Supporting information for

**Self-Encapsulation of Homogeneous Catalyst Species into Polymer Gel Leading
to a Facile and Efficient Separation System of Amine Products in the
Ru-Catalyzed Reduction of Carboxamides with Polymethylhydrosiloxane
(PMHS)**

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1. General methods	--- P. S-2
2. Synthesis and ^1H and ^{13}C NMR data of the amides 2a-2e	--- P. S-2
3. General procedure for the reduction of amines with PMHS	--- P. S-4
4. ^1H , ^{13}C NMR and GLC data of the amines 3a-3d	--- P. S-6
5. Photos of Figure 1	--- P. S-7
6. ^{29}Si NMR spectra of PMHS and silicone resin (<i>Ru/Si</i>). (Figure S1)	--- P. S-8
7. IR spectrum of (ACE) $\text{Ru}_3(\text{CO})_7$ 1 (Figure S2)	--- P. S-9
8. IR data of (ACE) $\text{Ru}_3(\text{CO})_6(\text{H})(\text{SiR}_3)$ 1 (Table S1)	--- P. S-9
9. IR data of (trimethylazulene) $\text{Ru}_3(\text{CO})_6(\text{H})(\text{SiMe}_2\text{Ph})$ 1 (Scheme S1)	--- P. S-10
10. IR spectrum of silicone resin (<i>Ru/Si</i>). (Figure S3)	--- P. S-10
11. References	--- p. S-11

General Methods: All reactions were carried out under a nitrogen or argon atmosphere. Solvents were distilled under an inert atmosphere from sodium/benzophenone [tetrahydropyran (THP), diethyl ether (Et₂O), dimethoxyethane (DME), cyclopentyl methyl ether (CPME), toluene] prior to use. Sodium hydride, formic acid and *N*-methylbenzylamine were purchased from Wako Pure Chemical Ind., Ltd. 3-Phenylpropionyl chloride and 3-phenylpropyl bromide were purchased from Tokyo Chemical Industry Co., Ltd. ϵ -Caprolactam was purchased from Yoneyama Chemical Ind., Ltd. Benzoyl chloride and piperidine were purchased from Kishida Chemical Co., Ltd. Polymethylhydrosiloxane (PMHS) was purchased from AZmax Co., Ltd. ¹H, ¹³C, and ²⁹Si NMR spectra were measured on JEOL GSX-270 (270 MHz), Lambda 400 (400 MHz), Lambda 600 (600 MHz) spectrometers. Chemical shifts for ¹H NMR were described in parts per million downfield from tetramethylsilane as an internal standard (δ = 0) in CDCl₃, unless otherwise noted. Chemical shifts for ¹³C NMR were expressed in parts per million in CDCl₃ as an internal standard (δ = 77.1), unless otherwise noted. Chemical shifts for ²⁹Si NMR were described in parts per million downfield from tetramethylsilane as an external standard. IR spectra were measured on a JASCO FT/IR-550 spectrometer. Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F₂₅₄, layer thickness 0.25 and 0.2 mm, respectively). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. ($\mu_3, \eta^2, \eta^3, \eta^5$ -acenaphthylene)Ru₃(CO)₇ (**1**) was prepared by the method reported previously.¹

Synthesis of Carboxamides.

***N,N*-Dimethyl-3-phenylpropionamide (2a).** This compound was prepared from dihydrocinnamoyl chloride (5 mL, 33.8 mmol) and dimethylamine (large excess) in the presence of triethylamine (11.7 mL, 84.5 mmol) in Et₂O (85 mL). Purification by vacuum distillation (108 °C/2 Torr) gave **2a** in 93% yield. ¹H NMR (600 MHz, CDCl₃) δ : 2.62 (t, *J* = 8.2 Hz, 2H), 2.93 (s, 3H), 2.95 (s, 3H), 2.97 (t, *J* = 8.2 Hz, 2H), 7.18-7.24 (m, 3H), 7.31 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ : 31.4, 35.3, 35.4, 37.1, 126.1, 128.40, 128.44, 141.5, 172.2.

