Dendrimer *N*-heterocyclic carbene complexes with rhodium(I) at the core†

Tetsuaki Fujihara, Yasushi Obora, Makoto Tokunaga, Hiromichi Sato and Yasushi Tsuji*

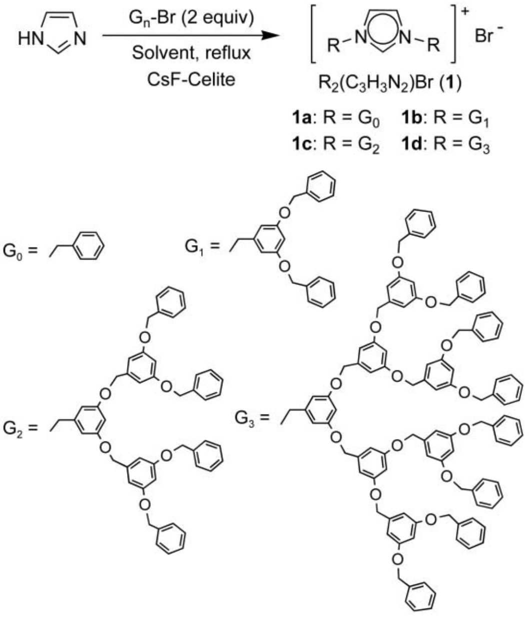
Received (in Cambridge, UK) 17th May 2005, Accepted 27th July 2005
First published as an Advance Article on the web 19th August 2005
DOI: 10.1039/b506927k

Novel dendrimer *N*-heterocyclic carbene complexes with rhodium(I) located at the core were synthesized, and a positive dendrimer effect was found in the hydrosilylation of ketones catalyzed by them.

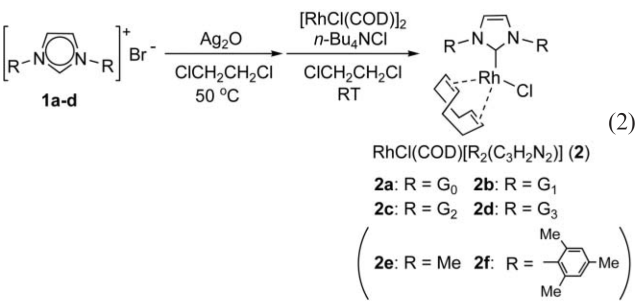
Dendrimers are intriguing molecules owing to the distinct physical and chemical properties caused by their well-defined hyperbranched frameworks.[1] In particular, the development of organometallic dendrimers is imperative, since the dendritic moieties will bring about unique catalytic environments to realize novel catalytic performance. Thus, a number of organometallic dendrimers with catalytic sites at either their core or periphery have been reported.[2] Among them however, examples of the positive dendrimer effect, in which the dendrimers play active roles in enhancing catalytic ability, have been limited.[3] We have recently reported dendrimer ligands with a pyridine[4] or phosphine[5] functionality at their core, and found that palladium acetates with the dendrimer pyridine ligands successfully suppress Pd black formation in the air oxidation of alcohols.[4]

N-Heterocyclic carbene (NHC) ligands have attracted considerable attention in both homogeneous catalysis and organometallic chemistry.[6] Stronger bonds to the metals associated with NHC ligands, compared to conventional ligands such as phosphines, diminish their dissociation from metal centers. As for dendrimer NHC complexes, there is the only one precedent,[7] a complex with four ruthenium metal atoms located at the periphery of a low generation dendrimer. The complex worked as a recyclable metathesis catalyst, but the dendrimer effect for different generations was not explored. In the present study, we synthesized a series of dendrimer (zeroth to the third generations: G_0–G_3) NHC complexes with rhodium(I) at the core, and employed the complexes as catalysts for the hydrosilylation of ketones. In the catalytic reaction, the evident positive dendrimer effect using the dendrimer NHC complexes was observed for the first time; the yields of the products increased with increasing dendrimer generation.

