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Süleyman Gülcemal, Agnès Labande, Jean-Claude Daran, Bekir Çetinkaya, Rinaldo Poli. Rhodium(I) Complexes of New Ferrocenyl Benzimidazol-2-ylidene Ligands: The Importance of the Chelating Effect for Ketone Hydrosilylation Catalysis. *European Journal of Inorganic Chemistry*, 2009, N-Heterocyclic carbene complexes, 2009 (13), pp.1806-1815. 10.1002/ejic.200801163 . hal-03184576

**HAL Id: hal-03184576**

**<https://hal.science/hal-03184576>**

Submitted on 29 Mar 2021

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## Rhodium(I) complexes of new ferrocenyl benzimidazol-2-ylidene ligands: The importance of the chelating effect for ketone hydrosilylation catalysis.

Süleyman Gülcemal,<sup>[a]</sup> Agnès Labande,<sup>\*[b][c]</sup> Jean-Claude Daran,<sup>[b][c]</sup> Bekir Çetinkaya<sup>[a]</sup> and Rinaldo Poli<sup>[b][c][d]</sup>

**Keywords:** N-heterocyclic carbenes / benzimidazole / ferrocene / Rhodium / hydrosilylation

*N*-[(1-Phosphanylferrocen-1'-yl)methyl]-*N'*-[(2,4,6-trimethylphenyl)methyl]-5,6-di-X-benzimidazolium tetrafluoroborate salts (X = H, **5a** and Me, **5b**), precursors of new phosphane-benzimidazol-2-ylidene bifunctional ligands, and related ferrocenyl 5,6-di-X-benzimidazol-2-ylidene iodide salts (X = H, **6a** and Me, **6b**), precursors of monodentate benzimidazol-2-ylidene ligands, have been prepared for the first time. Cationic rhodium(I) complexes **7a** and **7b** and neutral rhodium(I) complexes **8a** and **8b** have been obtained in good yields and fully characterised. Cationic rhodium(I) complexes **10a** and **10b** were prepared from **8a** and **8b**, for comparison with complexes **7**, but not isolated.

All complexes showed good activities for the catalytic hydrosilylation of acetophenone derivatives. Activities are much greater than for related imidazol-2-ylidene systems and the cationic complexes are more active than the neutral ones, the highest activities being recorded for the more soluble **7b** system. The use of bidentate ligands proved essential to obtain good selectivities in the desired alcohol.

- [a] Ege University, Department of Chemistry, Bornova, 35100 Izmir, Turkey.  
 [b] CNRS; LCC (Laboratoire de Chimie de Coordination); 205, route de Narbonne, F-31077 Toulouse, France.  
 Fax: +33 5 61 55 30 03.  
 E-mail : agnes.labande@lcc-toulouse.fr  
 [c] Université de Toulouse; UPS, INPT; F-31077 Toulouse, France.  
 [d] Institut Universitaire de France; 103, bd Saint-Michel; F-75005 Paris, France.

### Introduction

The recent developments in the field of functionalised N-heterocyclic carbene (NHC) ligands have proved their great potential in transition metal catalysis.<sup>[1-3]</sup> Indeed, the presence of an NHC and a second, structurally different donating group on the metal can radically alter the catalytic properties. On the other hand, the chelating nature of these ligands results in the production of highly stable complexes. In our search for more efficient catalysts, we have shown that very small structural variations on bifunctional ligands could change dramatically the reactivity of rhodium(I) catalysts for the hydrosilylation of ketones.<sup>[4,5]</sup>

Although NHC ligands bearing a benzimidazole backbone offer a vast potential for catalytic applications, their coordination chemistry has remained relatively unexplored.<sup>[6-12]</sup> The  $\sigma$ -donating properties of benzimidazol-2-ylidene ligands stand between those of unsaturated imidazol-2-ylidenes and of saturated imidazolin-2-ylidenes. Thus, although they have the topology of unsaturated NHCs, they show a reactivity typical of saturated carbenes.<sup>[11,13]</sup>

We have tried to improve the catalytic activity of rhodium(I) complexes bearing ferrocenylphosphanyl-NHC ligands. Indeed, ferrocenyl-substituted NHCs are a class of ligands that has been little developed and has a great potential in both asymmetric and non-asymmetric catalysis.<sup>[2,14]</sup> We thus prepared new ferrocenylphosphane ligand precursors bearing a benzimidazolium

moiety, and the corresponding rhodium(I) complexes. Although benzimidazolium salts with a ferrocenyl substituent are already known,<sup>[15]</sup> we report here the first example of a ferrocenylphosphane bearing a benzimidazolium unit. In order to evaluate the contribution of the phosphanyl group to catalysis, rhodium(I) complexes bearing monodentate ferrocenyl NHC ligands were also prepared.

### Results and Discussion

#### (a) Synthesis and characterisation of ligand precursors **5** and **6**

The benzimidazolium salts **4a** and **4b** were obtained in very good yields from ferrocenyl alcohol **1** and, respectively, substituted benzimidazoles **2a** and **2b**<sup>[7],[16]</sup> (Figure 1, Scheme 1), following the procedure developed previously in our group for related imidazolium salts.<sup>[4]</sup>

The phosphane group was deprotected by desulfurisation with Raney nickel to afford the ligand precursors **5a** and **5b**. Two related systems, either with (**b**) or without (**a**) methyl groups at positions 5 and 6 of the benzimidazole moiety were developed, in order to check whether subtle variations could induce electronic changes on the metal centre or modify the physical properties of the metal complexes.<sup>[12]</sup>

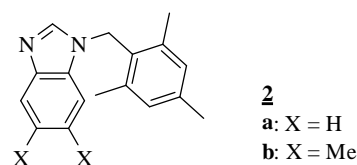
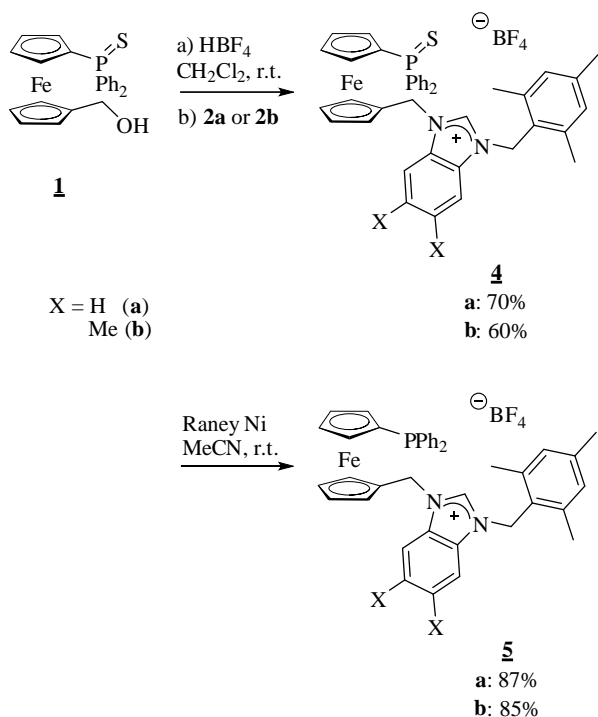
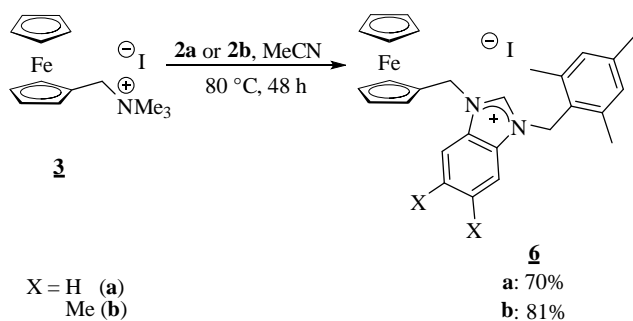


Figure 1. Substituted benzimidazoles.

In parallel, compounds **6a** and **6b** were prepared by reaction of N-(ferrocenylmethyl) trimethylammonium iodide (**3**) with substituted benzimidazoles in refluxing acetonitrile (Scheme 2), following the literature procedure.<sup>[17]</sup> These systems will allow a performance comparison of the benzimidazol-2-ylidene/phosphine ligand systems either in the presence or absence of a chelating effect.



Scheme 1. Synthesis of 1,1'-disubstituted ferrocenyl benzimidazolium salts.



Scheme 2. Synthesis of ferrocenyl benzimidazolium salts.

