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Rhodium(III) complexes with a bidentate *N*-heterocyclic carbene ligand bearing flexible dendritic frameworks†‡

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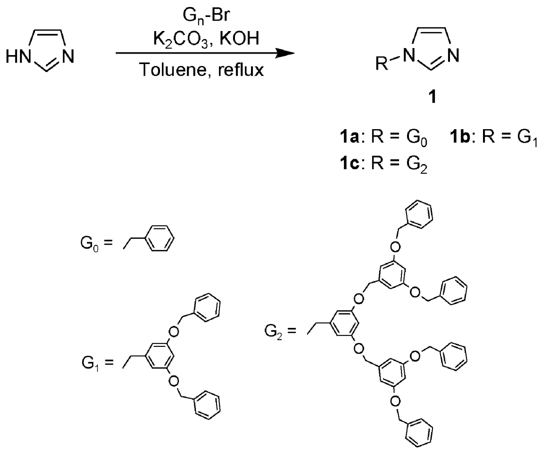
Rh(III) complexes with a bidentate *N*-heterocyclic carbene ligand bearing flexible dendritic frameworks have been synthesized and fully characterized by X-ray crystallographic analysis, NMR measurements and theoretical calculations.

Much attention has been paid to dendrimers with organometallic centers since the well-defined hyperbranched frameworks will bring about unique chemical properties including novel catalysis.[1,2] We have reported various dendritic ligands with pyridine,[3] phosphine[4] and *N*-heterocyclic carbene (NHC)[5,6] functionalities at the core and used as transition-metal-catalyzed reactions. Recently, we have synthesized a series of Rh(I) complexes with a *mono*dentate NHC ligand bearing Fréchet-type[7] flexible dendritic frameworks. In the hydrosilylation of ketones catalyzed by them, yields of the corresponding alcohols increased with higher dendrimer generation: a positive dendrimer effect was evident.[5] Furthermore, Rh(I) complexes with a NHC ligand having a rigid 2,3,4,5-tetraphenylphenyl and its higher dendritic frameworks were efficient catalysts in the hydrosilylation of α,β-unsaturated ketones.[6]

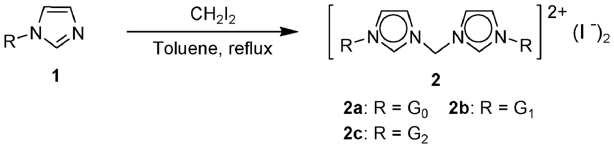
The NHC ligands have been widely used in the field of homogeneous catalysis and organometallic chemistry.[8] Formation of stronger bonds to the metals associated with NHC ligands as compared with phosphines diminish their dissociation from metal centers. Among them, *bi*dentate NHC ligands are of special interest since stability of their metal complexes is considerably enhanced by the chelating effect.[9] However, examples of the *bi*dentate NHC ligands are very limited as compared to those of *mono*dentate NHC cases. As for Rh(III) complexes,[10] the complexes are efficient catalysts in hydrosilylation[10a] and transfer hydrogenation.[10b] In this study, novel Rh(III) complexes with a bidentate NHC ligand having Fréchet-type[7] flexible polybenzylether dendrimers were synthesized and fully characterized. Then, these complexes were employed as catalysts in the hydrosilylation of 2-cyclohexen-1-one and good 1,4-selectivity was observed.

A series of imidazolium salts, which are precursors for the desired bidentate NHC ligands, were synthesized in two steps. At first, *N*-substituted imidazoles bearing the Fréchet-type[7] polybenzylether dendrimers (**1a–c**) were synthesized by the reaction of imidazole with one equivalent of the corresponding dendrimer-bromides, G_n–Br (n = 0, 1 and 2) as shown in eqn (1).[11] Subsequently, the reaction of **1a–c** with CH_2I_2 in toluene afforded the corresponding imidazolium salts $[(G_0)(C_3H_3N_2)CH_2(C_3H_3N_2)(G_0)]I_2$ (**2a**),[9a] $[(G_1)(C_3H_3N_2)CH_2(C_3H_3N_2)(G_1)]I_2$ (**2b**), and $[(G_2)(C_3H_3N_2)CH_2(C_3H_3N_2)(G_2)]I_2$ (**2c**) (eqn (2)). The new compounds (**1b**, **1c**, **2b** and **2c**) were fully characterized by elemental analysis, FD-MS spectra and NMR measurements.

