Synthesis, Structure, and Reactivity of New Rhodium and Iridium Complexes, Bearing a Highly Electron-Donating PNP System. Iridium-Mediated Vinylic C−H Bond Activation

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Reaction of the new highly electron-donating PNP ligand [2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine] (**1**) with $[Rh(COE)_2Cl]_2$ (COE = cyclooctene) at room temperature resulted in formation of the neutral Rh(I) complex [Rh(PNP)Cl] (**2**). Unsaturated cationic complexes $[Rh(PNP)(CH_3CN)]BF_4$ (**3**) and $[Rh(PNP)(C_2H_4)]SO_3CF_3$ (**4**) were obtained in reaction of **1** with $[(COE)_2Rh(CH_3CN)_2]BF_4$ and $[(C_2H_4)_2Rh(THF)_2]SO_3CF_3$, respectively. Upon reaction of the PNP ligand **1** with $[Ir(COE)_2Cl]_2$, facile vinylic C−H activation takes place, yielding the hydrido-vinyl complex $[ClIr(PNP)(H)(C_8H_{13})]$ (**5**). Also, coordination of ligand **1** to the cationic iridium complex $[Ir(COD)_2]BF_4$ (COD = cyclooctadiene) in RCN (R = CH_3, $CH(CH_3)_2$, $C(CH_3)_3$) led to iridium insertion into a vinylic C−H bond, resulting in complexes $[(RCN)Ir(PNP)(H)(C_8H_{11})]BF_4$ (**6a**−**c**). The hydrido-vinyl complexes **6a**,**c** readily react with H_2 (2 atm) at room temperature, affording the iridium dihydride complexes $[(RCN)Ir(PNP)(H)_2]BF_4$ (R = CH_3, $C(CH_3)_3$) (**7a**,**b**).

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Introduction

Multidentate ligands play an important role in transition metal chemistry, enhancing stability of complexes and allowing the manipulation of steric and electronic parameters which control reactivity at the metal center. An attractive multidentate ligand is a neutral mixed nitrogen-phosphorus tridentate ligand of the PNP type, in which the central pyridine-based ring donor contains phosphine substituents in the ortho positions.[1] Upon coordination to transition metals, the rigid bis-chelate framework may confer on such complexes interesting stoichiometric[2] and catalytic [3,5] reactivities. Although several PNP-based late transition metal complexes have been reported,[1−4] examples of the related Ir complexes are extremely scarce. To our knowledge, only one example of a PNP−Ir complex has been reported.[5] Moreover, in all PNP systems reported to date, the phosphine donors bear phenyl substituents. Following our interest in the chemistry of electron-rich tridentate PCP,[6] PCN,[7] and PCO[8] systems, we have synthesized a novel highly electron-donating PNP ligand bearing *tert*-butyl groups as substituents on the phosphines. We report here the synthesis, structure, and reactivity of new Rh and Ir complexes, bearing this PNP ligand [(2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine]. Significantly, in contrast to the reported $PNP(C_6H_5)$[9]-based Ir compound,[5] the new PNP−Ir complexes undergo facile vinylic C−H bond activation, resulting in metal hydrido-vinyl complexes. Such species are increasingly implicated in a number of interesting chemical transformations.[10,19a]

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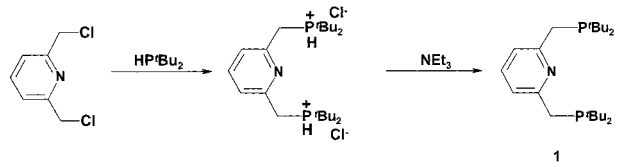
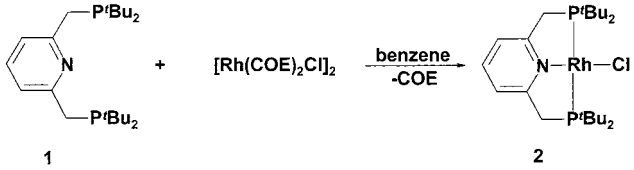
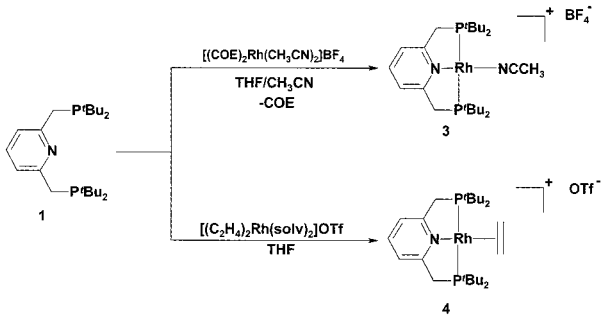
Scheme 1



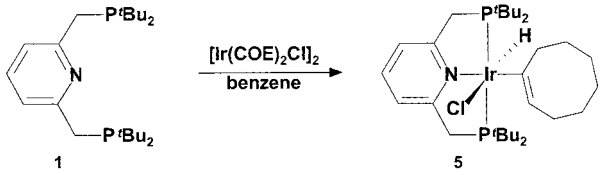
Scheme 2



Scheme 3



Scheme 4



Results and Discussion

Ligand Synthesis. The new PNP-type ligand **1** was synthesized from the commercially available 2,6-bis-(chloromethyl)pyridine. Reaction of this compound with 2 equiv of di-*tert*-butylphosphine resulted in the corresponding diphosphonium salt (Scheme 1), which was deprotonated with an excess of triethylamine, affording the crude PNP ligand. Purification of the reaction mixture by chromatography on a silica column yielded the pure compound **1** as a white solid in 79% yield.

Synthesis and Characterization of PNP-Based Rh Complexes. When a benzene solution of ligand **1** was slowly added at room temperature to $[(COE)_2RhCl]_2$ (COE = cyclooctene, 1 equiv), formation of the neutral PNP-based Rh chloride complex **2** was observed (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum shows one doublet at 59.28 ppm (J_{RhP} = 145 Hz), indicating that the two phosphorus atoms are magnetically equivalent and that the complex is symmetric. This is confirmed by the ^1H NMR spectrum, that shows the same chemical shift for both CH_2-P protons, which appear at 2.57 ppm as a virtual triplet due to coupling with the P and Rh atoms.

Interestingly, the dimeric byproduct $Rh_2Cl_2(PNP)_3$, which was found in the analogous reaction of PNP-(C_6H_5),[2a] was not observed here. Its formation is prevented, most likely, by the bulky substituents on the phosphine ligand.