A series of imidazolium salts bearing Fréchet-type polybenzyl ether dendrimers (G_0–G_3):[8] $(G_0)_2(C_3H_3N_2)Br$ (**1a**),[9] $(G_1)_2(C_3H_3N_2)Br$ (**1b**), $(G_2)_2(C_3H_3N_2)Br$ (**1c**) and $(G_3)_2(C_3H_3N_2)Br$ (**1d**) were synthesized[10] by the reaction of imidazole with 2 equiv. of the corresponding dendrimer bromides G_n–Br (n = 0, 1, 2 and 3)[8] (eqn. (1)) and the new compounds (**1b–d**) fully characterized. The rhodium(I) complexes with dendrimer NHC ligands: $RhCl(COD)[(G_0)_2(C_3H_2N_2)]$ (**2a**),[11] $RhCl(COD)[(G_1)_2(C_3H_2N_2)]$ (**2b**), $RhCl(COD)[(G_2)_2(C_3H_2N_2)]$ (**2c**) and $RhCl(COD)[(G_3)_2(C_3H_2N_2)]$ (**2d**) (COD = 1,5-cyclooctadiene) were synthesized in good yields (74, 72, 73 and 71% respectively) by the carbene-transfer method[12] using the NHC–Ag species derived from **1a–d** (eqn. (2)). The newly isolated complexes (**2b-d**) were fully characterized, their FD-MS spectra showing molecular ion peaks at m/z = 918, 1762 and 3466 respectively. In the $^{13}C\{^1H\}$ NMR spectra of **2b-d**, the coordinated carbene carbons appeared as sharp doublets at 183.3 ppm ($J_{Rh–C}$ = 50.8 Hz), 183.4 ppm (50.7 Hz) and 183.3 ppm (47.6 Hz) respectively. **2a–d** were also highly stable both to air and moisture in the solid state. The ^1H NMR spectra of **2a–d** measured in $CDCl_3$ did not change over two weeks, indicating they are also considerably stable in solution.



(1)



(2)

Catalysis Research Center and Division of Chemistry, Graduate School of Science, Hokkaido University, CREST, Japan Science and Technology Agency (JST), Sapporo, 001-0021, Japan.
E-mail: tsuji@cat.hokudai.ac.jp; Fax: +81-11-706-9156

† Electronic supplementary information (ESI) available: Synthetic methods and analytical data for **1b–1d** and **2b–2d**. See http://dx.doi.org/10.1039/b506927k

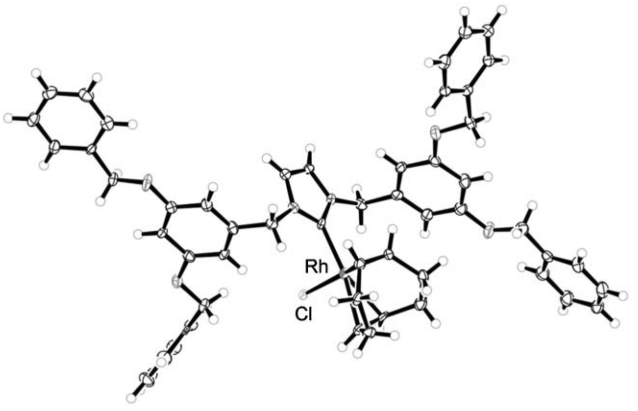


Fig. 1 ORTEP drawing of **2b** with thermal ellipsoids drawn at a 50% probability level.

The molecular structure of **2b** has been successfully determined by X-ray structural analysis (Fig. 1).‡ The rhodium complex is a 2.2 nm-sized molecule and has a distorted square-planar coordination geometry. The Rh–C bond length of **2b** (2.042(4) Å) is similar to those of other Rh–NHC complexes.[13]

The electrochemically active rhodium cores of **2a–d** could be sensitive to an electrode, depending on the dendrimer moiety (G_0–G_3). Therefore, cyclic voltammograms (CV) of these complexes were measured in CH_2Cl_2 with n-Bu_4NClO_4 as a supporting electrolyte.[14] The G_0 complex (**2a**) exhibited the irreversible oxidation process that can be assigned to a metal-centered oxidation peak (Fig. 2(a)). The G_1 and G_2 complexes (**2b** and **2c** respectively) also showed similar irreversible oxidation peaks (Fig. 2(b) and 2(c)), although the peak height of **2c** decreased noticeably compared with **2b**. Finally, the G_3 complex (**2d**) did not exhibit a distinguishable oxidation peak (Fig. 2(d)). These different electrochemical responses suggest that electron transfer from the Rh core to the electrode was hampered by the large dendritic structures.

