Synthesis, structure and reactivity of Pd and Ir complexes based on new lutidine-derived NHC/phosphine mixed pincer ligands†

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Coordination studies of new lutidine-derived hybrid NHC/phosphine ligands (CNP) to Pd and Ir have been performed. Treatment of the square-planar [Pd(CNP)Cl](AgCl₂) complex 2a with KHMDS produces the selective deprotonation at the CH₂P arm of the pincer to yield the pyridine-dearomatised complex 3a. A series of cationic [Ir(CNP)(cod)]⁺ complexes 4 has been prepared by reaction of the imidazolium salts 1 with Ir(acac)(cod). These derivatives exhibit in the solid state, and in solution, a distorted trigonal bipyramidal structure in which the CNP ligands adopt an unusual C(axial)–N(equatorial)–P(equatorial) coordination mode. Reactions of complexes 4 with CO and H₂ yield the carbonyl species 5a(Cl) and 6a(Cl), and the dihydrido derivatives 7, respectively. Furthermore, upon reaction of complex 4b(Br) with base, selective deprotonation at the methylene CH₂P arms is observed. The, thus formed, deprotonated Ir complex 8b reacts with H₂ in a ligand-assisted process leading to the trihydrido complex 9b, which can also be obtained by reaction of 7b(Cl) with H₂ in the presence of KO₂Bu. Finally, the catalytic activity of Ir–CNP complexes in the hydrogenation of ketones has been briefly assessed.

Introduction

Metal complexes based on lutidine-derived PNP pincer ligands have gained considerable attention due to their applications in organometallic chemistry and catalysis (Fig. 1a).¹ In these derivatives metal–ligand cooperativity, triggered by deprotonation of the methylene arms of the ligand accompanied by de-aromatisation of the pyridine ring, has led to unique reactivity in the activation of a diversity of X–H (X = H, C, O, N) bonds. While significantly less studied, analogous complexes based on CNC pincers (C stands for a N-heterocyclic carbene, NHC) have also been described (Fig. 1b).²–⁴ As shown with Ru–CNC complexes,³,⁴ these derivatives can also be deprotonated at the methylene CH₂N bridges, and participate in metal–ligand cooperation processes. Furthermore, the larger Py–CH₂–NHC linkage, which forms 6-membered metallacycles upon coordination, confers a greater flexibility on the ligand in comparison to 5-membered rings formed in PNP pincers. This flexibility should permit stabilizing metal complexes in a variety of coordination geometries, a relevant issue in catalysis where the intermediates in the catalytic cycle may need to adopt different structural arrangements. For example, while PNP...
ligands have only exhibited meridional coordination modes, facial coordination of CNC ligands in Ru complexes has been observed.\(^5\) More remarkable, as demonstrated by the Pidko’s group, is that the increased flexibility of the CNC pincer results in enhanced reactivities towards H\(_2\) and CO\(_2\) in comparison to Ru–PNP systems.\(^4\,^b\)

In addition, non-symmetric pincer ligands, \emph{i.e.} having two inequivalent flanking donor groups, allow for a larger electronic and steric diversity derived from the potential tuning of two different side donors.\(^5\) With respect to lutidine-derived pincer complexes, some examples of PNP\(^6\) and CNC\(^4\)\(^d\) derivatives have been reported. Unsymmetrical PXN and CNX pincer complexes have also been described, although these derivatives are usually of the type PNN\(^1\) and CNN\(^7\) where hemilabile coordination of the N-donor flanking group has been proposed. In marked contrast, complexes based on CNP ligands having a pyridine central moiety and in which the two side functionalities are two significantly different strong σ-donors, such as a phosphine and a NHC, have not been investigated. In fact, a limited number of hybrid tridentate ligands possessing both phosphine and NHC donors have been reported, and these have either a ligand backbone based on a 1,3-disubstituted phenyl ring\(^8\) or a different arrangement of the donor moieties, where the NHC group is the central unit of the pincer ligand.\(^8\)\(^b\)\(^f\) Also, recently Danopoulos, Brauneist et al. have prepared Co and Cr complexes based on deprotonated NHC/phosphine mixed pincer ligands having a central picoline motif (Fig. 1c).\(^9\)

Based on these precedents, we aimed to develop a new class of ligands having NHC and phosphine side donors and a lutidine central fragment (CNP, Fig. 1d). A fundamental difference of these ligands with the previous picoline-based pincer derivatives reported by Danopoulos, Brauneist \emph{et al.} resides in the presence of a methane linker between the pyridine and the NHC functionalities, which could also be susceptible to deprotonation and should enhance pincer flexibility. In this contribution, we report on the synthesis of the precursors of these ligands as well as their coordination to Pd and Ir complexes. In particular, the ability of CNP ligands to adapt to different coordination geometries and participate in ligand-assisted processes has been assessed.

**Results and discussion**

**Syntheses of imidazolium salts**

Syntheses of imidazolium salts 1a(Cl), 1b(Cl) and 1b(Br) were effected as shown in Scheme 1. Derivative 1a(Cl) was prepared by reaction of the corresponding 2-chloromethyl-6-imidazolylmethyl-pyridine with diphenyl phosphine in the presence of KO’Bu. Alternatively, in the case of salts 1b(Cl) and 1b(Br), higher product yields were obtained when diphenyl phosphine–borane adduct was used for the introduction of the P-donor fragment, followed by phosphine protection by simple treatment with refluxing MeOH. The CNP ligands precursors were obtained with moderate to good yields (55–85%) as white to brown solids.

**Synthesis and deprotonation of Pd–CNP complex 2a**

For an evaluation of the coordination capabilities of these new CNP ligands, we initially studied the formation of Pd derivatives. Thus, salt 1a(Cl) was reacted with Ag\(_2\)O in CH\(_2\)Cl\(_2\), followed by addition of PdCl\(_2\)(cod) to yield complex 2a (Scheme 2).\(^10\) The spectroscopic data support the formation of a complex in which the CNP ligand is coordinated to the metal centre as a pincer. For example, its \(^1\)H NMR spectrum shows distinctly two signals for the bridging methylene. The CH\(_2\)P protons appear at 4.32 ppm (d, \(^2\)J\(_{HP} = 11.3\) Hz), whereas the NCH\(_2\) hydrogens produce a singlet at 6.05 ppm. The \(^{13}\)C\({}^1\)H NMR spectrum exhibits a doublet at 166.4 ppm with a large \(^3\)J\(_{CP}\) (183 Hz, carbene carbon, C\(_2\), of the NHC moiety), indicating the trans disposition of the NHC and phosphine moieties.

A single crystal X-ray diffraction study of 2a confirmed the proposed structure (Fig. 2). Thus, complex 2a in the solid state is comprised of a Pd atom in an square-planar coordination geometry, with the carbene and phosphine fragments of the pincer disposed trans to each other ([C\(_7\)(NHC)–Pd–P = 168.65°], and the chloride ligand trans to the pyridine (N(Py)–Pd–Cl = 175.03°). The NHC–Pd–Py chelate ring has a boat conformation as determined by the torsion angle C(14)–N(3)–Pd(1)–C(1) of 32.4°, whereas the 5-membered ring involving the phosphine donor has an envelope conformation with a C(18)–N(3)–Pd(1)–P(1) torsion angle of 28.4°.

Since it can be expected that CNP ligands can be deprotonated in either the CH\(_2\)P or CH\(_2\)–NHC arms, the acid/base responsiveness of 2a was tested by adding KH\(_2\)MS to a suspension of the complex in THF.\(^11\) In the \(^1\)H NMR spectrum of the resulting product 3a, a significant up-field shift for the signals of the pyridine protons (5.55–6.46 ppm) in accord with the dearomatisation of this moiety is observed. Meanwhile, the...
CHP fragment produces a singlet signal at 3.41 ppm (integrating to 1H) in the 1H NMR spectrum and a doublet at $\delta = 3.3$ ppm ($^1J_{CP} = 66$ Hz) in the $^{13}$C{1H} NMR experiment, evidencing the selective deprotonation of the CNP ligand at the CH$_2$P arm.

