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Journal Name

ARTICLE

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](AgCl$_2$) complex **2a** with KHMDS produces the selective deprotonation at the CH$_2$P 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 H$_2$ 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 CH$_2$P arms is observed. The, thus formed, deprotonated Ir complex **8b** reacts with H$_2$ in a ligand-assisted process leading to the trihydrido complex **9b**, which can also be obtained by reaction of **7b(Cl)** with H$_2$ in the presence of KO^{t}Bu. 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 dearomatisation 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 CH$_2$N bridges, and participate in metal-ligand cooperation processes. Furthermore, the larger Py-CH$_2$-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.[3] 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.[4b]
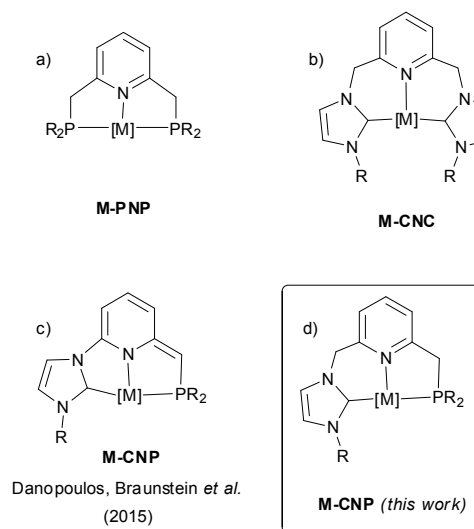
Fig. 1 General structure of metal complexes with a) lutidine-derived PNP ligands, b) lutidine-derived CNC ligands, c) deprotonated picoline-derived CNP ligands, and d) lutidine-derived CNP ligands (this work).
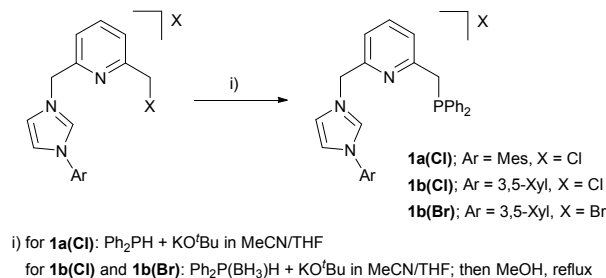
In addition, non-symmetric pincer ligands, i.e. having two inequivalent flanking donor groups, allow for a larger electronic and steric diversity derived from the potential

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tuning of two different side donors.[5] With respect to lutidine-derived pincer complexes, some examples of PNP'[6] and CNC'[4a] derivatives have been reported. Unsymmetrical PNX 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,[8a] or a different arrangement of the donor moieties, where the NHC group is the central unit of the pincer ligand.[8b-f] Also, recently Danopoulos, Braunstein 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, Braunstein et al. resides in the presence of a methylene 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.

i) for **1a(Cl)**: $Ph_2PH + KO^tBu$ in MeCN/THF
for **1b(Cl)** and **1b(Br)**: $Ph_2P(BH_3)H + KO^tBu$ in MeCN/THF; then MeOH, reflux

Scheme 1 Syntheses of CNP ligands precursors.

Results and discussion

Syntheses of imidazolium salts 1

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^tBu. 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 deprotection 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_2O in CH_2Cl_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 ^1H NMR spectrum shows distinctly two signals for the bridging methylenes. The CH_2P protons appear at 4.32 ppm (d, $^2J_{HP}$ = 11.3 Hz), whereas the NCH_2 hydrogens produce a singlet at 6.05 ppm. The $^{13}C\{^1H\}$ NMR spectrum exhibits a doublet at 166.4 ppm with a large $^2J_{CP}$ (183 Hz, carbene carbon, C^2, of the NHC moiety), indicating the *trans* disposition of the NHC and phosphine moieties.
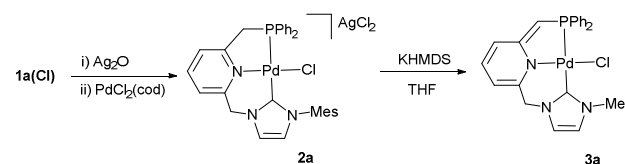
Scheme 2 Synthesis and reactivity of Pd complex **2a**.

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^2(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_2P or CH_2-NHC arms, the acid/base responsiveness of **2a** was tested by adding KHMDS to a suspension of the complex in THF.[11] In the ^1H 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 63.3 ppm ($^1J_{CP}$ = 66 Hz) in the $^{13}C\{^1H\}$ NMR experiment, evidencing the selective deprotonation of the CNP ligand at the CH_2P arm.
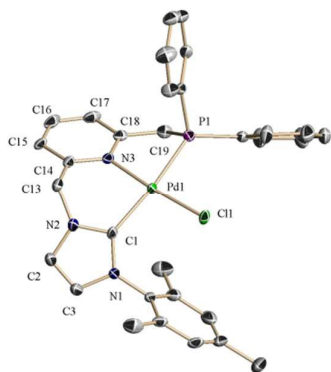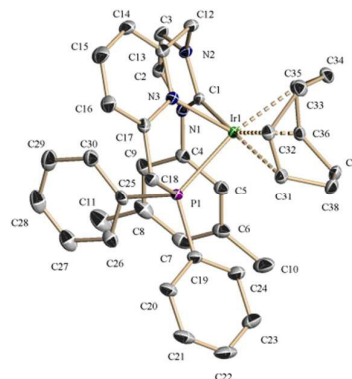
Fig. 2 ORTEP drawing at 30% ellipsoid probability of the cationic component of complex **2a**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)-C(1) 2.038(6), Pd(1)-N(3) 2.071(4), Pd(1)-P(1) 2.2623(15), Pd(1)-Cl(1) 2.2758(14), C(1)-Pd(1)-P(1) 168.65(16), N(3)-Pd(1)-Cl(1) 175.03(14), P(1)-Pd(1)-Cl(1) 93.97(5), P(1)-Pd(1)-N(3) 81.34(14), C(1)-Pd(1)-Cl(1) 95.93(16), C(1)-Pd(1)-N(3) 88.6(2).

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 ^{1}H NMR spectrum of **4b(Br)**, the CH_2P protons are diastereotopic and appear as doublet of doublets at δ 3.36 ($^2J_{HP}$ = 2.1 Hz) and 4.17 ppm ($^2J_{HH}$ = 15.5 Hz and $^2J_{HP}$ = 11.6 Hz). Similarly, protons for the CH_2N bridge produce two doublets at δ 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(BAr$_F$)** (Fig. 3), obtained by anion exchange in complex **4b(Br)** with NaBAr$_F$.

The structure of complex **4b(BAr$_F$)** is best described as adopting a distorted trigonal bipyramidal geometry despite the acute P-Ir-N(Py) bond angle of 75.98(8)°. The CNP ligand exhibits a facial coordination, with the NHC donor in the apical position (P-Ir-C(NHC) angle of 95.61(10)°). In addition, the six-membered chelate ring involving the NHC and pyridine donors adopts a boat–like conformation as defined by the dihedral angle C(13)-N(3)-Ir(1)-C(1) of −50.6°, 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°. 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 $C_{(axial)}$-$N_{(equatorial)}$-$P_{(equatorial)}$ 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 pentacoordinated 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 *trans* to the NHC than for the olefin placed in the meridional position (Δd(Ir-centroid C=C) = 0.14 Å).


Fig. 3 ORTEP drawing at 30% ellipsoid probability of the cationic component of complex **4b(BAr$_F$)**. 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) 2.3412(9), Ir(1)-C(31) 2.263(4), Ir(1)-C(32) 2.217(4), Ir(1)-C(35) 2.140(3), Ir(1)-C(36) 2.101(4), C(1)-Ir(1)-P(1) 95.61(10), N(3)-Ir(1)-P(1) 75.98(8), N(3)-Ir(1)-C(1) 81.07(13).

