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Mechanistic Investigations of Imine Hydrogenation Catalyzed by Dinuclear Iridium Complexes

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Abstract: Treatment of $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_3(NCMe)(P\textit{i}Pr_3)_2]$ (**1**) with one equivalent of HBF_4 or [PhNH=CHPh]BF_4 affords efficient catalysts for the homogeneous hydrogenation of *N*-benzylideneaniline. The reaction of **1** with HBF_4 leads to the trihydride–dihydrogen complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(\eta^2\text{-}H_2)(NCMe)(P\textit{i}Pr_3)_2]BF_4$ (**2**), which has been characterized by NMR spectroscopy and DFT calculations on a model complex. Complex **2** reacts with imines such as *t*BuN=CHPh or PhN=CHPh to afford amine complexes $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)\{L\}(P\textit{i}Pr_3)_2]BF_4$ (L = NH(*t*Bu)CH_2Ph, **3**; NH(Ph)CH_2Ph, **4**) through a sequence of proton- and hydride-transfer steps. Dihydrogen partially displaces the amine ligand of **4** to form **2**; this complements a possible catalytic cycle for the *N*-benzylideneaniline hydrogenation in which the amine-by-dihydrogen substitution is the turnover-determining step. The rates of ligand substitution in **4** and its analogues with labile ligands other than amine are dependent upon the nature of the leaving ligand and independent on the incoming ligand concentration, in agreement with dissociative substitutions. Water complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)(OH_2)(P\textit{i}Pr_3)_2]BF_4$ (**7**) hydrolyzes *N*-benzylideneaniline, which eventually affords the poor hydrogenation catalyst $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)(NH_2Ph)(P\textit{i}Pr_3)_2]BF_4$ (**11**). The rate law for the catalytic hydrogenation in 1,2-dichloroethane with complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(OSO_2CF_3)(NCMe)(P\textit{i}Pr_3)_2]$ (**8**) as catalyst precursor is rate = $k[\mathbf{8}]\{p(H_2)\}$; this is in agreement with the catalytic cycle deduced from the stochiometric experiments. The hydrogenation reaction takes place at a single iridium center of the dinuclear catalyst, although ligand modifications at the neighboring iridium center provoke changes in the hydrogenation rate. Even though this catalyst system is also capable of effectively hydrogenating alkenes, *N*-benzylideneaniline can be selectively hydrogenated in the presence of simple alkenes.

Keywords: homogeneous catalysis · hydrogenation · imines · iridium · reaction mechanisms

Introduction

Di- and polynuclear metal complexes can display distinctive chemical properties as a consequence of their multimetallic reaction sites and intermetallic cooperation phenomena. These features can drive unusual transformations inaccessible to mononuclear complexes and might enable new facile alternative pathways for conventional reactions.[1,2] Such advantages seem to be widely exploited by nature, through enzymes containing polymetallic active sites,[3] although their use in technological catalytic applications remains a challenge.

Recent investigations on intermetallic cooperation phenomena during catalysis allowed us to identify a new dinuclear hydrogenation mechanism,[4] which operates in alkene and alkyne hydrogenations, by using complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2(H)_3(NCMe)(P\textit{i}Pr_3)_2]$ (**1**) as the catalyst precursor. In such a mechanism [illustrated for diphenylacetylene in Equation (1)], the transmission of ligands *trans* effects between metals,[5] together with the high mobility of hydrides, permit an alternate use of the two-metal centers for substrate activation and product release. Apart from this peculiarity, the catalysis seems to involve the concerted elementary steps common to most conventional hydrogenation cycles. After recognizing the ionic mechanism for imine hydrogenation described in the preceding paper,[6] we became

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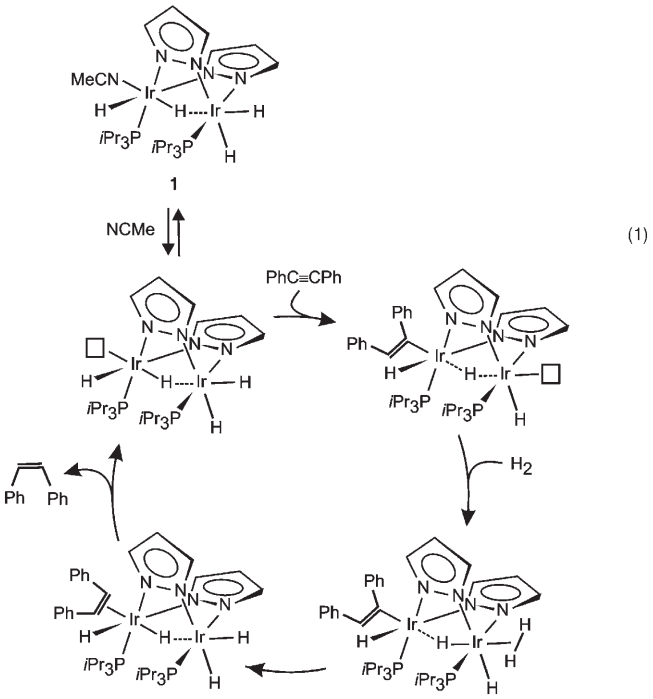
interested in how such hydrogenations could proceed in a more versatile dinuclear environment. Our investigation on the hydrogenation of *N*-benzylideneaniline catalyzed by derivatives of **1** has again concluded with a mechanism of ionic type, which comprises the sequential transfer to the imine of the two hydrogens of an η^2-H_2 ligand, in the form of H^+ and H^- moieties. Noteworthy, such a mechanism does not have any elementary step in common with that described in the preceding paper for the same substrate and closely related catalyst precursors, thus illustrating the variety of mechanistic resources available for ionic hydrogenation.[7] The deduced mechanism also displays very significant differences with that previously recognized for C=C hydrogenations of **1** [Eq. (1)]. Such differences have been exploited to achieve selective imine hydrogenations in the presence of readily hydrogenable alkenes: a desirable and previously anticipated consequence of the mechanistic understanding of C=N hydrogenations.[8]



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Results and Discussion

Neutral complex **1** has been recognized as inactive for the catalytic hydrogenation of *N*-benzylideneaniline. However, this compound has been observed to afford very effective C=N hydrogenation catalysts upon addition of catalytic amounts of a protic acid, either in the form of a diethyl ether solution of HBF_4 or as the iminium salt [PhNH=CHPh]BF_4. As illustrated in Figure 1, the use of one equivalent of acid per mol of catalyst leads to the fast hydrogenation of the imine under mild conditions, whereas larger amounts of acid diminish the catalytic activity.

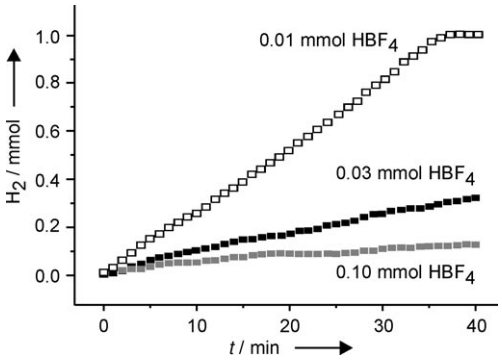


Figure 1. H_2-uptake profiles for the hydrogenation of *N*-benzylideneaniline catalyzed by **1** in the presence of HBF_4. Conditions: 1,2-dichloroethane (8 mL), $T = 333$ K, $p = 1.0$ bar, $[PhN{=}CHPh]_0 = 0.125\ mol\,L^{-1}$, $[\mathbf{1}] = 1.25 \times 10^{-3}\ mol\,L^{-1}$ (0.01 mmol).

Protonation and hydride-transfer reactions: The possible effect of the acidic additive on the catalyst precursor and the catalysis has been examined through NMR studies of stoichiometric reactions. The reaction of complex **1** with one equivalent of HBF_4 in CD_2Cl_2 has been found to quantitatively afford a new compound; the ^1H NMR hydride resonances are shown in Figure 2. The two signals at higher

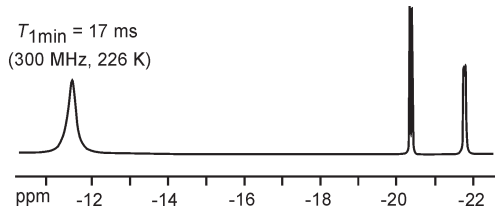
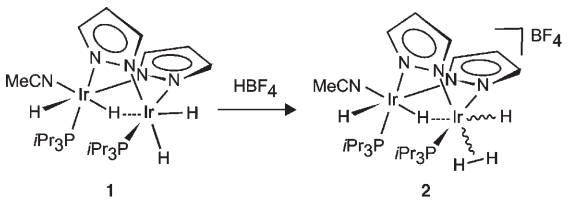


Figure 2. High-field region of the ^1H NMR spectrum of **2** in CD_2Cl_2 at 293 K.

field, two doublets displaying a mutual J(H,H) coupling constant of 3 Hz and J(H,P) couplings of 9 and 18 Hz, are attributable to a bridging and a terminal hydride, respectively. The remaining broad signal corresponds to three protons and displays a short T_1 relaxation time, which indicates short H–H distances and suggests the presence of a dihydrogen ligand. On the basis of this information, the most likely result of the reaction seems to be the trihydride–η^2-dihydrogen complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(\eta^2\text{-}H_2)(NCMe)(P\mathit{i}Pr_3)_2]BF_4$ (**2**) [Eq. (2)], in which a terminal hydride would rapidly exchange in the NMR time scale with a dihydrogen ligand, as usually found in *cis* hydride–dihydrogen species.[9]



(2)

Unfortunately, the proposed hydride/dihydrogen exchange has been observed to remain fast at the lowest temperature attainable in CD_2Cl_2 solution, thus precluding identification of the ground-state structure of **2**. In order to provide a more accurate structural description, we have carried out the structure optimization of model cation $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_4(NCMe)(PH_3)_2]^+$ (**2′**) by use of DFT (B3LYP) calculations. The calculations indicate the existence of the two minima shown in Figure 3, both corresponding to trihydride–dihydrogen compounds. The minima are separated by an energy of 6.9 kcal mol^{-1}, in agreement with the experimentally observed fast exchange. Interestingly, the most stable structure, **2b′**, is also that featuring a more intact dihydrogen moiety, which is coordinated *trans* to a pyrazolate nitrogen.