Synthesis and structural features of Ir–CNP complexes

Reaction of imidazolium salts 1 with Ir(acac)(cod) provided cationic olefin complexes 4, isolated as yellow to orange solids in moderate to good yields (30–80%) (Scheme 3). These derivatives are stable in the solid state to the atmospheric agents, and have been fully characterised by NMR. For example, in the 3H NMR spectrum of 4b(Br), the CH$_3$P protons are diastereotopic and appear as doublet of doublets at $\delta = 3.36$ ppm ($^2J_{HP} = 2.1$ Hz) and 4.17 ppm ($^2J_{HH} = 15.5$ Hz and $^2J_{HP} = 11.6$ Hz).

Similarly, protons for the CH$_2$N bridge produce two doublets at $\delta = 5.65$ and 6.91 ($^2J_{HH} = 14.1$ Hz). The $^{13}$C{1H} NMR spectrum shows a doublet at 164.8 ppm for the C$^2$ NHC carbon with a very small $^2J_{CP}$ coupling constant of 8 Hz. These data suggest a cis coordination of the phosphine and NHC donors, also confirmed in the solid state by a single crystal X-ray diffraction study of 4b(BArF) (Fig. 3), obtained by anion exchange in complex 4b(Br) with NaBArF.

The structure of complex 4b(BArF) is best described as adopting a distorted trigonal bipyramidal geometry despite the acute P–Ir–N(Py) bond angle of 75.98(8)$^\circ$. The CNP ligand exhibits a facial coordination, with the NHC donor in the apical position (P–Ir–C(NHC) angle of 95.61(10)$^\circ$). In addition, the six-membered chelate ring involving the NHC and pyridine donors adopts a boat-like conformation as defined by the

![Fig. 3 ORTEP drawing at 30% ellipsoid probability of the cationic component of complex 4b(BArF). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.029(4), Ir(1)–N(3) 2.253(3), Ir(1)–P(1) 2.341(2), Ir(1)–Cl(31) 2.263(4), Ir(1)–Cl(32) 2.217(4), Ir(1)–Cl(35) 2.140(3), Ir(1)–Cl(36) 2.101(4), P(1)–Ir(1)–P(3) 95.61(10), N(3)–Ir(1)–P(3) 75.98(8), N(3)–Ir(1)–Cl(31) 81.07(13).](image-url)
dihedral angle \( C(13) - N(3) - Ir(1) - C(1) \) of \(-50.6^\circ\), while the chelate ring containing the phosphine fragment exhibits an envelope conformation with a \( C(17) - N(3) - Ir(1) - P(1) \) angle of \( 29.5^\circ\). This facial coordination mode is unprecedented in \( M - PNP \) complexes and may be ascribed to the larger flexibility of the six-membered Py\(-M\)-NHC chelate ring, as previously observed in Ru\(-CNC\) complexes.\(^3\) In addition, the \( C(\text{axial}) - N(\text{equatorial}) - P(\text{equatorial}) \) coordination mode of the pincer differs significantly from previously reported pentacoordinated \( d^8 \) pincer complexes,\(^{12}\) for which an eq-ax-eq distribution is usually observed.\(^{13}\) Finally, as observed with other penta-coordinated diolefin \( Ir \) complexes,\(^{13}\) the distance from the \( Ir \) atom to the centroid of the \( C=C \) bonds is slightly longer for the alkene coordinated \textit{trans} to the NHC than for the olefin placed in the meridional position (\( \Delta d(\text{Ir-centroid C}=C) = 0.14 \) Å).

As exemplified with complex \( 4a(Cl) \), a dynamic behaviour in solution for complexes 4 has been evidenced by NMR. VT\(^1\)H NMR spectra of \( 4a(Cl) \) registered in the temperature range between 50 and \(-80^\circ C\) show sharp signals for the resonances attributable to the CNP ligand. In contrast, broad signals at 2.98 and 3.49 ppm, integrating for two protons each, are observed for the olefinic protons at \( 25^\circ C\). \(^1\)H\(-\)\(^1\)H COSY and \(^1\)H\(-\)\(^1\)H NOESY experiments indicate that each signal is produced by protons of different olefins; \( i.e. H^{b1}, H^{b2} \) and \( H^{a1}, H^{a2} \) produce signals at 2.98 and 3.49 ppm, respectively (Fig. 4a). In addition, these signals broaden upon lowering the temperature and eventually split at temperatures below \(-25^\circ C\) into two sets of two signals each, appearing at \( \delta 2.23 \) (\( H^{b2} \)) and 3.39 (\( H^{b1} \)), and 2.86 (\( H^{a2} \)) and 3.90 (\( H^{a1} \)), respectively. An approximate value of \( \Delta G^\ddagger = 10.9 \text{ kcal mol}^{-1} \) at the coalescence temperature (244 K) can be estimated for the fluxional process. This dynamic behaviour can be ascribed to alkene site exchange allowed by the decoordination of the \( C=C \) fragment \textit{trans} to the NHC moiety to produce the distorted tetrahedral intermediate \( A \), followed by re-coordination of the free olefin moiety to the opposite side without a net change of the \textit{fac} coordination mode of the CNP ligand (Fig. 4a).

In addition, the \(^1\)H\(-\)^\(^1\)H-exchange spectroscopy (EXSY) experiment of \( 4a(Cl) \) registered at \( 50^\circ C \) demonstrates the existence of additional dynamic processes with higher energy barriers. Thus, intense exchange cross-peaks between the signals for the olefinic protons appearing at 2.98 and 3.49 ppm are observed, which can be explained by the formal rotation of the diolefin ligand allowed by the decoordination of one of the \( Ir \)-alkene bonds (Fig. 4a). Furthermore, the observation of strong correlation peaks between the resonances of the \( \sigma-, m- \) and \( p- \)protons of one of the PPh groups with the aromatic protons of the other phenyl group, as well as between the signals of the methylene protons in each of the \( CH_2P \) and \( CH_2N \) arms, indicates that the CNP pincer in complexes 4 also undergoes structural changes, which could be assigned to a slow interconversion between the two enantiomeric forms of the complex. Previously, mirror-image isomer exchange involving a pseudo-Berry rotation has been observed for pentacoordinated pincer \( Ir \) complexes containing diolefin ligands.\(^{13}\) However, this process should not be possible in complexes 4 due to the

Fig. 4 Proposed dynamic processes in solution operating in the cationic part of complexes 4 (positive charges have been supressed for clarity; \( PR_2 = PPh_2, Ar = \text{mesityl or 3,5-xylyl} \)).
C_{(axial)}-N_{(equatorial)}-P_{(equatorial)} coordination mode of the pincer. Since, as discussed above, olefin decoordination seems facile, the observed fluxional process could likely involve the intermediary of the square-planar structure B (Fig. 4b).