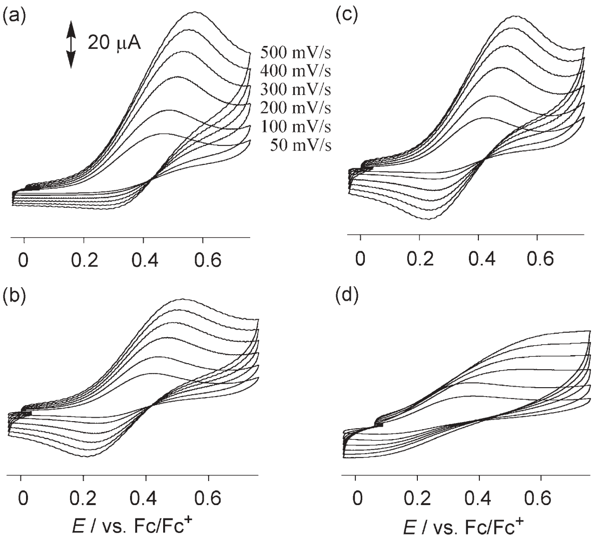


Fig. 2 Cyclic voltammograms of (a) **2a**, (b) **2b**, (c) **2c** and (d) **2d** in CH_2Cl_2 (1×10^{-3} mol dm^{-3}) containing n-Bu_4NClO_4 (0.1 mol dm^{-3}) at varying scan rate (50, 100, 200, 300, 400 and 500 mV s^{-1}).

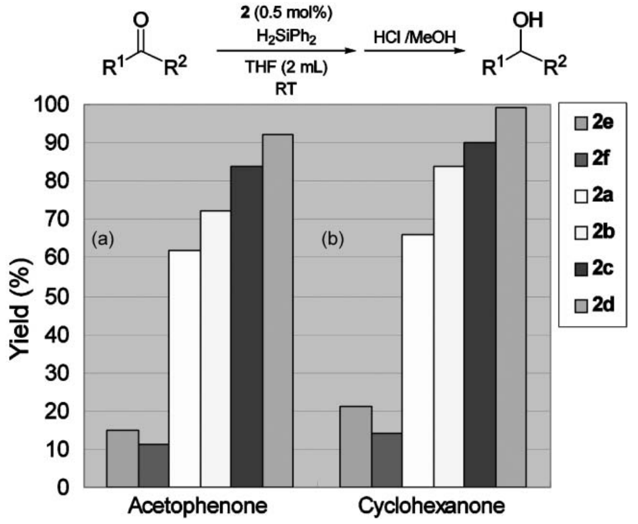


Fig. 3 Hydrosilylation of ketones with H_2SiPh_2 catalyzed by **2**. (a) Yields of 1-phenylethanol from actophenone after 20 h: 15% with **2e** as the catalyst, 11% with **2f**, 62% with **2a**, 72% with **2b**, 84% with **2c** and 92% with **2d**. (b) Yields of cyclohexanol from cyclohexanone after 3h: 21% with **2e** as the catalyst, 14% with **2f**, 66% with **2a**, 84% with **2b**, 90% with **2c** and 99% with **2d**.

Catalytic performance as well as the dendrimer effect of **2a–d** were examined by the hydrosilylation of ketones.[11,15] $RhCl(COD)[Me_2(C_3H_2N_2)]$[13a] (**2e**) and $RhCl(COD)[(Mes)_2(C_3H_2N_2)]$[16] (**2f**) (see eqn. (2)) were also employed as catalysts for comparison. The reaction was carried out in the presence of a catalytic amount (0.5 mol%) of **2** and diphenylsilane (1.2 equiv.) in THF.§ In the hydrosilylation of acetophenone, **2e** and **2f** showed only low catalytic activities; yields of 1-phenylethanol after 20 h were 15% and 11% respectively (Fig. 3(a)). The catalytic activity was enhanced by introducing G_0–G_3 substituents onto the NHC ligand; the product was obtained in 62, 72, 84 and 92% yields with **2a–d** as the catalyst respectively. It is noteworthy that the yields gradually increased with increasing dendrimer generation. This positive dendrimer effect was also found in benzene and dichloromethane solvents. The same behavior was observed in the reaction of cyclohexanone (Fig. 3(b)). The rhodium–NHC complexes **2e** and **2f** afforded cyclohexanol after 3 h in only 21 and 14% yields respectively, whereas **2a–d** provided the product in 66, 84, 90 and 99% yields respectively. Again, the yield of the product increased with increasing dendrimer generation. Aromatic rings of G_0–G_3 might interact with the rhodium metal and cause the positive dendrimer effect, as suggested by the lowest energy conformation of **1d** calculated by CONFLEX5[17]/MMFF94s[18] (Fig. 4). Interestingly, the dendrimer effect was influenced by the concentration of the catalytic reaction. When the hydrosilylation of acetophenone was carried out under more dilute conditions (0.29 mol dm^{-3}, *cf.* 0.41 mol dm^{-3} in Fig. 3), the yield of 1-phenylethanol decreased considerably to 44% after 46 h (*cf.* 62% after 20 h in Fig. 3) with the lower generation (G_0) catalyst (**2a**), while with the higher generation (G_1–G_3) catalysts (**2b–2d**), the product yields (70, 83 and 89% yields after 46 h respectively) were almost comparable to those in Fig. 3 (72, 84 and 92% respectively).

