

Synthesis of Novel Ruthenium and Rhodium Complexes with a Silsesquioxane-Based Phosphine Ligand

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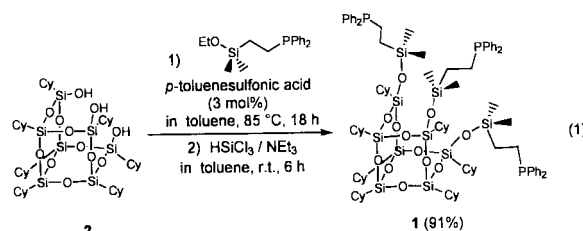
Novel silsesquioxane-containing ruthenium and rhodium complexes were prepared by the reaction of $[\text{RuCl}_2(p\text{-cymene})]_2$ and $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ with a new silsesquioxane-based tridentate phosphine ligand, $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (**1**).

Transition metal-containing silsesquioxanes of cube-like core structure are very interesting as homogeneous catalysts which mimic the active sites of silica-supported catalysts and zeolites,¹ as well as precursors for heterogeneous catalysts with the characteristic structures.² Numbers of main group element- or early transition metal-containing silsesquioxanes have been synthesized,¹ whereas few examples of late transition metal-containing silsesquioxanes have been reported to date.^{1a,3} On the other hand, silsesquioxane-based ligands, which has one thiol or phosphine group attached to a completely condensed T_8 -oligosilsesquioxane cage, have been prepared.⁴ Starburst-type silsesquioxane-based ligands, which are composed of one cubic silsesquioxane or spherosilicate core together with eight or more dative groups on the periphery, are also prepared, and have been employed as a core ligand of metallodendrimers.⁵ The positive effects of silsesquioxane-based dendritic phosphine ligands on the catalytic activities towards the rhodium-catalyzed hydroformylation of terminal olefins were observed.^{5d,e} However, synthesis of transition metal complexes with multi-dentate silsesquioxane-based ligands of novel core structures is strongly required, since the size and flexibility of the ligand would significantly affect the catalytic activity of the complex.

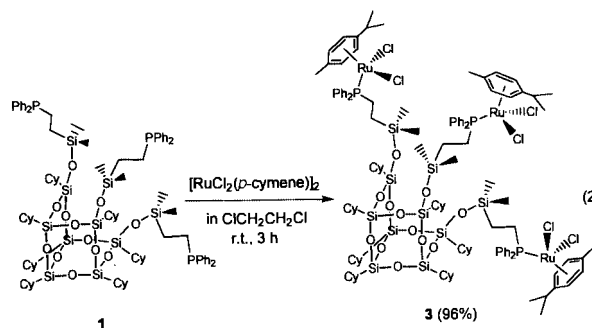
Here we report the synthesis of novel ruthenium or rhodium complexes containing a newly-prepared silsesquioxane-based tridentate phosphine ligand, $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (**1**). The reaction of **1** with $[\text{RuCl}_2(p\text{-cymene})]_2$ and $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ successfully gave novel silsesquioxane-containing ruthenium or rhodium complexes.

A silsesquioxane-based ligand with three diphenylphosphinoethyl groups was synthesized by the reaction of incompletely condensed silsesquioxane trisilanol **2** with (3-ethoxy-3-methyl-3-silabutyl)diphenylphosphine in the presence of 3 mol% of *p*-toluenesulfonic acid at 85 °C for 18 h. The crude products contained **1** and its phosphine oxide. Analytically pure **1** was obtained in the yield of 91% by the reduction of the crude mixture with trichlorosilane in the presence of triethylamine (eq 1).⁶ The product **1** was fully characterized by NMR, IR, and FAB-MASS. The ^{29}Si NMR spectrum of **1** consists of one set of three peaks in a 1 : 3 : 3 ratio for seven silicon atoms in the silsesquioxane cage, which are in good accordance with the local C_{3v} -symmetry of the siloxane framework. The FAB-MASS analysis clearly shows peaks at around m/z of 1685, $[\text{M} + \text{H}]^+$, and the isotope distribution pattern coincides with the composition of **1**.

The reactions of the phosphine ligand **1** with several late

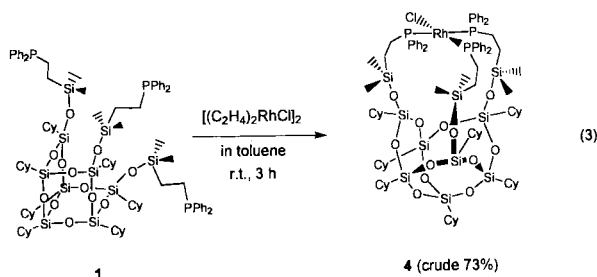


transition metal complexes were examined. Among them, the reaction of **1** with $[\text{RuCl}_2(p\text{-cymene})]_2$ successfully proceeded in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at room temperature to give red solids of a novel ruthenium complex **3** in almost quantitative yield (eq 2).⁷ In the ^{31}P NMR spectrum of **3**, the signal for three terminal PPh_2 groups was equivalently observed at 21.22 ppm as a singlet, and the ^{29}Si NMR spectrum consists of one set of three peaks in a 1 : 3 : 3 ratio for seven silicon atoms in the silsesquioxane cage, which is in consistent with the local C_{3v} -symmetry of the siloxane framework. In the FAB-MASS spectrum, the signals for $[\text{M} - \text{Cl}]^+$ were clearly observed at around m/z of 2569, and the isotope distribution pattern is completely consistent with the composition of $[\text{M} - \text{Cl}]^+$, $\text{C}_{113}\text{H}_{165}\text{Cl}_5\text{O}_{12}\text{P}_3\text{Ru}_3\text{Si}_{10}$.



