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New Iridium Catalysts for the Efficient Alkylation of Anilines by Alcohols under Mild Conditions

Stefan Michlik and Rhett Kempe*[a]

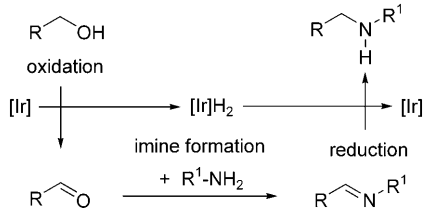
Abstract: The synthesis of eight new iridium complexes containing anionic P,N ligands is described. These complexes have been investigated as catalysts for amine alkylation reactions, resulting in a highly active catalyst for the selective monoalkylation of anilines with primary alcohols, under mild reaction conditions. Nearly quantitative conversion was observed at 70 °C with a catalyst loading as low as 0.05 mol % iridium.

Keywords: alcohols · alkylation · anilines · iridium · N,P ligands

Introduction

P,N-ligand-stabilised iridium complexes are efficient catalysts for selective C–N[1–3] and C–C[4] coupling reactions involving the borrowing-hydrogen (BH)[5] or hydrogen-autotransfer (HA)[6] catalysis protocols.[7] These protocols proceed for Ir-complex-catalysed amine alkylations as shown in Scheme 1 and have been developed into efficient synthetic methods by (for instance) the groups of Beller,[8] Grigg,[9] Fujita,[10] Williams[8a,11] and Yus,[12] as well as by us.[1–4]

The P,N-ligand-based Ir catalyst system developed by us is especially active in the alkylation of aminopyridines[2,3] and usually requires a stoichiometric amount of base. Both of these observations were not fully understood by us and we became interested in obtaining a more detailed insight into how the catalyst operates within an HA/BH scenario. The observations made led to a new class of catalysts that operates very efficiently under mild conditions.

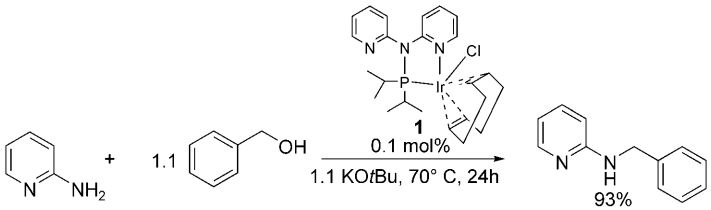


Scheme 1. The metal-complex catalysed borrowing-hydrogen or hydrogen-autotransfer protocol to selectively alkylate amines ([Ir] = iridium complex).

Results and Discussion

Detection of the catalytically active species in aminopyridine alkylation reactions: In previous work, it has been shown that our catalyst system is highly active in the alkylation of 2-aminopyridines with primary alcohols.[2,3] Therefore, 2-aminopyridine (1.0 equiv), alcohol (1.1 equiv) and KO*t*Bu were reacted, at 70 °C, in the presence of the Ir catalyst (0.1 mol %; Scheme 2). Under these conditions, *N*-(2-pyridyl)benzylamine was isolated in a very good yield of up to 93 %.[2]

However, these mild reaction conditions could not simply be transferred to the alkylation of anilines. For these compounds it was necessary to increase the catalyst loading to 0.6 mol % iridium to obtain comparable results. It was con-



Scheme 2. Alkylation of aminopyridines under mild conditions.

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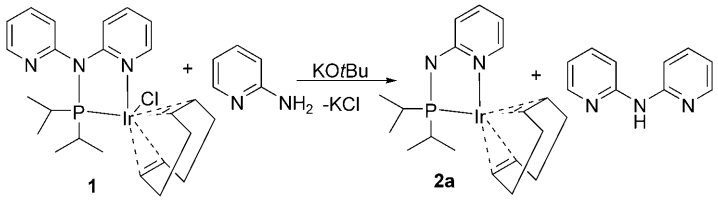
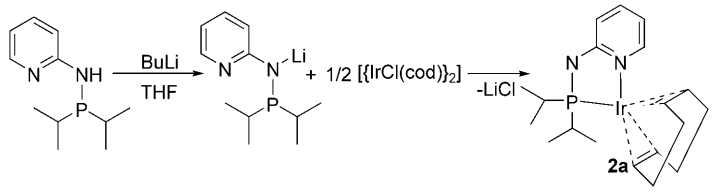
cluded that the presence of aminopyridines may change the nature of the catalyst. NMR experiments were carried out to investigate whether the catalyst reacts with the aminopyridine substrate. Stoichiometric amounts of 2-aminopyridine and KO*t*Bu were added to catalyst **1**, under equivalent conditions to the catalysis experiments



