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Rhodium(I) Complexes of New Ferrocenyl Benzimidazol-2-ylidene Ligands: The Importance of the Chelating Effect for Ketone Hydrosilylation Catalysis

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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 have been 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. The activities are much greater than for related imidazol-2-ylidene systems, and the cationic complexes are more active than the neutral complexes; the highest activity is observed for the more soluble complex **7b**. The use of bidentate ligands proved to be essential for obtaining good selectivities of the desired alcohol.

Introduction

Recent developments in the field of functionalised N-heterocyclic carbene (NHC) ligands have proved that they have great potential in transition-metal catalysis.[1–3] Indeed, the presence of an NHC ligand 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 the bifunctional ligands dramatically change the reactivity of rhodium(I) catalysts in the hydrosilylation of ketones.[4,5]

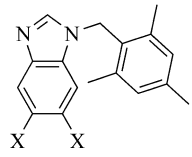
Although NHC ligands bearing a benzimidazole backbone offer a vast potential in catalytic applications, their coordination chemistry has remained relatively unexplored.[6–12] The σ-donating properties of benzimidazol-2-ylidene ligands are between those of unsaturated imidazol-2-ylidenes and of saturated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

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.[2,14] 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,[15] 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

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 the substituted benzimidazoles **2a** and **2b**[7,16] (Figure 1, Scheme 1),



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a: X = H
b: X = Me

Figure 1. Substituted benzimidazoles.

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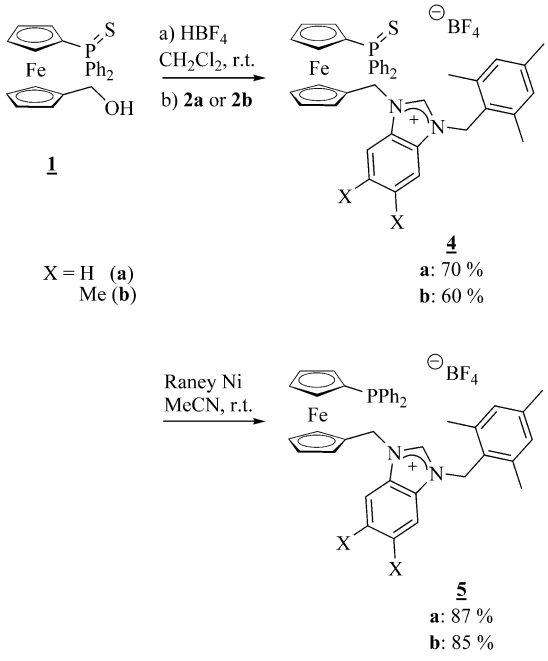
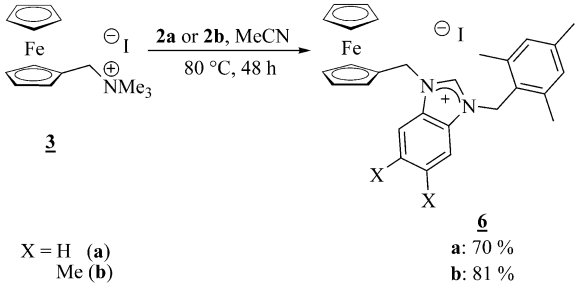


Scheme 1. Synthesis of 1,1′-disubstituted ferrocenyl benzimidazolium salts.

respectively, by following the procedure developed previously in our group for related imidazolium salts.[4]

The phosphane group was deprotected by desulfurisation with Raney nickel to afford the ligand precursors **5a** and **5b**. Two related systems, either with or without methyl groups (**b** and **a**, respectively) 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.[12]

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



Scheme 2. Synthesis of ferrocenyl benzimidazolium salts.

All compounds were fully characterised by standard analytical methods. The ^{1}H NMR spectra of compounds **5a** and **5b** show signals at 9.10 and 8.86 ppm, respectively, which are 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) because of the stronger C–H···X$^-$ bond polarisation when X = I.[3] The crystal structures of compounds **5a** and **6b** have been solved 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] than that of the 1,1′-ferrocenylphosphane imidazolium salt previously described by us [1.330(6) Å].[4] This denotes the delocalisation of the C–C bond π-electron density over the condensed benzene ring (the C–C bond lengths within the ring are in the range 1.372–1.402 Å for **5a** and in the range 1.354–1.424 Å for **6b**), which could be responsible for the different reactivity of the resulting carbenes. The two structures exhibit hydrogen bonds, as is typically observed for imidazolium salts, between a fluorine atom of the BF_4^- anion and the C62 proton (F3···H62–C62, 2.312 Å) for **5a** and between the iodide anion and the C1 proton (I1···H1–C1, 2.962 Å) for **6b**. The H bond is significantly shorter in the case of the benz-

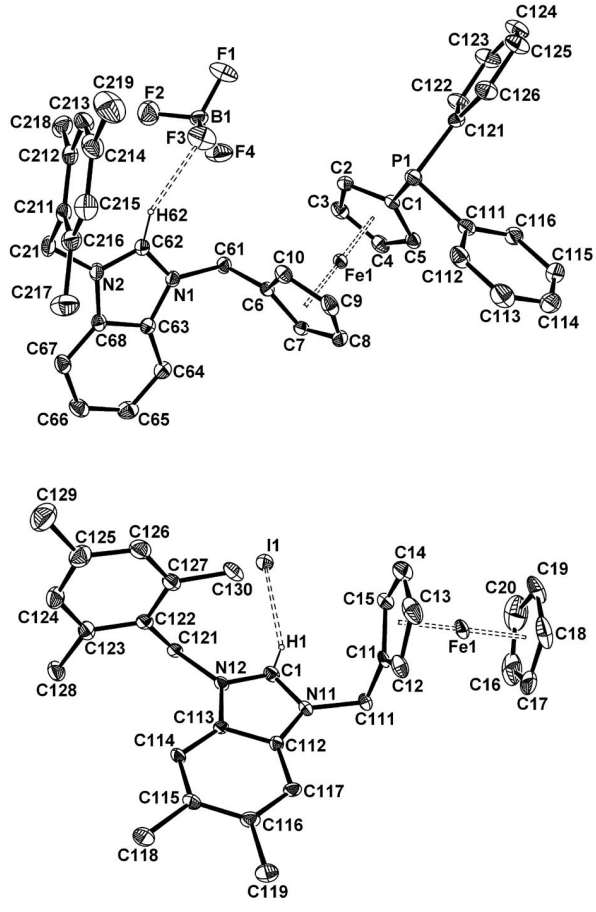
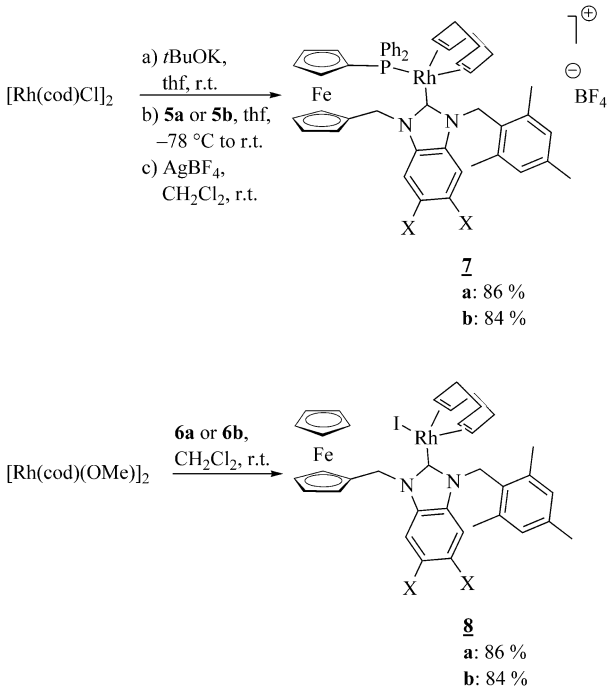


