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Synthesis and Structural Characterization of Pincer Pyridine Diphosphite Complexes of Rhodium and Iridium

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The synthesis of a novel pyridine diphosphite ligand **1** has been described. From this ligand, rhodium– and iridium–chlorido complexes of formula [MCl(**1**)] (M = Rh, Ir) have been prepared. Chloride abstraction by treatment with $NaBPh_4$ and a phosphane produced the corresponding cationic phosphane derivatives [M(**1**)**L**][BPh_4] [**L** = PPh_3 (Rh, Ir), PPh_2Me (Ir)]. The analogous reaction of [RhCl(**1**)] with CNXy (Xy = 2,6-Me_2-C_6H_3) and $NaBPh_4$ yielded the monosubstituted complex [Rh(**1**)(CNXy)][BPh_4], whereas the reaction between [IrCl(**1**)] and isonitriles led to the disubstituted complexes [Ir(**1**)(**L**)$_2$][BPh_4] (**L** = CNBn, CNCy). Ethylene compound [Rh(**1**)(C_2H_4)][BPh_4] was obtained from the reaction of [RhCl(**1**)] with $NaBPh_4$ under ethylene, whereas [Ir(**1**)(C_2H_4)][BPh_4] was synthesized by a treatment of [{IrCl(COE)$_2$}$_2$] with ethylene followed by addition of **1** and $NaBPh_4$. An IR analysis of the isocyanide complexes indicates a very poor π-donor ability of the [M(**1**)]$^+$ fragment, therefore the isocyanide metal bond is mostly due to σ donation from the isocyanide. Characterization by X-ray crystallography of [Rh(**1**)(PPh_3)][BPh_4], [Rh(**1**)(MeCN)][BPh_4] and [Ir(**1**)(PPh_2Me)][BPh_4] displays a square-planar structure with ligand **1** coordinated in a pincer fashion for these complexes. In addition, the ethylene derivative [Rh(**1**)(C_2H_4)][BPh_4] shows a near in-plane conformation of the ethylene ligand, with a short C–C distance (1.319 Å). Moreover, in all the structures, the diphosphite ligand exhibits a *meso* conformation irrespective of the size of the neutral ancillary ligand. An examination of the behaviour of some of these complexes in catalytic hydrogenation has shown that [IrCl(**1**)] is an active catalyst in the reduction of 2-methylquinoline and 2-methylquinoxaline.

Introduction

Rh and Ir complexes with phosphorus-based pincer ligands constitute a prominent class of derivatives in organometallic chemistry.[1] These complexes have exhibited a vast chemistry that includes many challenging transformations like the activation of C–H,[2] N–H,[3] C–C[4] or C–O[5] bonds among other reactions.[6] Moreover, the unique properties of pincer ligands for stabilizing transition-metal complexes have greatly helped in the detection of reaction intermediates and therefore in understanding the mechanistic aspects of some of these reactions.[1b]

Since the first examples, which correspond to cyclometalated phosphane derivatives,[7] attention has long been focused on phosphane-based donor ligands. In recent years, however, growing attention has been given to accepting pincer ligands.[8] A comparison of the reactivity of complexes based on pincer diphosphanes with those that bear accepting pincer ligands have demonstrated the profound influence that the ligand acidity can exert on the reactivity of the metal centre. For instance, in the catalytic dehydrogenation of alkanes, it has been observed that Ir diphosphinite complexes are more reactive than their diphosphane counterparts.[9] In addition, important differences between diphosphane– and diphosphinite–rhodium complexes in C–H activation reactions have recently been revealed.[10] Moreover, computational studies support a strong ability of accepting pincer ligands to stabilize pentacoordinate complexes of d^8 metals by adopting a *fac* coordination.[8a] In connection with this, the structural characterization of a family of pentacoordinate Ir complexes based on a pincer fluorophosphane that exhibits a significant bending of the pincer ligand has been reported recently.[11]

With regards to the modulation of reactivity at the metal centre, it is pertinent to recall the difference in π-accepting ability of phosphorus ligands. Then, a decrease on acidity it is expected in the order: fluoroalkylphosphane, *N*-pyrrolylphosphane, fluoroarylphosphane, phosphite, phosphoramidite and phosphinite.[12] Notably, a wide variety of PCP-type accepting ligands that cover most of these frag-

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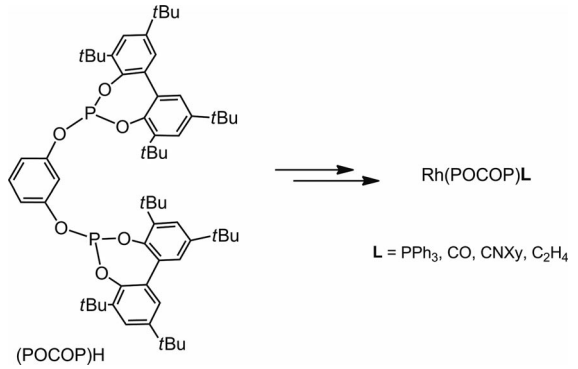
ments have been prepared.[13] On the contrary, for neutral PNP accepting ligands, only phosphinite[14] and phosphoramidite[15] derivatives have been reported. Therefore, the preparation of more acidic ligands is highly interesting.[16]

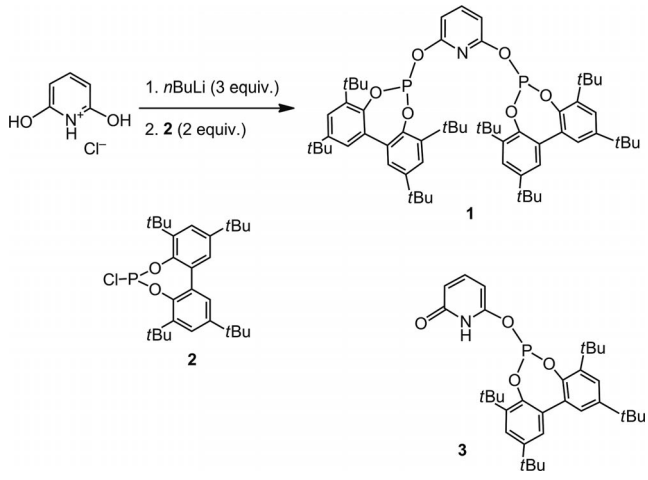
In a previous study, we described a family of Rh^I complexes with pincer anionic diphosphite ligands based on resorcinol (POCOP; Scheme 1).[17] The design of these ligands allows an easy modulation of their structure and is very suitable for the introduction of chirality into the complex. Most notably, the Rh(POCOP) fragment favoured for steric reasons an unusual in-plane coordination of an olefin ligand. Alternatively, we have become interested in an analogous neutral ligand based on a pyridine backbone that can lead to more electrophilic cationic Rh^I and Ir^I complexes. In the present contribution we therefore report a study of the synthesis and characterization of a new pyridine diphosphite pincer ligand and its coordination in a series of Rh^I and Ir^I complexes. The structural characterization of some selected examples as well as an examination of π-donor strength of the metal centre has also been included. Finally, the behaviour of some of these complexes in several catalytic hydrogenations has also been examined.



Scheme 1. Pincer complexes based on a resorcinol diphosphite.