Scheme 3. The reaction of **1** with 2-aminopyridine, in the presence of KO*t*Bu.

(Scheme 3). In the ^{31}P NMR spectrum (161 MHz, CD_2Cl_2, 298 K) only one peak, at $\delta = 94.9$ ppm, was detected, which is shifted to higher field in comparison with the chemical shift of complex **1** ($\delta = 110.4$ ppm). This observation indicates that complex **1** does react with 2-aminopyridine, in the presence of a base, to form a new compound. Independent synthesis of this new compound, complex **2a**, through deprotonation of PyHNP(*i*Pr)$_2$ (Py = pyridine) with *n*BuLi, followed by the addition of [{IrCl(cod)}$_2$] (cod = 1,5-cyclooctadiene), led to **2a** in 80% isolated yield (Scheme 4).



Scheme 4. Synthesis of **2a**.

Crystals suitable for X-ray crystal structure analysis were obtained from a hexane solution. The molecular structure of **2a** is shown in Figure 1. In complex **2a**, both the Ir1–N1 (2.071(5) Å), and the P1–N2 (1.659(5) Å) bond lengths are slightly shorter than those in complex **1**, which contains a neutral P,N-ligand (Ir1–N1 (2.119(3) Å), P1–N2 (1.730(3) Å)), because deprotonation of the amino group means that the electron density is delocalised over the P-N-C-N backbone. Similar observations have been made by Woollins and co-workers for platinum and palladium complexes stabilised by deprotonated 2-(diphenylphosphinoamino)pyridine (dppap).[13] Seidel already succeeded in 1967 in synthesising a neutral nickel(II) complex by using the deprotonated dppap ligand.[14]

It is possible that if complexes like **2a** are formed under the catalytic conditions with alkylated aminopyridines, similar complexes may be formed with anilines. However, no reaction of complex **1** with aniline in the presence of a base was observed.

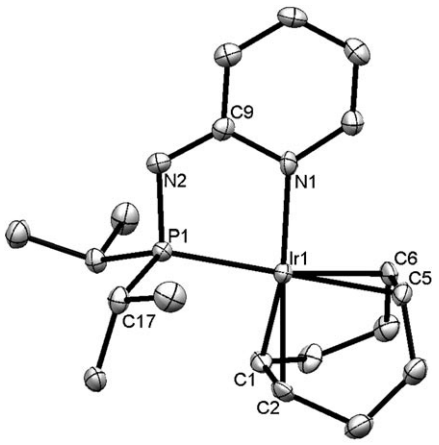
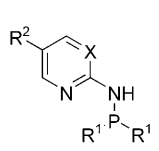


Figure 1. Molecular structure of **2a**. Selected bond length [Å] and angles [°]: Ir1–N1 2.071(5), Ir1–C1 2.109(6), Ir1–C2 2.140(6), Ir1–C5 2.191(6), Ir1–C6 2.216(6), Ir1–P1 2.2806(15), C1–C2 1.402(9), C5–C6 1.381(9), P1–N2 1.659(5), N1–C9 1.405(7), P1–C14 1.835(6), N1-Ir1-C1 157.0(2), N1-Ir1-C2 164.3(2), C1-Ir1-C2 38.5(2), N1-Ir1-C5 95.2(2), N1-Ir1-P1 79.23(14), N2-P1-Ir1 105.53(19), N2-C9-N1 121.7(5).

