

# Synthesis of novel axially chiral Rh–NHC complexes derived from BINAM and application in the enantioselective hydrosilylation of methyl ketones†

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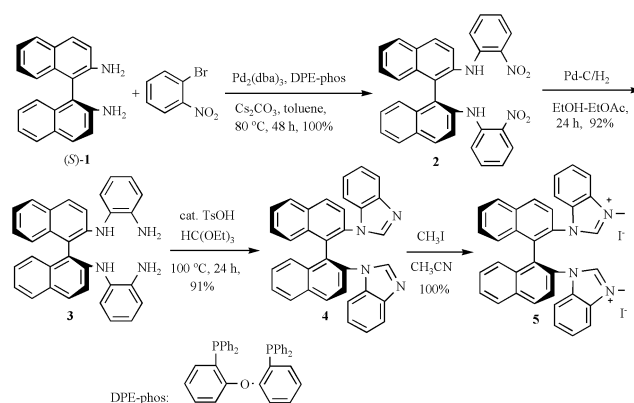
Novel axially chiral Rh *N*-heterocyclic carbene complexes were prepared from axially dissymmetric 1,1'-binaphthalenyl-2,2'-diamine and applied in the Rh-catalyzed enantioselective hydrosilylation of methyl ketones. The corresponding *sec*-alcohols can be obtained in high yields with good to excellent ee.

In 1968, Öfele and Wanzlick concurrently prepared the first authentic metal complex of an *N*-heterocyclic carbene.<sup>1</sup> These two reports received little attention until Arduengo synthesized a stable free carbene.<sup>2</sup> The pioneering work from Herrmann's group made progress in this field by preparing numerous *N*-heterocyclic carbenes and their metal complexes, and further applied them in homogeneous catalysis.<sup>3</sup> Numerous papers concerning this topic have appeared in the past few years. The complexes of *N*-heterocyclic carbenes have been applied to a broad spectrum of catalytic reactions.<sup>3a</sup> On the other hand, although a few examples of good or excellent enantioselectivities exist,<sup>4</sup> asymmetric catalytic using chiral metal–NHC complexes has to date not been extensively investigated.<sup>5</sup> Therefore, we wish to report in this paper the synthesis and application of novel axially chiral Rh–NHC complexes<sup>6</sup> derived from axially dissymmetric 1,1'-binaphthalenyl-2,2'-diamine **1** (BINAM) giving excellent chiral induction in the enantioselective hydrosilylation of methyl ketones.

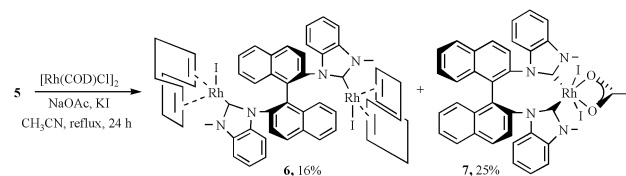
The preparation of the NHC complexes began with the bis(2-diphenylphosphinophenyl) ether (DPEphos)-Pd catalyzed coupling reaction of 2-bromo-nitrobenzene with (*S*)-1,1'-binaphthalenyl-2,2'-diamine **1** (BINAM) in toluene in the presence of Cs<sub>2</sub>CO<sub>3</sub> to give compound **2** in quantitative yield.<sup>7</sup> Reduction of **2** by means of Pd/C–H<sub>2</sub> produced compound **3**. Subsequent cyclization with triethyl orthoformate catalyzed by TsOH at 100 °C afforded the product **4**, and then quaternization of the benzimidazole ring of **4** with methyl iodide gave the dibenzimidazolium salt **5** in quantitative yield (Scheme 1). The desired compound **5** was treated with [Rh(COD)Cl]<sub>2</sub> without further purification in acetonitrile in the presence of base NaOAc to give Rh(I)-complex **6**<sup>8</sup> and Rh(III)-complex **7**, which were separated by silica gel column chromatography as a yellow and an orange solid, respectively (Scheme 2).<sup>9</sup> They are stable at ambient atmosphere and their structures are determined by spectroscopic data, microanalysis and X-ray diffraction (Figures 1 and 2 in ESI†).<sup>10</sup> From their crystal structures,<sup>10</sup> it can be seen that Rh(I)–NHC complex **6** has a completely different crystal structure from Rh(III)–NHC complex **7**. For chiral Rh(I)–NHC complex **6**, dibenzimidazolium precursor **5** binds two Rh atoms with two *N*-heterocyclic carbenes and the dihedral angle of the two naphthyl rings is 70.65°. The X-ray structure shows the Rh atom with a square-planar arrangement of the ligands