Ligand **1** can also coordinate to cationic Rh precursors, resulting in stable PNP-based Rh(I) cationic complexes. A monomeric Rh species $[(COE)_2Rh(CH_3CN)_2]BF_4$ was prepared by chloride abstraction from $[(COE)_2RhCl]_2$ in CH_3CN.[11] This species reacted with ligand **1** to give, after stirring for 10 min at room temperature, the 16-e cationic rhodium complex **3** (Scheme 3). The rhodium center in this complex is stabilized by coordination of a CH_3CN molecule as a fourth ligand, as confirmed by IR spectroscopy ($\nu_{C\equiv N}$ = 2272 cm^{-1}). The phosphines exhibit a doublet at 67.95 ppm, ca. 8 ppm downfield from that observed for the neutral complex **2**. The tetrafluoroborate anion gives rise to a sharp singlet at 151.91 ppm in ^{19}F NMR, indicating a free, noncoordinated BF_4^-.

A similar reaction takes place with $[(C_2H_4)_2Rh(solv)_2]$-OTf, obtained by reaction of $[(C_2H_4)_2RhCl]_2$ with 2 equiv of AgOTf in THF. Upon reaction of this complex with the PNP ligand **1**, the cationic complex **4** was obtained as a red solid (Scheme 3). The ethylene protons appear at 3.42−3.47 ppm as a multiplet in the ^1H NMR spectrum, indicating coordination of C_2H_4 to the metal. The chemical shift is significantly upfield from that of free ethylene, indicating strong back-bonding from the metal to the olefin ligand. Complex **4** is similar to the analogous compound $[PNP(C_6H_5)Rh(C_2H_4)]OTf$, recently reported by Taube et al.[2c]

Synthesis and Characterization of PNP-Based Iridium Complexes. Iridium-Mediated Vinylic C−H Bond Activation. In contrast to the rhodium complexes **2**−**4**, the analogous iridium compounds exhibit high activity in vinylic C−H bond activation. Thus, reaction of the neutral iridium dimer $[(COE)_2IrCl]_2$ with ligand **1** results in facile room-temperature insertion of the metal into the C_{sp^2}−H bond of cyclooctene (Scheme 4).

The resulting hydrido-vinyl complex **5** was fully characterized by multinuclear NMR techniques. The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits a singlet at 39.58 ppm, indicating the existence of a N−Ir−H plane of symmetry. In the ^1H NMR spectrum the signal due to the hydride ligand appears at −22.54 ppm as a broad singlet. The cyclooctenyl ligand gives rise to a characteristic set of signals in the aliphatic area.

The molecular structure of **5** was confirmed by an X-ray diffraction study of colorless single crystals obtained by slow evaporation of its benzene solution. The crystal contains two independent, structurally analogous molecules in the asymmetric unit. An ORTEP drawing of one of these molecules is shown in Figure 1, and the averages of selected bond distances and bond angles for two independent molecules are given in Table 1.

The iridium atom of complex **5** is located in the center of a distorted octahedron with the hydride group occupying the position trans to the chloride. The metal−carbon(vinylic) bond distance is 2.094(8) Å, which is slightly longer then the only other known Ir(III)−cyclooctenyl bond distance (2.054(7) Å) in [IrH(HB-(pyrazolyl)$_3$)(σ-C_8H_{13})(η^2-C_8H_{14})].[12] However, the C=C

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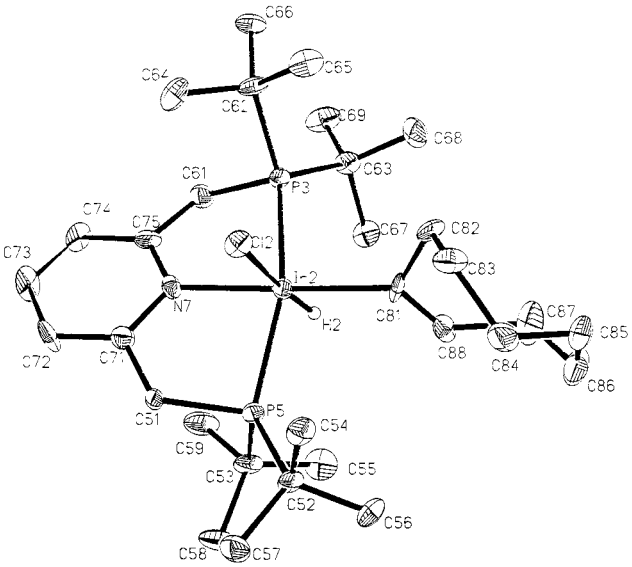
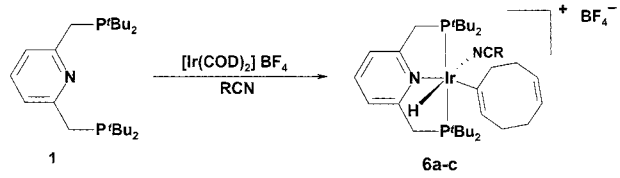


Figure 1. ORTEP drawing of a molecule of **5** (50% of probability). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 5

Ir(2)−N(7)	2.148(7)	Ir(2)−Cl(2)	2.536(2)
Ir(2)−C(81)	2.094(8)	Ir(2)−P(3)	2.335(2)
Ir(2)−P(5)	2.323(2)		
C(81)−Ir(2)−N(7)	178.6(3)	P(5)−Ir(2)−P(3)	157.18(8)
C(81)−Ir(2)−P(5)	101.3(3)	C(81)−Ir(2)−Cl(2)	95.0(3)
N(7)−Ir(2)−P(5)	79.6(2)	N(7)−Ir(2)−Cl(2)	85.93(19)
C(81)−Ir(2)−P(3)	97.1(3)	P(5)−Ir(2)−Cl(2)	93.81(8)
N(7)−Ir(2)−P(3)	81.86(19)	P(3)−Ir(2)−Cl(2)	98.09(8)

Scheme 5



6a: R=CH$_3$; 6b: R=CH(CH$_3$)$_2$; 6c: R=C(CH$_3$)$_3$

bond distance in **5** (1.329(12) Å) is practically identical to that in the latter complex (1.335(6) Å) as well as to the C═C bond length in free *trans*-cyclooctene (1.332(17) Å),[13] indicating that no significant interaction is present between the vinylic double bond and iridium. Notably, compound **5** represents the first example of a PNP-based Ir(III) complex.