1-(3-Phenylpropionyl)piperidine (2b). This compound was prepared from dihydrocinnamoyl

chloride (5 mL, 33.8 mmol) and piperidine (4 mL, 40.6 mmol) in the presence of triethylamine (11.7 mL, 84.5 mmol) in Et₂O (85 mL). Purification by vacuum distillation (120 °C/0.002 Torr) gave **2b** in 82% yield. ¹H NMR (396 MHz, CDCl₃) δ: 1.44-1.72 (m, 6H), 2.65 (t, *J* = 7.7 Hz, 2H), 3.00 (t, *J* = 8.2 Hz, 2H), 3.36 (t, *J* = 5.3 Hz, 2H), 3.53 (t, *J* = 5.3 Hz, 2H), 7.19-7.28 (m, 3H), 7.31 (m, 2H). ¹³C NMR (99 MHz, CDCl₃) δ: 27.4, 28.5, 26.4, 31.8, 35.3, 42.7, 46.7, 126.1, 128.5, 128.6, 170.4.

1-(3-Phenylpropyl)azepan-2-on (2c). This compound was prepared from ε-caprolactam (2.6 g, 23 mmol) and 3-phenylpropyl bromide (5 g, 25.3 mmol) in the presence of 60% NaH (1.2 g, 30 mmol; pre-washed with *n*-hexane) in THF (60 mL). Purification by vacuum distillation (130 °C/0.002 Torr) gave **2c** in 80% yield. ¹H NMR (396 MHz, CDCl₃) δ: 1.57-1.76 (m, 6H), 1.84 (m, 2H), 2.50 (m, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 3.30 (m, 2H), 3.42 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.27 (dd, *J* = 7.7, 7.3 Hz, 2H). ¹³C NMR (99 MHz, CDCl₃) δ: 23.4, 28.7, 29.7, 29.9, 33.2, 37.3, 48.0, 49.5, 125.8, 128.2, 128.3, 141.7, 175.6.

***N,N*-Dimethylbenzamide (2d).** This compound was prepared from benzoyl chloride (3.9 mL, 33.8 mmol) and dimethylamine (large excess) in the presence of triethylamine (11.7 mL, 84.5 mmol) in Et₂O (85 mL). Purification by recrystallization from Et₂O-hexane gave **2d** in 90% yield. Mp. 44 °C. ¹H NMR (600 MHz, CDCl₃) δ: 2.97 (s, 3H), 3.11 (s, 3H), 7.38-7.41 (m, 5H). ¹³C NMR (150 MHz, CDCl₃) δ: 35.3, 39.5, 127.0, 128.3, 129.4, 136.3, 171.6.

***N*-Benzyl-*N*-methylformamide (2e).** This compound was prepared from *N*-benzylmethylaniline (6 mL, 46.5 mmol) and formic acid (53 mL, 1.39 mol) in toluene (75 mL) under refluxing condition for 6 h. Purification by vacuum distillation (84 °C/0.5 Torr) gave **2e** in 85% yield with a mixture of rotational isomers. **major isomer:** ¹H NMR (600 MHz, CDCl₃) δ: 2.87 (s, 3H), 4.39 (s, 2H), 7.20-7.38 (m, 5H), 8.29 (s, 1H). ¹³C NMR (150 MHz, CDCl₃) δ: 29.4, 53.5, 127.4, 128.2, 128.7, 135.7, 162.7. **minor isomer:** ¹H NMR (600 MHz, CDCl₃) δ: 2.84 (s, 3H), 4.52 (s, 2H), 7.20-7.38 (m, 5H), 8.16 (s, 1H). ¹³C NMR (150 MHz, CDCl₃) δ: 34.0, 47.8, 127.6, 128.1, 128.9, 136.0, 162.6.

General Procedure for the Reduction of Carboxamide with PMHS Catalyzed by 1.

i) **Solvent Effects in the Reaction of 2a.** To a solution of (acenaphthylene)Ru₃(CO)₇ **1** (6.3 mg, 0.01 mmol) in the solvent **A** in Table S1 (0.5 mL) was added PMHS (0.3 mL, Si-H = 4.4 mmol), and the mixture was stirred at ambient temperature for 30 min. The initial dark orange color of the solution gradually turned to light orange. Then, *N,N*-dimethyl-3-phenylpropionamide **2a** (170 μ L, 1.0 mmol) was added and the solution was stirred at 30 °C. The homogeneous solution turns to gel after 1 h. After it was allowed to stand for 15 h, the solvent was removed *in vacuo* (5 Torr) to form a silicone resin insoluble in common organic solvents. The resultant residue was washed seven times with the solvent **B** in Table S1 (totally 14 mL), then the combined organic solution was evaporated under reduced pressure. The chemical yield of **3a** was determined by ¹H NMR analysis in the presence of anisole as an internal standard. The ruthenium content in the obtained amine **3a** was determined by ICP mass analysis: **3a** obtained by the above procedure (not distilled) was dissolved in an aqueous solution of HCl, and the concentration of HCl was adjusted to 5 x 10⁻³ wt%. The amine content in this solution was 6.2 x 10⁻³ mol/L. The measurement was performed using this solution. The ruthenium content was calibrated with a commercially available standard reagent (ACROS: ruthenium atomic absorption standard solution, 1 mg/mL Ru in 5% HCl); five standard solutions, of which Ru concentration is in a range from 5ppb to 200ppb, were used for calibration.