Figure 2. ORTEP views of **5a** (top) and **6b** (bottom). Ellipsoids are shown at the 30% probability level. All hydrogen atoms except H2 (top) and H1 (bottom) are omitted for clarity. Selected bond lengths [Å] and angles [°], **5a**: C1–P1 1.811(2), C62–N1 1.325(3), C62–N2 1.331(3), C63–C68 1.395(3), N1–C62–N2 110.5(2); **6b**: C1–N11 1.321(6), C1–N12 1.321(6), C112–C113 1.399(6), N11–C1–N12 110.4(6).

imidazolium salt **5a**, which possesses 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.

Synthesis and Characterisation of Rhodium(I) Complexes 7 and 8

Addition of compounds **5a** or **5b** to $[Rh(cod)(OtBu)]_2$ – prepared in situ from $[Rh(cod)Cl]_2$ and *t*BuOK[18] – in thf led to rhodium(I) complexes **7a** or **7b**. $[Rh(OMe)(cod)]_2$ reacted with benzimidazolium salts **6a** or **6b** in dichloromethane to give complexes **8a** or **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 coordination of the iodido ligand.



Scheme 3. Synthesis of rhodium complexes.

The ^{13}C NMR signals of the carbene C atoms of complexes **7** appear at δ = 192.5 ppm (**7a**) and 189.9 ppm (**7b**) and lie within the expected range for cationic NHC–Rh^{I} complexes with a benzimidazol-2-ylidene moiety.[10,19] These signals are found at slightly lower fields for complexes **8a** (δ =196.4 ppm) and **8b** (δ =194.5 ppm).[8,18]

Complexes **7** and **8** gave X-ray quality crystals by slow diffusion of diethyl ether into a dichloromethane solution (Figures 3 and 4, respectively). Selected bond lengths and angles are listed in Table 1 and are compared to those of a previously described complex **9a** (Figure 5).[4] The square-planar coordination environment in complexes **7** and **8** was confirmed by X-ray diffraction studies. The *cis*-NHC–Rh–P angles in complexes **7a** and **7b** [92.06(18)° and 93.78(12)°,

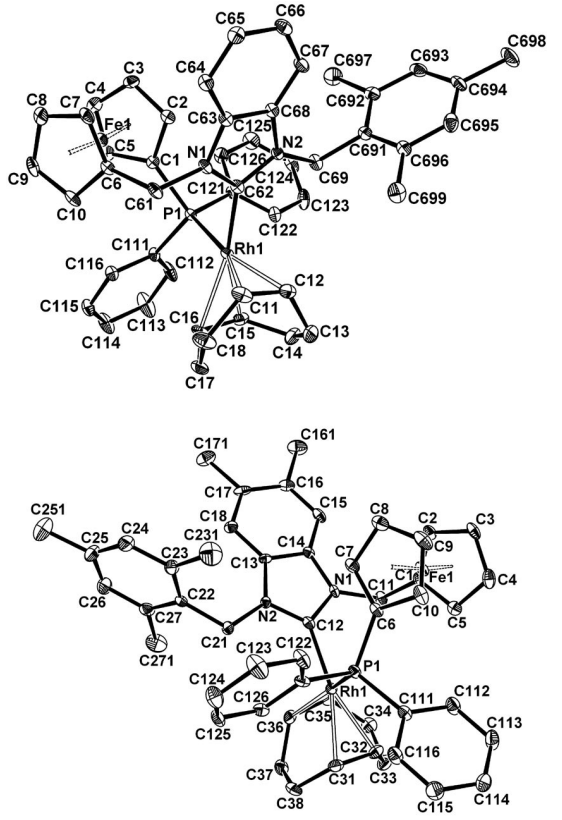


Figure 3. ORTEP views of **7a** (top) and **7b** (bottom). Ellipsoids are shown at the 50% (**7a**) or 30% (**7b**) probability level. All hydrogen atoms are omitted for clarity.