As in the case of the neutral complex, cationic iridium complexes of the ligand **1** are also active in vinylic C−H activation. Thus, the compounds [(COD)Ir(RCN)$_2$]BF$_4$ (COD = cyclooctadiene; R = CH$_3$, HC(CH$_3$)$_2$, C(CH$_3$)$_3$), prepared by reaction of [(COD)$_2$IrCl]$_2$ with AgBF$_4$ in the corresponding alkyl nitrile, react with **1** at room temperature to give the Ir(III) hydrido-vinyl complexes **6a**−**c** in high yield (Scheme 5).

The compounds were fully characterized by multinuclear NMR spectroscopy. The ^{31}P{^{1}H} NMR spectra of **6a**−**c** show a broad signal at 23 °C. Also, the hydride protons appear as a very broad peak at an upfield region, indicating a dynamic behavior of these compounds. Variable-temperature NMR studies were carried out for compound **6a** in order to clarify the nature of the dynamic process. At −30 °C, two sharp singlets were observed by ^{31}P{^{1}H} NMR at 36.01 and 40.82 ppm, and the ^{1}H NMR spectrum showed two metal-hydride signals as triplets at −20.83 and −20.25 ppm. These observations indicate the presence of two species in equilibrium. Coalescence of the phosphine signals and that of the hydrides took place at around +30 °C. Only one clear triplet at −20.57 ppm for Ir-*H* and a sharp singlet in the ^{31}P NMR spectrum at 39.72 ppm were observed at elevated temperatures (+70 °C). The reversible coordination of the CH$_3$CN molecule in **6a** is, most likely, responsible for the presence of the two equilibrating complexes in solution. The possible dissociation of the nitrile ligand is supported by the observation of an easy exchange of *tert*-butylnitrile in **6c** with CH$_3$CN when the complex is dissolved in the latter. Spin saturation transfer experiments indicated that an equilibrium between **6a** and the corresponding Ir(I)-olefin species is unlikely at room temperature.

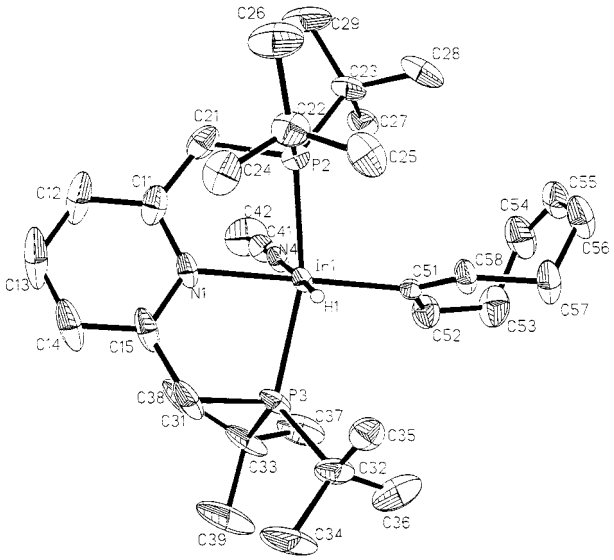


Figure 2. ORTEP drawing of a molecule of **6a** (50% of probability). Hydrogen atoms and BF_4^- are omitted for clarity

The molecular structures of **6a** and **6b** were confirmed by X-ray diffraction studies. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a benzene solution in both cases. The structures display a distorted octahedral geometry around the metal, with the PNP ligand coordinated in a meridional fashion (Figures 2 and 3). The hydride is located trans to the nitrile ligand, and the cyclooctadienyl unit is trans to the pyridinic ring in both molecules. The bond distances and bond angles in complexes **6a** and **6b** are very similar. Selected values are given in Tables 2 and 3.

Complexes **5** and **6a**−**c** represent a second example of PNP-based iridium complexes. The only reported PNP-Ir complex, the monovalent [(PNP)Ir(η^2-COD)]-ClO$_4$, was synthesized by reaction of the corresponding cationic iridium precursor with PNP(C$_6$H$_5$).[5] Interestingly, this compound coordinates cyclooctadiene in an η^2 fashion and does not undergo vinylic C−H activation. Thus, changing the phenyl substituents on the phosphines in the PNP system to the more electron-donating *tert*-butyl groups sufficiently increases the electron density on the iridium center to make it highly active

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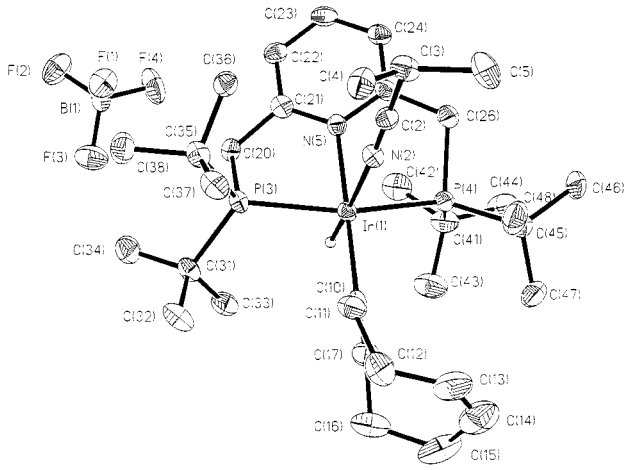


Figure 3. ORTEP drawing of a molecule of **6b** (50% of probability). Hydrogen atoms (except Ir-H) and BF_4^- are omitted for clarity

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 6a

Ir(1)−N(4)	2.127(4)	Ir(1)−N(1)	2.147(3)
Ir(1)−C(51)	2.091(4)	Ir(1)−P(3)	2.3225(12)
Ir(1)−P(2)	2.3184(13)		
C(51)−Ir(1)−N(4)	93.30(14)	N(1)−Ir(1)−P(2)	80.19(11)
C(51)−Ir(1)−N(1)	179.75(16)	C(51)−Ir(1)−P(3)	97.62(11)
N(4)−Ir(1)−N(1)	86.78(13)	N(4)−Ir(1)−P(3)	98.28(9)
C(51)−Ir(1)−P(2)	100.05(11)	N(1)−Ir(1)−P(3)	82.13(11)
N(4)−Ir(1)−P(2)	92.34(10)	P(3)−Ir(2)−P(2)	158.79(4)

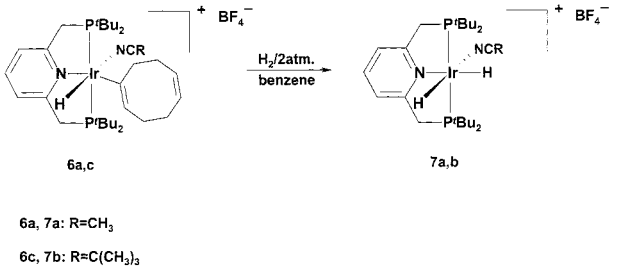
Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 6b