To evaluate the donating properties of the CNP ligands, we prepared the carbonyl derivative 5a(Cl) by bubbling CO through a CH₂Cl₂ solution of complex 4a(Cl) (Scheme 3). Signals of the bridging CH₂P and CH₂N protons in the ¹H NMR spectrum support a planar coordination of the CNP pincer. Thus, the CH₂P protons produce a doublet signal at 4.18 ppm (J_HP = 10.0 Hz) while the CH₂N hydrogens appear as a singlet at 6.11 ppm. In the IR spectrum, the carbonyl ligand absorbs at 1985 cm⁻¹, which is a higher frequency than that corresponding to the (²Bu–PNP)–Ir analogue (1964 cm⁻¹), suggesting a lower electron density at the metal centre in the Ir–CNP system. The CO ligand is detected in the ¹³C{¹H} NMR spectrum by the appearance of a doublet signal at 177.2 ppm (J_CP = 10 Hz), while the C² NHC carbon appears at 178.1 ppm (J_CP = 99 Hz).

Interestingly, complex 5a(Cl) reversibly coordinates a new CO molecule yielding complex 6a(Cl), as inferred from the absorption bands corresponding to the CO ligands, which appear in the IR spectrum at 1946 and 2021 cm⁻¹. In the ¹H NMR spectrum of 6a(Cl), the presence of a singlet signal at 6.09 ppm (2H) for the CH₂N arm and a doublet at 4.29 ppm (2H, J_HP = 10.9 Hz) attributable to the CH₂P moiety suggests the existence of a symmetry plane containing the CNP–Ir coordination plane and points out to a meridional coordination of the pincer ligand,¹³b in variance with the coordination geometry in the also pentacoordinated compounds 4.

As determined by VT-¹H NMR spectroscopy (see ESI†), carbonyl complexes 5a(Cl) and 6a(Cl) exhibit a dynamic behaviour in solution, which equilibrates the two otherwise diastereotopic hydrogens of both methylene bridges. In square-planar Pd¹⁶ and octahedral Ru complexes incorporating CNC ligands,¹⁶b similar dynamic processes have been ascribed to a slow interconversion between the two twisted conformations adopted by both C²(NHC)–N[Py]–M chelate rings of the pincer ligand. Similarly, the observed fluxionality in derivatives 5a(Cl) and 6a(Cl) can be attributed to the fast atropoisomerism between the two limiting enantiomeric forms shown in Fig. 5.

Complexes 4a(Cl) and 4b(Cl) react with H₂ producing the dihydrido derivatives 7 and cyclooctene (Scheme 3). At room temperature, the ¹H NMR spectrum of complex 7a(Cl) shows two doublets of doublets at -20.19 (J_HH = 13.8 Hz, J_HP = 7.0 Hz) and -23.30 ppm (J_HP = 18.9 Hz) due to the hydrido ligands placed trans to the pyridine and trans to the chloride, respectively. In the ¹³C{¹H} NMR spectrum, the C² NHC appears at 172.9 ppm as a doublet signal (J_CP = 119 Hz). Exposure of a sample of 7a(Cl) in CD₂Cl₂ to deuterium gas (2 bar) or addition of CD₃OD causes fast H/D exchange of the hydrido ligands.

Furthermore, the structural features of complex 7a(Cl) have been studied in the solid state by single crystal X-ray diffraction (Fig. 6). This derivative has an octahedral geometry with the two hydrido ligands occupying mutually cis positions and the CNP ligand adopting a meridional coordination, as defined by the C(1)–Ir(1)–P(1) angle value of 166.5(3)°. The chelate ring incorporating the NHC fragment has a boat-like conformation as shown by the C(14)–N(3)–Ir(1)–C(1)₁ torsion angle of -26.5°, whereas an envelope conformation for the N(Py)–Ir–P ring is observed with a C(18)–N(3)–Ir(1)–P(1) dihedral angle of -14.9(8)°.

**Deprotonation and ligand-assisted H₂ activation**

We have also explored the deprotonation of the Ir–CNP complexes 4.¹⁷ Treatment of 4b(Br) with KO'Bu produces the selective deprotonation of the CH₂P arm (Scheme 4). The resulting complex 8b is characterised in the ¹H NMR spectrum by the presence of significantly high-field shifted signals for the pyridine protons (5.6–6.4 ppm), evidencing the dearomatisation of the pyridine ring. The =CHP proton appears as a singlet at 3.86 ppm, while the CH₂–NHC hydrogens generate two doublets at 4.93 and 5.29 ppm (J_HH = 13.6 Hz). In the ¹³C{¹H} NMR spectrum, the resonance caused by the C² NHC carbon appears as an overlapped doublet at 170.6 ppm. Although the J_CP value cannot be unambiguously calculated, a value of 2 to
smoother catalysed the hydrogenation of acetophenone under 4 bar of H₂ at 30 °C in 2-methyltetrahydrofuran, using a S/C/B ratio of 100/1/15 (entry 1). By using the same pressure, catalyst loading could be decreased to a S/C ratio of 250 after heating to 60 °C (entry 2). Also, at this temperature, a lower H₂ pressure (1 bar) could be employed (entry 3). Under the latter conditions, complex 4b(Cl) was found to be slightly less active, whereas a significantly lower catalytic activity was obtained with the carbonyl derivative 5a(Cl) (entries 4 and 5). Finally, the hydrogenation of a series of ketones was performed with complex 4a(Cl). High conversions were obtained in the case of acetophenone derivatives substituted with p-methoxy, p-chloro and o-bromo substituents (entries 6–8). Alternatively, the presence of fluoro substituents seems somewhat detrimental since 2-fluoroacetophenone was reduced with a slightly lower yield (entry 9). Also, the hydrogenation of a cyclic ketone, α-tetralone, proceeded with a high conversion (entry 10).

Conclusions

In summary, Pd and Ir complexes based on novel lutidine-derived CNP pincer ligands have been synthesised. The flexibility of the chelating Py–CH₂–NHC fragment of the ligands allows for both facial and meridional coordination modes in five- and six-coordinated Ir–CNP complexes. Furthermore, selective deprotonation of the CH₂P arm in Ir–CNP complexes promotes ligand-assisted H–H activation, leading to active species in ketone hydrogenation. Further studies involving the application of metal complexes based on CNP ligands in X–H (X = H, C, heteroatom) bond activation and as catalysts in the (de)hydrogenation of polar substrates are currently in progress in our laboratory.

Experimental

General procedures

All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen with the following desiccants: sodiumbenzophenone-ketyl for diethyl ether (Et₂O) and tetrahydrofuran (THF); sodium for hexane, pentane and toluene; CaH₂ for dichloromethane (CH₂Cl₂) and acetonitrile (CH₃CN); and NaOMe for methanol (MeOH). 1-(3,5-Dimethylphenyl)-1H-imidazole and 1-(2,4,6-trimethylphenyl)-1H-imidazole were prepared as previously described.19 Ir(acac)(cod)₂ and NaBArF₆ were synthesized according to literature procedures. All other reagents were purchased from commercial suppliers and used as received. NMR spectra were obtained on Bruker DPX-300, DRX-400, AVANCEIII/ASCEND 400R or DRX-500 spectrometers. ³¹P{¹H} NMR shifts were referenced to external 85% H₃PO₄, while ¹³C{¹H} and ¹H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me₄Si. All NMR measurements were

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Table 1 Hydrogenation of ketones catalysed by Ir–CNP complexes

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<th>Entry</th>
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<th>T (°C)</th>
<th>Conv. (%)</th>
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<td>4a(Cl)</td>
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<td>95</td>
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<td>4a(Cl)</td>
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<td>93</td>
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<td>60 &gt;99</td>
<td>98</td>
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<tr>
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<td>α-Tetralone</td>
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*Reaction conditions, unless otherwise noted: 1 bar of H₂, 2-methyltetrahydrofuran, S/C/B = 100/1/15, base: KO'Bu, 16 h. [S] = 0.13 M. Conversion was determined by ¹H NMR spectroscopy. *4 bar of H₂, S/C/B = 250/1/15.
carried out at 25 °C, unless otherwise stated. NMR signal assignments were confirmed by 2D NMR spectroscopy (1H–1H COSY, 1H–13C HMQC and 1H–13C HMBC). HRMS data were obtained on a JEOL JMS-SX 102A mass spectrometer at the Instrumental Services of Universidad de Sevilla (CITIUS). ESI-MS experiments were carried out on a Bruker 6000 apparatus by the Mass Spectrometry Service of the Instituto de Investigaciones Químicas. Elemental analyses were run by the Analytical Service of the Instituto de Investigaciones Químicas in a Leco TrueSpec CHN elemental analyzer. IR spectra were acquired on a Bruker Tensor 27 instrument.