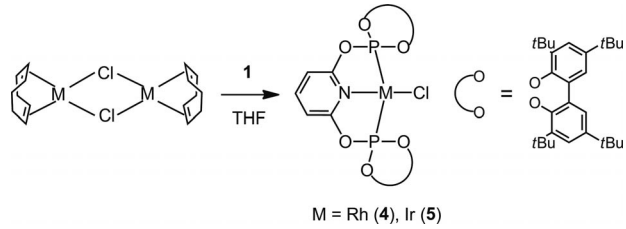
Results and Discussion

Initially, several attempts were made to prepare the pyridine diphosphite ligand **1** by treating 2,6-dihydroxypyridinium chloride with chlorophosphite **2** in the presence of different bases. Pyridine, NEt_3 or KH produced unsatisfactory results, as the reactions showed the presence of significant amounts of the monophosphite **3** as a byproduct (Scheme 2). In this system, a tautomeric rearrangement of the phosphite hydroxypyridine to the corresponding lactam phosphite **3** is expected, which hinders the formation of the second phosphite functionality. Otherwise, diphosphite **1** was obtained in good yield by converting 2,6-dihydroxypyridinium chloride into the corresponding dilithium salt by treatment with three equivalents of Li*n*Bu, followed by the reaction with two equivalents of **2**. Characterization of **1** by NMR spectroscopic techniques showed the expected signals for the bridged pyridine and the phosphite fragments. In addition, the spectra are in good accord with a rapid atropisomerization of the biphenyl moieties at room temperature.



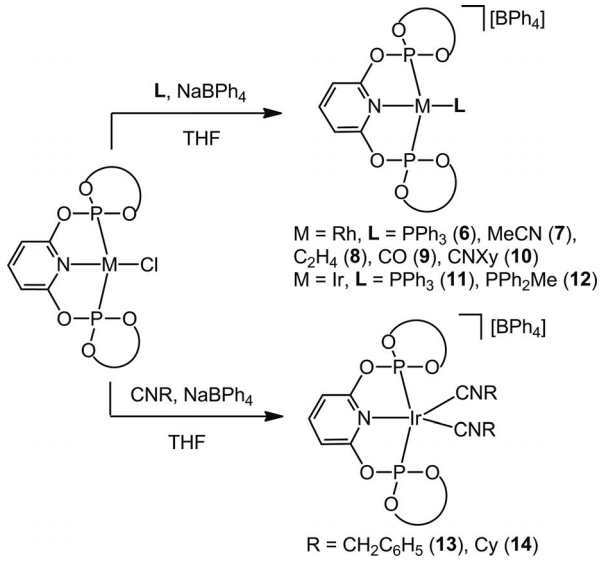
Scheme 2. Synthesis of diphosphite **1**.

From ligand **1**, complexes of formula [MCl(**1**)] [M = Rh (**4**), Ir (**5**)] were readily prepared by treatment of [{MCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) with the diphosphite at a metal-to-ligand ratio of 1:1 (Scheme 3). Characterization of these compounds indicates the P,N,P-trihapto coordination of the pyridine diphosphite. For instance, for complex **4**, a doublet at δ = 139.0 ppm with $J_{Rh,P}$ = 250 Hz is observed. Moreover, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy experiments show the equivalence of the two phosphite fragments and of the two aromatic halves of each biphenyl due to a fast conformer interconversion. In addition, the IR spectrum also accounts for pyridine coordination. Two bands at 1615 and 1560 cm^{-1} are observed, the former being at higher energy than in the free ligand.[18]



Scheme 3. Synthesis of compounds **4** and **5**.

At the next stage the preparation of cationic derivatives was examined. Chloride exchange by a neutral ligand **L** was easily performed by reaction of **4**, $NaBPh_4$ and **L** (Scheme 4). This reaction led to a series of complexes of formula [Rh(**1**)**L**][BPh_4] [**L** = PPh_3 (**6**), NCMe (**7**), C_2H_4 (**8**), CO (**9**), CNXy (Xy = 2,6-Me_2-C_6H_3; **10**)]. Moreover, Ir derivatives [Ir(**1**)**L**][BPh_4] that bear a phosphane [**L** = PPh_3 (**11**), $PMePh_2$ (**12**)] were prepared from **5** by the same procedure. On the contrary, attempts to abstract the chloride with $AgBF_4$ did not provide satisfactory results.[19,20]

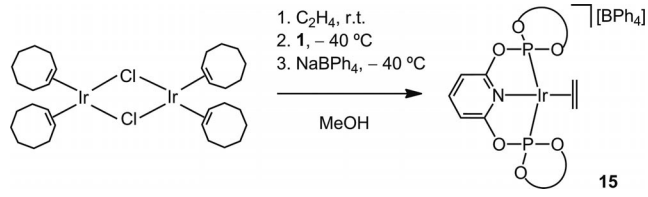


Scheme 4. Synthesis of compounds **6**–**14**.

Characterization data for compounds **6**–**12** are in good accord with square-planar structures, with the diphosphite ligand coordinated in a pincer mode and the **L** ligand occupying the remaining coordination position. For instance, complexes **6**, **11** and **12** show the typical *cis* $^2J_{P,P}$ constants (35–49 Hz) for the phosphane ligand in the $^{31}P\{^1H\}$ NMR spectra. Moreover, in the ^1H and $^{13}C\{^1H\}$ NMR spectra compound **7** shows resonances that correspond to a coordinated acetonitrile molecule. On the other hand, the olefin derivative **8** exhibits the expected signals for a coordinated ethylene. Thus, in the ^1H NMR spectroscopy experiment a broad singlet for four protons is observed at δ = 2.98 ppm, whereas the corresponding resonance in the $^{13}C\{^1H\}$ NMR spectroscopic experiment appears at δ = 57.7 ppm. The chemical shift of the ^{13}C resonance is very close to that observed in the related derivative of a pyridine diphosphane ligand (δ = 58.8 ppm).[21] Therefore, the π-acidic nature of **1** is not reflected in a lower-field shift of this resonance. The existence of only two singlets for the *t*Bu groups in the ^1H NMR spectrum is indicative of a fast phosphite atropisomerization at room temperature. To investigate this dynamic process in more detail, we performed ^1H and $^{31}P\{^1H\}$ NMR spectroscopy at variable temperature for **8** in CD_2Cl_2. Upon cooling, the doublet observed in the $^{31}P\{^1H\}$ NMR spectrum broadens and at –50 °C appears split into two doublets centred at 158.4 ($^2J_{P,P}$ = 213 Hz) and 158.1 ppm ($^2J_{P,P}$ = 211 Hz) at around a 5:1 ratio. On the other hand, in the ^1H NMR spectroscopy characteristic region for coordinated ethylene, the broad singlet observed at room temperature splits into three broad singlets upon cooling. At –80 °C, these resonances appear at δ = 3.49, 3.29 and 2.38 ppm in a 1.0:0.4:1.0 ratio. In addition, an ^1H COSY experiment at this temperature shows a cross-peak between the resonances at δ = 3.49 and 2.38 ppm. These signals can then be assigned to the *rac* conformer. Moreover, the resonance at δ = 3.29 ppm should correspond to the four ethylene protons of the *meso* isomer due to a symmetry plane perpendicular to the coordination one and fast olefin rotation. The *rac* conformer is therefore preferred in solution at low temperature (*rac*/*meso* 5:1) despite the *meso* conformer being observed in the solid state. Finally, in-plane and perpendicular rotamers could not be observed separately at the lowest temperature investigated. This solution behaviour is similar to that observed for [Rh(POCOP)(C_2H_4)].[17]

An interesting difference between complexes **4** and **5** is constituted by the reactions with isonitriles. The Ir complex shows a clear preference for the formation of pentacoordinate disubstituted complexes [Ir(**1**)$(CNR)_2$][BPh_4] [R = CH_2Ph (**13**), Cy (**14**)]. Thus, even in reactions run at an Ir/isocyanide 1:1 ratio, the presence of the disubstituted complex along with **5** was observed.

