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Reactions of Hydridoirida-β-diketones with Amines or with 2-Aminopyridines: Formation of Hydridoirida-β-ketoimines, PCN Terdentate Ligands, and Acyl Decarbonylation

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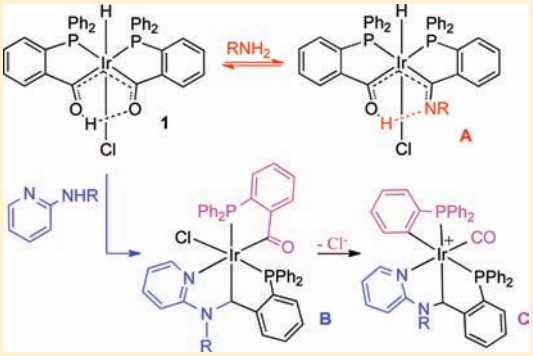
Supporting Information

ABSTRACT: The hydridoirida-β-diketone [IrHCl{(PPh_2(o-C_6H_4CO))$_2$H}] (**1**) reacts with benzylamine ($C_6H_5CH_2NH_2$) to give the hydridoirida-β-ketoimine [IrHCl{(PPh_2(o-C_6H_4CO))(PPh_2(o-$C_6H_4CNCH_2C_6H_5$))H}] (**2**), stabilized by an intramolecular hydrogen bond. **2** reacts with water to undergo hydrolysis and amine coordination giving hydridodiacylamino [IrH(PPh_2(o-C_6H_4CO))$_2$($C_6H_5CH_2NH_2$)] (**3**). Cyclohexylamine or dimethylamine lead to hydridodiacylamino [IrH(PPh_2(o-C_6H_4CO))$_2$L] (**4**–**5**). In chlorinated solvents hydridodiacylamino complexes undergo exchange of hydride by chloride to afford [IrCl(PPh_2(o-C_6H_4CO))$_2$L] (**6**–**9**). The reaction of **1** with hydrazine (H_2NNH_2) gives hydridoirida-β-ketoimine [IrHCl{(PPh_2(o-C_6H_4CO))(PPh_2(o-$C_6H_4CNNH_2$))H}] (**10**), fluxional in solution with values for $\Delta H^{\ddagger}$ of 2.5 ± 0.3 kcal mol^{-1} and for $\Delta S^{\ddagger}$ of −32.9 ± 3 eu. A hydrolysis/imination sequence can be responsible for fluxionality. 2-Aminopyridines (RHNC$_5$H$_3$R′N) react with **1** to afford *cis*-[IrCl(PPh_2(o-C_6H_4CO))(PPh_2(o-$C_6H_4CHNRC_5H_3R'N$))] (R = R′ = H (**11**), R = CH_3, R′ = H (**12**), R = H, R′ = CH_3 (**13**)) containing new terdentate PCN ligands in a facial disposition and cis phosphorus atoms as kinetic products. The formation of **11**–**13** requires imination of the hydroxycarbene moiety of **1**, coordination of the nitrogen atom of pyridine to iridium, and iridium to carbon hydrogen transfer. In refluxing methanol, complexes **11**–**13** isomerize to afford the thermodynamic products **14**–**16** with trans phosphorus atoms. Chloride abstraction from complexes [IrCl(PPh_2(o-C_6H_4CO))(PPh_2(o-$C_6H_4CHNRC_5H_4N$))] (R = H or CH_3) leads to decarbonylation of the acylphosphine chelating group to afford cationic complexes [Ir(CO)(PPh_2(o-C_6H_4))(PPh_2(o-$C_6H_4CHNRC_5H_4N$))]A, **17** (R = H, A = ClO_4) and **18** (R = CH_3, A = BF_4) as a cis/trans = 4:1 mixture of isomers. Single crystal X-ray diffraction analysis was performed on **6**, **9**, **13**, and **14**.



INTRODUCTION

Hydridoirida-β-diketones such as [IrHCl{(PPh_2(o-C_6H_4CO))$_2$H}] (**1**) can be considered as acylhydroxycarbene complexes, stabilized by a strong intramolecular hydrogen bond between the acyl and the hydroxycarbene moieties. These complexes can be easily obtained by the reaction of the hydridoacyliridium(III) complex [Ir(Cod)(Cl)H(PPh_2(o-C_6H_4CO))] (Cod = 1,5-cyclooctadiene) with chelating aldehydes in methanol.[1] Hydridoirida-β-diketones may undergo reversible deprotonation and/or dehydrogenation reactions to afford diacyl [IrH(PPh_2(o-C_6H_4CO))$_2$L] (L = CO, C_2H_4, DMSO, PPh_3, py), [Ir(Cl)(PPh_2(o-C_6H_4CO))$_2$(py)], [Ir_2H_2(PPh_2(o-C_6H_4CO))$_2$(μ-PPh_2(o-C_6H_4CO))$_2$], [Ir_2(μ-H){μ-PPh_2(o-C_6H_4CO)}$_2$(PPh_2(o-C_6H_4CO))$_2$]$^+$, [Ir_2H(PPh_2(o-C_6H_4CO)){μ-PPh_2(o-C_6H_4CO)}$_3$]$^+$, or [Ir_2(μ-Cl){μ-PPh_2(o-C_6H_4CO)}$_2$(PPh_2(o-C_6H_4CO))$_2$]$^+$ species.[2−4] Recently, we have found that complex **1** is an efficient homogeneous catalyst for the hydrolysis of ammonia- or amine-borane adducts for hydrogen generation.[5] The transition-metal catalyzed dehydrogenation of these potential hydrogen storage materials for hydrogen production is the subject of recent intensive research.[6] Plausible mechanisms considered to account for the heterogeneous transition metal catalyzed hydrolysis of NH_3BH_3 (AB) include the formation of an activated complex species between AB and the metal particle surface to which attack by a H_2O molecule leads to concerted dissociation of the B−N bond and the hydrolysis of the resulting BH_3 intermediate.[7] The cleavage of the B−N bond may afford the amine. Metalla-β-diketones are known to react with ammonia or amines to afford metalla-β-ketoimines.[8] In our preliminary communication we have reported that the hydridoirida-β-diketone [IrHCl{(PPh_2(o-C_6H_4CO))$_2$H}] (**1**) reacts with methylamine to afford a hydridometalla-β-ketoimine, which was characterized by single crystal X-ray diffraction.[5]

We report now on the reaction of **1** with primary or secondary amines, hydrazine, or 2-aminopyridines to afford hydridoirida-β-ketoimines, which can undergo reversible

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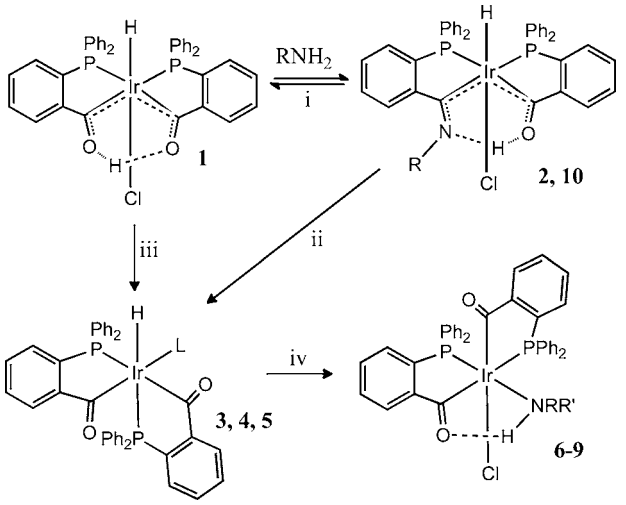
hydrolysis reactions, or new iridium coordinated terdentate PCN ligands.