All compounds were fully characterised by standard analytical methods. The  $^1\text{H}$  NMR spectra of compounds **5a** and **5b** showed signals at respectively 9.10 and 8.86 ppm, characteristic of the acidic C2 proton of the benzimidazolium group. Comparatively, the signal of the same proton in compounds **6a** and **6b** is shifted downfield (10.60 and 10.21 ppm respectively), due to the stronger C-H $\cdots$ X bond polarisation when X = I.<sup>[3]</sup> The crystal structures of compounds **5a** and **6b** have been resolved by X-ray diffraction analysis (Figure 2). The C-C bond of the imidazolium motif is significantly longer in the case of benzimidazolium salts **5a** and **6b** (1.395(3) Å and 1.399(6) Å, respectively), compared to a 1,1'-ferrocenylphosphane imidazolium salt previously described by us [1.330(6) Å]. This denotes the delocalization of the C-C bond  $\pi$  electron density into the condensed benzene ring (the C-C bond lengths within the ring are in the 1.372-1.402 Å range for **5a** and in

the 1.354-1.424 Å range for **6b**) and could be responsible for the different reactivity of the resulting carbenes. The two structures show hydrogen bonds, as is typically observed for imidazolium salts, between a fluorine atom of the  $\text{BF}_4^-$  anion and the C62 proton ( $\text{F3}\cdots\text{H62}-\text{C62} = 2.312$  Å) for **5a**, and between the iodide anion and the C1 proton ( $\text{I1}\cdots\text{H1}-\text{C1} = 2.962$  Å) for **6b**. The H-bond is significantly shorter in the case of benzimidazolium salt **5a**, possessing a weakly-coordinating anion, certainly because the F atom is much smaller than the I atom, although the NMR study (*vide supra*) indicates a stronger H bond for the iodide salt.

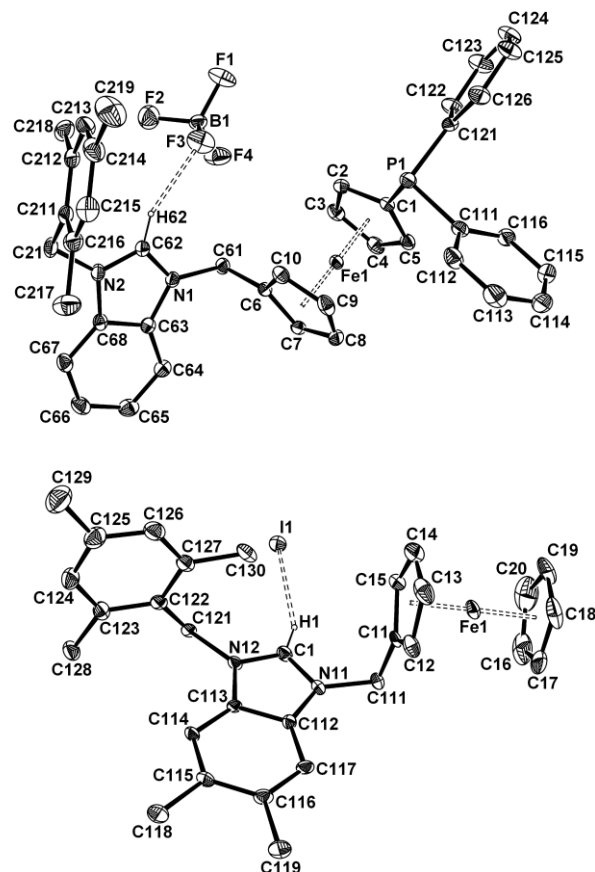


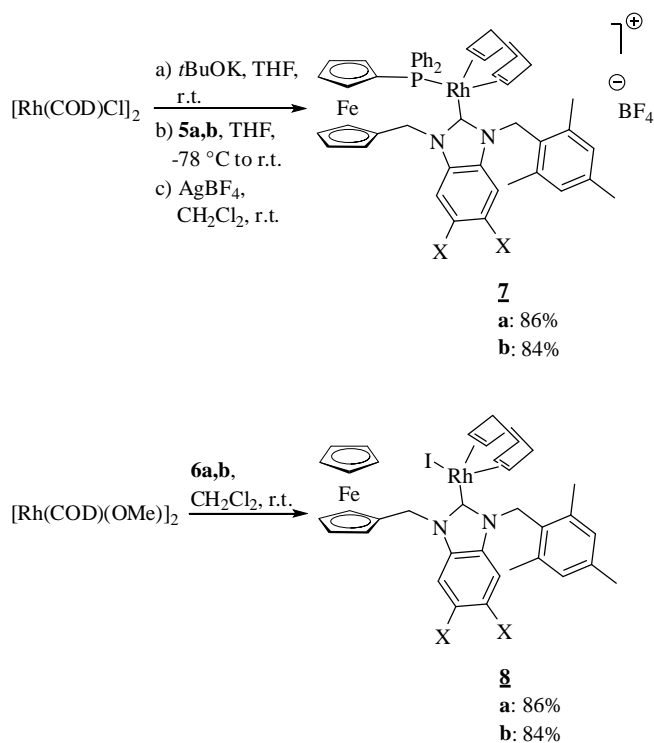
Figure 2. ORTEP views of **5a** (top) and **6b** (bottom). Ellipsoids are shown at the 30% probability level. All hydrogen atoms except H(62) (top) and H(1) (bottom) are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ), **5a**: C(1)-P(1) 1.811 (2), C(62)-N(1) 1.325 (3), C(62)-N(2) 1.331 (3), C(63)-C(68) 1.395 (3), N(1)-C(62)-N(2) 110.5 (2); **6b**: C(1)-N(11) 1.321 (6), C(1)-N(12) 1.321 (6), C(112)-C(113) 1.399 (6), N(11)(C(1)-N(12) 110.4 (6).

### (b) Synthesis and characterisation of rhodium(I) complexes **7** and **8**

Addition of compounds **5a** or **5b** to  $[\text{Rh}(\text{COD})(\text{O}i\text{Bu})]_2$  – prepared in situ from  $[\text{Rh}(\text{COD})\text{Cl}]_2$  and  $t\text{BuOK}$ <sup>[18]</sup> – in THF led to rhodium(I) complexes **7a** and **7b**.  $[\text{Rh}(\text{OMe})(\text{COD})]_2$  reacted with benzimidazolium salts **6a** and **6b** in dichloromethane to give complexes **8a** and **8b**, respectively (Scheme 3). The reaction with ligand precursors **5a** and **5b** led directly to cationic complexes, whereas the neutral form was obtained in the case of precursors **6a** and **6b**, with iodide coordination.

The  $^{13}\text{C}$  NMR signals of the carbene C atoms of complexes **7** appear at 192.5 ppm (**7a**) and 189.9 ppm (**7b**), within the expected range for cationic NHC–Rh(I) complexes with a benzimidazol-2-

ylidene moiety.<sup>[10,19]</sup> These signals are found at slightly lower fields for complexes **8a** (196.4 ppm) and **8b** (194.5 ppm).<sup>[8,18]</sup>



Scheme 3. Synthesis of rhodium complexes.

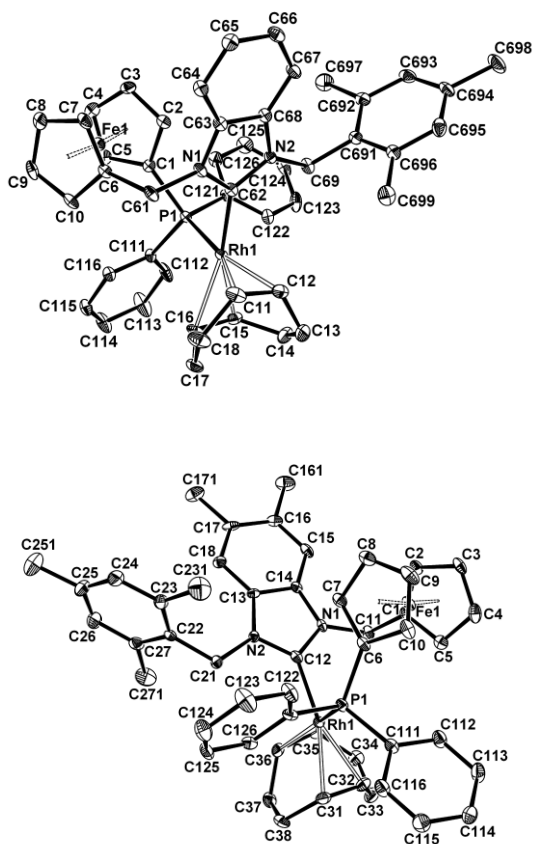


Figure 3. ORTEP views of **7a** (top) and **7b** (bottom). Ellipsoids are shown at the 50% (**7a**) or 30% (**7b**) probability level. All hydrogen atoms are omitted for clarity.

Complexes **7** and **8** gave X-ray quality crystals by slow diffusion of ether into a dichloromethane solution (Figures 3 and 4). Selected bond distances and angles are listed in Table 1, and compared to those of previously described complex **9a** (Figure 5).<sup>[4]</sup> The square-planar coordination environment in complexes **7-8** was confirmed by X-ray diffraction studies (Figures 3 and 4). The *cis*-NHC-Rh-P angles in complexes **7a**, **7b** (92.06(18)° and 93.78(12)°, respectively) and the *cis*-NHC-Rh-I angles in complexes **8a**, **8b** (89.57(6)° and 86.1(3)°, respectively) are close to the expected 90° value. The structures of complexes **7a** and **7b** reveal slightly shorter Rh1-C(NHC) bond lengths than in imidazol-2-ylidene/phosphane complex **9a**, as well as in a related complex described by Field et al. [2.064(2) Å]<sup>[20]</sup>.