Ir(1)−N(2)	2.134(4)	Ir(1)−N(5)	2.149(3)
Ir(1)−C(10)	2.101(4)	Ir(1)−P(3)	2.3348(12)
Ir(1)−P(4)	2.3234(12)	Ir(1)−H(1)	1.43(4)
C(10)−Ir(1)−N(2)	95.71(15)		
C(10)−Ir(1)−N(5)	178.25(15)	N(5)−Ir(1)−P(4)	80.20(9)
N(2)−Ir(1)−N(5)	86.04(13)	C(10)−Ir(1)−P(3)	98.16(12)
C(10)−Ir(1)−P(4)	99.61(12)	N(2)−Ir(1)−P(3)	97.61(10)
N(2)−Ir(1)−P(4)	91.95(10)	N(5)−Ir(1)−P(3)	81.69(9)
C(10)−Ir(1)−H(1)	88.1(17)	P(3)−Ir(2)−P(4)	158.85(4)
N(2)−Ir(1)−H(1)	176.2(17)	P(4)−Ir(1)−H(1)	87.5(17)
N(5)−Ir(1)−H(1)	90.2(17)	P(3)−Ir(1)−H(1)	81.7(17)

in C−H oxidative addition. Notably, a closely related PCP-based iridium system bearing *tert*-butyl substituents on the phosphines was also active in C_{sp^2}−H activation.[14]

It should be noted that Ir(I) complexes were not observed in the reactions leading to the formation of **5** and **6a**−**c**; only stable metal hydrido-vinyl species were detected. Such species are proposed as active intermediates in various metal-catalyzed processes, such as C−C coupling,[15] deuteration of vinylic protons,[16] and dimerization of olefins.[17] Hydrido-vinyl compounds can be obtained from Ir(I) and an olefin both photochemically[18,19a] and thermally.[12,18b,19] Many Ir(H)(vinyl) species are kinetic rather than thermodynamic products, rearranging to a more stable Ir(I)(η^2-olefin) at elevated

Scheme 6



temperatures.[18a,c,19b] Compounds **5** and **6a**−**c** are very likely thermodynamic products, because they are obtained, most probably, from the corresponding (PNP)-Ir(I)-olefin intermediates. Moreover, complex **6a** was stable upon heating to 70 °C. Other examples of thermodynamically stable metal hydrido-vinyl compounds were reported.[12,19a,20]

Reaction of Complex 6 with H_2. Formation of (PNP)-Ir Dihydride Species. Recently it was demonstrated that a PCP-based Ir(III) dihydride complex can be used as a catalyst for dehydrogenation of hydrocarbons.[21] To prepare a related PNP-based iridium dihydride derivative, we have explored the reaction of **6** with H_2.

When compounds **6a**,**c** were reacted with 2 atm of hydrogen, formation of the *cis*-dihydride complexes **7a**,**b** was observed by NMR after 18 h (Scheme 6).

Complex **7a** gives rise to two high-field signals at −20.97 and −19.40 ppm in the ^{1}H NMR spectrum, indicating a mutually cis-configuration of the hydride ligands. These signals, which are broad at room temperature, appear at −30 °C as two clear double triplets. Upon raising the temperature, the hydride signals shift toward each other and a coalescence is observed at about +50 °C. Thus, exchange of the hydrides takes place at room temperature or above, probably involving reversible dissociation of the acetonitrile ligand. Complex **7b** exhibits similar NMR characteristics.

Colorless single crystals of **7a** suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution. The geometry around the iridium atom in this complex is distorted octahedral, with the two hydrides occupying mutually cis positions (Figure 4). Selected bond lengths and bond angles are given in Table 4.

Reaction of complex **7a** with D_2 led to H/D exchange, forming an $Ir(D)_2$ complex. One of the possible mechanisms for this reaction may involve generation of an Ir(I) intermediate by a possible $Ir(H)_2 = Ir(H_2)$ equilibrium. If this equilibrium is operative, reaction with an H_2/D_2 mixture should lead to the formation of the $Ir(D)_2$

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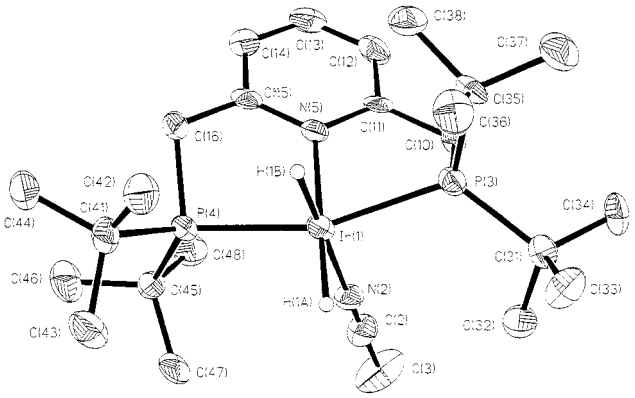

Figure 4. ORTEP drawing of a molecule of **7a** (50% of probability). Hydrogen atoms (except Ir-H) and BF_4^- are omitted for clarity

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 7a

Ir(1)−N(2)	2.101(6)	Ir(1)−N(5)	2.145(5)
Ir(1)−H(1A)	1.65(7)	Ir(1)−P(3)	2.3150(18)
Ir(1)−P(4)	2.3123 (19)	Ir(1)−H(1B)	1.55(6)
H(1B)−Ir(1)−N(2)	179(2)		
H(1B)−Ir(1)−N(5)	91(2)	N(5)−Ir(1)−P(4)	82.80(15)
N(2)−Ir(1)−N(5)	89.7(2)	H(1B)−Ir(1)−P(3)	87(2)
H(1B)−Ir(1)−P(4)	83(2)	N(2)−Ir(1)−P(3)	92.79(16)
N(2)−Ir(1)−P(4)	97.16(16)	N(5)−Ir(1)−P(3)	81.12(15)
H(1B)−Ir(1)−H(1A)	85(3)	P(3)−Ir(2)−P(4)	161.02(6)
N(2)−Ir(1)−H(1A)	94(2)	P(4)−Ir(1)−H(1A)	98(2)
N(5)−Ir(1)−H(1A)	176(2)	P(3)−Ir(1)−H(1A)	97(2)

complex (in addition to the starting $Ir(H)_2$) as the only product. However, reaction of **7a** with 1:1 H_2/D_2 led to formation of mixed Ir(H)(D) derivatives together with $Ir(D)_2$ as observed by ^1H and ^2H NMR spectroscopy. Thus, the possibility of an Ir(I)-mediated (reductive elimination−oxidative addition) mechanism in the reaction of **7a** with D_2 is unlikely. The reaction products might be formed by σ-bond metathesis or by involvement of an Ir(V) intermediate such as $(PNP)Ir(H)_4$,[22] formed by oxidative addition of H_2. The reversible formation of a similar $(PCP)Ir(H)_3$(vinyl) species was also observed in the reaction of $(PCP)Ir(H)_2$ with *tert*-butylethylene.[23] Furthermore, a mechanism involving Ir(V) intermediates was proposed for Ir(III)-mediated C−H bond actvation.[24]