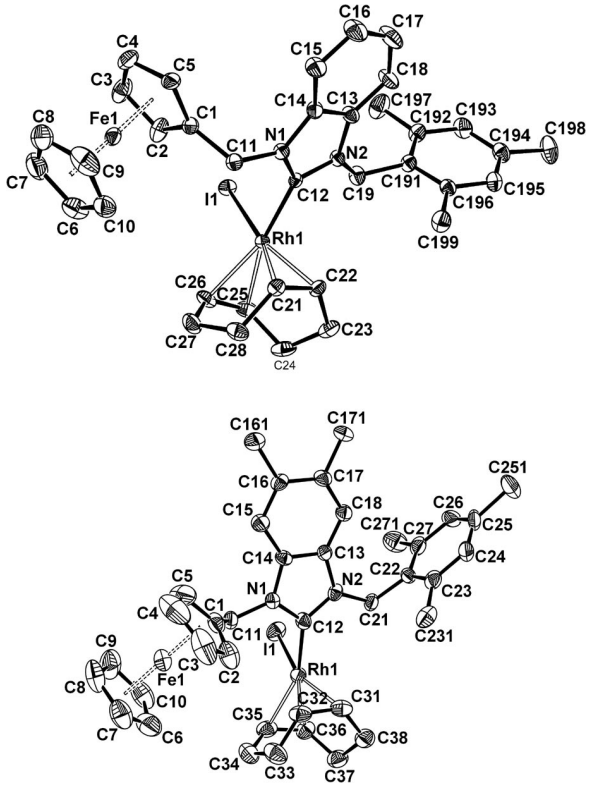


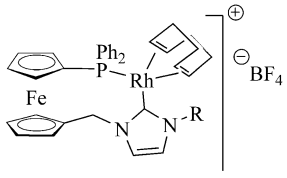
Figure 4. ORTEP views of **8a** (top) and **8b** (bottom). Ellipsoids are shown at the 50% (**8a**) or 30% (**8b**) probability level. All hydrogen atoms are omitted for clarity.

respectively] and the *cis*-NHC–Rh–I angles in complexes **8a** and **8b** [89.57(6)° and 86.1(3)°, respectively] are close to the expected value of 90°. The structures of complexes **7a** and **7b** reveal slightly shorter Rh1–C(NHC) bond lengths than those in the imidazol-2-ylidene/phosphane complex **9a** as well as those in a related complex described by Field et al.

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

	7a	**7b**	**9a**[a]	**8a**	**8b**
Bond lengths					
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)
Rh1–C(cod)	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)
	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)
Bond angles					
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)

[a] Data from ref.[4]; chemically equivalent parameters are given on the same row for all compounds.



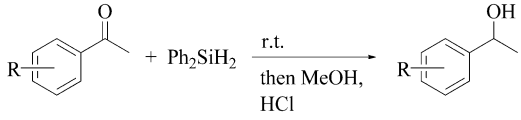
9
a: R = Me
b: R = 2,4,6-trimethylphenyl

Figure 5. Previously described Rh^I complexes with an imidazol-2-ylidene moiety.[4]

[2.064(2) Å].[20] 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 coordination of iodido ligands.[8,9,21] 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 cannot observe any significant variation in the Rh1–C(NHC) bond lengths related to this parameter. The mesityl group is found in a roughly orthogonal position to the benzimidazole backbone, and dihedral angles range from 86 to 90°, to limit steric interactions.

Catalytic Hydrosilylation of Methyl Aryl Ketones

The catalytic activity of NHC complexes **7** and **8** was evaluated in the hydrosilylation of carbonyl compounds.[22,23] The reactions were typically carried out with 2 mol-% 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 ^{1}H NMR spectroscopy.



Scheme 4. Hydrosilylation of acetophenone and its derivatives with Rh^I 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 the alcohol were much higher in the case of bifunctional, cationic complexes **7a** and **7b**. As observed in some of our previous work, the concentration of acetophenone in the medium can dramatically alter the reaction rate.[5] We thus carried out the next catalytic tests with a more concentrated medium (2 M instead of 1 M). The

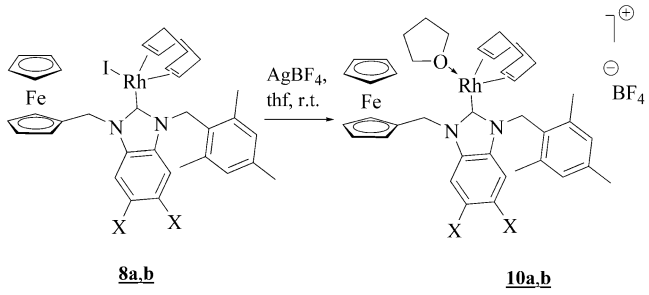
Table 2. Hydrosilylation of acetophenone (R = H).[a]

Entry	Catalyst (mol-%)	Additive	Concentration [M]	*t* [h]	Conversion[b] [%]	Ratio silyl ether/silyl enol ether[b]	Yield (1-phenylethanol)[c] [%]
1	**7a** (2)	–	1	20	n.c.	n.c.	73
2	**7b** (2)	–	1	20	n.c.	n.c.	85
3	**7a** (2)	–	2	20	80	96:4	78[d]
4	**7b** (2)	–	2	2	100	98:2	98
5	**7b** (1)	–	2	2	100	96:4	95
6	**8a** (2)	–	1	20	n.c.	n.c.	43[d]
7	**8b** (2)	–	1	20	n.c.	n.c.	23
8	**8a** (2)	–	2	8	n.c.	n.c.	49[d]
9	**8b** (2)	–	2	8	n.c.	n.c.	32
10	**10a** (2)	–	2	2	100	n.c.; 50:50; 59:41[e]	62; 46; 60[e]
11	**10b** (2)	–	2	2	100	n.c.; 69:31; 58:42[e]	83; 66; 58[e]
12	**10a** (2)	PPh_3 (1 equiv.)	2	20	100	78:22	76[d]
13	**10b** (2)	PPh_3 (1 equiv.)	2	2	100	87:13	84
14[f]	**9a** (2)	–	2	5 d	63	>99:1	63[d]
15[f]	**9b** (2)	–	2	5 d	90	99:1	87[d]

[a] Ketone (1 equiv.), diphenylsilane (1.1 equiv.), room temperature, thf, then hydrolysis with MeOH/HCl. [b] Determined by ^{1}H NMR signal integration of the crude reaction mixture before hydrolysis, n.c. = not calculated. [c] Determined by ^{1}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.[4]

results were very encouraging, since we obtained a nearly quantitative yield of the alcohol in 2 h with complex **7b** (Entry 4). A reaction time of 20 h was still needed with complex **7a** to reach 80% conversion of the ketone (Entry 3), probably because of the poor solubility of the catalyst in thf. In comparison, our previously described complexes **9a** and **9b** were poorly active,[4] even at this concentration, as the reactions were not complete after 5 d at room temperature (Entries 14 and 15).

