its sandwich composition; however, a precise structural determination was prevented by the positional disorder between the skeletal Si and Ge atoms.



Scheme 2. Synthesis of heavy cyclobutadiene complexes **2** and **4**.

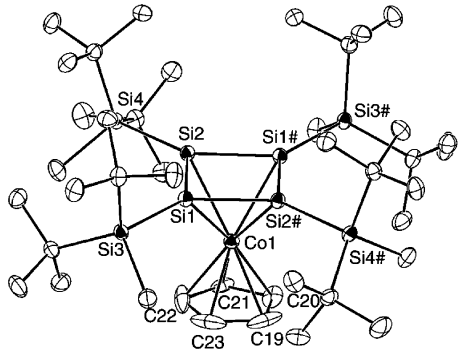


Figure 1. ORTEP drawing of **2** (30% probability level, hydrogen atoms are not shown). Selected bond lengths [Å]: Si1–Si2 2.2725(9), Si1–Si2# 2.2718(10), Si1–Co1 2.3862(7), Si2–Co1 2.3990(7), Si1–Si3 2.3784(9), Si2–Si4 2.3846(8). Selected bond angles [°]: Si2–Si1–Si2# 90.08(3), Si1–Si2–Si1# 89.92(3). Dihedral angle [°]: Si1–Si2–Si1#/Si1–Si2#–Si1# 1.10(2).

In order to gain a deeper insight into the structures of these novel sandwich complexes, we performed computations on the Me_3Si-substituted model [(η^4-R′$_4Si_4$)CoCp] (R′ = $SiMe_3$) (**2′**) and the complex [η^4-$(Me_3Si)_4C_4$]CoCp (**A**). The structural parameters for experimental compounds **2** and **A**[3d] and those of calculated **2′** and **A** are summarized in Table 1. The structural features of **2** were fairly well reproduced in the calculated structure **2′**, except for the location of the silyl substituents' Si atoms. Thus, whereas these Si atoms in **2** are nearly coplanar with the Si_4 ring, in the optimized structure of **2′** they are tilted towards the Co atom from the Si_4 mean plane by 0.236–0.261 Å. In contrast, the silyl substituents' Si atoms in the calculated structure of **A** are bent away from the Co atom, being situated 0.294–0.330 Å above the C_4 ring. Such a distinction in the position of the silyl substituents in the calculated structures of **2′** and **A** would be reasonably explained by the difference in the ring size of cyclobutadienes R_4E_4 (E = Si, C; R = $SiMe_3$), implying different extents of the effective π(R_4E_4)–3d(Co) orbitals' interaction depending on the size of the carbon 2pπ- and silicon 3pπ-orbitals, as schematically illustrated in Figure 2. The experimentally observed in-plane positions of the silyl substituents in **2** are due to the balance between the two opposite tendencies: favorable orbital interactions and unfavorable steric repulsion between the bulky silyl substituents and Cp ligand.

Table 1. Geometrical parameters of the experimental (**2** and **A**) and calculated (**2′** and **A**) structures of the cyclobutadiene cobalt complexes [(η^4-R_4E_4)CoCp] (E = Si, C).

	2 (E = Si) experimental	**2′** (E = Si) calculated	**A** (E = C)[a] experimental	**A** (E = C) calculated
E–Co [Å]	2.3862(7)	2.389	1.989(2)	1.980
	2.3990(7)	2.390	1.992(2)	1.983
		2.392	1.995(2)	1.986
		2.395	2.012(2)	1.987
Endocyclic E–E [Å]	2.2718(10)	2.262	1.480(3)	1.481
	2.2725(9)	2.262	1.481(3)	1.482
		2.264	1.486(3)	1.482
		2.264	1.486(3)	1.482
Si substituent–	+0.0198(7)	–0.236	+0.3954(8)	+0.330
E_4-mean plane [Å][b]	–0.0043(7)	–0.257	+0.3798(7)	+0.314
		–0.260	+0.0010(7)	+0.295
		–0.261	–0.0798(8)	+0.294

[a] From ref.[3d] [b] Positive and negative values correspond to the location of Si substituents above and below the E_4 mean plane, respectively.