and a bond angle I1–Rh1–C11(carbene) of 90.1(4)°. The Rh–C(carbene) distances, 2.059(12) and 1.924(19) Å, are normal for Rh–C σ bonds. The two Rh metal centers are far away from the axially chiral environment (ESI†).<sup>10</sup> For chiral Rh(III)–NHC complex **7**, dibenzimidazolium precursor **5** acts as a bidentate ligand to coordinate the Rh metal together with one acetate and the *N*-heterocyclic carbene is chelating with a ruffled conformation and a bite angle (C1–Rh1–C34) of 98.1° (*cis*-geometry). The Rh–C distances, 1.956(14) and 1.972(13) Å, are normal for Rh–C σ bonds and imply a symmetric ligand coordination mode. The dihedral angle of two naphthyl rings is 78.67° and the Rh metal center is embedded into the axially chiral environment.<sup>10</sup> The high *trans*-effect of the *N*-heterocyclic carbenes is evident in the rather long Rh–OAc distances (Rh–O 2.175(9), 2.174(9) Å) compared to those in the parent carboxylate complexes [Rh(OAc)<sub>2</sub>(L)]<sub>2</sub> (2.01–2.06 Å).<sup>10</sup>

Rh-catalyzed enantioselective hydrosilylation of ketone is a versatile method providing optically active secondary alcohols.<sup>11</sup> It was first performed by using (4*S*,5*S*)-(+)-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane [(*S,S*)-DIOP] and a rhodium complex for the reduction of acetophenone with 58% ee.<sup>12</sup> Later, numerous ligands were applied and high enantioselectivities were produced in some cases.<sup>13</sup> Rh–NHC complexes also were used as catalyst in this reaction with > 70% ee and 44% ee respectively.<sup>3a,14</sup> Thus, we attempted to utilize the two novel axially chiral Rh–NHC complexes **6** and **7** in this process. As a result, we found that



Scheme 1 The synthesis of the axially chiral dibenzimidazolium salt.



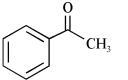
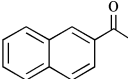
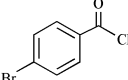
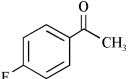
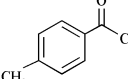
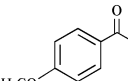
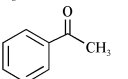
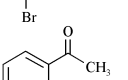
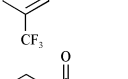
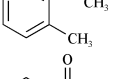
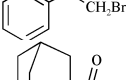
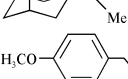
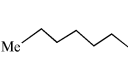
Scheme 2 The synthesis of the axially chiral Rh–NHC complexes.

† Electronic supplementary information (ESI) available: <sup>13</sup>C NMR and <sup>1</sup>H NMR spectral and analytic data for compounds **2–7**, reduction products, and chiral HPLC and GC charts for *sec*-alcohols **9a–m**. See <http://www.rsc.org/suppdata/cc/b3/b309185f/>

various aryl alkyl ketones and dialkyl ketones **8** can be reduced using chiral Rh–NHC catalyst **7** in high yields (82–96%) with good to excellent ee (67–98% ee) (Table 1).<sup>15</sup>

In conclusion, two novel axially chiral Rh–NHC complexes derived from BINAM were designed and synthesized and their crystal structures have been determined by X-ray diffraction. They were applied in the catalytic enantioselective hydrosilylation of methyl ketones process. For a broad range of substrates such as aryl alkyl ketones as well as dialkyl ketones, Rh(III)–NHC complex **7** furnishes good to excellent enantioselectivities and yields. In the view of both scope and stereoselectivity, this novel chiral Rh–NHC complex compares favorably with previously described catalysts for this process. Efforts are under way to elucidate the mechanistic details of this catalytic system and to extend the scope and limitations of these

**Table 1** The chiral Rh complexes catalyzed enantioselective hydrosilylation of methyl ketones

$\text{R}^1-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2$ <b>8a-m</b>		$\xrightarrow[2) \text{ hydrolysis}]{1) 1.5 \text{ equiv Ph}_2\text{SiH}_2, \text{ 7 (2 mol\%), THF, 15 }^\circ\text{C, 24 h}}$		$\text{R}^1-\overset{\text{OH}}{\text{C}}-\text{R}^2$ <b>(R)-9a-m</b>	
1		<b>a</b>	87		98
2		<b>b</b>	91		96
3		<b>c</b>	88		95
4		<b>d</b>	86		95
5		<b>e</b>	93		98
6		<b>f</b>	96		92
7		<b>g</b>	93		98
8		<b>h</b>	82		98
9		<b>i</b>	85		92
10		<b>j</b>	92		97
11		<b>k</b>	96		96 <sup>c</sup>
12		<b>l</b>	87		71
13		<b>m</b>	86		67 <sup>d</sup>

<sup>a</sup> Isolated yields. <sup>b</sup> Determined by chiral HPLC or GC. <sup>c</sup> Determined by chiral HPLC analysis of its *N*-phenyl carbamate derivative. <sup>d</sup> Determined by chiral GC analysis of its acetate derivative.

novel chiral Rh–NHC complexes in other asymmetric catalysis.

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