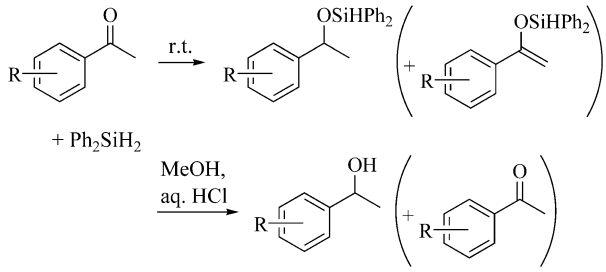
However, by increasing the concentration, the yield did not improve in the case of neutral complexes **8a** and **8b** (Entries 8 and 9). In order to have a better comparison with cationic complexes **7a** and 7**b**, 1 equiv. $AgBF_4$ was added to compounds **8a** and **8b** to give cationic complexes **10a** and **10b**, respectively (Scheme 5), in which 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 in the catalytic reactions.



Scheme 5. Generation of cationic Rh^I 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_2CF_3, BF_4, PF_6) was required in order to improve the catalytic activity,[23–25] 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 ^1H 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, which shows a lack of selectivity of these systems for the formation of the expected alcohol. The ^1H 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 ^1H NMR spectra before hydrolysis show two doublets at δ = 4.65 and 5.05 ppm (=CH_2, J = 2.4 Hz), which is characteristic of the silyl enol ether (the doublet at δ = 5.05 ppm, however, is often hidden by the Si–H singlet of Ph_2SiH_2 at δ = 5.06 ppm). These signals are absent from the ^1H NMR spectra of the mixtures after hydrolysis, whereas two new signals, typical of acetophenone, appear at 2.6 ppm (CH_3, s) and 8.0 ppm (Ar-H, d, J = 7.5 Hz). This process is frequently observed in ketone hydrosilylation.[26]



Scheme 6. Side products generated during hydrosilylation reactions.

In order to see whether the phosphane was necessary to maintain a good selectivity, we added 1 equiv. 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_3 decreases the solubility of the complex in thf. Analysis of the reaction mixture before and after hydrolysis showed an increase in selectivity in both cases, which confirms our hypothesis. However, the selectivity was lower than that obtained with complexes **7a** and **7b**, which shows clearly that the chelating effect is beneficial for reaction selectivity.

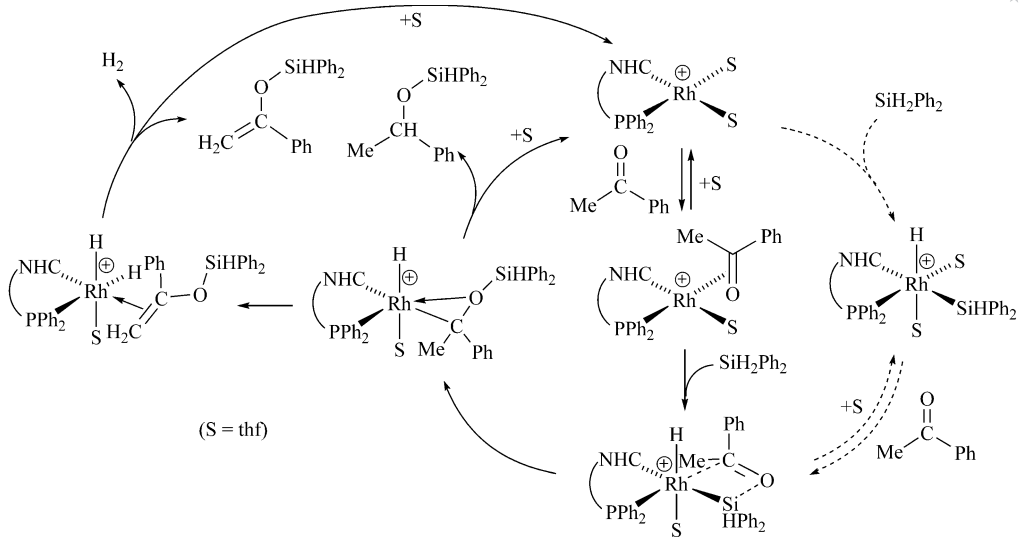
Encouraged by the results obtained with complex **7b**, we decided to lower the catalyst loading to 1 mol-% (Entry 5) and were pleased to observe that the activity was preserved, with a total conversion and 95% yield in only 2 h. Catalytic tests with the acetophenone derivatives allowed us to determine the efficiency of complexes **7a** and **7b** (2 mol-%) with a variation in the electronic or steric properties (Scheme 4, Table 3). Whereas marked differences were observed with complex **7a**, catalyst **7b** shows a very high activity irrespective of the substituents on acetophenone. Indeed, even the presence of an *ortho* substituent did not lower the yield (Entry 6).

Table 3. Hydrosilylation of acetophenone derivatives.[a]

Entry	R	Catalyst	t [h]	Yield [%][b]
1	4-OMe	**7a**	20	87
2	4-OMe	**7b**	2	97
3	4-F	**7a**	20	71
4	4-F	**7b**	2	98
5	2-Me	**7a**	20	52
6	2-Me	**7b**	2	92

[a] Ketone (1 equiv.), diphenylsilane (1.1 equiv.), room temperature, 2 mol-% catalyst, thf, then hydrolysis with MeOH/HCl. [b] Determined by ^1H NMR signal integration of the crude products after hydrolysis.

The higher catalytic activity observed at higher ketone concentrations agrees with previous reports of a saturation effect: the reaction was found to be first order with respect to the ketone at low concentrations, but eventually became independent of the ketone concentration at high concentrations.[27–29] 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 that originally proposed,[27,30–32] which is based on a rate-determining Si–H oxidative addition pro-



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

cess to yield a Rh^{III} 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 Hetflejs of a saturation effect (while working with a cationic system) was interpreted as indicative of reversible complexation of the ketone prior to the rate-determining silane addition,[28] but Giering later discarded this variant when he could properly model, on the basis of the other mechanism, the kinetic results that he obtained with a neutral system, which also included a saturation effect in the ketone.[27] 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 Hetflejs is reasonable and probably applies to our system, for the following reasons. The cod ligand is probably lost rapidly from the coordination sphere by the hydrosilylation or hydrogenation processes, as also observed or proposed in other cases.[27,32–34] The resulting $[(NHCFcPPh_2)Rh]^+$ system is then likely to be coordinated by two solvent molecules, but the lability of these should easily allow ketone coordination, at a rate faster than that of the rate-determining silane oxidative addition step. 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.

Finally, the formation of the unsaturated silyl ether can be easily rationalised on the basis of a competition between the reductive elimination of the hydrosilylation product and a β-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,[35] 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.[24,36] Supposedly, the absence of the phosphane ligand renders the β-H elimination pathway more easily accessible through the availability of an additional open coordination site.