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 °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 °C. ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY experiments indicate that each signal is produced by protons of different olefinic moieties; 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 °C into two sets of two signals each, appearing at δ 2.23 (H^{b2}) and 3.39 (H^{b1}), and 2.86 (H^{a2}) and 3.90 (H^{a1}), respectively. An approximate value of $\Delta G^‡$ = 10.9 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 *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 *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 °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 *o*-, *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 CH₂P and CH₂N 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.[13c] However, this process should not be possible in complexes **4** due to the $C_{(axial)}$-$N_{(equatorial)}$-$P_{(equatorial)}$ coordination mode of the pincer. Since, as discussed above, olefin decoordination seems facile, the observed fluxional process could likely involve the intermediacy of the square-planar structure **B** (Fig. 4b).
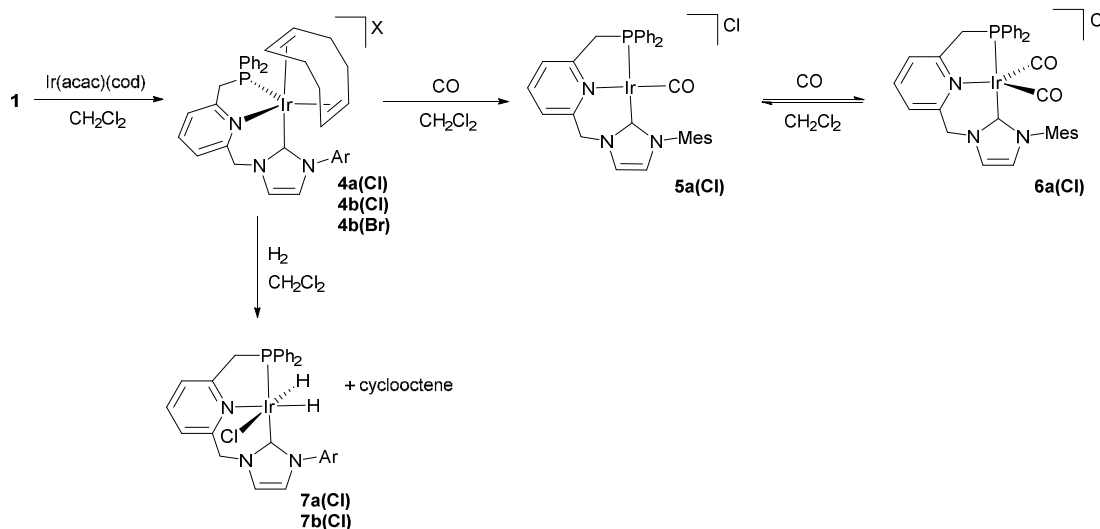
**Scheme 3** Synthesis and reactivity of Ir-CNP complexes **4**.
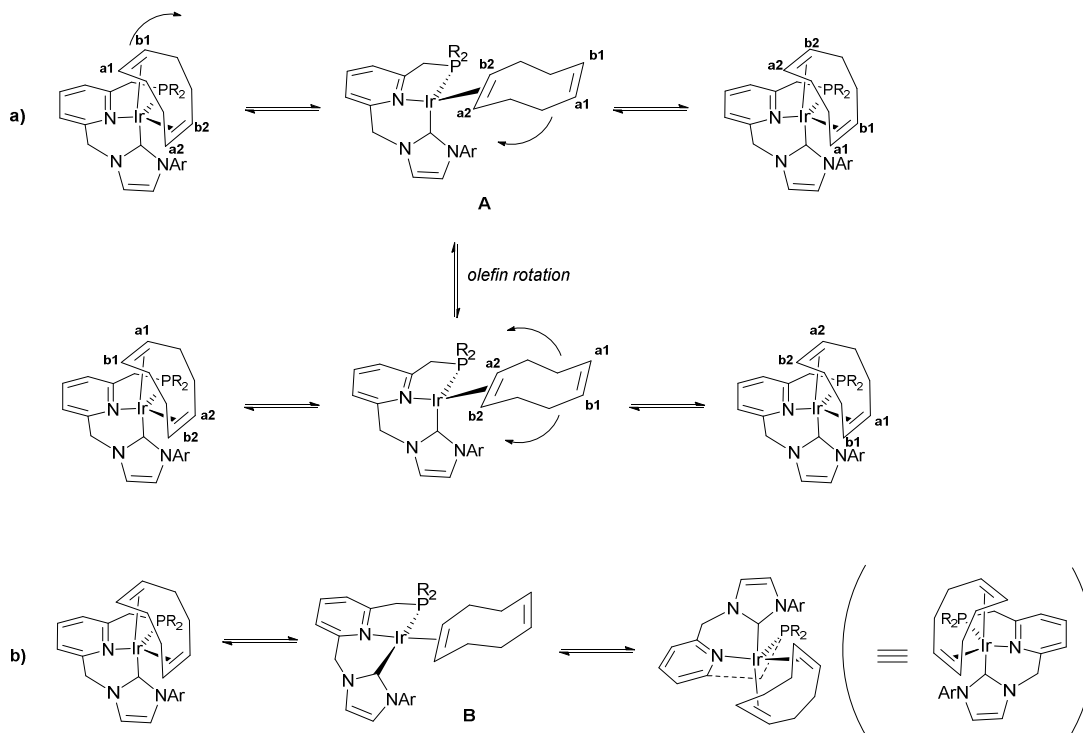
Fig. 4 Proposed dynamic processes in solution operating in the cationic part of complexes **4** (positive charges have been supressed for clarity; PR₂ = PPh₂, Ar = mesityl or 3,5-xylyl).

To evaluate the donating properties of the CNP ligands, we prepared the carbonyl derivative **5a(Cl)** by bubbling CO through a CH_2Cl_2 solution of complex **4a(Cl)** (Scheme 3). Signals of the bridging CH_2P and CH_2N protons in the ^{1}H NMR spectrum support a planar coordination of the CNP pincer. Thus, the CH_2P protons produce a doublet signal at 4.18 ppm ($^2J_{HP}$ = 10.0 Hz) while the CH_2N 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 (^tBu-PNP)-Ir analogue (1964 cm^{-1}),[14] suggesting a lower electron density at the metal centre in the Ir-CNP system. The CO ligand is detected in the $^{13}C\{^1H\}$ NMR spectrum by the appearance of a doublet signal at 177.2 ppm ($^2J_{CP}$ = 10 Hz), while the C^2 NHC carbon appears at 178.1 ppm ($^2J_{CP}$ = 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}.[15] In the ^{1}H NMR spectrum of **6a(Cl)**, the presence of a singlet signal at 6.09 ppm (2H) for the CH_2N arm and a doublet at 4.29 ppm (2H, $^2J_{HP}$ = 10.9 Hz) attributable to the CH_2P 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] at variance with the coordination geometry in the also pentacoordinated compounds **4**.

As determined by VT-^{1}H NMR spectroscopy (see SI), 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 Pd[16] and octahedral Ru complexes incorporating CNC ligands,[3b] similar dynamic processes have been ascribed to a slow interconversion between the two twisted conformations adopted by both C^2(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.


[Ir] = Ir(CO), **5a(Cl)**; Ir(CO)$_2$, **6a(Cl)**
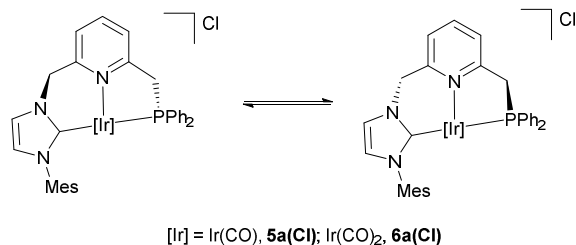
Fig. 5 Interconversion between the limiting conformations of **5a(Cl)** and **6a(Cl)**.

Complexes **4a(Cl)** and **4b(Cl)** react with H_2 producing the dihydrido derivatives **7** and cyclooctene (Scheme 3). At room temperature, the ^{1}H NMR spectrum of complex **7a(Cl)** shows two doublets of doublets at −20.19 ($^2J_{HP}$ = 13.8 Hz, $^2J_{HH}$ = 7.0

Hz) and −23.30 ppm ($^2J_{HP}$ = 18.9 Hz) due to the hydrido ligands placed *trans* to the pyridine and *trans* to the chloride, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the C^2 NHC appears at 172.9 ppm as a doublet signal ($^2J_{CP}$ = 119 Hz). Exposure of a sample of **7a(Cl)** in CD_2Cl_2 to deuterium gas (2 bar) or addition of CD_3OD 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) torsion angle of −26.5(9)°, 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)°.
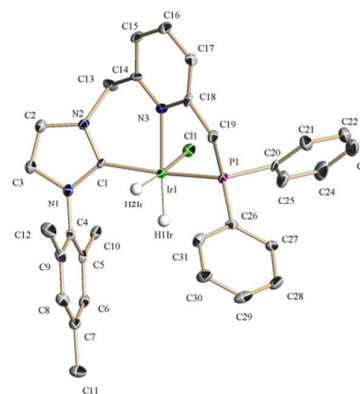

Fig. 6 ORTEP drawing at 30% ellipsoid probability of complex **7a(Cl)**. Hydrogen atoms, except hydrido ligands, and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)-C(1) 2.037(10), Ir(1)-N(3) 2.192(9), Ir(1)-P(1) 2.262(3), Ir(1)-H(1)Ir 1.600, Ir(1)-H(2)Ir 1.599, Ir(1)-Cl(1) 2.509(3), C(1)-Ir(1)-P(1) 166.5(3), N(3)-Ir(1)-H(1)Ir 173.9, P(1)-Ir(1)-H(1)Ir 92.7, P(1)-Ir(1)-N(3) 82.2(3), C(1)-Ir(1)-H(1)Ir 95.4, C(1)-Ir(1)-N(3) 89.0(4).

Deprotonation and ligand-assisted H$_2$ activation

We have also explored the deprotonation of the Ir-CNP complexes **4**.[17] Treatment of **4b(Br)** with KO^{t}Bu produces the selective deprotonation of the CH_2P arm (Scheme 4). The resulting complex **8b** is characterised in the ^{1}H 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 CH_2-NHC hydrogens generate two doublets at 4.93 and 5.29 ppm ($^2J_{HH}$ = 13.6 Hz). In the $^{13}C\{^1H\}$ NMR spectrum, the resonance caused by the C^2 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 20 Hz is estimated, suggesting a *cis* coordination of the phosphine and NHC fragments. This coordination mode is further supported by the existence of strong NOE contacts between the protons of the xylyl and PPh$_2$ groups.