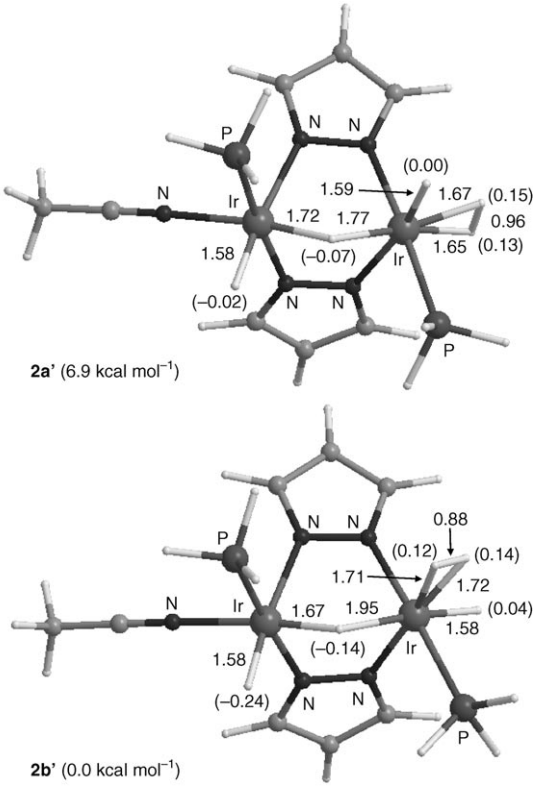
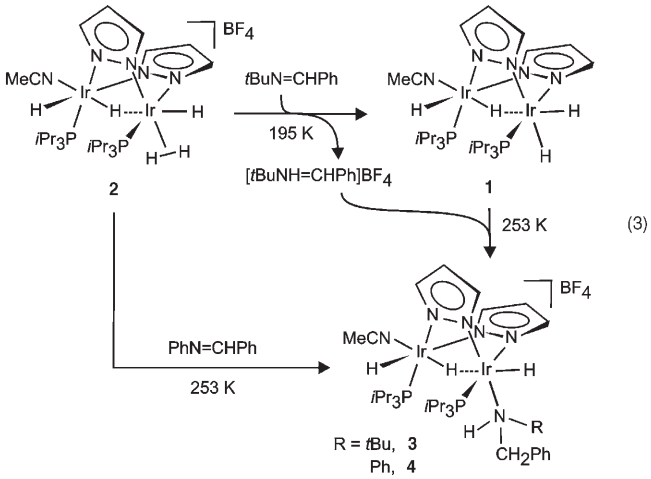
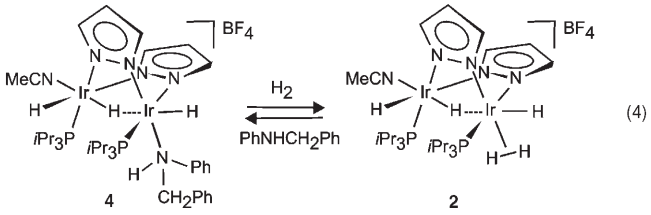


Figure 3. DFT (B3LYP) optimized structures for the stable isomers of the model complex **2′**. Interatomic distances are in Å. Values in parentheses are natural charges of the hydride ligands. Relative energies are free energies in standard conditions.

The analysis of the hydride ligands natural population analysis partial charges in these calculated structures (in parentheses in Figure 3) indicates the dihydrogen ligand H atoms to be acidic.[10] Therefore, it could be expected the protonation reaction of Equation (2) would revert in the presence of a base. The base can be, for example, imine *t*BuN=CHPh, which has been observed by NMR to react with **2** affording the corresponding iminium cation and complex **1** [Eq. (3)]. In CD_2Cl_2, this reaction is fast and quantitative already at 195 K. Interestingly, the mixture of reaction products has been found to evolve at temperatures above 253 K, affording trihydride complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)\{NH(tBu)CH_2Ph\}(PiPr_3)_2]BF_4$ (**3**). The NMR data obtained for this new complex are consistent with the presence of a *tert*-butylbenzylamine ligand, also confirming the structural disposition of hydride and phosphine ligands shown in Equation (3). The formation of this compound indicates that the imine has been able to consecutively extract the two H atoms of the dihydrogen ligand to complete its hydrogenation to an amine ligand.

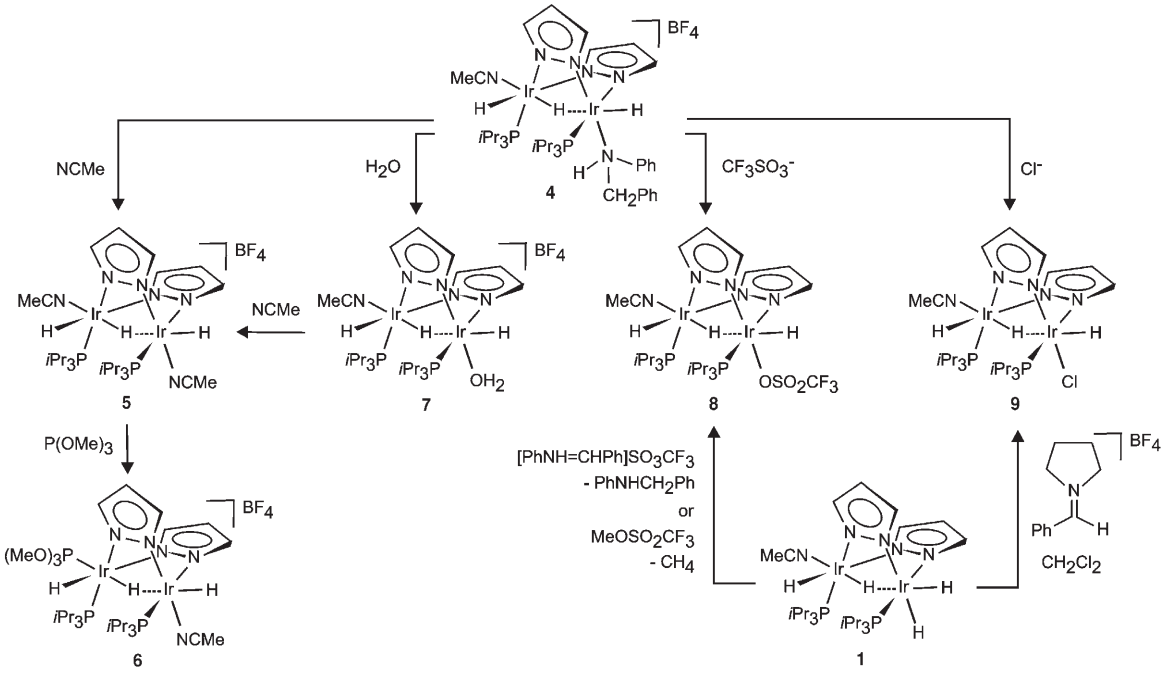


The use of the *N*-benzylideneaniline substrate as a base in this reaction has led to the formation of an analogue of **3**, the complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)\{NH(Ph)CH_2Ph\}(PiPr_3)_2]BF_4$ (**4**), which has been isolated and characterized by analytic and spectroscopic methods. In this case, the two steps of the reaction could not be observed separately, a likely result of the lower basicity of this phenyl-substituted imine which is expected to relatively disfavor the initial deprotonation against the hydride-transfer step. In any case, compound **4** has also been obtained in good yield by reaction of **1** with the corresponding iminium salt [PhNH=CHPh]BF_4, in agreement with the proposed sequence of H^+ and H^- transfer steps leading to hydrogenation. The latter reaction between **1** and [PhNH=CHPh]BF_4 is also one of those experimentally observed to promote fast catalysis, so that complex **4**, as well as **2**, could be considered likely components of the catalytic reaction and potential hydrogenation intermediates. In fact, the completion of a catalytic cycle on the basis of the experimentally observed stoichiometric reactions of Equation (3) just requires the amine by dihydrogen substitution reaction of Equation (4) to be feasible.



