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η^5 -1,2,3-Trisilacyclopentadienyl - A Ligand for Transition Metal Complexes: Rhodium Half-Sandwich and Ruthenium Sandwich

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Coordination chemistry is greatly dominated by the transition metal complexes featuring cyclic polyene ligands, such as cyclopropenyls η^3 -C₃R₃, cyclobutadienes η^4 -C₄R₄, cyclopentadienyls η^5 -C₅R₅, arenes η^6 -C₆R₆, cycloheptatrienyls η^7 -C₇R₇, cyclooctatetraenes η^8 -C₈R₈, etc.¹ Among them, complexes with cyclopentadienyl ligands are most abundant. One can recall milestone metallocenes known since the synthesis of ferrocene (η^5 -H₅C₅)₂Fe by Kelly and Pauson in 1951.² Apart from fascinating structures and nonclassical bonding modes, sandwich metallocenes as well as cyclopentadienyl half-sandwich complexes have found widespread utilization in material science: asymmetric catalysis, polymerization of alkenes, and fluorescent materials.³ Analogues of metallocenes with the heavy group 14 elements (Si, Ge) in the cyclopentadienyl ring are particularly challenging because of the novel physicochemical properties anticipated upon the introduction of metalloid elements. However, until now, only a few compounds of such type based on the group 4, 5, and 8 transition metals have been isolated, including ruthenocenes and ferrocene featuring sila- and germacyclopentadienyl ligands.⁴ We have also contributed to the field with the recent report on the synthesis of a heavy analogue of ferrocene with a disilagermacyclopentadienyl ligand.⁵ In this contribution, we describe the synthesis of two complexes featuring a novel trisilacyclopentadienyl ligand: Rh half-sandwich (piano-stool) and Ru sandwich (ruthenocene). The former is particularly important, being the first group 9 metal complex with the heavy cyclopentadienyl ligand and the first heavy cyclopentadienyl complex of half-sandwich type.

Stoichiometric ligand exchange between the recently prepared lithium salt of trisilacyclopentadienide derivative **1**[−]•[Li⁺(thf)]⁶ and (acac)dicarbonylrhodium Rh(CO)₂(acac) in toluene resulted in formation of the desired (trisilacyclopentadienyl)dicarbonylrhodium **2**, isolated as air- and moisture-sensitive orange crystals in 47% yield (Scheme 1).⁷

Scheme 1

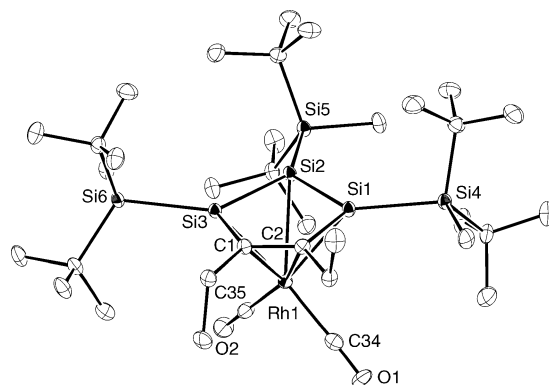
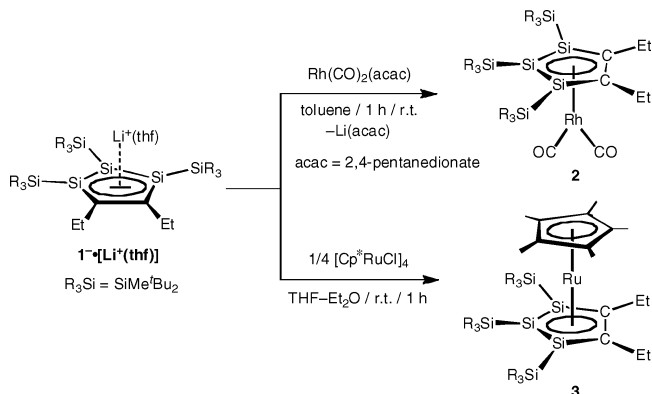


