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Palladium, iridium and ruthenium complexes with acyclic imino-N-heterocyclic carbenes and their application in aqua-phase Suzuki–Miyaura cross-coupling reaction and transfer hydrogenation†

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Palladium (**4a–4c**), iridium (**5a–5c**) and ruthenium (**6a–6c**) complexes have been prepared by *in situ* transmetalation from the corresponding silver complexes of acyclic imino-functionalized imidazolium chlorides [1-(Me)-imidazolium-3-{C(*p*-CH_3–Ph)═N(Ar)}]Cl (**3**) (Ar = 2,4,6-trimethylphenyl (**3a**), 2,6-diisopropylphenyl (**3b**) and phenyl (**3c**)) with [Pd(COD)Cl_2], [Cp*IrCl_2]$_2$ or [Ru(*p*-cymene)Cl_2]$_2$, respectively. Iridium and ruthenium complexes, **5a[PF_6]–5c[PF_6]**, **6a[PF_6]–6c[PF_6]**, **6c[BF_4]**, **6c[BPh_4]** and **6c[NTf_2]**, were obtained directly from **5a–5c** and **6a–6c** through an anion-exchange process with KPF_6, $NaBF_4$, $NaBPh_4$ and $LiNTf_2$ (bis(trifluoromethylsulfonyl)imide lithium), respectively. All complexes were characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. Crystal structures of **4a**, **5a** and **6c[NTf_2]** show that five-membered chelate ring is formed in these complexes by the coordination of the carbene carbon and the imino nitrogen atom, and the latter two are cationic compounds with Cl^- and NTf_2^- as counteranion respectively. The catalytic performance of Pd complexes for Suzuki–Miyaura cross-coupling reactions in pure water and Ir and Ru complexes for transfer hydrogenation of ketones and imines was tested in a wide scope of substrates. Pd complex **4b** with the largest steric hinder exhibited the best performance to gain moderate to excellent yields on catalyzing Suzuki–Miyaura cross-coupling of aryl chlorides and arylboronic acids in water. While in transfer hydrogenation of various ketones, all the Ir and Ru complexes were effective with good to excellent yields. Among all these complexes, **6c[PF_6]** was found most effective, and moderate yields could be obtained even in the transfer hydrogenation of imines. Moreover, different counteranions of Ru complexes are influential on catalyzing the transfer hydrogenation, with the sequence of $PF_6^- \approx BF_4^- > BPh_4^- > Cl^- > NTf_2^-$.

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Introduction

The N-heterocyclic carbene (NHC) ligands have been proved to be efficient as ancillary ligands because of their strong coordination ability and their tunable character of the steric and electronic properties on the coordinated metal center.[1] NHCs functionalized with an additional donor group have become important ligands due to the potential hemilability of the new donor group, which can play a dual role in a catalyst since they can easily enable coordination sites and, at the same time, protect the coordination sites by a dynamic "on and off" chelating effect.[2]

NHC ligands with P,[3] O,[4] S[5] and N[6–10] donors have been developed, among which the design and synthesis of N donor ligands continue drawing numerous attention. N atom as chelate has been incorporated to the N-terminated carbene in the form of cyclic imines like pyridine[6]/pyrimidine[7] or oxazoline,[8] acylic imines, or in the form of amino[9]/amido.[10] They bond to carbene nitrogen directly or *via* one or more CH_2 linkage through the α carbon. However, the design and application of metal complexes bearing pyridine/pyrimidine, oxazoline and amino/amido group are restrained in that the introduction of appropriate substituents on these N-ligands is inaccessible. We are interested in a kind of acyclic imino-funtionlized N-heterocyclic carbene ligands, where the imino carbon bonds directly to the carbene nitrogen. These ligands are prone to form stable five-membered ring complexes when coordinated to metal, which avoids dynamic behavior in

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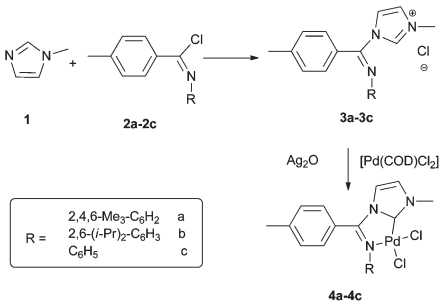
†Electronic supplementary information (ESI) available: X-Ray crystallographic data (CIF) for **4a**, **5a** and **6c[NTf_2]**, and ^{1}H NMR and ^{13}C NMR spectra of all the complexes. CCDC 872878 (**4a**), 872879 (**5a**) and 872880 (**6c[NTf_2]**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31989f



Scheme 1 Synthesis of ligands and Pd complexes **4a–4c**.

solution such as conformational "ring-flip" of the chelating ring and solvent-dependent interconversion of chelating and nonchelating species.[11] Furthermore, the synthesis method of these ligands is rather general and allows systematic variations of sterics and electronics by introduction of substituents to the imino carbon and nitrogen atoms and to the other nitrogen atom of carbene.[12] Researches on this kind of ligands mainly concentrate on the synthesis and characterization of their corresponding group 4, 10 and 11 transition metal complexes,[13,14] whereas information on their catalytic application is limited.[14,15]

Our group has been interested in the synthesis and catalytic performance of well-defined N-heterocyclic carbene metal complexes for the past few years.[16] In this work, we report the synthesis and characterization of acyclic imino-N-heterocyclic carbene ligands chelating complexes of Pd, Ir and Ru, and the catalytic performance of Pd complexes in Suzuki–Miyaura cross-coupling reactions in pure water and Ir, Ru complexes in transfer hydrogenation of ketones and imines.

Results and discussion

Synthesis and characterization of Pd complexes 4a–4c

The acyclic imino-functionalized imidazolium chlorides **3** were prepared according to similar procedures[12a] reported before by the reaction of the corresponding imidoyl chlorides ClC(*p*-CH_3–Ph)=N(Ar) (Ar = 2,4,6-trimethylphenyl (**2a**), 2,6-diisopropylphenyl (**2b**) and phenyl (**2c**)) with 1-methylimidazole (**1**) in high yields. (Scheme 1) They were characterized by FT-IR, elemental analysis, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Metal-NHC complexes are frequently prepared by reaction of the imidazolium salts with appropriate metal salts, by *in situ* carbene generation through treatment of imidazolium salts with strong bases or transmetalation through silver carbene complexes. We attempted to treat the imidazolium salts with $Pd(OAc)_2$ or $PdCl_2$ to prepare Pd iminoylcarbene complexes, or with $NaN[Si(CH_3)_3]_2$, *t*BuOK and *n*BuLi to obtain the free carbene, but failed.[12a] However, Pd complexes **4a–4c** were successfully synthesized by the transfer of the ligands from the corresponding silver complexes[17] to $[Pd(COD)Cl_2]$ (Scheme 1) in yields around 60% and characterized by FT-IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, elemental analysis and in the case of **4a**, by X-ray crystallography. The C=N stretching frequency is found at 1617 (**4a**), 1611 (**4b**) and 1615 (**4c**) cm^{-1}, significantly lowered compared with that of the ligands (1664 (**3a**), 1660 (**3b**), 1666 (**3c**) cm^{-1}) and quite indicative of coordination of the imino nitrogen to the Pd center. In the ^{1}H NMR spectra of **4a–4c**, the disappearance of downfield-shifted N*CH*N resonance indicates the deprotonation of the acidic proton of **3a–3c**. The ^{13}C{^{1}H} NMR spectra provide more evidence for the metalation. Signals at δ 162.5 and 161.5 ppm are assigned to the Pd–$C_{carbene}$ of **4a** and **4b**, respectively. All these results prove that the ligands are coordinated to the Pd center through carbene carbon and imino nitrogen atom. **4c** is practically insoluble in nearly all solvents (only slightly soluble in acetonitrile and DMSO); the ^{13}C NMR spectrum is thus failed to record.

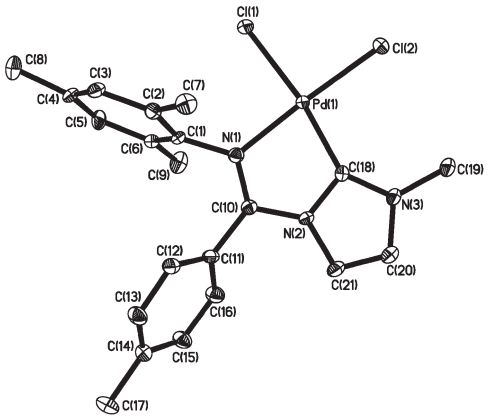
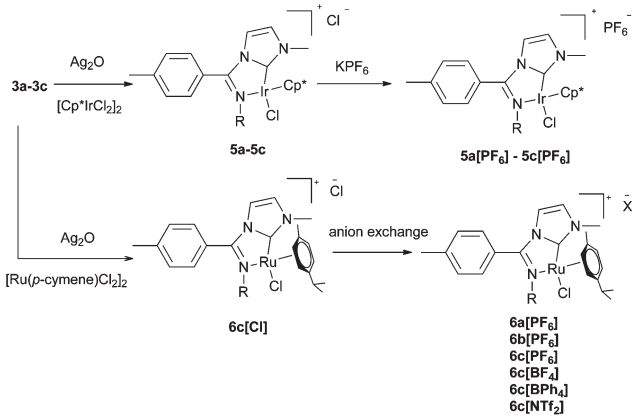


Fig. 1 Crystal structure of **4a**. Ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(18) 1.960(2), Pd(1)–N(1) 2.0478(19), Pd(1)–Cl(2) 2.2929(6), Pd(1)–Cl(1) 2.3335(6); C(18)–Pd(1)–N(1) 79.78(9).

Crystals of complex **4a** suitable for X-ray crystallography were grown by the layering of diethyl ether onto a saturated acetonitrile solution. The molecular structure of **4a** is shown in Fig. 1. The palladium complex **4a** has a distorted square-planar geometry in which the coordinated carbene carbon, imino nitrogen atom, and one of the chloride ligands are all approximately coplanar, with the remaining chloride ligand distorted away from this plane. The dihedral angle of the imidazole ring with the trimethylphenyl ring and that of the imidazole ring with the *p*-methylphenyl ring are 77.3 and 59.4°, respectively. The Pd(1)–N(1) bond distance of 2.0478(19) Å, Pd(1)–C(18) bond distance of 1.960(2) Å and the bite angle C(18)–Pd(1)–N(1) of 79.78(9)° are similar to those of other palladium(II) NHC complexes.[12a] The Pd–Cl(1) distance of 2.3335(6) Å and the Pd–Cl(2) distance of 2.2929(6) Å, with the longer Pd–Cl bond *trans* to the carbene, are considered a consequence of the greater *trans* influence.