On the other hand, for the preparation of the desired Ir–ethylene derivative, chloride abstraction from **5** in an atmosphere of ethylene did not produce satisfactory results. On the contrary, treatment of [{IrCl(COE)$_2$}$_2$] under an atmosphere of ethylene followed by addition of ligand **1** and $NaBPh_4$ provided the olefin compound **15** in good yield (Scheme 5). This complex shows the expected resonances for the olefin ligand in the ^1H and $^{13}C\{^1H\}$ NMR spectra. Thus, resonances at δ = 2.89 and 44.6 ppm are observed, respectively.



Scheme 5. Synthesis of compound **15**.

The most prominent feature of cationic complexes [M(**1**)**L**][BPh_4] is the low π basicity of the metal centre, favoured by both the formal positive charge and the strong acceptor properties of the phosphite groups. Thus, the ν̃(CO) for **9** has a very high value of 2093 cm^{-1}. This frequency is significantly higher than the value observed for the cyclometalated diphosphite analogue [Rh(POCOP)(CO)] (2017 cm^{-1}),[17] whereas for cationic derivatives of pincer pyridine diphosphanes the corresponding band appears around 1980 cm^{-1}.[7c,20] However, compound **9** is unstable in solution and showed decomposition after several hours at room temperature. Isocyanide compounds exhibited a higher stability and also demonstrate the low donor ability of the [M(**1**)]$^+$ fragment. Thus, the ν̃(CN) band appears in **10** at 2153 cm^{-1}, which is significantly higher than the value observed for [Rh(POCOP)(CNXy)] (2099 cm^{-1})[17] and even higher than that for the free isocyanide (2114 cm^{-1}). The comparison of these data indicates that in this compound the isocyanide acts very predominantly as a σ donor, whereas the π component of the bond should be minimal.[22,23] Likewise, the Ir isocyanides show results that reinforce this assumption. Thus, for **13** and **14** the values for ν̃(CN) are around 40 cm^{-1} above the free ligand. These values are very high for late-transition metals in a low oxi-

dation state. For comparison, it can be mentioned that similar values have been reported for Ln^{III} complexes {e.g., 2150 cm^{-1} for $[Ce(Cp')_3(CNXy)]$}.[22]

To gain insight into the structure of coordinated **1** in these complexes, phosphane derivatives **6** and **12** (see Figures 1 and 2, respectively), acetonitrile adduct **7** (Figure 3) and ethylene complex **8** (Figure 4) have been characterized by X-ray crystallography.[24] As a general feature, all complexes along the series showed for the [M(**1**)] fragment similar values for the M–P bond lengths and the P–M–P bond angle, whereas the M–N bond length changes between 2.01 and 2.08 Å depending on the nature of the ancillary ligand (Table 1). The angle determined by the metal and the two P atoms of the pincer ligand, between 158 and 160°, is similar to those observed in related square-planar complexes with pincer diphosphane[21] and diphosphinite[9] ligands. Moreover, the M–P bond lengths (2.22–2.25 Å) are similar to those observed in a pyridine diphosphinite complex (2.22 and 2.28 Å),[9] yet somewhat lower than in a diphosphane

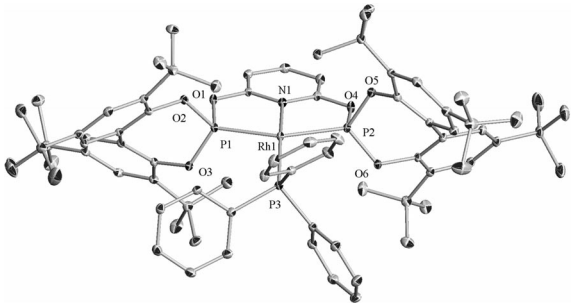


Figure 1. ORTEP diagram at 30% ellipsoid probability of complex **6**. Hydrogen atoms and the BPh_4 anion have been omitted for clarity.

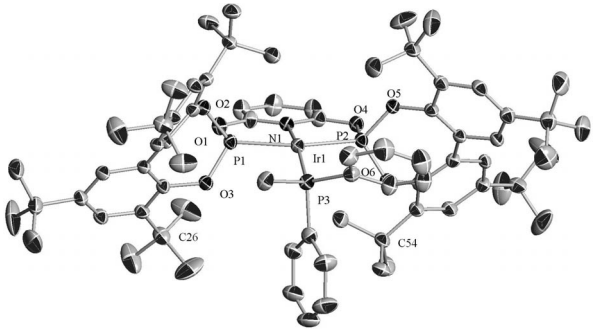


Figure 2. ORTEP diagram at 30% ellipsoid probability of complex **12**. Hydrogen atoms and the BPh_4 anion have been omitted for clarity.

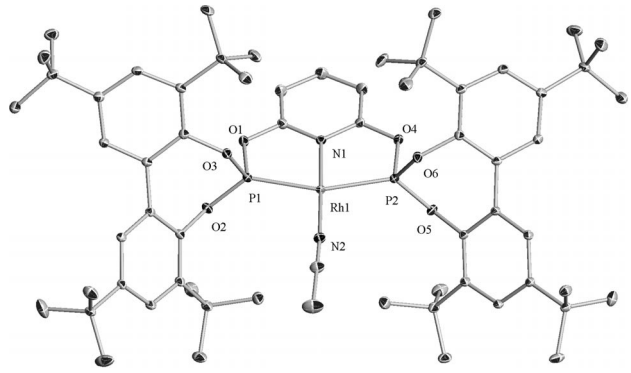


Figure 3. ORTEP diagram at 30% ellipsoid probability of complex **7**. Hydrogen atoms and the BPh_4 anion have been omitted for clarity.

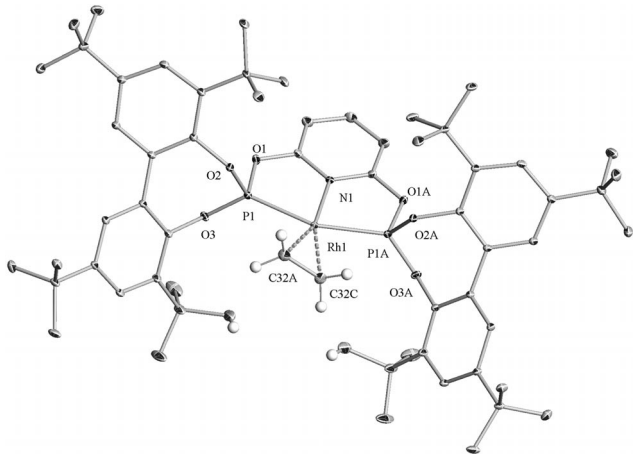


Figure 4. ORTEP diagram at 30% ellipsoid probability of complex **8**. Hydrogen atoms, except for the ethylene ligand, and the BPh_4 anion have been omitted for clarity.

complex (2.27 and 2.30 Å).[21] Noteworthy is that phosphane derivatives **6** and **12** showed a slight displacement of the phosphane ligand from the coordination plane denoted by P–M–N angles around 168°, probably caused by a steric repulsion with the phosphite groups. For these complexes, the metal phosphite bond is slightly shorter (ca. 0.05 Å) than the metal phosphane one, as observed before for complexes of the POCOP ligand.[17]

A comparison between these structures indicates that irrespective of the size of the **L** ligand, a *meso* conformation was observed in all the structures. This feature can be clearly observed by comparison of structures of phosphane complexes **6** and **12** with that of acetonitrile **7** and ethylene

Table 1. Bond lengths [Å] and angles [°] in complexes **6**–**8** and **12**.