RESULTS AND DISCUSSION

Reaction with Amines or Hydrazine. The reaction of **1** with benzylamine ($C_6H_5CH_2NH_2$) (see Scheme 1i) in CH_2Cl_2 leads to the condensation reaction product, hydridoirida-β-ketoimine [IrHCl{(PPh_2(o-C_6H_4CO))(PPh_2(o-$C_6H_4CNCH_2C_6H_5$))H}] **2**, stabilized by an intramolecular hydrogen bond between the keto and the enamine moieties. Complex **2** was fully characterized spectroscopically. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets at 30.4 and 15.3 ppm with ^2J(P,P) of 7 Hz, the $^{13}C\{^1H\}$ NMR spectrum shows two doublets at 243.3 and 223.0 ppm due to acyl and imino groups trans to phosphorus atoms (^2J(P,C) of 106 and 103 Hz respectively), and the ^1H NMR spectrum shows a hydride resonance in the high field region, at −20.47 ppm, as triplet due to ^2J(P,H) of 14.2 Hz, which agrees with the hydride being trans to chlorine and cis to two phosphines, and a low field singlet at 13.40 ppm that supports the presence of fairly strong N···H···O hydrogen bonds and the existence of a irida-β-ketoimine. In tetrahydrofuran (THF) solution, **2** reacts with water to undergo hydrolysis and amine coordination thus affording the hydridodiacylamino complex [IrH(PPh_2(o-C_6H_4CO))$_2$($C_6H_5CH_2NH_2$)] **3**, as shown in Scheme 1ii. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two doublets at 31.0 and 25.4 ppm with ^2J(P,P) of 4 Hz. In the ^{31}P NMR spectrum, the signal at 31.0 ppm appears as doublet with $^2J(H,P)_{trans}$ of 130 Hz. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet at 239.0 (^2J(P,C) of 102 Hz) and a singlet at 213.6 ppm respectively due to acyl groups trans or cis to phosphorus atoms, and the ^1H NMR spectrum shows a hydride resonance in the high field region, at −7.83 ppm, as doublet of doublet due to $^2J(P,H)_{trans}$ of 130.2 Hz and $^2J(P,H)_{cis}$ of 19.8 Hz, along with the resonances due to the coordinated amine at 2.61 and 1.87 ppm, at lower field than that of the free ligand. All these data agree with the structure shown in Scheme 1. Complex **3** is most conveniently prepared by the reaction of **1** with $C_6H_5CH_2NH_2$ in a THF/H_2O = 1/1 mixture (Scheme 1iii).

Scheme 1[a]



[a](i) R = $C_6H_5CH_2$ (**2**) in CH_2Cl_2; R = NH_2 (**10**) in THF or THF/H_2O. (ii) **2** in THF/H_2O. (iii) L = $C_6H_5CH_2NH_2$ (**3**); $C_6H_{11}NH_2$ (**4**); $(CH_3)_2NH$ (**5**) in THF/H_2O. (iv) L = $C_6H_5CH_2NH_2$ (**6**); $C_6H_{11}NH_2$ (**7**); CH_3NH_2 (**8**); $(CH_3)_2NH$ (**9**) in refluxing CCl_4.

The reaction of **1** with cyclohexylamine ($C_6H_{11}NH_2$) in CH_2Cl_2 leads only to complex **4**. The reaction of **1** with cyclohexylamine or with the secondary amine $(CH_3)_2NH$ in a THF/H_2O = 1/1 mixture, leads to **4** or **5**, respectively. Complex **1** fails to react with the tertiary amine NEt_3 in dry solvents and reacts in THF/H_2O = 1/1 mixtures to afford the known acyl-bridged species [Ir_2H_2(PPh_2(o-C_6H_4CO))$_2$(μ-PPh_2(o-C_6H_4CO))$_2$], reported to react with different donor ligands to form hydridodiacyliridium(III) complexes analogous to **3**−**5**.[3] We observe now that the dimer [Ir_2H_2(PPh_2(o-C_6H_4CO))$_2$(μ-PPh_2(o-C_6H_4CO))$_2$] fails to react with cyclohexylamine or with dimethylamine. Therefore, we believe that the transformation of **1** into **4** or **5** may proceed via the sequence shown in Scheme 1. Formation of a condensation reaction product (i), unstable for compounds with bulky amino substituents, cyclohexylamine, or when the condensation reaction cannot result in the formation of the N---H---O hydrogen bond, dimethylamine, followed by hydrolysis (ii). An aromatic amine, aniline, fails to react with **1** under the studied reaction conditions.

In chlorinated solvents hydridodiacylamino complexes **3**−**5**, and also [IrH(PPh_2(o-C_6H_4CO))$_2$(CH_3NH_2)],[5] undergo the exchange of hydride by chloride to afford complexes [Ir(Cl)-(PPh_2(o-C_6H_4CO))$_2$L] **6**−**9** (Scheme 1iv). Such a reaction has several precedents.[9] This exchange occurs with concomitant isomerization as shown by an X-ray diffraction study. While in complexes **3**−**5** the amino group is trans to the acyl group, in complexes **6**−**9** the acyl group is trans to chloride and the amino goup is trans to phosphine. The formation of **6**−**9** was demonstrated spectroscopically. The $^{13}C\{^1H\}$ NMR spectra show doublets in the 233−230 ppm range (^2J(P,C) of 108 Hz) and resonances in the 210−207 ppm range due to acyl groups trans or cis to phosphorus atoms respectively. The ^1H NMR spectra show one of the resonances due to the amino groups at rather high field, in the 5.99−5.29 ppm range, and suggest the presence of intramolecular hydrogen bonds. The $^{31}P\{^1H\}$ NMR spectra show two doublets at 23 and 9 ppm respectively with ^2J(P,P) of 4 Hz, for complexes **6**−**8**, containing primary amines and two singlets at higher field, 17.5 and 7.7 ppm, for complex **9**. On account of these spectroscopic data it is not possible to distinguish between the disposition shown in Scheme 1 and an isomer containing the amino group trans to the acyl group as in complexes **3**−**5**.

An X-ray diffraction study on complexes **6**, [$C_{45}H_{37}$Cl-NO_2P_2Ir]·1/2$C_4H_{10}O$ and **9**, [$C_{40}H_{35}ClNO_2P_2Ir$] confirms the isomerization reaction. These compounds crystallized in the $C2/c$ monoclinic group. Figure 1 and Figure 2 show ORTEP views of complexes **6** and **9**, respectively. Selected bond distances and angles are reported in Table 1. In both compounds the crystal consists of neutral Ir complexes and for **6** half a solvent molecule of diethyl ether is also present. The coordinative environment of the Ir atom is slightly distorted octahedral with four positions occupied by the two bidentate acylphosphine ligands and the other two positions occupied by the amino and the chloride ligands. The P1−Ir−P2 bond angles (100.2 (1) and 98.4(1)°) confirm that, in both cases, the phosphorus atoms are mutually cis, with P1 trans to one acyl group and P2 trans to the amino group. Inspection of the bond lengths in these complexes shows that the Ir−N, Ir−P, Ir−C, and Ir−Cl bond distances are in the expected ranges.[4,10] The Ir−P bond distance values of 2.360(2) Å for P1, trans to the acyl group, and of 2.275(2) Å for P2, trans to the amino group, agree with the trans influence order of the ligands: acyl ≫ amine.[11] In these complexes the amino group forms a strong intramolecular hydrogen bond with the oxygen

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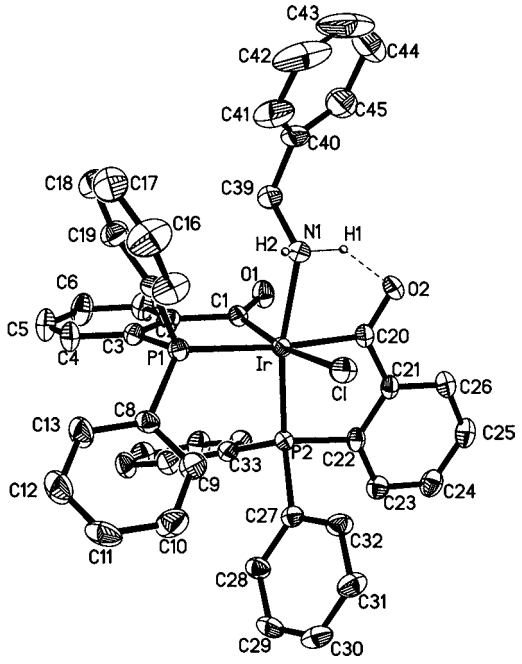

Figure 1. ORTEP plot (25% probability ellipsoids) of complex **6**, showing the labeling of the asymmetric unit. The solvent molecule and the hydrogen atoms except two, have been omitted for clarity.

atom of an acyl group N1−H1---O2 (N1---O2 = 2.752(9) Å or 2.70(1) Å for **6** or **9** respectively). We observe that the intramolecular hydrogen bond formation occurs between the amino group and the acyl group trans to P with the longest Ir−C bond distance (2.066(8) Å), rather than with the acyl group trans to chloride, with shorter Ir−C bond distance (2.005(8) Å). This preference has also been observed in related diacyldiaminerhodium(III) complexes.[11b]