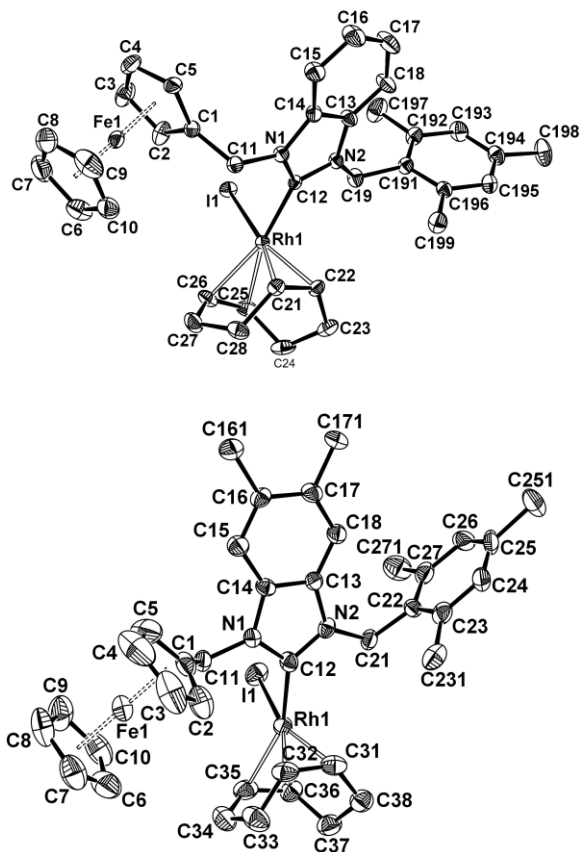
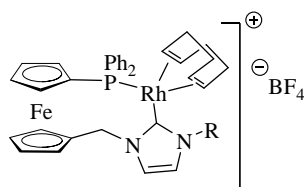


Figure 4. ORTEP views of **8a** (top) and **8b** (bottom). Ellipsoids are shown at the 50% (**8a**) or 30% (**8b**) probability level. All hydrogen atoms are omitted for clarity.

However, this difference is not observed with neutral complexes **8a** and **8b**: the Rh1-C(NHC) bond lengths are in the typical range observed for NHC-Rh complexes with iodide coordination.<sup>[8,9,21]</sup> There is no evidence for a structural effect of the methyl groups in positions 5 and 6 of the benzene ring (complexes **7b** and **8b**), as we can not observe any significant variation in the Rh1-C(NHC) bond lengths related to this parameter. The mesityl group is found roughly orthogonal to the benzimidazole backbone, with dihedral angles ranging from 86 to 90°, to limit steric interactions.

Table 1. Selected bond lengths (Å) and bond angles (°) for complexes **7**, **8** and **9a**.

	<b>7a</b>	<b>7b</b>	<b>9a</b> [a]	<b>8a</b>	<b>8b</b>
<i>Bond lengths (Å)</i>					
Rh1-C(NHC)	2.018 (7)	2.031 (5)	2.047 (3)	2.012 (2)	1.993 (10)
Rh1-P1	2.3138 (18)	2.3233 (12)	2.3345 (8)	-	-
Rh1-I1	-	-	-	2.6848 (3)	2.6784 (11)
	2.180 (7)	2.209 (5)	2.215 (3)	2.143 (2)	2.100 (10)
	2.181 (7)	2.209 (5)	2.231 (3)	2.109 (2)	2.091 (11)
Rh1-C(COD)	2.209 (7)	2.239 (4)	2.220 (3)	2.234 (2)	2.187 (10)
	2.248 (7)	2.229 (4)	2.217 (3)	2.204 (2)	2.226 (10)
N1-C(NHC)	1.355 (8)	1.367 (5)	1.359 (4)	1.366 (3)	1.364 (11)
N2-C(NHC)	1.362 (8)	1.373 (6)	1.357 (4)	1.360 (3)	1.382 (11)
<i>Bond angles (°)</i>					
N1-C(NHC)-N2	105.5 (6)	105.2 (4)	104.5 (2)	106.02 (18)	104.7 (8)
C(NHC)-Rh1-P1	92.06 (18)	93.78 (12)	90.83 (8)	-	-
C(NHC)-Rh1-I1	-	-	-	89.57 (6)	86.1 (3)



**9**

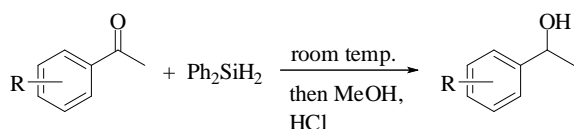
a: R = Me

b: R = 2,4,6-trimethylphenyl

Figure 5. Previously described Rh<sup>I</sup> complexes with an imidazol-2-ylidene moiety.<sup>[4]</sup>

### (c) Catalytic hydrosilylation of methyl aryl ketones

The catalytic activity of NHC complexes **7** and **8** was evaluated in the hydrosilylation of carbonyl compounds.<sup>[22,23]</sup> The reactions were typically carried out with 2 mol% of catalyst, in THF at room temperature (Scheme 4, Table 2). The conversion of acetophenone was followed by TLC and the crude mixture was analysed by <sup>1</sup>H NMR.

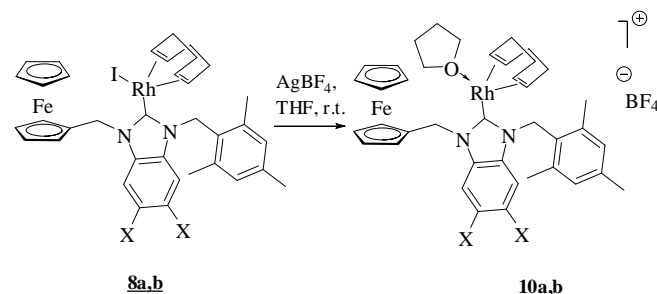


Scheme 4. Hydrosilylation of acetophenone and its derivatives with Rh<sup>I</sup> complexes.

In our first attempts, we were pleased to note that all complexes were active (entries 1-2 and 6-7), although a reaction time of 20 h was needed to obtain reasonable yields. The yields of alcohol were much higher in the case of bifunctional, cationic complexes **7a,b**. As observed in some of our previous work, the concentration of acetophenone in the medium can alter dramatically the reaction rate.<sup>[5]</sup> We thus carried out the next catalytic tests with a more concentrated medium (2 M instead of 1 M). The results were very encouraging, since we obtained a nearly quantitative yield of alcohol in 2 h with complex **7b** (entry 4). 20 h were still needed with complex **7a** to reach 80% conversion of the ketone (entry 3), probably due to the poor solubility of the catalyst in THF. In

comparison, our previously described complexes **9a** and **9b** were poorly active,<sup>[4]</sup> even at this concentration, as the reactions were not complete after 5 days at room temperature (entries 14 and 15).

However, increasing the concentration did not improve the yield in the case of neutral complexes **8a,b** (entries 8 and 9). In order to have a better comparison with cationic complexes **7a** and **b**, one equivalent of AgBF<sub>4</sub> was added to compounds **8a** and **b** to give, respectively, cationic complexes **10a** and **10b** (Scheme 5), where the Rh(I) centre is probably coordinated by one THF molecule in order to achieve the preferred square planar configuration. These complexes were not isolated but used directly for catalytic reactions.



Scheme 5. Generation of cationic Rh<sup>I</sup> complexes bearing monodentate NHC ligands.

Both complexes were completely soluble in THF, in contrast to their neutral precursors. It has been reported in some other cases that the use of AgX (X = OSO<sub>2</sub>CF<sub>3</sub>, BF<sub>4</sub>, PF<sub>6</sub>) was required in order to improve the catalytic activity,<sup>[23-25]</sup> and this proved to be the case also with our systems. Indeed, the conversion of acetophenone was complete after only 2 h, as shown by the <sup>1</sup>H NMR spectra of the reaction mixture before hydrolysis of the silyl ether (entries 10 and 11). However, the NMR yields calculated after hydrolysis were rather low and hardly reproducible, showing a lack of selectivity of these systems for the formation of the expected alcohol. The <sup>1</sup>H NMR spectra of the reaction mixtures before hydrolysis suggest the formation of a silyl enol ether as by-product (Scheme 6), which would then be reconverted to acetophenone by the hydrolysis step.