Conclusions

The benzimidazol-2-ylidene unit gives highly active hydrosilylation rhodium catalysts that prove to be superior to 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 enhances 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 Bruker ARX250, AV300 or DPX300 spectrometers. All spectra were recorded in $CDCl_3$, unless otherwise stated. Mass spectra were obtained from acetonitrile solutions on a TSQ7000 instrument from ThermoElectron. (1′-Diphenylthiophosphanylferrocen-1-yl)methanol (**1**) was prepared according to our previously published procedure.[4,37] $[Rh(OMe)(cod)]_2$,[38] **2a**, **2b**[7]and **3**[39] were prepared according to literature procedures.

Benzimidazolium Salt 4a: HBF_4 (35 μL, 54 wt.-% in Et_2O) was added quickly to a solution of ferrocenyl alcohol **1** (100 mg, 0.23 mmol) in degassed dichloromethane (5 mL). *N*-(2,4,6-Trimethylbenzyl) benzimidazole (**2a**, 86 mg, 0.35 mmol) was then added immediately. The mixture was washed with 2 M aq. HCl, water, saturated aq. $NaHCO_3$ and water again. The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was

purified by column chromatography on silica gel (eluent: CH_2Cl_2/acetone, 9:1) to give a yellow–orange solid (121 mg, 70% yield). $C_{40}H_{38}BF_4FeN_2PS$ (752.1): calcd. C 63.82, H 5.05, N 3.72; found C 63.60, H 5.32, N 3.64. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.30 (s, 1 H, NC*H*N$^+$), 7.98 (d, $J_{H,H}$ = 8.4 Hz, 1 H, benzimidazole), 7.29 (d, $J_{H,H}$ = 8.4 Hz, 1 H, benzimidazole), 7.43–7.67 (m, 12 H, benzimidazole + Ar*H*), 6.98 (s, 2 H, Mes), 5.61 (s, 2 H, CH_2-Mes), 5.50 (s, 2 H, CH_2-Fc), 4.75, 4.71, 4.48, 4.08 (t, $J_{H,H}$ = 1.8 Hz, 8 H, Cp), 2.33 (s, 3 H, *p*-CH_3 Mes), 2.26 (s, 6 H, *o*-CH_3 Mes) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 141.32 (N*C*N$^+$), 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 (*C*H$_2$-Mes), 46.98 (*C*H$_2$-Fc), 21.09 (*p*-*C*H$_3$ Mes), 19.84 (*o*-*C*H$_3$ Mes) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 41.6 ppm.

Benzimidazolium Salt 4b: HBF_4 (35 μL, 54 wt.-% in Et_2O) was added quickly to a solution of ferrocenyl alcohol **1** (100 mg, 0.23 mmol) in degassed dichloromethane (5 mL). *N*-(2,4,6-Trimethylbenzyl)-5,6-dimethyl benzimidazole (**2b**, 96 mg, 0.35 mmol) was then added immediately. The mixture was washed with 2 M aq. HCl, water, saturated aq. $NaHCO_3$ and water again. The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/acetone, 9:1) to give a yellow–orange solid (108 mg, 60% yield). $C_{42}H_{42}BF_4FeN_2PS$ (780.1): calcd. C 64.61, H 5.38, N 3.59; found C 64.67, H 5.82, N 3.85. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.01 (s, 1 H, NC*H*N$^+$), 7.78–7.70 (m, 3 H), 7.58 (s, 1 H), 7.51–7.45 (m, 5 H), 7.31 (s, 1 H), 7.26 (s, 1 H), 7.10 (s, 1 H, benzimidazole + Ar-*H*), 6.99 (s, 2 H, Mes), 5.51, 5.39 (s, 2 H, CH_2-Mes), 5.32, 5.21 (s, 2 H, CH_2-Fc), 4.74, (t, $J_{H,H}$ = 1.8 Hz, 1 H, Cp), 4.66 (t, $J_{H,H}$ = 1.8 Hz, 1 H, Cp), 4.55 (d, $J_{H,H}$ = 1.8 Hz, 2 H, Cp), 4.48–4.47 (m, 1 H, Cp), 4.30 (s, 1 H, Cp), 4.07 (t, $J_{H,H}$ = 1.8 Hz, 1 H, Cp), 4.00 (s, 1 H, Cp), 2.49, 2.44, 2.41 (s, 6 H, *o*-CH_3 Mes), 2.33 (t, $J_{H,H}$ =.3 Hz, 3 H, *p*-CH_3 Mes), 2.26 (d, $J_{H,H}$ = 1.2 Hz, 6 H, CH_3 benzimidazole) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 139.71 (N*C*N$^+$), 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 (*C*H$_2$-Mes), 43.03 (*C*H$_2$-Fc), 21.08, 21.04 (*o*-*C*H$_3$ Mes), 20.78, 20.65, 20.29 (*p*-*C*H$_3$ Mes), 19.78, 19.56 (*C*H$_3$ benzimidazole) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 41.5 ppm.

Benzimidazolium Salt 5a: Raney nickel (2.2 g, suspension in water) was washed with degassed methanol (3 × 10 mL), degassed diethyl ether (3 × 10 mL) and, finally, degassed acetonitrile (3 × 10 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 through 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). $C_{40}H_{38}BF_4FeN_2P$ (720.1): calcd. C 66.66, H 5.28, N 3.89; found C 65.01, H 5.99, N 3.92. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.10 (s, 1 H, NC*H*N$^+$), 7.70–7.32 (m, 12 H, benzimidazole + Ar-*H*), 6.96 (s, 2 H, Mes), 5.60 (s, 2 H, CH_2-Mes), 5.15 (s, 2 H, CH_2-Fc), 4.58, 4.36, 4.22, 4.13 (t, $J_{H,H}$ = 1.8 Hz, 8 H, Cp), 2.32 (s, 3 H, *p*-CH_3 Mes), 2.25 (s, 6 H, *o*-CH_3 Mes) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 141.20 (N*C*N$^+$), 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 (*C*H$_2$-Mes), 46.91 (*C*H$_2$-Fc), 21.07 (*p*-*C*H$_3$ Mes), 19.85 (*o*-*C*H$_3$ Mes) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = –17.2 ppm.