The reaction of **1** with hydrazine (H_2NNH_2) (see Scheme 1i) in dry THF leads to the hydridoirida-*β*-ketoimine [IrHCl{(PPh_2(*o*-C_6H_4CO))(PPh_2(*o*-$C_6H_4CNNH_2$))H}] **10**. This compound is fluxional in solution as shown by inspection of the $^{31}P\{^1H\}$ and ^1H NMR spectra in THF-d_8. At 173 K the $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 19.8 and 13.3 ppm and the ^1H NMR spectrum shows a resonance in the high field region, at −19.11 ppm, as triplet (^2J(P,H) of 16.8 Hz) due to a hydride cis

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6 and 9

6		9	
Ir−P1	2.360(2)	Ir−P1	2.361(3)
Ir−P2	2.275(2)	Ir−P2	2.279(3)
Ir−C1	2.005(8)	Ir−C1	2.02(1)
Ir−C20	2.066(8)	Ir−C20	2.06(1)
Ir−CL	2.511(2)	Ir−CL	2.510(2)
Ir−N1	2.164(6)	Ir−N1	2.21(1)
C1−O1	1.232(9)	C1−O1	1.22(1)
C20−O2	1.226(9)	C20−O2	1.22(1)
N1−H1	0.94	N1−H1	0.98
N1−H2	1.09		
N1---O2	2.752(9)	N1---O2	2.70(1)
O2···H1	2.10	O2···H1	2.06
P1−Ir−CL	96.3(1)	P1−Ir−CL	96.3(1)
P1−Ir−C20	173.2(2)	P1−Ir−C20	174.0(3)
P1−Ir−C1	84.0(2)	P1−Ir−C1	84.9(3)
P1−Ir−P2	100.2(1)	P1−Ir−P2	98.4(1)
P1−Ir−N1	92.5(2)	P1−Ir−N1	96.0(3)
CL−Ir−C20	88.6(2)	CL−Ir−C20	88.9(3)
CL−Ir−C1	170.7(2)	CL−Ir−C1	176.1(3)
CL−Ir−P2	100.4(1)	CL−Ir−P2	97.4(1)
CL−Ir−N1	79.0(2)	CL−Ir−N1	86.7(3)
C20−Ir−C1	90.4(3)	C20−Ir−C1	89.7(4)
C20−Ir−P2	83.4(2)	C20−Ir−P2	83.7(3)
C20−Ir−N1	83.9(3)	C20−Ir−N1	81.4(4)
C1−Ir−P2	88.7(3)	C1−Ir−P2	86.0(3)
C1−Ir−N1	91.7(3)	C1−Ir−N1	89.5(4)
P2−Ir−N1	167.3(2)	P2−Ir−N1	164.5(3)
N1−H1−O2	125.5	N1−H1−O2	120.5

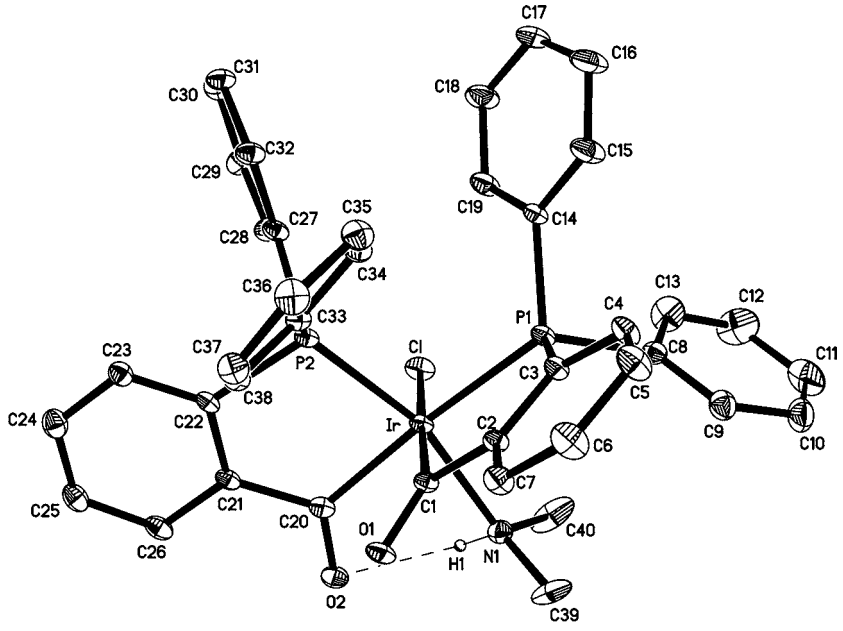

Figure 2. ORTEP plot (20% probability ellipsoids) of complex **9**, showing the labeling of the asymmetric unit. The solvent molecule and the hydrogen atoms except one, have been omitted for clarity.

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to two phosphorus atoms, a resonance at 3.21 ppm due to the amino group and a low field singlet at 14.16 ppm due to the N···H···O hydrogen bond of the irida-β-ketoimine. On raising the temperature the signals due to the phosphorus atoms broaden and coalescence occurs at 263 K (see Figure 3), while the

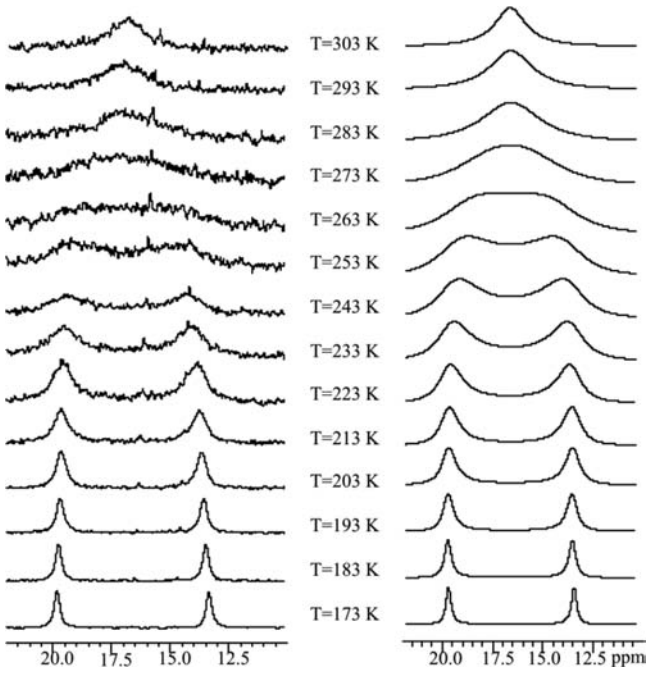
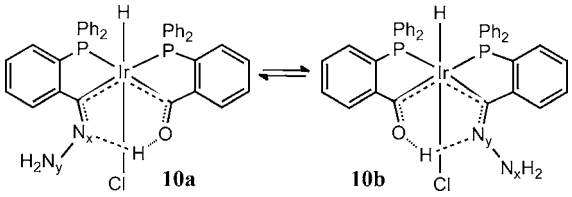


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **10** in THF-d_8: (left) experimental and (right) calculated.

resonances due to the amino group and to the N···H···O moiety also broaden and coalesce. The resonance due to the hydride remains as a triplet. These features indicate exchange between the keto and the imine moieties as shown in Scheme 2. From

Scheme 2. Exchange between the Keto and the Imine Moieties in 10



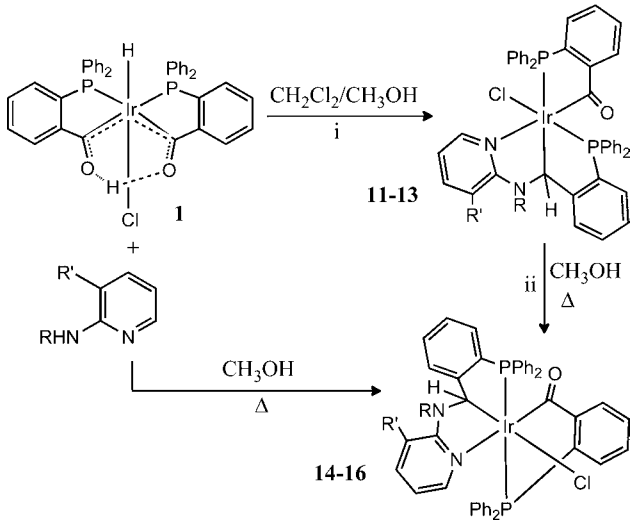
line-shape analysis[12] of the variable temperature $^{31}P\{^1H\}$ NMR spectra of complex **10**, the activation parameters $\Delta H^{\ddagger}$ = 2.5 ± 0.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −32.9 ± 3 cal K^{-1} mol^{-1} have been determined. The enthalpy of activation indicates a low activation barrier. The high entropy of activation suggests an associative mechanism,[13] which could occur by interaction of adventitious water with the imino fragment in **10a** to afford its hydrolysis and deliver free hydrazine, which could promote again the imination reaction giving **10b** and the observed site exchange. This behavior suggests that the irida-β-ketoimine formation shown in Scheme 1i can be a reversible reaction.