Synthesis and characterization of Ir complexes 5a–5c and 5a[PF_6]–5c[PF_6]

Iridium complexes **5a–5c** were prepared by *in situ* transmetalation from the silver carbene complexes of ligands **3a–3c** with



Scheme 2 Synthesis of Ir and Ru complexes.

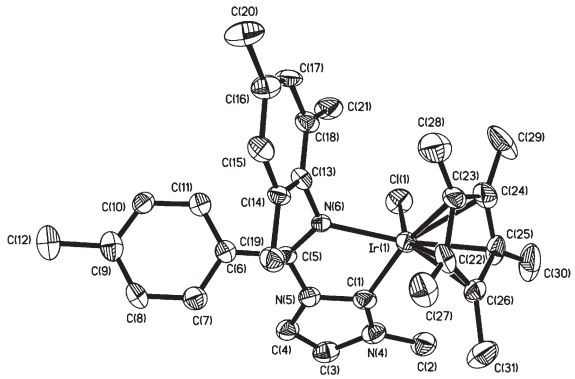


Fig. 2 Crystal structure of **5a**. Ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 1.997(11), Ir(1)–N(6) 2.129(7), Ir(1)–Cl(1) 2.414(3), Ir(1)–Cp*(centroid) 1.8219(8); C(1)–Ir(1)–N(6) 75.8(4), C(1)–Ir(1)–Cl(1) 82.1(3), N(6)–Ir(1)–Cl(1) 91.1(2).

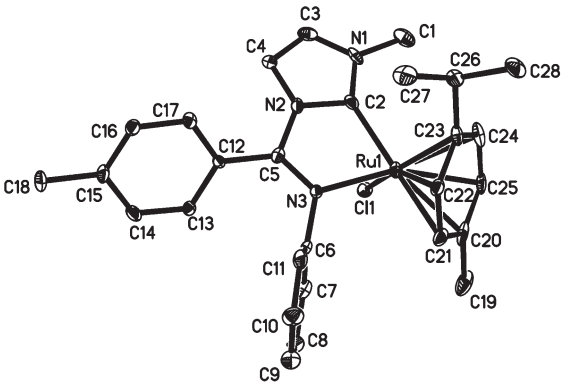


Fig. 3 Crystal structure of **6c[NTf$_2$]**. Ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)–C(2) 2.015(5), Ru(1)–N(3) 2.081(4), Ru(1)–Cl(1) 2.4011(11), Ru(1)–C(centroid) 1.7086(4); C(2)–Ru(1)–N(3) 76.29(16), C(2)–Ru(1)–Cl(1) 82.04(11), N(3)–Ru(1)–Cl(1) 86.08(10).

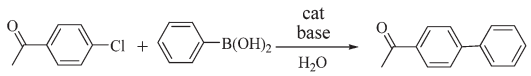
[Cp*IrCl$_2$]$_2$ in yields of 62%, 59% and 48%, respectively. Complexes **5a[PF$_6$]–5c[PF$_6$]** were obtained quantitatively from **5a–5c** through an anion-exchange procedure with KPF_6 as anion-exchange reagent (Scheme 2). All these complexes were purified by column chromatography and characterized by FT-IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy, elemental analysis and in the case of **5a**, by X-ray crystallography. A decrease in the C=N stretching frequency (around 1610 cm^{-1} for **5a–5c**, and 1630 cm^{-1} for **5a[PF$_6$]–5c[PF$_6$]**) compared with that of the ligands (around 1660 cm^{-1}) is observed, suggesting coordination of the imino nitrogen to the metal center. The ^{1}H NMR spectra show the NC*H*N proton resonance disappeared, indicating the deprotonation of the acidic proton of the ligands. From the $^{13}C\{^1H\}$ NMR spectra, signals at δ 167–170 ppm are attributed to Ir–$C_{carbene}$, implying the metalation of Ir with the carbene carbon of the ligands.

Crystals of complex **5a** suitable for X-ray crystallography were grown by slow diffusion of diethyl ether to a nearly saturated dichloromethane solution. The molecular structure of **5a** is illustrated in Fig. 2. It is found that there are two molecules in one unit cell, and one of them has been eliminated for clarity. **5a** is revealed to be a cationic compound with chloride as counteranion. The Ir center is in a distorted octahedral environment with Cp* as a three-coordinated ligand, and other three coordination sites occupied by carbene carbon, imino nitrogen and chlorine atom, respectively. The five-membered chelate ring Ir(1)–C(1)–N(5)–C(5)–N(6) is approximately coplanar with the imidazole ring. The dihedral angle of the imidazole ring with the trimethylphenyl ring and that of the imidazole ring with the *p*-methylphenyl ring are 72.2 and 58.7°, respectively. The Ir–Cl and Ir–Cp*(centroid) distances are 2.414(3) and 1.8219(8) Å, respectively. The Ir–$C_{carbene}$ (1.997 (11) Å) and Ir–N (2.129(7) Å) distances lie in the expected range for other known Cp*Ir(NHC) complexes.[7a] The bite angle of C(1)–Ir(1)–N(6) is 75.8(4)°.

Synthesis and characterization of Ru complexes 6a[PF$_6$]–6c[PF$_6$], 6c[Cl], 6c[BF$_4$], 6c[BPh$_4$], 6c[NTf$_2$]

The ruthenium complexes **6a[PF$_6$]–6c[PF$_6$]** were prepared in an analogous manner with **5a–5c**, using [Ru(*p*-cymene)Cl$_2$]$_2$ as metalation reagent, followed by an anion-exchange procedure with KPF_6 and isolated as orange powders. Complex **6c[Cl]** was isolated before anion-exchanging and **6c[BF$_4$]**, **6c[BPh$_4$]** and **6c[NTf$_2$]** were prepared by anion-exchange of **6c[Cl]** with $NaBF_4$, $NaBPh_4$ and $LiNTf_2$, respectively. (Scheme 2) Similar to the corresponding Ir complexes, the C=N stretching frequency of all the Ru complexes is lower than that of the ligands, indicating the coordination of the imino nitrogen to the Ru center. The absence of the NC*H*N proton resonances in ^{1}H NMR spectra associated with the presence of the Ru–$C_{carbene}$ carbon signals (around 190 ppm) in $^{13}C\{^1H\}$ NMR spectra proves that the coordination also occurs at the carbene carbon atom. Besides, we notice that the $\nu_{C=N}$ frequency of **6c[PF$_6$]**, **6c[BF$_4$]** and **6c[BPh$_4$]** (around 1630 cm^{-1}) is higher than that of **6c[Cl]** and **6c[NTf$_2$]** (around 1610 cm^{-1}), suggesting a weaker C=N double bond, which might be attributed to the influence of the counteranion. The carbene N–C*H*$_3$ resonance of **6c[BPh$_4$]** is found

Table 1 Optimization of the Suzuki–Miyaura coupling reaction conditions in pure water[a]



Entry	Cat.	Base	Yield[b] (%)
1	**4a**	KOH	64
2	**4b**	KOH	99
3	**4c**	KOH	17
4	**4b**	K_2CO_3	22
5	**4b**	Cs_2CO_3	46
6[c]	**4b**	KOH	67
7[d]	**4b**	KOH	Trace

[a] Reaction conditions: 4-chloroacetophenone (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (1 mol%), KOH (2.0 mmol), water (6 mL), 100 °C, 24 h. [b] Yields determined by ^{1}H NMR spectroscopy. [c] 0.5 mol% of catalyst loading. [d] Temperature reduced to 25 °C.

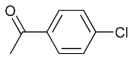
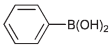
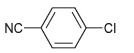
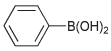
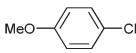
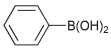
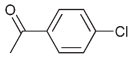
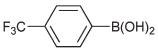
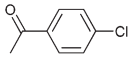
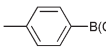
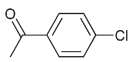
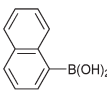
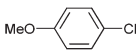
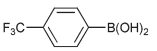
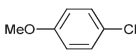
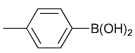
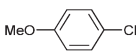
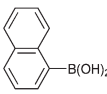
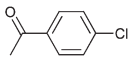
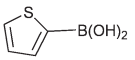
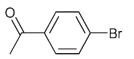
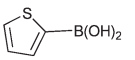
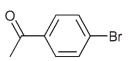
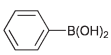
upfield shifted than the others, which is possibly due to the ring current effect of BPh_4^- anion.[18]

Crystals of complex **6c[NTf$_2$]** suitable for X-ray crystallography were grown by slow diffusion of diethyl ether to a nearly saturated dichloromethane solution. The molecular structure of **6c[NTf$_2$]** is shown in Fig. 3. It is found a cationic compound with a NTf_2^- as anion. The NTf_2^- anion of **6c[NTf$_2$]** is highly disordered and divided into two parts.[19] The center metal Ru displays a distorted octahedral geometry in which the *p*-cymene group occupies three coordination sites, and the carbene carbon, imino nitrogen and chlorine atom occupy others. The chloride ligand is found to adopt the opposite orientation to the iPr substituent of the *p*-cymene ligand, which is probably due to steric repulsion. The five-membered chelate ring Ru(1)–C(2)–N(2)–C(5)–N(3) is approximately coplanar with the imidazole ring. The dihedral angle of the imidazole ring with the phenyl ring and that of the imidazole ring with the *p*-methylphenyl ring are 80.5 and 60.0°, respectively. The Ru–$C_{carbene}$ distance and Ru–N distance are 2.015(5) and 2.081(4), respectively, similar to those of analogous complexes.[6c]

Suzuki–Miyaura coupling reactions catalyzed by Pd complexes in water

Well-defined Pd(NHC) complexes with nitrogen donors as ancillary ligands have attracted much attention for Suzuki–Miyaura cross-coupling reactions.[20] Analogous Pd complexes have also been employed in Suzuki–Miyaura reactions with aryl bromides as substrates in organic solvents to attain good yields,[12a] and solvent with higher polarity may benefit the activity.[12b] On the basis of these precious results, catalytic performance of **4a–4c** in Suzuki–Miyaura cross-coupling reactions is tested in pure water as an environmental benign solvent. Surprisingly, catalyst **4b** exhibited excellent activity on catalyzing cross-coupling of deactivated aryl chlorides and arylboronic acids.