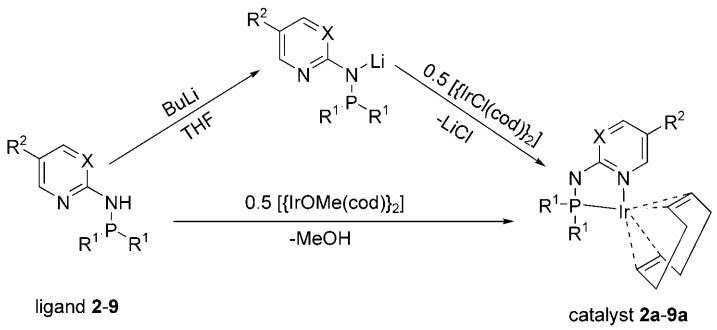
Iridium complexes like **2a**, that is, compounds stabilised by anionic P,N ligands, might be responsible for the enhanced activity in alkylation reactions of aminopyridines and might be a better class of catalyst than complexes like **1**, namely, ones stabilised by neutral P,N ligands. To investigate the potential of this "novel" class of Ir catalysts, a small library of ligands was synthesised from different substituted 2-aminopyridines and 2-aminopyrimidines by reacting them with chlorodiisoproylphosphane or chlorodiphenylphosphane in the presence of a base.



2: X = C; R^1 = *i*Pr; R^2 = H
3: X = C; R^1 = Ph; R^2 = H
4: X = N; R^1 = *i*Pr; R^2 = H
5: X = N; R^1 = Ph; R^2 = H
6: X = C; R^1 = *i*Pr; R^2 = CH_3
7: X = C; R^1 = Ph; R^2 = CH_3
8: X = C; R^1 = *i*Pr; R^2 = Cl
9: X = C; R^1 = Ph; R^2 = Cl

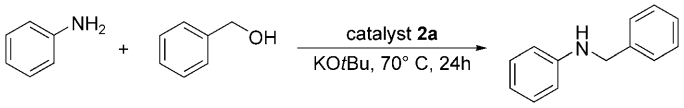
Iridium complexes based upon these ligands were synthesised in two different ways. The first was deprotonation of the corresponding ligand by *n*BuLi, followed by the addition of [{IrCl(cod)}$_2$] (0.5 equiv). The resulting LiCl was filtered off and the solvent removed under vacuum. The more elegant method was a one-step synthesis of the complexes. For this, the dissolved ligand was added to [{IrOMe(cod)}$_2$] (0.5 equiv) and the complex was formed by elimination of methanol in quantitative yield. Iridium complexes **2a**–**9a** were synthesised and characterised (Scheme 5).

Catalyst development: If catalyst systems based upon **2a**–**9a** are responsible for the high efficiency of the alkylation reactions of aminopyridines they should do well in the alkylation of anilines. Since catalyst efficiency depends upon the reac-



Scheme 5. Synthesis of **2a–9a**.

tion conditions, these had to be optimised for the new catalyst system. Catalyst **2a** was used for the optimisation of the reaction conditions (Scheme 6).



Scheme 6. The model reaction used for finding the optimum reaction conditions.

First of all, the influence of the solvent was determined and various organic solvents were tested. As can be seen from Table 1, diethylene glycol dimethyl ether (diglyme) appears to be the most suitable solvent, because complete conversion and a very good yield (99%) could only be achieved by using this solvent (Table 1, entry A5). When using THF, toluene or dimethoxyethane (DME), the yields were substantially lower (Table 1, entries A2–A4), indicating an inhibitory influence of the solvent on the reaction. It was also observed that the yield of *N*-phenylbenzylamine remains the same even with higher catalyst loadings. Interestingly, when DMSO was used as the solvent, no conversion was observed (Table 1, entry A1). Unfortunately, in all recent work the catalyst stock solution was in THF,[1–4] even for the solvent screenings. Since THF seems to deactivate our catalyst, all further stock solutions were made in diglyme.