Some hydridohydrazineiridium(III) complexes are known,[14] so we thought that the reaction of **1** with hydrazine (H_2NNH_2) in THF/H_2O = 1:1 could afford a complex similar to **3**−**5**. This last reaction gave only complex **10**, and the formation of the corresponding hydridodiacylhydrazineiridium(III) derivative of the **3**−**5** type was not observed.

Reaction with 2-Aminopyridines. 2-Aminopyridines are well-known to form a variety of complexes behaving as a monodentate *N*-pyridine ligand.[15] Their reaction with acylhydroxycarbene platinum(II) complexes has been reported to yield cyclic five-membered PtNCNC aminocarbene derivatives;[16] therefore, we thought it interesting to study the reaction of complex **1** with these ligands. These reactions could also be of interest because the catalytic hydrolysis of ammonia- or amine-boranes with complex **1** could involve interactions of the iridium atom with the borane fragment and of the hydroxycarbene moiety with the amino fragment thus affording IrHBNC metallocycles. Ammonia- or amine-borane adducts can coordinate to transition metals to afford a variety of σ-borane complexes, or compounds containing M−H−BH_nR_{2-n}−NH_nR_{3-n} fragments.[17]

2-Aminopyridines react with **1** in a dichloromethane/methanol mixture, at room temperature, to afford complexes **11**−**13** containing new terdentate PCN ligands with a coordinated sp^3 carbon atom as shown in Scheme 3i. The NMR spectra, including 2D experiments, agree with the formation of the new C−N bonds and with the structure shown in Scheme 3i. The $^{31}P\{^1H\}$ NMR spectra show two

Scheme 3[a]



[a](i) R = R′ = H (**11**), R = CH_3, R′ = H (**12**), R = H, R′ = CH_3 (**13**) in CH_2Cl_2/CH_3OH; (ii) R = R′ = H (**14**), R = CH_3, R′ = H (**15**), R = H, R′ = CH_3 (**16**) in refluxing CH_3OH.

doublets at 24 and 17 ppm respectively with ^2J(P,P) of 4 Hz, due to phosphorus atoms in mutually cis positions. The $^{13}C\{^1H\}$ NMR spectra show singlets in the 219−216 ppm range due to terminal acyl groups bonded to iridium and doublets in the 76−66 ppm range due to benzylic carbon atoms trans to phosphorus (^2J(P,C) of 84 Hz), which correlate with resonances in the 6.2−5.8 ppm range in the ^1H NMR spectra that also contain the resonances due to the amino groups at 5.29 or 5.78 ppm for compounds **11** or **13**, respectively. PCN ligands may adopt meridional or facial coordination patterns in octahedral transition metal complexes, and some cationic Ir(III) complexes have been reported to undergo the fac-mer isomerization reaction.[18] As indicated by an X-ray diffraction

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study (vide infra), the PCN terdentate ligand in complexes **11**−**13** adopts a facial disposition.

We believe that the formation of complexes **11**−**13** involves a condensation reaction to yield a transient aminocarbene followed by iridium to carbon hydrogen transfer, with concomitant coordination of the nitrogen atom of pyridine to iridium. Most likely, in the present reaction the coordination of pyridine makes the formed aminocarbene fragment to be involved in a five-membered IrNCNC metallacycle thus inhibiting the formation of a N---H---O hydrogen bond with the keto group. The lack of stabilization would be responsible for the observed iridium to carbon hydrogen transfer to afford complexes **11**−**13**. α-Hydrogen transfer has been reported for hydrido-carbene iridium complexes.[19] As indicated previously we have observed that aromatic amines fail to afford the imination reaction and in a previous report we described that the reaction of **1** with pyridine in refluxing methanol led to a diacylpyridine complex with hydrogen loss.[4] In contrast, 2-aminopyridines afford a new reaction, most likely favored by chelate formation, to give the five-membered IrNCNC metallacycle.

Complexes **11**−**13** are the kinetic products of this reaction. When refluxed in methanol for 90 min, the isomerization reaction occurs to afford the thermodynamic products **14**−**16** with also a facial disposition of the PCN ligand, trans phosphorus atoms and with the chloride trans to the benzyl group as shown in Scheme 3ii. Complexes **14**−**16** can be more easily obtained by the reaction of **1** with the corresponding 2-aminopyridine in refluxing methanol. The $^{31}P\{^{1}H\}$ NMR spectra show two doublets at slightly lower field than in complexes **11**−**13**, in the 33−23 ppm range, with $^{2}J(P,P)$ of 390 Hz, due to phosphorus atoms in mutually trans positions. The $^{13}C\{^{1}H\}$ NMR spectra show the expected singlets at 218 ppm due to the terminal acyl groups bonded to iridium and in the 54−44 ppm range due to the benzyl groups. The latter resonances correlate with resonances in the 4.6−4.2 ppm range in the ^{1}H NMR spectra that also show resonances at 4.09 and 3.83 ppm due to the amino groups in **14** and **16**, respectively. Complexes **11**−**16** contain an asymmetric sp^3 carbon atom newly formed. These complexes are diastereomeric because the iridium atom is also chiral. In all cases only one group of resonances is observed and indicates the formation of only a pair of enantiomers of the four possible diastereomers.

An X-ray diffraction study on complexes **13** and **14** was undertaken and confirms the formation of new C−N bonds and the Ir-to-C hydrogen transfer to give the final products. These compounds crystallized in the $P\bar{1}$ triclinic group and in the $P2_1/c$ monoclinic group respectively. The crystals consist of $[C_{44}H_{36}ClN_2OP_2Ir]$ neutral molecules and diethyl ether solvent molecules bonded by weak hydrogen bond for **13**, and of $[C_{43}H_{34}ClN_2OP_2Ir]$ neutral molecules and dichloromethane solvent molecules for **14**. In the latter compound the intermolecular hydrogen bond (Table 2) led to chains along the *a* axis. Figure 4 and Figure 5 show the ORTEP views of the complexes with the atomic numbering scheme. Selected bond distances and angles are listed in Table 2. The C20−N2 bond distances, 1.467(3) and 1.47(1) Å for **13** and **14** respectively, along with the C21−C20−N2 bond angle of 110.8(2)° and 108.3(7) for **13** and **14**, respectively, show the new C−N bond formation, with C20 changing from sp^2 to sp^3. The iridium atom in compounds **13** and **14** is coordinated in a slightly distorted octahedral fashion because of the presence of a bidentate and a terdentate ligand. The maxima deviation from

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 13 and 14[a]

13		14	
Ir−P1	2.3552(7)	Ir−P1	2.307(3)
Ir−P2	2.2526(7)	Ir−P2	2.307(3)
Ir−C1	2.020(3)	Ir−C1	1.98(1)
Ir−C20	2.110(3)	Ir−C20	2.082(8)
Ir−CL1	2.4304(7)	Ir−CL1	2.468(2)
Ir−N1	2.160(2)	Ir−N1	2.145(7)
C1−O1	1.224(3)	C1−O1	1.23(1)
C20−N2	1.467(3)	C20−N2	1.47(1)
N2−H2	0.93	N2−H2	1.04
N2---O2	3.584(4)	N2---CL1′	3.244(7)
O2···H2	2.70	CL1′···H2	2.29
P1−Ir−CL1	90.17(3)	P1−Ir−CL1	88.03(9)
P1−Ir−C20	173.29(7)	P1−Ir−C20	97.2(3)
P1−Ir−C1	83.47(8)	P1−Ir−C1	83.2(3)
P1−Ir−P2	102.52(3)	P1−Ir−P2	172.29(9)
P1−Ir−N1	104.63(7)	P1−Ir−N1	95.0(2)
CL1−Ir−C20	85.51(8)	CL1−Ir−C20	170.6(3)
CL1−Ir−C1	83.71(8)	CL1−Ir−C1	95.2(2)
CL1−Ir−P2	165.42(3)	CL1−Ir−P2	94.93(9)
CL1−Ir−N1	86.35(7)	CL1−Ir−N1	90.5(2)
C20−Ir−C1	91.0(1)	C20−Ir−C1	93.2(3)
C20−Ir−P2	81.18(8)	C20−Ir−P2	80.9(3)
C20−Ir−N1	80.3(1)	C20−Ir−N1	81.3(3)
C1−Ir−P2	90.56(8)	C1−Ir−P2	89.4(3)
C1−Ir−N1	167.2(1)	C1−Ir−N1	174.0(3)
P2−Ir−N1	97.17(7)	P2−Ir−N1	92.1(2)
C21−C20−N2	110.8(2)	C21−C20−N2	108.3(7)
N2−H2−O2	158.9	N2−H2−CL1′	151.8

[a] (′) $-x+2$, $y+1/2$, $-z+1/2$.