**Synthesis of imidazolium salts** 1. Imidazolium salts 1 were synthesised in two steps from the corresponding 2,6-bis(halo-methyl)pyridines and imidazoles as shown below.

**[2-(Diphenylphosphinyl)methyl-6-(3-mesitylimidazolium-1-yl)methyl]pyridine chloride, 1a(Cl)**: A solution of 2,6-bis(chloro-methyl)pyridines and imidazoles as shown below.

**[2-Chloromethyl-6-(3-(3,5-xylylimidazolium-1-yl)methyl]pyridine chloride, 1b(Cl)**: A solution of 2,6-bis(chloro-methyl)pyridine (3.96 g, 22.5 mmol) and 1-xylyl-1H-imidazole (1.93 g, 11.2 mmol) in THF (20 mL) was heated to 45 °C for 7 days. The solution was reduced to half the initial volume by solvent evaporation, and Et2O (10 mL) was added to precipitate the product. The solid was filtered, washed with Et2O (2 × 10 mL) and pentane (3 × 5 mL) and dried under vacuum. 

**[2-Chloromethyl-6-(3-(3,5-xylylimidazolium-1-yl)methyl]pyridine chloride was isolated as a white solid (2.21 g, 57%).**

1H NMR (400 MHz, CDCl3): δ 10.85 (s, 1H, H arom Imid), 8.13 (s, 1H, H arom Imid), 8.06 (dd, JHH = 7.7 Hz, 1H, H arom Py), 7.84 (dd, JHH = 7.7 Hz, JHH = 7.7 Hz, 1H, H arom Py), 7.48 (dd, JHH = 7.7 Hz, 1H, H arom Py), 7.10 (s, 1H, H arom Imid), 6.99 (s, 2H, 2H arom Mes), 6.24 (s, 2H, CH2N), 4.63 (s, 2H, CH2Cl), 2.33 (s, 3H, CH3), 2.04 (s, 6H, 2CH3). 

**13C{1H} NMR (125 MHz, CDCl3):** δ 156.0 (Cq arom), 151.9 (Cq arom), 141.5 (Cq arom), 137.9 (CH arom), 136.4 (CH arom), 134.3 (CH arom), 132.1 (CH arom), 125.2 (CH arom), 124.1 (Cq arom), 123.8 (CH arom), 121.9 (2 CH arom), 119.5 (2 CH arom), 52.3 (CH2N), 45.1 (CH2Cl), 21.2 (CH3), 17.7 (2 CH2). HRMS (ESI): m/z 312.1256 [(M – Cl)+] (exact mass calculated for C18H19ClN3P: 476.2243).

In a subsequent step, to a solution of Ph3P(BH3)H (0.288 g, 0.44 mmol) in THF (10 mL) was added a solution of KOH (0.161 g, 1.44 mmol) in THF (5 mL). The mixture was stirred for 15 min, and added to a suspension of 2-[chloromethyl-6-(3-(3,5-xylylimidazolium-1-yl)methyl]pyridine chloride (0.500 g, 0.500 g, 4.55 mmol) in MeCN (10 mL). The suspension was stirred over night, and MeOH (15 mL) was added to quench the reaction. The solvent was evaporated under vacuum, and the solid was extracted with CH2Cl2 (3 × 10 mL). Solvent removal followed by washings with Et2O (2 × 10 mL) yields a light brown solid (2.40 g, 72%).

**1H NMR (500 MHz, CDCl3):** δ 10.30 (s, 1H, H arom Imid), 7.85 (s, 1H, H arom Imid), 7.60 (d, JHH = 7.5 Hz, 1H, H arom Py), 7.54 (dd, JHH = 7.6 Hz, JHH = 7.6 Hz, 1H, H arom Py), 7.36 (m, 4H, 4H arom PPh), 7.28 (m, 6H, 6H arom PPh), 7.12 (s, 1H, H arom Imid), 7.03 (d, JCP = 7.7 Hz, 1H, H arom Py), 7.70 (s, 1H, 2H arom Mes), 5.94 (s, 2H, CH2N), 3.59 (s, 2H, CH3P), 2.33 (s, 3H, CH3), 2.01 (s, 6H, 2CH3). 

**13C{1H} NMR (125 MHz, CDCl3):** δ 156.7 (Cq arom), 156.0 (Cq arom), 151.9 (Cq arom), 141.5 (Cq arom), 140.8 (CH arom), 138.9 (CH arom), 134.3 (2Cq arom), 130.8 (Cq arom), 130.0 (2CH arom), 125.1 (CH arom), 124.1 (CH arom), 124.0 (CH arom), 122.8 (CH arom), 52.3 (CH2N), 45.1 (CH2Cl), 21.2 (CH3), 17.7 (2CH2). HRMS (ESI): m/z 312.1411 [(M – Cl)+] (exact mass calculated for C18H19ClN3P: 476.2142).

In a subsequent step, to a solution of Ph3P(BH3)H (0.288 g, 0.44 mmol) in THF (10 mL) was added a solution of KOH (0.161 g, 1.44 mmol) in THF (5 mL). The mixture was stirred for 10 min, and added to a suspension of 2-[chloromethyl-6-(3-(3,5-xylylimidazolium-1-yl)methyl]pyridine chloride (0.500 g, 0.500 g, 4.55 mmol) in MeCN (10 mL). The resulting suspension was stirred over night, and MeOH (10 mL) was added to quench the reaction. The solvent was evaporated under vacuum, and the solid was extracted with CH2Cl2 (3 × 10 mL). Solvent removal followed by washings with Et2O (2 × 10 mL) yields a light orange solid which should correspond to the borane adduct of 1b(Cl). This solid was dissolved in MeOH (10 mL), and the solution was transferred to a Fisher-Porter vessel and heated to 75 °C for 24 h. Volatiles were removed under vacuum, and MeOH (10 mL) was newly added and the previous procedure repeated. The resulting solid was washed with toluene (2 × 5 mL) and Et2O (3 × 5 mL) to give an off-white solid (0.444 g, 62%). 

**1H NMR (400 MHz, CD2Cl2):** δ 11.28 (s, 1H, H arom Imid), 7.74 (d, JHH = 7.6 Hz, 1H, H arom Py), 7.64 (dd, JHH = 7.7 Hz, JHH = 7.7 Hz, 1H, H arom Py), 7.55 (d, JHH = 1.1 Hz, 1H, H arom Imid), 7.44 (m, 4H, 4H arom PPh), 7.36 (m, 7H, 7H arom), 7.29 (s, 2H, 2H arom Xyl), 7.21 (s, 1H, H arom Xyl), 7.12 (d, JHH = 7.8 Hz, 1H, H arom Py), 5.91 (s, 2H, CH2N), 3.69 (s, 2H, CH2P), 2.45 (s, 6H, 2CH3). 