Table 1. Screening of solvent, base and substrate/base ratio.[a]

	A		B		C	
	Solvent	Yield [%][b,c]	Base	Yield [%][b]	Substrate/Base	Yield [%][b,d]
1	DMSO	n.d.	K_3PO_4	23	1:1.1	99
2	THF	32	NaOH	10	1:1.0	72
3	toluene	34	KOH	9	1:0.7	68
4	DME	50	NaO*t*Bu	25	1:0.5	45
5	diglyme	99	KO*t*Bu	99	1:0.3	36
6					1:0.1	31
7					1:0	n.d.

[a] Reaction conditions: aniline (1.0 mmol), benzyl alcohol (1.1 mmol), catalyst **2a** (0.4 mol%), base (1.1 mmol), solvent (0.2 mL), 70°C, 24 h; n.d. = not determined. [b] Yield determined by GC analysis with dodecane as the internal standard. [c] Catalyst stock solutions were made with the corresponding solvent. [d] Mean values after three runs.

Next, the influence of the base was investigated to determine whether the results obtained with KO*t*Bu could be improved upon. As can be seen in Table 1, entries B1–B5, only some bases achieved a reasonable yield. However, the problem was that with all bases, except NaO*t*Bu and KO*t*Bu (Table 1, entries B4 and B5), simultaneous to the amine formation, the corresponding imine was also observed. The better results achieved with KO*t*Bu compared with NaO*t*Bu are explained by its excellent solubility in diglyme. The bases used, with the exception of KO*t*Bu, were generally very poorly soluble in diglyme, which could have caused the incomplete conversions.

After these optimisations, we were interested to see if the addition of stoichiometric amounts of base was needed to allow complete conversion or whether catalytic quantities of base are sufficient. Therefore, the influence of the substrate/base ratio was investigated (Table 1, entries C1–C7). The results shown in Table 1, entries C1–C5, suggest that it is necessary to use a substrate/base ratio of 1:1.1, because only in this case (Table 1, entry C1) was it possible to obtain complete conversion and an excellent yield (99%) within 24 h. However, at a base loading of only 10 mol%, it was possible to achieve a yield of 31% (Table 1, entry C5), which contradicts the aforementioned stoichiometric requirement for base. For this reason, we investigated whether it is possible to bring the reaction to complete conversion by the use of 10 mol% of KO*t*Bu. To this end, the reaction time was increased; after 48 h a yield of 45% and after 4 days a yield of 60% were obtained.

To examine the reaction with catalyst **2a** in detail, a kinetic experiment for the reaction of aniline with benzyl alcohol was performed by utilising continuous sampling by gas chromatography. As can be seen in Figure 2, it is possible to come to complete conversion and a very good yield (94%) with catalytic amounts of base. However, a very long reaction time (≈150 h) and a high catalyst loading (2.0 mol% iridium) is needed to get this result. Since these reaction conditions are unfavourable, it is reasonable to use an

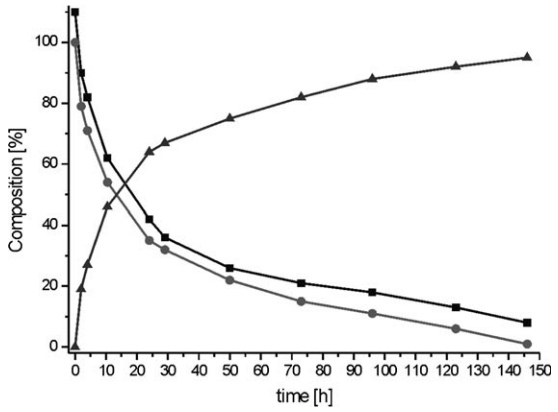
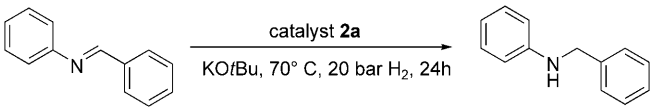


Figure 2. Time conversion plot for the reaction of aniline with benzyl alcohol (■: benzyl alcohol; ●: aniline; ▲: *N*-phenylbenzylamine). Reaction conditions: aniline (4.0 mmol), benzyl alcohol (4.4 mmol), catalyst **2a** (2 mol%), diglyme (1 mL), KO*t*Bu (0.4 mmol) and dodecane (1 mmol) as an internal standard.

excess of base to accelerate the reaction and to reduce the catalyst loading.

