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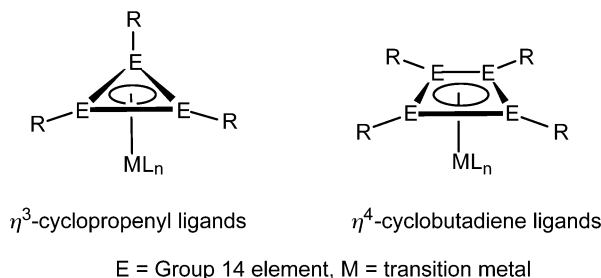
Kazunori Takanashi, Vladimir Ya. Lee, Tadahiro Matsuno, Masaaki Ichinohe, and Akira Sekiguchi*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Received February 14, 2005; E-mail: sekiguchi@staff.chem.tsukuba.ac.jp

The chemistry of organotransition-metal compounds is one of the most important and well-studied subdivisions of organometallic chemistry.¹ Although many kinds of ligands are now commonly available for coordination compounds, the quest for new ligands for transition-metal complexes is still a topic of major importance. Thus, recently there has been an increasing interest in the possible utilization of small ring unsaturated aromatic compounds consisting of heavier group 14 elements (such as E_3H_3^+ ($\text{E} = \text{Si}, \text{Ge}$) and its derivatives) as a new generation of π -ligands for transition-metal complexes.² However, in contrast to those commonly used in a variety of coordination and main group compounds, namely η^3 -cyclopropenyl and η^4 -cyclobutadiene ligands (Chart 1, $\text{E} = \text{C}$),¹ their homologues of heavier group 14 elements (Chart 1, $\text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) have remained elusive.³ We now report the synthesis and properties of the first stable Co complexes with a new type of ligand, η^4 -tetrasilacyclobutadiene.

Chart 1



The reaction of tetrasilacyclobutadiene dianion dipotassium salt $[\text{R}_4\text{Si}_4]^{2-} \cdot 2\text{K}^+$ ($\text{R} = \text{SiMe}^t\text{Bu}_2$) **1**⁴ with an excess of $\text{CpCo}(\text{CO})_2$ in THF immediately took place, accompanied by a color change from dark green to dark brown. After the removal of THF and excess of $\text{CpCo}(\text{CO})_2$, the reaction mixture was washed with dry hexane, and the residue was crystallized from hexane–THF mixed solvent to give [tetrakis(di-*tert*-butylmethylsilyl)tetrasilacyclobutadiene]dicarbonylcobalt $[(\text{R}_4\text{Si}_4)\text{Co}(\text{CO})_2]^- \cdot 2^-$, in the form of a dimer $\{2^- \cdot [\text{K}^+(\text{THF})_3]\}_2$, isolated as orange crystals in 48% yield (Scheme 1).^{5,6} The subsequent addition of diglyme resulted in the formation of the anionic complex of the potassium salt $2^- \cdot [\text{K}^+(\text{diglyme})_2(\text{THF})]$ (Scheme 1).^{6,7}

As an overall result of this reaction, a stable 18-electron anionic Co complex $2^- \cdot [\text{K}^+(\text{diglyme})_2(\text{THF})]$ was produced following the fast elimination of CpK. This ligand exchange reaction proceeded in an unexpected way, resulting in elimination of the Cp ligand rather than the loosely bound and easily removable CO group. Such a reaction path seems to be unusual, since it is well-known that the Cp groups usually bind quite firmly to a transition metal, being typically an innocent ligand that plays a purely spectator role in ligand exchange reactions.¹ However, in our case the situation is different: the nonaromatic heavy CBD^{2-} **1**⁴ is heavily overloaded

