

Supplementary Information

Catalytic hydrosilylation by immobilized Co-terpyridine complex activated by inorganic salts and its application to flow reactor

Katsuaki Kobayashi, Norihisa Fukaya, Hiroshi Nakawaza

General information

^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded using a JEOL JNM-AL 400 spectrometer. The residual peaks of the solvent or TMS were used as internal standards. GC analyses were carried out using a Shimadzu GC-2014 equipped with a DB-1 (Agilent, 30 m, 0.25 mm ID, 0.25 μm) capillary column. The product yields were determined based on the calibration curve of each authentic sample. Continuous flow experiment was performed using EYLA FLOWREACTOR MCR-1000 which was connected to a fraction collector, EYELA DC-1500. The mixture of substrates was supplied to the reactor through the pump unit, EYELA EUI-22.

The energy-dispersive X-ray fluorescence spectrometer (EDXRF) measurement was carried out using a Shimadzu EDX-800HS spectrometer. Elemental analysis measurement of carbon and nitrogen content was conducted using a PerkinElmer 2400II instrument. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed using an Agilent ICP 8800.

Materials

All other reagents were purchased from commercial sources and used as received. Hydrosilylated products **3**,¹ **4**,² **5**,³ **6**,⁴ **7**,¹ **8**,⁵ **9**⁵ and **10**⁵ were synthesized as authentic samples according to the literatures.

Characterization of Co(tpy)Br₂@SiO₂

The content of Co and Br in the **Co(tpy)Br₂@SiO₂** catalyst was analyzed by EDXRF measurement with accelerating voltage of 15 kV, while the content of C and N in the tpy ligand unit in catalyst was determined by elemental analysis to disclose the overall elemental composition of **Co(tpy)Br₂@SiO₂**.

Study on detachment of the Co complex from the silica gel

2.5 mL of nitric acid was added to the products of hydrosilylation reaction of 1-octene and Ph₂SiH₂ using **Co(tpy)Br₂@SiO₂** catalyst, then all organic compounds were decomposed by microwave irradiation. 0.25 mL of hydrofluoric acid was added to the resulting sample to dissolve the metallic components, and then the mixture was diluted with water to 25 mL. The amount of Co in the resulting aqueous solution was determined by ICP-MS analysis. The content of Co in the resulting aqueous solution was lower than the detection limit of ICP-MS (0.5 µg/g).

Hydrosilylation by various amount of Co(tpy)Br₂@SiO₂ activated by K₂CO₃.

Hydrosilylation catalyzed by various amount of **Co(tpy)Br₂@SiO₂** was conducted in the presence of 2.5 mol% K₂CO₃.

Table S1 Hydrosilylation by various amount of **Co(tpy)Br₂@SiO₂** activated by K₂CO₃.

Entry	amount of Co(tpy)Br₂@SiO₂	olefin	hydrosilane	Yield (%) ^a
1	10 mg	styrene	(EtO) ₃ SiH	1 : 90
2	20 mg	styrene	(EtO) ₃ SiH	1 : 89
3	30 mg	styrene	(EtO) ₃ SiH	1 : 89
4	40 mg	styrene	(EtO) ₃ SiH	1 : 91
5	50 mg	styrene	(EtO) ₃ SiH	1 : 92
6	10 mg	1-octene	Ph ₂ SiH ₂	2l : 39 (2b : 1.6)
7	20 mg	1-octene	Ph ₂ SiH ₂	2l : 57 (2b : 2.8)
8	30 mg	1-octene	Ph ₂ SiH ₂	2l : 67 (2b : 2.1)
9	40 mg	1-octene	Ph ₂ SiH ₂	2l : 72 (2b : 3.3)
10	50 mg	1-octene	Ph ₂ SiH ₂	2l : 88 (2b : 2.1)

^aDetermined by GC.

Hydrosilylation by $\text{Co}(\text{tpy})\text{Br}_2@\text{SiO}_2/\text{K}_2\text{CO}_3$ in various solvents.