Table 2 Suzuki–Miyaura coupling reactions with various substrates[a]

Entry	Aryl halide	Arylboronic acid	Yield[b] (%)
1			99 (97[c])
2			93[c]
3			90
4			62
5			54
6			51
7			48
8			74
9			70
10			Trace
11			69
12			99

[a] Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), **4b** (1 mol%), KOH (2.0 mmol), water (6 mL), 100 °C, 24 h. [b] Yields determined by ^{1}H NMR spectroscopy. [c] Isolated yield.

Initially the cross-coupling of 4-chloroacetophenone with phenylboronic acid was used as a representative reaction, and the reaction conditions were briefly optimized (Table 1). Complex **4b** with 2,6-diisopropylphenyl as substituent in the imine moiety was more effective than **4a** and **4c** under the same conditions, showing quantitative yield (entry 2). This behavior demonstrates that steric effects may be playing an important role in the catalytic activity.[21] Several bases were also employed in this reaction, and KOH was found most effective (entries 4 and 5). Then we attempted to decrease the loading of catalyst and moderate yield (67%) was obtained when the catalyst loading was 0.5 mol% (entry 6). An attempt at room temperature gave a depressed result (entry 7).

Several aryl halides and arylboronic acids were then chosen to explore the activity of **4b**, with KOH as the base at 100 °C in water. The results are summarized in Table 2. Aryl chlorides containing either electron-withdrawing group (–CN, entry 2) or electron-donating group (–OMe, entry 3) obtained yield above 90%. Then the cross-coupling reactions of 4-chloroacetophenone or 4-chloroanisole with different arylboronic acids were tested to obtain moderate to good yield (entries 4–9). It was interesting to observe that 4-chloroacetophenone obtained

higher yield than 4-chloroanisole when reacted with 4-(trifluoromethyl)phenylboronic acid (entries 4 and 7), however, when reacted with 4-methylphenylboronic acid or 1-naphthaleneboronic acid, 4-chloroanisole, on contrary, exhibited higher yield (entries 5–6 and 8–9). No product was observed when thiophen-2-ylboronic acid was reacted with 4-chloroacetophenone, however, it underwent smoothly reaction to get yield of 69% when 4-chloroacetophenone was replaced by higher activated 4-bromoacetophenone (entries 10 and 11), providing a useful way for the synthesis of aryl-substituted sulfur heterocycles. Summarily, palladium complex **4b** with the largest steric hinder proves to be most effective to gain moderate to excellent yields for the coupling of various aryl chlorides and arylboronic acids in pure water.

In order to clarify the possibility of Pd nanoparticle acting as catalytic species during the cross-coupling process, the mercury tests[22] were performed under optimal conditions with 4-chloroacetophenone and phenylboronic acid in pure water. One drop of Hg (excess amount with respect to the palladium resource) was added to the reaction mixture after 0 and 12 hours resulting in 83% and 90% yields respectively, demonstrating that the reaction may not follow the Pd nanoparticle catalytic route.

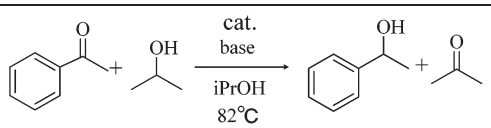
Transfer hydrogenation catalyzed by Ir and Ru complexes

Transfer hydrogenation of C═O and C═NR groups have drawn great attention, providing environmentally friendly and simple processes for the production of alcohols and amines[23] which play a significant role in organic synthesis. Several NHC complexes of iridium[24] and ruthenium[25] have been developed as catalysts for the transfer hydrogenation of ketones. Herein, acyclic imino-N-heterocyclic carbene Ir and Ru complexes were tested for these transformations.

The reduction of acetophenone to 1-phenylethanol was initially used as a model reaction with Ir or Ru complexes as catalyst in the presence of 1.0 mmol of potassium *tert*-butoxide (*t*BuOK) as the base. All the complexes exhibited excellent catalytic activity (above 80% isolated yield), as shown in Table 3. Among which, Ru complex **6c[PF$_6$]** with the smallest steric hinder proved to be most effective with yield up to 96% (entries 1–7). The decrease of *t*BuOK or loading of **6c[PF$_6$]**, or the replacement of *t*BuOK by KOH lowered the yield (entries 8–11). From an environmental as well as from an economic point of view, the following reactions were performed with 10 mol% of *t*BuOK as the base and 1 mol% of **6c[PF$_6$]** as the catalyst in iPrOH.

Under optimal conditions, several aromatic and aliphatic ketones as well as imines were selected to investigate the activity of **6c[PF$_6$]**, as shown in Table 4. It is obviously observed that *p*-substituted acetophenones with both electron-withdrawing halo groups (entries 2 and 3) and electron-donating methyl group (entry 5) obtained good to excellent yields. However, 4-

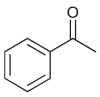
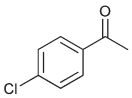
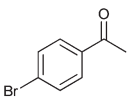
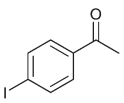
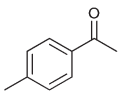
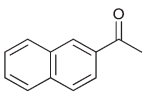
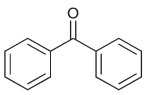
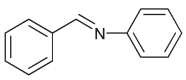
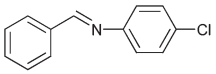
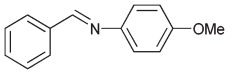
Table 3 Optimization of reaction conditions of transfer hydrogenation[a]



Entry	Cat.	Base	Time (h)	Yield[b] (%)
1	**5a**	*t*BuOK (1.0 mmol)	12	82
2	**5a[PF$_6$]**	*t*BuOK (1.0 mmol)	10	83
3	**5b[PF$_6$]**	*t*BuOK (1.0 mmol)	9	85
4	**5c[PF$_6$]**	*t*BuOK (1.0 mmol)	9	85
5	**6a[PF$_6$]**	*t*BuOK (1.0 mmol)	12	82
6	**6b[PF$_6$]**	*t*BuOK (1.0 mmol)	9	82
7	**6c[PF$_6$]**	*t*BuOK (1.0 mmol)	9	96
8	**6c[PF$_6$]**	*t*BuOK (0.1 mmol)	5	91
9[c]	**6c[PF$_6$]**	*t*BuOK (0.1 mmol)	24	Trace
10	**6c[PF$_6$]**	KOH (1.0 mmol)	9	76
11	**6c[PF$_6$]**	KOH (0.5 mmol)	9	69

[a] Reaction conditions: acetophenone (1.0 mmol), base, catalyst (1 mol%), iPrOH (5 mL), 82 °C. [b] Isolated yield. [c] 0.1 mol% of catalyst loading.

Table 4 Transfer hydrogenation of different substrates[a]

Entry	Substrate	Time (h)	Yield[b] (%)
1		5	91
2		5	>99
3		5	94
4		22	64
5		17	88
6		22	89
7		17	>99
8		17	92
9		22	45
10		22	59
11		22	58

[a] Reaction conditions: substrate (1.0 mmol), *t*BuOK (0.1 mmol), **6c[PF$_6$]** (1 mol%), iPrOH (5 mL), 82 °C. [b] Isolated yield.

Table 5 Influence of counterions on the transfer hydrogenation of 4-iodoacetophenone[a]

Entry	Cat.	Yield[b] (%)
1	**6c[PF_6]**	64
2	**6c[Cl]**	31
3	**6c[BF_4]**	62
4	**6c[BPh_4]**	49
5	**6c[NTf_2]**	23

[a] Reaction conditions: 4-iodoacetophenone (1.0 mmol), *t*BuOK (0.1 mmol), catalyst (1 mol%), iPrOH (5 mL), 82 °C, 22 h. [b] Isolated yield.

iodoacetophenone showed lower yield even with an increased reaction time (entry 4). Besides, 2-acetylnaphthalene and benzophenone were hydrogenated to corresponding alcohols with excellent yields (entries 6 and 7). On the other hand, **6c[PF_6]** was also demonstrated to be active for the reduction of aliphatic 2-decanone (entry 8).

Imines are harder to reduce by transfer hydrogenation catalysis than ketones mainly because of the drawbacks such as the coordination of the imine nitrogen lone pair to the metal center, which inhibits the η^2-(C=N) coordination required for the insertion into metal-hydride bonds, or the poisoning effect of the resultant amines on the catalyst.[26] We have found **6c[PF_6]** works effectively in the transfer hydrogenation of imines with both electron-drawing and electron-donating groups in moderate yields (entries 9–11). All these results demonstrate the versatility of **6c[PF_6]** towards the transfer hydrogenation of both ketones and imines.