In addition, the synthesis of a new rhodium complex with **1**, in which all three of phosphorus atoms are coordinated to one rhodium center, was performed. The tridentate phosphine ligand **1** readily reacted with $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ in a very dilute solution of toluene at room temperature to give yellow solids of a crude rhodium complex **4** in ca. 73% yield (eq 3).⁸ The purity of the product **4** is over 95%, but further purification is now attempted. The spectroscopic analyses of **4** indicate that the complex consists of one triphosphine ligand **1** and one rhodium atom. In the ^1H NMR spectrum of **4**, three peaks of almost the same intensity for six CH_3 groups were observed, and the ^{29}Si NMR spectrum consists of one set of five peaks in a 1 : 2 : 1 : 1 : 2 ratio for seven silicon atoms in the silsesquioxane cage, which are compatible with the local C_s -symmetry of the siloxane framework. The ^{31}P NMR spectrum of **4** in CD_2Cl_2 consists of a simple first-order AM_2X splitting pattern, which produces a

doublet of triplets for one phosphorus atom of **4** and a doublet of doublets for the other two phosphorus atoms in a 1 : 2 ratio. In the FAB-MASS measurement, the signals for $[M-Cl]^+$ were observed at around m/z of 1789, and there is no sign of intermolecular coordinated complexes. These results suggest that **4** is composed of a discrete mononuclear species in which the rhodium atom is in a distorted square-planar environment. The proposed structure is analogous to that of Wilkinson complex $RhCl(PPh_3)_3$.



As described above, a new silsesquioxane-based phosphine ligand **1** was found to be easily prepared from an incompletely condensed silsesquioxane **2** in high yields. The reaction of **1** with $[RuCl_2(p\text{-cymene})]_2$ and $[(C_2H_4)_2RhCl]_2$ successfully gave novel silsesquioxane-containing ruthenium (**3**) and rhodium (**4**) complexes. The complexes **3** and **4** are expected to provide unique and characteristic catalytic processes in which plural metals participate and ability of molecular recognition due to the cage-like structure and steric bulkiness, respectively.