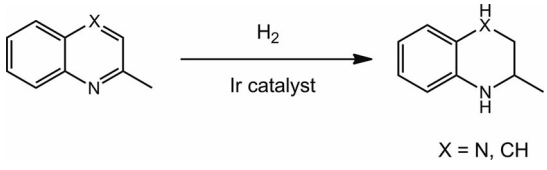
Compound	M–N	M–P[a]	M–**L**	P–M–P	N–M–**L**
6	2.082(2)	2.2529(7)	2.3081(7)	157.78(2)	167.64(6)
7	2.013(3)	2.2251(7)	1.994(3)	160.25(3)	178.94(9)
8	2.0428(17)	2.2251(5)	2.221(6)[b]	159.21(2)	172.97[c]
12	2.075(7)	2.235(2)	2.285(2)	158.74(9)	168.4(2)

[a] Average of the two M–P(phosphite) bond lengths. [b] Average of the two Rh–C bond lengths. [c] Angle determined by the olefin centroid and Ir and N atoms.

complex **8**. Accordingly, the phosphite groups form a rather flexible cavity which accommodates the steric requirements of ligand **L**. Thus, the distances between the quaternary carbons of *endo*-*tert*-butyl groups below the coordination plane in **6** and **12** (i.e., 7.30 Å between C26 and C54 in **6** and 7.43 Å between C26 and C54 in **12**) are larger than the corresponding distances in complexes **7** and **8** (6.76 and 6.60 Å, respectively). This observation contrasts with the trend outlined by structures of complexes [Rh(POCOP)**L**], which showed a *meso* conformation for sterically encumbered **L** ligands (PPh_3, CNXy) and a *rac* conformation for smaller ones (CO, C_2H_4).[17]

A remarkable feature of complex **8** is a near in-plane orientation of the olefin ligand (Figure 4). Thus, the angle between the plane defined by the Rh and the olefinic carbon atoms and the best plane defined by Rh, N and P atoms amounts to 23.7°. This orientation is clearly different from the angle of 90° that is characteristic of the usual perpendicular orientation for an ethylene ligand in a square-planar complex. As discussed in detail for the resorcinol diphosphite derivatives,[17] this uncommon conformation should be favoured over the perpendicular one by steric effects, as well as by the reduction from 180° of the P–Rh–P angle.[25] The Rh–C distances in **8** are 2.121 Å which is shorter than those found in the analogue complex of the POCOP diphosphite (2.218 and 2.235 Å),[17] yet slightly shorter than the distance found in the cationic derivative of a pyridine diphosphane (2.142 and 2.157 Å).[21b] Most remarkably, the C=C bond length in the ethylene ligand is rather short (1.319 Å). This value is appreciably smaller than the distances observed in the mentioned diphosphite (1.377 Å) and in the cationic pyridine diphosphane (1.352 Å) complexes. The short C=C distance can be attributed to a very low back-donation from the metal, already mentioned above.

Finally, we were interested in exploring the ability of some complexes based on ligand **1** to perform catalytic hydrogenations. Despite [Rh(POCOP)(C_2H_4)] being active in the hydrogenation of dimethyl itaconate, no activity was shown by compound **8**. Moreover, the hydrogenation of C=N bonds of imines and heterocycles with Ir complex **5** was also examined (Scheme 6). Thus, this catalyst precursor showed full conversion in the hydrogenation of 2-methylquinoline and 2-methylquinoxaline at a substrate (S)/catalyst (C) ratio of 100 (Table 2, entries 1 and 2). Likewise, catalyst generated in situ from [{IrCl(cod)}$_2$] and **1** at an Ir/diphosphite ratio of 1 also showed conversions over 95% (entries 3 and 6). The reaction was also effected in the presence of acid additives (entries 4 and 5). A control reaction performed with [{IrCl(cod)}$_2$] also showed complete conversion in the hydrogenation of 2-methylquinoline (entry 7), although a black deposit was observed at the end of the reaction, which points to the stabilizing role of the pincer ligand. On the contrary, no conversion was observed in the reduction of 2-methylquinoxaline (entry 8).



Scheme 6. Catalytic hydrogenation of nitrogen heterocycles.

Table 2. Hydrogenation reactions performed with Ir complexes.[a]

Entry[a]	Substrate	Cat. precursor	Conv. [%]
1	2-methylquinoline	**5**	100
2	2-methylquinoxaline	**5**	100
3	2-methylquinoline	0.5 [{IrCl(cod)}$_2$] + **1**	98
4[b]	2-methylquinoline	0.5 [{IrCl(cod)}$_2$] + **1**	100
5[c]	2-methylquinoline	0.5 [{IrCl(cod)}$_2$] + **1**	100
6	2-methylquinoxaline	0.5 [{IrCl(cod)}$_2$] + **1**	100
7[d]	2-methylquinoline	0.5 [{IrCl(cod)}$_2$]	100
8	2-methylquinoxaline	0.5 [{IrCl(cod)}$_2$]	0
9	*N*-benzylideneaniline	0.5 [{IrCl(cod)}$_2$] + **1**	0
10	*trans*-cinnamaldehyde	0.5 [{IrCl(cod)}$_2$] + **1**	55[e]
11	methyl itaconate	0.5 [{IrCl(cod)}$_2$] + **1**	0

[a] Conditions: 30 atm H_2, 25 °C, toluene, S/C = 100, 24 h. [S] = 0.6 M. Conversion was determined by ^{1}H NMR spectroscopy. [b] $(PhO)_2P(O)OH$ (10 equiv.) was added as additive. [c] [(*S*)-BINOL]P(O)OH (10 equiv.; BINOL = 1,1′-bi-2-naphthol) was added as additive; product obtained as a racemic mixture. [d] Heterogeneous reaction mixture. [e] Ratio allyl alcohol/saturated alcohol/aldehyde: 45:5:5.

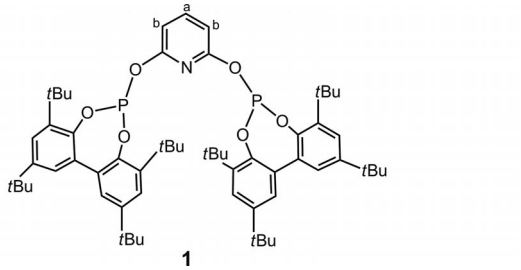
Alternatively, no reaction was observed with methyl itaconate or (*E*)-*N*-benzylideneaniline, which do not possess the α,β-unsaturated scaffold (Table 2, entries 9, 11). Moreover, the complex is active in the hydrogenation of *trans*-cinnamaldehyde, although it does not provide a selective reaction and both reductions of the C=C and C=O bonds were observed (entry 10).