Benzimidazolium Salt 5b: Raney nickel (2.4 g, suspension in water) was washed with degassed methanol (3 × 10 mL), degassed diethyl ether (3 × 10 mL) and, finally, degassed acetonitrile (3 × 10 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 through 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). $C_{42}H_{42}BF_4FeN_2P$ (748.1): calcd. C 67.37, H 5.61, N 3.74; found C 67.23, H 5.62, N 3.88. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.86 (s, 1 H, NC*H*N$^+$), 7.59 (s, 1 H), 7.41–7.32 (m, 8 H), 7.31 (s, 1 H), 7.26 (s, 1 H), 7.11 (s, 1 H, benzimidazole + Ar-*H*), 6.98 (s, 2 H, Mes), 5.51, (s, 2 H, CH_2-Mes), 5.21, 5.07 (s, 2 H, CH_2-Fc), 4.58, (t, $J_{H,H}$ = 1.8 Hz, 2 H, Cp), 4.41 (s, 1 H, Cp), 4.33 (t, $J_{H,H}$ = 1.8 Hz, 2 H, Cp), 4.21 (t, $J_{H,H}$ = 1.8 Hz, 1 H, Cp), 4.13 (d, $J_{H,H}$ = 1.8 Hz, 2 H, Cp), 2.45, 2.41 (s, 6 H, *o*-CH_3 Mes), 2.35, 2.33 (s, 3 H, *p*-CH_3 Mes), 2.25 (d, $J_{H,H}$ = 4.2 Hz, 6 H, CH_3 benzimidazole) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 139.66 (N*C*N$^+$), 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 (*C*H$_2$-Mes), 46.40 (*C*H$_2$-Fc), 21.06, 20.76, 20.73 (*C*H$_3$ Mes), 19.75 (*C*H$_3$ benzimidazole) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = –17.1 ppm.

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, after which the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/acetone, 8:2) to give an orange solid (485 mg, 70% yield). $C_{28}H_{29}FeIN_2$ (578.8): calcd. C 58.05, H 5.01, N 4.84; found C 58.10, H 5.08, N 4.37. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.60 (s, 1 H, NC*H*N$^+$), 7.77, 7.30 (dd, $J_{H,H}$ = 8.4 Hz, 2 H, benzimidazole), 7.57, 7.48 (dt, $J_{H,H}$ = 6.2 Hz, 2 H, benzimidazole), 6.96 (s, 2 H, Mes), 5.72 (s, 2 H, CH_2-Mes), 5.32 (s, 2 H, CH_2-Fc), 4.55, 4.31, 4.23 (t, $J_{H,H}$ = 1.8 Hz, 9 H, Cp), 2.32 (s, 9 H, CH_3Mes) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 140.96 (N*C*N$^+$), 140.03, 137.98, 131.35 (d, $J_{C,H}$ = 4.5 Hz), 127.22 (d, $J_{C,H}$ = 10.6 Hz), 124.65, 113.67 (d, $J_{C,H}$ = 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 (*C*H$_2$-Mes), 47.12 (*C*H$_2$-Fc), 21.13 (*p*-*C*H$_3$ Mes), 20.44 (d, $J_{C,H}$ = 4.5 Hz, *o*-*C*H$_3$ Mes) ppm.

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, after which the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/acetone, 8:2) to give an orange solid (590 mg, 81% yield). $C_{30}H_{33}FeIN_2$ (606.8): calcd. C 59.33, H 5.44, N 4.61; found C 61.01, H 6.08, N 4.80. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.21 (s, 1 H, NC*H*N$^+$), 7.11, 7.27, 7.32, 7.50, 7.59 (s, 2 H, benzimidazole), 6.98 (s, 2 H, Mes), 5.64 (d, $J_{H,H}$ = 8.7 Hz, 2 H, CH_2-Mes), 5.22 (s, 2 H, CH_2-Fc), 4.52, (t, $J_{H,H}$ = 2.1 Hz, 2 H, Cp), 4.30, (s, 5 H, Cp), 4.22 (t, $J_{H,H}$ = 2.1 Hz, 2 H, Cp), 2.43 (d, $J_{H,H}$ = 10.2 Hz, 6 H, *o*-CH_3-Mes), 2.34 (d, $J_{H,H}$ = 8.1 Hz, 6 H, CH_3 benzimidazole), 2.27 (s, 3 H, *p*-CH_3-Mes) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 140.95 (N*C*N$^+$), 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 (*C*H$_2$-Mes), 43.05 (*C*H$_2$-Fc), 19.58 (*p*-*C*H$_3$ Mes), 20.31, 20.42 (*C*H$_3$ benzimidazole), 20.75, 21.92 (*o*-*C*H$_3$ Mes) ppm.

Rhodium Complex 7a: *t*BuOK (23.3 mg, 0.21 mmol) and [Rh(cod)Cl]$_2$ (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 and 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 and at room temperature for 2 h. The solvent was evaporated, and the residue taken up into degassed CH_2Cl_2 (10 mL). $AgBF_4$ (56.7 mg, 0.291 mmol) was added, and the mixture was stirred for 30 min at room temperature and filtered through Celite®. The solvent was evaporated in vacuo, and the residue was filtered through silica gel (eluent: CH_2Cl_2/acetone, 95:5) to give **7a** as an orange solid (154 mg, 86% yield). $C_{48}H_{49}BF_4FeN_2PRh$ (929.6): calcd. C 61.96, H 5.27, N 3.01; found C 61.55, H 5.60, N 2.98. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.30 (m, 10 H, Ar-*H*), 7.62 (d, $J_{H,H}$ = 8.4 Hz, 1 H, benzimidazole), 7.46 (d, $J_{H,H}$ = 15.3 Hz, 1 H, benzimidazole), 6.26 (d, $J_{H,H}$ = 15.3 Hz, 1 H, benzimidazole), 5.77 (d, $J_{H,H}$ = 8.4 Hz, 1 H, benzimidazole), 6.93 (s, 2 H, Mes), 5.47 (d, $J_{H,H}$ = 15 Hz, 2 H, CH_2-Mes), 4.97 (d, $J_{H,H}$ = 15 Hz, 2 H, CH_2-Fc), 4.49, 4.24, 4.11 (s, 8 H, Cp), 5.18 (s, 2 H, cod-C*H*), 4.40 (s, 2 H, cod-C*H*), 2.53 (s, 4 H, cod-CH_2), 2.31 (s, 4 H, cod-CH_2), 2.37 (s, 6 H, *o*-CH_3 Mes), 1.82 (s, 3 H, *p*-CH_3 Mes) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 192.52 (d, $J_{Rh,C}$ = 50.8 Hz, $C_{carbene}$), 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-C*H*), 30.90, 30.42 (cod-CH_2), 50.80 (*C*H_2-Fc), 47.12 (*C*H_2-Mes), 21.12 (*o*-CH_3 Mes), 19.89 (*p*-CH_3 Mes) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 18.4 (d, $J_{P,Rh}$ = 154.3 Hz) ppm.