Table S1. Reduction of 2a using PMHS.

entry	solvent		3a	
	A (reaction)	B (extraction)	yield (%)	Ru (ppm)
1	THP	Et ₂ O	88	15
2	Et ₂ O	Et ₂ O	82	28
3	DME	Et ₂ O	87	43
4	CPME	Et ₂ O	94	42
5	toluene	Et ₂ O	95	18
6	THP	hexane	84	16
7	THP	toluene	82	17

ii) The Reduction of 2a-2e in Which the Chemical Yield was Determined by ^1H NMR. *The experimental procedure shown in Table 1, entry 1 is described as a representative:* To a solution of (acenaphthylene) $\text{Ru}_3(\text{CO})_7$ **1** (32.1 mg, 0.05 mmol) in THP (2.5 mL) was added PMHS (1.45 mL, Si-H = 22.0 mmol), and the mixture was stirred at ambient temperature for 30 min. The initial dark orange color of the solution gradually turned to light orange. Then, *N,N*-dimethyl-3-phenylpropionamide **2a** (850 μL , 5.0 mmol) was added and the solution was stirred at 30 $^\circ\text{C}$. The homogeneous solution turns to gel after 1 h. After it was allowed to stand for 15 h, the solvent was removed *in vacuo* (5 Torr) to form a silicone resin insoluble in common organic solvents. The resultant residue was washed seven times with ether (totally 70 mL), then the combined organic solution was evaporated under reduced pressure. Addition of anisole (1 mmol) to the crude product as an internal standard was followed by ^1H NMR analysis. The yield was determined by comparison of integral values of the product and the internal standard. In similar manners, the reduction of **2b-e** was performed.

iii) Isolation by Distillation in the Reduction of 2a-2e. *The experimental procedure shown in Table 1, entry 1 is described as a representative:* To a solution of (acenaphthylene) $\text{Ru}_3(\text{CO})_7$ **1** (32.1 mg, 0.05 mmol) in THP (2.5 mL) was added PMHS (1.45 mL, Si-H = 22.0 mmol), and the mixture was stirred at ambient temperature for 30 min. The initial dark orange color of the solution gradually turned to light orange. Then, *N,N*-dimethyl-3-phenylpropionamide **2a** (850 μL , 5.0 mmol) was added and the solution was stirred at 30 $^\circ\text{C}$. The homogeneous solution turns to gel after 1 h. After it was allowed to stand for 15 h, the solvent was removed *in vacuo* (5 Torr) to form a silicone resin insoluble in common organic solvents. The resultant residue was washed seven times with ether (totally 70 mL), then the combined organic solution was evaporated under reduced pressure. Purification of the crude amine by distillation at 60 $^\circ\text{C}$ (2.3 Torr) gave *N,N*-dimethyl-3-phenylpropylamine **3a** in 79% yield: the purity of the product was determined by capillary GLC analysis. In similar manners, the reduction of **2b-e** was performed.

iv) Reduction of 2a Using the Recovered *Ru/Si*. To a suspension of recovered *Ru/Si* (1 mol% of Ru species) in THP (0.5 mL) was added PMHS (0.24 mL, Si-H = 3.3 mmol), and this mixture was

stirred at ambient temperature for 30 min. Then, amide **2a** (170 μ L, 1.0 mmol) was added, and this mixture was stirred at 30 $^{\circ}$ C. After it was allowed to stand for 15 h, the reaction mixture set to gel. The solvent was removed *in vacuo* (5 Torr) to form a silicone resin insoluble in common organic solvents. The resultant residue was washed ten times with ether (totally 20 mL), then the combined organic solution was evaporated under reduced pressure. Chemical yield of **3a** was determined by ^1H NMR analysis using anisole as an internal standard (75% yield).