The reaction has been experimentally observed to be relatively slow and slightly disfavored in thermodynamic terms. The exposition of 3.0×10^{-2} mol L^{-1} solutions of **4** in CD_2Cl_2 to dihydrogen (1 bar) at 273 K has consistently led to the formation of *N*-benzylaniline and thermodynamic distributions of complexes **4** and **2** of relative molar composition 85:15, which require several minutes to be developed. In the frame of the proposed hydrogenation catalytic cycle, these latter features indicate the amine by dihydrogen substitution to be the most likely turnover-determining step.

Substitution reactions: The substitution of the amine ligand of **4** has allowed the systematic preparation of several isostructural derivatives. Equation (5) depicts some selected examples for such substitution reactions with neutral or anionic incoming ligands, which lead to compounds relevant to the following discussion on imine hydrogenation catalysis. Figure 4 shows the structures determined for three of these substitution products and Table 1 gives their most relevant structural parameters.



(5)

All substitution reactions have been observed to be slow at room temperature and require reaction times of about 30 min to be complete, irrespective of the incoming ligand. The behavior of the bis-acetonitrile compound $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)_2(PiPr_3)_2]BF_4$ (**5**) in the reaction leading to $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)\{P(OMe)_3\}(PiPr_3)_2]BF_4$ (**6**) allows to conclude that the most labile coordination position of the dinuclear compound is that *trans* to the bridging hydride. This indicates that the selective substitution reactions of Equation (5) are caused by a very weak imine coordination, which is attributable to its large steric demands. Nevertheless, smaller ligands such as water or triflate can also be released from the coordination position *trans* to nitrogen, as illustrated by the reaction of $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)(OH_2)(PiPr_3)_2]BF_4$ (**7**) with acetonitrile leading to **5**, or by the transformation of $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(OSO_2CF_3)(NCMe)(PiPr_3)_2]$ (**8**) into analogue **5** with triflate as the anion. This triflate ligand substitution has been observed to proceed at a rate comparable to those of amine substitutions in **4**, while the replacement of the water ligand of **7** has been found to be clearly slower. Furthermore, the rate of 2.1×10^{-6} mol L^{-1} s^{-1} estimated by ^{31}P NMR spectroscopy for this latter reaction (in CD_2Cl_2 at 253 K) has been found to be independent upon the concentration of the incoming acetonitrile ligand. The dependence of the substitution rate upon the nature of the leaving ligand and its independence upon the incoming ligand concentration indicates these substitution reactions to proceed through a dissociative mechanism. Taking into account that the amine-by-dihydrogen substitution constitutes the slow step of the proposed catalytic cycle, the feasibility of hydrogenation with this catalyst and the hydrogenation rates are expected to strongly depend upon the coordination capability of the amine products and, in particular, on the size of the substituents at the nitrogen.

Equation (5) also describes alternative routes to the neutral substitution products **8** and **9**, starting from complex **1**, that provide further support for the occurrence of a hydride transfer elementary step during hydrogenation. Thus, triflate complex **8** can be alternatively obtained by treatment of **1** with methyl triflate, in a reaction also producing methane. The use of 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate as hydride acceptor has been found to readily produce the corresponding amine, which is too hindered to ef-

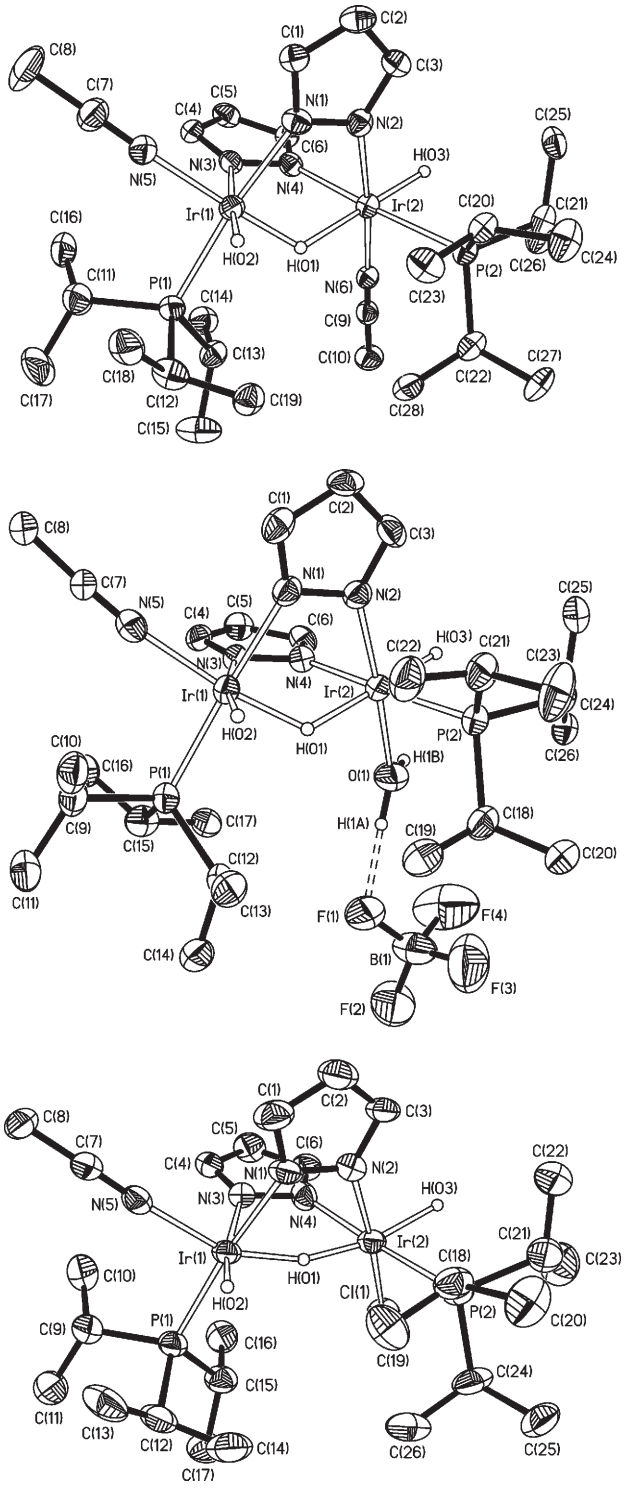


Figure 4. Molecular structures of the cations of complexes **5** (top) and **7** (middle), and complex **9** (bottom).

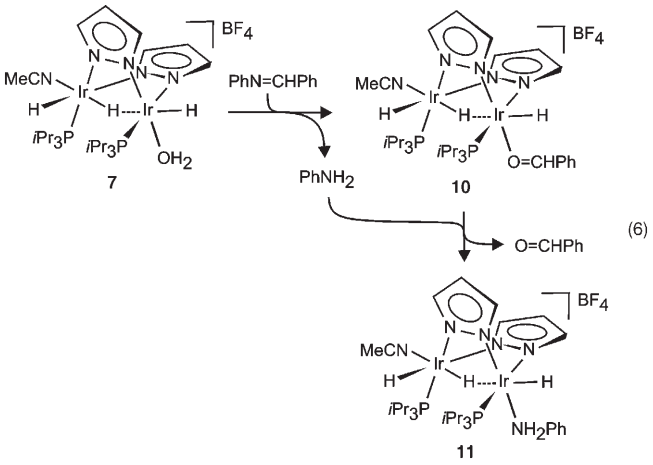
fectively coordinate to the resulting unsaturated complex. This reaction can result in a wealth of substitution products just by addition of the desired incoming ligand, although in the absence of potential ligands and in chlorinated solvents, the reaction has been found to afford chloride complex [Ir_2-(μ-H)(μ-Pz)$_2$H$_2$(Cl)(NCMe)(P*i*Pr$_3$)$_2$] (**9**). Formation of **9** seems to involve the cleavage of a solvent C–Cl bond at the unsaturated species generated after hydride transfer. Interestingly, the same reaction in the absence of hydride acceptor was found to slowly afford an isomer of **9** with the chloride ligand *trans* to the bridging hydride.[5,11]

Table 1. Selected bond lengths [Å] and angles [°] for complexes **5**, **7** and **9**.