Rh(III) complexes with the NHC ligand $RhI_2(OAc)[(G_0)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_0)]$ (**3a**), $RhI_2(OAc)[(G_1)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_1)]$ (**3b**), and $RhI_2(OAc)[(G_2)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_2)]$ (**3c**) were synthesized by the reaction of **2a–2c** with $[RhCl(COD)]_2$ in the presence of KI and KOAc (eqn (3)).[10a] In addition, a methyl derivative $RhI_2(OAc)[Me(C_3H_2N_2)CH_2(C_3H_2N_2)Me]$ (**3d**) was also synthesized with the same method using $[Me(C_3H_3N_2)CH_2(C_3H_3N_2)Me]I_2$.[12] The new complexes (**3a–3d**) were also fully characterized. In $^{13}C\{^1H\}$ NMR spectra of **3a–3d**, the coordinated carbene carbons appeared as sharp doublets at δ = 151.5 ppm (J_{Rh-C} = 41.6 Hz), 155.0 ppm (41.6 Hz), 154.8 ppm (41.7 Hz), and 151.3 ppm (43.1 Hz), respectively. The isolated complexes were highly stable both to air and moisture in the solid state. The ^1H NMR spectra of **3a–3d** did not change over a week, indicating these complexes are also considerably stable in solution.



(1)



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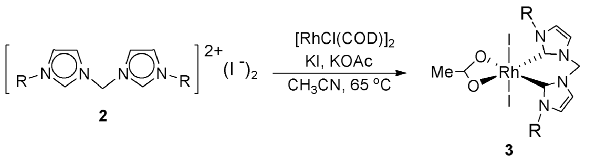
† The HTML version of this article has been enhanced with additional colour images.

‡ Electronic supplementary information (ESI) available: Synthetic method and analytical data of **1**, **2** and **3**. See DOI: 10.1039/b701104k



(3)

3a: R = G_0 **3b**: R = G_1
3c: R = G_2 (**3d**: R = Me)

The molecular structures of **3a**, **3b** and **3d** have been successfully determined by X-ray diffraction study. Fig. 1 shows the ORTEP drawing of **3a**, **3b** and **3d**.§¶ In the structures, each rhodium atom has distorted octahedral coordination geometry. The average Rh–C bond lengths of **3a**, **3b** and **3d** were 1.962(4), 1.969(4) and 1.965(3) Å, respectively. These bond lengths are similar to those of other Rh(III)–NHC complexes.[10] Fig. 1(b) showed that in the solid state the benzylether moiety on the NHC ligand spatially spreads out and covers the wide area from the Rh center.

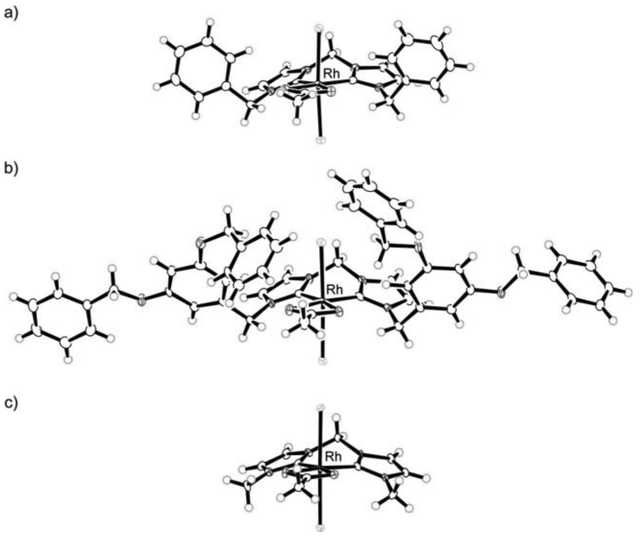


Fig. 1 ORTEP drawings of (a) **3a**, (b) **3b** and (c) **3d** with thermal ellipsoids at 50% probability levels.