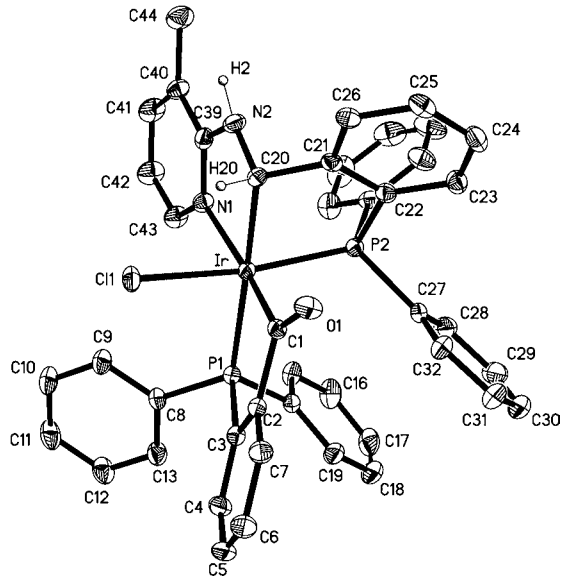

Figure 4. ORTEP plot (20% probability ellipsoids) of complex **13**, showing the labeling of the asymmetric unit. The solvent molecule and the hydrogen atoms except two have been omitted for clarity.

the octahedral geometry corresponds to 15° for the angle CL1−Ir−P2 for **14** and 13° for the angle C1−Ir−N1 for **13**. Compounds **13** and **14** can be considered as geometric isomers, although the terdentate ligands derive from 2-amino-3-methylpyridine or 2-aminopyridine, respectively. The most

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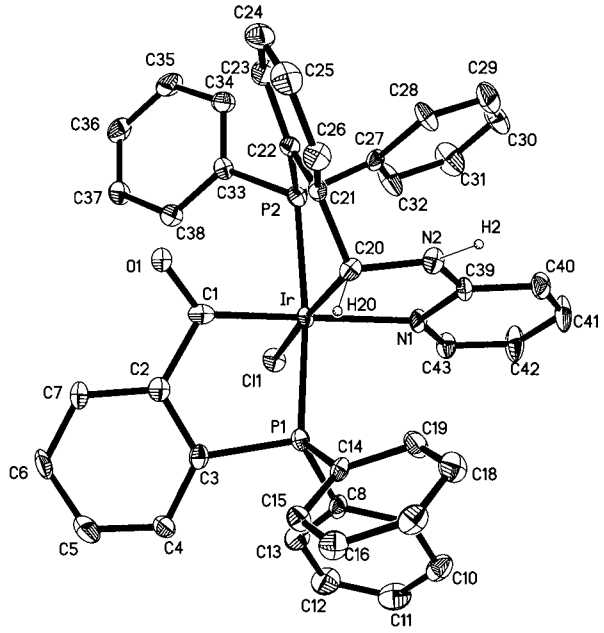
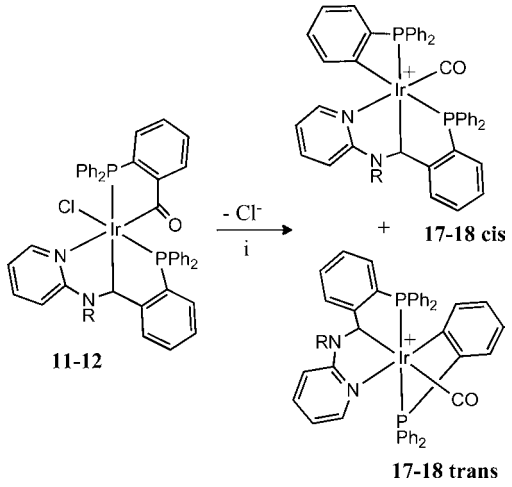


Figure 5. ORTEP plot (20% probability ellipsoids) of complex **14**, showing the labeling of the asymmetric unit. The solvent molecule and the hydrogen atoms except two have been omitted for clarity.

notable difference observed in these compounds is the cis coordination of the phosphorus atoms in **13** while they are trans coordinated in **14**. The bond angles closest to the linearity correspond to P1−Ir−C20 for **13** (173.29(7)°) and P1−Ir−P2 for **14** (172.29(9)°). For this reason, those donor atoms were considered to occupy the apical positions. In consequence the equatorial plane is formed by [P2, C1, CL1, N1] for **13** and by [C1, C20, N1, CL1] for **14**. The Ir atom is shifted away from the best least-squares plane by 0.22 Å in the former, while it is practically on the equatorial plane in the latter. In **13**, the Ir−P bond distances, shorter for P2, trans to chloride, than for P1, trans to the C20 atom of the terdentate ligand, reflect the higher trans influence of alkyl than that of chloride. In **14**, the Ir−P bond distances are equal as expected. Also, the Ir−C1 bond distances are shorter than the Ir−C20 bond distances as a consequence of the different hybridization for C1 (sp^2) than for C20 (sp^3).[10a,20]

In an attempt to obtain PCN unsaturated 16e species, we have studied the chloride abstraction reaction from complexes **11** or **12** by using $AgClO_4$ or Et_3OBF_4. Unsaturated pincer complexes, especially those involving a meridional disposition for the terdentate ligand, are of considerable current interest, as they may lead to a variety of bond activation and catalytic processes.[21] An unsaturated Ir-pincer complex is an efficient catalyst for the dehydrocoupling of amine-boranes under anhydrous conditions.[22] As shown in Scheme 4, the formation of stable unsaturated 16e species does not occur. Instead, the decarbonylation of the acylphosphine chelating group occurs to afford coordinatively saturated complexes **17** and **18** as a cis/trans = 4:1 mixture of isomers. By starting from complexes **14** or **16**, the same mixture of isomers was obtained. Orthometalated complexes containing the M[PPh_2(o-C_6H_4)] fragment are well-known.[23] However, the formation of **17** and **18** was unexpected to some extent because it requires decarbonylation of an acylphosphine chelate. Transition metal acyl complexes may undergo decarbonylation to afford carbonylated metal complexes. The transition metal promoted

Scheme 4[a]



[a](i) $AgClO_4$ in CH_2Cl_2, **17** (R = H); Et_3OBF_4 in CH_2Cl_2, **18** (R = CH_3).

decarbonylation of acyl halides or of aldehydes has been established as a useful synthetic transformation. Nevertheless, chelate formation frequently renders the decarbonylation reaction more difficult and halide abstraction from rhodium or iridium complexes containing acylphosphine chelates frequently results in the formation of dimer species with acyl bridging groups.[24]

Complexes **17** and **18** behave as 1:1 electrolytes and were identified spectroscopically. The appearance of resonances in the $^{31}P\{^1H\}$ NMR spectra at very high field, −66 ppm, which represents shifts over +80 ppm to higher fields with respect to the starting materials, indicates the formation of four-membered metallacycles.[25] The trans isomers, show two doublets with ^2J(P,P) of 340 Hz. The ***cis*-17** isomer also shows two doublets with ^2J(P,P) of 7 Hz, and the ***cis*-18** isomer shows two singlets due to unobservable ^2J(P,P). The presence of the coordinated carbonyl group, cis to phosphorus atoms in these compounds, is identified by the appearance of strong absorptions at 2040 cm^{-1} in the IR spectra and by the presence of triplets at 168 ppm (^2J(P,C) = 5 Hz) in the $^{13}C\{^1H\}$ NMR spectra. The carbon atoms of the PCN ligands appear as doublets ($^2J(P,C)_{trans}$ = 70 Hz) in the cis isomers and as singlets in the trans isomers. Assuming a facial disposition of the PCN ligand these NMR data indicate the structure shown in Scheme 4 for the cis isomers. For the trans isomers a disposition with the nitrogen atom trans to the aryl ligand, with larger structural trans effect than CO,[11a] appears more likely though the other disposition, trans to CO, cannot be totally excluded.