Deprotonated complex **8b** reacts with H$_2$ at 0 ^{o}C to produce the trihydrido derivative **9b** in a ligand-assisted process leading to the re-aromatisation of the pyridine fragment. Complex **9b** is only stable under an atmosphere of H$_2$ and can be also obtained by reaction of **7b(Cl)** with KO^{t}Bu followed by exposure to H$_2$. The trihydrido complex **9b** shows in the ^{1}H NMR spectrum a doublet of doublets at –9.98 ppm (2H, $^2J_{HP}$ = 18.2 Hz, $^2J_{HH}$ = 4.8 Hz) due to the apical hydrido ligands and a doublet of triplets at –19.64 ppm (1H, $^2J_{HP}$ = 14.4 Hz) produced by the hydride *trans* to the pyridine N. The C^2 of the NHC fragment appears in the ^{13}C{^{1}H} NMR spectrum as a doublet at 176.9 ppm with a large $^2J_{CP}$ (121 Hz), in agreement with a *trans* disposition of the NHC and phosphine donors of the CNP ligand.
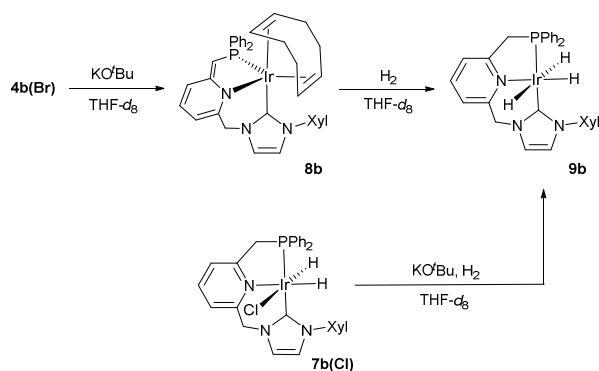
Scheme 4 Selective deprotonation of complex **4b(Br)**, and formation of complex **9b**.

Hydrogenation of ketones catalysed by Ir-CNP complexes

In order to assess the catalytic potential of these Ir-CNP complexes, their performance in the hydrogenation of ketones was studied (Table 1).[18] In the presence of KO^{t}Bu, complex **4a(Cl)** smoothly catalysed the hydrogenation of acetophenone under 4 bar of H$_2$ at 30 ^{o}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 ^{o}C (entry 2). Also, at this temperature, a lower H$_2$ 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*-methoxi, *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-CH$_2$-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 CH$_2$P 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.

Table 1 Hydrogenation of ketones catalysed by Ir-CNP complexes[a]

Entry	Ketone	Ir-CNP	T (^{o}C)	Conv. (%)
1[b]		**4a(Cl)**	30	95
2[b,c]			60	93
3	Acetophenone		60	>99
4		**4b(Cl)**	60	98
5		**5a(Cl)**	60	43
6	4´-Methoxiacetophenone	**4a(Cl)**	80	96
7	4´-Chloroacetophenone			>99
8	2´-Bromoacetophenone			99
9	2´-Fluoroacetophenone			82
10	α-Tetralone			89

[a] Reaction conditions, unless otherwise noted: 1 bar of H$_2$, 2-methyltetrahydrofuran, S/C/B = 100/1/15, base: KO^{t}Bu, 16 h. [S] = 0.13 M. Conversion was determined by ^{1}H NMR spectroscopy. [b] 4 bar of H$_2$. [c] S/C/B = 250/1/15.

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: sodium-benzophenone-ketyl for diethyl ether (Et$_2$O) and tetrahydrofuran (THF); sodium for hexane, pentane and toluene; CaH$_2$ for dichloromethane (CH$_2$Cl$_2$) and acetonitrile (CH$_3$CN); 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)[20] and NaBAr$_F$[21] 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. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. All NMR measurements were carried out at 25 ^{o}C, unless otherwise stated. NMR signal assignations were confirmed by 2D NMR spectroscopy (^1H-^1H COSY, ^1H-^1H NOESY, ^1H-^{13}C HSQC and ^1H-^{13}C 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 in 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(halomethyl)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(chloromethyl)pyridine (4.00 g, 22.7 mmol) and 1-mesityl-1*H*-imidazole (2.12 g, 11.4 mmol) in toluene (80 mL) was refluxed for 7 days. The precipitate was filtered, washed with cold THF (2 x 20 mL) and pentane (3 x 20 mL), and dried under vacuum to yield [2-chloromethyl-6-(3-mesitylimidazolium-1-yl)methyl]pyridine chloride as a brown solid (2.91 g, 70%). ^1H NMR (400 MHz, CDCl$_3$): δ 10.56 (s, 1H, H arom Imid), 8.13 (s, 1H, H arom Imid), 8.06 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.84 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.48 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.10 (s, 1H, H arom Imid), 6.99 (s, 2H, 2 H arom Mes), 6.24 (s, 2H, CH$_2$N), 4.63 (s, 2H, CH$_2$Cl), 2.33 (s, 3H, CH$_3$), 2.04 (s, 6H, 2 CH$_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CDCl$_3$): δ 156.0 (C$_q$ arom), 151.9 (C$_q$ arom), 141.5 (C$_q$ arom), 140.8 (CH arom), 138.9 (CH arom), 134.3 (2 C$_q$ arom), 130.8 (C$_q$ arom), 130.0 (2 CH arom), 125.1 (CH arom), 124.1 (CH arom), 124.0 (CH arom), 122.8 (CH arom), 52.3 (CH$_2$N), 45.1 (CH$_2$Cl), 21.2 (CH$_3$), 17.7 (2 CH$_3$). HRMS (ESI): m/z 326.1411 [(*M*−Cl)$^+$] (exact mass calculated for C$_{19}$H$_{21}$ClN$_3$: 326.1424).

In subsequent step, to a solution of PPh$_2$H (1.08 g, 5.80 mmol) in THF (10 mL) was added a solution of KO^{t}Bu (0.650 g, 5.80 mmol) in THF (10 mL). The resulting mixture stirred for 5 min, and added to a solution of [2-chloromethyl-6-(3-mesitylimidazolium-1-yl)methyl]pyridine chloride (2.00 g, 5.52 mmol) in MeCN (40 mL). The suspension was stirred overnight, and MeOH (15 mL) was added to quench the reaction. Solvent was evaporated, and the residue was extracted with CH$_2$Cl$_2$ (2 x 15 mL). The solid obtained after removal of the solvent was washed with diethyl ether (3 x 20 mL) and pentane (3 x 20 mL). Imidazolium salt **1a(Cl)** was isolated as a light brown solid (2.40 g, 85%). ^1H NMR (500 MHz, CDCl$_3$): δ 10.30 (s, 1H, H arom Imid), 7.85 (s, 1H, H arom Imid), 7.60 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.54 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py),

7.36 (m, 4H, 4 H arom PPh), 7.28 (m, 6H, 6 H arom PPh), 7.12 (s, 1H, H arom Imid), 7.03 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.01 (s, 2H, 2 H arom Mes), 5.94 (s, 2H, CH$_2$N), 3.59 (s, 2H, CH$_2$P), 2.33 (s, 3H, CH$_3$), 2.01 (s, 6H, 2 CH$_3$). $^{31}P\{^1H\}$ NMR (202 MHz, CD$_2$Cl$_2$): δ −11.7. $^{13}C\{^1H\}$ NMR (126 MHz, CD$_2$Cl$_2$): δ 158.8 (d, J_{CP} = 8 Hz, C$_q$ arom), 152.7 (C$_q$ arom), 141.4 (C$_q$ arom), 138.7 (d, J_{CP} = 3 Hz, CH arom), 138.5 (d, J_{CP} = 15 Hz, 2 C$_q$ arom), 137.9 (CH arom), 134.7 (2 C$_q$ arom), 133.0 (d, J_{CP} = 19 Hz, 4 CH arom), 131.2 (C$_q$ arom), 129.9 (2 CH arom), 129.0 (2 CH arom), 128.7 (d, J_{CP} = 7 Hz, 4 CH arom), 124.0 (d, J_{CP} = 5 Hz, CH arom), 123.9 (CH arom), 122.7 (CH arom), 121.3 (d, J_{CP} = 2 Hz, CH arom), 53.7 (CH$_2$N), 38.3 (d, J_{CP} = 17 Hz, CH$_2$P), 21.1 (CH$_3$), 17.7 (2 CH$_3$). HRMS (ESI): m/z 476.2243 [(*M*−Cl)$^+$] (exact mass calculated for C$_{31}$H$_{31}$N$_3$P: 476.2256).