Fig. 2 showed the ^1H NMR spectra of **3a–3c** in $CDCl_3$. All the ^1H and ^{13}C NMR resonances were unambiguously assigned with the aid of H–H COSY and HSQC spectroscopy. The ^1H NMR spectrum of **3a** exhibited the NHC ring proton resonances as two doublet peaks at $\delta = 6.98$ and 6.82 ppm ($J = 1.8$ Hz; signals *a* and *b* in Fig. 2(a)). A bridging methylene proton resonance was observed at $\delta = 6.05$ ppm (signal *c* in Fig. 2(a)). Similarly, the ^1H NMR spectrum of **3b** showed signals of two NHC ring protons at $\delta = 6.92$ and 6.84 ppm, and the bridging methylene proton at $\delta = 5.95$ ppm (Fig. 2(b)). However, the ^1H NMR spectrum of the second generation (G_2) complex **3c** displayed the NHC ring proton resonances at $\delta = 6.68$ and 6.62 ppm, and a bridging methylene proton at $\delta = 5.58$ ppm (Fig. 2(c)). In the spectrum, one of the NHC ring proton resonance (signal *a*) and the bridging methylene proton resonance (signal *c*) showed considerable up-field shifts. The latter peak (signal *c*) overlapped with the methylene resonance of the benzyl moiety on the NHC ring (signal *d* in Fig. 2(c)). Interestingly, these shifts were not observed in the ^1H NMR spectrum of the corresponding imidazolium salt **2c**. Although no noe interaction between the aromatic ring protons and the NHC ring protons was observed, such up-field shifts might be caused by the ring-current effect of aromatic rings of the dendritic framework: the second generation dendritic moieties would then come closer to the NHC center. Actually, ONIOM[13] (B3LYP/LANL2DZ:UFF)-CAChe[14]/CONFLEX[15]/MM3[16] calculations afforded the significantly folded structure shown in Fig. 3. It is noteworthy that this structure is quite different from the open structure in Fig. 1(b) determined by X-ray crystallography.

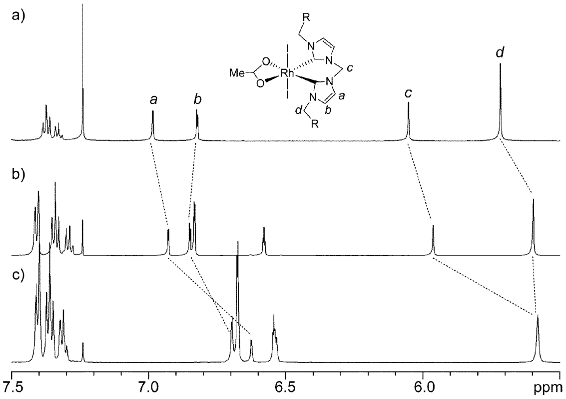


Fig. 2 ^1H NMR spectra of (a) **3a**, (b) **3b** and (c) **3c** in $CDCl_3$.

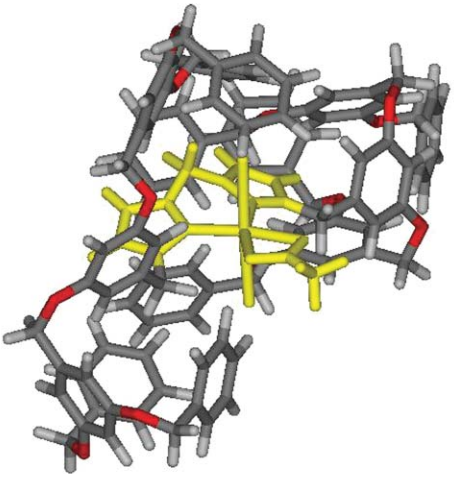
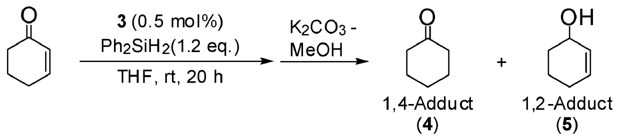


Fig. 3 An optimized structure of **3c** calculated by ONIOM (B3LYP/LANL2DZ:UFF)-CAChe/CONFLEX/MM3. The yellow part indicates the $RhI_2(OAc)[(C_3H_2N_2)CH_2(C_3H_2N_2)]$ core.