In conclusion, a series of novel dendrimer NHC complexes with rhodium(I) located at the core (**2a–d**) were synthesized and

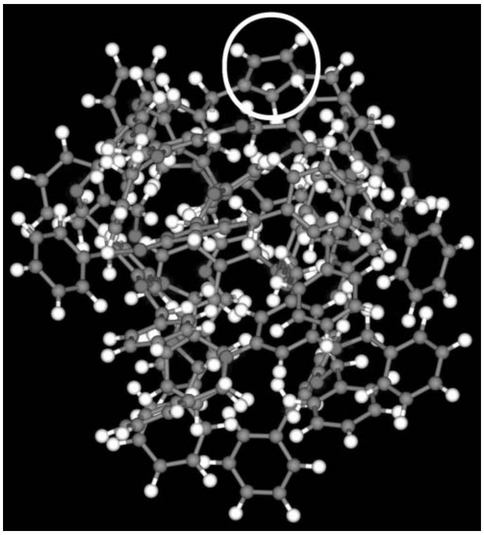


Fig. 4 The lowest energy conformation of **1d**, calculated by CONFLEX5/MMFF94s. A white circle indicates the $C_3H_3N_2$ ring.

characterized. The positive dendrimer effect was evident in the hydrosilylation reactions of ketones they catalyzed. The yields of the corresponding alcohols increased with increasing dendrimer generation. Further studies on the mechanism of the dendrimer effect and applications to other catalytic reactions are currently under way.

Notes and references

‡ Crystal data for $\mathrm{RhCl(COD)[(G_1)_2(C_3H_2N_2)]\cdot CH_2Cl_2}$ (**2b**·CH_2Cl_2): $C_{54}H_{54}Cl_3N_2O_4Rh$, M = 1004.30, T = 113 K, triclinic, space group $P\bar{1}$ (no. 2), a = 10.936(8), b = 12.458(9), c = 17.56(1) Å, α = 98.94(2), β = 101.480(10), γ = 91.966(11) °, U = 2310(3) Å^3, Z = 2, μ(Mo-Kα) = 5.92 cm^{-1}, observed reflections 12898 ($I > 3\sigma(I)$), $R1$ = 0.062, $wR2$ = 0.159. GOF = 1.013. CCDC 269270. See http://dx.doi.org/10.1039/b506927k for crystallographic data in CIF or other electronic format.

§ General procedure for hydrosilylation: A rhodium catalyst **2** (0.005 mmol) was placed in a 10 cm^3 Schlenk tube under an Ar atmosphere. Anhydrous THF (2.0 cm^3, or 3.0 cm^3 for the diluted conditions), acetophenone (1 mmol) and tridecane as an internal standard (0.25 mmol) were added by syringe under an Ar flow. After the reaction mixture had been stirred for 5 min, diphenylsilane (1.2 mmol) was added *via* a syringe. The reaction mixture was stirred at room temperature (22 ± 1 °C) for 20 h (3 h in the case of cyclohexanone). The desilylation was performed with HCl/MeOH (2 mol dm^{-3}, 1 cm^3) and the mixture stirred for 1 h. After neutralization with $NaHCO_3$, the reaction mixture was passed through a short silica gel column. The yield of the product was determined by GC using the internal standard method.