Rhodium Complex 7b: *t*BuOK (19 mg, 0.171 mmol) and [Rh(cod)Cl]$_2$ (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 and 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 and at room temperature for 2 h. The solvent was evaporated, and the residue taken up into degassed CH_2Cl_2 (10 mL). $AgBF_4$ (45.6 mg, 0.234 mmol) was added, and the mixture was stirred for 30 min at room temperature and filtered through Celite®. The solvent was evaporated in vacuo, and the residue was filtered through silica gel (eluent: CH_2Cl_2/acetone, 95:5) to give **7b** as an orange solid (126 mg, 84% yield). $C_{50}H_{53}BF_4FeN_2PRh$ (957.6): calcd. C 62.66, H 5.54, N 2.92; found C 61.40, H 5.66, N 2.89. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.51–7.39 (m, 10 H, Ar-*H*), 7.33 (s, 1 H, benzimidazole), 5.39 (s, 1 H, benzimidazole), 6.94 (s, 2 H, Mes), 5.33 (d, $J_{H,H}$ = 9 Hz, 2 H, CH_2-Mes), 4.87 (d, $J_{H,H}$ = 15 Hz, 2 H, CH_2-Fc), 4.48, 4.45, 4.25, 4.15 (s, 8 H, Cp), 5.14 (s, 2 H, cod-C*H*), 4.38 (s, 2 H, cod-C*H*), 2.52 (s, 4 H, cod-CH_2), 2.41 (s, 4 H, cod-CH_2), 2.39 (s, 6 H, *o*-CH_3 Mes), 1.99 (s, 3 H, *p*-CH_3 Mes), 1.81 (s, 6 H, CH_3 benzimidazole) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 189.84 (d, $J_{Rh,C}$ = 50.7 Hz, $C_{carbene}$), 139.69, 138.68, 134.27, 134.10, 133.87, 132.80, 132.67, 131.64, 130.86, 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-C*H*), 30.93, 30.43, 22.34 (cod-CH_2), 50.52 (*C*H_2-Fc), 46.99 (*C*H_2-Mes), 21.06 (*o*-CH_3 Mes), 20.57, 20.26 (*p*-CH_3 Mes), 19.89 (*C*H_3 benzimidazole) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 18.55 (d, $J_{P,Rh}$ = 159.2 Hz) ppm.

Rhodium Complex 8a: A mixture of **6a** (116 mg, 0.2 mmol) and [Rh(OMe)(cod)]$_2$ (48.4 mg, 0.1 mmol) in CH_2Cl_2 (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_2Cl_2) to give a yellow–orange solid (135 mg, 86% yield). $C_{36}H_{40}FeIN_2Rh$ (785.7): calcd. C 54.98, H 5.09, N 3.56; found C 52.85, H 4.71, N 3.32. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.21 (d, $J_{H,H}$ = 15 Hz, 1 H, benzimidazole), 6.94 (t, $J_{H,H}$ = 7.5 Hz, 1 H, benzimidazole), 6.78 (t, $J_{H,H}$ = 7.5 Hz, 1 H, benzimidazole), 6.32 (benzimidazole), 6.95 (s, 2 H, Mes), 6.10 (t, $J_{H,H}$ = 12.5 Hz, 2 H, CH_2-Mes), 5.83 (q, $J_{H,H}$ = 15 Hz, 2 H, CH_2-Fc), 4.83 (d, $J_{H,H}$ = 1.8 Hz, 2 H, Cp), 4.48 (d, $J_{H,H}$ = 1.8 Hz, 2 H, Cp), 4.35 (s, 2 H, Cp), 4.19 (t, $J_{H,H}$ = 1.8 Hz, 2 H, Cp), 5.52, 5.39 (s, 2 H, cod-C*H*), 3.66 (s, 2 H, cod-C*H*), 2.49 (s, 4 H, cod-CH_2), 1.94 (s, 4 H, cod-CH_2), 2.37 (s, 3 H, *p*-CH_3 Mes), 2.32 (s, 6 H, *o*-CH_3 Mes) ppm. ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 196.38 (d, $J_{Rh,C}$ = 50.6 Hz, $C_{carbene}$), 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-C*H*), 32.73, 32.08, 30.16, 29.00 (cod-CH_2), 50.45 (*C*H_2-Mes), 49.92 (*C*H_2-Fc), 21.11 (*p*-CH_3 Mes) 21.07 (*o*-CH_3 Mes) ppm.

Rhodium Complex 8b: A mixture of **6b** (121 mg, 0.2 mmol) and [Rh(OMe)(cod)]$_2$ (48.4 mg, 0.1 mmol) in CH_2Cl_2 (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_2Cl_2) to give a yellow–orange solid (138 mg, 84% yield). $C_{38}H_{44}FeIN_2Rh$ (813.7): calcd. C 56.04, H 5.41, N 3.44; found C 56.85, H 5.81, N 3.33. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.97 (s, 2 H, benzimidazole), 6.95 (s, 2 H, Mes), 6.03 (d, $J_{H,H}$ = 15 Hz, 1 H, CH_2-Mes), 6.23 (d, $J_{H,H}$ = 15 Hz, 1 H, CH_2-Mes), 5.78 (q, $J_{H,H}$ = 12 Hz, 2 H, CH_2-Fc), 4.80 (d, $J_{H,H}$ = 1.2 Hz, 2 H, Cp), 4.47 (d, $J_{H,H}$ = 1.2 Hz, 2 H, Cp), 4.33 (d, $J_{H,H}$ = 1.2 Hz, 2 H, Cp), 4.17 (t, $J_{H,H}$ = 1.2 Hz, 2 H, Cp), 5.46, 5.35 (s, 2 H, cod-C*H*), 3.60 (s, 2 H, cod-C*H*), 2.47 (s, 4 H, cod-CH_2), 1.95 (s, 4 H, cod-CH_2), 2.37 (s, 3 H, *p*-CH_3 Mes), 2.31 (s, 6 H, *o*-CH_3 Mes), 2.17 (s, 6 H, CH_3 benzimidazole) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 194.51 (d, $J_{Rh,C}$ = 50.8 Hz, $C_{carbene}$), 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-C*H*), 32.70, 32.10, 30.11, 29.03 (cod-CH_2), 50.08 (*C*H_2-Mes), 49.68 (*C*H_2-Fc), 21.06 (*p*-CH_3 Mes) 20.29 (*o*-CH_3 Mes), 20.15 (*C*H_3 benzimidazole) ppm.