Summary

Rh and Ir complexes bearing a new highly electron-donating PNP ligand were synthesized. The latter complexes represent the first examples of PNP-based Ir(III) compounds. The PNP-Ir complexes are highly active in vinylic C−H bond activation, resulting in thermodynamically stable hydrido-vinyl compounds. The new (PNP)Ir(III) compounds can easily activate H_2 under mild conditions. Our efforts are currently directed toward investigation of the reactivity of such compounds in the activation of various strong bonds and their catalytic activity.

(22) Likewise, reaction of **6a** with H_2 might involve an Ir(V) complex such as $(PNP)Ir(H)_3$(cyclooctadienyl).
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Experimental Section

General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The complexes $[Rh(COE)_2Cl]_2$,[25] $[Rh(C_2H_4)_2Cl]_2$,[26] and $[(COE)_2IrCl]_2$[27] were prepared according to literature procedures.

^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at 400, 100, 376, and 162 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 23 °C. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.15 ppm, benzene; 7.24 ppm, chloroform; 1.96 ppm, acetonitrile; 5.32 ppm, dichloromethane). In $^{13}C\{^1H\}$ NMR measurements the signals of C_6D_6 (128.0 ppm), $CDCl_3$ (77.0 ppm), CD_3CN (1.3 ppm), and CD_2Cl_2 (53.8 ppm) were used as a reference. ^{31}P NMR chemical shifts are reported in parts per million downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. ^{19}F NMR chemical shifts were referenced to C_6F_6 (−163 ppm). Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet, v, virtual. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Germany.

Synthesis of 2,6-Bis(di-*tert*-butylphosphinomethyl)-pyridine (1). Di-*tert*-butylphosphine (1.25 g, 8.6 mmol) was added dropwise to a suspension of 2,6-bis(chloromethyl)-pyridine (710 mg, 4.0 mmol) in methanol (3 mL). The mixture was heated to 45 °C for 2 days. After cooling to room temperature, triethylamine (1.25 mL) was added slowly, and a white precipitate was formed. The solvent was evaporated under vacuum, and compound **1** was isolated from the residue by column chromatography (silica, solvent: chloroform) as a white solid (second fraction). Yield: 1.25 g (79%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 37.49 (s). ^1H NMR ($CDCl_3$): 1.14 (d, $^3J_{PH}$ = 11.0 Hz, 36H, $PC(CH_3)_3$), 3.01 (d, $^2J_{PH}$ = 3.3 Hz, 4H, CH_2P), 7.25 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyridine-H3,5), 7.47 (dd, $^3J_{HH}$ = 7.8 Hz, 1H, pyridine-H4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 29.69 (d, $^2J_{PC}$ = 13.2 Hz, $PC(CH_3)_3$), 31.67 (d, $^1J_{PC}$ = 23.4 Hz, CH_2P), 31.83 (d, $^1J_{PC}$ = 21.4 Hz, CH_2P), 120.69 (dd, $^3J_{PC}$ = 10.8 Hz, $^5J_{PC}$ = 1.35 Hz, pyridine-C3,5), 136.08 (s, pyridine-C4), 161.89 (d, $^2J_{PC}$ = 14.6 Hz, pyridine-C2,5) (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). MS (EI), *m*/*z* (%): 396 (5) [M^+], 338 (100) [$M^+ - C(CH_3)_3$]. Anal. Calcd: C, 69.75; H, 10.87. Found: C, 69.36; H, 11.08.

Reaction of the PNP Ligand 1 with $[Rh(COE)_2Cl]_2$. Formation of $[C_5H_3N(CH_2P(tBu)_2)_2]RhCl$ (2). A benzene solution of **1** (0.5 mL, 27 mg, 38 mmol) was added within 5 min. to a stirred solution of $[Rh(COE)_2Cl]_2$ (30 mg, 76 mmol) in benzene (1.5 mL). The color changed to red and finally to brown. The solvent was removed under vacuum, and the residue was washed with pentane, resulting in the pure compound **2**. Yield: 14 mg (35%). $^{31}P\{^1H\}$ NMR (C_6D_6): 59.28 (d, $^1J_{RhP}$ = 145 Hz). ^1H NMR (C_6D_6): 1.46 (vt, J_{PH} = 6.4 Hz, 36H, $PC(CH_3)_3$), 2.57 (vt, J_{PH} = 3.4 Hz, 4H, CH_2P), 6.31 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyridine-H3,5), 6.92 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyridine-H4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 29.49 (vt, J_{PC} = 3.6 Hz,

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PC(CH_3)$_3$), 34.83 (dvt, J_{PC} = 5.0 Hz, $^2J_{RhC}$ = 1.6 Hz, PC(CH$_3$)$_3$), 36.44 (dvt, J_{PC} = 5.0 Hz, $^2J_{RhC}$ = 1.0 Hz, CH$_2$P), 119.75 (dvt, J_{PC} = 5.4 Hz, $^2J_{RhC}$ = 1.5 Hz, pyridine-C3,5), 128.35 (s, pyridine-C4), 164.29 (dvt, J_{PC} = 6.5 Hz, $^2J_{RhC}$ = 1.4 Hz, pyridine-C2,6) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). Anal. Calcd: C, 51.69; H, 8.05. Found: C, 51.87; H, 7.95.