[2-(Diphenylphosphinyl)methyl-6-(3-(3,5-xylyl)imidazolium-1-yl)methyl]pyridine chloride, 1b(Cl)

A solution of 2,6-bis(chloromethyl)pyridine (3.96 g, 22.5 mmol) and 1-xylyl-1*H*-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 Et$_2$O (10 mL) was added to precipitate the product. The solid was filtered, washed with Et$_2$O (2 x 10 mL) and pentane (3 x 5 mL) and dried under vacuum. [2-Chloromethyl-6-(3-(3,5-xylyl)imidazolium-1-yl)methyl]pyridine chloride was isolated as a white solid (2.21 g, 57%). ^1H NMR (400 MHz, CDCl$_3$): δ 11.09 (s, 1H, H arom Imid), 8.19 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H arom Py), 8.09 (s, 1H, H arom Imid), 7.89 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, H arom Py), 7.54 (m, 2H, H arom Py + H arom Imid), 7.23 (s, 2H, 2 H arom Xyl), 7.11 (s, 1H, H arom Xyl), 6.10 (s, 2H, CH$_2$N), 4.69 (s, 2H, CH$_2$Cl), 2.36 (s, 6H, 2 CH$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$): δ 156.1 (C$_q$ arom), 151.7 (C$_q$ arom), 140.9 (CH arom), 140.5 (2 C$_q$ arom), 136.4 (CH arom), 134.3 (CH arom), 132.1 (CH arom), 125.2 (CH arom), 124.1 (C$_q$ arom), 123.8 (CH arom), 120.31 (CH arom), 119.58 (2 CH arom), 52.7 (CH$_2$N), 45.4 (CH$_2$Cl), 21.4 (2 CH$_3$). HRMS (ESI): m/z 312.1256 [(*M*−Cl)$^+$] (exact mass calculated for C$_{18}$H$_{19}$ClN$_3$: 312.1268).

In a subsequent step, to a solution of Ph$_2$P(BH$_3$)H (0.288 g, 1.44 mmol) in THF (10 mL) was added a solution of KO^{t}Bu (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-xylyl)imidazolium-1-yl)methyl]pyridine chloride (0.500 g, 1.44 mmol) in MeCN (10 mL). The resulting suspension was stirred overnight, and MeOH (10 mL) was added to quench the reaction. The solvent was evaporated under vacuum, and the solid was extracted with CH$_2$Cl$_2$ (3 x 10 mL). Solvent removal followed by washings with Et$_2$O (2 x 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 ^{o}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 x 5 mL) and Et$_2$O (3 x 5 mL) to give an off-white solid (0.444 g, 62%). ^1H NMR (400 MHz, CD$_2$Cl$_2$): δ 11.28 (s, 1H, H arom Imid), 7.74 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.64 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.55 (d, $^3J_{HH}$ = 1.1 Hz, 1H, H arom Imid), 7.44 (m, 4H, 4 H arom), 7.36 (m, 7H, 7 H

arom), 7.29 (s, 2H, 2 H arom Xyl), 7.21 (s, 1H, H arom Xyl), 7.12 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H arom Py), 5.91 (s, 2H, CH$_2$N), 3.69 (s, 2H, CH$_2$P), 2.45 (s, 6H, 2 CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$): δ –11.8. ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): δ 159.0 (d, J_{CP} = 8 Hz, C$_q$ arom), 152.6 (C$_q$ arom), 141.0 (2 C$_q$ arom), 138.5 (d, J_{CP} = 15 Hz, 2 C$_q$ arom), 138.0 (CH arom), 136.6 (CH arom), 134.9 (C$_q$ arom), 133.0 (d, J_{CP} = 19 Hz, 4 CH arom), 131.9 (CH arom), 129.1 (2 CH arom), 128.7 (d, J_{CP} = 7 Hz, 4 CH arom), 124.2 (d, J_{CP} = 5 Hz, CH arom), 123.7 (CH arom), 121.8 (CH arom), 120.2 (CH arom), 119.7 (2 CH arom), 54.0 (CH$_2$N), 38.3 (d, J_{CP} = 16 Hz, CH$_2$P), 21.3 (2 CH$_3$). HRMS (ESI): m/z 462.2082 [(M–Cl)$^+$] (exact mass calculated for C$_{30}$H$_{29}$N$_3$P: 462.2094).

[2-(Diphenylphosphinyl)methyl-6-(3-(3,5-xylyl)imidazolium-1-yl)methyl]pyridine 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, 11.6 mmol) in THF (20 mL). The solution was stirred for 7 days at room temperature. The resulting precipitate was filtered, washed with cold THF (2 x 10 mL) and hexane (2 x 10 mL), and dried to give [2-bromomethyl-6-(3-(3,5-xylyl)imidazolium-1-yl)methyl]pyridine bromide as a light brown solid (2.00 g, 79%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 10.86 (s, 1H, H arom Imid), 7.98 (s, 1H, H arom Imid), 7.80 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.75 (s, 1H, H arom Imid), 7.72 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.42 (d, $^3J_{HH}$ = 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, CH$_2$N), 4.51 (s, 2H, CH$_2$Br), 2.36 (s, 6H, 2 CH$_3$). ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 157.4 (C$_q$ arom), 152.9 (C$_q$ arom), 141.0 (2 C$_q$ arom), 138.9 (CH arom), 136.1 (CH arom), 134.7 (C$_q$ 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 (CH$_2$N), 34.0 (CH$_2$Br), 21.2 (2 CH$_3$). HRMS (ESI): m/z 356.0751 [(M–Br)$^+$] (exact mass calculated for C$_{18}$H$_{19}$BrN$_3$: 356.0757).

In a subsequent step, to a solution of Ph$_2$P(BH$_3$)H (0.483 g, 2.42 mmol) in THF (10 mL) was added a solution of KO^{t}Bu (0.271 g, 2.42 mmol) in THF (10 mL). The resulting mixture was stirred for 10 min, and added to a solution of [2-bromomethyl-6-(3-(3,5-xylyl)imidazolium-1-yl)methyl]pyridine bromide (1.01 g, 2.39 mmol) in MeCN (20 mL). The suspension was stirred overnight, and MeOH (15 mL) was added to quench the reaction. The solvent was evaporated under vacuum, and the resulting solid was extracted with CH$_2$Cl$_2$ (3 x 10 mL). Solvent removal followed by washings with Et$_2$O (2 x 10 mL) yields a light orange solid which should correspond to the borane adduct of 1b(Br). This solid was dissolved in MeOH (10 mL), and the solution was transferred to a Fisher-Porter vessel and heated to 75 ^{o}C for 24 h. Volatiles were removed under vacuum, and MeOH was newly added and the previous procedure was repeated. The resulting solid was washed with toluene (10 mL) and Et$_2$O (10 mL) to give an off-white solid (0.693 g, 55% yield). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 10.77 (s, 1H, H arom Imid), 7.65 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.61 (t, $^3J_{HH}$ = 1.2 Hz, 1H, H arom Imid), 7.56 (m, 2H, H arom Py + H arom Imid), 7.38 (m, 4H, 4 H arom PPh), 7.32 (s, 2H, 2 H arom Xyl), 7.29 (m, 6H, 6 H arom PPh), 7.13 (s, 1H, H arom Xyl), 7.07 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 5.84 (s, 2H, CH$_2$N), 3.62 (s, 2H, CH$_2$P), 2.37 (s, 6H, 2 CH$_3$). ^{31}P{^{1}H} NMR (202 MHz,

CD$_2$Cl$_2$): δ –11.7. ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 159.0 (d, J_{CP} = 8 Hz, C$_q$ arom), 152.3 (C$_q$ arom), 141.0 (2 C$_q$ arom), 138.4 (d, J_{CP} = 15 Hz, 2 C$_q$ arom), 137.9 (CH arom), 135.9 (CH arom), 134.8 (C$_q$ arom), 132.9 (d, J_{CP} = 19 Hz, 4 CH arom), 131.9 (CH arom), 129.1 (2 CH arom), 128.7 (d, J_{CP} = 7 Hz, 4 CH arom), 124.2 (d, J_{CP} = 5 Hz, CH arom), 123.9 (CH arom), 121.6 (CH arom), 120.3 (CH arom), 119.7 (2 CH arom), 54.0 (CH$_2$N), 38.3 (d, J_{CP} = 16 Hz, CH$_2$P), 21.3 (2 CH$_3$). HRMS (ESI): m/z 462.2089 [(M–Br)$^+$] (exact mass calculated for C$_{30}$H$_{29}$N$_3$P: 462.2099).