Indeed, the <sup>1</sup>H NMR spectra before hydrolysis show two doublets at 4.65 and 5.05 ppm (=CH<sub>2</sub>, J = 2.4 Hz), characteristic of

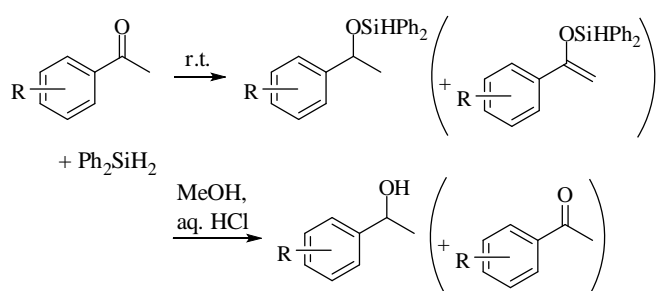
Table 2. Hydrosilylation of acetophenone (R=H).<sup>[a]</sup>

Entry	Catalyst (mol%)	Additive	Concentration (M)	t (h)	Conversion (%) <sup>[b]</sup>	Ratio silyl ether/silyl enol ether <sup>[b]</sup>	Yield of 1-phenylethanol (%) <sup>[c]</sup>
1	<b>7a</b> (2)	-	1	20	n/c	n/c	73
2	<b>7b</b> (2)	-	1	20	n/c	n/c	85
3	<b>7a</b> (2)	-	2	20	80	96:4	78 <sup>[d]</sup>
4	<b>7b</b> (2)	-	2	2	100	98:2	98
5	<b>7b</b> (1)	-	2	2	100	96:4	95
6	<b>8a</b> (2)	-	1	20	n/c	n/c	43 <sup>[d]</sup>
7	<b>8b</b> (2)	-	1	20	n/c	n/c	23
8	<b>8a</b> (2)	-	2	8	n/c	n/c	49 <sup>[d]</sup>
9	<b>8b</b> (2)	-	2	8	n/c	n/c	32
10	<b>10a</b> (2)	-	2	2	100	n/c ; 50:50 ; 59:41 <sup>[e]</sup>	62 ; 46 ; 60 <sup>[e]</sup>
11	<b>10b</b> (2)	-	2	2	100	n/c ; 69:31 ; 58:42 <sup>[e]</sup>	83 ; 66 ; 58 <sup>[e]</sup>
12	<b>10a</b> (2)	PPh <sub>3</sub> (1 eq.)	2	20	100	78:22	76 <sup>[d]</sup>
13	<b>10b</b> (2)	PPh <sub>3</sub> (1 eq.)	2	2	100	87:13	84
14 <sup>f</sup>	<b>9a</b> (2)	-	2	5 days	63	>99:1	63 <sup>[d]</sup>
15 <sup>f</sup>	<b>9b</b> (2)	-	2	5 days	90	99:1	87 <sup>[d]</sup>

[a] Ketone (1 eq.), diphenylsilane (1.1 eq.), room temperature, THF, then hydrolysis with MeOH/HCl. [b] Determined by <sup>1</sup>H NMR signal integration of the crude reaction mixture before hydrolysis, n/c = not calculated. [c] Determined by <sup>1</sup>H NMR signal integration of the crude reaction mixture after hydrolysis. [d] Catalyst only partially soluble in THF. [e] Results of three runs. [f] Data from ref. <sup>[4]</sup>.

the silyl enol ether (the doublet at 5.05 ppm, however, is often hidden by the Si-*H* singlet of Ph<sub>2</sub>SiH<sub>2</sub>, showing at 5.06 ppm). These signals are absent from the <sup>1</sup>H spectra of the mixtures after hydrolysis, whereas two new signals, typical of acetophenone, appear at 2.6 ppm (*CH*<sub>3</sub>, s) and 8.0 ppm (*Ar-H*, d, *J* = 7.5 Hz). This process is frequently observed in ketone hydrosilylation.<sup>[26]</sup>

In order to see whether the phosphane was necessary to maintain a good selectivity, we added 1 equivalent of triphenylphosphane to complexes **10a** and **10b** prior to the reaction (entries 12 and 13). The reaction was complete after 2 h with complex **10b**, but needed 20 h with complex **10a**, as the addition of PPh<sub>3</sub> decreased the solubility of the complex in THF. The analysis of the reaction mixture before and after hydrolysis showed a selectivity increase in both cases, which confirmed our hypothesis. However, the selectivity was lower than that reached with complexes **7a** and **7b**, showing clearly that the chelating effect is beneficial for the reaction selectivity.

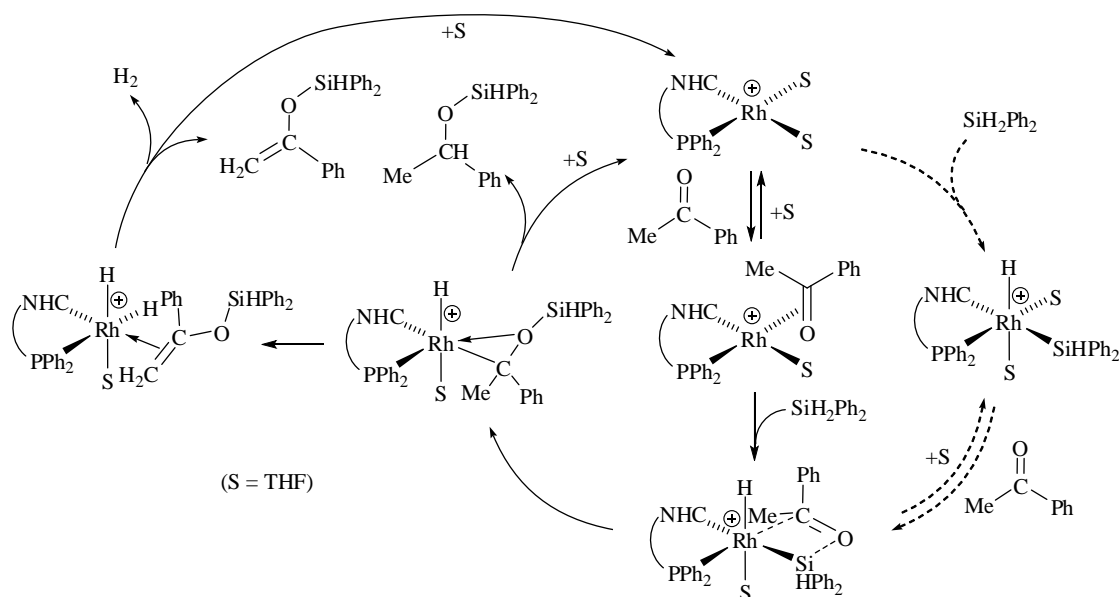


Scheme 6. Side-products generated during hydrosilylation reactions.

Encouraged by the results obtained with complex **7b**, we decided to lower the catalyst loading to 1 mol% (entry 5), and were pleased to observe that the activity was preserved, with a total conversion and 95% yield in only 2 h. Catalytic tests with acetophenone derivatives allowed us to determine the efficiency of complexes **7a** and **7b** (2 mol%) with a variation of electronic or steric properties (Scheme 4, Table 3). Whereas marked differences were observed

with complex **7a**, catalyst **7b** showed a very high activity whatever the substituents of acetophenone. Indeed, even the presence of an ortho substituent did not lower the yield (entry 6).

The higher catalytic activity observed at higher ketone concentration agrees with previous reports of a saturation effect: the reaction was found first order in ketone at low concentrations, but eventually became [ketone] independent at high concentrations.<sup>[27-29]</sup> The mechanism of this catalytic process has been addressed by many authors. Although a few variations have been discussed, the most commonly accepted mechanism remains the originally proposed one,<sup>[27,30-32]</sup> which is based on a rate determining Si-H oxidative addition process, yielding a Rh<sup>III</sup> silyl hydride intermediate. This step would be followed by ketone coordination, insertion into the metal-silyl bond, and final reductive elimination. Interestingly, the observation by Kolb and Hetflejš of a saturation effect (while working with a cationic system) was interpreted as indicating reversible complexation of the ketone prior to the rate determining silane addition,<sup>[28]</sup> but Giering later discarded this variant when he could properly model, on the basis of the other mechanism, kinetic results that he obtained with a neutral system, which also included a saturation effect in [ketone].<sup>[27]</sup> However, the data fittings were described as unsatisfactory unless additional processes of catalyst decomposition were included at various places in the catalytic cycle. We believe that the interpretation offered by Kolb and Hetflejš is reasonable and probably applies to our system, for the following reasons. The COD ligand is probably lost rapidly from the coordination sphere by hydrosilylation or hydrogenation processes, as also observed or proposed in other cases.<sup>[27,32-34]</sup> The resulting [(NHCFcPPh<sub>2</sub>)Rh]<sup>+</sup> system is then likely coordinated by two solvent molecules, but the lability of these should easily allow ketone coordination, faster than the rate-determining silane oxidative addition. Thus, the rate-determining silane oxidative addition may preferentially occur on the ketone substituted complex, as shown in Scheme 7, when the ketone concentration is high, whereas the order of events may be inverted (pathway indicated with dashed arrows in Scheme 7) at low ketone concentrations.



Scheme 7. Proposed mechanism for the formation of saturated and unsaturated hydrosilylation products.

Finally, the formation of the unsaturated silyl ether can be easily rationalized on the basis of a competition between the reductive elimination of the hydrosilylation product and a  $\beta$ -H elimination step from a common intermediate (Scheme 7). Although the mechanism of ketone hydrosilylation is not as well established as that of olefin hydrosilylation,<sup>[35]</sup> there is good evidence supporting a ketone insertion into the Rh-Si bond followed by C-H reductive elimination, rather than the alternative insertion into the Rh-H bond followed by Si-C reductive elimination.<sup>[24,36]</sup> Supposedly, the absence of the phosphane ligand renders the  $\beta$ -H elimination pathway more easily accessible through the availability of an additional open coordination site.

## Conclusions

In conclusion, the benzimidazol-2-ylidene unit gives highly active hydrosilylation rhodium catalysts, proving superior to the imidazol-2-ylidene. Moreover, bidentate NHC ligands bearing a phosphanyl group ensure a much better selectivity in the desired product than monodentate NHC ligands. The introduction of methyl substituents on the benzene ring of the benzimidazol-2-ylidene ligand enhanced the solubility of the rhodium complex in the reaction medium. This work was carried out with achiral ligands, and we are now planning to prepare planar chiral 1,2-disubstituted ferrocenyl ligands, using the methodology developed here, for applications to asymmetric hydrosilylation.