The properties of counteranions may play an important role in catalytic process,[27] and the counteranion effects on catalytic reactions have been researched.[28] In order to give some information on counteranion effect in transfer hydrogenation, less-activated 4-iodoacetophenone was selected as substrate to explore the activity of complexes **6c** with various counteranions. As shown in Table 5, **6c** with PF_6^- or BF_4^- as counteranion display better reactivity than others. This outcome may result from their weak interaction with the cation, which benefit the generation of catalytically active species.[29] Moreover, their weakly coordinating ability will hinder them from coordinating to the Ru intermediate to block the catalytic cycle.[30] BPh_4^- is also a weakly coordinating anion, but it has the ability to ligate to metal through one of its phenyl ring to exhibit η^6-coordinating structure.[31] The poor activity of **6c[Cl]** is probably due to its poor stability in solution so that the dehalogenation process of the catalyst by base might be restrained by the high concentration of Cl^- in the solvent. The fact that **6c[NTf_2]** displays the worst catalytic performance perhaps result from the special coordination property of the NTf_2^- anion to Ru intermediate through N or O atom.[32]

Conclusions

In this article, Pd, Ir and Ru complexes bearing acylic imino-funtionlized N-heterocyclic carbene ligands where the imino carbon bonds directly to the carbene nitrogen, were synthesized and characterized. The crystal structures of **4a**, **5a** and **6c[NTf_2]** indicate that N atom of the imino moiety and C atom of the NHC moiety of the ligand are coordinated to the metal (Pd, Ir or Ru) center and a five-membered chelate ring is formed. **5a** and **6c[NTf_2]** are found cationic complexes with Cl^- and NTf_2^- as counteranion, respectively. Pd complex **4b** with the largest steric hinder proves to be most effective to gain moderate to excellent yields for the cross-coupling of various aryl chlorides and arylboronic acids in pure water. All Ir and Ru complexes work well for the transfer hydrogenation of ketones with iPrOH as a hydrogen source and *t*BuOK as an activator, and especially Ru complex **6c[PF_6]** with the smallest steric hinder exhibits excellent performance in a wide range of substrates. Noticeably, moderate yields were obtained in the transfer hydrogenation of imines, providing potential application in the construction of C–N bond. Besides, we found that different counteranions in those Ru complexes had an obvious influence on the yield of the transfer hydrogenation of less-activated 4-iodoacetophenone, with **6c[PF_6]** and **6c[BF_4]** displaying the best catalytic reactivity. These results demonstrate the high versatility and application potential of acylic imino-N-heterocyclic carbene ligands in the design of effective homogeneous catalysts.

Experimental

General

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (*n*-hexane, diethyl ether, toluene) or calcium hydride (dichloromethane), methanol and i-propanol was distilled over Mg/I_2. The starting materials $[Pd(COD)Cl_2]$,[33] $[Cp^*IrCl_2]_2$,[34] $[Ru(p\text{-cymene})Cl_2]_2$[35] and imines[36] were synthesized according to the literature procedures. The imidoyl chloride was prepared by refluxing the corresponding amide with $SOCl_2$ in the absence of solvent.[37] Other chemical reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded using Bruker spectrometers operating at 400 or 500 (^1H) and 100 or 125 MHz ($^{13}C\{^1H\}$), respectively. NMR spectra were recorded at room temperature in $CDCl_3$ or $[D_6]DMSO$, unless otherwise stated. FT-IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer using KBr disc in the range of 4000–400 cm^{-1}; only characteristic frequency of each product was listed. Elemental analysis was performed using an Elementar Vario EL III analyzer.

Synthesis of 3a–3c. **3a–3c** were synthesized by similar procedures reported before.[12a] 1-methylimidazole (12 mmol) was added dropwise to a solution of corresponding imidoyl chlorides (10 mmol) in 10 mL of dry THF with constant stirring at room temperature. The mixture was stirred under nitrogen at room temperature for 12–48 h, during which time the product precipitated. After removal of the solvent by filtration, the

precipitate was washed with dry THF for three times and dried under vacuum to obtain the products.

3a. Yellow solid, yield: 80%. ^{1}H NMR (Z-isomer) ($CDCl_3$, 400 MHz, ppm): δ 10.22 (s, 1H, NC*H*N), 8.14 (s, 1H, NC*H*CHN near imine), 7.46 (s, 1H, NCHC*H*N near N–CH_3), 7.18 (m, 4H, C–Ph), 6.74 (s, 2H, N–Ph), 4.33 (s, 3H, N–CH_3), 2.32 (s, 3H, CH_3–Ph), 2.20 (s, 3H, *p*-CH_3–Ph), 1.96 (s, 6H, *o*-CH_3–Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 147.9 (*C*═N), 143.2 (N–Ph–*C*), 140.8 (C–Ph–*C*), 137.5 (N*C*N), 135.3 (Ph), 133.9 (Ph), 130.0 (Ph), 128.7 (CH_3–Ph–*C*), 127.2 (Ph), 126.0 (Ph) 124.6 (N*C*CN, near N–CH_3), 119.5 (NC*C*N, near imine), 37.6 (N–*C*H_3), 21.6 (*C*H_3–Ph), 20.6 (*p*-*C*H_3–Ph), 18.2 (*o*-*C*H_3–Ph). ^{1}H NMR (*E*-isomer) ($CDCl_3$, 400 MHz, ppm): δ 9.49 (s, 1H, NC*H*N), 7.74 (s, 1H, NC*H*CHN near imine), 7.31 (s, 1H, NCHC*H*N near N–CH_3), 7.18 (m, 4H, C–Ph), 6.74 (s, 2H, N–Ph), 4.08 (s, 3H, N–CH_3), 2.32 (s, 3H, CH_3–Ph), 2.20 (s, 3H, *p*-CH_3–Ph), 1.96 (s, 6H, *o*-CH_3–Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 166.1 (*C*═N), 141.5 (N–Ph–*C*), 136.1 (C–Ph–*C*), 135.3 (N*C*N), 134.8 (Ph), 131.7 (Ph), 130.9 (Ph), 128.7 (CH_3–Ph–*C*), 128.4 (Ph), 124.3 (Ph), 122.0 (N*C*CN, near N–CH_3), 119.3 (NC*C*N, near imine), 35.6 (N–*C*H_3), 21.0 (*C*H_3–Ph), 20.5 (*p*-*C*H_3–Ph), 18.0 (*o*-*C*H_3–Ph). FT-IR (KBr) $\nu_{C=N}$ 1664 cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_3Cl$: C, 71.27; H, 6.84; N, 11.87. Found: C, 71.25; H, 6.85; N, 11.88.

3b. White solid, yield: 75%. ^{1}H NMR (Z-isomer) ($CDCl_3$, 400 MHz, ppm): δ 10.04 (s, 1H, NC*H*N), 8.17 (s, 1H, NC*H*CHN near imine), 7.89 (s, 1H, NCHC*H*N near N–CH_3), 7.16 (m, 4H, C–Ph), 7.05 (m, 3H, N–Ph), 4.20 (s, 3H, N–CH_3), 2.74 (m, 2H, C*H*(CH_3)$_2$), 2.29 (s, 3H, CH_3–Ph), 1.14 (d, J = 6.4 Hz, 6H, CH(CH_3)$_2$), 1.09 (d, J = 6.4 Hz, 6H, CH(CH_3)$_2$). ^{1}H NMR (*E*-isomer) ($CDCl_3$, 400 MHz, ppm): δ 9.12 (s, 1H, NC*H*N), 7.79 (s, 1H, NC*H*CHN near imine), 7.44 (s, 1H, NCHC*H*N near N–CH_3), 7.16 (m, 4H, C–Ph), 7.05 (m, 3H, N–Ph), 3.97 (s, 3H, N–CH_3), 3.16 (m, 2H, C*H*(CH_3)$_2$), 2.38 (s, 3H, CH_3–Ph), 1.14 (d, J = 6.4 Hz, 6H, CH(CH_3)$_2$), 0.89 (d, J = 6.4 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 146.5 (*C*═N), 142.5 (N–Ph–*C*), 140.1 (C–Ph–*C*), 136.8 (N*C*N), 135.8 (Ph), 129.4 (Ph), 128.7 (CH_3–Ph–*C*), 124.8 (Ph), 124.7 (Ph), 123.5 (N*C*CN, near N–CH_3), 122.8 (Ph), 119.0 (NC*C*N, near imine), 37.1 (N–*C*H_3), 27.9 (C*H*(CH_3)$_2$), 23.5 (CH(CH_3)$_2$), 21.4 (CH(CH_3)$_2$), 21.0 (*C*H_3–Ph). FT-IR (KBr) $\nu_{C=N}$ 1660 cm^{-1}. Anal. Calcd for $C_{24}H_{30}N_3Cl$: C, 72.80; H, 7.64; N, 10.61. Found: C, 72.83; H, 7.61; N, 10.62.

3c. White solid, yield: 83%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.93 (s, 1H, NC*H*N), 8.05 (s, 1H, NC*H*CHN near imine), 7.66 (s, 1H, NCHC*H*N, near N–CH_3), 7.23 (m, 7H, Ph), 6.76 (d, 2H, Ph), 4.28 (s, 3H, N–CH_3), 2.34 (s, 3H, CH_3–Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 148.7 (*C*═N), 145.1 (N–Ph–*C*), 142.6 (C–Ph–*C*), 137.1 (N*C*N), 129.9 (Ph), 129.5 (Ph), 128.8 (Ph), 125.2 (CH_3–Ph–*C*), 124.7 (N*C*CN, near N–CH_3), 123.7 (Ph), 121.0 (Ph), 119.3 (NC*C*N, near imine), 37.4 (N–*C*H_3), 21.4 (*C*H_3–Ph). FT-IR (KBr) $\nu_{C=N}$ 1666 cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_3Cl$: C, 69.34; H, 5.82; N, 13.48. Found: C, 69.36; H, 5.79; N, 13.46.

Synthesis of Pd complexes 4a–4c. To a solution of ligand **3a**, **3b** or **3c** (0.2 mmol) in 15 mL of dry CH_2Cl_2 with constant stirring, Ag_2O (0.1 mmol, 0.5 equiv) was added in the absence of light under nitrogen. After having been stirred at room temperature for 2–4 h, the suspension was filtered and the filtrate was added dropwise at −78 °C to a solution of [Pd(COD)Cl_2] in 10 mL of CH_2Cl_2 over a period of 15 min. The mixture was slowly warmed to room temperature and stirred overnight. All the volatiles were removed under vacuum and the crude product was dissolved in acetonitrile (15 mL) and filtered to remove precipitated silver chloride. The solvent was removed *in vacuo* and the crude product was purified by column chromatography or recrystallization.