Representative Procedure for Rh^I-Catalysed Hydrosilylation of Ketones: The Rh^I complex (10^{-6} mol, 2 mol-%) was placed in a flame-dried Schlenk flask under argon. Anhydrous thf (0.25 mL) and then acetophenone (56 μL, 4.8×10^{-4} mol) were added by syringe. Diphenylsilane (100 μL, 5.4×10^{-4} 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 complete, the solvent was evaporated in vacuo, and the residue analysed by ^{1}H NMR ($CDCl_3$) spectroscopy. The NMR sample was taken up into CH_2Cl_2, MeOH (1 mL) was added, and the reaction mixture stirred for 1 h at room temperature. After the addition of 1 M HCl (1 mL), the reaction mixture was stirred for one additional hour at room temperature. The phases were separated, the aqueous phase extracted with CH_2Cl_2, and the organic phases were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was analysed by ^{1}H NMR spectroscopy.

X-ray Diffraction Studies: A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a 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

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

Compound	**5a**	**6b**
Empirical formula	$C_{40}H_{38}BF_4FeN_2P$	$(C_{30}H_{33}FeIN_2)_2$
Formula weight	720.35	1208.67
Temperature [K]	180(2)	180(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
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	103.671(6)
β [°]	92.832(5)	97.411(6)
γ [°]	90	102.822(7)
Volume [Å^3]	3592.0(6)	2916.3(4)
Z	4	2
Density (calculated) [Mg/m^3]	1.332	1.376
Absorption coefficient [mm^{-1}]	0.516	1.594
F(000)	1496	1224
Crystal size [mm]	$0.84 \times 0.163 \times 0.068$	$0.75 \times 0.43 \times 0.26$
θ range [°]	2.38–27.02	2.77–27.10
Reflections collected	120450	23199
Independent reflections (R_{int})	7757 (0.0836)	12820 (0.0407)
Completeness [%]	98.7	99.5
Absorption correction	multiscan	multiscan
Max., min. transmission	1.0, 0.404	1.0, 0.635
Refinement method	F^2	F^2
Data/restraints/parameters	7757/0/445	12820/0/623
Goodness-of-fit on F^2	1.031	1.078
R_1, wR_2 [$I > 2\sigma(I)$]	0.0418, 0.1013	0.0608, 0.1374
R_1, wR_2 (all data)	0.0686, 0.1154	0.0766, 0.1434
Residual density [e Å^{-3}]	0.611/–0.467	1.536/–1.232

5a. Data were collected by using the monochromatic Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SIR97) [40] and refined by least-squares procedures on F^2 with SHELXL-97.[41] All H atoms attached to carbon were introduced in the calculation in idealised positions and treated as riding models. In compound **6b**, some residual electron density was difficult to model, and, therefore, the SQUEEZE function of PLATON [42] 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^3 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 was also used. In **7b**, there are two cavities of 470 Å^3 per unit cell. PLATON estimated that each cavity contains 190 electrons, which may correspond to roughly a mixture of four CH_2Cl_2 and four $(C_2H_5)_2O$ molecules within the cell. In compound **8a**, there are two cavities of 172 Å^3 per unit cell, which may roughly correspond to a mixture of two CH_2Cl_2 and two $(C_2H_5)_2O$ molecules within the cell. The drawing of the molecules was realised with the help of ORTEP32.[43] Crystal data and refinement parameters are shown in Tables 4 and 5. CCDC-710144, -710145, -710146, -710147, CCDC-711381, and -711382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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

Compound	**7a**	**7b**	**8a**	**8b**
Empirical formula	$C_{46}H_{45}BF_4FeN_2PRh$	$C_{50}H_{51}BF_4FeN_2PRh$	$C_{36}H_{40}FeIN_2Rh$	$C_{38}H_{44}FeIN_2Rh$
Formula weight	891.57	956.47	786.36	814.41
Temperature [K]	180(2)	180(2)	180(2)	296(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	tetragonal	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$I\bar{4}$	$P2_1/n$
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	90	90	90
β [°]	91.019	91.663(3)	90	98.151(13)
γ [°]	90	90	90	90
Volume [Å^3]	4080.1(3)	4975.3(8)	6445.7(6)	3421.9(6)
Z	4	4	8	4
Density (calculated) [Mg/m^3]	1.515	1.277	1.621	1.581
Absorption coefficient [mm^{-1}]	0.855	0.703	1.947	1.837
F(000)	1912	1968	3152	1640
Crystal size [mm]	$0.336 \times 0.125 \times 0.080$	$0.293 \times 0.085 \times 0.039$	$0.44 \times 0.08 \times 0.071$	$0.40 \times 0.40 \times 0.16$
θ range [°]	2.82–26.37	1.64–22.12	2.27–33.22	1.76–24.20
Reflections collected	30948	79794	128931	27214
Independent reflections (R_{int})	8322 (0.0756)	6134 (0.1124)	12376 (0.0463)	5458 (0.1564)
Completeness [%]	99.9	98.8	99.9	99.0
Absorption correction	multiscan	semiempirical from equivalents	semiempirical from equivalents	multiscan
Max., min. transmission	1.0, 0.970	1.0, 0.784	1.0, 0.881	0.5312, 0.4354
Refinement method	F^2	F^2	F^2	F^2
Data/restraints/parameters	8322/51/526	6134/0/546	12376/1/373	5458/0/393
Goodness-of-fit on F^2	1.243	1.076	1.035	0.790
R_1, wR_2 [$I > 2\sigma(I)$]	0.0792, 0.1418	0.0406, 0.0978	0.0294, 0.0674	0.0544, 0.1175
R_1, wR_2 (all data)	0.1146, 0.1500	0.0598, 0.1051	0.0336, 0.0689	0.1360, 0.1409
Residual density [e Å^{-3}]	1.068/–1.517	0.508/–0.403	0.600/–0.359	1.200/–1.130

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