**13C{1H} NMR (121 MHz, CD2Cl2):** δ –11.8. 

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134.9 (Cq arom), 133.0 (d, JCP = 19 Hz, 4 CH arom), 131.9 (CH arom), 129.1 (2 CH arom), 128.7 (d, JCP = 7 Hz, 4 CH arom), 124.2 (d, JCP = 5 Hz, 2 CH arom), 123.7 (CH arom), 121.8 (CH arom), 120.2 (CH arom), 119.7 (2 CH arom), 54.0 (CHN), 38.3 (d, JCP = 16 Hz, CH2P), 21.3 (2 CH3). HRMS (ESI): m/z 462.2082 [(M – Cl)+] (exact mass calculated for Cs3H25N3P: 462.094).

[2-(Diphenylphosphinyl)methyl-6-(3,5-xylyl)imidazolium-1-yl]methylpyridine bromide, 1b(Br). A solution of 1-(3,5-xylyl)-1H-imidazole (1.00 g, 5.81 mmol) in THF (20 mL) was added to a solution of 2,6-bis(bromomethyl)pyridine (3.08 g, 16.93 mmol) in THF (10 mL), and dried to give [2-bromomethyl-6-(3,5-xylyl)imidazolium-1-yl]methylpyridine bromide as a light brown solid (0.025 g, 0.04 mmol) in THF (10 mL) to give an off-white solid which should correspond to the borane adduct of 1b(Br). This solid was dissolved in MeOH (10 mL) and the reaction was transferred to a Fisher–Porter vessel and heated to 75 °C for 24 h. Volatiles were removed under vacuum, and MeOH (15 mL) was added to quench the reaction. The solvent was evaporated under vacuum, and the resulting solid was extracted with CH2Cl2 (3 × 20 mL), and the resulting mixture was stirred for 7 days at room temperature. The resulting precipitate was filtered, washed with cold THF (2 × 10 mL) and hexane (2 × 10 mL), dried to give [2-bromomethyl-6-(3,5-xylyl)imidazolium-1-yl]methylpyridine bromide as a light brown solid (0.693 g, 55% yield). 1H NMR (500 MHz, CD2Cl2): δ 10.86 (s, 1H, H arom Imid), 7.98 (s, 1H, H arom Imid), 7.80 (d, JHH = 7.6 Hz, 1H, H arom Py), 7.75 (s, 1H, H arom Imid), 7.72 (dd, JHH = 7.7 Hz, 7.7 Hz, 1H, H arom Py, 1H, H arom Py), 7.42 (d, JHH = 7.6 Hz, 1H, H arom Py), 7.34 (s, 2H, 2 H arom Xyl), 7.12 (s, 1H, H arom Xyl), 5.98 (s, 2H, CH2N), 4.51 (s, 2H, CH3Br), 2.36 (s, 2 CH3). 13C{1H} NMR (125 MHz, CD2Cl2): δ 157.4 (Cq arom), 152.9 (Cq arom), 141.0 (2 Cq arom), 138.9 (Cq arom), 136.1 (CH arom), 134.7 (Cq arom), 132.0 (CH arom), 124.0 (CH arom), 123.9 (CH arom), 123.6 (CH arom), 120.7 (CH arom), 119.7 (2 CH arom), 53.9 (CHN), 34.0 (CH3Br), 21.2 (2 CH3). HRMS (ESI): m/z 356.0751 [(M – Br)+] (exact mass calculated for Cs16H19BrN3P: 356.0757).

In a subsequent step, to a solution of Ph2P(BH3)H (0.483 g, 2.07 mmol) in THF (20 mL) was added a solution of KOH (0.157 g, 2.42 mmol) in THF (10 mL) to give an off-white solid which should correspond to the borane adduct of 1b(Br). This solid was dissolved in MeOH (10 mL) and the reaction was transferred to a Fisher–Porter vessel and heated to 75 °C for 24 h. Volatiles were removed under vacuum, and the resulting solid was extracted with CH2Cl2 (2 × 5 mL), and dried to give [2-bromomethyl-6-(3,5-xylyl)imidazolium-1-yl]methylpyridine bromide (1.00 g, 5.81 mmol) in THF (20 mL) to give an off-white solid which should correspond to the borane adduct of 1b(Br). This solid was dissolved in MeOH (20 mL) and the resulting mixture was stirred for 30 min, and solvent was evaporated under reduced pressure. The residue was washed with Et2O (2 × 5 mL) and extracted with THF (2 × 5 mL). The suspension was stirred for 2 h, and filtered. To the resulting mixture was added PdCl2(cod) (0.057 g, 0.20 mmol). After stirring for 2 h, the resulting precipitate was filtered, washed with cold THF (2 × 10 mL) and hexane (2 × 10 mL), dried to give [2-bromomethyl-6-(3,5-xylyl)imidazolium-1-yl]methylpyridine bromide as a light brown solid (0.096 g, 60%). Anal. calcd (%) for C31H30AgCl3N3PPd: C 46.8; H 3.8; N 5.3; found: C 47.2; H 3.6; N 4.8. 1H NMR (500 MHz, CD2Cl2): δ 8.30 (d, JHH = 7.4 Hz, 1H, H arom Py), 8.21 (s, 1H, H arom NHC), 8.05 (dd, JHH = 7.5 Hz, 7.5 Hz, 1H, H arom Py), 7.92 (d, JHH = 7.6 Hz, 1H, H arom Py), 7.73 (dd, JHH = 12.1 Hz, 12.1 Hz, JHP = 8.1 Hz, 4H, 4 H arom PPh), 7.58 (t, JHH = 7.7 Hz, 2H, 2 H arom PPh), 7.50 (m, 4H, 4 H arom PPh2), 7.03 (s, 2H, 2 H arom Mes), 6.95 (s, 1H, H arom NHC), 6.05 (s, 2H, CH2N), 4.32 (d, JHH = 11.3 Hz, 2H, CH2P), 3.29 (s, 3H, CH3), 1.83 (s, 6H, 2 CH3). 31P{1H} NMR (121 MHz, CD2Cl2): δ 34.8. 13C{1H} NMR (126 MHz, CD2Cl2): δ 166.4 (d, JCP = 183 Hz, C-2 NHC), 161.9 (d, JCP = 7 Hz, Cq arom), 155.1 (Cq arom), 142.1 (CH arom), 139.6 (Cq arom), 135.8 (Cq arom), 135.5 (2 Cq arom), 133.3 (d, JCP = 11 Hz, 4 CH arom), 132.7 (2 CH arom), 129.7 (d, JCP = 12 Hz, 4 CH arom), 129.0 (2 CH arom), 126.6 (d, JCP = 46 Hz, 2 Cq arom), 126.4 (CH arom), 125.4 (d, JCP = 10 Hz, CH arom), 124.0 (d, JCP = 5 Hz, CH arom), 123.4 (d, JCP = 5 Hz, CH arom), 55.2 (CHN), 41.7 (d, JCP = 28 Hz, CH2P), 21.3 (CH3), 18.6 (2 CH3). MS (ESI, CD2Cl2): m/z (%): 616 (100) [(M – AgCl2)+].