4a. Yellow solid, yield: 56%. ^{1}H NMR ([D_6]DMSO, 400 MHz, ppm): δ 7.49 (s, 1H, Ph), 7.28 (m, 5H, Ph), 6.70 (s, 2H, Ph), 4.17 (s, 3H, N–CH_3), 2.29 (s, 3H, CH_3–Ph), 2.16 (s, 6H, *o*-CH_3–Ph), 2.12 (s, 3H, *p*-CH_3–Ph). ^{13}C{^{1}H} NMR ([D_6]DMSO, 100 MHz, ppm): δ 162.5 (*C*–Pd), 156.9 (*C*═N), 142.4 (Ph), 139.1 (Ph), 135.4 (Ph), 131.1 (Ph), 129.1 (Ph), 128.1 (Ph), 127.9 (Ph), 125.0 (N*C*CN), 122.4 (Ph), 119.5 (NC*C*N), 37.7 (N–*C*H_3), 30.6 (*C*H_3–Ph), 20.9, 20.4 (*o*-*C*H_3), 18.5 (*p*-*C*H_3). FT-IR (KBr) $\nu_{C=N}$ 1617 cm^{-1}. Anal. Calcd for $C_{21}H_{23}N_3Cl_2Pd$: C, 50.98; H, 4.69; N, 8.49. Found: C, 50.95; H, 4.71; N 8.47.

4b. Yellow solid, yield: 63%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.48 (m, 4H, Ph), 7.20 (m, 1H, NC*H*CHN near imine), 7.19 (m, 1H, H_p, DIPP), 7.17 (d, 1H, NCHC*H*N near N–Me), 7.09 (m, 2H, H_m, DiPP), 4.38 (s, 3H, N–CH_3), 3.12 (m, 2H, C*H*(CH_3)$_2$), 2.35 (s, 3H, CH_3–Ph), 1.44 (d, J = 8.5 Hz, 6H, CH_3), 0.89 (d, J = 8.5 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 161.5 (*C*–Pd), 158.9 (*C*═N), 143.7 (Ph), 141.3 (Ph), 138.4 (Ph), 129.5 (Ph), 129.0 (Ph), 128.3 (Ph), 125.8 (N*C*CN), 123.3 (Ph), 121.8 (NC*C*N), 118.7 (Ph), 38.8 (N–*C*H_3), 28.6 (*C*H(CH_3)$_2$), 24.2, 23.1 (*o*-*C*H_3), 21.5 (*C*H_3–Ph). FT-IR (KBr) $\nu_{C=N}$ 1611 cm^{-1}. Anal. Calcd for $C_{24}H_{29}N_3Cl_2Pd$: C, 53.70; H, 5.44; N, 7.83. Found: C, 53.69; H, 5.42; N, 7.80.

4c. Yellow solid, yield: 58%. ^{1}H NMR ([D_6]DMSO, 400 MHz, ppm): δ 7.43 (s, 1H, Ph), 7.30 (d, 2H, imi), 7.16 (m, 5H, Ph), 6.99 (m, 3H, Ph), 4.11 (s, 3H, N–CH_3), 2.27 (s, 3H, CH_3–Ph). FT-IR (KBr) $\nu_{C=N}$ 1615 cm^{-1}. Anal. Calcd for $C_{18}H_{17}N_3Cl_2Pd$: C, 47.76; H, 3.79; N, 9.28. Found: C, 47.78; H, 3.76; N, 9.30.

Synthesis of Ir complexes 5a–5c and 5a[PF_6]–5c[PF_6]. Ag_2O (0.1 mmol, 0.5 equiv) was added to a solution of ligand **3a**, **3b** or **3c** (0.2 mmol) in 15 mL of dry CH_2Cl_2 with constant stirring in the absence of light under nitrogen, and the suspension was stirred at room temperature for 2–4 h. After the addition of [Cp*$IrCl_2$]$_2$ (0.1 mmol, 0.5 equiv), the mixture was stirred for another 12 h at room temperature in the dark. The precipitate was filtered off and the residue was purified by column chromatography to obtain **5a–5c**. **5a[PF_6]–5c[PF_6]** were produced through anion-exchange procedure by addition of potassium hexafluorophosphate (0.24 mmol, 1.2 equiv) to the unpurified residue, and purified by column chromatography.

5a. Yellow solid, yield: 62%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.19 (s, 3H, N–CH_3), 2.41 (s, 3H, *o*-CH_3–Ph), 2.35 (s, 3H, *o*-CH_3–Ph), 2.25 (s, 3H, CH_3–Ph), 1.74 (s, 3H, *p*-CH_3–Ph), 1.55 (s, 15H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, ppm): δ 168.4 (*C*–Ir), 164.4 (*C*═N), 143.8 (Ph), 141.3 (Ph), 137.4 (Ph), 133.4 (Ph), 129.9 (Ph), 129.6 (Ph), 129.2 (Ph), 127.2 (N*C*CN near imine), 123.0 (Ph), 119.4 (NC*C*N near N–CH_3), 93.6 (Cp*),

37.9 (N–CH_3), 21.6 (CH_3–Ph), 20.4, 20.6 (*o*-CH_3), 19.4 (*p*-CH_3), 9.2 (Cp*, CH_3). FT-IR (KBr) $\nu_{C=N}$ 1612 cm^{-1}. Anal. Calcd for $C_{31}H_{38}N_3Cl_2Ir$: C, 52.02; H, 5.35; N, 5.87. Found: C, 52.04; H, 5.34; N, 5.85.

5a[PF_6]. Yellow solid, yield: 60%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.04 (s, 3H, N–CH_3), 2.41 (s, 3H, *o*-CH_3–Ph), 2.34 (s, 3H, *o*-CH_3–Ph), 2.24 (s, 3H, CH_3–Ph), 1.78 (s, 3H, *p*-CH_3–Ph), 1.55 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, ppm): δ 169.0 (*C*–Ir), 164.4 (*C*═N), 143.7 (Ph), 141.3 (Ph), 137.4 (Ph), 133.3 (Ph), 130.1 (Ph), 129.8 (Ph), 129.3 (Ph), 125.8 (N*C*CN near imine), 123.1 (Ph), 119.5 (NC*C*N near N–CH_3), 93.7 (Cp*), 37.5 (N–CH_3), 21.6 (CH_3–Ph), 20.4, 20.6 (*o*-CH_3), 19.1 (*p*-CH_3), 8.9 (Cp*, CH_3). FT-IR (KBr) $\nu_{C=N}$ 1633 cm^{-1}. Anal. Calcd for $C_{31}H_{38}N_3ClF_6PIr$: C, 45.12; H, 4.64; N, 5.09. Found: C, 45.15; H, 4.72; N, 5.06.

5b. Yellow solid, yield: 59%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.01 (s, 1H, Ph), 7.32 (d, J = 8.0 Hz, 2H, Ph), 7.20 (m, 2H, Ph), 7.14 (d, J = 8.0 Hz, 2H, Ph), 7.08 (d, J = 7.6 Hz, 2H, imi), δ 4.22 (s, 3H, N–CH_3), 3.45 (m, 1H, C*H*(CH_3)$_2$), 2.61 (m, 1H, C*H*(CH_3)$_2$), 2.34 (s, 3H, CH_3), 1.60 (s, 15H, Cp*), 1.37 (d, J = 6.0 Hz, 3H, iPr–CH_3), 1.12 (d, J = 6.0 Hz, 3H, iPr–CH_3), 0.64 (d, J = 6.0 Hz, 3H, iPr–CH_3), 0.52 (d, J = 6.0 Hz, 3H, iPr–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, ppm): δ 167.2 (*C*–Ir), 164.3 (*C*═N), 143.7 (Ph), 142.8 (Ph), 142.1 (Ph), 139.4 (Ph), 130.6 (Ph), 129.3 (Ph), 128.8 (Ph), 126.8 (Ph), 125.5 (Ph), 124.2 (N*C*CN near imine), 122.8 (Ph), 119.8 (NC*C*N near N–CH_3), 93.7 (Cp*), 38.3 (N–CH_3), 27.3 (CH(CH_3)$_2$), 25.6, 25.5 (CH(CH_3)$_2$), 24.7 (*C*H(CH_3)$_2$), 23.5 (*C*H(CH_3)$_2$), 21.3 (CH_3–Ph), 9.2 (Cp*, CH_3). FT-IR (KBr) $\nu_{C=N}$ 1610 cm^{-1}. Anal. Calcd for $C_{34}H_{44}N_3Cl_2Ir$: C, 53.88; H, 5.85; N, 5.54. Found: C, 53.92; H, 5.89; N, 5.51.

5b[PF_6]. Yellow solid, yield: 58%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.05 (s, 3H, N–CH_3), 3.53 (m, 1H, C*H*(CH_3)$_2$), 2.63 (m, 1H, C*H*(CH_3)$_2$), 2.33 (s, 3H, CH_3), 1.58 (s, 15H, Cp*), 1.35 (d, J = 6.0 Hz, 3H, iPr–CH_3), 1.15 (d, J = 6.0 Hz, 3H, iPr–CH_3), 0.65 (d, J = 6.0 Hz, 3H, iPr–CH_3), 0.52 (d, J = 6.0 Hz, 3H, iPr–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, ppm): δ 168.4 (*C*–Ir), 164.3 (*C*═N), 143.7 (Ph), 142.9 (Ph), 142.3 (Ph), 139.7 (Ph), 130.8 (Ph), 129.4 (Ph), 128.8 (Ph), 126.8 (Ph), 125.5 (Ph), 125.3 (Ph), 124.5 (N*C*CN near imine), 122.9 (Ph), 120.2 (NC*C*N near N–CH_3), 93.8 (Cp*), 37.8 (N–CH_3), 27.5, 27.2 (CH(*C*H_3)$_2$), 25.7, 25.6 (CH(*C*H_3)$_2$), 24.7 (*C*H(CH_3)$_2$), 23.9 (*C*H(CH_3)$_2$), 21.4 (CH_3–Ph), 9.2 (Cp*, CH_3). FT-IR (KBr) $\nu_{C=N}$ 1636 cm^{-1}. Anal. Calcd for $C_{34}H_{44}N_3ClF_6PIr$: C, 47.08; H, 5.11; N, 4.84. Found: C, 47.12; H, 5.14; N, 4.87.

5c. Yellow solid, yield: 48%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.19 (s, 3H, N–CH_3), 2.34 (s, 3H, CH_3), 1.63 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, ppm): δ 170.3 (*C*–Ir), 164.1 (*C*═N), 145.8 (Ph), 142.8 (Ph), 129.7 (Ph), 127.7 (Ph), 126.2 (Ph), 123.8 (Ph), 121.9 (N*C*CN near imine), 119.4 (NC*C*N near N–CH_3), 93.2 (Cp*), 37.9 (N–CH_3), 21.5 (CH_3–Ph), 9.0 (Cp*, CH_3). FT-IR (KBr) $\nu_{C=N}$ 1610 cm^{-1}. Anal. Calcd for $C_{28}H_{32}N_3Cl_2Ir$: C, 49.92; H, 4.79; N, 6.24. Found: C, 49.94; H, 4.76; N, 6.27.

