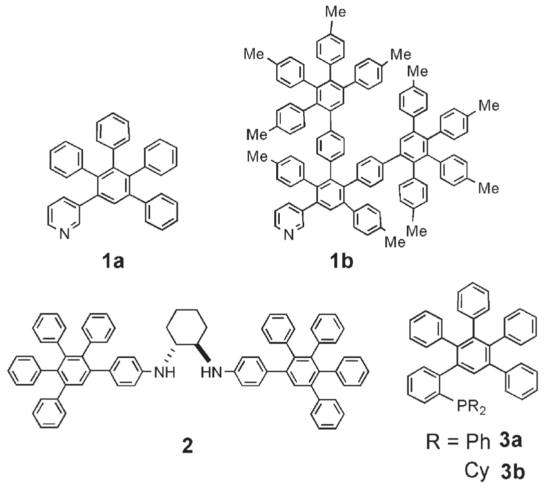
Rhodium(I) complexes with *N*-heterocyclic carbenes bearing a 2,3,4,5-tetraphenylphenyl and its higher dendritic frameworks†

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

Received (in Cambridge, UK) 30th August 2006, Accepted 29th September 2006
First published as an Advance Article on the web 25th October 2006
DOI: 10.1039/b612385f

Novel rhodium(I) complexes with *N*-heterocyclic carbenes bearing a 2,3,4,5-tetraphenylphenyl and its higher dendritic frameworks were synthesized and the complexes were used as catalysts in rhodium-catalyzed hydrosilylation of α,β-unsaturated ketones to show high 1,4-adduct selectivity.

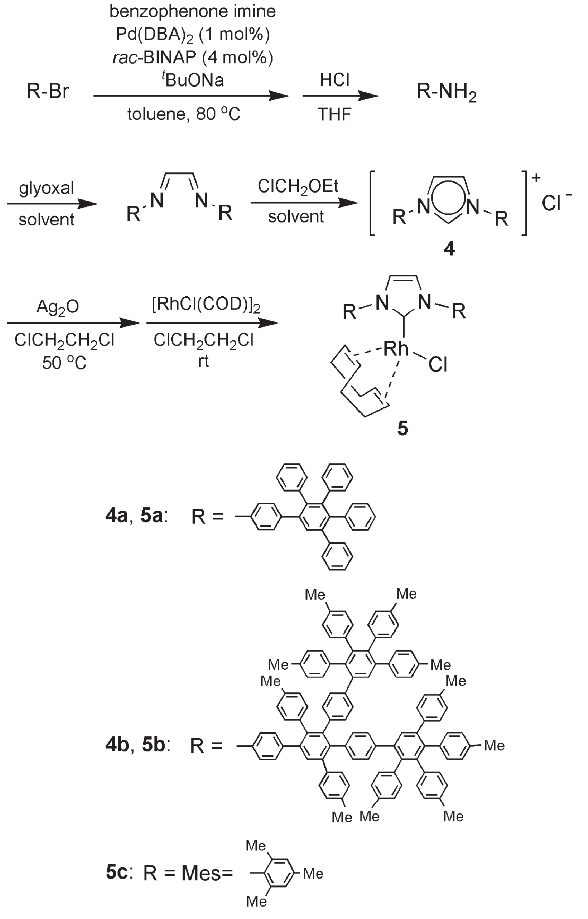
Dendritic frameworks have received considerable attention to develop new materials[1] including catalysts.[2] Among them, a 2,3,4,5-tetraphenylphenyl (TPPh) moiety developed by Müllen and co-workers have been utilized as building blocks for polyphenylene nanomaterials.[3] We are interested in their spatially spread and rigid structures. Palladium acetates with pyridine ligands having a TPPh moiety (**1a**) and its higher dendritic framework (**1b**) successfully suppressed Pd black formation in the air-oxidation of alcohols (Scheme 1).[4] The diamine (**2**) with TPPh groups was effectively employed as a ligand in a palladium-catalyzed kinetic resolution of various biaryl compounds.[5] Recently, we found that the phosphines (**3**) having a TPPh moiety are effective ligands to utilize unactivated aryl chlorides in palladium-catalyzed Suzuki–Miyaura and Mizoroki–Heck reactions.[6]



Scheme 1 Ligands bearing a 2,3,4,5-tetraphenylphenyl (TPPh) moiety.

In this communication, we have selected an *N*-heterocyclic carbene (NHC) as a ligand. A use of NHC would be beneficial because stronger bonds to metals as compared with conventional ligands such as phosphines diminish their dissociation from metal centers.[7] Here, we designed and synthesized novel rhodium(I) complexes with NHC ligands bearing a TPPh and its higher dendritic moieties. These complexes are active catalysts and provide 1,4-adducts predominantly in the hydrosilylation of α,β-unsaturated ketones with Ph_2SiH_2, which has opposite regioselectivity to the one obtained with conventional Rh-phosphine and Rh-NHC catalyst systems.

