Supplementary Material (ESI) for Dalton Transactions

A two-and-a-half-layer sandwich: potassium salt of anionic (η^4-tetrasilacyclobutadiene)(η^5-cyclopenta-dienyl)ruthenium

*Vladimir Ya. Lee, Kazunori Takanashi and Akira Sekiguchi**

SUPPORTING INFORMATION

Dr. V. Ya. Lee, Dr. K. Takanashi,
Prof. A. Sekiguchi
Department of Chemistry
Graduate School of Pure and Applied Sciences
University of Tsukuba
Tsukuba, Ibaraki 305-8571, Japan
E-mail: sekiguch@chem.tsukuba.ac.jp

General Procedures.

All experiments were performed using high-vacuum line techniques or in an argon atmosphere using MBRAUN MB 150B-G glove box. 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) and AV-400FT NMR (^{1}H NMR at 400 MHz; ^{13}C NMR at 100.6 MHz; ^{29}Si NMR at 79.5 MHz) spectrometers. The dipotassium salt of the tetrasilacyclobutadiene dianion $\mathbf{2^{2-}\bullet[K^+(thf)_2]_2}$ and ruthenium complex $[Cp^*RuCl]_4$ were prepared according to the published procedures [1] and [2], respectively.

Experimental Procedure and Spectral Data for $\{[\eta^4\text{-}(^t\mathbf{Bu_2MeSi})_4\mathbf{Si_4}]\mathbf{RuCp^*}\}^-\bullet[K^+(thf)_2]$ ($\mathbf{1^-\bullet[K^+(thf)_2]}$).

The dipotassium salt of the tetrasilacyclobutadiene dianion $\mathbf{2^{2-}\bullet[K^+(thf)_2]_2}$ (125 mg, 0.113 mmol) and $[Cp^*RuCl]_4$ (31 mg, 0.029 mmol) were placed in a reaction tube with a magnetic stirring bar. Dry oxygen-free THF (2 ml) was introduced into this tube by vacuum transfer, and the reaction mixture was stirred at room temperature to give a red solution within 1 h. After evaporation of the solvent and removal of the inorganic salt, the reaction mixture was recrystallized from hexane–THF to give $\mathbf{1^-\bullet[K^+(thf)_2]}$ (85 mg, 65%) as as air- and moisture-sensitive red crystals. Mp > 300 °C (dec.); ^{1}H NMR (THF-d_8, δ) 0.04 (s, 12 H, CH_3), 1.14 (s, 72 H, $C(CH_3)_3$), 2.28 (s, 15 H, $(CH_3)_5C_5$); ^{13}C NMR (THF-d_8, δ) –2.7 (CH_3), 16.1 ($(CH_3)_5C_5$), 22.0 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 88.6 ($(CH_3)_5C_5$); ^{29}Si NMR (THF-d_8, δ) –49.8 (skeletal Si), 20.4 (substituent Si).

X-ray Diffraction Study and Crystallographic Data for $\mathbf{1^-\bullet[K^+(thf)_2]}$).

The single crystals of $\mathbf{1^-\bullet[K^+(thf)_2]}$ for X–ray diffraction analysis were grown from a hexane–THF solution at –30 °C. Diffraction data were collected at 150 K on a MacScience DIP2030 Image Plate diffractometer equipped with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-$K\alpha$ radiation (λ = 0.71070 Å). The structure was solved by the direct method using SIR-92 [3] program and refined by the full-matrix least-squares method by SHELXL–97 program [4]. Crystallographic data for $\mathbf{1^-\bullet[K^+(thf)_2]}$ at 150 K: MF = $C_{54}H_{115}K_1O_2Ru_1Si_8$, MW = 1161.35, orthorhombic, *Pccn*,

a = 20.5640(5), b = 44.9360(4), c = 14.2880(13) Å, V = 13203.0(12) Å^3, Z = 8, D_{calcd} = 1.169 g•cm^{-3}. The final R factor was 0.0639 for 9512 reflections with $I_0 > 2\sigma(I_0)$ (R_w = 0.1697 for all data, 14892 reflections) with $I > 2\sigma(I)$, GOF = 1.019. CCDC-764194 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.

References:

[1] V. Ya. Lee, K. Takanashi, T. Matsuno, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.*, 2004, **126**, 4758.

[2] P. J. Fagan, M. D. Ward, J. V. Caspar, J. C. Calabrese, P. J. Krusic, *J. Am. Chem. Soc.,* 1988, **110**, 2981.

[3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

[4] G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.