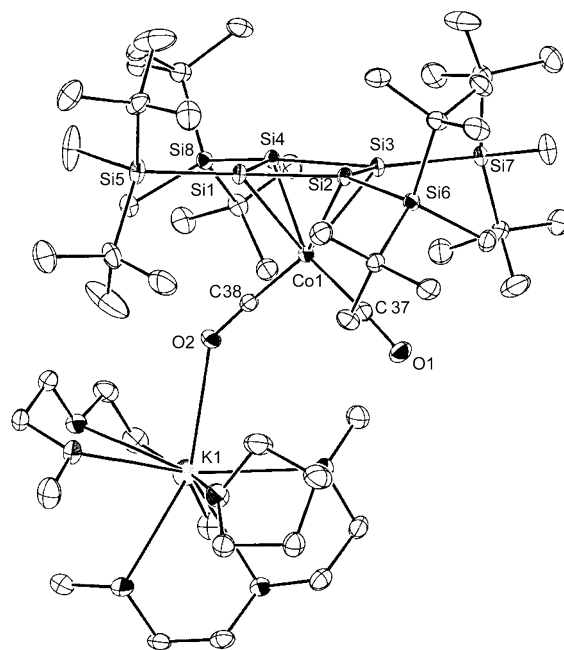


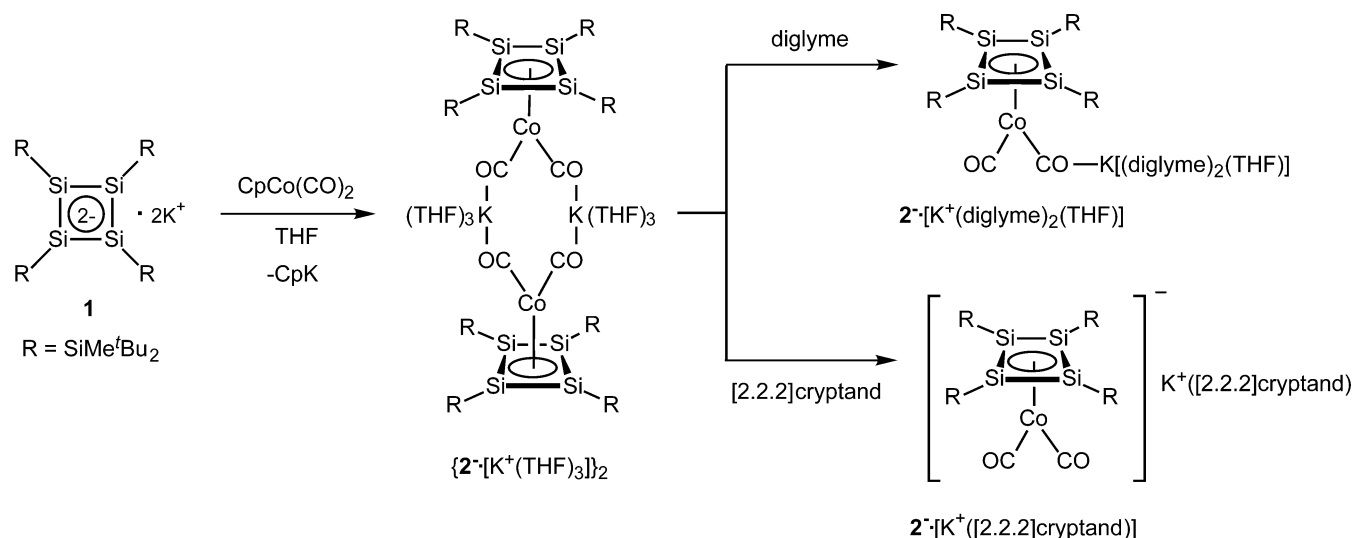
Figure 1. ORTEP drawing of $2^- \cdot [\text{K}^+(\text{diglyme})_2(\text{THF})]$. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.2570(9), Si2–Si3 = 2.3081(8), Si3–Si4 = 2.2588(9), Si1–Si4 = 2.3154(8), Si1–Co1 = 2.3935(7), Si2–Co1 = 2.4225(7), Si3–Co1 = 2.4054(7), Si4–Co1 = 2.4082(7), C38–Co1 = 1.718(2), C37–Co1 = 1.741(3), C38–O2 = 1.184(3), C37–O1 = 1.170(3), O2–K1 = 2.8168(18). Selected bond angles (deg): Si1–Si2–Si3 = 91.49(3), Si2–Si3–Si4 = 88.63(3), Si3–Si4–Si1 = 91.25(3), Si2–Si1–Si4 = 88.49(3).

with the two negative charges and consequently strongly favors the loss of one electron, which can be eliminated in the form of an aromatic Cp anion.

Due to its highly symmetrical structure, $2^- \cdot [\text{K}^+(\text{diglyme})_2(\text{THF})]$ exhibited only one set of signals for the Me and $t\text{Bu}$ groups in both ^1H and ^{13}C NMR spectra. The most important observation is the resonance of the skeletal Si atoms in the ^{29}Si NMR spectrum at -43.2 ppm, which is well outside the expected low-field region for the conjugated tetrasilacyclobutadiene system.^{8,9} This provides evidence that the negative charge is at least partially distributed over the Si_4 ring. Such a significant shielding of the skeletal Si atoms indicates the strong π -back-bonding from $3d(\text{Co})$ orbitals to Si_4 fragment, which increases the electron density inside the four-membered ring.