Conclusion

A family of Rh^I and Ir^I square-planar complexes based on a pyridine diphosphite ligand **1** has been prepared and characterized. The set contains both neutral chloridocomplexes [MCl(**1**)] and cationic ones of formula [M(**1**)**L**][BPh_4] with diverse ligands such as phosphanes, acetonitrile, isocyanides or ethylene. On the contrary, isonitriles led to pentacoordinate complexes [Ir(**1**)$(CNR)_2$][BPh_4] in the case of Ir. An important feature of these compounds is the very low back-donor ability of the [M(**1**)]$^+$ fragment as determined by IR spectroscopy analysis of carbonyl and isocyanide complexes. Structural characterization of complexes of the formula [M(**1**)**L**][BPh_4] by X-ray crystallography show the expected pincer coordination mode, with a preferred *meso* conformation for the diphosphite. Moreover, the ethylene derivative **8** shows a near in-plane conformation of the ethylene ligand. This structure shows, in addition, a remarkably short C–C bond for the ethylene ligand, which can be attributed to a rather reduced π back-donation. A screening that explores the reactivity of these complexes in catalytic hydrogenation has shown that [IrCl(**1**)] is able to reduce the heteroaromatic ring of 2-methylquinoline and 2-methylquinoxaline, whereas it is not active in the hydrogenation of simple *N*-benzylideneaniline or dimethyl itaconate.

Experimental Section

General Procedures: All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or by using standard Schlenk-type techniques. All solvents were distilled under nitrogen using the following desiccants: sodium benzophenone ketyl for diethyl ether (Et_2O) and tetrahydrofuran (THF); sodium for *n*-hexane and toluene; CaH_2 for dichloromethane (CH_2Cl_2) and NaOMe for methanol (MeOH). $[\{Rh(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})\}_2]$,[26] $[\{Ir(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})\}_2]$[27] and $[\{Ir(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})_2\}_2]$[28] were prepared by reported methods. Phosphanes and isocyanides were purchased from commercial suppliers and used as received. IR spectra were recorded with a Perkin–Elmer 1720-XFT or with a Bruker Vector 22 spectrometer. NMR spectra were obtained with Bruker DPX-300, DRX-400, AV400 or DRX-500 spectrometers. $^{31}P\{^1H\}$ NMR spectroscopic shifts were referenced to external 85% H_3PO_4, whereas $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. The C,H,N analyses were carried out with a LECO CHNS-TruSpec microanalyzer. HRMS data was obtained at the Instrumental Services of Universidad de Sevilla (CITIUS) with a Jeol JMS-SX 102A mass spectrometer. The following atom labels have been used for the ^1H NMR spectroscopic data of the diphosphite ligand.



1

Diphosphite 1: *n*BuLi (5.0 mL, 8.0 mmol, 1.6 M in hexanes) was added dropwise to a suspension of 2,6-dihydroxypyridinium chloride (0.352 g, 2.4 mmol) in THF (10 mL). The mixture was stirred for 1 h and a solution of 3,3′,5,5′-tetra-*tert*-butylbisphen-2,2′-diylphosphochloridite (2.73 g, 5.7 mmol) in THF (10 mL) was added slowly to the white suspension. The reaction mixture was stirred for 12 h, volatile compounds were evaporated under vacuum and the resulting solid was washed with *n*-hexane (3 × 30 mL), dissolved in CH_2Cl_2 and the solution was filtered through Celite. Evaporation of the solvent yielded **1** as a white solid (1.15 g, 48%). IR (nujol mull): $\tilde{\nu}$ = 1600 (m, py), 1573 (m, py) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.53 (t, $^3J_{H,H}$ = 8 Hz, 1 H, H arom, H^a), 7.44 (d, $^4J_{H,H}$ = 2.5 Hz, 4 H, 4 H arom.), 7.19 (d, $^4J_{H,H}$ = 2.5 Hz, 4 H, 4 H arom.), 6.46 (d, $^3J_{H,H}$ = 8 Hz, 2 H, 2 H arom., H^b), 1.46 (s, 36 H, 4 CMe_3), 1.36 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 138.8 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 158.4 (d, $J_{P,C}$ = 6 Hz), 146.7, 145.5 (br.), 142.2, 140.5, 132.9, 126.5, 124.3, 106.9, 35.5, 34.7, 31.6, 31.3 ppm. HRMS (FAB): *m*/*z* exact mass calcd. for $C_{61}H_{84}NO_6P_2$ 988.5774; found 988.5821 $[M + H]^+$.

[RhCl(1)] (4): A solution of $[\{RhCl(cod)\}_2]$ (0.157 g, 0.32 mmol) in THF (5 mL) was added to a solution of diphosphite **1** (0.63 g, 0.64 mmol) in THF (10 mL). The reaction mixture was stirred for 24 h, volatile compounds were removed under vacuum and the resulting residue was washed with *n*-hexane (3 × 10 mL), dissolved in CH_2Cl_2 and the resulting mixture was filtered through a pad of Celite. Evaporation of the solution obtained yielded **4** as a yellow solid (0.53 g, 75%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.66 (t, $^3J_{H,H}$ = 8 Hz, 1 H, H arom, H^a), 7.43 (d, $^4J_{HH}$ = 2 Hz, 4 H, 4 H arom), 7.17 (d, $^4J_{H,H}$ = 2 Hz, 4 H, 4 H arom), 6.62 (d, $^3J_{H,H}$ = 8 Hz, 2 H, 2 H arom, 2 H^b), 1.47 (s, 36 H, 4 CMe_3), 1.34 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 298 K): δ = 139.0 (d, $J_{P,Rh}$ = 250 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, 298 K): δ = 159.7 (br.), 147.6, 144.8, 140.2, 138.4, 131.1, 126.8, 124.9, 103.4 (br.), 35.6, 34.7, 31.8, 31.5 ppm. $C_{61}H_{83}ClNO_6P_2Rh$ (1126.62): calcd. C 65.03, H 7.43, N 1.24; found C 65.14, H 7.34, N 1.26.

[IrCl(1)] (5): A solution of complex $[\{IrCl(cod)\}_2]$ (0.067 g, 0.1 mmol) in THF (10 mL) was slowly added to a solution of diphosphite **1** (0.198 g, 0.2 mmol) in THF (20 mL). The resulting solution was stirred vigorously for 24 h. Then the solvent was removed under vacuum and the residue was washed with *n*-hexane (3 × 10 mL). The orange residue was extracted with dichloromethane. Subsequently, the filtered solution was concentrated to around 2 mL and *n*-hexane (15 mL) was added. The resulting orange solid was washed with *n*-hexane (3 × 5 mL) and vacuum-dried to give **5** as an orange solid (0.186 g, 77%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.93 (t, $^3J_{H,H}$ = 8.3 Hz, 1 H, H^a arom.), 7.48 (d, $^4J_{H,H}$ = 2.1 Hz, 4 H, H arom.), 7.22 (d, $^4J_{H,H}$ = 2.1 Hz, 4 H, H arom.), 6.56 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, H^b arom.), 1.49 (s, 36 H, 4 CMe_3), 1.36 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ = 140.0 (s) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 155.4 (br.), 147.1, 144.8 (br.), 140.9, 137.9, 129.1, 128.1, 124.9, 102.9 (br.), 35.8, 34.9, 32.5, 31.8 ppm. $C_{61}H_{83}ClIrNO_6P_2$ (1215.93): calcd. C 60.25, H 6.88, N 1.15; found C 60.25, H 6.81, N 1.12.