5c[PF_6]. Yellow solid, yield: 45%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.09 (s, 3H, N–CH_3), 2.33 (s, 3H, CH_3), 1.57 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, ppm): δ 170.8 (*C*–Ir), 164.4 (*C*═N), 145.9 (Ph), 142.7 (Ph), 129.8 (Ph), 124.9 (Ph), 123.9 (Ph), 123.8 (Ph), 122.1 (N*C*CN near imine), 119.7 (NC*C*N near N–CH_3), 93.4 (Cp*), 37.6 (N–CH_3), 21.5 (CH_3–Ph), 8.8 (Cp*, CH_3). FT-IR (KBr) $\nu_{C=N}$ 1633 cm^{-1}. Anal. Calcd for $C_{28}H_{32}N_3ClF_6PIr$: C, 42.94; H, 4.12; N, 5.37. Found: C, 42.98; H, 4.15; N, 5.34.

Synthesis of Ru complexes 6A[PF_6]–6C[PF_6], 6C[Cl], 6C[BF_4], 6C[BPh_4] and 6C[NTf_2]. Ag_2O (0.11 mmol, 0.55 equiv) was added to a solution of ligand **3a**, **3b** or **3c** (0.2 mmol) in 15 mL of dry CH_2Cl_2 with constant stirring in the absence of light under nitrogen, and the suspension was stirred at room temperature for 2–4 h. After the addition of [Ru(*p*-cymene)Cl_2]$_2$ (0.1 mmol, 0.5 equiv), the mixture was stirred for another 12 h at room temperature in the dark. The precipitate was filtered off and the residue was purified by column chromatography to obtain **6c[Cl]**. **6a[PF_6]–6c[PF_6]** were produced through anion-exchange procedure by addition of potassium hexafluorophosphate (0.24 mmol, 1.2 equiv) to the unpurified residue, and purified by column chromatography. **6c[BF_4]**, **6c[BPh_4]** and **6c[NTf_2]** were synthesized by addition of 1.2 equiv of sodium tetrafluoroborate, sodium tetraphenylborate and bis (trifluoromethylsulfonyl)imide lithium to the unpurified residue and purified by column chromatography, respectively.

6a[PF_6]. Orange solid, yield: 76%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.78 (d, J = 6.0 Hz, 1H, Cy), 5.36 (d, J = 6.0 Hz, 1H, Cy), 4.98 (d, J = 6.0 Hz, 1H, Cy), 4.83 (d, J = 6.0 Hz, 1H, Cy), 4.19 (s, 3H, N–CH_3), 2.61 (m, 1H, *C*H(CH_3)$_2$), 2.58 (s, 3H, CH_3), 2.35 (s, 3H, *p*-CH_3), 2.29 (d, 6H, *o*-CH_3), 1.76 (s, 3H, Cymene *p*-CH_3), 1.23 (dd, 6H, CH(*C*H_3)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, ppm): δ 189.8 (*C*–Ru), 163.4 (*C*═N), 146.0 (Ph), 144.0 (Ph), 137.5 (Ph), 133.0 (Ph), 130.2 (Ph), 129.8 (Ph), 129.3 (Ph), 129.0 (Ph), 127.8 (Ph), 126.2 (Ph), 123.1 (N*C*CN near imine), 119.3 (NC*C*N near N–CH_3), 112.6 (Ph), 107.7 (Ph), 85.0 (Cy, *C*H), 85.6 (Cy, *C*H), 87.0 (Cy, *C*H), 92.1 (Cy, *C*H), 38.7 (N–CH_3), 31.7 (Cy, *C*H(CH_3)$_2$), 22.0, 24.0 (Cy, CH(*C*H_3)$_2$), 21.6 (CH_3–Ph), 20.6, 20.8 (*o*-CH_3), 19.2 (*p*-CH_3–Ph), 18.6 (Cy, *p*-CH_3). FT-IR (KBr) $\nu_{C=N}$ 1637 cm^{-1}. Anal. Calcd for $C_{31}H_{37}N_3ClF_6PRu$: C, 50.79; H, 5.09; N, 5.73. Found: C, 50.82; H, 5.12; N, 5.75.

6b[PF_6]. Orange solid, yield: 65%. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.21 (d, J = 6.0 Hz, 1H, Cy), 5.20 (d, J = 6.0 Hz, 1H, Cy), 5.07 (d, J = 6.0 Hz, 1H, Cy), 5.04 (d, J = 6.0 Hz, 1H, Cy), 4.20 (s, 3H, N–CH_3), 3.85 (m, 1H, *C*H(CH_3)$_2$), 2.50 (m, 1H, *C*H(CH_3)$_2$), 2.35 (m, 1H, *C*H(CH_3)$_2$), 2.33 (s, 3H, CH_3), 2.29 (s, 3H, *p*-CH_3), 1.36 (d, J = 6.5 Hz, 3H, iPr–CH_3), 1.34 (d, J = 6.5 Hz, 3H, iPr–CH_3), 1.21 (dd, 6H, CH(*C*H_3)$_2$), 1.09 (d, J = 6.5 Hz, 3H, iPr–CH_3), 0.21 (d, J = 6.5 Hz, 3H, iPr–CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, ppm): δ 189.9 (*C*–Ru), 162.9 (*C*═N), 144.7 (Ph), 144.2 (Ph), 143.8 (Ph), 138.8 (Ph), 130.7 (Ph), 129.7 (Ph), 128.8 (Ph), 126.0 (Ph), 125.6 (Ph), 124.9 (Ph), 122.6 (N*C*CN near imine), 120.4 (NC*C*N near N–CH_3), 113.9 (Ph), 108.3 (Ph), 91.8 (Cy, *C*H), 86.1 (Cy, *C*H), 85.9 (Cy, *C*H), 82.0 (Cy, *C*H), 38.8 (N–CH_3), 30.9 (*C*H(CH_3)$_2$), 28.1, 27.4 (CH(*C*H_3)$_2$), 26.1 (*C*H(CH_3)$_2$), 25.2, 24.9 (CH(*C*H_3)$_2$), 24.6, 24.2 (CH(*C*H_3)$_2$), 22.2 (*C*H(CH_3)$_2$), 21.5 (CH_3–Ph), 19.0 (CH_3–Cy). FT-IR (KBr) $\nu_{C=N}$

Table 6 Crystal data and structure refinement for **4a**, **5a**·0.5(CH_2Cl_2)·1.5(H_2O) and **6c[NTf_2]**

	4a	**5a**·0.5(CH_2Cl_2)·1.5(H_2O)	**6c[NTf_2]**
Formula	$C_{21}H_{23}Cl_2N_3$ Pd	($C_{31}H_{38}N_3Cl_2Ir$)·0.5(CH_2Cl_2)·1.5(H_2O)	$C_{30}H_{31}ClF_6N_4O_4RuS_2$
M_r	494.72	785.23	826.23
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	*C*2/*c*	$P\bar{1}$
a [Å]	16.9571(17)	41.54(3)	8.8397(12)
b [Å]	14.9440(15)	11.423(5)	11.0339(15)
c [Å]	19.461(2)	32.26(2)	17.918(2)
α [°]	90	90	91.615(2)
β [°]	90	113.60(4)	102.572(2)
γ [°]	90	90	96.477(2)
V [Å^3]	4931.6(9)	14 025(14)	1692.4(4)
Z	8	16	2
μ [mm^{-1}]	0.978	4.065	0.740
ρ_{calcd} [mg m^{-3}]	1.333	1.488	1.621
F [000]	2000	6272	836
T [K]	173(2)	293(2)	173(2)
θ range [°]	2.09 to 27.58	1.38 to 25.01	2.14 to 25.50
Reflns collected/indep reflns	34 264/5681	24 896/12 350	10 193/6170
$R_{(int)}$	0.0229	0.0627	0.0183
Data/restraints/params	5681/0/249	12 350/12/765	6170/6/539
GOF	1.122	0.991	1.055
R_1 ($I > 2\sigma(I)$)	0.0313	0.0596	0.0501
wR_2	0.0842	0.1544	0.1263

1638 cm^{-1}. Anal. Calcd for $C_{34}H_{43}N_3ClF_6PRu$: C, 52.68; H, 5.59; N, 5.42. Found: C, 52.65; H, 5.56; N, 5.38.

6c[PF_6]. Orange solid, yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.87 (d, *J* = 6.0 Hz, 1H, Cy), 5.54 (d, *J* = 6.0 Hz, 1H, Cy), 5.27 (d, *J* = 6.0 Hz, 1H, Cy), 5.23 (d, *J* = 6.0 Hz, 1H, Cy), 4.22 (s, 3H, N–C*H*$_3$), 2.66 (m, 1H, *CH*(CH_3)$_2$), 2.34 (s, 3H, *p*-C*H*$_3$), 2.19 (s, 3H, Cymene *p*-CH_3), 1.13 (dd, 6H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 190.5 (*C*–Ru), 162.7 (*C*═N), 150.1 (Ph), 143.1 (Ph), 130.0 (Ph), 129.4 (Ph), 127.9 (Ph), 125.7 (N*C*CN near imine), 122.3 (Ph), 119.0 (NC*C*N near N–CH_3), 109.7 (Ph), 106.8 (Ph), 91.4 (Cy, *C*H), 89.3 (Cy, *C*H), 87.8 (Cy, *C*H), 85.5 (Cy, *C*H), 38.7 (N–*C*H$_3$), 31.0 (Cy, *C*H(CH_3)$_2$), 22.6, 22.4 (Cy, CH(*C*H$_3$)$_2$), 21.7 (*C*H$_3$–Ph), 19.0 (Cy, *p*-*C*H$_3$). FT-IR (KBr) $\nu_{C=N}$ 1637 cm^{-1}. Anal. Calcd for $C_{28}H_{31}N_3ClF_6PRu$: C, 48.66; H, 4.52; N, 6.08. Found: C, 48.63; H, 4.55; N, 6.07.