As a probe reaction to investigate the catalytic activity of **3**, hydrosilylation of 2-cyclohexen-1-one[17] was carried out (Scheme 1).* As catalysts, **3a**, **3b** and **3c** showed high catalytic activity to afford mixtures of cyclohexanone (1,4-adduct: **4**) and 2-cyclohexen-1-ol (1,2-adduct: **5**) in 91–99% yields with the 1,4-adduct as a major product (79–81% selectivities). Although the yield and 1,4-regioselectivity decreased, the corresponding methyl derivative (**3d**) also showed moderate catalytic activity. Recently, we reported that the 1,2-adduct (**5**) was obtained as the major product (61–69% selectivities in 62–83% total yields) in the same hydrosilylation of 2-cyclohexen-1-one catalyzed by Rh(I) complexes having the *mono*dentate NHC ligand: RhCl(COD)-$[(G_n)_2(C_3H_2N_2)]$ (G_n: $n = 0$–3).[6] With the bidentate NHC ligand,



catalyst	total yield (%)	selectivity (**4**/**5**)
3a	99	79/21
3b	96	81/19
3c	91	80/20
3d	62	65/35

Scheme 1 Hydrosilylation of 2-cyclohexen-1-one catalyzed by **3**. The products were obtained after hydrolysis.

the dendrimer moiety of higher generation must affect the catalytic environment as shown in Fig. 2 and 3. However, almost no effect of the dendrimer generation was observed in the hydrosilylation as shown in Scheme 1. In the catalytic reaction, the robust chelating structures of **3** are more important and successfully realized the good 1,4-regioselectivity.

Notes and references

§ *Crystal data for* $RhI_2(OAc)[(G_0)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_0)]\cdot C_4H_8O$ (**3a**·*THF*): $C_{27}H_{31}I_2N_4O_3Rh$, $M = 816.28$, $T = 113$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.126(5)$, $b = 14.786(6)$, $c = 15.987(6)$ Å, $\beta = 92.446(6)°$, $U = 2863(2)$ Å^3, $Z = 4$, μ(Mo Kα) = 2.78 cm^{-1}, observed reflections 5511 ($I > 2\sigma(I)$), $R1$, $wR2$ (all data) = 0.042, 0.098. *For* $RhI_2(OAc)[(G_1)(C_3H_2N_2)CH_2(C_3H_2N_2)(G_1)]\cdot CH_3CN$ (**3b**·*CH$_3$*CN): $C_{53}H_{50}I_2N_5O_6Rh$, $M = 1209.72$, $T = 113$ K, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.338(4)$, $b = 13.972(6)$, $c = 20.243(8)$ Å, $\alpha = 20.243(8)$, $\beta = 85.57(1)$, $\gamma = 78.379(9)°$, $U = 2461(2)$ Å^3, $Z = 2$, μ(Mo Kα) = 1.66 cm^{-1}, observed reflections 8789 ($I > 2\sigma(I)$), $R1$, $wR2$ (all data) = 0.043, 0.102. *For* $RhI_2(OAc)[Me(C_3H_2N_2)CH_2(C_3H_2N_2)Me]$ (**3d**): $C_{11}H_{15}I_2N_4O_2Rh$, $M = 591.98$, $T = 113$ K, monoclinic, space group Cc (No. 5), $a = 9.685(2)$, $b = 13.321(3)$, $c = 12.691(3)$ Å, $\beta = 94.340(2)°$, $U = 1632.6(7)$ Å^3, $Z = 4$, μ(Mo Kα) = 4.83 cm^{-1}, Flack parameter = 0.222(16), observed reflections 2074 ($I > 2\sigma(I)$), $R1$, $wR2$ (all data) = 0.019, 0.059.

¶ CCDC reference numbers 633257, 633258 and 633259. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701104k

* *General procedure for hydrosilylation of 2-cyclohexen-1-one.* A rhodium catalyst **3a** (3.7 mg, 0.005 mmol) was placed in a 10-cm^3 Schlenk tube under an Ar atmosphere. Anhydrous THF (1.0 cm^3), 2-cyclohexen-1-one (9.7×10^{-2} dm^3, 1 mmol), and bibenzyl (45.6 mg, 0.25 mmol as an internal standard) were added under an Ar flow and the solution was stirred for 5 min. Ph_2SiH_2 (0.22 dm^3, 1.2 mmol) was added *via* a syringe and the reaction mixture was stirred at room temperature (22 ± 1 °C) for 20 h. The desilylation was performed by adding K_2CO_3 (*ca.* 1 mg) and MeOH (1 cm^3), then the mixture was stirred for 30 min. A total yield (99%) and a ratio (79/21) of cyclohexanone and 2-cyclohexen-1-ol were determined by a GC (Shimadzu CPB10 column, 25 m length, 0.25 mm i.d.).

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