Complex 2a. A solution of 1a(Cl) (0.100 g, 0.20 mmol) in CH2Cl2 (7 mL) was added Ag2O (0.049 g, 0.21 mmol). The suspension was stirred for 24 h, and filtered. To the resulting solution was added PdCl2(cod) (0.057 g, 0.20 mmol) in THF (2 × 5 mL) and extracted with CH2Cl2 (2 × 5 mL). The residue was washed with Et2O (2 × 5 mL) and extracted with THF (2 × 5 mL). Solvent removal under vacuum provides complex 3a as an orange solid (0.020 g, 85%). An analytical pure sample of 3a could not be obtained due to significant decomposition of the complex during purification.
Synthesis of Ir–CNP complexes 4–9

Complex 4a(Cl). A solution of 1a(Cl) (0.769 g, 1.50 mmol) in CH2Cl2 (8 mL) was added to a solution of Ir(acac)(cod) (0.600 g, 1.50 mmol) in CH2Cl2 (8 mL). The resulting solution was stirred overnight. Solvent was evaporated, and the solid was recrystallized from cold THF. The obtained solid was washed with Et2O (2 × 10 mL) and pentane (2 × 10 mL). Yellow solid (0.682 g, 56%). 1H NMR (400 MHz, CD2Cl2): δ 8.46 (s, 1H, H arom NHC), 8.33 (d, JCP = 7.5 Hz, 1H, 1H arom Py), 7.88 (dd, JHH = 7.5 Hz, 7.5 Hz, 1H, 1H arom Py), 7.79 (dd, JHH = 8.5 Hz, 2H arom PPh, 2H arom Py), 7.62 (m, 3H, 3H arom), 7.38 (d, JCP = 7.5 Hz, 1H, 1H arom Py), 7.12 (d, JCP = 14.0 Hz, 1H, NHCN), 6.78 (t, JHH = 7.5 Hz, 1H, 1H arom), 6.89 (m, 3H, 3H arom), 6.75 (s, 1H, 1H arom), 6.65 (s, 1H, 1H arom NHC), 5.87 (dd, JHH = 8.0 Hz, 1H, 2H arom PPh), 5.56 (d, JCP = 14.0 Hz, 1H, NHCN), 3.97 (dd, JHH = 14.8 Hz, 1H, 1H arom Py), 2.93 (br, 2H, 2CH2 COD), 2.23 (m, 2H, 2CH2 COD), 1.71 (br, 2H, 2CH2 COD), 1.28 (br, 2H, 2CH2 COD), 0.98 (s, 3H, 3H arom). 13P1H1 NMR (162 MHz, CD2Cl2): δ 16.9. 13C1H1 NMR (126 MHz, CD2Cl2): δ 164.4 (d, JCP = 8 Hz, C2 NHC), 160.1 (d, JCP = 4 Hz, Cq arom), 158.5 (d, JCP = 6 Hz, Cq arom), 139.5 (CH arom + Cq arom), 137.7 (Cq arom), 136.8 (d, JCP = 18 Hz, Cq arom), 135.9 (Cq arom), 135.3 (Cq arom), 134.0 (CH arom), 133.8 (CH arom), 131.6 (d, JCP = 2 Hz, CH arom), 130.3 (d, JCP = 10 Hz, 2CH arom), 130.1 (d, JCP = 2 Hz, CH arom), 130.1 (d, JCP = 39 Hz, Cq arom), 129.3 (d, JCP = 10 Hz, 2CH arom), 129.2 (d, JCP = 8 Hz, 2CH arom), 128.8 (d, JCP = 10 Hz, 2CH arom), 125.0 (d, JCP = 5 Hz, CH arom), 124.7 (CH arom), 124.3 (CH arom), 123.6 (d, JCP = 2 Hz, CH arom), 63.5 (br, 4CH = COD), 59.5 (NHCN), 44.3 (d, JCP = 29 Hz, PCH2), 37.7 (d, JCP = 6 Hz, 2CH2 COD), 28.8 (br, 2CH2 COD), 21.0 (CH3), 18.0 (CH3), 17.5 (CH3). MS (ESI, CH2Cl2): m/z (%): 776 (100) [M – Cl]− (fragmentation of ion m/z 776: 666 (100) [M – HCl – C4H4N]−). HRMS (ESI): m/z 776.2740 [M – Cl]− (exact mass calculated for C39H40N3IrP2: 776.2746).

Complex 4b(Cl). To a solution of Ir(acac)(cod) (0.269 g, 0.92 mmol) in CH2Cl2 was added a solution of 1b(Cl) (0.500 g, 0.92 mmol) in CH2Cl2, and the solution was stirred overnight. Solvent was evaporated, and the residue was extracted with CH2Cl2 (5 mL). The solution was dried by rotary evaporative vacuum, and the resulting solid was washed with toluene (7 mL) and Et2O (7 mL) and dried. Pale orange solid (0.238 g, 31%). Anal. caled (%) for C39H40BrIrN3P: C 54.2, H 4.8, N 5.0; found: C 54.4, H 5.05, N 4.7. 1H NMR (400 MHz, CD2Cl2): δ 8.28 (d, JHH = 7.7 Hz, 1H, 1H arom Py), 8.26 (d, JHH = 1.5 Hz, 1H, 1H arom NHC), 7.92 (dd, JHH = 7.7 Hz, JHH = 7.7 Hz, 1H, 1H arom Py), 7.83 (dd, JHH = 8.9 Hz, JHH = 8.9 Hz, 2H, 2H arom PPh), 7.64 (m, 3H, 3H arom PPh), 7.49 (d, JHH = 7.8 Hz, 1H, 1H arom Py), 7.09 (d, JHH = 7.5 Hz, 1H, 1H arom Py), 6.91 (d, JHH = 14.1 Hz, 1H, NHCN), 6.88 (d, JHH = 1.5 Hz, 1H, 1H arom NHC), 6.85 (s, 1H, 1H arom Xyl), 6.79 (dd, JHH = 6.6 Hz, JHH = 6.6 Hz, 2H, 2H arom PPh), 6.53 (s, 2H, 2H arom Xyl), 5.65 (d, JCP = 14.1 Hz, 1H, NHCN), 5.45 (dd, JCP = 8.4 Hz, JCP = 8.4 Hz, 2H, 2H arom PPh), 4.17 (dd, JCP = 15.5 Hz, JCP = 11.6 Hz, 1H, 1H arom Py), 3.49 (br, 2H, 2CH = COD), 3.36 (dd, JHH = 15.7 Hz, JHH = 15.7 Hz, 2H, 2H arom PPh), 2.98 (br, 2H, 2CH = COD), 2.35 (br, 4H, 2CH2 COD), 2.14 (s, 6H, 2CH3), 1.92 (br, 2H, 2CH2 COD), 1.42 (br, 2H, 2CH2 COD). 13P1H1 NMR (162 MHz, CD2Cl2): δ 20.0. 13C1H1 NMR (101 MHz, CD2Cl2): δ 164.8 (d, JCP = 8 Hz, C2 NHC), 160.4 (d, JCP = 3 Hz, Cq arom), 158.8 (d, JCP = 6 Hz, Cq arom), 139.6 (CH arom), 139.2 (Cq arom), 138.5 (2Cq arom), 135.3 (d, JCP = 25 Hz, Cq arom), 134.5 (d, JCP = 13 Hz, 2CH arom), 131.9 (CH arom), 129.8 (CH arom), 129.7 (CH arom), 129.5 (d, JCP = 9 Hz, 2CH arom), 129.3 (d, JCP = 10 Hz, 2CH arom), 129.2 (d, JCP = 2 Hz, CH arom), 63.5 (br, 4CH = COD), 59.5 (NHCN), 44.3 (d, JCP = 29 Hz, PCH2), 37.7 (d, JCP = 6 Hz, 2CH2 COD), 28.8 (br, 2CH2 COD), 21.0 (CH3), 18.0 (CH3), 17.5 (CH3). MS (ESI, CH2Cl2): m/z (%): 776 (100) [M – Cl]− (fragmentation of ion m/z 776: 666 (100) [M – HCl – C4H4N]−). HRMS (ESI): m/z 776.2740 [M – Cl]− (exact mass calculated for C39H40N3IrP2: 776.2746).
Complex 4b(BArF). A solution of 4b(Br) (0.100 g, 0.12 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a solution of NaBArF (0.105 g, 0.12 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting suspension was stirred for 4 h. The precipitate was filtered off, and the solvent was removed under vacuum to yield the complex as an orange solid (0.164 g, 85%). Crystals of complex 4b(BArF) suitable for X-ray diffraction analysis were grown by layering pentane over a CH$_2$Cl$_2$ solution. Anal. calcd (%) for C$_{30}$H$_{24}$Br$_2$B$_2$Ir$_2$N$_2$: C 51.7, H 3.2; found: C 51.6, H 3.1. H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.86 (dd, $^3$J$_{HH}$ = 7.6 Hz, 1H, H arom), 7.63 (m, 10H, 10 H arom PPh), 7.47 (m, 10H, 10 H arom PPh), 7.40 (m, 6H, 6 H arom), 6.95 (dd, $^3$J$_{HH}$ = 7.6 Hz, 1H, H arom NHC), 6.58 (d, $^3$J$_{HH}$ = 7.7 Hz, 1H, H arom), 6.32 (d, $^3$J$_{HH}$ = 8.1 Hz, 1H, H arom), 6.09 (s, 2H, 2 H arom Xyl), 5.86 (d, $^3$J$_{HH}$ = 14.2 Hz, 1H, NCHH), 5.48 (dd, $^3$J$_{HH}$ = 8.7 Hz, $^3$J$_{HP}$ = 8.7 Hz, 2H, 2 H arom PPh), 5.44 (d, $^3$J$_{HH}$ = 14.2 Hz, 1H, NCHH), 4.16 (dd, $^3$J$_{HH}$ = 15.6 Hz, $^3$J$_{HP}$ = 3.0 Hz, 1H, PCHR), 3.02 (br, 2H, 2 CH = COD), 2.41 (s, 3H, CH$_3$), 1.95 (m, 2H, 2 CHH COD), 1.49 (m, 2H, 2 CHH COD). 31P{1H} NMR (202 MHz, CD$_2$Cl$_2$): δ 3.0. 13C{1H} NMR (126 MHz, CD$_2$Cl$_2$): δ 76.2 (100) [(M − Br)]$^3$ (fragmentation of ion m/z 762: 654 (100) ([M − Br = C$_9$H$_8$I$_2$]).