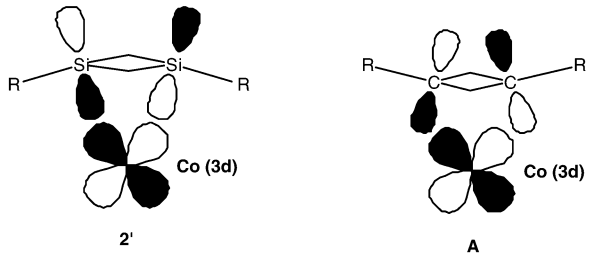


Figure 2. Systematic illustration of the interaction between the R_4E_4 (E = Si, C; R = $SiMe_3$) pπ- and Co 3d-orbitals in calculated **2′** and **A**.

Conclusions

New sandwich complexes featuring heavy cyclobutadiene ligands (η^5-cyclopentadienyl)(η^4-tetrasilacyclobutadiene)-cobalt {[(η^4-R_4Si_4)CoCp], **2**} and (η^5-cyclopentadienyl)(η^4-trisilagermacyclobutadiene)cobalt {[(η^4-R_4Si_3Ge)CoCp], **4**} (R = $SiMe$*t*Bu_2) were synthesized by the reaction of the corresponding dipotassium salts of the tetrasilacyclobutadiene dianion K^+_2·$[R_4Si_4]^{2-}$ (**1**) and the trisilagermacyclobutadiene dianion K^+_2·$[R_4Si_3Ge]^{2-}$ (**3**) with [$CpCoI_2(PPh_3)$]. The systematic comparison between **2** and its carbon analog, (η^5-cyclopentadienyl)[η^4-tetrakis(trimethylsilyl)cyclobutadiene]cobalt {[η^4-$(Me_3Si)_4C_4$]CoCp (**A**)}, showed significant structural differences between them caused by the difference in the ring size of the cyclobutadiene ligand R_4E_4 (R = $SiMe$*t*Bu_2, E = Si vs. R = $SiMe_3$, E = C).

Experimental Section

Starting Materials: The dipotassium salt of the tetrasilacyclobutadiene dianion, K^+_2·$[R_4Si_4]^{2-}$ (R = $SiMe$*t*Bu_2) (**1**), was prepared according to a published experimental procedure.[5] The dipotassium salt of the trisilagermacyclobutadiene dianion, K^+_2·$[R_4Si_3Ge]^{2-}$ (R = $SiMe$*t*Bu_2) (**3**), was also synthesized in a similar manner.[8] The cobalt complex [$CpCoI_2(PPh_3)$] was synthesized according to a literature procedure,[10] whereas complex $[Cp_2Co]^+$·$[PF_6]^-$ was commercially available and purchased from Tokyo Kasei Co.

(η^5-Cyclopentadienyl)[η^4-tetrakis(di-*tert*-butylmethylsilyl)tetrasilacyclobutadiene]cobalt {[η^4-(*t*Bu_2MeSi)$_4Si_4$]CoCp} (2): The dipotassium salt of the tetrasilacyclobutadiene dianion, K^+_2·$[R_4Si_4]^{2-}$ (R = $SiMe$*t*Bu_2) (**1**) (104 mg, 0.094 mmol), and [$CpCoI_2(PPh_3)$] (55 mg, 0.095 mmol) were placed in a reaction tube with a magnetic stirring bar. Oxygen-free dry THF (2 mL) was introduced by vacuum transfer, and the reaction mixture was stirred at room temperature to give an orange solution within 1 h. Then the solvent was removed in vacuo, and dry hexane was introduced. After inorganic salt was removed by centrifugation, the residue was recrystallized from hexane (1 mL) at –30 °C to give **2** (29 mg, 36%) as orange crystals; m.p. 290–292 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.30 (s, 12 H, *t*Bu_2*Me*Si), 1.22 (s, 72 H, *tBu*$_2$MeSi), 5.33 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = –3.6, 21.5, 30.4, 80.3 ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = 0.4 (skeletal Si), 22.2 (substituents Si) ppm. UV/Vis (THF): λ (ε) = 294 (23000), 347 (6100), 407 (3200) nm. $C_{41}H_{89}CoSi_8$ (865.78): calcd. C 56.88, H 10.36; found C 57.26, H 10.30.