Hydrosilylation of 1-octene with Ph_2SiH_2 catalyzed by $\text{Co}(\text{tpy})\text{Br}_2@\text{SiO}_2/\text{K}_2\text{CO}_3$ in the presence of various solvents was conducted. Toluene, THF, acetonitrile, and MeOH were selected as a solvent (Eq. 3).

$\text{Co}(\text{tpy})\text{Br}_2@\text{SiO}_2$ (50 mg) and K_2CO_3 (19 mg, 2.5 mol%) were placed in a Schlenk tube. The air in the tube was replaced with N_2 . 1-Octene (0.85 mL, 5.4 mmol), Ph_2SiH_2 (1.0 mL, 5.4 mmol), and a solvent (1.0 mL) were added to the tube. The suspension was heated at 100 °C and stirred for 24 h. Then, the solution was cooled to room temperature. $\text{Co}(\text{tpy})\text{Br}_2@\text{SiO}_2$ and K_2CO_3 were separated by centrifugation and the supernatant was analyzed by GC. Results are summarized in Table S4. Toluene and THF were suitable solvents (Table S2, entries 1 and 2). Especially with THF, the total yield of products (**2I** + **2b**) was 99%. In contrast, when acetonitrile and MeOH were used, the hydrosilylated products were not obtained at all (entries 3 and 4).

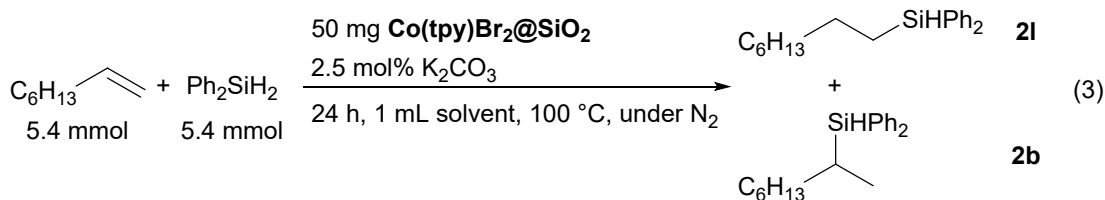


Table S2 Hydrosilylation of 1-octene with Ph₂SiH₂ by Co(tpy)Br₂@SiO₂/K₂CO₃ in the presence of various solvents.

entry	solvent	yield ^a
1	toluene	2l : 81% (2b : 2.6%)
2	THF	2l : 97% (2b : 2.6%)
3	acetonitrile	N.D. ^b
4	MeOH	N.D. ^b

^aDetermined by GC. ^bNot detected.

Hydrosilylation by Co(tpy)Br₂@SiO₂/K₂CO₃ through the continuous flow reactor.

500 mg Co(tpy)Br₂@SiO₂ and 200 mg K₂CO₃ were mixed and packed into a stainless-steel tubular reactor (5 mm internal diameter, 100 mm length) in air. The tube reactor was attached with two filters at the both ends, and was set into the temperature controller. Reaction temperature was dependent on the solvent (toluene: 100 °C, THF: 60 °C). Substrate solution was degassed by N₂ bubbling for 30 min. Flow rate of the substrate mixture was 0.03 mL/min, which continued for 24 h. The product was fractionated at hourly intervals using a fraction collector. Each fraction was analyzed by GC.

References

1. M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.*, 2014, **356**, 584-590.
2. B. Raya, S. Jing, V. Balasanthiran and T. V. RajanBabu, *ACS Catal.*, 2017, **7**, 2275-2283.
3. D. Taguchi, K. Kobayashi, T. Moriuchi and H. Nakazawa, *Bull. Chem. Soc. Jpn.*, 2020, **93**, 1086-1094.
4. S. Gutiérrez-Tarriño, P. Concepción and P. Oña-Burgos, *Eur. J. Inorg. Chem.*, 2018, 4867-4874.
5. K. Kobayashi and H. Nakazawa, *Dalton Trans.*, 2022, **51**, 18685-18692.