Figure 1. ORTEP drawing of **2** (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.2294(8), Si2–Si3 = 2.2807(8), Si1–C2 = 1.871(2), Si3–C1 = 1.857(2), C1–C2 = 1.413(3), Si1–Si4 = 2.3864(8), Si2–Si5 = 2.3821(8), Si3–Si6 = 2.4001(8), Rh1–Si1 = 2.5231(6), Rh1–Si2 = 2.6845(6), Rh1–Si3 = 2.4806(6), Rh1–C1 = 2.371(2), Rh1–C2 = 2.323(2), Rh1–C34 = 1.900(2), Rh1–C35 = 1.873(2), C34–O1 = 1.141(3), C35–O2 = 1.147(3). Selected bond angles (deg): C2–Si1–Si2 = 102.74(7), Si1–Si2–Si3 = 93.22(3), Si2–Si3–C1 = 103.99(7), Si3–C1–C2 = 117.58(15), C1–C2–Si1 = 122.41(15), C34–Rh1–C35 = 97.78(10), O1–C34–Rh1 = 176.7(2), O2–C35–Rh1 = 176.9(2).

Spectral characteristics of **2** are noteworthy. First of all, all skeletal atoms in **2** were remarkably shielded compared with those of the starting **1**[−]•[Li⁺(thf)]: 124.4 vs 159.6 ppm (–C–C–), –67.6 vs 22.0 ppm (–Si–Si–Si–), 24.7 vs 29.9 ppm (broad, –Si–Si–Si–).^{8,9} Although the ¹J_{Rh–C} coupling constant for the skeletal carbons of 4.7 Hz in **2** was comparable with that of [(η^5 -Me₅C₅)Rh(CO)₂] (101.7 ppm, 3.5 Hz),¹⁰ the magnitude of the Rh–Si coupling (¹J_{Rh–Si} = 7.1 Hz) in **2** was smaller than those of known silyl-rhodium complexes (15–48 Hz),¹¹ evidently because of the higher hapticity of coordination in **2**. The shielding of ring carbons and silicons taking place upon complexation, as well as observation of coupling to the Rh center, provides clear evidence for the appreciable delocalization of the 6 π -electrons over the Si₃C₂ ring and its pentahaptocoordination to the Rh center.¹² On the other hand, shielding of skeletal atoms is indicative of strong Si₃C₂–ligand \leftarrow 5d(Rh) π -back-donation (δ -bonding), supportive of the high electron-accepting properties of the heavy cyclopentadienyl ligand. The resonance of the carbonyl carbons was observed at 199.4 ppm as a doublet with a ¹J_{Rh–C} coupling constant of 76.5 Hz, a value smaller than that in [(η^5 -Me₅C₅)Rh(CO)₂] (195.4 ppm, ¹J_{Rh–C} = 83.2 Hz),¹⁰ implying weaker Rh–CO back-bonding in **2**.¹³

The crystal structure of **2** is shown in Figure 1.⁷ Remarkable cyclic π -delocalization within the Si₃C₂ heavy cyclopentadienyl ligand was manifested in its diagnostic pentahaptocoordination to the Rh atom. The values of all skeletal bond lengths were

intermediate between those of the normal single and double bonds: Si1–Si2 = 2.2294(8), Si2–Si3 = 2.2807(8), Si3–C1 = 1.857(2), Si1–C2 = 1.871(2), C1–C2 = 1.413(3) Å. They were comparable with those of the previously reported $\text{Bu}_2\text{C}=\text{O}$ -coordinated lithium trisilacyclopentadienide $1^-\cdot[\text{Li}^+(\text{O}=\text{C}^+\text{Bu}_2)]$,⁶ which was classified as 6π -electron aromatics: Si1–Si2 = 2.2508(10), Si2–Si3 = 2.2438(10), Si3–C1 = 1.844(3), Si1–C2 = 1.829(3), C1–C2 = 1.418(4) Å. Complexation of the trisilacyclopentadienyl ligand to the transition metal in **2** resulted in a significant flattening of the five-membered ring, which was even more pronounced than that of the lithium salt $1^-\cdot[\text{Li}^+(\text{O}=\text{C}^+\text{Bu}_2)]$ ⁶ (the sum of the interior bond angles: 539.9° vs 538.5°). Accordingly, the geometry around all skeletal atoms in **2** is almost perfectly planar (the sum of the bond angles): Si1 (359.6°), Si2 (359.2°), Si3 (359.3°), C1 (359.9°), C2 (360.0°). Interestingly, the Si2–Si3 and Si1–C2 bonds in **2** are slightly longer than the Si1–Si2 and Si3–C1 bonds. Such distortions, resulting in the departure of the Si_3C_2 ring from the expected pentagonal geometry of C_s -symmetry, apparently stem from the staggered conformation of the CO ligands in **2**, in which Si2–Si3 and Si1–C2 bonds are superimposed by carbonyl groups (angle between the Rh1–Si2–Si3 plane and O1–C34–Rh1–C35–O2 mean plane = 56.3°) (Figure 2). The staggered conformation of the CO groups may result from their appreciable steric interplay with the bulky Bu_2MeSi substituents.¹⁴ In contrast, in the model compound $[\eta^5\text{-(Me}_3\text{Si)}_3\text{Si}_3\text{C}_2\text{Me}_2]\text{Rh}(\text{CO})_2$ **2'**, the conformation of the CO ligands is eclipsed (89.9°), thus reflecting the remarkably smaller steric bulk of the Me_3Si groups.