■ CONCLUSIONS

Hydridoirida-β-diketones react with aliphatic amines or with hydrazine to afford, reversibly, hydridoirida-β-ketoimines that may also undergo hydrolysis to afford hydridodiacylaminoiridium(III) derivatives. The reaction of hydridoirida-β-diketones with 2-aminopyridines leads to imination and to iridium to carbon hydrogen transfer to afford the formation of complexes containing new terdentate PCN ligands. These complexes containing pincer and acylphosphine ligands may undergo decarbonylation of the chelating acylphosphine ligands at room temperature.

■ EXPERIMENTAL SECTION

General Procedures. The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk

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techniques. The complexes $[IrHCl\{(PPh_2(o\text{-}C_6H_4CO))_2H\}]$[1a] (**1**) and $[IrH(PPh_2(o\text{-}C_6H_4CO))_2(CH_3NH_2)]$[5] were prepared as previously reported. Microanalysis were carried out with a Leco CHNS-932 microanalyzer. Conductivities were measured in acetone solution with a Metrohm 712 conductimeter. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000−400 cm^{-1} using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers; ^1H and $^{13}C\{^1H\}$ (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard) and 2D spectra were measured from $CDCl_3$ or THF-d_8 solutions.

Preparation of $[IrHCl\{(PPh_2(o\text{-}C_6H_4CO)(PPh_2(o\text{-}C_6H_4CN\text{-}(CH_2C_6H_5))H\}]$ (2). To a dichloromethane solution of **1** (50 mg, 0.062 mmol) was added benzylamine (6.8 μL, 0.062 mmol) and 4 Å molecular sieve. Stirring during 2 h and evaporation of the solvent gave a yellow solid that was washed with diethyl ether and vacuum-dried. Yield: 41 mg, 74%. IR (cm^{-1}): 2169 (m), ν(IrH); 1592 (s), 1566 (s), ν(C═O). Anal. Calc. for $C_{45}H_{36}ClIrNOP_2$: C 60.30, H 4.05, N 1.56; found: C 60.39, H 3.64, N 1.89. ^1H NMR ($CDCl_3$): δ 13.40 (s, 1H, N···H···O); 3.93 (s, 2H, CH_2); −20.47 (t, 1H, $J_{P,H}$ = 14.2 Hz, IrH). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 30.4 (d, $J_{P,P}$ = 7 Hz); 15.3 (d). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 243.3 (d, $J_{P,C}$ = 106 Hz, IrC═O); 223.0 (d, $J_{P,C}$ = 103 Hz, IrC═N); 46.5 (s, CH_2).

Preparation of $[IrH(PPh_2(o\text{-}C_6H_4CO))_2L]$ (L = $(H_2NCH_2C_6H_5$ (3); $H_2NC_6H_{11}$ (4)). To a THF/H_2O (1/1) suspension of **1** (50 mg, 0.062 mmol) was added the corresponding ligand (13.6 or 14.2 μL, 0.124 mmol). Stirring during 4 h and decantation gave pale yellow solids that were washed with diethyl ether and vacuum-dried. **Data for 3.** Yield: 35 mg, 63%. IR (cm^{-1}): 3310 (m), 3272 (w), ν(NH); 2031 (s), ν(IrH); 1596 (s), 1560 (s), ν(C═O). Anal. Calc. for $C_{45}H_{38}IrNO_2P_2$: C 61.49, H 4.36, N 1.50; found: C 61.07, H 4.29, N 1.68. ^1H NMR ($CDCl_3$): δ 3.43 (s, 2H, CH_2); 2.61 (s, br, 1H, NH); 1.87 (s, br, 1H, NH); −7.83 (dd, 1H, $J_{(P,H)cis}$ = 19.8 Hz; $J_{(P,H)trans}$ = 130.2 Hz, IrH). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 31.0 (d, $J_{P,P}$ = 4 Hz); 25.4 (d). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 239.0 (d, $J_{P,C}$ = 102 Hz, IrC═O); 213.6 (s, IrC═O); 54.8 (s, CH_2). **Data for 4.** Yield: 43 mg, 87%. IR (cm^{-1}): 3309 (w), 3220 (w), ν(NH); 2050 (m), ν(IrH); 1609 (s), 1563(s), ν(C═O). Anal. Calc. for $C_{44}H_{42}IrNO_2P_2{\cdot}CH_2Cl_2$: C, 56.54; H, 4.64; N, 1.47; found: C, 56.43; H, 4.62; N, 1.67. ^1H NMR ($CDCl_3$): δ 3.09 (s, br, 2H, NH); 2.92 − 0.25 (m, 11H, cyclohexyl); −7.98 (dd, 1H, $J_{(P,H)cis}$ = 19.7 Hz; $J_{(P,H)trans}$ = 130.1 Hz, IrH). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 30.1 (d, $J_{P,P}$ = 5 Hz); 24.7 (d). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 238.7 (d, $J_{P,C}$ = 103 Hz, IrC═O); 214.0 (s, IrC═O).

Preparation of $[IrH(PPh_2(o\text{-}C_6H_4CO))_2(NH(CH_3)_2)]$ (5). To a THF/H_2O (1/1) suspension of **1** (50 mg, 0.062 mmol) at 0 °C was added dimethylamine in 2 M THF solution (31 μL, 0.062 mmol) whereupon a solution was obtained. Stirring during 5 min and evaporation of THF gave a pale yellow solid that was decanted, washed with diethyl ether, and vacuum-dried. Yield: 27 mg, 52%. IR (cm^{-1}): 3282 (w) ν(NH); 2038 (m), ν(IrH); 1606 (s), 1564 (s), ν(C═O). Anal. Calc. for $C_{40}H_{36}IrNO_2P_2{\cdot}2H_2O$: C 56.33, H 4.73, N 1.64; found: C 56.00, H 4.56, N 1.48. ^1H NMR ($CDCl_3$): δ 2.35 (d, 3H, $J_{H,H}$ = 5.8 Hz, CH_3); 2.24 (d, 3H, $J_{H,H}$ = 5.8 Hz, CH_3); 1.79 (m, 1H, NH); −7.70 (dd, 1H, $J_{(P,H)cis}$ = 19.8 Hz; $J_{(P,H)trans}$ = 131.6 Hz, IrH). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 30.6 (d, $J_{P,P}$ = 3 Hz); 24.9 (d). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 234.8 (d, $J_{P,C}$ = 106 Hz, IrC═O); 212.4 (m, IrC═O); 49.8 (s, CH_3); 47.9 (s, CH_3).