Reaction of the PNP Ligand 1 with [(COE)$_2$Rh(CH$_3$CN)$_2$]BF$_4$. Formation of [C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$Rh(CH$_3$CN)]BF$_4$ (3). A THF solution of **1** (0.5 mL, 15 mg, 38 mmol) was added to a solution of [(COE)$_2$Rh(CH$_3$CN)$_2$]BF$_4$ (14.5 mg, 38 mmol) in acetonitrile (1.0 mL). The mixture was stirred for 10 min. The solvent was removed under vacuum, and the residue was washed with pentane. Yield: 16 mg (67%). ^{31}P{^{1}H} NMR (CD$_3$CN): 67.95 (d, $^1J_{RhP}$ = 137 Hz). ^{1}H NMR (CD$_3$CN): 1.37 (vt, J_{PH} = 6.7 Hz, 36H, PC(CH_3)$_3$), 3.43 (vt, J_{PH} = 3.8 Hz, 4H, CH_2P), 7.25 (d, $^3J_{HH}$ = 7.8 Hz, 2H, pyridine-H3,5), 7.63 (t, $^3J_{HH}$ = 7.8 Hz, 1H, pyridine-H4). ^{13}C{^{1}H} NMR (CD$_3$CN): 29.90 (vt, J_{PC} = 3.4 Hz, PC(CH_3)$_3$), 36.07 (dvt, J_{PC} = 7.6 Hz, $^2J_{RhC}$ = 1.6 Hz, PC(CH$_3$)$_3$), 36.30 (dvt, J_{PC} = 7.6 Hz, $^2J_{RhC}$ = 0.7 Hz, CH$_2$P), 122.04 (dvt, J_{PC} = 5.6 Hz, $^2J_{RhC}$ = 1.1 Hz, pyridine-C3,5), 137.13 (vt, J_{PC} = 1.1 Hz, pyridine-C4), 167.18 (dvt, J_{PC} = 6.1 Hz, $^2J_{RhC}$ = 1.6 Hz, pyridine-C2,6) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). Anal. Calcd: C, 47.94; H, 7.40. Found: C, 48.11; H, 7.34.

Reaction of the PNP Ligand 1 with [(C$_2$H$_4$)$_2$Rh(solv)$_2$]OTf. Formation of [C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$Rh(C$_2$H$_4$)]OTf (4). AgOTf (7.0 mg, 27 μmol) was added to a suspension of [Rh(C$_2$H$_4$)$_2$Cl]$_2$ (5.5 mg, 14 μmol) in THF (0.5 mL). The dark mixture was stirred for 10 min and filtered over Celite. A suspension of **1** (10 mg, 25 μmol) in THF (0.5 mL) was added to the filtrate, and the mixture was stirred for another 3 h. The solvent was removed under vacuum, and the red residue was washed with pentane and ether. Yield: 6 mg (39%). ^{31}P{^{1}H} NMR (CD$_3$CN): 65.04 (d, $^1J_{RhP}$ = 121 Hz). ^{1}H NMR (C$_6$D$_6$): 1.01 (vt, J_{PH} = 6.5 Hz, 36H, PC(CH_3)$_3$), 3.42−3.47 (m, 4H, CH$_2$CH$_2$), 3.60 (vt, J_{PH} = 3.6 Hz, 4H, CH_2P), 7.60 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyridine-H3,5), 8.07 (t, $^3J_{HH}$ = 7.8 Hz, 1H, pyridine-H4). MS (EI), m/z (%): 526 (100) [M$^+$ − OTf].

Reaction of the PNP Ligand 1 with [Ir(COE)$_2$Cl]$_2$. Formation of [C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$]IrH(C$_8$H$_{13}$)Cl (5). A benzene solution (0.5 mL) of **1** (20 mg, 51 μmol) was added within 30 min to a suspension of [Ir(COE)$_2$Cl]$_2$ (23 mg, 26 μmol) in benzene (1.5 mL). The mixture was stirred for 24 h, after which the color changed to red and a colorless precipitate was formed. The precipitate was filtered off and washed with a little pentane. Yield: 25 mg (68%). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 39.58 (s). ^{1}H NMR (CD$_2$Cl$_2$): −22.54 (bs, 1H, Ir-H), 1.21 (vt, J_{PH} = 6.4 Hz, 18H, PC(CH_3)$_3$), 1.43 (vt, J_{PH} = 6.4 Hz, 18H, PC(CH_3)$_3$), 1.99−2.05 (m, 3H, cyclooctene-CH_2), 2.72−2.75 (m, 2H, cyclooctene-CH_2), 3.28−3.34 (m, 2H, cyclooctene-CH_2), 3.95 (vt, J_{PH} = 3.4 Hz, 2H, CH_2P), 3.99 (vt, J_{PH} = 3.4 Hz, 2H, CH_2P), 5.86 (t, $^4J_{PH}$ = 7.3 Hz, 1H, cyclooctene-H), 7.21 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyridine-H3,5), 7.55 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyridine-H4). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 29.18 (s, PC(CH_3)$_3$), 30.36 (s, PC(CH_3)$_3$), 38.61 (vt, J_{PC} = 7.9 Hz, PC(CH$_3$)$_3$), 39.87 (vt, J_{PC} = 10.8 Hz, CH$_2$P), 119.20 (vt, J_{PC} = 3.9 Hz, pyridine-C3,5), 136.20 (s, pyridine-C4), 162.97 (vt, J_{PC} = 2.2 Hz, pyridine-C2,6) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). MS (EI), m/z (%): 698 (100) [M$^+$ − Cl], 588 (80) [M$^+$ − Cl − C(CH)(CH$_2$)$_6$]. Anal. Calcd: C, 50.77; H, 7.84. Found: C, 50.85; H, 7.78.