[Rh(1)(PPh$_3$)][BPh$_4$] (6): PPh_3 (0.025 g, 0.095 mmol) and $NaBPh_4$ (0.031 g, 0.09 mmol) were added to a solution of **4** (0.1 g, 0.089 mmol) in THF (10 mL). The mixture was stirred for 1 h and the solvent evaporated. The resulting residue was extracted with toluene (3 × 5 mL), the obtained solution evaporated and the obtained solid was washed with *n*-hexane (3 × 5 mL) to yield **6** as a yellow-orange solid (0.09 g, 60%). ^1H NMR (C_6D_6, 500 MHz, 298 K): δ = 8.09 (br. s, 8 H, 8 H arom., BPh_4), 7.55 (br. s, 4 H, 4 H arom.), 7.50 (t, $J_{H,H}$ = 9 Hz, 6 H, 6 H arom., PPh_3), 7.25 (br. s, 4 H, 4 H arom.), 7.22 (t, $J_{H,H}$ = 7 Hz, 8 H, 8 H arom., BPh_4), 7.05 (t, $J_{H,H}$ = 7 Hz, 4 H, 4 H arom., BPh_4), 6.83 (t, $J_{H,H}$ = 7 Hz, 3 H, 3 H arom., PPh_3), 6.61 (m, 6 H, 6 H arom., PPh_3), 6.33 (t, $^3J_{H,H}$ = 8 Hz, 1 H, H arom., H^a), 5.34 (d, $^3J_{H,H}$ = 8 Hz, 2 H, 2 H arom., 2 H^b), 1.31 (s, 36 H, 4 CMe_3), 1.28 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 298 K): δ = 32.8 (dt, $J_{P,Rh}$ = 159 Hz, $J_{P,P}$ = 49 Hz, P–C), 150.3 (dd, $J_{P,Rh}$ = 243, $J_{P,P}$ = 49 Hz, P–O) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz, 298 K): δ = 165.2 (q, $^1J_{C,B}$ = 49 Hz), 156.3 (br.), 148.7, 147.5, 146.2 (br.), 139.8, 137.0, 133.9 (d, $J_{P,C}$ = 49 Hz), 133.4 (d, $J_{P,C}$ = 12 Hz), 130.6, 130.5 (d, $J_{P,C}$ = 10 Hz), 130.4, 128.1, 125.9 (br.), 125.5, 121.6, 104.6, 35.5, 34.5, 31.1 ppm. $C_{103}H_{118}BNO_6P_3Rh$ (1672.68): calcd. C 73.96, H 7.11, N 0.84; found C 73.52, H 7.41, N 0.78.

[Rh(1)(MeCN)][BPh$_4$] (7): $NaBPPh_4$ (0.02 g, 0.058 mmol) was added to a solution of complex **4** (0.06 g, 0.053 mmol) in a THF/MeCN (5:1) mixture (6 mL). The mixture was stirred for 5 h and the solvent evaporated. The resulting residue was washed with *n*-hexane (3 × 5 mL) and dissolved in toluene (10 mL). Precipitation by addition of *n*-hexane (20 mL) yielded **7** as a yellow solid (0.075 g, 95%). ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.51 (br. s, 4 H, 4 H arom.), 7.48 (t, $^3J_{H,H}$ = 8 Hz, 1 H, H arom., H^a), 7.34 (br. s, 4 H, 4 H arom.), 7.26 (br. s, 4 H, 4 H arom.), 6.87 (t, $J_{H,H}$ = 7 Hz, 8 H, 8 H arom., BPh_4), 6.70 (t, $J_{H,H}$ = 7 Hz, 4 H, 4 H arom., BPh_4), 6.60 (d, $^3J_{H,H}$ = 8 Hz, 2 H, 2 H arom., 2 H^b), 1.45 (s, 36 H, 4 CMe_3), 1.35 (s, 36 H, 4 CMe_3), 0.58 (s, 3 H, MeCN)

ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 139.5 (d, $J_{P,Rh}$ = 238 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 164.2 (q, $^1J_{C,B}$ = 49 Hz), 159.1 (br.), 149.0, 147.6, 144.0, 140.0, 136.0 (br.), 130.8, 129.0 (br.), 127.3, 125.5 (br.), 125.4, 121.5, 104.7, 35.7, 34.9, 31.5, 31.4, 1.3 ppm. $C_{87}H_{106}BN_2O_6P_2Rh$ (1451.45): calcd. C 71.92, H 7.36, N 1.93; found C 72.31, H 7.45, N 1.75.

[Rh(1)(η²-C₂H₄)][BPh₄] (8): A solution of **4** (0.1 g, 0.089 mmol) in CH_2Cl_2 (10 mL) was introduced into a glass pressure reactor and $NaBPh_4$ (0.03 g, 0.09 mmol) was added. After 1 h, the vessel was charged with 1 atm of C_2H_4 and the reaction stirred for 15 h. The mixture was evaporated down to one-fourth of the volume and *n*-hexane (5 mL) was added to yield **8** as orange crystals (0.045 g, 35%). ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.53 (d, $^4J_{H,H}$ = 2 Hz, 4 H, 4 H arom.), 7.44 (m, 8 H, 8 H arom., BPh_4), 7.29 (d, $^4J_{H,H}$ = 2 Hz, 4 H, 4 H arom.), 7.17 (t, $^3J_{H,H}$ = 8 Hz, 1 H, H arom., H^a), 7.00 (t, $J_{H,H}$ = 7 Hz, 8 H, 8 H arom., BPh_4), 6.83 (t, $J_{H,H}$ = 7 Hz, 4 H, 4 H arom., BPh_4), 6.56 (d, $^3J_{H,H}$ = 8 Hz, 2 H, 2 H arom., 2 H^b), 2.98 (br. s, 4 H, C_2H_4), 1.38 (s, 36 H, 4 CMe_3), 1.31 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 298 K): δ = 154.2 (d, $J_{P,Rh}$ = 211 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 298 K): δ = 164.3 (q, $^1J_{C,B}$ = 49 Hz), 156.9 (t, $J_{P,C}$ = 6 Hz), 149.8, 147.1, 144.2 (br.), 139.7, 136.3 (br.), 130.4, 127.6, 125.8, 125.6 (br.), 121.6, 105.6 (br.), 57.7 (br.), 35.7, 35.0, 31.4, 31.3 ppm. $C_{87}H_{107}BNO_6P_2Rh$ (1438.45): calcd. C 72.64, H 7.50, N 0.97; found C 72.81, H 7.98, N 0.90.

[Rh(1)(CO)][BPh₄] (9): Obtained as yellow crystals as described for **8** using CO instead of C_2H_4 (0.05 g, 40%). IR (nujol mull): $\tilde{\nu}$ = 2093 (s, CO) cm^{-1}. ^1H NMR (CD_2Cl_2, 500 MHz): δ = 7.80 (t, $^3J_{H,H}$ = 8 Hz, 1 H, H arom.), 7.61 (br. s, 4 H, 4 H arom.), 7.34 (br. s, 12 H, 12 H arom.), 7.02 (t, $J_{H,H}$ = 7 Hz, 8 H, 8 H arom., BPh_4), 6.86 (m, 6 H, 6 H arom.), 1.46 (s, 36 H, 4 CMe_3), 1.40 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz, 298 K): δ = 145.6 (d, $J_{P,Rh}$ = 220 Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 298 K): δ = 185.7 (m, $^1J_{C,Rh}$ = 72, $^2J_{C,P}$ = 16 Hz), 164.4 (q, $^1J_{C,B}$ = 49 Hz), 157.8 (br.), 150.4, 147.1, 144.1 (br.), 140.2, 136.2 (br.), 130.7, 127.9, 126.6, 126.3, 125.9, 122.0, 106.4, 36.0, 35.2, 31.6, 31.3 ppm. $C_{86}H_{103}BNO_7P_2Rh$ (1438.40): calcd. C 71.81, H 7.22, N 0.97; found C 71.81, H 7.54, N 0.76.