	5	**7**	**9**
Ir(1)···Ir(2)	3.0210(4)	3.0150(5)	3.0481(5)
Ir(1)–P(1)	2.2672(17)	2.268(2)	2.271(2)
Ir(1)–N(1)	2.073(5)	2.104(6)	2.098(6)
Ir(1)–N(3)	2.166(5)	2.162(6)	2.167(6)
Ir(1)–N(5)	2.032(6)	2.059(7)	2.021(7)
Ir(1)–H(01)	1.58(2)	1.65(6)	1.434(13)
Ir(1)–H(02)	1.60(4)	1.52(6)	1.57(6)
Ir(2)–P(2)	2.2955(17)	2.280(2)	2.278(2)
Ir(2)–N(2)	2.034(5)	1.995(6)	2.034(6)
Ir(2)–N(4)	2.067(5)	2.072(6)	2.063(6)
Ir(2)–N(6)	2.002(5)		
Ir(2)–O(1)		2.187(6)	
Ir(2)–Cl(1)			2.379(2)
Ir(2)–H(01)	1.83(2)	1.77(6)	1.661(14)
Ir(2)–H(03)	1.61(5)	1.68(6)	1.70(6)
P(1)-Ir(1)-N(1)	171.82(15)	172.60(17)	172.43(18)
P(1)-Ir(1)-N(3)	102.99(13)	102.95(16)	102.04(16)
P(1)-Ir(1)-N(5)	94.22(16)	94.94(17)	94.56(17)
P(1)-Ir(1)-H(01)	87.4(15)	94(2)	104(2)
P(1)-Ir(1)-H(02)	82.4(15)	82(2)	92(2)
P(2)-Ir(2)-N(2)	94.93(15)	93.92(17)	93.89(18)
P(2)-Ir(2)-N(4)	175.38(15)	175.63(17)	176.54(17)
P(2)-Ir(2)-H(01)	101.1(13)	96.0(19)	113(2)
P(2)-Ir(2)-H(03)	78.2(16)	89(2)	81(2)
P(2)-Ir(2)-N(6)	90.57(14)		
P(2)-Ir(2)-O(1)		92.00(17)	
P(2)-Ir(2)-Cl(1)			92.72(8)

Imine hydrolysis: Water complex **7**, which crystallizes as an ion pair, featuring a short H(1A)···F(1) distance of 1.76(2) Å, is depicted in Figure 4. This interaction suggests the acidic character of the water ligand hydrogen atoms, which could be responsible for the observed fast reaction between **7** and the basic imine substrate. This reaction has been found to eventually afford aniline complex [Ir_2(μ-H)-(μ-Pz)$_2$H$_2$(NCMe)(NH$_2$Ph)(P*i*Pr$_3$)$_2$]BF$_4$ (**11**) and benzaldehyde [Eq. (6)], although the NMR examination of the process at low temperature ($CDCl_3$, 273 K) revealed benzaldehyde complex [Ir_2(μ-H)(μ-Pz)$_2$H$_2$(NCMe)(OCHPh)-(P*i*Pr$_3$)$_2$]BF$_4$ (**10**) and aniline as the hydrolysis kinetic products. Again, the substitution of the benzaldehyde ligand of **10** by aniline produced in the hydrolysis has been observed to be slow. The identity of complexes **10** and **11** has been established by comparison of the NMR spectra of the "in situ" hydrolysis reactions with those of pure samples, which can easily be obtained from **4** through substitution reactions similar to those in Equation (5) using benzaldehyde and aniline, respectively.

The hydrolysis reaction of Equation (6) has been found to readily take place under the conditions of catalytic hydroge-



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nation, constituting a very effective catalyst poisoning process in the presence of water traces. In fact, complex **11** has been observed to be a poor hydrogenation catalyst, as expected from the strong coordinating capability and small size of its aniline ligand.

Hydrogenation kinetics and mechanism: Due to the effectiveness of the hydrolysis process, the catalytic hydrogenation reactions were found to hardly afford reproducible kinetic results when using hygroscopic co-catalyst such as HBF_4 or iminium salts. For this reason, the kinetic study of this hydrogenation was based on the neutral triflate complex **8**, which avoided the use of additives and simplifies the reactions set-up. The use of this compound as a catalyst precursor adds a potential competitor for the catalyst coordination vacancy, the triflate anion, although this has been experimentally observed to have a very minor effect in the reaction rates. Indeed, the H_2-uptake profile shown in Figure 5 clearly illustrates that the use of **8** still leads to very fast hydrogenations under mild conditions. This linear profile also indicates the hydrogenation rate to be independent upon *N*-benzylideneaniline concentration.

The logarithmic representations in Figure 5, based on the rates collected in Table 2, indicate a first-order dependence of the reaction rate upon catalyst concentration and dihydrogen pressure. This is in agreement with the catalytic cycle deduced from the aforementioned reactivity studies [Eq. (7)] in which the reaction between **4** and dihydrogen is the rate-determining step. The cycle consists of fast elementary steps of H^+ transfer to the imine and H^- transfer to the iminium cation, followed by a slow amine by dihydrogen substitution. This mechanism is similar to that recently reported by Norton et al. for the hydrogenation of iminium to ammonium cations catalyzed by [CpRu(diphosphine)H] complexes, in which H^- transfer was found to be slow step.[12] A similar cycle has also been recently proposed for high-pressure imine hydrogenations catalyzed by rhenium complexes.[13]

The catalytic cycle in Equation (7) is likely to be interfered by the basic *N*-benzylaniline hydrogenation product,

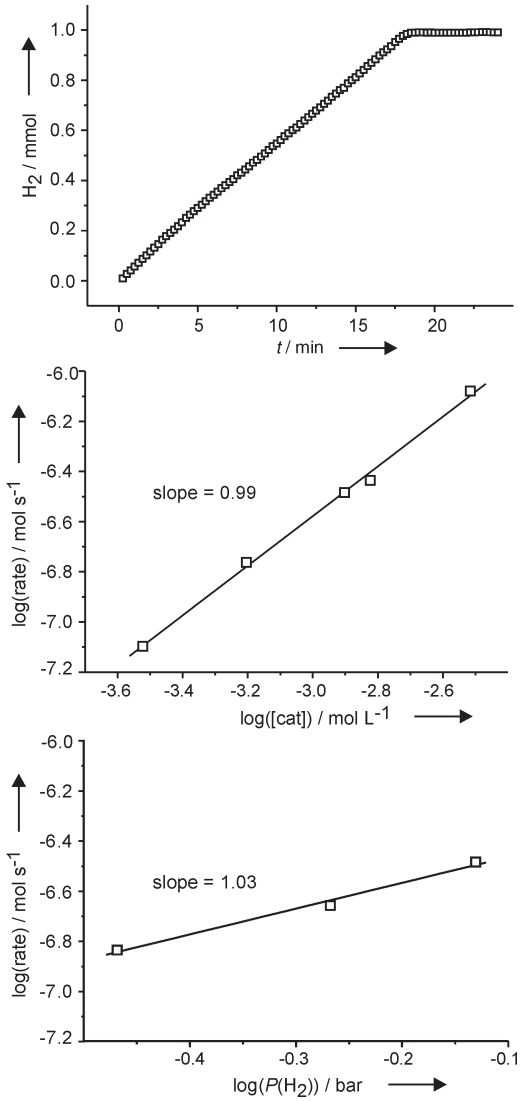

Figure 5. H_2-uptake profile (top) for the hydrogenation of *N*-benzylideneaniline catalyzed by **8**. Conditions: 1,2-dichloroethane (8 mL), T = 323 K, p = 1.0 bar, $[PhN{=}CHPh]_0$ = 0.125 mol L^{-1}, [**8**] = 3.0×10^{-3} mol L^{-1}. Logarithmic plots for the dependence of the hydrogenation rates upon catalyst concentration (middle), and dihydrogen partial pressure pressure (bottom).

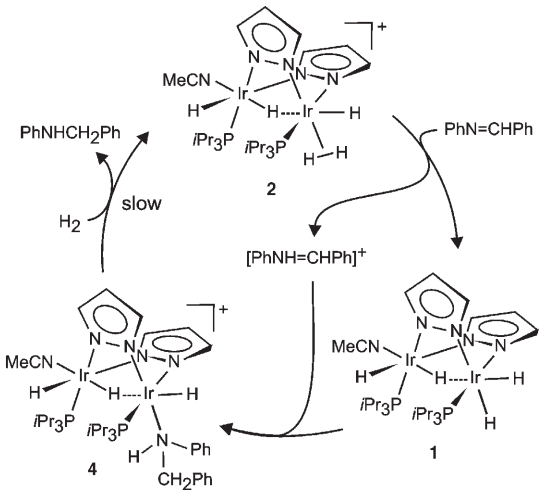

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Table 2. Initial reaction rates for the hydrogenation of *N*-benzylideneaniline catalyzed by **8** in 1,2-dichloroethane at 323 K.[a]

[**8**] [mol L^{-1}]	$p(H_2)$ [bar][b]	Rate [mol s^{-1}]
3.00×10^{-4}	0.74	7.99×10^{-8}
6.25×10^{-4}	0.74	1.73×10^{-7}
1.25×10^{-3}	0.74	3.28×10^{-7}
1.50×10^{-3}	0.74	3.67×10^{-7}
3.05×10^{-3}	0.74	8.33×10^{-7}
1.25×10^{-3}	0.54	2.20×10^{-7}
1.25×10^{-3}	0.34	1.46×10^{-7}

[a] $[PhN{=}CHPh]_0 = 0.125$ mol L^{-1}. [b] 1,2-Dichloroethane vapor pressure 0.31 bar (323 K).

which has been observed to readily deprotonate complex **2** under the same experimental conditions shown for imines *t*BuN=CHPh and PhN=CHPh in Equation (3). Nevertheless, such a competing process, which affects the steps prior to the rate-determining step, does not have any apparent effect in the hydrogenation rate, which remains constant despite the increasing of amine concentration during the reaction (Figure 5).