6c[Cl]. Orange solid, yield: 72%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.30 (d, *J* = 6.0 Hz, 1H, Cy), 5.66 (d, *J* = 6.0 Hz, 1H, Cy), 5.49 (d, *J* = 6.0 Hz, 1H, Cy), 5.24 (d, *J* = 6.0 Hz, 1H, Cy), 4.45 (s, 3H, N–C*H*$_3$), 2.67 (m, 1H, *CH*(CH_3)$_2$), 2.35 (s, 3H, *p*-C*H*$_3$), 2.25 (s, 3H, Cymene *p*-CH_3), 1.11 (dd, 6H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 190.2 (*C*–Ru), 162.3 (*C*═N), 149.9 (Ph), 142.9 (Ph), 129.8 (Ph), 129.1 (Ph), 127.7 (Ph), 126.2 (N*C*CN near imine), 122.2 (Ph), 118.5 (NC*C*N near N–CH_3), 108.7 (Ph), 107.0 (Ph), 91.7 (Cy, *C*H), 89.3 (Cy, *C*H), 88.0 (Cy, *C*H), 85.1 (Cy, *C*H), 39.4 (N–*C*H$_3$), 31.2 (Cy, *C*H(CH_3)$_2$), 22.5, 22.4 (Cy, CH(*C*H$_3$)$_2$), 21.4 (*C*H$_3$–Ph), 19.1 (Cy, *p*-*C*H$_3$). FT-IR (KBr) $\nu_{C=N}$ 1615 cm^{-1}. Anal. Calcd for $C_{28}H_{31}N_3Cl_2Ru$: C, 57.83; H, 5.37; N, 7.23. Found: C, 57.85; H, 5.34; N, 7.26.

6c[BF_4]. Orange solid, yield: 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.92 (d, *J* = 6.0 Hz, 1H, Cy), 5.56 (d, *J* = 6.0 Hz, 1H, Cy), 5.33 (d, *J* = 6.0 Hz, 1H, Cy), 5.24 (d, *J* = 6.0 Hz, 1H, Cy), 4.26 (s, 3H, N–C*H*$_3$), 2.65 (m, 1H, *CH*(CH_3)$_2$), 2.33 (s, 3H, *p*-C*H*$_3$), 2.21 (s, 3H, Cymene *p*-CH_3), 1.13 (dd, 6H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 190.4 (*C*–Ru), 162.8 (*C*═N), 150.2 (Ph), 143.0 (Ph), 129.9 (Ph), 129.3 (Ph), 127.9 (Ph), 125.9 (N*C*CN near imine), 122.5 (Ph), 119.0 (NC*C*N near N–CH_3), 110.0 (Ph), 106.3 (Ph), 91.2 (Cy, *C*H), 89.6 (Cy, *C*H), 87.7 (Cy, *C*H), 85.6 (Cy, *C*H), 38.9 (N–*C*H$_3$), 31.4 (Cy, *C*H(CH_3)$_2$), 22.6, 22.4 (Cy, CH(*C*H$_3$)$_2$), 21.7 (*C*H$_3$–Ph), 19.1 (Cy, *p*-*C*H$_3$). FT-IR (KBr) $\nu_{C=N}$ 1634 cm^{-1}. Anal. Calcd for $C_{28}H_{31}N_3BClF_4Ru$: C, 53.14; H, 4.94; N, 6.64. Found: C, 53.17; H, 4.98; N, 6.63.

6c[BPh_4]. Orange solid, yield: 65%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.37 (d, *J* = 6.0 Hz, 1H, Cy), 5.02 (d, *J* = 6.0 Hz, 1H, Cy), 4.89 (d, *J* = 6.0 Hz, 1H, Cy), 4.78 (d, *J* = 6.0 Hz, 1H, Cy), 3.37 (s, 3H, N–C*H*$_3$), 2.38 (m, 1H, *CH*(CH_3)$_2$), 2.32 (s, 3H, *p*-C*H*$_3$), 2.00 (s, 3H, Cymene *p*-CH_3), 0.99 (dd, 6H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 189.7 (*C*–Ru), 164.9 (Ph), 164.4 (Ph), 163.9 (Ph), 163.4 (Ph), 162.5 (*C*═N), 149.9 (Ph), 143.4 (Ph), 130.4 (Ph), 130.2 (Ph), 129.4 (Ph), 128.1 (Ph), 125.7 (N*C*CN near imine), 122.0 (Ph), 118.8 (NC*C*N near N–CH_3), 108.2 (Ph), 92.3 (Cy, *C*H), 88.2 (Cy, *C*H), 87.9 (Cy, *C*H), 84.5 (Cy, *C*H), 38.3 (N–*C*H$_3$), 31.5 (Cy, *C*H(CH_3)$_2$), 22.8, 22.5 (Cy, CH(*C*H$_3$)$_2$), 21.7 (*C*H$_3$–Ph), 19.2 (Cy, *p*-*C*H$_3$). FT-IR (KBr) $\nu_{C=N}$ 1635 cm^{-1}. Anal. Calcd for $C_{52}H_{51}N_3BClRu$: C, 72.18; H, 5.94; N, 4.86. Found: C, 72.16; H, 5.89; N, 4.83.

6c[NTf_2]. Orange solid, yield: 68%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.93 (d, *J* = 6.0 Hz, 1H, Cy), 5.46 (d, *J* = 6.0 Hz, 1H, Cy), 5.25 (d, *J* = 6.0 Hz, 1H, Cy), 5.21 (d, *J* = 6.0 Hz, 1H, Cy), 4.21 (s, 3H, N–C*H*$_3$), 2.62 (m, 1H, *CH*(CH_3)$_2$), 2.34 (s, 3H, *p*-C*H*$_3$), 2.20 (s, 3H, Cymene *p*-CH_3), 1.10 (dd, 6H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 190.4 (*C*–Ru), 162.7 (*C*═N), 150.1 (Ph), 143.3 (Ph), 130.1 (Ph), 129.4 (Ph), 128.1 (Ph), 125.8 (N*C*CN near imine), 122.2 (Ph), 119.1 (NC*C*N near N–CH_3), 109.2 (Ph), 107.4 (Ph), 91.9 (Cy, *C*H), 88.9 (Cy,

*C*H), 87.7 (Cy, *C*H), 85.6 (Cy, *C*H), 38.8 (N–CH_3), 31.5 (Cy, *C*H(CH_3)$_2$), 22.6, 22.3 (Cy, CH(*C*H_3)$_2$), 21.7 (*C*H_3–Ph), 19.1 (Cy, *p*-*C*H_3). FT-IR (KBr) $\nu_{C=N}$ 1616 cm^{-1}. Anal. Calcd for $C_{30}H_{31}N_4ClF_6O_4S_2Ru$: C, 43.61; H, 3.78; N, 6.78. Found: C, 43.58; H, 3.76; N, 6.75.

General procedure for Suzuki–Miyaura cross-coupling reaction in pure water

A 25 mL flask fitted with a reflux condenser was charged with catalyst (1.0 mol%), aryl halides (1.0 mmol), KOH (2.0 mmol) and boronic acid (1.5 mmol), then 6.0 mL of H_2O was added. The flask was placed in a preheated oil bath (100 °C) under air atmosphere for 24 h. The reaction mixture was extracted with dichloromethane (3 × 5 mL). The combined dichloromethane phase was dried with anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to gain a crude product, which was purified by column chromatography.

General procedure for the transfer hydrogenation

Substrate (1.0 mmol), potassium *tert*-butoxide (0.1 mmol), catalyst (1.0 mol%) and 2-propanol (5 mL) were placed in an oven-dried 25 mL Schlenk flask flushed with nitrogen and stirred on a prehetaed oil bath (82 °C) for a constant time. The volatiles were then evaporated and the crude product was purified by column chromatography.

X-ray crystallography

Intensity data for the compounds were collected on Bruker Smart APEX (at 293 K) (**5a**) and Bruker APEX DUO diffractometers (at 173 K) (**4a** and **6c[NTf$_2$]**), respectively. Both are equipped with 2.4 kW sealed tube X-ray source (Mo-Kα radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. A hemisphere of intensity data was collected at room temperature with a scan width of 0.60° in ω. Empirical absorption corrections were based on SADABS program.[38] The structures were solved by direct methods and refined by full-matrix least-squares refinement using the SHELXTL-97 program.[39] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The NTf_2^- anion of **6c[NTf$_2$]** are highly disordered and are divided into two parts. A summary of the crystal data and processing parameters are given in Table 6.

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Notes and references

1 (*a*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39; (*b*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*c*) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247; (*d*) H. M. Lee, C. C. Lee and P. Y. Cheng, *Curr. Org. Chem.*, 2007, **11**, 1491; (*e*) O. Kühl, *Chem. Soc. Rev.*, 2007, **36**, 592; (*f*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (*g*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.

2 (*a*) A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27; (*b*) P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680.

3 (*a*) C. C. Lee, W. C. Ke, K. T. Chan, C. L. Lai, C. H. Hu and H. M. Lee, *Chem.–Eur. J.*, 2007, **13**, 582; (*b*) A. A. Danopoulos, N. Tsoureas, S. A. Macgregor and C. Smith, *Organometallics*, 2007, **26**, 253; (*c*) G. Song, X. Li, Z. Song, J. Zhao and H. Zhang, *Chem.–Eur. J.*, 2009, **15**, 5535; (*d*) F. E. Hahn, A. R. Naziruddin, A. Hepp and T. Pape, *Organometallics*, 2010, **29**, 5283; (*e*) J. A. Cabeza, M. Damonte, P. García-Álvarez, A. R. Kennedy and E. Pérez-Carreño, *Organometallics*, 2011, **30**, 826.

4 (*a*) W. A. Herrman, L. J. Gooßen and M. Spiegler, *J. Organomet. Chem.*, 1997, **547**, 357; (*b*) D. J. Nielsen, K. J. Cavell, B. W. Skelton and A. H. White, *Organometallics*, 2006, **25**, 4850.