Synthesis of Pd-CNP complexes 2a and 3a

Complex 2a. A solution of 1a(Cl) (0.100 g, 0.20 mmol) in CH$_2$Cl$_2$ (7 mL) was added Ag$_2$O (0.049 g, 0.21 mmol). The suspension was stirred for 24 h, and filtered. To the resulting solution was added PdCl$_2$(cod) (0.057 g, 0.20 mmol). After stirring for 4 h, solvent was removed under vacuum, and the residue was washed with Et$_2$O (2 × 5 mL), extracted with CH$_2$Cl$_2$ (2 × 5 mL), and crystallized from a CH$_2$Cl$_2$/toluene solvent mixture. Pale yellow solid (0.096 g, 60%). Anal. calcd (%) for C$_{31}$H$_{30}$AgCl$_3$N$_3$PPd: C 46.8; H 3.8; N 5.3; found: C 47.2; H 3.7; N 4.8. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 8.30 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 8.21 (s, 1H, H arom NHC), 8.05 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.92 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.73 (dd, $^3J_{HP}$ = 12.1 Hz, $^3J_{HH}$ = 8.1 Hz, 4H, 4 H arom PPh), 7.58 (t, $^3J_{HH}$ = 7.5 Hz, 2H, 2 H arom PPh), 7.50 (m, 4H, 4 H arom PPh$_2$), 7.03 (s, 2H, 2 H arom Mes), 6.95 (s, 1H, H arom NHC), 6.05 (s, 2H, CH$_2$N), 4.32 (d, $^2J_{HP}$ = 11.3 Hz, 2H, CH$_2$P), 2.39 (s, 3H, CH$_3$), 2.17 (s, 6H, 2 CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$): δ 34.8. ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$): δ 166.4 (d, J_{CP} = 183 Hz, C-2 NHC), 161.9 (d, J_{CP} = 7 Hz, C$_q$ arom), 155.1 (C$_q$ arom), 142.1 (CH arom), 139.6 (C$_q$ arom), 135.8 (C$_q$ arom), 135.5 (2 C$_q$ arom), 133.3 (d, J_{CP} = 11 Hz, 4 CH arom), 132.7 (2 CH arom), 129.7 (d, J_{CP} = 12 Hz, 4 CH arom), 129.0 (2 CH arom), 126.6 (d, J_{CP} = 46 Hz, 2 C$_q$ arom), 126.4 (CH arom), 125.4 (d, J_{CP} = 10 Hz, CH arom), 124.0 (d, J_{CP} = 5 Hz, CH arom), 123.4 (d, J_{CP} = 5 Hz, CH arom), 55.2 (CH$_2$N), 41.7 (d, J_{CP} = 28 Hz, CH$_2$P), 21.3 (CH$_3$), 18.6 (2 CH$_3$). MS (ESI, CH$_2$Cl$_2$): m/z (%): 616 (100) [(M–AgCl$_2$)$^+$].

Complex 3a. To a suspension of 2a (0.025 g, 0.04 mmol) in THF (2 mL) was added KHMDS (0.007 g, 0.04 mmol). The mixture was stirred for 30 min, and solvent was evaporated under reduced pressure. The residue was washed with Et$_2$O (2 x 2 mL) and extracted with THF (2 x 2 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.
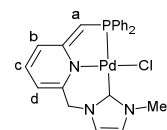
^{1}H NMR (400 MHz, THF-d_8): δ 7.71 (m, 4H, 4 H arom PPh$_2$), 7.44 (s, 1H, H arom NHC), 7.22 (m, 6H, 6 H arom PPh$_2$), 6.98 (s, 1H, H arom NHC), 6.87 (s, 2H, 2 H arom Mes), 6.46 (ddd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 6.4 Hz, $^5J_{HP}$ = 2.8 Hz, 1H, H^c), 6.30 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H^b), 5.55 (d, $^3J_{HH}$ = 6.3 Hz,1H, H^d), 4.87 (s, 2H, CH$_2$N), 3.41 (s, 1H, H^a), 2.30 (s, 3H, CH$_3$), 2.08 (s, 6H, 2 CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ 25.3.

^{13}C{^{1}H} NMR (126 MHz, THF-d_8): δ 175.1 (d, J_{CP} = 166 Hz, C-2 NHC), 174.8 (d, J_{CP} = 26 Hz, C$_q$ arom), 150.0 (C$_q$ arom), 138.7 (C$_q$ arom), 137.9 (C$_q$ arom), 137.4 (d, J_{CP} = 8 Hz, 2 C$_q$ arom), 136.2 (2 C$_q$ arom), 133.3 (d, J_{CP} = 11 Hz, 4 CH arom), 132.7 (C^c), 129.6 (2 CH arom), 129.0 (2 CH arom), 128.2 (d, J_{CP} = 11 Hz, 4 CH arom), 123.4 (d, J_{CP} = 5 Hz, CH arom), 121.2 (d, J_{CP} = 4 Hz, CH arom), 117.0 (d, J_{CP} = 21 Hz, C^b), 102.9 (C^d), 63.3 (d, J_{CP} = 66 Hz, C^a), 56.9 (CH$_2$N), 21.2 (CH$_3$), 18.6 (2 CH$_3$).

Synthesis of Ir-CNP complexes 4-9

Complex 4a(Cl). A solution of **1a(Cl)** (0.769 g, 1.50 mmol) in CH$_2$Cl$_2$ (8 mL) was added to a solution of Ir(acac)(cod) (0.600 g, 1.50 mmol) in CH$_2$Cl$_2$ (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 Et$_2$O (2 x 10 mL) and pentane (2 x 10 mL). Yellow solid (0.682 g, 56%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.46 (s, 1H, H arom NHC), 8.33 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.88 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.79 (dd, $^3J_{HP}$ = 8.5 Hz, $^3J_{HH}$ = 8.5 Hz, 2H, 2 H arom PPh), 7.62 (m, 3H, 3 H arom), 7.38 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.12 (d, $^2J_{HH}$ = 14.0 Hz, 1H, NCHH), 7.08 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H arom), 6.89 (m, 3H, 3 H arom), 6.75 (s, 1H, H arom), 6.65 (s, 1H, 1H, H arom NHC), 5.87 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, 2 H arom PPh), 5.56 (d, $^2J_{HH}$ = 14.0 Hz, 1H, NCHH), 3.97 (dd, $^2J_{HH}$ = 14.8 Hz, $^2J_{HP}$ = 11.5 Hz, 1H, PCHH), 3.45 (m, 3H, 2 CH= COD + PCHH), 2.93 (br, 2H, 2 CH= COD), 2.31 (s, 3H, CH$_3$), 2.05 (br, 4H, 4 CHH COD), 1.75 (s, 3H, CH$_3$), 1.71 (br, 2H, 2 CHH COD), 1.28 (br, 2H, 2 CHH COD), 0.98 (s, 3H, CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 16.9. ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$): δ 164.4 (d, J_{CP} = 8 Hz, C-2 NHC), 160.1 (d, J_{CP} = 4 Hz, C$_q$ arom), 158.5 (d, J_{CP} = 6 Hz, C$_q$ arom), 139.5 (CH arom + C$_q$ arom), 137.7 (C$_q$ arom), 136.8 (d, J_{CP} = 18 Hz, C$_q$ arom), 135.9 (C$_q$ arom), 135.3 (C$_q$ arom), 134.0 (CH arom), 133.8 (CH arom), 131.6 (d, J_{CP} = 2 Hz, CH arom), 130.3 (d, J_{CP} = 10 Hz, 2 CH arom), 130.1 (d, J_{CP} = 2 Hz, CH arom), 130.1 (d, J_{CP} = 39 Hz, C$_q$ arom), 129.3 (d, J_{CP} = 10 Hz, 2 CH arom), 129.2 (d, J_{CP} = 8 Hz, 2 CH arom), 128.8 (d, J_{CP} = 10 Hz, 2 CH arom), 125.0 (d, J_{CP} = 5 Hz, CH arom), 124.7 (CH arom), 124.3 (CH arom), 123.6 (d, J_{CP} = 2 Hz, CH arom), 63.5 (br, 4 CH= COD), 59.5 (NCH$_2$), 44.3 (d, J_{CP} = 29 Hz, PCH$_2$), 37.7 (d, J_{CP} = 6 Hz, 2 CH$_2$ COD), 28.8 (br, 2 CH$_2$ COD), 21.0 (CH$_3$), 18.0 (CH$_3$), 17.5 (CH$_3$). MS (ESI, CH$_2$Cl$_2$): m/z (%): 776 (100) [(M–Cl)$^+$] (fragmentation of ion m/z 776: 666 (100) [(M–HCl–C$_8$H$_{12}$)$^+$]). HRMS (ESI): m/z 776.2740 [(M–Cl)$^+$] (exact mass calculated for C$_{39}$H$_{42}$N$_3$IrP: 776.2746).