[Rh(1)(CNXy)][BPh₄] (10): $NaBPh_4$ (0.013 g, 0.04 mmol) was added to a solution of **4** (0.043 g, 0.04 mmol) in THF (2 mL). The mixture was stirred for 1 h, and CNXy (0.005 g, 0.04 mmol) was added. The reaction was stirred overnight. Solvent was removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and filtered through a short pad of Celite. The solution was dried and the solid was washed with Et_2O (2 × 5 mL) to yield **10** as an orange solid (0.042 g, 80%). IR (CH_2Cl_2): $\tilde{\nu}$ = 2153 (s, CN) cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz, 298 K): δ = 7.86 (t, $^3J_{H,H}$ = 9.0 Hz, 1 H, 1 H arom.), 7.59 (d, $^4J_{H,H}$ = 2.1 Hz, 4 H, 4 H arom.), 7.36 (m, 13 H, 13 H arom.), 7.08 (m, 8 H, 8 H arom.), 6.89 (m, 8 H, 8 H arom.), 1.58 (s, 6 H, 2 Me), 1.49 (s, 36 H, 4 CMe_3), 1.42 (s, 36 H, 4 CMe_3) ppm. $^1P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 298 K): δ = 149.8 (d, $J_{P,Rh}$ = 235 Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 298 K): δ = 164.4 (q, $J_{C,B}$ = 52 Hz), 164.4 (m), 158.4 (m), 149.9, 147.1, 144.2, 140.6, 136.3, 135.6, 131.1, 129.9, 128.2, 127.8, 127.0, 126.1, 125.9, 122.0, 105.7, 36.0, 35.2, 31.8, 31.5, 18.1 ppm. $C_{94}H_{112}BN_2O_6P_2Rh$ (1541.57): calcd. C 73.24, H 7.32, N 1.82; found C 72.67, H 7.33, N 1.73.

[Ir(1)(PPh₃)][BPh₄] (11): PPh_3 (0.010 g, 0.04 mmol) and $NaBPh_4$ (0.013 g, 0.04 mmol) was added to a solution of complex **5** (0.036 g, 0.03 mmol) in THF (10 mL). The resulting solution was stirred at room temperature for 1 h and the volatile compounds were removed under vacuum. The residue was extracted with toluene (15 mL). Subsequently, the filtered solution was concentrated to around 2 mL and *n*-hexane (15 mL) was added. The resulting orange solid was washed with *n*-hexane (3 × 10 mL) and vacuum-dried; yield 64% (0.033 g). ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 8.26 (br. s, 8 H, H arom., BPh_4), 7.67 (br. s, 4 H, H arom.), 7.65 (m, 6 H, H arom., PPh_3), 7.37 (br. s, 4 H, H arom.), 7.24 (m, 8 H, H arom., BPh_4), 7.14 (m, 4 H, H arom., BPh_4), 6.93 (m, 3 H, H arom., PPh_3), 6.72 (m, 6 H, H arom., PPh_3), 6.54 (t, $^3J_{H,H}$ = 8.1 Hz, 1 H, H^a arom.), 5.45 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H^b arom.), 1.42 (s, 36 H, 4 CMe_3), 1.40 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ = 144.1 (d, $^2J_{P,P}$ = 38.9 Hz, P-O), 11.0 (t, $^2J_{P,P}$ = 38.9 Hz, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 165.3 (q, $J_{C,B}$ = 47.9 Hz), 157.4 (br.), 149.6, 148.8, 146.9, 140.5, 137.0, 135.5 (br.), 134.1 (d, $J_{C,P}$ = 12 Hz), 131.2, 130.7, 129.8 (br.), 128.1, 126.9 (br.), 126.5, 122.9, 104.4 (br.), 36.1, 35.1, 31.6 ppm. $C_{103}H_{118}BIrNO_6P_3$ (1761.99): calcd. C 70.21, H 6.75, N 0.79; found C 70.18, H 6.68, N 0.77.

[Ir(1)(PPh₂Me)][BPh₄] (12): Prepared as described for **11** using PPh_2Me. Orange solid, yield 67% (0.034 g). ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 8.22 (br. s, 8 H, H arom., BPh_4), 7.70 (br. s, 4 H, H arom.), 7.63 (m, 5 H, H arom., P*Ph*$_2$Me), 7.37 (br. s, 4 H, H arom.), 7.25 (m, 8 H, H arom., BPh_4), 7.12 (m, 4 H, H arom., BPh_4), 6.92 (m, 5 H, H arom., P*Ph*$_2$Me), 6.55 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, H^a arom.), 5.62 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H^b arom.), 1.48 (s, 36 H, 4 CMe_3), 1.43 (br. s, 3 H, PPh_2*Me*), 1.37 (s, 36 H, 4 CMe_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ = 146.5 (d, $^2J_{P,P}$ = 35.1 Hz, P–O), 6.2 (t, $^2J_{P,P}$ = 35.1 Hz, PPh_2Me) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 169.3 (q, $J_{C,B}$ = 42 Hz), 153.2 (br.), 149.8, 148.6, 144.9, 140.6, 137.3, 132.7 (br.), 131.7, 131.5 (br.), 130.9 (br.), 129.7, 129.5 (br.), 126.7, 125.8, 101.4 (br.), 35.9, 35.1, 31.6, 31.1 ppm. $C_{98}H_{116}BIrNO_6P_3$ (1699.92): calcd. C 69.24, H 6.88, N 0.82; found C 69.21, H 6.88, N 0.75.

[Ir(1)(CNBn)₂][BPh₄] (13): Isocyanide (0.04 mmol) and $NaBPh_4$ (0.013 g, 0.04 mmol) were added to a solution of complex **5** (0.036 g, 0.03 mmol) in THF (10 mL). The resulting solution was stirred at room temperature for 1 h and the volatile compounds were removed under vacuum. The residue was extracted with toluene (15 mL). Subsequently, the filtered solution was concentrated to around 2 mL and *n*-hexane (15 mL) was added. The resulting yellow solid was washed with *n*-hexane (3 × 10 mL) and vacuum-dried; yield 71% (0.037 g). IR (KBr): $\tilde{\nu}$ = 2191 (br. s, CN) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ = 145.2 (s) ppm. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 8.22 (br. s, 8 H, H arom., BPh_4), 7.74 (d, $J_{H,H}$ = 2.4 Hz, 4 H, H arom.), 7.49 (d, $J_{H,H}$ = 2.4 Hz, 4 H, H arom.), 7.36 (t, $J_{H,H}$ = 7.0 Hz, 8 H, H arom., BPh_4), 7.24 (m, 4 H, H arom., BPh_4), 7.15 (br. s, 4 H, 10 H, $CNCH_2C_6H_5$), 6.83 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, H^a arom.), 6.18 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H^b arom.), 2.22 (s, 4 H, 2CNCH_2C$_6$H$_5$), 1.42 (s, 36 H, 4 CMe_3), 1.40 (s, 36 H, 4 CMe_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 164.8 (q, $J_{C,B}$ = 52.0 Hz), 157.9 (br.), 149.5, 148.7, 146.0, 144.8 (br.), 140.8, 137.0 (br.), 136.9, 133.9, 132.8, 131.0, 128.3, 127.2 (br.), 126.2, 122.1, 104.7 (br.), 48.0, 35.5, 34.3, 31.2 ppm. $C_{101}H_{117}BIrN_3O_6P_2$ (1734.00): calcd. C 69.95, H 6.80, N 2.42; found C 69.93, H 6.88, N 2.45.