^1H , ^{13}C NMR and GLC Data of the Amines 3a-3d.

***N,N*-Dimethyl-3-phenylpropylamine (3a).** ^1H NMR (600 MHz, CDCl_3) δ : 1.81 (tt, $J = 7.8, 7.5$ Hz, 2H), 2.24 (s, 6H), 2.31 (t, $J = 7.5$ Hz, 2H), 2.65 (t, $J = 7.8$ Hz, 2H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.20 (d, $J = 7.1$ Hz, 2H), 7.29 (dd, $J = 7.6, 7.1$ Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ : 29.5, 33.7, 45.5, 59.3, 125.7, 128.3, 128.4, 142.3. TC-WAX; 0.25 mm x 30 m, column temperature 120 $^{\circ}$ C, detection FID, $t_{\text{R}} = 16.1$ min.

1-(3-Phenylpropyl)piperidine (3b). ^1H NMR (396 MHz, CDCl_3) δ : 1.44 (m, 2H), 1.60 (m, 4H), 1.84 (tt, $J = 7.7, 6.3$ Hz, 2H), 2.29-2.45 (m, 6H), 2.63 (t, $J = 7.7$ Hz, 2H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.19 (d, $J = 7.3$ Hz, 2H), 7.27 (t, $J = 7.3$ Hz, 2H). ^{13}C NMR (99 MHz, CDCl_3) δ : 24.4, 25.9, 28.5, 33.7, 54.4, 58.3, 125.5, 128.0, 128.2, 142.1. TC-WAX; 0.25 mm x 30 m, column temperature 200 $^{\circ}$ C, detection FID, $t_{\text{R}} = 9.4$ min.

1-(3-Phenylpropyl)azepane (3c). ^1H NMR (396 MHz, CDCl_3) δ : 1.55-1.71 (m, 8H), 1.81 (tt, $J = 7.5, 6.3$ Hz, 2H), 2.51 (t, $J = 7.5$ Hz, 2H), 2.57-2.70 (m, 6H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.20 (d, $J = 7.7$ Hz, 2H), 7.28 (dd, $J = 7.7, 7.2$ Hz, 2H). ^{13}C NMR (99 MHz, CDCl_3) δ : 26.9, 28.1, 29.4, 33.6, 55.4, 57.6, 125.5, 128.1, 128.3, 142.4. TC-WAX; 0.25 mm x 30 m, column temperature 250 $^{\circ}$ C, detection FID, $t_{\text{R}} = 7.0$ min.

***N,N*-Dimethyl-benzylamine (3d).** ^1H NMR (600 MHz, CDCl_3) δ : 2.24 (s, 6H), 3.42 (s, 2H), 7.24-7.34 (m, 5H). ^{13}C NMR (150 MHz, CDCl_3) δ : 45.4, 64.4, 127.0, 128.2, 129.1, 138.9. TC-WAX; 0.25 mm x 30 m, column temperature 150 $^{\circ}$ C, detection FID, $t_{\text{R}} = 5.4$ min.

Photos of Figure 1.

Step A

Step B

Step C

Step D

After Et₂O extraction

Silicon resin "Ru/Si"

^{29}Si NMR (CP/MAS: 5000 Hz) of PMHS and Silocon Resin (*Ru/Si*).

In Figure S1 are illustrated the ^{29}Si NMR spectra of PMHS (DEPT, $J = 11$ Hz) and silicone resin (*Ru/Si*) (CP/MAS, 5000 Hz). The spectrum of PMHS (i) showed two signals at δ 10.1 ($-\text{OSiMe}_3$) and -34.3 ppm ($-\text{OSi(H)Me}-$). In contrast, four signals (**A~D**) at δ 10.4, -35.0 , -56.5 and -64.8 ppm appeared in the spectrum of silicone resin (ii). Comparing to the reported data of siloxane polymers,² these signals were assignable to the terminal $-\text{OSiMe}_3$ (**A**), $-\text{OSi(H)Me}-$ (**B**), *Si* in the trisiloxane ring (**C**), and $-\text{OSiMe(O-)}_2$ (**D**), respectively. Similar results of cross-linked silicone were reported for the siloxane-stabilized Pd nanoclusters prepared by the reaction of PMHS and Pd(OAc)_2 under air.³

Figure S1. ^{29}Si NMR spectra of PMHS (DEPT; $J = 11$ Hz) and silicone resin (CP/MAS; 5000 Hz).