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- All manipulations were performed under an argon atmosphere using standard Schlenk techniques. To a mixture of **2** (2.19 g, 2.5 mmol) and *p*-toluenesulfonic acid (0.014 g, 0.075 mmol) in toluene (30 cm³), (3-ethoxy-3-methyl-3-silabutyl)diphenylphosphine (3.7 cm³, 10 mmol) was added dropwise, and it was stirred at 85 °C for 18 h. After separation by a recycling preparative HPLC, the resulting clear solution was then evaporated at room temperature to leave a pink viscous liquid. To a toluene solution (30 cm³) of this crude liquid, trichlorosilane (1.8 cm³) and triethylamine (1.8 cm³) was added and stirred at room temperature for 18 h. After filtration, the resulting clear solution was then evaporated at room temperature to leave a product **1** as a pale yellow viscous liquid. Yield 91%. ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 7.48–7.29 (br, 30H, PPh₂), 2.11 (br, 6H, SiCH₂CH₂PPh₂), 1.81–1.52 (br m, 56H, CH₂ of Cy), 1.08–0.90 (br m, 7H, CH of Cy), 0.72 (br, 6H, SiCH₂CH₂PPh₂), 0.20 (s, 18H, Si(CH₃)₂). ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 139.10–128.26 (PPh₂), 27.66–26.82 (CH₂ of Cy), 24.51, 23.67, 22.40 (3 : 3 : 1 for CH of Cy), 20.90 (d, *J*_{CP} = 13.1 Hz, SiCH₂CH₂PPh₂), 13.54 (d, *J*_{CP} = 8.1 Hz, SiCH₂CH₂PPh₂), 0.17 (Si(CH₃)₂). ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.02 M Cr(acac)₃, 25 °C) δ 8.65 (d, *J*_{SIP} = 23.5 Hz, Si(CH₃)₂), –66.18, –67.48, –67.59 (1 : 3 : 3); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ –11.99 (s). IR (neat): 3070, 3053, 2950, 2864, 1587, 1480, 1434, 1252, 1134, 912, 842, 781, 739, 697 cm^{–1}. MS (FAB) *m/z* : 1685 [M + H]⁺, 1615 [M – C₅H₉]⁺.
- To a solution of **1** (0.24 g, 0.14 mmol) in ClCH₂CH₂Cl (30 cm³), $[RuCl_2(p\text{-cymene})]_2$ (0.13 g, 0.21 mmol) in ClCH₂CH₂Cl (20 cm³) was added dropwise, and the mixture was stirred at room temperature for 3 h. The resulting red solution was then evaporated at room temperature to leave red solids. Complex **3** was obtained by reprecipitation by slow diffusion of pentane into a CH₂Cl₂ solution. Yield 96%. M.p. (decomp.) 186–187 °C; ¹H NMR (300 MHz, CD₂Cl₂, 25 °C) δ 7.79–7.43 (br m, 30H, PPh₂), 5.22 (br s, 6H, CH of *p*-cymene), 5.07 (br s, 6H, CH of *p*-cymene), 3.72 (br s, 3H, CH(CH₃)₂ of *p*-cymene), 2.42 (br s, 6H, SiCH₂CH₂PPh₂), 1.83 (s, 9H, C(CH₃)₃ of *p*-cymene), 1.57–1.24 (br m, 56H, CH₂ of Cy), 0.81 (br m, 25H, CH(CH₃)₂ of *p*-cymene and CH of Cy), 0.18 (br m, 6H, SiCH₂CH₂PPh₂), –0.20 (s, 18H, Si(CH₃)₂). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 25 °C) δ 133.62 (d, *J*_{CP} = 8.1 Hz, PPh₂), 132.94 (PPh₂), 132.38 (PPh₂), 130.63 (PPh₂), 128.31 (d, *J*_{CP} = 9.3 Hz, PPh₂), 107.51 (CCH(CH₃)₂ of *p*-cymene), 93.62 (CCH₃ of *p*-cymene), 90.79 (d, *J*_{CP} = 5.0 Hz, CH for *p*-cymene), 85.68 (d, *J*_{CP} = 5.6 Hz, CH for *p*-cymene), 30.18 (CH(CH₃)₂ of *p*-cymene), 27.78–27.01 (CH₂ of Cy), 24.58, 23.78, 22.53 (3 : 3 : 1 for CH of Cy), 21.32 (CH(CH₃)₂ of *p*-cymene), 17.68 (SiCH₂CH₂PPh₂), 17.31 (CCH₃ of *p*-cymene), 10.71 (d, *J*_{CP} = 9.3 Hz, SiCH₂CH₂PPh₂), –0.16 (Si(CH₃)₂). ²⁹Si{¹H} NMR (76 MHz, CD₂Cl₂, 0.02 M Cr(acac)₃, 25 °C) δ 9.22 (d, *J*_{SIP} = 21.5 Hz, Si(CH₃)₂), –66.38, –67.44, –67.81 (1 : 3 : 3); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ 21.22 (s, P–Ru). IR (KBr): 2874, 2866, 2503, 2206, 1813, 1685, 1557, 1488, 1393, 1131, 1042, 988, 899 cm^{–1}. MS (FAB) *m/z* : 2569 [M – Cl]⁺. Anal. Calcd for C₁₁₃H₁₆₅ClO₁₂P₃Ru₃Si₁₀ (2605.21): C, 52.10; H, 6.38%. Found C, 51.15; H, 6.74%.
- To a solution of **1** (0.22 g, 0.13 mmol) in toluene (70 cm³), $[(C_2H_4)_2RhCl]_2$ (0.026 g, 0.065 mmol) in toluene (30 cm³) was added slowly and dropwise for 1.5 h, and the mixture was further stirred at room temperature for 1.5 h. The resulting yellow solution was then evaporated at room temperature to leave yellow solids. Complex **4** was obtained by repeated reprecipitation by slow diffusion of pentane into a CH₂Cl₂ solution. Yield 73% (crude). M.p. (decomp.) 141–142 °C; ¹H NMR (300 MHz, CD₂Cl₂, 25 °C) δ 8.11–6.75 (30H, PPh₂), 2.57–2.29 (6H, SiCH₂CH₂PPh₂), 1.80–1.29 (br m, 56H, CH₂ of Cy), 1.11–1.04 (6H, SiCH₂CH₂PPh₂), 0.92 (7H, CH of Cy), 0.21 (6H, Si(CH₃)₂), 0.17 (6H, Si(CH₃)₂), 0.12 (6H, Si(CH₃)₂). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 25 °C) δ 137.07–127.94 (PPh₂), 28.41–27.48 (CH₂ of Cy), 25.46, 25.39, 24.53, 24.30, 23.14 (1 : 2 : 2 : 1 : 1 for CH of Cy), 0.79, 0.05 (2 : 1 for Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CD₂Cl₂, 0.02 M Cr(acac)₃, 25 °C) δ 8.74 (Si(CH₃)₂), 8.28 (Si(CH₃)₂), –66.16, –67.59, –67.76, –67.83, –68.23 (1 : 2 : 1 : 1 : 2); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ 40.26 (dt, *J*_{PRh} = 189 Hz, *J*_{PP} = 37 Hz, Rh–P(*trans* for Cl)), 28.05 (dd, *J*_{PRh} = 140 Hz, *J*_{PP} = 37 Hz, Rh–P(*cis* for Cl)). IR (KBr): 3424, 3048, 2950, 2865, 1437, 1254, 1117, 842, 696, 593 cm^{–1}. MS (FAB) *m/z* : 1789 [M – Cl]⁺.