According to Equation (7), this catalytic imine hydrogenation involves the participation of a single metal center of the dinuclear compound. Nevertheless, taking into account the effective intermetallic communication through the bridging hydride previously recognized in these compounds,[5] the replacement of acetonitrile by other ligands was expected to influence the electronic properties of the neighboring metal center and, as a consequence, the hydrogenation rates. Indeed, our exploratory experiments using analogues of **8** with ligands such as CO, pyridine or ethylene instead of acetonitrile, $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(OSO_2CF_3)(L)(P\textit{i}Pr_3)_2]$ (L = CO, **12**; py, **13**; η^2-C_2H_4, **14**), have evidenced a strong influence of the ligand occupying the position *trans* to the bridging hydride on the catalysis. Unfortunately, the catalyst precursors bearing CO (**12**) and pyridine (**13**) have led to hydrogenation rates much slower than those obtained with **1**, while the ethylene complex **14** has been observed to be just slightly faster than **1** (Table 3). In any case, these results indicate the nature of the axial ligand at the spectator iridium center to be a crucial aspect for catalyst optimization.

Table 3. Hydrogenation reactions catalyzed by $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(OSO_2CF_3)(L)(P\textit{i}Pr_3)_2]$ complexes.[a]

Catalyst precursor	Substrate	*t* [min]	Imine conversion [%]	Alkene conversion [%]
8	PhN=CHPh	25	> 99	–
12	PhN=CHPh	1020	81	–
13	PhN=CHPh	1080	73	–
14	PhN=CHPh	16	> 99	–
8	1-octene	30	–	> 99
8	PhN=CHPh 1-octene	90	81	12
8	$PhCH{=}CH_2$	90	–	94
8	PhN=CHPh $PhCH{=}CH_2$	35	> 99	5
8	$Ph(Me)C{=}CH_2$	240	–	26
8	PhN=CHPh $Ph(Me)C{=}CH_2$	40	> 99	0

[a] Conditions: 1,2-dichloroethane (8 mL), $T = 333$ K, initial concentration of each substrate = 0.125 mol L^{-1}, catalyst precursor concentration = 1.25×10^{-3} mol L^{-1}, $p = 1.0$ bar.

Selective imine hydrogenation in the presence of alkenes: Comparison of the imine hydrogenation mechanism in Equation (7) with that responsible for the C=C and C≡C hydrogenations in Equation (1) evidences profound mechanistic differences between the two hydrogenations, but a species common to both catalytic cycles, that is, precursor **1**. This suggests that, in the presence of substrate mixtures containing both C–C multiple bonds and C=N functionalities, complex **1** can be directed to selectively hydrogenate one type of bonds by simply adjusting the acidity of the reaction media, thus favoring the presence of neutral or cationic active species. This has been found to be facile for the selective hydrogenation of C–C multiple bonds, while our exploratory experiments on the reverse selectivity have reached very remarkable percentages of C=N versus C=C hydrogenation, in the range 90–100% depending on the alkene. Under the conditions employed in this study, the completely selective C=N hydrogenation has been found possible only in the presence of relatively hindered alkenes, due to the fact that the cationic derivatives involved in the C=N hydrogenation also are very efficient C=C hydrogenation catalysts, as illustrated for precursor **8** and several alkenes in Table 3.

A more detailed course of these selective C=N hydrogenations is shown in Figure 6 for a mixture of *N*-benzylideneaniline and cyclooctene, the selectivity of which reaches a 90%. Figure 6 and the values in Table 3 show that the hydrogenation of the mixture is much slower than the hydrogenation of each separate component. In the frame of the mechanism in Equation (7), this effect is likely to result from the competing alkene coordination at the catalyst, which should hinder the rate-determining dihydrogen coordination. However, we still do not have a plausible rationalization for the competing effect of the imine substrate (or the amine product) during C=C hydrogenations. This aspect of the catalytic properties of complex **1** and its derivatives is currently being investigated within our search for conditions which should allow completely selective C=N hydrogenations in presence of C–C multiple bonds.

Summary and Conclusions

Under simple experimental conditions, the dinuclear complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_3(NCMe)(P\textit{i}Pr_3)_2]$ (**1**) can be transformed into derivatives such as $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(L)(NCMe)(P\textit{i}Pr_3)_2]BF_4$ (L = η^2-H_2, **2**; NH(Ph)CH_2Ph, **4**) or $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(OSO_2CF_3)(NCMe)(P\textit{i}Pr_3)_2]$ (**8**), which are very efficient catalyst precursors for the hydrogenation of *N*-benzylideneaniline. The hydrogenation reaction proceeds through an ionic mechanism comprising the rate-determining substitution of the amine ligand of **4** by dihydrogen to give **2**, followed by fast elementary steps of proton and hydride transfer to the imine substrate. Such a mecha-

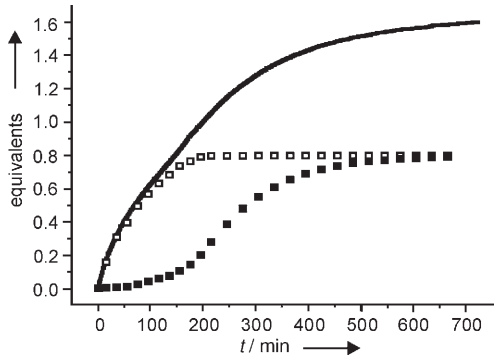

Figure 6. H_2-uptake (——) and product formation (GC) profiles for the competitive hydrogenation of *N*-benzylideneaniline (□) and cyclooctene (■) catalyzed by **8**. Conditions: 1,2-dichloroethane (8 mL), $T = 333$ K, $p = 1.0$ bar, $[PhN{=}CHPh]_0 = 0.125\ mol\,L^{-1}$, $[cyclooctene]_0 = 0.125\ mol\,L^{-1}$, $[\mathbf{8}] = 1.25\times10^{-3}\ mol\,L^{-1}$.

nism permits the selective hydrogenation of *N*-benzylideneaniline in the presence of readily hydrogenable alkenes, with selectivities toward C=N hydrogenation above 90%. The catalysis takes place at a single iridium center of the dinuclear compound although, in agreement with the effective intermetallic communication previously recognized in this type of compounds, ligand modifications at the spectator metal atom can provoke significant changes in the hydrogenation rate. The catalyst system is very sensitive to the presence of water, which favors the formation of complex $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(NCMe)(OH_2)(P\mathit{i}Pr_3)_2]BF_4$ (**7**). This compound effectively hydrolyzes the imine substrate, yielding an analogous complex with a hardly dissociable aniline ligand that displays poor catalytic activity.

The mechanistic studies in this work, together with those in the preceding paper, illustrate that imines can be effectively and selectively hydrogenated by iridium catalysts through mechanisms that are ionic and outer-sphere, since they involve steps of proton and hydride transfer (simultaneous or not), and use hydrogen bonds rather than metal coordination vacancies to anchor the imine substrate to the catalyst. Nevertheless, these C=N hydrogenations can also involve intermediates and elementary steps compatible with classical concerted mechanisms, such as dihydrogen compounds, concerted H_2 oxidative additions or ligand substitution reactions. Such a variety of mechanistic resources enables C=N hydrogenation to connect the existing rationalizations of catalytic C=C and C=O reductions, thus contributing to an enriched unified view of the transition-metal-catalyzed hydrogenations that could assist the rational development of more selective catalysts and applications.

Experimental Section

Details about equipment and catalytic reactions are given in the preceding article.[6] The *N*-benzylideneaniline solutions in 1,2-dichloroethane used in catalytic experiments were prepared under argon from the commercial imine (Aldrich), and dried with molecular sieves during one week before use.

Synthesis: All experiments were carried out under argon atmosphere by Schlenk techniques. Solvents were dried by known procedures and distilled under argon before use. Complex **1** and its derivatives with CO and ethylene axial ligands, $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_3(L)(P\mathit{i}Pr_3)_2]$ (L = CO, η^2-C_2H_4), were prepared as previously reported.[11] The pyridine analogue $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_3(py)(P\mathit{i}Pr_3)_2]$ was prepared by treatment of **1** (506.0 mg, 0.57 mmol) with pyridine (92.6 μL, 1.14 mmol) in toluene, followed by precipitation in methanol (466.0 mg, 78%). ^{1}H NMR (C_6D_6, 293 K): $\delta = -25.42$ (dddd, J(H,P) = 16.1, 4.4, J(H,H) = 4.4, 3.6 Hz, 1H; IrHIr), −23.18 (dddd, J(H,P) = 22.0, 3.6, J(H,H) = 8.0, 3.6 Hz, 1H; IrH), −21.24 (dd, J(H,P) = 19.8, J(H,H) = 8.0 Hz, 1H; IrH), −20.88 (dd, J(H,P) = 19.0, J(H,H) = 4.4 Hz, 1H; IrH), 1.01, 1.15 (2×dd, J(H,P) = 13.2, J(H,H) = 7.3 Hz, 9H each; PCHCH_3), 1.34, 1.35 (2×dd, J(H,P) = 12.5, J(H,H) = 7.3 Hz, 9H each; PCHCH_3), 2.26, 2.44 (2×m, 3H each; PCHCH$_3$), 6.23, 6.29 (2×dt, J(H,P) = 2.2, J(H,H) = 1.5 Hz, 1H each; CH), 6.30 (t, J(H,H) = 7.3 Hz, 2H; CH), 6.45 (d, J(H,H) = 1.5 Hz, 1H; CH), 6.94 (t, J(H,H) = 7.3 Hz, 1H; CH), 7.68, 7.81, 8.06 (3×d, J(H,H) = 1.5 Hz, 1H each; CH), 9.15 (br, 2H; CH); ^{31}P{^{1}H} NMR (C_6D_6, 293 K): $\delta = 8.80$, 30.30 (2×s); ^{13}C{^{1}H} NMR (C_6D_6, 293 K): $\delta = 17.2$, 18.8, 19.0, 19.1 (all s; PCHCH$_3$), 24.0 (d, J(C,P) = 28.5 Hz; PCHCH$_3$), 25.2 (d, J(C,P) = 30.0 Hz; PCHCH$_3$), 102.7, 103.2 (2×d, J(C,P) = 2.9 Hz; CH), 123.5 (s; CH), 132.3 (d, J(C,P) = 4.4 Hz; CH), 133.6 (br; CH), 134.5 (s; CH), 138.3 (br; CH), 142.8 (d, J(C,P) = 2.9 Hz; CH), 156.7 (s; CH); IR (KBr): $\tilde{\nu}$ = 2158 (IrH), 1661 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 921 (100) [M^+]; elemental analysis calcd (%) for $C_{29}H_{57}N_5Ir_2P_2$: C 37.77, H 6.23, N 7.59; found: C 37.52, H 6.10, N 7.49.