To determine whether the base is essential for the imine hydrogenation step or for the activation of the benzyl alcohol, imine hydrogenation experiments were carried out with different base loadings and by using *N*-benzylidene-(phenyl)amine as the starting material to get further insights



Scheme 7. The hydrogenation of benzylidene(phenyl)amine.

into this reaction (Scheme 7). As can be seen from Table 2, the excess of base is not needed for the hydrogenation of the imine, since even 10 mol% of base gives complete conversion and excellent yield (95%; Table 2, entry 2). At higher base loadings the yield of *N*-phenylbenzylamine declines (Table 2, entries 3 and 4) and various byproducts are formed.

Table 2. The influence of base ratio on the hydrogenation of benzylidene(phenyl)amine.[a]

	Base [mol%]	Conversion [%]	Yield [%][b]
1	0	10	9
2	10	100	95
3	50	100	90
4	110	100	70

[a] Reaction conditions: benzylidene(phenyl)amine (1.0 mmol), H_2 (20 bar), catalyst **2a** (0.4 mol%), diglyme (0.2 mL), 70°C, 24 h. [b] Yield determined by GC analysis with dodecane as the internal standard.

Additionally, the iridium complexes **2a–9a** were tested to determine what effect substitution at the phosphorus and the amino skeleton has on the reaction (Table 3). Evidently, all of the catalysts containing phenyl substituents on the phosphorus (Table 3, entries 2, 4, 6 and 8) gave better results than those containing an isopropyl substituent (Table 3, entries 1, 3, 5 and 7), although isopropyl was always favoured in our earlier work.[1–4] Moreover, it is noted that, by using 2-aminopyridines (Table 3, entries 1 and2, and 5–8) as the amine skeleton, better activities were generally observed

Table 3. Catalyst screening.[a]

	Catalyst	Yield [%][b]		Catalyst	Yield [%][b]
1	**2a**	47	5	**6a**	40
2	**3a**	61	6	**7a**	65
3	**4a**	36	7	**8a**	49
4	**5a**	41	8	**9a**	53

[a] Reaction conditions: aniline (1.0 mmol), benzyl alcohol (1.1 mmol), catalyst (0.05 mol%), KO*t*Bu (1.1 mmol), diglyme (0.2 mL), 70°C, 24 h. [b] Yield determined by GC analysis with dodecane as the internal standard; mean values after three runs.

than if the corresponding 2-aminopyrimidines (Table 3, entries 3 and 4) were used. The best catalyst for this reaction seems to be catalyst **7a** (Table 3, entry 6), which achieved a 65% yield at a very low catalyst loading (0.05 mol% iridium).

The final screening was performed on the catalyst loading to find the minimum catalyst loading necessary to achieve full conversion and good yields (Table 4). As shown in Table 4, it was sufficient to use a catalyst loading of 0.1 mol% to obtain a very good yield (92%) for this reaction (Table 4, entry 4). With catalyst **7a**, the catalyst loading can be reduced to approximately 1/6 of the catalyst loading required when using catalyst **1**. If no catalyst is used a conversion of only 3% is observed (Table 4, entry 6).

Table 4. Catalyst loading.[a]

	Ir loading [%]	Yield [%][b]		Ir loading [%]	Yield [%][b]
1	0.4	99	4	0.1	92
2	0.3	99	5	0.05	65
3	0.2	99	6	0.0	3

[a] Reaction conditions: aniline (1.0 mmol), benzyl alcohol (1.1 mmol), catalyst **7a**, KO*t*Bu (1.1 mmol), diglyme (0.2 mL), 70°C, 24 h. [b] Yield determined by GC analysis with dodecane as the internal standard; mean values after three runs.