Imidazolium salts (**4a** and **4b**) having the TPPh and its higher dendritc frameworks were synthesized in three steps *via* the amination with benzophenone imine[5,8,9] followed by the diimine formation[10] (Scheme 2). The dendritic moieties of **4b** and **5b** have



Scheme 2 Synthesis of NHC rhodium(I) complexes.

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, and CREST, Japan Science and Technology Agency (JST), Kyoto 615-8510, Japan and Catalysis Research Center and Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, 001-0021, Japan.
E-mail: ytsuji@scl.kyoto-u.ac.jp; Fax: +81-75-383-2514

† Electronic supplementary information (ESI) available: Experimental procedures and data for characterization of **4** and **5**. See DOI: 10.1039/b612385f

the methyl substituents to ensure good solubility of these materials.[4] The MALDI-TOF-MS spectra of **4a** and **4b** showed peaks at *m*/*z* = 981 ([M-Cl]$^+$) and 2782 ([M-Cl]$^+$), respectively. Rhodium(I) complexes with the corresponding NHC ligands (**5a** and **5b**) were synthesized in good yields (69 and 70%, respectively) by the carbene-transfer method[11] using NHC–Ag species derived from **4a** and **4b** (Scheme 2). The new complexes (**5a** and **5b**) were fully characterized, and their mass spectra showed peaks at *m*/*z* = 1227 (FD-MS: [M]$^+$) and 2992 (MALDI-TOF-MS: [M-Cl]$^+$), respectively. In $^{13}C\{^1H\}$ NMR spectra of **5a** and **5b**, the coordinated carbene carbons appeared with distinct ^{13}C–^{103}Rh couplings at 184.4 ppm ($^1J_{Rh–C}$ = 48.7 Hz) and 184.3 ppm ($^1J_{Rh–C}$ = 47.7 Hz), respectively, indicating their tight coordination to the rhodium atoms in solution.

The molecular structure of **5a** has been successfully determined by X-ray crystal structural analysis (Fig. 1a).‡ It is evident that the TPPh moiety of the NHC ligand spatially spreads out. The structure of **5a** shows that the longest distance between the edge of the two TPPh groups is 2.9 nm. The Rh–C(carbene) bond length of **5a** (2.010(5) Å) is similar to those of other Rh(I)–NHC complexes.[12,13b] As for **5b**, all the trials to obtain single crystals suitable for crystallographic analysis were unsuccessful. Therefore, the optimized structure of **5b** (Fig. 1b) were obtained by ONIOM calculation[14] (B3LYP/LANL2DZ:UFF) using an initial structure based on the X-ray structure of **5a**. As a result, **5b** is a bigger nano-sized complex with the longest distance between the edge of the two dendritic frameworks being 4.9 nm.