Iminium salts [PhNH=CHPh]BF_4, [*t*BuNH=CHPh]BF_4, [PhNH=CHPh]SO_3CF_3 were prepared as white solids in ca. 90% yield by treatment of diethyl ether solutions of the commercial imines with the corresponding commercial acids: HBF_4 (54% in diethyl ether) and $HOSO_2CF_3$, respectively.

[PhNH=CHPh]BF_4: ^{1}H NMR (CD_2Cl_2, 293 K): $\delta = 7.55$ (m, 3H; CH), 7.66 (t, J(H,H) = 7.9 Hz, 2H; CH), 7.78 (m, 2H; CH), 7.86 (tt, J(H,H) = 7.5, 1.0 Hz, 1H; CH), 8.26 (dt, J(H,H) = 8.2, 1.0 Hz, 2H; CH), 9.06 (s, 1H; =CH), 12.55 (br, 1H; NH); ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, all s): δ = 121.4 (CH), 126.8 (C), 130.9, 131.0, 132.1, 133.7 (all CH), 136.5 (C), 139.7 (CH), 165.6 (=CH); IR (KBr): $\tilde{\nu}$ = 3333 (NH), 1667 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{13}H_{12}NBF_4$: C 58.03, H 4.50, N 5.20; found: C 57.76, H 4.52, N 5.28.

[*t*BuNH=CHPh]BF_4: ^{1}H NMR (CD_2Cl_2, 293 K): $\delta = 1.63$ (s, 9H; C(CH$_3$)), 7.66 (t, J(H,H) = 7.8 Hz, 2H; CH), 7.85 (t, J(H,H) = 7.6 Hz, 1H; CH), 8.16 (d, J(H,H) = 8.4 Hz, 2H; CH), 8.63 (s, 1H; =CH), 11.45 (br, 1H; NH); ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, all s): δ = 27.9 (C(CH$_3$)$_3$), 37.0 (C(CH$_3$)$_3$), 126.6 (C), 130.5, 132.7, 138.5 (all CH), 167.0 (s; =CH); IR (KBr): $\tilde{\nu}$ = 3332 (NH), 1663 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{11}H_{16}NBF_4$: C 53.04, H 6.47, N 5.62; found: C 52.70, H 6.15, N 5.62.

[PhNH=CHPh]SO_3CF_3: The NMR spectra were similar to those of the tetrafluoroborate analogue with an additional signal in the ^{13}C{^{1}H} spectrum: $\delta = 120.6$ (q, J(C,F) = 319.8 Hz; CF_3SO_3); elemental analysis calcd (%) for $C_{14}H_{12}NSF_3O_3$: C 50.76, H 3.65, N 4.23, S 9.66; found: C 50.60, H 3.66, N 4.30, S 9.61.

1-(1-Phenylethylidene)pyrrolidinium tetrafluoroborate was prepared as described in the literature.[14] All other reagents were obtained from commercial sources and used as received. All new compounds described below are air-sensitive in solution.

$[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2(\eta^2\text{-}H_2)(NCMe)(P\mathit{i}Pr_3)_2]BF_4$ (2): A solution of **1** (44.9 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) in a NMR tube at 195 K was treated with (6.9 μL, 0.05 mmol) of a HBF_4 solution (54% in diethyl ether). The NMR spectra of the resulting orange solution indicated the quantitative formation of complex **2**. ^{1}H NMR (CD_2Cl_2, 233 K): $\delta = -21.81$ (dd, J(H,P) = 9.0, J(H,H) = 3.0 Hz, 1H; IrHIr), −20.43 (dd, J(H,P) = 18.0, J(H,H) = 3.0 Hz, 1H; IrH), −11.43 (br, 3H; IrH), 1.02 (dd, J(H,P) = 14.3, J(H,H) = 7.1 Hz, 18H; PCHCH_3), 1.06 (dd, J(H,P) = 14.3, J(H,H) = 7.0 Hz, 9H; PCHCH_3), 1.21 (dd, J(H,P) = 13.7, J(H,H) = 7.1 Hz, 9H; PCHCH_3), 2.08, 2.30 (2×m, 3H each; PCHCH$_3$), 2.64 (s, 3H; NCCH$_3$), 5.99, 6.07 (2×td, J(H,H) = 1.8, J(H,P) = 1.3 Hz, 1H each; CH),

7.22 (m, 2H; CH), 7.46, 7.53 (2×d, J(H,H) = 1.8 Hz, 1H each; CH); ^{31}P{^{1}H} NMR (CD_2Cl_2, 233 K): δ = 15.21, 20.60 (2×s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K): δ = 4.65 (s; NC*C*H$_3$), 19.03, 19.14, 19.34, 19.67 (all s; PCH*C*H$_3$), 24.31 (d, J(C,P) = 31.6 Hz; P*C*HCH$_3$), 27.41 (d, J(C,P) = 32.8 Hz; P*C*HCH$_3$), 106.02 (d, J(C,P) = 3.3 Hz; CH), 106.92 (d, J(C,P) = 2.8 Hz; CH), 119.74 (s; N*C*CH$_3$), 136.17 (d, J(C,P) = 4.3 Hz; CH), 138.16 (d, J(C,P) = 3.6 Hz; CH), 140.26 (d, J(C,P) = 3.3 Hz; CH), 142.78 (d, J(C,P) = 5.3 Hz; CH).

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(NCMe){NH(*t*Bu)CH$_2$Ph}(P*i*Pr$_3$)$_2$]BF$_4$ (3): A NMR tube containing a solution of **2** (0.05 mmol) in CD_2Cl_2 at 195 K was treated with *t*BuN=CHPh (5.2 μL, 0.05 mmol). The NMR spectra of the resulting solution at 195 K indicated the quantitative formation of **1** and iminium cation [*t*BuN=CHPh]$^+$, which were identified by their ^{1}H NMR spectra. After increasing the sample temperature to 253 K, this mixture was observed to partially transform (ca. 70%) into complex **3**. Selected NMR data: ^{1}H NMR (CD_2Cl_2, 213 K): δ = −21.78 (dd, J(H,P) = 19.5, J(H,H) = 3.3 Hz, 1H; IrH), −21.24 (dddd, J(H,P) = 13.2, 3.3, J(H,H) = 3.3, 3.3 Hz, 1H; IrHIr), −20.71 (dd, J(H,P) = 19.5, J(H,H) = 3.3 Hz, 1H; IrH), 1.11 (s, 9H; C*C*H$_3$), 2.55 (s, 3H; NCCH$_3$), 3.99 (s, 2H; CH$_2$), 4.30 (br, 1H; NH), 5.82, 6.08, 6.82 (all m, 1H each; CH); ^{31}P{^{1}H} NMR (CD_2Cl_2, 213 K): δ = 12.63, 16.05 (2×s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K): δ = 4.44 (s; NC*C*H$_3$), 18.64, 18.76, 19.36, 19.77 (all s; PCH*C*H$_3$), 24.02 (d, J(C,P) = 30.2 Hz; P*C*HCH$_3$), 27.39 (d, J(C,P) = 31.4 Hz; P*C*HCH$_3$), 46.84 (s; CH$_2$), 104.98 (d, J(C,P) = 2.9 Hz; CH), 106.04 (d, J(C,P) = 2.5 Hz; CH), 119.04 (s; N*C*CH$_3$), 129.55, 130.07, 130.44 (all s; CH), 134.70 (d, J(C,P) = 3.6 Hz; CH), 134.76 (s; C), 135.53 (d, J(C,P) = 3.7 Hz; CH), 138.50 (d, J(C,P) = 3.4 Hz; CH), 141.70 (d, J(C,P) = 2.8 Hz; CH).