Reaction of the PNP Ligand 1 with Ir(COD)$_2$BF$_4$ in Acetonitrile. Formation of [(C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$)IrH(C$_8$H$_{11}$)(NCCH$_3$)]BF$_4$ (6a). Ligand **1** (75 mg, 190 mmol) was added slowly to a solution of Ir(COD)$_2$BF$_4$ (94 mg, 190 mmol) in acetonitrile (5 mL). The mixture was stirred for 24 h, after which the color changed to light red. The solvent was removed under vacuum, and the residue was washed with pentane and diethyl ether. Yield: 137 mg (88%). ^{31}P{^{1}H} NMR (CD$_3$CN): 40.96 (s). ^{1}H NMR (CD$_3$CN): −20.35 (bs, 1H, Ir-H), 1.21 (vt, J_{PH} = 6.7 Hz, 18H, PC(CH_3)$_3$), 1.33 (vt, J_{PH} = 6.7 Hz, 18H, PC(CH_3)$_3$), 2.15 (s, 3H, IrNCCH$_3$), 2.15−2.74 (m, 8H, cyclooctadiene-CH$_2$), 3.71 (m, 4H, CH_2P), 5.40−5.90 (m, 3H, cyclooctadiene-CH), 7.42 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyridine-H3,5), 7.74 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyridine-H4). ^{13}C{^{1}H} NMR (CD$_3$CN): 29.83 (s, PC(CH_3)$_3$), 30.52 (s, PC(CH_3)$_3$), 38.02 (vt, J_{PC} = 12.2 Hz, PC(CH$_3$)$_3$), 40.54 (vt, J_{PC} = 11.9 Hz, CH$_2$P), 121.95 (vt, J_{PC} = 4.0 Hz, pyridine-C3,5), 139.54 (s, pyridine-C4), 164.40 (s, pyridine-C2,6) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). MS (ESI), m/z (%): 588 (100) [M$^+$ − BF$_4$ − CH$_3$CN − C(CH)$_3$(CH$_2$)$_4$], 532 (22) [M$^+$ − BF$_4$ − CH$_3$CN − C(CH)$_3$(CH$_2$)$_4$ − C(CH$_3$)$_3$]. Anal. Calcd: C, 48.11; H, 7.10. Found: C, 47.96; H, 7.14.

Reaction of the PNP Ligand 1 with Ir(COD)$_2$BF$_4$ in Isopropyl Cyanide. Formation of [(C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$)IrH(C$_8$H$_{11}$)(NCCH(CH$_3$)$_2$)]BF$_4$ (6b). Ligand **1** (50 mg, 126 mmol) was added in portions to a solution of Ir(COD)$_2$BF$_4$ (62.5 mg, 126 mmol) in isopropyl cyanide (2.5 mL). The mixture was stirred for 24 h. During the reaction the color changed first to red and became colorless again after 1 h. The solvent was distilled off, and the residue was washed with pentane, diethyl ether, and a small portion of benzene. Yield: 72.4 mg (66%). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 40.91 (s). ^{1}H NMR (CD$_2$Cl$_2$): −20.09 (bs, 1H, Ir-H), 1.23 (vt, J_{PH} = 6.8 Hz, 18H, PC(CH_3)$_3$), 1.28 (d, J_{PH} = 6.7 Hz, 6H, (CH_3)$_2$CHCN), 1.36 (vt, J_{PH} = 6.8 Hz, 18H, PC(CH$_3$)$_3$), 2.15−2.71 (m, 8H, cyclooctadiene-CH$_2$), 2.97 (m, 1H, (CH$_3$)$_2$CHCN), 3.60−3.66 (m, 4H, CH_2P), 5.43−5.95 (m, 3H, cyclooctadiene-CH), 7.45 (d, $^3J_{HH}$ = 7.8 Hz, 2H, pyridine-H3,5), 7.75 (t, $^3J_{HH}$ = 7.8 Hz, 1H, pyridine-H4). ^{13}C{^{1}H} NMR (400 MHz, CD$_2$Cl$_2$): 19.31 (s, (CH_3)$_2$CHCN), 29.24 (s, PC(CH_3)$_3$), 29.90 (s, PC(CH_3)$_3$), 37.19 (vt, J_{PC} = 12.2 Hz, PC(CH$_3$)$_3$), 39.80 (vt, J_{PC} = 11.3 Hz, CH$_2$P), 121.12 (s, pyridine-C3,5), 138.78 (s, pyridine-C4), 162.68 (s, pyridine-C2,6) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). MS (ESI), m/z (%): 696 (12) [M$^+$ − BF$_4$ − (CH$_3$)$_2$CHCN], 588 (100) [M$^+$ − BF$_4$ − (CH$_3$)$_2$CHCN − C(CH)$_3$(CH$_2$)$_4$], 531 (21) [M$^+$ − BF$_4$ − (CH$_3$)$_2$CHCN − C(CH)$_3$(CH$_2$)$_4$ − C(CH$_3$)$_3$]. IR (KBr): ν 2255 cm^{-1} (CN). Anal. Calcd: C, 49.35; H, 7.34. Found: C, 49.22; H, 7.40.

Reaction of the PNP Ligand 1 with Ir(COD)$_2$BF$_4$ in *tert*-Butyl Cyanide. Formation of [(C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$)IrH(C$_8$H$_{11}$)(NCC(CH$_3$)$_3$)]BF$_4$ (6c). Ligand **1** (50 mg, 126 μmol) was added in portions to a solution of Ir(COD)$_2$BF$_4$ (63 mg, 126 μmol) in *tert*-butyl cyanide (2.5 mL). The mixture was stirred 24 h. During the reaction the color changed first to red and became colorless again after 1 h. The solvent was removed under vacuum, and the residue was washed with pentane and diethyl ether. Yield: 64 mg (59%). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 41.14 (s). ^{1}H NMR (CD$_2$Cl$_2$): −20.06 (bs, 1H, Ir-H), 1.23 (vt, J_{PH} = 6.8 Hz, 18H, PC(CH_3)$_3$), 1.32 (s, 9H, (CH_3)$_3$CCN), 1.36 (vt, J_{PH} = 6.8 Hz, 18H, PC(CH_3)$_3$), 2.14−2.70 (m, 8H, cyclooctadiene-CH$_2$), 3.61 (s, 4H, CH$_2$P), 5.44−5.98 (m, 3H, cyclooctadiene-CH), 7.47 (d, $^3J_{HH}$ = 7.8 Hz, 2H, pyridine-H3,5), 7.77 (t, $^3J_{HH}$ = 7.8 Hz, 1H, pyridine-H4). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 27.75 (s, (CH_3)$_3$CCN), 29.21 (s, PC(CH_3)$_3$), 30.33 (s, PC(CH_3)$_3$), 37.20 (vt, J_{PC} = 12.2 Hz, PC(CH$_3$)$_3$), 39.63 (vt, J_{PC} = 11.2 Hz, CH$_2$P), 121.17 (s, pyridine-C3,5), 138.94 (s, pyridine-C4), 162.55 (s, pyridine-C2,6) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). MS (ESI), m/z (%): 588 (100) [M$^+$ − BF$_4$ − (CH$_3$)$_3$CCN − C(CH)$_3$(CH$_2$)$_4$], 531 (20) [M$^+$ − BF$_4$ − (CH$_3$)$_3$CCN − C(CH)$_3$(CH$_2$)$_4$ − C(CH$_3$)$_3$]. IR (KBr): ν 2298 cm^{-1} (CN). Anal. Calcd: C, 49.95; H, 7.46. Found: C, 50.11; H, 7.55.