Complex 4b(Cl). To a solution of Ir(acac)(cod) (0.269 g, 0.67 mmol) in CH$_2$Cl$_2$ (5 mL) was added **1b(Cl)** (0.335 g, 0.67 mmol) in CH$_2$Cl$_2$ (8 mL), and the reaction mixture was stirred for 4 h. After solvent evaporation, the solid was extracted with CH$_3$CN (5 mL). The solvent was removed in vacuo, and the resulting solid was washed with toluene (3 x 3 mL) and Et$_2$O (3 x 5 mL), and dried. Orange-yellow solid (0.412 g, 77%). Anal. calcd (%) for C$_{38}$H$_{40}$ClIrN$_3$P·CH$_2$Cl$_2$: C 53.1, H 4.8, N 4.8; found: C 53.4, H 5.0, N 4.75. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.42 (d, $^3J_{HH}$ = 4.0 Hz, 1H, H arom NHC), 8.32 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H arom Py), 7.90 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, H arom Py), 7.83 (ddd, $^3J_{HP}$ = 10.4 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, 2 H arom PPh), 7.63 (m, 3H, 3 H arom PPh), 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H

arom Py), 7.20 (d, $^2J_{HH}$ = 12.0 Hz, 1H, NCHH), 7.05 (td, $^3J_{HH}$ = 7.6 Hz, $^5J_{HP}$ = 1.2, 1H, H arom PPh), 6.84 (d, $^3J_{HH}$ = 4.0 Hz, 1H, H arom NHC), 6.83 (s, 1H, H arom Xyl), 6.76 (m, 2H, 2 H arom PPh), 6.53 (s, 2H, 2 H arom Xyl), 5.59 (d, $^2J_{HH}$ = 12.0 Hz, 1H, NCHH), 5.43 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, 2 H arom PPh), 4.19 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{HP}$ = 11.6, 1H, PCHH), 3.46 (br, 2H, 2 CH= COD), 3.35 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{HP}$ = 3.2 Hz, 1H, PCHH), 2.96 (br, 2H, 2 CH= COD), 2.32 (m, 4H, 4 CHH COD), 2.12 (s, 6H, 2 CH$_3$), 1.94 (m, 2H, 2 CHH COD), 1.39 (m, 2H, 2 CHH COD). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 19.9. ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$): δ 164.5 (d, J_{CP} = 8 Hz, C-2 NHC), 160.3 (d, J_{CP} = 4.0 Hz, C$_q$ arom), 159.0 (d, J_{CP} = 6 Hz, C$_q$ arom), 139.5 (2 C$_q$ arom), 139.2 (C$_q$ arom), 138.4 (CH arom), 135.2 (d, J_{CP} = 25 Hz, C$_q$ arom), 134.4 (d, J_{CP} = 13 Hz, 2 CH arom), 131.8 (d, J_{CP} = 2 Hz, CH arom), 129.6 (CH arom), 129.4 (m, 3 CH arom), 129.2 (d, J_{CP} = 10 Hz, 2 CH arom), 129.0 (d, J_{CP} = 8 Hz, 2 CH arom), 128.5 (d, J_{CP} = 47 Hz, C$_q$ arom), 124.6 (d, J_{CP} = 4 Hz, CH arom), 124.1 (CH arom), 123.4 (d, J_{CP} = 2 Hz, CH arom), 122.1 (2 CH arom), 121.8 (CH arom), 66.1 (br, 4 CH= COD), 59.1 (NCH$_2$), 44.7 (d, J_{CP} = 27 Hz, PCH$_2$), 38.4 (d, J_{CP} = 6 Hz, 2 CH$_2$ COD), 28.3 (2 CH$_2$ COD), 21.3 (2 CH$_3$).

Complex 4b(Br). A solution of Ir(acac)(cod) (0.368 g, 0.92 mmol) in CH$_2$Cl$_2$ was added a solution of **1b(Br)** (0.500 g, 0.92 mmol) in CH$_2$Cl$_2$, and the solution was stirred overnight. Solvent was evaporated, and the residue was extracted with CH$_3$CN (5 mL). The solution was brought to dryness, and the resulting solid was washed with toluene (7 mL) and Et$_2$O (7 mL) and dried. Pale orange solid (0.238 g, 31%). Anal. calcd (%) for C$_{38}$H$_{40}$BrIrN$_3$P: C 54.2, H 4.8, N 5.00; found: C 54.4, H 5.05, N 4.7. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.28 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 8.26 (d, $^3J_{HH}$ = 1.5 Hz, 1H, H arom NHC), 7.92 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.83 (dd, $^3J_{HP}$ = 8.9 Hz, $^3J_{HH}$ = 8.9 Hz, 2H, 2 H arom PPh), 7.64 (m, 3H, 3 H arom PPh), 7.49 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H arom Py), 7.09 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H arom PPh), 6.91 (d, $^2J_{HH}$ = 14.1 Hz, 1H, NCHH), 6.88 (d, $^3J_{HH}$ = 1.5 Hz, 1H, H arom NHC), 6.85 (s, 1H, H arom Xyl), 6.79 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, 2H, 2 H arom PPh), 6.53 (s, 2H, 2 H arom Xyl), 5.65 (d, $^2J_{HH}$ = 14.1 Hz, 1H, NCHH), 5.45 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 8.4 Hz, 2H, 2 H arom PPh), 4.17 (dd, $^2J_{HH}$ = 15.5 Hz, $^2J_{HP}$ = 11.6 Hz, 1H, PCHH), 3.49 (br, 2H, 2 CH= COD), 3.36 (dd, $^2J_{HH}$ = 15.7 Hz, $^2J_{HP}$ = 2.1 Hz, 1H, PCHH), 2.98 (br, 2H, 2 CH= COD), 2.35 (br, 4H, 2 CH$_2$ COD), 2.14 (s, 6H, 2 CH$_3$), 1.92 (br, 2H, CH$_2$ COD), 1.42 (br, 2H, CH$_2$ COD). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 20.0. ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): δ 164.8 (d, J_{CP} = 8 Hz, C-2 NHC), 160.4 (d, J_{CP} = 3 Hz, C$_q$ arom), 158.8 (d, J_{CP} = 6 Hz, C$_q$ arom), 139.6 (CH arom), 139.2 (C$_q$ arom), 138.5 (2 C$_q$ arom), 135.3 (d, J_{CP} = 25 Hz, C$_q$ arom), 134.5 (d, J_{CP} = 13 Hz, 2 CH arom), 131.9 (CH arom), 129.8 (CH arom), 129.7 (CH arom), 129.5 (d, J_{CP} = 9 Hz, 2 CH arom), 129.3 (d, J_{CP} = 10 Hz, 2 CH arom), 129.1 (d, J_{CP} = 8 Hz, 2 CH arom), 128.6 (d, J_{CP} = 43 Hz, C$_q$ arom), 124.7 (d, J_{CP} = 4 Hz, CH arom), 123.8 (CH arom), 123.4 (CH arom), 122.3 (2 CH arom), 122.2 (CH arom), 66.0 (br, 4 CH= COD), 59.4 (CH$_2$N), 44.7 (d, J_{CP} = 28 Hz, CH$_2$P), 38.5 (d, J_{CP} = 6 Hz, 2 CH$_2$ COD), 28.4 (2 CH$_2$ COD), 21.4 (2 CH$_3$). MS (ESI, CH$_2$Cl$_2$): m/z (%): 762 (100) [(M–Br)$^+$] (fragmentation of ion m/z 762: 654 (100) [(M–Br–C$_8$H$_{12}$)$^+$]).

Complex 4b(BAr$_F$). A solution of **4b(Br)** (0.100 g, 0.12 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a solution of NaBAr$_F$ (0.105 g, 0.12

mmol) in CH_2Cl_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(BAr$_F$)** suitable for X-ray diffraction analysis were grown by layering pentane over a CH_2Cl_2 solution. Anal. calcd (%) for $C_{70}H_{52}BF_{24}IrN_3P$: C 51.7, H 3.2, N 2.6; found: C 51.6, H 3.25, N 2.5. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.86 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.81 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 6.7 Hz, 2H, 2 H arom PPh), 7.76 (s, 8H, 8 H arom BAr$_F$), 7.66 (m, 4H, 3 H arom PPh + H arom Py), 7.58 (s, 4H, 4 H arom BAr$_F$), 7.48 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.33 (d, $^3J_{HH}$ = 2.0 Hz, 1H, H arom NHC), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H arom PPh), 6.95 (d, $^3J_{HH}$ = 2.0 Hz, 1H, H arom NHC), 6.93 (s, 1H, H arom Xyl), 6.82 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HP}$ = 1.9 Hz, 2H, 2 H arom PPh), 6.49 (s, 2H, 2 H arom Xyl), 5.86 (d, $^2J_{HH}$ = 14.2 Hz, 1H, NCH*H*), 5.48 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HP}$ = 8.7 Hz, 2H, 2 H arom PPh), 5.44 (d, $^2J_{HH}$ = 14.2 Hz, 1H, NCH*H*), 4.16 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{HP}$ = 11.3 Hz, 1H, PCH*H*), 3.55 (br, 2H, 2 CH= COD), 3.39 (dd, $^2J_{HH}$ = 15.6 Hz, $^2J_{PH}$ = 3.0 Hz, 1H, PCH*H*), 3.02 (br, 2H, 2 CH= COD), 2.39 (m, 4H, 4 C*H*H COD), 2.16 (s, 6H, 2 CH$_3$), 1.95 (m, 2H, 2 C*H*H COD), 1.49 (m, 2H, 2 C*H*H COD). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 20.3. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 166.1 (d, J_{CP} = 8 Hz, C-2 NHC), 162.2 (q, J_{CB} = 50 Hz, 4 BC$_q$ arom BAr$_F$), 161.5 (d, J_{CP} = 3 Hz, C$_q$ arom), 157.5 (d, J_{CP} = 6 Hz, C$_q$ arom), 139.7 (CH arom), 139.0 (d, J_{CP} = 10 Hz, C$_q$ arom), 139.0 (2 C$_q$ arom), 135.3 (m, 8 CH arom BAr$_F$), 135.1 (overlapped, C$_q$ arom), 134.5 (d, J_{CP} = 14 Hz, 2 CH arom), 132.2 (d, J_{CP} = 2 Hz, CH arom), 130.5 (CH arom), 130.1 (d, J_{CP} = 2 Hz, CH arom), 129.7 (d, J_{CP} = 10 Hz, 2 CH arom), 129.5 (d, J_{CP} = 10 Hz, 2 CH arom), 129.3 (d, J_{CP} = 8 Hz, 2 CH arom), 129.3 (q, J_{CF} = 32 Hz, 8 C$_q$ arom BAr$_F$), 128.2 (d, J_{CP} = 38 Hz, C$_q$ arom), 125.3 (d, J_{CP} = 5 Hz, CH arom), 124.8 (q, J_{CF} = 272 Hz, 8 CF$_3$), 123.4 (CH arom), 122.6 (2 CH arom), 122.2 (CH arom), 122.0 (CH arom), 117.9 (m, 4 CH arom BAr$_F$), 66.2 (br, 4 CH= COD), 60.7 (NCH$_2$), 44.7 (d, J_{CP} = 28 Hz, PCH$_2$), 38.3 (d, J_{CP} = 6 Hz, 2 CH$_2$ COD), 28.6 (2 CH$_2$ COD), 21.4 (2 CH$_3$). MS (ESI, CH_2Cl_2): m/z (%): 762 (100) [(M–C$_{32}$H$_{12}$BF$_{24}$)$^+$] (fragmentation of ion m/z 762: 654 (100) [(M–C$_{32}$H$_{12}$BF$_{24}$–C$_8$H$_{12}$)$^+$]).