To confirm the results we achieved for the alkylation of aniline with benzyl alcohol with catalyst **7a**, different aniline derivatives were reacted with primary alcohols (Table 5). To compare results, batches were made both with catalyst **7a** and the original catalyst **1** to show the superiority of the new catalyst system. As can be seen in Table 5, complex **7a** is a significantly better catalyst than **1**. All products were obtained in very good to excellent yields by using complex **7a**. The catalyst loadings are very low and the reaction conditions are very mild in comparison with protocols previously developed for this reaction.[5–12]

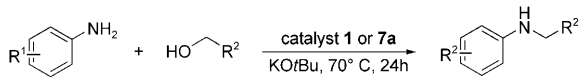
Conclusion

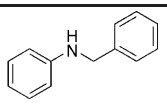
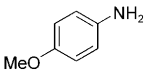
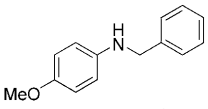
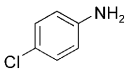
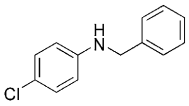
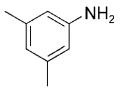
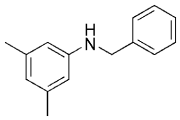
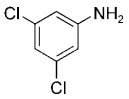
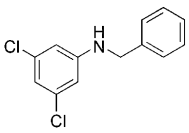
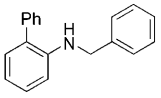
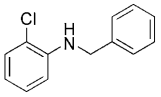
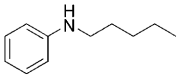
It was shown that our new catalyst system, based upon anionic P,N ligands, is highly active towards the alkylation of aniline with primary alcohols and far surpasses the original catalyst (based upon a neutral P,N ligand). Furthermore, the catalysts are characterised by good long-term stability, as confirmed by kinetic experiments over more than five days. In addition, ligands and complexes are easily accessible in very good yields. Further work is directed towards the application of these catalysts to selective C–N and/or C–C coupling reactions using the HA/BH protocol.

Experimental Section

General considerations: All reactions were carried out in a dry argon or nitrogen atmosphere using standard Schlenk or glove box techniques.

Table 5. Catalytic N-alkylation of aniline derivatives with primary alcohols.[a]



	Catalyst loading [mol %]	Amine	Product	Yield [%][b] Catalyst 1	Catalyst 7a
1	0.1			38	92
2	0.2			29	92
3	0.05			75	98
4	0.2			33	81
5	0.2			54	98
6	0.4			48	91
7	0.2			73	97
8	0.2			52	98

[a] Reaction conditions: amine (1.0 mmol), benzyl alcohol (1.1 mmol), KO*t*Bu (1.1 mmol), diglyme (0.2 mL), 70 °C, 24 h. [b] Yield determined by GC analysis with dodecane as the internal standard.

Halogenated solvents were dried over P_2O_5 and non-halogenated solvents were dried over sodium benzophenone ketyl. Deuterated solvents were ordered from Cambridge Isotope Laboratories, vented, stored over molecular sieves and distilled. All chemicals were purchased from commercial sources with a purity over 97% and used without further purification, with the exception of aniline, which was distilled before use in the screening reactions. NMR spectra were performed by using an INOVA 400 MHz spectrometer at 298 K. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analysis was carried out on a Vario elementar EL III. GC analyses were carried out on an Agilent 6890N Network GC system equipped with an HP-5 column (30 m × 0.32 μm × 0.25 μm).

General procedure for the screening reactions: The pressure tube was closed with a Teflon cap and stirred at 70 °C for 24 h. The reaction mixture was cooled to room temperature and quenched by the addition of water (2 mL). Then, diethyl ether (10 mL) and dodecane (1.0 mmol, 226 μL, as an internal standard) were added. After agitation, a small fraction of the organic phase was analysed by GC analysis. In a pressure tube, the catalyst stock solution (200 μL, 0.02 M) in diethyl glycol dimethyl ether, aniline (1.0 mmol, 91 μL), benzyl alcohol (1.1 mmol, 114 μL), solvent (0.2 mL) and base (1.1 mmol) were combined.