Preparation of $[IrCl(PPh_2(o\text{-}C_6H_4CO))_2L]$ (L = $H_2NCH_2C_6H_5$ (6); $H_2NC_6H_{11}$ (7); H_2NCH_3 (8); $HN(CH_3)_2$ (9)). A CCl_4 suspension of the corresponding $[IrH(PPh_2(o\text{-}C_6H_4CO))_2L]$ (0.034 mmol) was refluxed during 1 h until a solution was obtained. The evaporation of the solvent gave pale yellow solids that were washed with diethyl ether and vacuum-dried. **Data for 6.** Yield: 18 mg, 58%. IR (cm^{-1}): 3289 (w), 3173 (w), ν(NH); 1620 (s), 1575 (s), ν(C═O). Anal. Calc. for $C_{45}H_{37}ClIrNO_2P_2.0.5CH_2Cl_2$: C 57.44, H 3.98, N 1.46; found C 57.67, H 4.06, N 1.59. ^1H NMR ($CDCl_3$): 5.73 (s, br, 1H, NH), 3.54 (m, 1H, CH_2), 3.24 (s, br, 1H, NH), 2.38 (m, 1H, CH_2). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 23.2 (d, $J_{P,P}$ = 5 Hz); 9.3 (d). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 231.0 (d, $J_{P,C}$ = 108 Hz, IrC═O); 208.4 (d, $J_{P,C}$ = 7 Hz, IrC═O); 49.5 (s, CH_2). **Data for 7.** Yield: 30 mg, 99%. IR (cm^{-1}): 3292 (w), 3167 (w), ν(NH); 1622 (s), ν(C═O). Anal. Calc. for $C_{44}H_{41}ClIrNO_2P_2$: C, 58.37, H, 4.56, N, 1.55; found: C, 58.49, H, 4.47, N, 1.74. ^1H NMR ($CDCl_3$): δ 5.39 (m, 1H, NH); 3.10 (m, 1H, NH and 1H, CH cyclohexyl), 2.50 to −0.02(m, 10H, cyclohexyl). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 22.6 (d, $J_{P,P}$ = 3 Hz); 8.4 (d). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 230.9 (d, $J_{P,C}$ = 108 Hz, IrC═O); 207.2 (s, IrC═O). **Data for 8.** Yield: 28 mg, 90%. IR (cm^{-1}): 3312 (w), 3145 (w), ν(NH); 1621 (s), ν(C═O). Anal. Calc. for $C_{39}H_{33}ClIrNO_2$-$P_2{\cdot}0.25CH_3Cl$: C, 54.92, H, 3.91, N, 1.63; found: C, 54.78, H, 3.95, N, 1.61. ^1H NMR ($CDCl_3$): δ 5.29 (s, br, 1H, NH); 2.81 (s, br, 1H, NH); 1.78 (m, 3H, CH_3). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 22.9 (d, $J_{P,P}$ = 5 Hz); 10.5 (d). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 231.8 (d, $J_{P,C}$ = 109 Hz, IrC═O); 208.2 (d, $J_{P,C}$ = 7 Hz); 31.6 (s, CH_3). **Data for 9.** Yield: 32 mg, 59%. IR (cm^{-1}): 3134 (w), ν(NH); 1614 (s), 1571 ν(C═O). Anal. Calc. for $C_{39}H_{33}ClIrNO_2P_2{\cdot}0.5CH_2Cl_2$: C, 54.42, H, 4.06, N, 1.57; found: C, 54.72, H, 4.06, N, 1.63. ^1H NMR ($CDCl_3$): δ 5.99 (s, br, 1H, NH); 2.00 (m, 6H, CH_3). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 17.5 (s); 7.7 (s). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 232.7 (d, $J_{P,C}$ = 109 Hz, IrC═O); 210.0 (d, $J_{P,C}$ = 8 Hz); 44.6 (s, CH_3); 40.8 (s, CH_3).

Preparation of $[IrHCl\{(PPh_2(o\text{-}C_6H_4CO)(PPh_2(o\text{-}C_6H_4CNNH_2)\text{-}H\}]$ (10). To a THF solution of **1** (50 mg, 0.062 mmol) was added hydrazine (1.8 μL, 0.062 mmol). Stirring during 90 min and evaporation of the solvent gave an orange solid that was washed with diethyl ether and vacuum-dried. Yield: 40 mg, 79%. IR (cm^{-1}): 3175 (m), ν(NH); 2190 (m), ν(IrH); 1587 (s), ν(C═O). Anal. Calc. for $C_{38}H_{32}ClIrN_2OP_2$: C 55.51, H 3.92, N 3.41; found: C 56.03, H 3.27, N 3.96. ^1H NMR (THF-d_8, 173 K): δ 14.16 (s, 1H, N···H···O); 3.21 (s, 2H, NH_2); −19.11 (t, 1H, $J_{P,H}$ = 16.8 Hz, IrH). $^{31}P\{^1H\}$NMR (THF-d_8, 173 K): δ 19.8 (s); 13.3 (s).

Preparation of *cis*-$[IrCl(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4CHNRC_5H_3R'N))]$ (R = R′ = H (11); R = CH_3, R′ = H (12); R = H, R′ = CH_3 (13)). To a dichloromethane/methanol (1:1) solution of **1** (50 mg, 0.062 mmol) was added the corresponding ligand (0.062 mmol). Stirring during 24 h and evaporation of CH_2Cl_2 gave yellow solids that were decanted, washed with methanol and vacuum-dried. **Data for 11**. Yield 42 mg, 77%. IR (cm^{-1}): 3273 (m), ν(NH); 1627 (s), ν(C═O). Anal. Calc. for $C_{43}H_{33}ClIrN_2OP_2{\cdot}0.5CH_2Cl_2$: C 56.43, H 3.70, N 3.03; found C 56.00, H 3.79, N 3.16. ^1H NMR ($CDCl_3$): δ 6.07 (m, 1H, IrCH); 5.29 (d, 1H, $J_{P,H}$ = 7.9 Hz, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.8 (d, $J_{P,P}$ = 4 Hz); 17.4 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 216.3 (s, IrC═O); 67.4 (d, $J_{P,C}$ = 86 Hz, IrCH). **Data for 12.** Yield 35 mg, 63%. IR (cm^{-1}): 1616 (s), ν(C═O). Anal. Calc. for $C_{44}H_{35}ClIrN_2OP_2{\cdot}0.75CH_2Cl_2$: C 55.93, H 3.83, N 2.92; found C 55.89, H 3.85, N 2.89. ^1H NMR ($CDCl_3$): δ 5.86 (d, 1H, $J_{P,H}$ = 5.7 Hz, IrCH); 3.14 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.0 (d, $J_{P,P}$ = 4 Hz); 16.4 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 217.9 (s, IrC═O); 75.2 (d, $J_{P,C}$ = 83 Hz, IrCH); 37.5 (s, CH_3). **Data for 13.** Yield 40 mg, 72%. IR (cm^{-1}): 3420 (w), ν(NH); 1615(s), ν(C═O). Anal. Calc. for $C_{44}H_{35}ClIrN_2OP_2{\cdot}0.5CH_2Cl_2$: C 56.87, H 3.86, N 2.98; found C 56.60, H 3.78, N 3.31. ^1H NMR ($CDCl_3$): δ 6.11 (d, 1H, $J_{P,H}$ = 5.3 Hz, IrCH); 5.78 (m, 1H, NH); 1.87 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.8 (d, $J_{P,P}$ = 4 Hz); 16.9 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 216.4 (d, $J_{P,C}$ = 5 Hz, IrC═O); 66.6 (d, $J_{P,C}$ = 87 Hz, IrCH); 18.1 (s, CH_3).

Preparation of *trans*-$[IrCl\{(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4CHNRC_5H_3R'N))\}]$ (R = R′ = H (14); R = CH_3, R′ = H (15); R = H, R′ = CH_3 (16)). To a methanol suspension of **1** (50 mg, 0.062 mmol) was added the corresponding ligand (0.062 mmol). The suspension was refluxed whereupon the formation of a yellow solution occurs, followed by the appearance of a yellow precipitate. After 4 h reflux and cooling, the solids were decanted, washed with methanol, and vacuum-dried. **Data for 14**. Yield 28 mg, 52%. IR (cm^{-1}): 3315 (w), ν(NH); 1621 (s), ν(C═O). Anal. Calc. for $C_{43}H_{33}ClIrN_2$-$OP_2{\cdot}2CH_3OH$: C 57.05, H 4.36, N 2.96; found C 56.76, H 4.01, N 3.55. ^1H NMR ($CDCl_3$): δ 4.61 (dd, 1H, $J_{P,H}$ = 4.3 Hz, $J_{P,H}$ = 10.4 Hz, IrCH); 4.09 (s, br, 1H, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.2 (d, $J_{P,P}$ = 390 Hz); 23.4 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 218.6 (s, IrC═O); 45.1 (s, IrCH). **Data for 15**. Yield 34 mg, 62%. IR (cm^{-1}): 1607 (s), ν(C═O). Anal. Calc. for $C_{44}H_{35}ClIrN_2OP_2{\cdot}2CH_3OH$: C 57.46, H 4.51, N 2.91; found C 57.11, H 4.21, N 2.83. ^1H NMR ($CDCl_3$): δ 4.27 (dd, 1H, $J_{P,H}$ = 4.1 Hz, $J_{P,H}$ = 10.7 Hz, IrCH); 2.26 (s, 3H, CH_3). $^{31}P\{^1H\}$

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Table 3. Crystal Data and Refinement Data for 6, 9, 13, and 14