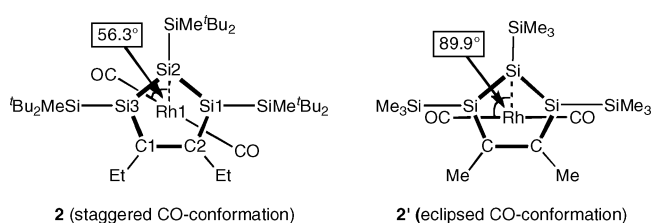


Figure 2. Conformation of the CO ligands in exptl **2** and calcd **2'**.

The utility of Si_3C_2 as a novel ligand was further demonstrated by the reaction of $1^-\cdot[\text{Li}^+(\text{thf})]$ ⁶ with 0.25 equiv of $[\text{Cp}^*\text{RuCl}]_4$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) to produce the heavy analogue of ruthenocene $\text{Cp}^*\text{Ru}[\eta^5\text{-(Bu}_2\text{MeSi)}_3\text{Si}_3\text{C}_2\text{Et}_2]$ **3**, isolated as yellow crystals in 35% yield (Scheme 1).⁷ The resonances of the skeletal atoms in sandwich complex **3** (-76.4 ppm for $-\text{Si}-\text{Si}-\text{Si}-$, -2.2 ppm for $-\text{Si}-\text{Si}-\text{Si}-$, 94.4 ppm for $-\text{C}-\text{C}-$)¹⁵ were observed at higher fields than those of half-sandwich **2** because of the pronounced π -donating effect of the Cp^* ligand compared with the high π -acidity of the CO groups. Preliminary crystal structure analysis of **3** revealed its sandwich-type composition with both five-membered rings being planar (and coplanar with each other) and with characteristic η^5 -coordination to the Ru atom.¹⁶ As is typical for Cp^* -metallocenes,¹⁷ the conformation of both the Cp^* and Si_3C_2 rings is staggered.

The CV measurement of **3** revealed an irreversible oxidation wave at $E(\text{ox}) = -0.30$ V (vs Ag/Ag^+ , CH_2Cl_2 , 0.1 M $[\text{Bu}_4\text{N}][\text{ClO}_4]$), whereas the parent decamethylruthenocene Cp^*Ru displayed a reversible oxidation wave at $+0.18$ V under the same measurement conditions.¹⁸ The remarkably low oxidation potential of **3**

compared with that of Cp^*Ru suggests that the novel heavy cyclopentadienyl ligand Si_3C_2 is an excellent electron donor, even surpassing such a powerful π -donor as the Cp^* group.