1 (*a*) G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendrimers and Dendrons: Concepts, Syntheses, Applications*, Wiley-VCH, Weinheim, 2001; (*b*) *Dendrimers and Other Dendritic Polymers*, ed. J. M. J. Fréchet and D. A. Tomalia, J. Wiley & Sons, New York, 2001; (*c*) S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2001, **40**, 74.

2 Selected reviews of organometallic dendrimers: (*a*) L. J. Twyman, A. S. H. King and I. K. Martin, *Chem. Soc. Rev.*, 2002, **31**, 69; (*b*) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Angew. Chem., Int. Ed.*, 2001, **40**, 1828; (*c*) D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991 and references cited therein.

3 (*a*) C. Müller, L. J. Ackerman, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.*, 2004, **126**, 14960; (*b*) M. Uyemura and T. Aida, *Chem.–Eur. J.*, 2003, **9**, 3492; (*c*) Y. Ribourdouille, G. D. Engel, M. Richard-Plouet and L. H. Gade, *Chem. Commun.*, 2003, 1228; (*d*) T. Mizugaki, M. Murata, M. Ooe, K. Ebitani and K. Kaneda, *Chem. Commun.*, 2002, 52; (*e*) R. B. Breinbauer and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, 2000, **39**, 3604; (*f*) Q.-H. Fan, Y.-M. Chen, X.-M. Chen, D.-Z. Jiang, F. Xi and A. S. C. Chan, *Chem. Commun.*, 2000, 789.

4 T. Iwasawa, M. Tokunaga, Y. Obora and Y. Tsuji, *J. Am. Chem. Soc.*, 2004, **126**, 6554.

5 B. S. Balaji, Y. Obora, D. Ohara, S. Koide and Y. Tsuji, *Organometallics*, 2001, **20**, 5342.

6 (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*b*) V. César, S. Bellemin-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619; (*c*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39 and references cited therein.

7 S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168.

8 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.

9 K. J. Harlow, A. F. Hill and T. Welton, *Synthesis*, 1996, 697.

10 S. Hayat, Atta-ur-Rahman, M. I. Choudhary, K. M. Khan, W. Schumann and E. Bayer, *Tetrahedron*, 2001, **57**, 9951.

11 R. Rivera and R. H. Crabtree, *J. Mol. Catal. A: Chem.*, 2004, **222**, 59.

12 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972.

13 (*a*) M. V. Baker, S. K. Brayshaw, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2004, **357**, 2841; (*b*) M. T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken and R. Weberskirch, *Organometallics*, 2004, **23**, 4817; (*c*) R. S. Simons, P. Custer, C. A. Tessier and W. J. Youngs, *Organometallics*, 2003, **22**, 1979; (*d*) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree, *Organometallics*, 2003, **22**, 1663.

14 CV studies on organometallic dendrimers: (*a*) M. Kimura, Y. Sugihara, T. Muto, K. Hanabusa, H. Shirai and N. Kobayashi, *Chem.–Eur. J.*, 1999, **5**, 3495; (*b*) C. B. Gorman, B. L. Parkhurst, W. Y. Su and K.-Y. Chen, *J. Am. Chem. Soc.*, 1997, **119**, 1141; (*c*) P. J. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati and E. M. Sanford, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1739.

15 (*a*) W. A. Herrmann, L. J. Goossen, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2805; (*b*) W.-L. Duan, M. Shi and G.-B. Rong, *Chem. Commun.*, 2003, 2916; (*c*) O. Niyomura, M. Tokunaga, Y. Obora, T. Iwasawa and Y. Tsuji, *Angew. Chem., Int. Ed.*, 2003, **42**, 1287.

16 (*a*) P. A. Evans, E. W. Baum, A. N. Fazal and M. Pink, *Chem. Commun.*, 2005, 63; (*b*) A. M. Seayad, K. Selvakumar, M. Ahmed and M. Bellar, *Tetrahedron Lett.*, 2003, **44**, 1679.

17 CONFLEX5: (*a*) H. Goto and E. Osawa, *J. Am. Chem. Soc.*, 1989, **111**, 8950; (*b*) H. Goto and E. Osawa, *J. Chem. Soc., Perkin Trans. 2*, 1993, 187.

18 MMFF94s: (*a*) T. A. Halgren, *J. Comput. Chem.*, 1999, **20**, 720; (*b*) T. A. Halgren, *J. Comput. Chem.*, 1996, **17**, 490.