Crystal Data	6	9	13	14
identification code	CCDC-830884	CCDC-830885	CCDC-830886	CCDC-830887
empirical formula	$[C_{45}H_{37}ClNO_2P_2Ir]\cdot 1/2C_4H_{10}O$	$[C_{40}H_{35}ClNO_2P_2Ir]$	$[C_{44}H_{36}ClN_2OP_2Ir]\cdot C_4H_{10}O$	$[C_{43}H_{34}ClN_2OP_2Ir]\cdot CH_2Cl_2$
formula wt	950.41	851.28	972.46	969.24
crystal sys.	monoclinic	monoclinic	triclinic	monoclinic
space group	$C2/c$	$C2/c$	$P\bar{1}$	$P2(1)/c$
a/Å	27.130(2)	26.411(3)	11.0825(7)	10.355(1)
b/Å	19.595(1)	19.349(2)	13.0297(8)	16.157(1)
c/Å	19.595(1)	19.978(2)	15.097(1)	24.241(2)
α /deg			89.345(1)	
β /deg	123.846(1)	123.279(2)	78.796(1)	100.505(1)
γ /deg			78.253(1)	
V/Å^3	8651.5(8)	8535(2)	2092.8(2)	3987.8(5)
Z	8	8	2	4
D_c /g/cm^3	1.459	1.325	1.543	1.614
μ(Mo−Kα) /mm^{-1}	3.261	3.296	3.372	3.667
F(000)	3800	3376	976	1920
θ range/deg	1.38 to 25	1.40 to 26.37	1.91 to 25	1.52 to 25
index ranges	−32,−23,−21 to 32,20,23	−32,−23,−24 to 23,24,24	−13,−15,−17 to 13,15,17	−11,−19,−28 to 12,19,26
reflections collected	32960	35824	21188	30207
unique reflections [R(int)]	7611 [R(int) = 0.052]	8706 [R(int) = 0.0393]	7349 [R(int) = 0.0284]	7031 [R(int) = 0.1311]
completeness to θ	99.9%	99.7%	99.7%	99.9%
data/restraints/params	7611/4/469	8706/0/424	7349/0/505	7031/0/478
R1 (reflns obsd) [$I > 2\sigma(I)$][a]	0.0379 (4636)	0.0473 (5768)	0.0212 (6539)	0.0469(3976)
wR2 (all data)[b]	0.1291	0.2568	0.0512	0.1098
largest diff. peak and hole/e Å^{-3}	1.124 and −0.482	1.867 and −0.794	0.935 and −0.815	1.468 and −1.992

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}$.

NMR ($CDCl_3$): δ 27.6 (d, $J_{P,P}$ = 391 Hz); 23.3 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 219.3 (d, $J_{P,C}$ = 4 Hz, IrC═O); 53.4 (s, IrCH); 34.5 (s, CH_3). **Data for 16**. Yield 34 mg, 62%. IR (cm^{-1}): 3408 (s), ν(NH); 1609(s), ν(C═O). Anal. Calc. for $C_{44}H_{35}ClIrN_2OP_2\cdot CH_3OH$: C 58.15, H 4.23, N 3.01; found C 58.07, H 4.24, N 2.97. ^1H NMR ($CDCl_3$): δ 4.60 (dd, 1H, $J_{P,H}$ = 4.3 Hz, $J_{P,H}$ = 10.3 Hz, CH); 3.83 (s, 1H, NH); 1.65 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.7 (d, $J_{P,P}$ = 392 Hz); 27.9 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 218.4 (d, $J_{P,C}$ = 4 Hz, IrC═O), 44.4 (s, IrCH); 17.6 (s, CH_3).

Preparation of [Ir(CO)(PPh$_2$(*o*-C$_6$H$_4$))(PPh$_2$(*o*-C$_6$H$_4$CHNHC$_5$H$_4$N))]ClO$_4$ (17). To a CH_2Cl_2 solution of **11** (50 mg, 0.057 mmol) was added $AgClO_4$ (12 mg, 0.057 mmol). After being stirred for 30 min the silver salts were filtered and the solvent was evaporated to give a yellow solid that was washed with diethyl ether and vacuum-dried. Yield 35 mg, 63%. IR (cm^{-1}): 3324 (m), ν(NH); 2041 (s), ν(C≡O). Λ_M (ohm^{-1} cm^2 mol^{-1}): 134 (acetone). Anal. Calc. for $C_{43}H_{43}IrN_2OP_2ClO_4\cdot 0.25CH_2Cl_2$: C 53.58, H 3.59, N 2.89; found C 53.42, H 3.54, N 3.03. **Data for *cis*-17**. ^1H NMR ($CDCl_3$): δ 6.49 (s, 1H, IrCH); 6.10 (m, 1H, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.5 (d, $J_{P,P}$ = 7 Hz); −65.2 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.4 (t, $J_{P,C}$ = 5 Hz, IrC≡O); 51.8 (d, $J_{P,C}$ = 71 Hz, IrCH). **Data for *trans*-17**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.4 (d, $J_{P,P}$ = 342 Hz); −65.7 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.4 (t, $J_{P,C}$ = 7 Hz, IrC≡O); 47.1 (s, IrCH).

Preparation of [Ir(CO)(PPh$_2$(*o*-C$_6$H$_4$))(PPh$_2$(*o*-C$_6$H$_4$CHN(CH$_3$)C$_5$H$_4$N))]BF$_4$ (18). To a CH_2Cl_2 solution of **12** (50 mg, 0.056 mmol) was added Et_3OBF_4 (11 mg, 0.056 mmol). Stirring during 30 min and evaporation of the solvent gave a yellow solid that was washed with diethyl ether and vacuum-dried. Yield 45 mg, 86%. IR (cm^{-1}): 2045 (s), ν(C≡O). Λ_M (ohm^{-1} cm^2 mol^{-1}): 132 (acetone). Anal. Calc. for $C_{43}H_{43}IrN_2OP_2BF_4\cdot 0.5CH_2Cl_2$: C 53.41, H 3.61, N 2.86; found C 53.48, H 3.91, N 3.09. **Data for *cis*-18**. ^1H NMR ($CDCl_3$): δ 6.16 (m, 1H, IrCH); 3.27 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.5 (s); −66.2 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.8 (t, $J_{P,C}$ = 6 Hz, IrC≡O]; 60.7 (d, $J_{P,C}$ = 70 Hz, IrCH); 37.4 (d, $J_{P,C}$ = 4 Hz, CH_3). **Data for *trans*-18**. ^1H NMR ($CDCl_3$): 3.33 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.5 (d, $J_{P,P}$ = 337 Hz); −65.9 (d). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 56.6 (s, IrCH); 37.0 (s, CH_3).

X-ray Structure Determination of [C$_{45}$H$_{37}$ClNO$_2$P$_2$Ir]·1/2C$_4$H$_{10}$O (6), [C$_{40}$H$_{35}$ClNO$_2$P$_2$Ir] (9), [C$_{44}$H$_{36}$ClN$_2$OP$_2$Ir]·C$_4$H$_{10}$O (13), and [C$_{43}$H$_{34}$ClN$_2$OP$_2$Ir]·CH$_2$Cl$_2$ (14). Suitable crystals for X-ray experiments were obtained by slow diffusion of diethyl ether into dichloromethane (**6**, **9**, and **14**) or chloroform (**13**) solutions. Data were collected on a Bruker Smart CCD diffractometer, with graphite-monochromated Mo−K$_\alpha$ (λ = 0.71073) radiation, operating at 50 kV and 20 or 30 mA. A summary of the fundamental crystal data and refinement data are given in Table 3. In all cases data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each frame exposure time was of 10 s or 20 s, covering 0.3° in ω. The cell parameters were determined and refined by a least-squares fit of all reflections collected. The first 100 frames were recollected at the end of the data collection to monitor crystal decay. No appreciable decay was observed. A semiempirical absorption correction was applied for **6**, **9**, and **13**. The structures of all the compounds were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXS-97).[26] All nonhydrogen atoms have been refined anisotropically, except the solvent molecules for **6**, which have been refined isotropically and with geometrical restraints. The hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameters related to the bonded atom, except the H atoms bonded to N atoms for all compounds and the hydrogen atoms bonded to C20 for **14** and **13**, which were located in a final Fourier difference synthesis and included with fixed isotropic factors and coordinates for **9**, **14**, and **13** while for **6** refined riding. The final R and Rw are shown in Table 3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data file of complexes **6**, **9**, **13**, and **14** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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