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(NCMe){NH(Ph)CH$_2$Ph}(P*i*Pr$_3$)$_2$]BF$_4$ (4): A solution of **1** (200.0 mg, 0.23 mmol) in CH_2Cl_2 (4 mL) was treated with [PhNH=CHPh]BF$_4$ (61.2 mg, 0.23 mmol) at 233 K. The resulting solution was concentrated, maintaining the solution temperature below 250 K, to ca. 0.5 mL. Addition of diethyl ether (ca. 4 mL) produced the formation of a pale yellow solid, which was separated by decantation, washed with Et_2O and dried in vacuo (190 mg, 73%). ^{1}H NMR (CD_2Cl_2, 243 K): δ = −22.94 (dd, J(H,P) = 19.8, J(H,H) = 3.3 Hz, 1H; IrH), −21.62 (dddd, J(H,P) = 13.2, 3.3, J(H,H) = 3.3, 3.3 Hz, 1H; IrHIr), −20.72 (dd, J(H,P) = 19.8, J(H,H) = 3.3 Hz, 1H; IrH), 1.03 (dd, J(H,P) = 13.8, J(H,H) = 7.1 Hz, 9H; PCHC*H*$_3$), 1.12 (dd, J(H,P) = 13.6, J(H,H) = 7.0 Hz, 9H; PCHC*H*$_3$), 1.22 (dd, J(H,P) = 14.0, J(H,H) = 7.0 Hz, 9H; PCHC*H*$_3$), 1.25 (dd, J(H,P) = 14.1, J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 2.04, 2.25 (2×m, 3H each; PC*H*CH$_3$), 2.53 (s, 3H; NCCH$_3$), 3.62 (s, 2H; CH$_2$), 4.40 (s, 1H; NH), 5.77, 6.09 (2×td, J(H,H) = 2.0, J(H,P) = 1.4 Hz, 1H each; CH), 6.57 (d, J(H,H) = 7.1 Hz, 1H; CH), 6.78 (m, 1H; CH), 6.85 (d, J(H,H) = 7.7 Hz, 1H; CH), 6.94, 7.12 (2×m, 1H each; CH), 7.16 (dd, J(H,H) = 7.5, 7.1 Hz, 1H; CH), 7.21 (t, J(H,H) = 8.4 Hz, 2H; CH), 7.27 (d, J(H,H) = 2.0 Hz, 1H; CH), 7.28 (m, 2H; CH), 7.32 (m, 1H; CH), 7.52, 7.62 (2×d, J(H,H) = 2.0 Hz, 1H each; CH); ^{31}P{^{1}H} NMR (CD_2Cl_2, 243 K): δ = 12.78, 16.54 (2×s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 243 K): δ = 4.62 (s; NC*C*H$_3$), 18.59, 18.94, 19.37 (all s; PCH*C*H$_3$), 23.68 (d, J(C,P) = 30.2 Hz; P*C*HCH$_3$), 27.27 (d, J(C,P) = 29.3 Hz; P*C*HCH$_3$), 67.75 (s; CH$_2$), 105.62 (d, J(C,P) = 3.0 Hz; CH), 105.77 (d, J(C,P) = 2.9 Hz; CH), 118.68 (s; N*C*CH$_3$), 128.62, 129.18, 129.25, 129.45, 129.64, 130.00 (all s; CH), 135.04 (d, J(C,P) = 3.6 Hz; CH), 135.25 (s; C), 138.26 (d, J(C,P) = 3.6 Hz; CH), 142.37 (d, J(C,P) = 2.6 Hz; CH), 143.17 (d, J(C,P) = 4.7 Hz; CH), 149.02 (s; C); ^{19}F NMR (CD_2Cl_2, 243 K): δ = −152.5 (s); IR (KBr): $\tilde{\nu}$ = 2185 (IrH), 1756 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 1066 (15) [M^+]; elemental analysis calcd (%) for $C_{39}H_{67}N_6BF_4Ir_2P_2$: C 40.61, H 5.86, N 7.28; found: C 40.23, H 5.99, N 7.01.

Reaction of 4 with H$_2$: A solution of **4** (16.0 mg, 0.015 mmol) in CD_2Cl_2 (0.5 mL) was allowed to react under dihydrogen atmosphere (1 bar) for 30 min at 273 K in a WILMAD NMR tube provided with a J-Young valve. The spectroscopic analysis of the resulting solution at 273 K indicated the presence of a mixture consisting of *N*-benzylaniline and compounds **2** and **4** in a 15:15:85 molar ratio, respectively. The identity of the components of the mixture was established by comparison of their ^{1}H NMR signals with those of pure samples in the same solvent.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(NCMe)$_2$(P*i*Pr$_3$)$_2$]BF$_4$ (5): A solution of **4** (230.0 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was treated with NCMe (100 μL) and allowed to react for 30 min at room temperature. The resulting solution was concentrated to ca. 0.5 mL and treated with diethyl ether to give a white solid. The solid was separated by decantation, washed with Et_2O, and dried in vacuo (186 mg, 92%). ^{1}H NMR ($CDCl_3$, 293 K): δ = −22.66 (dddd, J(H,P) = 12.6, 3.6, J(H,H) = 3.6, 2.7 Hz, 1H; IrHIr), −22.54 (dd, J(H,P) = 19.2, J(H,H) = 2.7 Hz, 1H; IrH), −20.70 (dd, J(H,P) = 19.2, J(H,H) = 3.6 Hz, 1H; IrH), 1.06 (dd, J(H,P) = 14.1, J(H,H) = 7.6 Hz, 9H; PCHC*H*$_3$), 1.08 (dd, J(H,P) = 14.7, J(H,H) = 7.8 Hz, 9H; PCHC*H*$_3$), 1.19 (dd, J(H,P) = 13.5, J(H,H) = 6.9 Hz, 9H; PCHC*H*$_3$), 1.22 (dd, J(H,P) = 13.5, J(H,H) = 6.9 Hz, 9H; PCHC*H*$_3$), 2.07, 2.25 (2×m, 3H each; PC*H*CH$_3$), 2.47, 2.56 (2×s, 3H each; NCCH$_3$), 5.75, 5.95 (2×td, J(H,H) = 2.0, J(H,P) = 1.2 Hz, 1H each; CH), 6.84, 7.21, 7.26, 7.42 (all d, J(H,H) = 2.0 Hz, 1H each; CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 12.80, 16.55 (2×s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 3.37, 3.40 (2×s; NC*C*H$_3$), 18.52 (d, J(C,P) = 1.2 Hz; PCH*C*H$_3$), 18.81 (d, J(C,P) = 1.1 Hz; PCH*C*H$_3$), 19.08 (d, J(C,P) = 1.4 Hz; PCH*C*H$_3$), 19.20 (d, J(C,P) = 1.3 Hz; PCH*C*H$_3$), 23.71 (d, J(C,P) = 30.2 Hz; P*C*HCH$_3$), 26.70 (d, J(C,P) = 31.1 Hz; P*C*HCH$_3$), 104.92 (d, J(C,P) = 3.2 Hz; CH), 105.42 (d, J(C,P) = 3.0 Hz; CH), 118.73, 118.78 (s; N*C*CH$_3$), 135.00 (d, J(C,P) = 4.0 Hz; CH), 137.39 (d, J(C,P) = 3.7 Hz; CH), 140.83 (d, J(C,P) = 3.0 Hz; CH), 141.29 (d, J(C,P) = 4.8 Hz; CH); ^{19}F NMR ($CDCl_3$, 293 K): δ = −155.7 (s); IR (KBr): $\tilde{\nu}$ = 2186 (Ir-H), 1744 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 923 (35) [M^+]; elemental analysis calcd (%) for $C_{28}H_{57}N_6BF_4Ir_2P_2$: C 33.27, H 5.68, N 8.31; found: C 33.14, H 5.48, N 8.06. The crystals used in the X-ray diffraction experiment were obtained by slow diffusion of diethyl ether into a saturated solution of **5** in CH_2Cl_2 at 253 K.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(NCMe){P(OMe)$_3$}(P*i*Pr$_3$)$_2$]BF$_4$ (6): A solution of **5** (100.0 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) was treated with P(OMe)$_3$ (35.1 μL, 0.30 mmol) and stirred for 1 h at 323 K. The resulting solution was concentrated to ca. 0.5 mL, cooled to 213 K, and treated with diethyl ether to give a white solid. The solid was separated by decantation, washed with Et_2O, and dried in vacuo (78.1 mg, 72%). ^{1}H NMR ($CDCl_3$, 293 K): δ = −19.92 (ddd, J(H,P) = 19.5, 18.3, J(H,H) = 1.1 Hz, 1H; IrH), −19.34 (ddd, J(H,P) = 60.0, 18.9, J(H,H) = 5.1 Hz, 1H; IrH), −12.33 (dddd, J(H,P) = 129.9, 7.8, J(H,H) = 5.1, 1.1 Hz, 1H; IrHIr), 0.81 (dd, J(H,P) = 13.8, J(H,H) = 7.1 Hz, 9H; PCHC*H*$_3$), 1.08 (dd, J(H,P) = 14.1, J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.16 (dd, J(H,P) = 14.0, J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.18 (dd, J(H,P) = 13.5, J(H,H) = 6.9 Hz, 9H; PCHC*H*$_3$), 2.04, 2.39 (2×m, 3H each; PC*H*CH$_3$), 2.51 (s, 3H; NCCH$_3$), 3.55 (d, J(H,P) = 11.1 Hz, 9H; POCH$_3$), 5.67, 5.88 (2×ddd, J(H,H) = 1.8, 1.6, J(H,P) = 1.3 Hz, 1H each; CH), 6.79, 7.19 (2×d, J(H,H) = 1.6 Hz, 1H each; CH), 7.42, 7.49 (2×d, J(H,H) = 1.8 Hz, 1H each; CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 11.99 (d, J(P,P) = 24.8 Hz; P*i*Pr$_3$), 13.07 (s; P*i*Pr$_3$), 84.92 (d, J(P,P) = 24.8; P(OMe)$_3$); ^{13}C{^{1}H} ($CDCl_3$, 293 K): δ = 3.16 (s; NC*C*H$_3$), 17.98, 18.51, 18.81, 20.30 (all s; PCH*C*H$_3$), 23.31, 28.54 (2×d, J(C,P) = 30.4 Hz; P*C*HCH$_3$), 52.44 (d, J(C,P) = 6.5 Hz; PO*C*H$_3$), 105.14 (d, J(C,P) = 3.7 Hz; CH), 105.66 (d, J(C,P) = 2.7 Hz; CH), 118.72 (s; N*C*CH$_3$), 138.89, 140.43, 142.63 (all d, J(C,P) = 3.7 Hz; CH), 143.91 (d, J(C,P) = 2.7 Hz; CH); ^{19}F NMR ($CDCl_3$, 293 K): δ = −156.3 (s); IR (KBr): $\tilde{\nu}$ = 2175 (Ir-H), 1736 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 1008 (100) [M^+]; elemental analysis calcd (%) for $C_{29}H_{63}N_5BF_4Ir_2O_3P_3$: C 31.83, H 5.80, N 6.40; found: C 31.81, H 5.89, N 6.17.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(NCMe)(OH$_2$)(P*i*Pr$_3$)$_2$]BF$_4$ (7): The compound was prepared as detailed for **5**, using **4** (104.2 mg, 0.09 mmol) and water (8.5 μL, 0.45 mmol); yield: 67.0 mg, 75%. ^{1}H NMR (CD_2Cl_2, 293 K): δ = −23.03 (dd, J(H,P) = 20.1, J(H,H) = 3.3 Hz, 1H; IrH), −21.60 (dddd, J(H,P) = 9.9, 3.6, J(H,H) = 3.3, 3.3 Hz, 1H; IrHIr), −20.74 (dd, J(H,P) = 19.8, J(H,H) = 3.3 Hz, 1H; IrH), 1.09, 1.14 (2×dd, J(H,P) = 13.9, J(H,H) = 7.2 Hz, 9H each; PCHC*H*$_3$), 1.26, 1.29 (2×dd, J(H,P) = 14.0, J(H,H) = 7.1 Hz, 9H each; PCHC*H*$_3$), 2.12, 2.30 (2×m, 3H each; PC*H*CH$_3$), 2.55 (s, 3H; NCCH$_3$), 3.50 (s, 2H; OH$_2$), 5.77 (td, J(H,H) = 2.1, J(H,P) = 1.5 Hz, 1H; CH), 6.09 (td, J(H,H) = 1.8, J(H,P) = 1.6 Hz, 1H; CH), 6.80 (m, 1H; CH), 7.27 (d, J(H,H) = 2.1 Hz, 1H; CH), 7.54 (d, J(H,P) = 1.8 Hz, 1H; CH), 7.60 (m, 1H; CH); ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K): δ = 12.55, 17.09 (2×s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K): δ = 5.58 (s; NC*C*H$_3$), 20.13, 20.44, 20.87 (all s; PCH*C*H$_3$), 25.33 (d, J(C,P) = 30.0 Hz; P*C*HCH$_3$), 28.73 (d, J(C,P) = 31.3 Hz; P*C*HCH$_3$), 107.07 (d, J(C,P) = 3.8 Hz; CH), 107.12 (d, J(C,P) = 3.5 Hz; CH), 120.16 (s; N*C*CH$_3$), 136.63 (d, J(C,P) = 4.7 Hz; CH), 139.67 (d, J(C,P) = 3.7 Hz; CH), 143.90 (d,