As shown in Fig. 1, the complexes **5a** and **5b** have the very unique rigid and spatially spread structures. Thus, catalytic behavior of **5a** and **5b** was intriguing and compared with the representative Rh(I) NHC complex, $RhCl(COD)[(Mes)_2(C_3H_2N_2)]$ (**5c**) (Scheme 2).[13] The hydrosilylation[15] of α,β-unsaturated ketones with Ph_2SiH_2 was carried out in the presence of a catalytic amount (1 mol%) of **5** in CH_2Cl_2 at room temperature (Table 1).§ It is well-established that regioselectivity in the Rh-catalyzed hydrosilylation of α,β-unsaturated ketones was preferentially determined by the nature of silanes employed:[16] use of di- or tri-hydrosilanes such as Ph_2SiH_2 or $PhSiH_3$ lead to 1,2-adducts giving allylic alcohols after the desilylation, whereas mono-hydrosilanes such as Et_3SiH or Me_2PhSiH afford 1,4-adducts giving ketones. The hydrosilylation of 2-cyclohexen-1-one with Ph_2SiH_2 in the presence of **5a** as a catalyst afforded the 1,4-adduct (cyclohexanone) in 91% selectivity with a smaller amount of the 1,2-adduct (2-cyclohexen-1-ol) in 77% total yield after the desilylation (entry 1). The complex **5b** as a catalyst also afforded the 1,4-adduct in 88% selectivity (entry 2). Noteworthy is that these 1,4-selectivities obtained with Ph_2SiH_2 in entries 1 and 2 were totally opposite to one obtained with $RhH(PPh_3)_4$ as a catalyst,[16b] in which only the 1,2-adduct was afforded exclusively. Furthermore, in contrast to **5a** and **5b**, **5c** as a catalyst afforded the 1,2-adduct as a major product in 92% selectivity (entry 3). Thus, the TPPh moieties of **5a** and **5b** play a critical role to reverse the typical regioselectivity associated with the dihydrosilane. Similar effect of the TPPh to reverse the regioselectivity was confirmed in the hydrosilylation of 3-octen-2-one: **5a** and **5b** afforded the 1,4-adduct (2-octanone) in 82 and 81% selectivities, respectively (entries 4 and 5), while **5c** provided the 1,2-adduct (3-octen-2-ol) in 91% selectivity (entry 6). In the hydrosilylation of benzylideneacetone, **5a** and **5b** provided the 1,4-adduct (4-phenyl-2-butanone) in 93 and 100% selectivities, respectively (entries 7 and 8), whereas selectivity of the 1,2-adduct (4-phenyl-3-buten-2-ol) increased considerably by using **5c** as a catalyst (entry 9). This selectivity with **5c** was comparable to that obtained with $RhCl(PPh_3)_3$ as the catalyst.[16a] With 4-methyl-3-penten-2-one having the two substituents at the β-position, **5a** realized the good 1,4-selectivity (entry 10), while **5b** lowered both the regioselectivity and yield of the products (entry 11). The steric bulk associated with the higher dendritic framework of **5b** might affect the selectivity and catalytic activity. In the hydrosilylation of 3-methyl-2-cyclohexen-1-one, even **5a** and **5b** as well as **5c** all provided the high 1,2-selectivities (84–100%), possibly due to significant steric congestion at the β-position (entries 13–15).

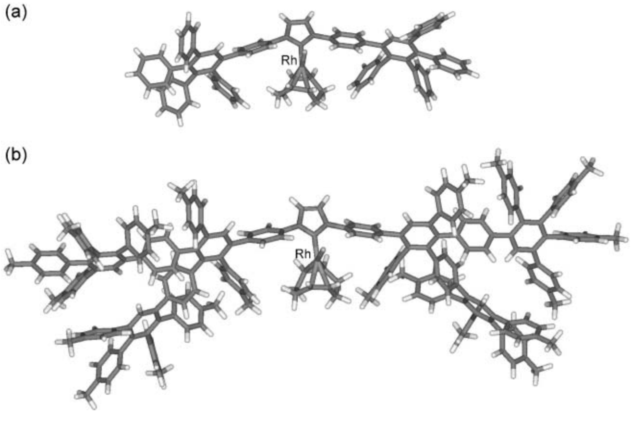
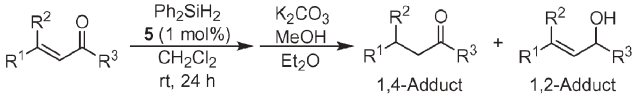
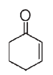
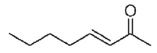
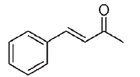
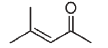
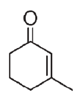


Fig. 1 Molecular structures of **5**. (a) Crystal structure of **5a**. (b) The optimized structure of **5b** calculated by ONIOM method.

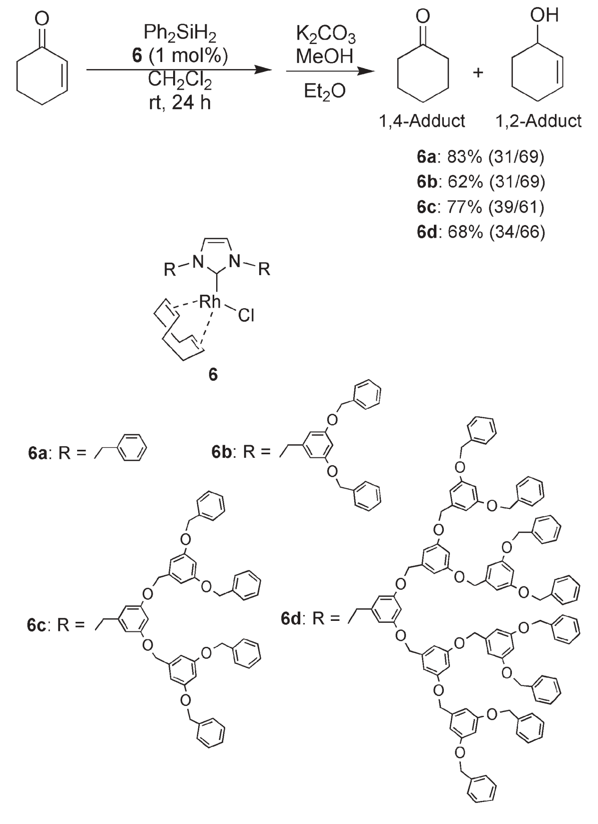
Table 1 Hydrosilylation of α,β-unsaturated ketones catalyzed by $\mathbf{5}^a$