(η^5-Cyclopentadienyl)[η^4-tetrakis(di-*tert*-butylmethylsilyl)trisilagermacyclobutadiene]cobalt {[η^4-(*t*Bu_2MeSi)$_4Si_3$Ge]CoCp} (4) by Reaction of K^+_2·$[R_4Si_3Ge]^{2-}$ (R = $SiMe$*t*Bu_2) and [$CpCoI_2(PPh_3)$]: The dipotassium salt of the trisilagermacyclobutadiene dianion, K^+_2·$[R_4Si_3Ge]^{2-}$ (R = $SiMe$*t*Bu_2) (**3**) (129 mg, 0.112 mmol), and [$CpCoI_2(PPh_3)$] (65 mg, 0.112 mmol) were placed in a reaction tube with a magnetic stirring bar. Oxygen-free dry THF (2 mL) was introduced by vacuum transfer, and the reaction mixture was stirred at room temperature to give an orange solution within 1 h. Then the solvent was removed in vacuo, and dry hexane was introduced. After inorganic salt was removed by centrifugation, the residue was recrystallized from hexane (1 mL) at –30 °C to give **4** (42 mg, 41%) as orange crystals; m.p. 287 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.26 (s, 3 H, *t*Bu_2*Me*Si), 0.30 (s, 3 H, *t*Bu_2*Me*Si), 0.32 (s, 6 H, *t*Bu_2*Me*Si), 1.18 (s, 18 H, *tBu*$_2$MeSi), 1.19 (s, 18 H, *tBu*$_2$MeSi), 1.23 (s, 18 H, *tBu*$_2$MeSi), 1.24 (s, 18 H, *tBu*$_2$MeSi), 5.29 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = –3.7 (2 C), –3.5, –2.9,

21.2, 21.26, 21.31, 21.9, 30.2, 30.32, 30.34, 30.4, 79.7 ppm. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = –13.7 (1 skeletal Si), 22.0 (2 Si), 24.1, 32.1 (substituents Si), 43.5 (2 skeletal Si) ppm. UV/Vis (THF): λ (ε) = 295 (14000), 410 (2100), 464 (770) nm. $C_{41}H_{89}CoGeSi_7$ (910.28): calcd. C 54.10, H 9.85; found C 53.79, H 9.74.

(η^5-Cyclopentadienyl)[η^4-tetrakis(di-*tert*-butylmethylsilyl)trisilagermacyclobutadiene]cobalt {[η^4-(*t*Bu$_2$MeSi)$_4$Si$_3$Ge]CoCp} (4) by Reaction of K$^+_2$·[R$_4$Si$_3$Ge]$^{2-}$ (R = SiMe*t*Bu$_2$) and [Cp$_2$Co]$^+$·[PF$_6$]$^-$: The dipotassium salt of the trisilagermacyclobutadiene dianion, K$^+_2$·[R$_4$Si$_3$Ge]$^{2-}$ (R = SiMe*t*Bu$_2$) (**3**) (129 mg, 0.112 mmol), and [Cp$_2$Co]$^+$·[PF$_6$]$^-$ (38 mg, 0.114 mmol) were placed in a reaction tube with a magnetic stirring bar. Oxygen-free dry toluene (2 mL) was introduced by vacuum transfer, and the reaction mixture was stirred at room temperature to give an orange solution within 0.5 h. Then the solvent was removed in vacuo, and dry hexane was introduced. After inorganic salt was removed by centrifugation, the residue was recrystallized from hexane to give **4** (63 mg, 62%) as orange crystals.

X-ray Diffraction Studies and Crystal Data for 2: A single crystal of **2** suitable for X-ray diffraction study was grown from a hexane solution. The diffraction data were collected with a MacScience DIP2030 image plate diffractometer equipped with a rotation anode using graphite-monochromatized Mo-K_α radiation (λ = 0.71070 Å) at 150 K. The structure was solved by direct methods using the SIR-92 program[11] and refined by full-matrix least-squares methods using the SHELXL-97 program.[12] Crystal data: $C_{41}H_{89}CoSi_8$, M = 865.77, orthorhombic, *Pccn*, a = 19.1700(5), b = 15.8280(9), c = 17.1620(10) Å, V = 5207.3(4) Å^3, Z = 4, $D_{calcd.}$ = 1.104 g/cm^3, R = 0.0437 (wR = 0.1259 for all data) for 6260 reflections with $I > 2\sigma(I)$, GOF = 0.924. CCDC-659562 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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