5 (*a*) J. Wolf, A. Labande, J.-C. Daran and R. Poli, *Eur. J. Inorg. Chem.*, 2007, 5069; (*b*) C. Fliedel and P. Braunstein, *Organometallics*, 2010, **29**, 5614; (*c*) C. Fliedel, A. Sabbatini and P. Braunstein, *Dalton Trans.*, 2010, **39**, 8820; (*d*) H. V. Huynh, C. H. Yeo and Y. X. Chew, *Organometallics*, 2010, **29**, 1479; (*e*) M. Bierenstiel and E. D. Cross, *Coord. Chem. Rev.*, 2011, **255**, 574–590.

6 (*a*) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz and M. B. Hursthouse, *Chem. Commun.*, 2000, 1247; (*b*) E. Peris, J. A. Loch, J. Mata and R. H. Crabtree, *Chem. Commun.*, 2001, 201; (*c*) F. E. Fernández, M. C. Puerta and P. Valerga, *Organometallics*, 2011, **30**, 5793; (*d*) P. Cao, J. Cabrera, R. Padilla, D. Serra, F. Rominger and M. Limbach, *Organometallics*, 2012, **31**, 921; (*e*) V. Khlebnikov, A. Meduri, H. Mueller-Bunz, T. Montini, P. Fornasiero, E. Zangrando, B. Milani and M. Albrecht, *Organometallics*, 2012, **31**, 976.

7 (*a*) D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics*, 2009, **28**, 321; (*b*) S. Warsink, I. Chang, J. J. Weigand, P. Hauwert, J. Chen and C. J. Elsevier, *Organometallics*, 2010, **29**, 4555.

8 (*a*) L. H. Gade, V. César and S. Bellemin-Laponnaz, *Angew. Chem., Int. Ed.*, 2004, **43**, 1014; (*b*) L. H. Gade and S. Bellemin-Laponnaz, *Coord. Chem. Rev.*, 2007, **251**, 718; (*c*) N. Schneider, M. Kruck, S. Bellemin-Laponnaz, H. Wadepohl and L. H. Gade, *Eur. J. Inorg. Chem.*, 2009, 493; (*d*) T. Makino, R. Yamasaki, I. Azumaya, H. Masu and S. Saito, *Organometallics*, 2010, **29**, 6291.

9 (*a*) P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.*, 2003, **42**, 5981; (*b*) M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahoz and L. A. Oro, *Organometallics*, 2008, **27**, 224; (*c*) W. W. N. O, A. J. Lough and R. H. Morris, *Organometallics*, 2009, **28**, 6755; (*d*) C. Topf, C. Hirtenlehner, M. Zabel, M. List, M. Fleck and U. Monkowius, *Organometallics*, 2011, **30**, 2755; (*e*) L. Busetto, M. C. Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni and G. Solinas, *Organometallics*, 2011, **30**, 5258; (*f*) W. W. N. O, A. J. Lough and R. H. Morris, *Organometallics*, 2012, **31**, 2137; (*g*) W. W. N. O, A. J. Lough and R. H. Morris, *Organometallics*, 2012, **31**, 2152.

10 C. Y. Liao, K. T. Chan, J. Y. Zeng, C. H. Hu, C. Y. Tu and H. M. Lee, *Organometallics*, 2007, **26**, 1692.

11 (*a*) M. Frøseth, A. Dhindsa, H. Røise and M. Tilset, *Dalton Trans.*, 2003, 4516; (*b*) M. Frøseth, K. A. Netland, K. W. Törnroos, A. Dhindsa and M. Tilset, *Dalton Trans.*, 2005, 1664; (*c*) M. Frøseth, K. A. Netland, C. Rømming and M. Tilset, *J. Organomet. Chem.*, 2005, **690**, 6125.

12 (*a*) S. Dastgir, K. S. Coleman, A. R. Cowley and M. L. H. Green, *Organometallics*, 2006, **25**, 300; (*b*) K. A. Netland, A. Krivokapic, M. Schröder, K. Boldt, F. Lundvall and M. Tilset, *J. Organomet. Chem.*, 2008, **693**, 3703; (*c*) A. C. Badaj, S. Dastgir, A. J. Lough and G. G. Lavoie, *Dalton Trans.*, 2010, **39**, 3361.

13 (*a*) J. A. Thagfi, S. Dastgir, A. J. Lough and G. G. Lavoie, *Organometallics*, 2010, **29**, 3133; (*b*) T. G. Larocque, A. C. Badaj, S. Dastgir and G. G. Lavoie, *Dalton Trans.*, 2011, **40**, 12705.

14 (*a*) A. C. Badaj and G. G. Lavoie, *Organometallics*, 2012, **31**, 1103; (*b*) J. A. Thagfi and G. G. Lavoie, *Organometallics*, 2012, **31**, 2463.

15 (*a*) M. L. Rosenberg, A. Krivokapic and M. Tilset, *Org. Lett.*, 2009, **11**, 547; (*b*) M. L. Rosenberg, E. Langseth, A. Krivokapic, N. S. Gupta and M. Tilset, *New J. Chem.*, 2011, **35**, 2306; (*c*) M. L. Rosenberg, K. Vlašaná, N. S. Gupta, D. Wragg and M. Tilset, *J. Org. Chem.*, 2011, **76**, 2465; (*d*) M. L. Rosenberg, A. Krapp and M. Tilset, *Organometallics*, 2011, **30**, 6562.

16 (*a*) R. Zhong, Y. N. Wang, X. Q. Guo, Z. X. Chen and X. F. Hou, *Chem.–Eur. J.*, 2011, **17**, 11041; (*b*) X. F. Hou, Y. N. Wang and I. Göttker-Schnetmann, *Organometallics*, 2011, **30**, 6053.

17 K. S. Coleman, S. Dastgir, G. Barnett, M. J. P. Alvite, A. R. Cowley and M. L. H. Green, *J. Organomet. Chem.*, 2005, **690**, 5591.

18 N. Saleh and J. A. Caruso, *J. Solution Chem.*, 1979, **8**, 197.

19 P. Illner, R. Puchta, F. W. Heinemann and R. van Eldik, *Dalton Trans.*, 2009, 2795.

20 (*a*) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson and M. G. Organ, *Chem.–Eur. J.*, 2006, **12**, 4743; (*b*) O. Navarro, N. Marion, Y. Oonishi, R. A. Kelly III and S. P. Nolan, *J. Org. Chem.*, 2006, **71**, 685; (*c*) G.-R. Peh, E. A. B. Kantchev, J.-C. Er and J. Y. Ying, *Chem.–Eur. J.*, 2010, **16**, 4010; (*d*) J. Nasielski, N. Hadei, G. Achonduh, E. A. B. Kantchev, C. J. O'Brien, A. Lough and M. G. Organ, *Chem.–Eur. J.*, 2010, **16**, 10844; (*e*) M.-T. Chen, D. A. Vicic, M. L. Turner and O. Navarro, *Organometallics*, 2011, **30**, 5052; (*f*) M.-T. Chen, D. A. Vicic, W. J. Chain, M. L. Turner and O. Navarro, *Organometallics*, 2011, **30**, 6770.

21 E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768.

22 N. T. S. Phan, M. Van Der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609.

23 (*a*) T. Ikariya and A. J. Blacker, *Acc. Chem. Res.*, 2007, **40**, 1300; (*b*) R. H. Morris, *Chem. Soc. Rev.*, 2009, **38**, 2282.

24 (*a*) M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller and R. H. Crabtree, *Organometallics*, 2002, **21**, 3596; (*b*) J. R. Miecznikowski and R. H. Crabtree, *Polyhedron*, 2004, **23**, 2857; (*c*) D. Gnanamgari, A. Moores, E. Rajaseelan and R. H. Crabtree, *Organometallics*, 2007, **26**, 1226; (*d*) W. B. Cross, C. G. Daly, Y. Boutadla and K. Singh, *Dalton Trans.*, 2011, **40**, 9722.

25 (*a*) V. Dragutan, I. Dragutan, L. Delaude and A. Demonceau, *Coord. Chem. Rev.*, 2007, **251**, 765; (*b*) N. Ding and T. S. A. Hor, *Dalton Trans.*, 2010, **39**, 10179; (*c*) W. W. N. O, A. J. Lough and R. H. Morris, *Organometallics*, 2011, **30**, 1236.

26 M. V. Jiménez, J. Fernández-Tornos, J. J. Pérez-Torrente, F. J. Modrego, S. Winterle, C. Cunchillos, F. J. Lahoz and L. A. Oro, *Organometallics*, 2011, **30**, 5493.

27 (*a*) E. Y. X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391; (*b*) A. Macchioni, *Chem. Rev.*, 2005, **105**, 2039.

28 (*a*) J. M. Buriak, J. C. Klein, D. G. Herrington and J. A. Osborn, *Chem.–Eur. J.*, 2000, **6**, 139; (*b*) S. P. Smidt, N. Zimmermann, M. Studer and A. Pfaltz, *Chem.–Eur. J.*, 2004, **10**, 4685; (*c*) J. Lacour and D. Moraleda, *Chem. Commun.*, 2009, 7073.

29 S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927.

30 (*a*) G. Ciancaleoni, S. Bolaño, J. Bravo, M. Peruzzini, L. Gonsalvi and A. Macchioni, *Dalton Trans.*, 2010, **39**, 3366; (*b*) R. Zhong, Y. N. Wang, X. Q. Guo and X. F. Hou, *J. Organomet. Chem.*, 2011, **696**, 1703.

31 P. Albano, M. Aresta and M. Manassero, *Inorg. Chem.*, 1980, **19**, 1069.

32 D. B. Williams, M. E. Stoll, B. L. Scott, D. A. Costa and W. J. Oldham Jr, *Chem. Commun.*, 2005, 1438.

33 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1990, **28**, 346.

34 R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson and S. T. Michel, *Inorg. Chem.*, 1990, **29**, 2023.

35 M. A. Bennett, T. N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 74.

36 K. Tanaka and R. Shiraishi, *Green Chem.*, 2000, **2**, 272.

37 R. T. Boeré, V. Klassen and G. Wolmershäuser, *J. Chem. Soc., Dalton Trans.*, 1998, 4147.

38 G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction*, University of Göttingen, Germany, 1998.

39 G. M. Sheldrick, *SHELXS-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.