Complex 5a(Cl). A solution of 4a(Cl) (0.080 g, 0.10 mmol) in CH$_2$Cl$_2$ (10 mL) was bubbled with CO for 5 min, and the solvent was evaporated. The resulting solid was washed with Et$_2$O (2 × 10 mL) and pentane (2 × 10 mL), and crystallized from THF. Orange solid (0.048 g, 70%). Anal. calcd (%) for C$_{31}$H$_{26}$ClIrN$_3$OP: C 52.8, H 4.6, N 5.5; found: C 52.2, H 4.6, N 5.5. IR (CH$_2$Cl$_2$): 1985 cm$^{-1}$ (v$_{CO}$). 1H NMR (300 MHz, CD$_2$Cl$_2$): δ 8.41 (s, 1H, H arom NHC), 8.28 (d, $^3$J$_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.97 (dd, $^3$J$_{HH}$ = 7.6 Hz, $^3$J$_{HP}$ = 7.6 Hz, 1H, H arom Py), 7.77 (dd, $^3$J$_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.61 (dd, $^3$J$_{HH}$ = 11.8 Hz, $^3$J$_{HP}$ = 7.7 Hz, $^3$J$_{HH}$ = 0.6 Hz, 4H, 4 H arom PPh), 7.46 (m, 6H, 6 H arom PPh), 7.02 (m, 3H, 3 H arom Mes + H arom NHC), 6.11 (s, 2H, CH$_2$N), 4.18 (d, $^3$J$_{HP}$ = 10.0 Hz, 2H, CH$_2$P), 2.34 (s, 3H, CH$_3$), 2.12 (s, 6H, 2 CH$_3$). 31P{1H} NMR (162 MHz, CD$_2$Cl$_2$): δ 45.7. 13C{1H} NMR (126 MHz, CD$_2$Cl$_2$): δ 178.1 (C$_{32}$H$_{30}$ClIrN$_3$PO: C 52.6, H 4.1, N 5.75; found: C 52.9, H 4.7, N 5.4). 1H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.57 (d, $^3$J$_{HH}$ = 0.8 Hz, 1H, H arom NHC), 8.41 (d, $^3$J$_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.98 (dd, $^3$J$_{HH}$ = 7.6 Hz, $^3$J$_{HP}$ = 7.6 Hz, 1H, H arom Py), 7.74 (d, $^3$J$_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.47 (m, 10H, 10 H arom PPh), 7.01 (d, $^3$J$_{HH}$ = 0.8 Hz, 1H, H arom NHC), 6.98 (s, 2H, 2 H arom Mes), 6.09 (s, 2H, CH$_2$N), 4.29 (d, $^3$J$_{HP}$ = 10.9 Hz, 2H, CH$_2$P), 2.32 (s, 3H, CH$_3$), 2.03 (s, 6H, 2 CH$_3$). 31P{1H} NMR (162 MHz, CD$_2$Cl$_2$): δ 17.4. 13C{1H} NMR (126 MHz, CD$_2$Cl$_2$): δ 76.2 (100) ([M − Br = C$_9$H$_8$I$_2$]).

Complex 7a(Cl). In a Fisher-Porter vessel, a solution of 4a(Cl) (0.120 g, 0.15 mmol) in CH$_2$Cl$_2$ (8 mL) was pressurised with 1 bar of CO. The system was analyzed by NMR spectroscopy. IR (CH$_2$Cl$_2$): 1946, 2021 cm$^{-1}$ (v$_{CO}$). 1H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.57 (d, $^3$J$_{HH}$ = 0.8 Hz, 1H, H arom NHC), 8.41 (d, $^3$J$_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.98 (dd, $^3$J$_{HH}$ = 7.6 Hz, $^3$J$_{HP}$ = 7.6 Hz, 1H, H arom Py), 7.74 (d, $^3$J$_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.47 (m, 10H, 10 H arom PPh), 7.01 (d, $^3$J$_{HH}$ = 0.8 Hz, 1H, H arom NHC), 6.98 (s, 2H, 2 H arom Mes), 6.09 (s, 2H, CH$_2$N), 4.29 (d, $^3$J$_{HP}$ = 10.9 Hz, 2H, CH$_2$P), 2.32 (s, 3H, CH$_3$), 2.03 (s, 6H, 2 CH$_3$). 31P{1H} NMR (162 MHz, CD$_2$Cl$_2$): δ 17.4. 13C{1H} NMR (126 MHz, CD$_2$Cl$_2$): δ 76.2 (100) ([M − Br = C$_9$H$_8$I$_2$]).
119 Hz, C-2 NHC), 164.8 (d, JCF = 6 Hz, Cq arom), 156.1 (Cq arom), 138.6 (Cq arom), 138.2 (Cq arom), 136.9 (Cq arom), 136.5 (CH arom), 135.7 (d, JCF = 50 Hz, Cq arom), 135.4 (Cq arom), 134.7 (d, JCF = 13 Hz, 2 CH arom), 132.4 (d, JCF = 11 Hz, 2 CH arom), 130.5 (d, JCF = 2 Hz, CH arom), 129.5 (CH arom), 129.2 (CH arom), 128.6 (CH arom), 128.3 (d, JCF = 10 Hz, 2 CH arom), 128.0 (d, JCF = 9 Hz, 2 CH arom), 122.7 (CH arom), 122.3 (d, JCF = 9 Hz, CH arom), 121.2 (d, JCF = 4 Hz, CH arom), 120.4 (d, JCF = 4 Hz, CH arom), 56.7 (CH, N), 47.1 (d, JCF = 33 Hz, CH, P), 21.3 (CH), 18.9 (CH), 18.5 (CH). Signals for one quaternary aromatic carbon could not be identified.