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Supporting Information Available: Experimental procedures and spectral data for compounds **2** and **3**, computational results of the model compounds **2'** and **3'**, tables of crystallographic data, including atomic positional and thermal parameters for **2** (PDF/CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Hill, A. F. *Organotransition Metal Chemistry*; Wiley–Interscience: Bristol, 2002.
- (2) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.
- (3) (a) *Ferrocenes. Homogenous Catalysis, Organic Synthesis, Material Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995. (b) *Metallocenes. Synthesis, Reactivity, Applications*; Togni, A., Halterman, R., Eds.; VCH: Weinheim, 1998. (c) *J. Organomet. Chem.* **2001**, *637*–639 (issue dedicated to 50th anniversary of ferrocene synthesis).
- (4) (a) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L.; Ostrander, R. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1744. (b) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8428. (c) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 8245. (d) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 3097. (e) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, *19*, 2671. (f) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, *19*, 4720. (g) Freeman, W. P.; Dysard, J. M.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **2002**, *21*, 1734. Review: (h) Lee, V. Ya.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 6596.
- (5) Lee, V. Ya.; Kato, R.; Sekiguchi, A.; Krapp, A.; Frenking, G. *J. Am. Chem. Soc.* **2007**, *129*, 10340.
- (6) Yasuda, H.; Lee, V. Ya.; Sekiguchi, A. *J. Am. Chem. Soc.* **2009**, *131*, 6352.
- (7) For the experimental procedure and the spectral data of compounds **2** and **3** and crystal data of compound **2**, see the Supporting Information.
- (8) The computed chemical shifts of complex **2** agreed reasonably with the experimental values: 123.6 ppm ($-\text{C}-\text{C}-$), -55.7 ppm ($-\text{Si}-\text{Si}-\text{Si}-$), and 46.2 ppm ($-\text{Si}-\text{Si}-\text{Si}-$).
- (9) All theoretical calculations were performed with the GAUSSIAN 98 program package: geometry optimization of the model compounds $[\eta^5\text{-(Me}_3\text{Si)}_3\text{Si}_3\text{C}_2\text{Me}_2]\text{Rh}(\text{CO})_2$ **2'** and $\text{Cp}^*\text{Ru}[\eta^5\text{-(Me}_3\text{Si)}_3\text{Si}_3\text{C}_2\text{Me}_2]$ **3'** at the B3PW91/6-31G(d) level for H, C, O, and Si and at the B3PW91/3-21G(d) level for Rh and Ru; GIAO NMR chemical shift calculations for **2** and **3'** at the B3PW91/6-311G(3d,p) level for H and C, at the B3PW91/6-311+G(3d,p) level for Si, and at the B3PW91/3-21G(d) level for Rh and Ru.
- (10) Herrmann, W. A.; Plank, J.; Bauer, Ch.; Ziegler, M. L.; Guggolz, E.; Alt, R. *Z. Anorg. Allg. Chem.* **1982**, *487*, 85.
- (11) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.
- (12) We previously observed the diagnostic shielding of the skeletal atoms of the heavy cyclic polyene ligand upon its complexation to the transition metal fragment. (a) Reference 5. (b) Takanashi, K.; Lee, V. Ya.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2005**, *127*, 5769. (c) Takanashi, K.; Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 3269. (d) Takanashi, K.; Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *Eur. J. Inorg. Chem.* **2007**, 5471.
- (13) The IR stretching frequencies of the CO group in **2** (1950 and 2002 cm^{-1}) are quite comparable to those of its carbon analogue $[\eta^5\text{-Me}_5\text{C}_5\text{Rh}(\text{CO})_2]$ (1943 and 2000 cm^{-1}).¹⁰
- (14) The decisive role of the conformation of the CO groups on the overall geometry of heavy cyclic polyene ligands was firmly established in preceding investigations: see refs 12b,c.
- (15) The computed chemical shifts of the model complex $\text{Cp}^*\text{Ru}[\eta^5\text{-(Me}_3\text{Si)}_3\text{Si}_3\text{C}_2\text{Me}_2]$ **3'** agreed reasonably with the experimental values: 93.3 ppm ($-\text{C}-\text{C}-$), -77.9 ppm ($-\text{Si}-\text{Si}-\text{Si}-$), and 35.6 ppm ($-\text{Si}-\text{Si}-\text{Si}-$).
- (16) The composition of **3** as the heavy ruthenocene was unambiguously established by X-ray crystallography; however, its structural parameters are not discussed here because of the poor refinement.
- (17) Elschenbroich, C. *Organometallics*, 3rd ed.; Wiley–VCH: Weinheim, 2006.
- (18) Such irreversibility of the oxidation wave points to an apparent instability of the resulting heavy ruthenocene cation radical under the measurement conditions, which contrasts with the stability of the ruthenocene cation radical.

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