Reaction of [(C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$)IrH(C$_8$H$_{11}$)(NCCH$_3$)]BF$_4$ (6a) with H$_2$. Formation of [(C$_5$H$_3$N(CH$_2$P(tBu)$_2$)$_2$)Ir(H)$_2$(NCCH$_3$)]BF$_4$ (7a). An acetonitrile solution (3 mL) of **6a** (50 mg, 61 μmol) was loaded into a Fischer−Porter pressure tube, charged with 2.0 bar (200 kPa) H$_2$, and stirred at room temperature for 18 h. The solvent was evaporated, and the colorless residue was washed with pentane. Yield: 27 mg

(62%). $^{31}P\{^1H\}$ NMR (CD_3CN): 59.49 (s). ^1H NMR (CD_2Cl_2): −20.97 (bs, 1H, Ir-*H*), −19.40 (bs, 1H, Ir-*H*), 1.28 (s, 36H, PC(CH_3)$_3$), 3.68−3.74 (m, 4H, CH_2P), 7.47 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyridine-H3,5), 7.75 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyridine-H4). $^{13}C\{^1H\}$ NMR (CD_3CN): 29.89 (s, PC(CH_3)$_3$), 36.90 (s, PC(CH_3)$_3$), 40.93 (vt, J_{PC} = 10.6 Hz, CH_2P), 121.91 (vt, J_{PC} = 4.3 Hz, pyridine-C3,5), 139.28 (s, pyridine-C4), 164.95 (vt, J_{PC} = 3.1 Hz, pyridine-C2,6) (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). MS (ESI), *m*/*z* (%): 588 (100) [M^+ − BF_4 − CH_3CN − H_2], 574 (24) [M^+ − BF_4 − CH_3CN − H_2 − CH_3]. Anal. Calcd: C, 41.84; H, 6.74. Found: C, 41.73; H, 6.71.

Reaction of [($C_5H_3N(CH_2P(tBu)_2)_2$)IrH(C_8H_{11})(NCCH$_3$)$_3$)]BF_4 (6c) with H_2. Formation of [($C_5H_3N(CH_2P(tBu)_2)_2$)Ir(H)$_2$(NCCH$_3$)]BF_4 (7b). A benzene solution (4 mL) of **6c** (15 mg, 17 mmol) was loaded into a Fischer−Porter pressure tube, charged with 3.0 bar (300 kPa) H_2, and stirred at room temperature for 18 h. The solvent was evaporated, and the colorless residue was washed with pentane. Yield: 2.7 mg (21%). $^{31}P\{^1H\}$ NMR (C_6D_6): 61.12 (s). ^1H NMR (250 MHz, C_6D_6): −21.01 (s, 1H, Ir-*H*), −19.10 (s, 1H, Ir-*H*), 0.93 (s, 9H, (CH_3)$_3$CCN), 0.98−1.39 (m, 36H, PC(CH_3)$_3$), 3.58−4.09 (m, 4H, CH_2P), 7.46 (d, $^3J_{HH}$ = 7.7 Hz, 2H, pyridine-H3,5), 7.68 (t, $^3J_{HH}$ = 7.7 Hz, 1H, pyridine-H4).

X-ray Crystal Structure Determination of 5, 6a,b, and 7a. Colorless crystals of complexes **5**, **6a**,**b**, and **7a** were obtained by slow evaporation of their benzene solutions. The crystals were mounted on the nylon loop and flash frozen in a nitrogen stream at 120 K. Data were collected on a Nonius KappaCCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The four structures were solved using direct methods with SHELXS-97 and refined by full-matrix least-squares technique with SHELXL-97 based on F^2.

Complex 5: 2($C_{31}H_{56}NP_2ClIr$)+2(C_6H_6), colorless plates, 0.2 × 0.1 × 0.1 mm^3, monoclinic, *C*2/*c* (No. 15), a = 35.238(7) Å, b = 11.561(2) Å, c = 35.895(7) Å, β = 99.51(3)°, V = 14422(5) Å^3, Z = 8, fw = 771.41, D_c = 1.421 Mg/m^3, μ = 3.888 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.048 for data with $I > 2\sigma(I)$ and R = 0.070 for all data (10 127 reflections) with a goodness-of-fit of 0.949. Idealized hydrogen atoms were placed and refined in the riding mode.

Complex 6a: $C_{33}H_{55}N_2P_2Ir+BF_4+1/2(C_6H_6)+1/2(H_2O)$, colorless plates, 0.3 × 0.15 × 0.05 mm^3, orthorhombic, *Fddd* (No. 70), a = 27.020(5) Å, b = 28.044(6) Å, c = 41.915(8) Å, V = 31761(11) Å^3, Z = 32, fw = 867.79, D_c = 1.452 Mg/m^3, μ = 3.490 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.033 for data with $I > 2\sigma(I)$ and R = 0.054 for all data (7817 reflections) with a goodness-of-fit of 1.123. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H1 (Ir−H), which was located in the difference map and refined independently.

Complex 6b: $C_{35}H_{66}N_2P_2Ir+BF_4+C_6H_6$, colorless, parallelogram, 0.4 × 0.1 × 0.1 mm^3, monoclinic, *P*2(1)/*c* (No. 14), a = 21.268(4) Å, b = 10.623(2) Å, c = 19.277(4) Å, β = 96.17(3)°, V = 4330.0(15) Å^3, Z = 4, fw = 933.96, D_c = 1.433 Mg/m^3, μ = 3.204 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.035 for data with $I > 2\sigma(I)$ and R = 0.050 for all data (8501 reflections) with a goodness-of-fit of 1.008. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H1 (Ir−H), which was located in the difference map and refined independently.

Complex 7a: $C_{25}H_{48}N_2P_2Ir+BF_4$, colorless, thin plates, 0.3 × 0.2 × 0.01 mm^3, monoclinic, *P*2(1)/*c* (No. 14), a = 16.996(3) Å, b = 10.584(2) Å, c = 18.266(4) Å, β = 108.75(3)°, V = 3111.3(11) Å^3, Z = 4, fw = 717.60, D_c = 1.532 Mg/m^3, μ = 4.434 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.034 for data with $I > 2\sigma(I)$ and R = 0.071 for all data (4460 reflections) with a goodness-of-fit of 1.004. Idealized hydrogen atoms were placed and refined in the riding mode.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **5**, **6a**, **6b**, and **7a**. This material is available free of charge via the Internet at http//pubs.acs.org.

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