Complex 5a(Cl). A solution of **4a(Cl)** (0.080 g, 0.10 mmol) in CH_2Cl_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 x 10 mL) and pentane (2 x 10 mL), and crystallized from THF. Orange solid (0.048 g, 70%). Anal. calcd (%) for $C_{32}H_{30}ClIrN_3OP$: C 52.6, H 4.1, N 5.75; found: C 52.2, H 4.6, N 5.5. IR (CH_2Cl_2): 1985 cm^{-1} (ν_{CO}). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.41 (s, 1H, H arom NHC), 8.28 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.97 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.77 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.61 (ddd, $^3J_{HP}$ = 11.8 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 0.6 Hz, 4H, 4 H arom PPh), 7.46 (m, 6H, 6 H arom PPh), 7.02 (m, 3H, 2 H arom Mes + H arom NHC), 6.11 (s, 2H, CH$_2$N), 4.18 (d, $^2J_{HP}$ = 10.0 Hz, 2H, CH$_2$P), 2.34 (s, 3H, CH$_3$), 2.12 (s, 6H, 2 CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 45.7. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 178.1 (d, J_{CP} = 99 Hz, C-2 NHC), 177.2 (d, J_{CP} = 10 Hz, CO), 164.7 (d, J_{CP} = 7 Hz, C$_q$ arom), 156.5 (C$_q$ arom), 141.4 (CH arom), 140.1 (C$_q$ arom), 136.3 (2 C$_q$ arom), 135.7 (C$_q$ arom), 133.2 (d, J_{CP} = 12 Hz, 4 CH arom), 131.9 (d, J_{CP} = 2 Hz, 2 CH arom), 130.3 (d, J_{CP} = 53 Hz, 2 C$_q$ arom), 129.4 (d, J_{CP} = 11 Hz, 4 CH arom), 129.2 (2 CH arom), 125.4 (CH arom), 124.4 (d, J_{CP} = 10 Hz, CH arom), 123.6

(d, J_{CP} = 3 Hz, CH arom), 122.0 (d, J_{CP} = 3 Hz, CH arom), 54.6 (CH$_2$N), 42.7 (d, J_{CP} = 31 Hz, CH$_2$P), 21.2 (CH$_3$), 18.5 (2 CH$_3$).

Complex 6a(Cl). In a J. Young valved NMR tube, a solution of **5a(Cl)** (0.011 g, 0.01 mmol) in CD_2Cl_2 (0.7 mL) was pressurised with 1 bar of CO. The solution was analyzed by NMR spectroscopy. IR (CH_2Cl_2): 1946, 2021 cm^{-1} (ν_{CO}). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.57 (d, $^3J_{HH}$ = 0.8 Hz, 1H, H arom NHC), 8.41 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H arom Py), 7.98 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.74 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.47 (m, 10H, 10 H arom PPh), 7.01 (d, $^3J_{HH}$ = 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, $^2J_{HP}$ = 10.9 Hz, 2H, CH$_2$P), 2.32 (s, 3H, CH$_3$), 2.03 (s, 6H, 2 CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 26.8. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 177.4 (CO), 161.5 (C$_q$ arom), 161.3 (d, J_{CP} = 94 Hz, C-2 NHC), 155.1 (C$_q$ arom), 140.5 (CH arom), 140.2 (C$_q$ arom), 136.1 (2 C$_q$ arom), 135.7 (C$_q$ arom), 132.5 (d, J_{CP} = 12 Hz, 4 CH arom), 131.1 (2 CH arom), 129.5 (d, J_{CP} = 11 Hz, 4 CH arom), 129.4 (d, J_{CP} = 55 Hz, 2 C$_q$ arom), 129.4 (2 CH arom), 125.2 (CH arom), 124.4 (CH arom), 124.0 (d, J_{CP} = 9 Hz, CH arom), 122.8 (CH arom), 56.7 (CH$_2$N), 44.9 (d, J_{CP} = 37 Hz, CH$_2$P), 21.2 (CH$_3$), 18.1 (2 CH$_3$).

Complex 7a(Cl). In a Fisher-Porter vessel, a solution of **4a(Cl)** (0.120 g, 0.15 mmol) in CH_2Cl_2 (8 mL) was pressurised with 2 bar of H$_2$ and stirred overnight. The system was depressurised, solvent was evaporated and the residue was washed with Et$_2$O (2 x 10 mL) and pentane (2 x 10 mL). Yellow solid (0.083 g, 80%). Crystals of complex **7a(Cl)** suitable for X-ray diffraction analysis were grown by layering hexane over a CH_2Cl_2 solution. Anal. calcd (%) for $C_{31}H_{32}ClIrN_3P$: C 52.8, H 4.6, N 5.9; found: C 52.9, H 4.7, N 5.4. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.79 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, 1H, H arom Py), 7.73 (dd, $^3J_{HP}$ = 10.6 Hz, $^3J_{HH}$ = 7.9 Hz, 2H, 2 H arom PPh), 7.57 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H arom Py), 7.40 (m, 6H, 6 H arom), 7.33 (m, 4H, 4 H arom), 7.09 (s, 1H, H arom NHC), 7.02 (s, 1H, H arom Mes), 6.97 (s, 1H, H arom Mes), 6.70 (d, $^2J_{HH}$ = 14.6 Hz, 1H, NC*H*H), 4.96 (d, $^2J_{HH}$ = 14.6 Hz, 1H, NC*H*H), 4.41 (dd, $^2J_{HH}$ = 16.3 Hz, $^2J_{HP}$ = 10.4 Hz, 1H, PC*H*H), 3.38 (dd, $^2J_{HH}$ = 16.3 Hz, $^2J_{PH}$ = 9.5 Hz, 1H, PC*H*H), 2.40 (s, 3H, CH$_3$), 2.20 (s, 3H, CH$_3$), 1.92 (s, 3H, CH$_3$), –20.19 (dd, $^2J_{HP}$ = 13.8 Hz, $^2J_{HH}$ = 7.0 Hz, 1H, IrH *trans* to Py), –23.30 (dd, $^2J_{HP}$ = 18.9 Hz, $^2J_{HH}$ = 7.0 Hz, 1H, IrH *cis* to Py). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 26.8. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 172.9 (d, J_{CP} = 119 Hz, C-2 NHC), 164.8 (d, J_{CP} = 6 Hz, C$_q$ arom), 156.1 (C$_q$ arom), 138.6 (C$_q$ arom), 138.2 (C$_q$ arom), 136.9 (C$_q$ arom), 136.5 (CH arom), 135.7 (d, J_{CP} = 50 Hz, C$_q$ arom), 135.4 (C$_q$ arom), 134.7 (d, J_{CP} = 13 Hz, 2 CH arom), 132.4 (d, J_{CP} = 11 Hz, 2 CH arom), 130.5 (d, J_{CP} = 2 Hz, CH arom), 129.5 (CH arom), 129.2 (CH arom), 128.6 (CH arom), 128.3 (d, J_{CP} = 10 Hz, 2 CH arom), 128.0 (d, J_{CP} = 9 Hz, 2 CH arom), 122.7 (CH arom), 122.3 (d, J_{CP} = 9 Hz, CH arom), 121.2 (d, J_{CP} = 4 Hz, CH arom), 120.4 (d, J_{CP} = 4 Hz, CH arom), 56.7 (CH$_2$N), 47.1 (d, J_{CP} = 33 Hz, CH$_2$P), 21.3 (CH$_3$), 18.9 (CH$_3$), 18.5 (CH$_3$). 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 CH_2Cl_2 (5 mL) was pressurised with 5 bar of H$_2$ and heated to 50 ^{o}C. After 16 h, the system was cooled to room temperature and depressurised. The solvent was evaporated and the residue was washed with Et$_2$O (3 x 3 mL) and pentane (3 x 3 mL). Pale yellow solid (0.073 g, 85%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ

7.85 (m, 2H, 2 H arom PPh), 7.74 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, H arom Py), 7.56 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H arom Py), 7.47 (m, 4H, 4 H arom), 7.36 (m, 4H, 4 H arom), 7.29 (m, 3H, 3 H arom), 7.24 (d, $^3J_{HH}$ = 1.5 Hz, 1H, H arom NHC), 7.18 (m, 1H, H arom), 7.11 (s, 1H, H arom), 6.53 (d, $^2J_{HH}$ = 14.4 Hz, 1H, NCH*H*), 4.96 (d, $^2J_{HH}$ = 14.8 Hz, 1H, NCH*H*), 4.49 (dd, $^2J_{HH}$ = 16.4 Hz, $^2J_{HP}$ = 10.4 Hz, 1H, CH*H*P), 3.54 (dd, $^2J_{HH}$ = 16.6 Hz, $^2J_{HP}$ = 10.0 Hz, 1H, CH*H*P), 2.44 (s, 6H, 2 CH$_3$), −19.73 (dd, $^2J_{HP}$ = 16.6 Hz, $^2J_{HH}$ = 7.2 Hz, 1H, IrH *trans* to Py), −23.24 (dd, $^2J_{HP}$ = 18.8 Hz, $^2J_{HH}$ = 7.2 Hz, 1H, IrH *cis* to Py). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 27.7. ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): δ 172.4 (d, J_{CP} = 122 Hz, C-2 NHC), 164.9 (d, J_{CP} = 5 Hz, C$_q$ arom), 155.8 (C$_q$ arom), 141.9 (C$_q$ arom), 138.5 (2 C$_q$ arom), 136.8 (2 CH arom), 136.3 (d, J_{CP} = 52 Hz, C$_q$ arom), 134.6 (d, J_{CP} = 12 Hz, 2 CH arom), 134.2 (d, J_{CP} = 38 Hz, C$_q$ arom), 132.9 (d, J_{CP} = 11 Hz, 2 CH arom), 130.7 (d, J_{CP} = 2 Hz, CH arom), 129.8 (d, J_{CP} = 1 Hz, CH arom), 128.6 (d, J_{CP} = 10 Hz, 2 CH arom), 128.2 (d, J_{CP} = 9 Hz, 2 CH arom), 125.7 (2 CH arom), 122.7 (CH arom), 122.6 (d, J_{CP} = 9.0 Hz, CH arom), 121.5 (d, J_{CP} = 4 Hz, CH arom), 121.4 (d, J_{CP} = 5 Hz, CH arom), 57.1 (CH$_2$N), 46.3 (d, J_{CP} = 32 Hz, CH$_2$P), 21.6 (2 CH$_3$). HRMS (ESI): *m/z* 656.1794 [(*M*–Cl)$^+$] (exact mass calculated for C$_{30}$H$_{30}$N$_3$IrP: 656.1801).

Complex 8b. In a J. Young valved NMR tube, a suspension of **4b(Br)** (0.030 g, 0.036 mmol) in THF-d_8 (0.7 mL) was treated with KO^{t}Bu (0.004 g, 0.039 mmol) forming a dark red solution. The solution was kept to 0 ^{o}C to avoid thermal decomposition of the product. Satisfactory elemental analysis could not be obtained due to the low thermal stability of the product.
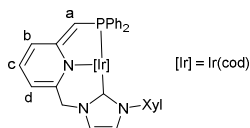
^{1}H NMR (400 MHz, THF-d_8, 273 K): δ 7.98 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HP}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, 2 H arom PPh), 7.50 (d, $^3J_{HH}$ = 2.0 Hz, 1H, H arom NHC), 7.45 (m, 3H, 3 H arom PPh), 7.22 (d, $^3J_{HH}$ = 2.0 Hz, 1H, H arom NHC), 7.00 (s, 2H, 2 H arom Xyl), 6.92 (td, $^3J_{HH}$ = 7.4 Hz, $^5J_{HP}$ = 1.5 Hz, 1H, H arom PPh), 6.81 (ddd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HP}$ = 1.4 Hz, 2H, 2 H arom PPh), 6.79 (s, 1H, H arom Xyl), 6.65 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, 2 H, 2 H arom PPh), 6.39 (ddd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.3 Hz, $^5J_{HP}$ = 1.9 Hz, 1H, H^c), 5.98 (d, $^3J_{HH}$ = 8.6 Hz, 1H, H^b), 5.58 (d, $^3J_{HH}$ = 6.2 Hz, 1H, H^d), 5.29 (d, $^2J_{HH}$ = 13.6 Hz, 1H, NC*H*H), 4.93 (d, $^2J_{HH}$ = 13.6 Hz, 1H, NCH*H*), 3.86 (s, 1H, H^a), 3.09 (br, 2H, 2 CH= COD), 2.62 (br, 2H, 2 CH= COD), 2.16 (s, 6H, 2 CH$_3$), 2.04 (br, 4H, 4 CH*H* COD), 1.89 (br, 2H, 2 CH*H* COD), 1.66 (br, 2H, 2 CH*H* COD). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, 273 K): δ 17.7. ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, 273 K): δ 170.6 (m, C-2 NHC + C$_q$ arom), 153.6 (d, J_{CP} = 6 Hz, C$_q$ arom), 148.8 (d, J_{CP} = 15 Hz, C$_q$ arom), 140.8 (C$_q$ arom), 138.5 (2 C$_q$ arom), 136.8 (d, J_{CP} = 53 Hz, C$_q$ arom), 134.0 (d, J_{CP} = 10 Hz, 2 CH arom), 131.4 (d, J_{CP} = 2 Hz, C^c), 130.3 (d, J_{CP} = 11 Hz, 2 CH arom), 129.2 (m, 2 CH arom), 128.4 (d, J_{CP} = 8 Hz, 2 CH arom), 128.3 (d, J_{CP} = 8 Hz, 2 CH arom), 127.1 (CH arom), 122.6 (2 CH arom), 122.0 (CH arom), 121.9 (CH arom), 114.2 (d, J_{CP} = 14 Hz, C^b), 100.3 (C^d), 76.5 (d, J_{CP} = 59 Hz, C^a), 61.6 (CH$_2$N), 37.3 (br d, J_{CP} = 3 Hz, 2 CH$_2$ COD), 30.7 (br, 2 CH$_2$ COD), 21.5 (2 CH$_3$). Signals for the four olefinic carbons could not be identified probably due to significant line broadening. *Cis* coordination of the phosphine and NHC fragments of the CNP ligand is proposed on the basis of the following NOE contacts:
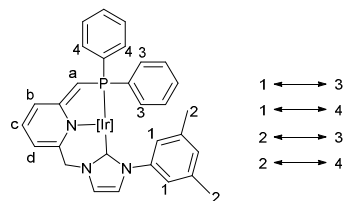
Complex 9b. In a J. Young valved NMR tube, a suspension of **4b(Br)** (0.030 g, 0.036 mmol) in THF-d_8 (0.7 mL) cooled to 0 ^{o}C was treated with KO^{t}Bu (0.004 g, 0.039 mmol). The NMR tube was charged with 5 bar of H$_2$ and kept to 0 ^{o}C to avoid thermal decomposition of the product. The resulting solution was analysed by NMR spectroscopy.

In a J. Young valved NMR tube, a suspension cooled to −20 ^{o}C of **7b(Cl)** (0.012 g, 0.017 mmol) in THF-d_8 (0.7 mL) was treated with KO^{t}Bu (0.002 g, 0.018 mmol). Immediately, the NMR tube was charged with 5 bar of H$_2$ and kept to 0 ^{o}C to avoid thermal decomposition of the product. After 1 h, the resulting solution was analysed by NMR spectroscopy.

^{1}H NMR (400 MHz, THF-d_8): δ 7.78 (dd, $^3J_{HP}$ = 8.5 Hz, $^3J_{HH}$ = 8.5 Hz, 4H, 4 H arom PPh), 7.82 (s, 2H, 2 H arom), 7.50 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, H arom Py), 7.35 (m, 2H, 2 H arom), 7.24 (m, 6H, 6 H arom), 7.11 (m, 1H, H arom), 7.07 (s, 1H, H arom NHC), 6.94 (s, 1H, H arom NHC), 5.18 (s, 2H, NCH$_2$), 3.98 (d, $^2J_{PH}$ = 10.0 Hz, 2H, PCH$_2$), 2.38 (s, 6H, 2 CH$_3$), −9.98 (dd, $^2J_{HP}$ = 18.2 Hz, $^2J_{HH}$ = 4.8 Hz, 2H, IrH *cis* to Py), −19.64 (dt, $^2J_{HP}$ = 14.4 Hz, $^2J_{HH}$ = 4.8 Hz, 1H, IrH *trans* to Py). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ 30.9. ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ 176.9 (d, J_{CP} = 121 Hz, C-2 NHC), 164.7 (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^{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 ^{o}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

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