**Complex 7b(Cl).** In a Fisher–Porter vessel, a solution of 4b (Cl) (0.100 g, 0.12 mmol) in CH2Cl2 (5 mL) was pressurised with 5 bar of H2 and heated to 50 °C. After 16 h, the system was cooled to room temperature and depressurised. The solvent was evaporated and the residue was washed with Et2O (3 × 3 mL) and pentane (3 × 3 mL). Pale yellow solid (0.073 g, 85%).

1H NMR (400 MHz, CD2Cl2): δ 7.85 (m, 2H, 2 H arom PPh), 7.45 (m, 3H, 3 H arom), 7.34 (d, JHH = 1.5 Hz, 1H, H arom NHC), 7.19 (m, 1H, H arom), 7.11 (s, 1H, H arom NHC), 3.86 (s, 1H, H arom NHC). Satisfactory elemental analysis could not be obtained due to the low thermal stability of the product. Satisfactory elemental analysis could not be obtained due to the low thermal stability of the product. The solution was kept to 0 °C to avoid thermal decomposition of the product. The resulting solution was analysed by NMR spectroscopy.

In a J. Young valved NMR tube, a suspension of 4b(0.036 mmol) in THF-d8, 273 K: δ 17.7. 31P{1H} NMR (101 MHz, THF-d8, 273 K): δ 170.6 (m, C-2 NHC + Cq arom), 153.6 (d, JCF = 15 Hz, Cq arom), 148.8 (d, JCF = 15 Hz, Cq arom), 136.8 (d, JCF = 53 Hz, Cq arom), 134.0 (d, JCF = 10 Hz, 2 CH arom), 131.4 (d, JCF = 2 Hz, C2), 130.3 (d, JCF = 11 Hz, 2 CH arom), 129.2 (m, 2 CH arom), 128.4 (d, JCF = 8 Hz, 2 CH arom), 128.3 (d, JCF = 8 Hz, 2 CH arom), 127.1 (CH arom), 122.6 (2 CH arom), 121.9 (CH arom), 114.2 (d, JCF = 14 Hz, C6), 100.3 (C7), 76.5 (d, JCF = 59 Hz, C8), 61.6 (CH2N), 37.3 (br d, JCF = 3 Hz, 2 CH2 COD), 30.7 (br, 2 CH2 COD), 21.5 (2 CH2). Signals for the four olefinic carbons could not be identified probably due to significant line broadening.

**Complex 9b.** In a J. Young valved NMR tube, a suspension of 4b(Br) (0.030 g, 0.036 mmol) in THF-d8 (0.7 mL) cooled to 0 °C was treated with KOtBu (0.004 g, 0.039 mmol). The NMR tube was charged with 5 bar of H2 and kept to 0 °C to avoid thermal decomposition of the product. The resulting solution was analysed by NMR spectroscopy.

In a J. Young valved NMR tube, a suspension cooled to −20 °C of 7b(Cl) (0.012 g, 0.017 mmol) in THF-d8 (0.7 mL) was treated with KOtBu (0.002 g, 0.018 mmol). The NMR tube was charged with 5 bar of H2 and kept to 0 °C to avoid thermal decomposition of the product. After 1 h, the resulting solution was analysed by NMR spectroscopy.

1H NMR (400 MHz, THF-d8, 273 K): δ 7.78 (dd, JHH = 8.5 Hz, 3H), 3JHH = 2.0 Hz, 1H, H arom NHC), 7.00 (s, 2H, 2 H arom Xyl), 6.92 (td, JHH = 7.4 Hz, 2JHP = 1.5 Hz, 1H, H arom PPh), 6.81 (dd, JHH = 7.7 Hz, 2JHP = 7.5 Hz, 2H, 2 H arom PPh), 6.79 (s, 1H, H arom Xyl), 6.65 (dd, JHH = 7.5 Hz, 1H, H arom PPh), 6.39 (dd, JHH = 8.5 Hz, 3JHH = 6.3 Hz, 1H, H arom NHC).Signals for one quaternary aromatic carbon could not be identified.

The solution was kept to 0 °C to avoid thermal decomposition of the product. The resulting solution was analysed by NMR spectroscopy.

1H NMR (400 MHz, THF-d8, 273 K): δ 7.87 (dd, JHH = 8.5 Hz, 3H), 3JHH = 2.0 Hz, 1H, H arom NHC), 7.00 (s, 2H, 2 H arom Xyl), 6.92 (td, JHH = 7.4 Hz, 2JHP = 1.5 Hz, 1H, H arom PPh), 6.81 (dd, JHH = 7.7 Hz, 2JHP = 7.5 Hz, 2H, 2 H arom PPh), 6.79 (s, 1H, H arom Xyl), 6.65 (dd, JHH = 7.5 Hz, 1H, H arom PPh), 6.39 (dd, JHH = 8.5 Hz, 3JHH = 6.3 Hz, 1H, H arom NHC).Signals for one quaternary aromatic carbon could not be identified.

The solution was kept to 0 °C to avoid thermal decomposition of the product. The resulting solution was analysed by NMR spectroscopy.

1H NMR (400 MHz, THF-d8, 273 K): δ 7.78 (dd, JHH = 8.5 Hz, 3H), 3JHH = 2.0 Hz, 1H, H arom NHC), 7.00 (s, 2H, 2 H arom Xyl), 6.92 (td, JHH = 7.4 Hz, 2JHP = 1.5 Hz, 1H, H arom PPh), 6.81 (dd, JHH = 7.7 Hz, 2JHP = 7.5 Hz, 2H, 2 H arom PPh), 6.79 (s, 1H, H arom Xyl), 6.65 (dd, JHH = 7.5 Hz, 1H, H arom PPh), 6.39 (dd, JHH = 8.5 Hz, 3JHH = 6.3 Hz, 1H, H arom NHC).Signals for one quaternary aromatic carbon could not be identified.
(d, $J_{CP} = 6$ Hz, C$_q$ arom), 155.9 (C$_q$ arom), 143.0 (C$_q$ arom), 139.1 (d, $J_{CP} = 42$ Hz, 2 C$_q$ arom), 137.2 (2 C$_q$ arom), 134.3 (d, $J_{CP} = 13$ Hz, 4 CH arom), 134.1 (CH arom), 129.4 (2 CH arom), 128.2 (CH arom), 127.8 (d, $J_{CP} = 10$ Hz, 4 CH arom), 125.5 (2 CH arom), 121.3 (CH arom), 121.1 (d, $J_{CP} = 9$ Hz, CH arom), 120.5 (CH arom), 120.1 (d, $J_{CP} = 4$ Hz, CH arom), 59.9 (CH$_2$N), 49.2 (d, $J_{CP} = 34$ Hz, CH$_2$P), 21.2 (2 CH$_3$).

**Representative procedure for ketone hydrogenation**

In a glovebox, a Fischer–Porter vessel was charged with a solution of complex 4a(Cl) (2.0 mg, 2.5 µmol), KO$\text{t}$Bu (2.7 mg, 37 µmol) and acetophenone (30 µL, 0.26 mmol) in 2-methyltetrahydrofuran (2.0 mL). The reactor was purged three times with H$_2$, and finally pressurized to 1 bar and heated to 60°C. After 16 h, the reactor was slowly cooled down to room temperature, the reaction solution was evaporated, and conversion was determined by $^1$H NMR spectroscopy using mesitylene as internal standard.

**Acknowledgements**


**Notes and references**


15 (a) L. Vaska, Science, 1966, 152, 769–771; (b) A. V. Polukeev and O. F. Wendt, Organometallics, 2015, 34, 4262–4271; (c) Ref. 13b and f.