General procedure for ligand synthesis (2–9): Arylamine (1.0 equiv) was dissolved in THF (70–120 mL), triethylamine (1.0 equiv) was added and the solution was cooled to 0 °C. Then, the corresponding chlorophosphane (1.0 equiv) was added dropwise, with a syringe. The solution was allowed to warm to room temperature and stirred overnight at 50 °C. The suspension was filtered through a glass filter frit with a pad of Celite (4 cm) and washed with THF. The solvent was concentrated in vacuo yielding the corresponding ligands as white solids.

General procedure for complex synthesis (2a–9a): [{IrOMe(cod)}$_2$] (0.5 equiv) was suspended in THF (5–25 mL) and subsequently a solution of the corresponding ligand (1.0 equiv, **2–9**) in THF (5 mL) was added dropwise. A red solution was obtained and, after 30 min, the solvent was removed in vacuo, affording dark red solids in almost quantitative yields.

Synthesis of (5-Me)PyNHPPh$_2$ (7): 5-Methyl-2-aminopyridine (10.0 mmol, 1.08 g) was suspended in THF (70 mL), triethylamine (10.0 mmol, 1.4 mL) was added and the solution was cooled to 0 °C. Then chlorodiphenylphosphane (10.0 mmol, 1.83 mL) was added dropwise, with a syringe. The solution was allowed to warm to room temperature and stirred for 4 d at room temperature and 12 h at 50 °C. The suspension was filtered over a glass filter frit with a pad of Celite (4 cm) and washed with THF (50 mL). The solvent was removed in vacuo, yielding compound **7** as a white solid (9.69 mmol, 97%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.92$ (s, 1H), 7.50–7.43 (m, 4H), 7.41–7.28 (m, 7H), 6.95 (d, $J = 8.6$ Hz, 1H), 5.25 (s, 1H), 2.19 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 147.7$, 139.6, 138.8, 131.2 (d, $J = 20.9$ Hz), 129.1, 128.5 (d, $J = 6.7$ Hz), 123.9, 108.4 (d, $J = 15.0$ Hz), 17.4 ppm; ^{31}P NMR (161 MHz, CD_2Cl_2, 298 K): $\delta = 27.21$ ppm; elemental analysis calcd (%) for $C_{18}H_{17}N_2P$: C 73.96, H 5.86, N 9.58; found: C 73.88, H 5.69, N 9.71.

Synthesis of [{(5-Me)PyNHPPh$_2$}Ir(cod)] (7a): [{IrOMe(cod)}$_2$] (1.2 mmol, 795 mg) was dissolved in THF (20 mL) and a solution of compound **7** (2.4 mmol, 701 mg) dissolved in THF (5 mL) was subsequently added dropwise. A red solution was obtained and, after 30 min, the solvent was removed in vacuo and the residue was recrystallised from hexane/THF (3:1), yielding red crystals (1.03 mmol, 86%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.59$ (ddd, $J = 10.8$, 7.3, 1.7 Hz, 4H), 7.41–7.36 (m, 6H), 7.23 (s, 1H), 7.04 (dt, $J = 8.9$, 2.4 Hz, 1H), 6.88 (d, $J = 8.9$ Hz, 1H), 4.94 (s, 2H), 3.54 (s, 2H), 2.25–2.19 (m, 4H), 2.02 (s, 3H), 2.04–1.94 ppm (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): $\delta =$ 143.8 (d, $J = 2.7$ Hz), 140.7 (d, $J = 2.9$ Hz), 138.4 (d, $J = 0.6$ Hz), 137.8 (d, $J = 0.5$ Hz), 132.5 (d, $J = 12.2$ Hz), 130.5 (d, $J = 2.3$ Hz), 128.8 (d, $J =$ 10.3 Hz), 116.6, 116.4 (d, $J = 0.5$ Hz), 115.9 (d, $J = 0.6$ Hz), 95.32, 91.7 (d, $J = 13.4$ Hz), 60.4, 33.5, 29.5, 17.3 ppm; ^{31}P NMR (161 MHz, CD_2Cl_2, 298 K): $\delta = 72.54$ ppm; elemental analysis calcd (%) for $C_{26}H_{28}IrN_2P$: C 52.78, H 4.77, N 4.73; found: C 52.83, H 4.86, N 4.72.

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