[Ir(1)(CNCy)₂][BPh₄] (14): Prepared as described for **13**. Yellow solid, yield 77% (0.034 g). IR (KBr): $\tilde{\nu}$ = 2178 (s, CN) cm^{-1}. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K): δ = 146.3 (s) ppm. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 8.13 (br. s, 8 H, H arom., BPh_4), 7.78 (m, 4 H, H arom.), 7.50 (br. s, 4 H, H arom), 7.43 (br. s, 8 H, H arom., BPh_4), 7.14 (br. s, 4 H, 4 H arom., BPh_4), 6.57 (m, 1 H, H^a arom.), 5.73 (d, $^3J_{H,H}$ = 9.8 Hz, 2 H, H^b arom.), 2.22 (br. s, 2 H, 2C*H*CNC$_6$H$_{11}$), 1.83 (m, 12 H, CNC$_6$H$_{11}$), 1.62 (s, 36 H, 4 CMe_3),

Table 3. Crystallographic data and structure refinement for **6**–**8** and **12**.

	6	**7**	**8**	**12**
Formula	$C_{107}H_{126}BNO_7PRh$	$C_{187}H_{241}B_2Cl_3N_4O_{12}P_4Rh_2$	$C_{93}H_{121}BNO_6P_2Rh$	$C_{398}H_{470}B_4Ir_4N_4O_{24}P_{12}$
M_r	1744.72	3194.51	1524.57	6877.46
T [K]	100(2)	100(2)	100(2)	293(2)
Crystal size [mm^3]	$0.36\times0.19\times0.13$	$0.25\times0.23\times0.22$	$0.28\times0.25\times0.14$	$0.074\times0.044\times0.015$
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/m$	$P2_1/c$
a [Å]	17.1399(16)	34.7797(14)	25.2664(19)	12.5992(5)
b [Å]	17.544(3)	26.4707(11)	26.4744(19)	28.1831(16)
c [Å]	18.7310(17)	25.3582(18)	14.6013(11)	27.1141(10)
α [°]	101.257(4)	90	90	90
β [°]	111.742(3)	124.6180(10)	100.366(2)	99.684(4)
γ [°]	103.737(4)	90	90	90
V [Å^3]	4825.5(10)	9212.6(18)	9607.6(12)	9490.6(7)
Z	2	4	4	1
$D_{calcd.}$ [g cm^{-3}]	1.201	1.104	1.054	1.203
Absorption coefficient [mm^{-1}]	0.281	0.301	0.257	3.587
F(000)	1852	6792	3256	3586
θ range [°]	2.14 to 30.69	1.82 to 30.55	2.35 to 30.61	3.14 to 73.82
Measured reflections	90629	199998	83189	36043
Unique reflections	28363 [R_{int} = 0.0571]	26069 [R(int) = 0.0355]	14794 [R(int) = 0.0389]	18389 [R(int) = 0.0887]
Data/restraints/parameters	28363/80/1126	26069/18/982	14794/74/502	18389/ 144/1136
Goodness-of-fit on F^2	1.051	1.030	1.108	0.883
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0498, wR_2 = 0.1267	R_1 = 0.0666, wR_2 = 0.2053	R_1 = 0.0424, wR_2 = 0.1236	R_1 = 0.0689, wR_2 = 0.1530
R indices (all data)	R_1 = 0.0903, wR_2 = 0.1473	R_1 = 0.0861, wR_2 = 0.2236	R_1 = 0.0521, wR_2 = 0.1291	R_1 = 0.1674, wR_2 = 0.1944
Largest diff. peak/hole [e Å^{-3}]	1.357/–1.261	4.432/–1.044	1.395/–0.638	0.788/–1.257

1.51 (m, 8 H, CH_2, CNC$_6$H$_{11}$), 1.35 (s, 36 H, 4 CMe$_3$) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 165.7 (q, $J_{C,B}$ = 34.0 Hz), 151.0 (br.), 148.5, 148.0, 146.7, 140.6, 137.6, 132.0, 128.2, 125.9, 125.4, 121.9, 115.7, 56.1, 35.7, 34.5, 31.3, 22.7, 21.5 ppm. $C_{99}H_{125}BIrN_3O_6P_2$ (1718.04): calcd. C 69.21, H 7.33, N 2.45; found C 69.26, H 7.40, N 2.44.

[Ir(1)(η^2-C$_2$H$_4$)][BPh$_4$] (15): A slow flow of ethylene was bubbled into a suspension of [{Ir(μ-Cl)(η^2-C$_8$H$_{14}$)$_2$}$_2$] (0.045 g, 0.05 mmol) in methanol (15 mL) at room temperature for 1 h. Then the mixture was cooled to –40 °C and a solution of diphosphite (0.099 g, 0.1 mmol) in THF (2 mL) was added. After 20 min, NaBPh$_4$ (0.032 g, 0.1 mmol) was added and the mixture was stirred at –40 °C for 30 min. Diethyl ether was added (30 mL) and the resulting pale orange solid was washed with cold diethyl ether (3×10 mL) and vacuum-dried; yield 62% (0.047 g). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 143.7 (s) ppm. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 8.21 (br. s, 8 H, H arom., BPh$_4$), 7.75 (br. s, 4 H, H arom.), 7.51 (br. s, 4 H, H arom.), 7.37 (m, 8 H, H arom., BPh$_4$), 7.14 (m, 4 H, H arom., BPh$_4$), 6.65 (m, 1 H, H^a arom.), 5.83 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H^b arom.), 2.89 (br. s, 4 H, C$_2H_4$), 1.42 (s, 36 H, 4 CMe$_3$), 1.35 (s, 36 H, 4 CMe$_3$) ppm. ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]tetrahydrofurane, 213 K): δ = 164.7 (q, $J_{C,B}$ = 48.2 Hz), 157.4 (br.), 150.0, 147.6, 144.7, 140.2, 137.0, 130.6, 128.9, 127.2 (br.), 125.9, 121.9, 105.7 (br.), 44.6, 35.7, 34.6, 31.3 ppm. $C_{87}H_{107}BIrNO_6P_2$ (1527.73): calcd. C 68.40, H 7.06, N 0.92; found C 68.43, H 7.08, N 0.92.

General Hydrogenation Procedure: In a glovebox, the appropriate substrate (0.3 mmol), diphosphite **1** (3.15 μmol), [{IrCl(cod)}$_2$] (1.5 μmol) and the additive (30 μmol) in toluene (0.5 mL) were added to a 2 mL glass vial. Vials were placed in a model HEL CAT18 pressure reactor that holds up to eighteen reactions. The reactor was purged three times with H_2 and finally pressurized. After 24 h, the reactor was slowly depressurized, solutions were evaporated and conversions were determined by ^{1}H NMR spectroscopy.

X-ray Structure Determinations: Crystallographic data for complexes **6**–**8** were collected with a Bruker-Nonius X8Apex-II CCD diffractometer using graphite-monochromated Mo-$K_{\alpha1}$ radiation (λ = 0.71073 Å), whereas diffraction data for **12** were recorded with an Oxford Diffraction Xcalibur Nova diffractometer using Cu-K_α radiation (λ = 1.5418 Å). The data were reduced (SAINT)[29] and corrected for Lorentz polarization and absorption effects by multiscan method (SADABS).[30] Structures were solved by direct methods (SIR-2002)[31] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL 6.12).[32] A summary of cell parameters, data collection and structure solution and refinement is given in Table 3.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra (CD_2Cl_2, 500 MHz) of compound **8** showing the ethylene signal region at several temperatures and the ^{31}P{^{1}H} NMR spectra (CD_2Cl_2, 202 MHz) of **8** at several temperatures.

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