## Experimental Section

All reactions were carried out under a dry argon atmosphere using Schlenk glassware and vacuum line techniques. Solvents for syntheses were dried and degassed by standard methods before use. Spectra were recorded on Brüker ARX250, AV300 or DPX300 spectrometers. All spectra were recorded in  $\text{CDCl}_3$ , unless otherwise stated. Mass spectra were obtained from acetonitrile solutions on a TSQ7000 instrument from ThermoElectron. (1'-diphenylthiophosferrocen-1-yl)methanol **1** was prepared according to our previously published procedure.<sup>[37]</sup>  $[\text{Rh}(\text{OMe})(\text{COD})]_2$ <sup>[38]</sup>, **2a** and **2b**<sup>[7]</sup> and **3**<sup>[39]</sup> were prepared according to literature procedures.

**Benzimidazolium salt 4a:** To a solution of ferrocenyl alcohol **1** (100 mg, 0.23 mmol) in degassed dichloromethane (5 mL) was quickly added  $\text{HBF}_4$

(35  $\mu\text{L}$ , 54 wt% in  $\text{Et}_2\text{O}$ ), immediately followed by *N*-(2,4,6-trimethylbenzyl) benzimidazole **2a** (86 mg, 0.35 mmol). The mixture was washed with 2 M aq. HCl, water, satd. aq.  $\text{NaHCO}_3$  and water again. The organic phase was dried ( $\text{MgSO}_4$ ), filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent:  $\text{CH}_2\text{Cl}_2/\text{acetone}$  9:1) to give a yellow-orange solid (121 mg, 70% yield).  $\text{C}_{40}\text{H}_{38}\text{BF}_4\text{FeN}_2\text{PS}$  (752.1): Calcd: C 63.82, H 5.05, N 3.72; found: C 63.60, H 5.32, N 3.64.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):  $\delta$  = 9.30 (s, 1H, NCHN<sup>+</sup>), 7.98 (d,  $J_{\text{H,H}}$  = 8.4 Hz, 1H, benzimidazole), 7.29 (d,  $J_{\text{H,H}}$  = 8.4 Hz, 1H, benzimidazole), 7.43-7.67 (m, 12H, benzimidazole + ArH), 6.98 (s, 2H, Mes), 5.61 (s, 2H,  $\text{CH}_2$ -Mes), 5.50 (s, 2H,  $\text{CH}_2$ -Fc), 4.75, 4.71, 4.48, 4.08 (t,  $J_{\text{H,H}}$  = 1.8 Hz, 8H, Cp), 2.33 (s, 3H, *p*- $\text{CH}_3$  Mes), 2.26 (s, 6H, *o*- $\text{CH}_3$  Mes).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):  $\delta$  = 141.32 (NCN<sup>+</sup>), 140.20, 137.93, 134.55, 133.39, 131.69, 131.55, 131.49, 131.41, 128.49, 128.33, 127.26, 124.32, 113.89, 113.41 (Ar-C), 130.31 (Mes), 80.73, 74.31, 74.15, 73.47, 73.33, 72.06, 70.91 (Cp), 47.01 ( $\text{CH}_2$ -Mes), 46.98 ( $\text{CH}_2$ -Fc), 21.09 (*p*- $\text{CH}_3$  Mes), 19.84 (*o*- $\text{CH}_3$  Mes).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):  $\delta$  = 41.6.

**Benzimidazolium salt 4b:** To a solution of ferrocenyl alcohol **1** (100 mg, 0.23 mmol) in degassed dichloromethane (5 mL) was quickly added  $\text{HBF}_4$  (35  $\mu\text{L}$ , 54 wt% in  $\text{Et}_2\text{O}$ ), immediately followed by *N*-(2,4,6-trimethylbenzyl)-5,6-dimethyl benzimidazole **2b** (96 mg, 0.35 mmol). The mixture was washed with 2 M aq. HCl, water, satd. aq.  $\text{NaHCO}_3$  and water again. The organic phase was dried ( $\text{MgSO}_4$ ), filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent:  $\text{CH}_2\text{Cl}_2/\text{acetone}$  9:1) to give a yellow-orange solid (108 mg, 60% yield).  $\text{C}_{42}\text{H}_{42}\text{BF}_4\text{FeN}_2\text{PS}$  (780.1): Calcd: C 64.61, H 5.38, N 3.59; found: C 64.67, H 5.82, N 3.85.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):  $\delta$  = 9.01 (s, 1H, NCHN<sup>+</sup>), 7.78-7.70 (m, 3H), 7.58 (s, 1H), 7.51-7.45 (m, 5H), 7.31 (s, 1H), 7.26 (s, 1H), 7.10 (s, 1H) (benzimidazole + Ar-H), 6.99 (s, 2H, Mes), 5.51, 5.39 (s, 2H,  $\text{CH}_2$ -Mes), 5.32, 5.21 (s, 2H,  $\text{CH}_2$ -Fc), 4.74 (t,  $J_{\text{H,H}}$  = 1.8 Hz, 1H, Cp), 4.66 (t,  $J_{\text{H,H}}$  = 1.8 Hz, 1H, Cp), 4.55 (d,  $J_{\text{H,H}}$  = 1.8 Hz, 2H, Cp), 4.48-4.47 (m, 1H, Cp), 4.30 (s, 1H, Cp), 4.07 (t,  $J_{\text{H,H}}$  = 1.8 Hz, 1H, Cp), 4.00 (s, 1H, Cp), 2.49, 2.44, 2.41 (s, 6H, *o*- $\text{CH}_3$  Mes), 2.33 (t,  $J_{\text{H,H}}$  = 3 Hz, 3H, *p*- $\text{CH}_3$  Mes), 2.26 (d,  $J_{\text{H,H}}$  = 1.2 Hz, 6H,  $\text{CH}_3$  benzimidazole).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):  $\delta$  = 139.71 (NCN<sup>+</sup>), 137.92, 137.87, 137.54, 137.42, 133.46, 131.69, 131.54, 131.40, 131.36, 128.48, 128.36, 128.32, 128.20, 124.49, 120.31, 113.51, 112.89, 109.77 (Ar-C), 130.22 (Mes), 81.01, 74.28, 74.11, 73.46, 73.33, 72.18, 72.05, 71.93, 70.84, 69.29, 69.22, 60.10 (Cp), 46.66, 46.49 ( $\text{CH}_2$ -Mes), 43.03 ( $\text{CH}_2$ -Fc), 21.08, 21.04

(*o*-CH<sub>3</sub> Mes), 20.78, 20.65, 20.29 (*p*-CH<sub>3</sub> Mes), 19.78, 19.56 (CH<sub>3</sub> benzimidazole). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 41.5.

**Benzimidazolium salt 5a:** Raney Nickel (2.2 g, suspension in water) was washed with degassed methanol (3x10 mL), degassed diethyl ether (3x10 mL) and finally degassed acetonitrile (3x10 mL). A solution of **4a** (500 mg, 0.67 mmol) in acetonitrile (10 mL) was added; the mixture was stirred at room temperature for 24 h, filtered on a short path of Celite® and rinsed with acetonitrile. The solution was concentrated and the orange solid was dried in vacuo (420 mg, 87% yield). C<sub>40</sub>H<sub>38</sub>BF<sub>4</sub>FeN<sub>2</sub>P (720.1): Calcd: C 66.66, H 5.28, N 3.89; found: C 65.01, H 5.99, N 3.92. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.10 (s, 1H, NCHN<sup>+</sup>), 7.70-7.32 (m, 12H, benzimidazole + Ar-H), 6.96 (s, 2H, Mes), 5.60 (s, 2H, CH<sub>2</sub>-Mes), 5.15 (s, 2H, CH<sub>2</sub>-Fc), 4.58, 4.36, 4.22, 4.13 (t, J<sub>H,H</sub> = 1.8 Hz, 8H, Cp), 2.32 (s, 3H, *p*-CH<sub>3</sub> Mes), 2.25 (s, 6H, *o*-CH<sub>3</sub> Mes). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 141.20 (NCN<sup>+</sup>), 140.14, 138.00, 133.64, 131.52, 131.33, 129.62, 128.89, 128.30, 127.22, 127.04, 124.49, 113.60, 113.53 (Ar-C), 130.26 (Mes), 79.54, 72.56, 70.73, 70.45 (Cp), 47.31 (CH<sub>2</sub>-Mes), 46.91 (CH<sub>2</sub>-Fc), 21.07 (*p*-CH<sub>3</sub> Mes), 19.85 (*o*-CH<sub>3</sub> Mes). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = -17.2.