Entry	Substrate	Catalyst	Yield^b/%	Selectivity^b (1,4-/1,2-)
1		**5a**	77	91 / 9
2		**5b**	91	88 / 12
3		**5c**	92	8 / 92
4		**5a**	67	82 / 18
5		**5b**	62	81 / 19
6		**5c**	88	9 / 91
7		**5a**	69	93 / 7
8		**5b**	76	100 / 0
9		**5c**	53	60 / 40
10		**5a**	96	94 / 6
11		**5b**	46	50 / 50
12		**5c**	43	12 / 88
13		**5a**	38	16 / 84
14		**5b**	51	4 / 96
15		**5c**	72	0 / 100

[a] α,β-Unsaturated ketone (1 mmol), Ph_2SiH_2 (1.2 mmol), **5** (0.01 mmol), CH_2Cl_2 (1 cm^3), rt, 24 h. [b] By GC analysis after the desilylation with K_2CO_3–MeOH.

Recently, we have synthesized analogous Rh(I) NHC complexes (**6a–d** in Scheme 3)[17] with very *flexible* dendritic frameworks consisting of the Fréchet-type benzyl ether moieties.[18] We are interested how rigid[4–6] and flexible[17–19] dendritic frameworks



Scheme 3 Hydrosilylation of 2-cyclohexen-1-one catalyzed by flexible dendrimer complexes **6**.

operate in the same hydrosilylation of α,β-unsaturated ketones. In the reaction of 2-cyclohexen-1-one, **6a–d** with a series of dendritic moieties of different generations all afforded the 1,2-adduct mainly in similar selectivities (61–69%, Scheme 3). In contrast to **5a** and **5b** having the rigid moieties, **6a–d** could not change the regioselectivity inherent to Ph$_2$SiH$_2$. These flexible dendrimer moieties tend to fold back around an active site.[17] The rigid and spatially spread structures of **5a** and **5b** might be crucial for causing the 1,4-regioselectivity.

In conclusion, novel rhodium(I) NHC complexes having a TPPh and its higher dendritic frameworks were synthesized and fully characterized. These complexes are efficient catalysts in the hydrosilylation of α,β-unsaturated ketones with Ph$_2$SiH$_2$which has the opposite regioselectivity to the one obtained with conventional Rh-phosphine or Rh–NHC catalysts. Further studies on transition-metal catalysts bearing rigid and flexible dendritic frameworks are under investigation.

Notes and references

‡ Single crystals of $\mathbf{5a}\cdot C_5H_{12}$ suitable for X-ray diffraction study were obtained by diffusion of *n*-pentane into **5a** in CH$_2$Cl$_2$. Crystal data for $\mathbf{5a}\cdot C_5H_{12}$: $C_{88}H_{76}ClN_2Rh$, $M = 1299.9$, $T = 113$ K, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.85(2)$, $b = 20.51(2)$, $c = 25.04(2)$ Å, $\alpha = 79.38(7)$, $\beta = 71.05(9)$, $\gamma = 81.10(10)°$, $U = 7054(1)$ Å^3, $Z = 4$, μ(Mo Kα) = 3.30 cm^{-1}, Unique reflections 31888, Observed reflections 16076 ($I > 3\sigma(I)$), $R1$, $wR2$ = 0.056, 0.164. GOF = 1.01. CCDC 617650. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612385f

§ General procedure for the hydrosilylation (entry 1 in Table 1): A mixture of **5a** (0.01 mmol, 12 mg), CH$_2$Cl$_2$ (1 cm^3), 2-cyclohexen-1-one (1 mmol, 9.7×10^{-2} dm^3), and bibenzyl (0.25 mmol, 45.6 mg) as an internal standard was placed in a 10-cm^3 Schlenk tube under an Ar atmosphere and the resulting solution was stirred for 5 min. Then, Ph$_2$SiH$_2$ (1.2 mmol, 0.22 dm^3) was added *via* a syringe and the reaction mixture was stirred at room temperature for 24 h. After removal of volatiles under vacuum at −30 °C, a residue was dissolved in Et$_2$O (1 cm^3). The solution was further stirred for 1 h with K$_2$CO$_3$ (1 mg) and MeOH (1 cm^3). Total yield (77%) and a ratio (91/9) of cyclohexanone and 2-cyclohexen-1-ol were determined by a GC (Shimadzu CPB10 column, 25 m length, 0.25 mm id).

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