IR (KBr) Spectra of (ACE)Ru₃(CO)₇ **1**, Oxidative Adducts of Triruthenium Complexes, and Silicone Resin (Ru/Si).

As reported previously, crystallography and NMR spectroscopy revealed existence of six terminal and one bridging CO ligands in **1**. Figure S2 showed the IR (KBr) spectrum of (μ₃,η²,η³,η⁵-acenaphthylene)Ru₃(CO)₇ **1**. The absorptions appeared at ν 2034, 1986 and 1944 cm⁻¹ is assignable to the terminal CO ligands, whereas the bridging CO gave the absorption at ν 1757 cm⁻¹.

Figure S2. IR (KBr) spectrum of (ACE)Ru₃(CO)₇ **1**: *terminal CO*: ν 2034, 1986, 1944 cm⁻¹; *bridging CO*: ν 1757 cm⁻¹.

The reaction of **1** with trialkylsilanes (R₃SiH) afforded the oxidative adducts, (μ₃,η²,η³,η⁵-acenaphthylene)Ru₃(CO)₆(H)(SiR₃) complexes (**4a**: R₃ = Me₂Ph, **4b**: R₃ = Et₃, **4c**: R₃ = Me₂Bn). These complexes contain a Ru-Si bond, and all of the CO ligands are in the terminal coordination mode (no bridging CO was observed) as reported previously.⁴ The IR (KBr) spectra of **4a-c** showed four to six absorptions in a range of ν 1924-2033 cm⁻¹ (Table S2).⁴

Table S2. IR absorptions of the oxidative adducts **4a-c**.

complex	IR ν _{CO} (cm ⁻¹)
4a (R ₃ Si = SiMe ₂ Ph)	2032, 1999, 1970, 1934
4b (R ₃ Si = SiEt ₃)	2030, 1998, 1968, 1952, 1924
4c (R ₃ Si = SiMe ₂ Bn)	2033, 1993, 1975, 1960, 1950, 1924

An azulene analogue of **1**, (μ_3 - η -4,6,8-trimethylazulene)Ru₃(CO)₇, also underwent the oxidative addition of a Si-H bond of Me₂PhSiH as shown in Scheme S1.⁵ The X-ray diffraction study showed that the product has a Ru-Si bond and six terminal CO ligands. Thus, characteristic absorptions in a range of ν 1911-2048 cm⁻¹ due to the terminal CO ligands are observed in its IR spectrum.⁵

Scheme S1. Reaction of (μ_3 - η -4,6,8-trimethylazulene)Ru₃(CO)₇ **1** with Me₂PhSi-H. IR (KBr): *terminal CO*: ν 2048, 2023, 1972, 1941, 1911 cm⁻¹.

The IR (KBr) spectrum of the silicon resin (**Ru/Si**) obtained in the reaction of carboxamide **2a** and PMHS catalyzed by **1** (10 mol%) is very similar to those of the oxidative adducts described above. In the IR spectrum of **Ru/Si**, a broad band appeared from 2118 to 1895 cm⁻¹, in which two peak tops are observed at ν 2018 and 1966 cm⁻¹ besides the Si-H absorption of the PMHS (ν 2174 cm⁻¹). The broad signal having two peak tops are assignable to the absorptions due to the terminal CO ligands in the Ru cluster.

Figure S3. IR (KBr) spectrum of silicon resin (**Ru/Si**). *CO*: ν 2018, 1966 cm⁻¹; *Si-H* (PMHS): ν 2174 cm⁻¹.

These three IR data indicate that the ruthenium species similar to the oxidative adducts described in the first two reactions would be included in the silicone resin ***Ru/Si***. The right orange color of ***Ru/S*** is typical for triruthenium carbonyl clusters, whereas existence of triruthenium species is supported by the fact that no product derived from the acenaphthylene ligand in **1** was recovered from the reaction mixture. Since the acenaphthylene ligand contributes to keep the triruthenium framework by a bridging ligand in the face-capping mode, no product derived from the acenaphthylene ligand suggests no cluster fragmentation. Although further detailed investigations for the analysis of ***Ru/Si*** are required, we consider from the above results that the oxidative addition of the triruthenium species to a Si-H bond in PMHS would take part in immobilizing the ruthenium species to the polymer chain of PMHS by a Ru-Si bond.

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