**Benzimidazolium salt 5b:** Raney Nickel (2.4 g, suspension in water) was washed with degassed methanol (3x10 mL), degassed diethyl ether (3x10 mL) and finally degassed acetonitrile (3x10 mL). A solution of **4b** (450 mg, 0.58 mmol) in acetonitrile (10 mL) was added; the mixture was stirred at room temperature for 24 h, filtered on a short path of Celite® and rinsed with acetonitrile. The solution was concentrated and the orange solid was dried in vacuo (370 mg, 85% yield). C<sub>42</sub>H<sub>42</sub>BF<sub>4</sub>FeN<sub>2</sub>P (748.1): Calcd: C 67.37, H 5.61, N 3.74; found: C 67.23, H 5.62, N 3.88. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 8.86 (s, 1H, NCHN<sup>+</sup>), 7.59 (s, 1H), 7.41-7.32 (m, 8H), 7.31 (s, 1H), 7.26 (s, 1H), 7.11 (s, 1H) (benzimidazole + Ar-H), 6.98 (s, 2H, Mes), 5.51 (s, 2H, CH<sub>2</sub>-Mes), 5.21, 5.07 (s, 2H, CH<sub>2</sub>-Fc), 4.58 (t, J<sub>H,H</sub> = 1.8 Hz, 2H, Cp), 4.41 (s, 1H, Cp), 4.33 (t, J<sub>H,H</sub> = 1.8 Hz, 2H, Cp), 4.21 (t, J<sub>H,H</sub> = 1.8 Hz, 1H, Cp), 4.13 (d, J<sub>H,H</sub> = 1.8 Hz, 2H, Cp), 2.45, 2.41 (s, 6H, *o*-CH<sub>3</sub> Mes), 2.35, 2.33 (s, 3H, *p*-CH<sub>3</sub> Mes), 2.25 (d, J<sub>H,H</sub> = 4.2 Hz, 6H, CH<sub>3</sub> benzimidazole). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 139.66 (NCN<sup>+</sup>), 138.87, 137.97, 137.33, 137.25, 133.53, 128.73, 128.31, 113.16, 112.97 (Ar-C), 130.19 (Mes), 79.82, 74.10, 72.45, 70.60, 70.37, 65.85 (Cp), 47.03 (CH<sub>2</sub>-Mes), 46.40 (CH<sub>2</sub>-Fc), 21.06, 20.76, 20.73 (CH<sub>3</sub> Mes), 19.75 (CH<sub>3</sub> benzimidazole). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = -17.1.

**Benzimidazolium salt 6a:** (Ferrocenylmethyl)trimethylammonium iodide **3** (465 mg, 1.2 mmol) was slowly added to a solution of *N*-(2,4,6-trimethylbenzyl) benzimidazole **2a** (325 mg, 1.3 mmol) in acetonitrile (10 mL). The mixture was heated to reflux for 48 h then the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/acetone 8:2) to give an orange solid (485 mg, 70% yield). C<sub>28</sub>H<sub>29</sub>FeIN<sub>2</sub> (578.8): Calcd: C 58.05, H 5.01, N 4.84; found: C 58.10, H 5.08, N 4.37. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 10.60 (s, 1H, NCHN<sup>+</sup>), 7.77, 7.30 (dd, J<sub>H,H</sub> = 8.4 Hz, 2H, benzimidazole), 7.57, 7.48 (dt, J<sub>H,H</sub> = 6.2 Hz, 2H, benzimidazole), 6.96 (s, 2H, Mes), 5.72 (s, 2H, CH<sub>2</sub>-Mes), 5.32 (s, 2H, CH<sub>2</sub>-Fc), 4.55, 4.31, 4.23 (t, J<sub>H,H</sub> = 1.8 Hz, 9H, Cp), 2.32 (s, 9H, CH<sub>3</sub>Mes). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 140.96 (NCN<sup>+</sup>), 140.03, 137.98, 131.35 (d, J<sub>C,H</sub> = 4.5 Hz), 127.22 (d, J<sub>C,H</sub> = 10.6 Hz), 124.65, 113.67 (d, J<sub>C,H</sub> = 12.8 Hz), (Ar-C), 130.32 (Mes), 79.20, 69.77, 69.64, 69.55, 69.48, 69.35, 69.30 (Cp), 48.09 (CH<sub>2</sub>-Mes), 47.12 (CH<sub>2</sub>-Fc), 21.13 (*p*-CH<sub>3</sub> Mes), 20.44 (d, J<sub>C,H</sub> = 4.5 Hz, *o*-CH<sub>3</sub> Mes).

**Benzimidazolium salt 6b:** (Ferrocenylmethyl)trimethylammonium iodide **3** (465 mg, 1.2 mmol) was slowly added to a solution of *N*-(2,4,6-trimethylbenzyl)-5,6-dimethyl benzimidazole **2b** (361 mg, 1.3 mmol) in acetonitrile (10 mL). The mixture was heated to reflux for 48 h then the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/acetone 8:2) to give an orange solid (590 mg, 81% yield). C<sub>30</sub>H<sub>33</sub>FeIN<sub>2</sub> (606.8): Calcd: C 59.33, H 5.44, N 4.61; found: C 61.01, H 6.08, N 4.80. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 10.21 (s, 1H, NCHN<sup>+</sup>), 7.11, 7.27, 7.32, 7.50, 7.59 (s, 2H,

benzimidazole), 6.98 (s, 2H, Mes), 5.64 (d, J<sub>H,H</sub> = 8.7 Hz, 2H, CH<sub>2</sub>-Mes), 5.22 (s, 2H, CH<sub>2</sub>-Fc), 4.52 (t, J<sub>H,H</sub> = 2.1 Hz, 2H, Cp), 4.30 (s, 5H, Cp), 4.22 (t, J<sub>H,H</sub> = 2.1 Hz, 2H, Cp), 2.43 (d, J<sub>H,H</sub> = 10.2 Hz, 6H, *o*-CH<sub>3</sub>-Mes), 2.34 (d, J<sub>H,H</sub> = 8.1 Hz, 6H, CH<sub>3</sub> benzimidazole), 2.27 (s, 3H, *p*-CH<sub>3</sub>-Mes). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 140.95 (NCN<sup>+</sup>), 140.00, 139.86, 138.72, 137.99, 137.90, 137.31, 137.26, 132.00, 130.29, 130.12, 129.97, 129.62, 127.37, 124.82, 120.35, 113.18, 113.04, 109.78, (Ar-C), 131.15 (Mes), 79.53 (Cp), 69.32 (m, Cp), 47.77, 46.59 (CH<sub>2</sub>-Mes), 43.05 (CH<sub>2</sub>-Fc), 19.58 (*p*-CH<sub>3</sub> Mes), 20.31, 20.42 (CH<sub>3</sub> benzimidazole), 20.75, 21.92 (*o*-CH<sub>3</sub> Mes).

**Rhodium complex 7a:** *t*-BuOK (23.3 mg, 0.21 mmol) and [Rh(COD)Cl]<sub>2</sub> (47.6 mg, 0.097 mmol) were placed in a Schlenk tube, the solids were degassed and THF (10 mL) was added. The solution was stirred for 30 min at room temperature, then slowly added to **5a** (139 mg, 0.194 mmol), which was precooled to -78 °C. The mixture was stirred at -78 °C for 15 min then 2 h at room temperature. The solvent was evaporated and the residue taken up into degassed CH<sub>2</sub>Cl<sub>2</sub> (10 mL). AgBF<sub>4</sub> (56.7 mg, 0.291 mmol) was added, the mixture was stirred for 30 min at room temperature then filtered on Celite®. The solvent was evaporated in vacuo and the residue was filtered on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/acetone 95:5) to give **7a** as an orange solid (154 mg, 86% yield). C<sub>48</sub>H<sub>49</sub>BF<sub>4</sub>FeN<sub>2</sub>PRh (929.6): Calcd: C 61.96, H 5.27, N 3.01; found: C 61.55, H 5.60, N 2.98. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.51-7.30 (m, 10H, Ar-H), 7.62 (d, J<sub>H,H</sub> = 8.4 Hz, 1H, benzimidazole), 7.46 (d, J<sub>H,H</sub> = 15.3 Hz, 1H, benzimidazole), 6.26 (d, J<sub>H,H</sub> = 15.3 Hz, 1H, benzimidazole), 5.77 (d, J<sub>H,H</sub> = 8.4 Hz, 1H, benzimidazole), 6.93 (s, 2H, Mes), 5.47 (d, J<sub>H,H</sub> = 15 Hz, 2H, CH<sub>2</sub>-Mes), 4.97 (d, J<sub>H,H</sub> = 15 Hz, 2H, CH<sub>2</sub>-Fc), 4.49, 4.24, 4.11 (s, 8H, Cp), 5.18 (s, 2H, COD-CH), 4.40 (s, 2H, COD-CH), 2.53 (s, 4H, COD-CH<sub>2</sub>), 2.31 (s, 4H, COD-CH<sub>2</sub>), 2.37 (s, 6H, *o*-CH<sub>3</sub> Mes), 1.82 (s, 3H, *p*-CH<sub>3</sub> Mes). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 192.52 (d, J<sub>Rh,C</sub> = 50.8 Hz, C<sub>carbene</sub>), 139.78, 138.55, 134.11, 131.96, 131.65, 130.92, 129.96, 128.71, 126.10, 123.65, 111.38, 110.93 (Ar-C), 129.82 (Mes), 71.26, 69.98, 69.31, 68.44 (Cp), 99.13, 96.50, 73.46 (COD-CH), 30.90, 30.42 (COD-CH<sub>2</sub>), 50.80 (CH<sub>2</sub>-Fc), 47.12 (CH<sub>2</sub>-Mes), 21.12 (*o*-CH<sub>3</sub> Mes), 19.89 (*p*-CH<sub>3</sub> Mes). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 18.4 (d, J<sub>P,Rh</sub> = 154.3 Hz) ppm.