The crystal structure of $2^- \cdot [\text{K}^+(\text{diglyme})_2(\text{THF})]$ was determined by X-ray crystallography (Figure 1),¹⁰ which showed that the R_4Si_4 four-membered ring is η^4 -coordinated to a Co center. Upon complexation, the four-membered ring of the Si_4 ligand became an almost planar (sum of the interior angles 359.9° , folding angles of 2.8 and 4.8°) rectangle with nearly equal opposite Si–Si bonds (Si1–Si2 = 2.2570(9) and Si3–Si4 = 2.2588(9) Å, Si1–Si4 =

Scheme 1



2.3154(8) and Si2–Si3 = 2.3081(8) Å) and an almost in-plane arrangement of all Si substituents (the sum of the bond angles around the Si1–Si4 = 358.6–359.5°), a geometry expected for the cyclobutadiene ligand in transition-metal complexes.¹ Such a geometry is quite different from the starting cyclobutadiene dianion **1**,⁴ which has a significantly folded four-membered ring (folding angle 34°) with highly pyramidalized skeletal Si atoms as a result of the repulsive interaction of the two negative charges inside the [R₄Si₄]²⁻ ring. The potassium ion in the complex **2**⁻·[K⁺(diglyme)₂(THF)] is exclusively bound to the oxygen atom of one of the CO ligands, being also coordinated to two diglyme and one THF molecules. Such specific accommodation of the negative charge on the O atom implies an enhanced 3d(Co)–π*(CO) π-back-donation, which results in an increase in the strength of the Co–CO bond accompanied by a decrease in the CO bond stretching vibration (observed⁷ value 1870 cm⁻¹, cf.¹ for anionic [Co(CO)₄]⁻ complexes, 1883 cm⁻¹). Such delocalization of the negative charge over the transition-metal moiety provides an extra stabilization of the anionic complex **2**⁻·[K⁺(diglyme)₂(THF)], particularly due to the presence of strongly π-acidic CO ligands.

The complex **2**⁻ was also prepared in the presence of [2.2.2]-cryptand: in this case the potassium ion was complexed with cryptand, thus leaving **2**⁻ as a free anion, **2**⁻·[K⁺[2.2.2]cryptand] (Scheme 1).⁶ However, the structural parameters of **2**⁻ moiety were not significantly affected by the cryptand complexation compared to those of **2**⁻·[K⁺(diglyme)₂(THF)].¹¹

Supporting Information Available: Experimental procedures and spectral data for **2**⁻·[K⁺(diglyme)₂(THF)], **2**⁻·[K⁺[2.2.2]cryptand](THF)₂, and {**2**⁻·[K⁺(THF)₃]}₂; tables of crystallographic data including atomic positional and thermal parameters for **2**⁻·[K⁺(diglyme)₂(THF)] and **2**⁻·[K⁺[2.2.2]cryptand](THF)₂ (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The structure of {**2**⁻·[K⁺(THF)₃]}₂ was determined by X-ray crystallography; however, the poor refinement of the X-ray data of the dimer prevents us from discussing its structural features.
- For the experimental procedures and spectral data, see Supporting Information.
- Spectral data for **2**⁻·[K⁺(diglyme)₂(THF)]: orange crystals; mp 252 °C (dec); ¹H NMR (THF-*d*₈, δ) 0.16 (s, 12 H), 1.16 (s, 72 H); ¹³C NMR (THF-*d*₈, δ) -3.2, 22.0, 31.0, 224.0 (C=O); ²⁹Si NMR (THF-*d*₈, δ) -43.2, 17.0; IR (KBr) 1870 cm⁻¹ (C=O).
- The typical ²⁹Si NMR resonances for doubly bonded Si atoms in disilenes lie in the region of +49 to +155 ppm. See: Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231.
- In cyclobutadiene systems, the resonances of the skeletal atoms are typically downfield shifted: (a) for tetrakis(trimethylsilyl)cyclobutadiene: 172.1 ppm (¹³C NMR). See: Sekiguchi, A.; Tanaka, M.; Matsuo, T.; Watanabe, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1675. (b) For the only known cyclobutadiene incorporating heavier group 14 elements, 1,2-digermylcyclobutadiene: 159.2 ppm (¹³C NMR), see: Cui, C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 5062.
- Crystal data for **2**⁻·[K⁺(diglyme)₂(THF)] at 120 K: MF = C₅₄H₁₂₀CoK₂O₉Si₈, MW = 1236.25, triclinic, *P*1, *a* = 14.2630(18), *b* = 15.8900(16), *c* = 16.2050(15) Å, α = 93.177(5), β = 94.693(6), γ = 95.974(6)°, *V* = 3632.9(7) Å³, *Z* = 2, *D*_{calc} = 1.130 g·cm⁻³. The final *R* factor was 0.0460 for 11 802 reflections with *I*_o > 2σ(*I*_o) (*R*_w = 0.1248 for all data, 16 127 reflections), GOF = 1.004.
- For the crystal data for **2**⁻·[K⁺[2.2.2]cryptand](THF)₂, see Supporting Information.

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