**Rhodium complex 7b:** *t*-BuOK (19 mg, 0.171 mmol) and [Rh(COD)Cl]<sub>2</sub> (38.5 mg, 0.078 mmol) were placed in a Schlenk tube, the solids were degassed and THF (10 mL) was added. The solution was stirred for 30 min at room temperature, then slowly added to **5b** (117 mg, 0.156 mmol), which was precooled to -78 °C. The mixture was stirred at -78 °C for 15 min then 2 h at room temperature. The solvent was evaporated and the residue taken up into degassed CH<sub>2</sub>Cl<sub>2</sub> (10 mL). AgBF<sub>4</sub> (45.6 mg, 0.234 mmol) was added, the mixture was stirred for 30 min at room temperature and then filtered on Celite®. The solvent was evaporated in vacuo and the residue was filtered on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/acetone 95:5) to give **7b** as an orange solid (126 mg, 84% yield). C<sub>50</sub>H<sub>53</sub>BF<sub>4</sub>FeN<sub>2</sub>PRh (957.6): Calcd: C 62.66, H 5.54, N 2.92; found: C 61.40, H 5.66, N 2.89. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.51-7.39 (m, 10H, Ar-H), 7.33 (s, 1H, benzimidazole), 5.39 (s, 1H, benzimidazole), 6.94 (s, 2H, Mes), 5.33 (d, J<sub>H,H</sub> = 9 Hz, 2H, CH<sub>2</sub>-Mes), 4.87 (d, J<sub>H,H</sub> = 15 Hz, 2H, CH<sub>2</sub>-Fc), 4.48, 4.45, 4.25, 4.15 (s, 8H, Cp), 5.14 (s, 2H, COD-CH), 4.38 (s, 2H, COD-CH), 2.52 (s, 4H, COD-CH<sub>2</sub>), 2.41 (s, 4H, COD-CH<sub>2</sub>), 2.39 (s, 6H, *o*-CH<sub>3</sub> Mes), 1.99 (s, 3H, *p*-CH<sub>3</sub> Mes) 1.81 (s, 6H, CH<sub>3</sub> benzimidazole). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 189.84 (d, J<sub>Rh,C</sub> = 50.7 Hz, C<sub>carbene</sub>), 139.69, 138.68, 134.27, 134.10, 133.87, 132.80, 132.67, 131.64, 130.86 (Mes), 129.33, 129.19, 128.75, 128.62, 126.40, 111.87, 110.87 (Ar-C), 129.60 (Mes), 71.31, 69.91, 69.24, 68.43 (Cp), 98.89, 96.47, 96.33, 73.58 (COD-CH), 30.93, 30.43, 22.34 (COD-CH<sub>2</sub>), 50.52 (CH<sub>2</sub>-Fc), 46.99 (CH<sub>2</sub>-Mes), 21.06 (*o*-CH<sub>3</sub> Mes), 20.57, 20.26 (*p*-CH<sub>3</sub> Mes), 19.89 (CH<sub>3</sub> benzimidazole). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 18.55 (d, J<sub>P,Rh</sub> = 159.2 Hz).

**Rhodium complex 8a:** A mixture of **6a** (116 mg, 0.2 mmol) and [Rh(OMe)(COD)]<sub>2</sub> (48.4 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred at room temperature for 6 h. The volume of the solvent was reduced to 2 mL,



pentane (10 mL) was added and the yellow precipitate was recovered by filtration. The residue was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>) to give a yellow-orange solid (135 mg, 86% yield). C<sub>36</sub>H<sub>40</sub>FeN<sub>2</sub>Rh (785.7): Calcd: C 54.98, H 5.09, N 3.56; found: C 52.85, H 4.71, N 3.32. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.21 (d, *J*<sub>H,H</sub> = 15 Hz, 1H, benzimidazole), 6.94 (t, *J*<sub>H,H</sub> = 7.5 Hz, 1H, benzimidazole), 6.78 (t, *J*<sub>H,H</sub> = 7.5 Hz, 1H, benzimidazole), 6.32 (benzimidazole), 6.95 (s, 2H, Mes), 6.10 (t, *J*<sub>H,H</sub> = 12.5 Hz, 2H, CH<sub>2</sub>-Mes), 5.83 (q, *J*<sub>H,H</sub> = 15 Hz, 2H, CH<sub>2</sub>-Fc), 4.83 (d, *J*<sub>H,H</sub> = 1.8 Hz, 2H, Cp), 4.48 (d, *J*<sub>H,H</sub> = 1.8 Hz, 2H, Cp), 4.35 (s, 2H, Cp), 4.19 (t, *J*<sub>H,H</sub> = 1.8 Hz, 2H, Cp), 5.52, 5.39 (s, 2H, COD-CH), 3.66 (s, 2H, COD-CH), 2.49 (s, 4H, COD-CH<sub>2</sub>), 1.94 (s, 4H, COD-CH<sub>2</sub>), 2.37 (s, 3H, *p*-CH<sub>3</sub> Mes), 2.32 (s, 6H, *o*-CH<sub>3</sub> Mes). <sup>13</sup>C{<sup>1</sup>H} NMR (62.9 MHz, CDCl<sub>3</sub>, 25 °C): δ = 196.38 (d, *J*<sub>Rh,C</sub> = 50.6 Hz, C<sub>carbene</sub>), 138.82, 138.53, 135.86, 134.69, 128.20, 122.05, 121.47, 110.71, 110.60 (Ar-C), 129.51 (Mes), 82.08, 71.15, 69.50, 69.22, 68.91, 67.76 (Cp), 97.74, 97.63, 97.55, 97.44, 72.50, 72.28, 72.11, 71.89 (COD-CH), 32.73, 32.08, 30.16, 29.00 (COD-CH<sub>2</sub>), 50.45 (CH<sub>2</sub>-Mes), 49.92 (CH<sub>2</sub>-Fc), 21.11 (*p*-CH<sub>3</sub> Mes) 21.07 (*o*-CH<sub>3</sub> Mes).

**Rhodium complex 8b:** A mixture of **6b** (121 mg, 0.2 mmol) and [Rh(OMe)(COD)]<sub>2</sub> (48.4 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred at room temperature for 6 h. The volume of the solvent reduced to 2 mL, pentane (10 mL) was added and the yellow precipitate was recovered by filtration. The residue was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>) to give a yellow-orange solid (138 mg, 84% yield). C<sub>38</sub>H<sub>44</sub>FeN<sub>2</sub>Rh (813.7): Calcd: C 56.04, H 5.41, N 3.44; found: C 56.85, H 5.81, N 3.33. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 6.97 (s, 2H, benzimidazole), 6.95 (s, 2H, Mes), 6.03 (d, *J*<sub>H,H</sub> = 15 Hz, 1H, CH<sub>2</sub>-Mes), 6.23 (d, *J*<sub>H,H</sub> = 15 Hz, 1H, CH<sub>2</sub>-Mes), 5.78 (q, *J*<sub>H,H</sub> = 12 Hz, 2H, CH<sub>2</sub>-Fc), 4.80 (d, *J*<sub>H,H</sub> = 1.2 Hz, 2H, Cp), 4.47 (d, *J*<sub>H,H</sub> = 1.2 Hz, 2H, Cp), 4.33 (d, *J*<sub>H,H</sub> = 1.2 Hz, 2H, Cp), 4.17 (t, *J*<sub>H,H</sub> = 1.2 Hz, 2H, Cp), 5.46, 5.35 (s, 2H, COD-CH), 3.60 (s, 2H, COD-CH), 2.47 (s, 4H, COD-CH<sub>2</sub>), 1.95 (s, 4H, COD-CH<sub>2</sub>), 2.37 (s, 3H, *p*-CH<sub>3</sub> Mes), 2.31 (s, 6H, *o*-CH<sub>3</sub> Mes), 2.17 (s, 6H, CH<sub>3</sub> benzimidazole). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 194.51 (d, *J*<sub>Rh,C</sub> = 50.8 Hz, C<sub>carbene</sub>), 138.83, 138.37, 134.51, 133.32, 130.61, 130.26, 129.35, 128.56, 111.15 (Ar-C), 129.47 (Mes), 82.43, 71.07, 69.38, 68.76, 67.69 (Cp), 97.36, 97.27, 97.16, 97.08, 72.35, 72.16, 71.98, 71.80 (COD-CH), 32.70, 32.10, 30.11, 29.03 (COD-CH<sub>2</sub>), 50.08 (CH<sub>2</sub>-Mes), 49.68 (CH<sub>2</sub>-Fc), 21.06 (*p*-CH<sub>3</sub> Mes) 20.29 (*o*-CH<sub>3</sub> Mes), 20.15 (CH<sub>3</sub> benzimidazole).

#### Representative procedure for Rh<sup>I</sup>-catalyzed hydrosilylation of ketones.

In a flame-dried Schlenk flask was placed the Rh<sup>I</sup> complex (10<sup>-6</sup> mol, 2 mol%) under argon. Anhydrous THF (0.25 mL) and then acetophenone (56 μL, 4.8 10<sup>-4</sup> mol) were added by syringe. Diphenylsilane (100 μL, 5.4 10<sup>-4</sup> mol) was added slowly, the reaction mixture was stirred at room temperature and the conversion of acetophenone followed by TLC analysis. After the reaction was finished, the solvent was evaporated in vacuo and the residue analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>). The NMR sample was taken up into CH<sub>2</sub>Cl<sub>2</sub>, MeOH (1 mL) was added, the reaction mixture stirred for 1h at room temperature. 1M HCl (1 mL) was then added, and the reaction mixture stirred for 1 additional hour at room temperature. The phases were separated, the aqueous phase extracted with CH<sub>2</sub>Cl<sub>2</sub>, the organic phases were dried (MgSO<sub>4</sub>), filtered and concentrated in vacuo. The residue was analyzed by <sup>1</sup>H NMR.

#### X-ray diffraction studies.

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of glass fibre and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR CCD diffractometer for **6b**, **7b**, **7a** and **8a**, a Stoe IPDS diffractometer for **8b** or a Bruker APEXII CCD diffractometer for **5a**. Data were collected using the monochromatic MoKα radiation (λ = 0.71073). The structures were solved by direct methods (SIR97)<sup>[40]</sup> and refined by least-squares procedures on F<sup>2</sup> using SHELXL-97.<sup>[41]</sup> All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. In compound **6b**, some residual electron density were difficult to model and therefore, the

SQUEEZE function of PLATON<sup>[42]</sup> was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. There are two cavities of about 173 Å<sup>3</sup> per unit cell. PLATON estimated that each cavity contains 12 electrons which may correspond to half a molecule of acetonitrile as suggested by chemical analyses. In compound **7b** and **8a**, the SQUEEZE function has been also used. In **7b**, there are two cavities of 470 Å<sup>3</sup> per unit cell. PLATON estimated that each cavity contains 190 electrons which may correspond to roughly a mixture of four CH<sub>2</sub>Cl<sub>2</sub> and four (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O molecules within the cell as suggested by the use of these solvents during the crystallization procedure. In compound **8a**, there are two cavities of 172 Å<sup>3</sup> per unit cell, which may roughly correspond to a mixture of two CH<sub>2</sub>Cl<sub>2</sub> and two (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O molecules within the cell. The drawing of the molecules was realised with the help of ORTEP32.<sup>[43]</sup> Crystal data and refinement parameters are shown in Tables 4 and 5.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 710144 – 710147 and 711381 – 711382. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-0033; e-mail: deposit@ccdc.cam.ac.uk).

Table 4. Crystal data and structure refinement parameters for benzimidazolium salts.

Compound	<b>5a</b>	<b>6b</b>
Empirical formula	C <sub>40</sub> H <sub>38</sub> FeN <sub>2</sub> P, BF <sub>4</sub>	(C <sub>30</sub> H <sub>33</sub> FeN <sub>2</sub> ) <sub>2</sub> , I <sub>2</sub>
Formula weight	720.35	1208.67
Temperature, K	180(2) K	180(2) K
Wavelength, Å	0.71073	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P 2 <sub>1</sub> /c	P -1
a, Å	16.5808(16)	10.0316(8)
b, Å	16.7482(15)	13.7879(10)
c, Å	12.9508(11)	22.6738(14)
α, °	90.0	103.671(6)
β, °	92.832(5)	97.411(6)
γ, °	90.0	102.822(7)
Volume, Å <sup>3</sup>	3592.0(6)	2916.3(4)
Z	4	2
Density (calculated), Mg/m <sup>3</sup>	1.332	1.376
Absorption coefficient, mm <sup>-1</sup>	0.516	1.594
F(000)	1496	1224
Crystal size, mm <sup>3</sup>	0.84 x 0.163 x 0.068	0.75 x 0.43 x 0.26
Theta range, °	2.38 to 27.02	2.77 to 27.10
Reflections collected	120450	23199
Independent reflections (R <sub>int</sub> )	7757 (0.0836)	12820 (0.0407)
Completeness, %	98.7	99.5 %
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	1.0 and 0.404	1.0 and 0.635
Refinement method	F <sup>2</sup>	F <sup>2</sup>
Data / restraints / parameters	7757 / 0 / 445	12820 / 0 / 623
Goodness-of-fit on F <sup>2</sup>	1.031	1.078
R1, wR2 [I > 2σ(I)]	0.0418, 0.1013	0.0608, 0.1374
R1, wR2 (all data)	0.0686, 0.1154	0.0766, 0.1434
Residual density, e.Å <sup>-3</sup>	0.611 / -0.467	1.536 / -1.232

Table 5. Crystal data and structure refinement parameters for rhodium complexes.

Compound	7a	7b	8a	8b
Empirical formula	C <sub>46</sub> H <sub>45</sub> FeN <sub>2</sub> PRh, BF <sub>4</sub>	C <sub>50</sub> H <sub>51</sub> FeN <sub>2</sub> PRh, BF <sub>4</sub>	C <sub>36</sub> H <sub>40</sub> FeIN <sub>2</sub> Rh	C <sub>38</sub> H <sub>44</sub> FeN <sub>2</sub> Rh, I
Formula weight	891.57	956.47	786.36	814.41
Temperature, K	180(2)	180(2) K	180(2) K	296(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Tetragonal	Monoclinic
Space group	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /n	I-4	P 2 <sub>1</sub> /n
a, Å	10.4291(4)	14.6210(15)	28.3187(10)	12.5094(14)
b, Å	27.7380(12)	13.7691(11)	28.3187(10)	15.0659(12)
c, Å	14.1065(6)	24.724(2)	8.0375(6)	18.3417(19)
α, °	90.0	90.0	90.0	90.0
β, °	91.019	91.663(3)	90.0	98.151(13)
γ, °	90.0	90.0	90.0	90.0
Volume, Å <sup>3</sup>	4080.1(3)	4975.3(8)	6445.7(6)	3421.9(6)
Z	4	4	8	4
Density (calculated), Mg/m <sup>3</sup>	1.515	1.277	1.621	1.581
Absorption coefficient, mm <sup>-1</sup>	0.855	0.703	1.947	1.837
F(000)	1912	1968	3152	1640
Crystal size, mm <sup>3</sup>	0.336 x 0.125 x 0.080	0.293 x 0.085 x 0.039	0.44 x 0.08 x 0.071	0.40 x 0.40 x 0.16
Theta range, °	2.82 to 26.37	1.64 to 22.12	2.27 to 33.22	1.76 to 24.20
Reflections collected	30948	79794	128931	27214
Independent reflections (R <sub>int</sub> )	8322 (0.0756)	6134 (0.1124)	12376 (0.0463)	5458 (0.1564)
Completeness, %	99.9	98.8	99.9	99.0
Absorption correction	Multi-scan	Semi-empirical equivalents	from Semi-empirical equivalents	from Multi-scan
Max. and min. transmission	1.0 and 0.970	1.0 and 0.784	1.0 and 0.881	0.5312 and 0.4354
Refinement method	F <sup>2</sup>	F <sup>2</sup>	F <sup>2</sup>	F <sup>2</sup>
Data / restraints / parameters	8322 / 51 / 526	6134 / 0 / 546	12376 / 1 / 373	5458 / 0 / 393
Goodness-of-fit on F <sup>2</sup>	1.243	1.076	1.035	0.790
R1, wR2 [I>2σ(I)]	0.0792, 0.1418	0.0406, 0.0978	0.0294, 0.0674	0.0544, 0.1175
R1, wR2 (all data)	0.1146, 0.1500	0.0598, 0.1051	0.0336, 0.0689	0.1360, 0.1409
Residual density, e.Å <sup>-3</sup>	1.068 / -1.517	0.508 / -0.403	0.600 / -0.359	1.200 / -1.130

## Acknowledgment

We thank the Centre National de la Recherche Scientifique (CNRS) and the Institut Universitaire de France (IUF) for support of this work.

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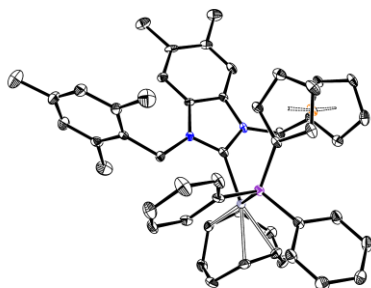
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## Entry for the Table of Contents ((Please choose one layout.))

### Layout 1:

Precursors of new ferrocenyl phosphane-benzimidazol-2-ylidene bifunctional ligands, and monodentate ferrocenyl benzimidazol-2-ylidene ligands, have been prepared. Cationic and neutral rhodium(I) complexes showed good activities for the catalytic hydrosilylation of ketones. The use of bidentate ligands proved essential to obtain good selectivities in the desired alcohol.



### Ferrocenyl benzimidazol-2-ylidene Rh<sup>I</sup> complexes

**Süleyman Gülcemal, Agnès Labande,  
\* Jean-Claude Daran, Bekir  
Çetinkaya and Rinaldo Poli** .....

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Rhodium(I) complexes of new ferrocenyl benzimidazol-2-ylidene ligands. The importance of chelating effect for ketone hydrosilylation catalysis.

**Keywords:** N-heterocyclic carbenes / benzimidazole / ferrocene / Rhodium / hydrosilylation