J(C,P) = 2.9 Hz; CH), 144.65 (d, J(C,P) = 4.8 Hz; CH); ^{19}F NMR (CD_2Cl_2, 293 K): $\delta = -152.5$ (s); IR (KBr): $\tilde{\nu} = 3412$ (O-H), 2179 (IrH), 1755 cm^{-1} (Ir-HI-r); MS (FAB+): m/z (%): 882 (45) [$M^+ - OH_2$]; elemental analysis calcd (%) for $C_{26}H_{56}N_5BF_4Ir_2OP_2$: C 31.61, H 5.71, N 7.09; found: C 32.01, H 5.57, N 6.97. The crystals used in the X-ray diffraction experiment were obtained by slow diffusion of hexane into a saturated solution of **7** in CH_2Cl_2 at 253 K.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(OSO$_2$CF$_3$)(NCMe)(P*i*Pr$_3$)$_2$] (8): *Method 1*: A solution of **4** (110.0 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) was treated with an excess of Na(SO_3CF_3) (ca. 200 mg) and stirred for 2 h at room temperature. The resulting suspension was taken to dryness and the residue was extracted with toluene (5 mL) and filtered through Celite. The resulting colorless solution was dried and the residue treated with hexane to give a white solid, which was separated by decantation, washed with hexane, and dried in vacuo (75.0 mg, 73 %).

Method 2: A solution of **1** (210.7 mg, 0.24 mmol) in toluene (5 mL) was treated with $MeOSO_2CF_3$ (27.0 μL, 0.24 mmol) and stirred for 1 h at 273 K. The resulting solution was filtered through Celite and taken to dryness. The residue was treated with hexane to give a white solid, which was separated by decantation, washed with hexane, and dried in vacuo (218.7 mg, 89 %). Compound **8** was also found by NMR to be quantitatively formed in the reaction of **1** with one equivalent of [PhNH=CHPh]SO_3CF_3 in CD_2Cl_2 at 233 K. ^{1}H NMR ([D$_8$]toluene, 293 K): $\delta = -23.71$ (dd, J(H,P) = 20.6, J(H,H) = 2.9 Hz, 1H; IrH), −20.98 (dddd, J(H,P) = 13.4, 6.3, J(H,H) = 3.4, 2.9 Hz, 1H; IrHIr), −20.09 (dd, J(H,P) = 20.2, J(H,H) = 3.4 Hz, 1H; IrH), 1.22 (dd, J(H,P) = 13.5, J(H,H) = 7.1 Hz, 9H; PCHCH_3), 1.29 (dd, J(H,P) = 14.5, J(H,H) = 7.3 Hz, 9H; PCHCH_3), 1.34 (dd, J(H,P) = 13.7, J(H,H) = 7.3 Hz, 9H; PCHCH_3), 1.35 (dd, J(H,P) = 13.2, J(H,H) = 6.9 Hz, 9H; PCHCH_3), 1.48 (s, 3H; NCCH_3), 2.17, 2.36 (2×m, 3H each; PCHCH$_3$), 5.84 (td, J(H,H) = 2.1, J(H,P) = 1.4 Hz, 1H; CH), 6.17 (td, J(H,H) = 2.1, J(H,P) = 1.5 Hz, 1H; CH), 7.00 (m, 1H; CH), 7.37 (d, J(H,H) = 2.1 Hz, 1H; CH), 7.65 (m, 1H; CH), 8.17 (d, J(H,H) = 2.1 Hz, 1H; CH); ^{31}P{^{1}H} NMR ([D$_8$]toluene, 293 K) δ 11.12, 18.26 (2×s); ^{13}C{^{1}H} NMR ([D$_8$]toluene, 293 K): $\delta = 1.29$ (s; NCCH$_3$), 18.65, 18.85, 19.22, 19.44 (all s; PCHCH$_3$), 23.86 (d, J(C,P) = 29.2 Hz; PCHCH$_3$), 26.51 (d, J(C,P) = 31.0 Hz; PCHCH$_3$), 104.15 (d, J(C,P) = 3.0 Hz; CH), 104.69 (d, J(C,P) = 2.9 Hz; CH), 117.06 (q, J(C,F) = 319.8 Hz; OSO_2CF_3), 117.71 (s; NCCH$_3$), 134.70 (d, J(C,P) = 3.8 Hz; CH), 136.21 (d, J(C,P) = 2.9 Hz; CH), 142.45 (d, J(C,P) = 2.8 Hz; CH), 143.75 (d, J(C,P) = 5.2 Hz; CH); ^{19}F NMR ([D$_8$]toluene, 293 K): $\delta = -77.4$ (s; CF_3SO_3); IR (KBr): $\tilde{\nu} = 2175$ (IrH), 1771 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 882 (24) [$M^+ - OSO_2CF_3$]; elemental analysis calcd (%) for $C_{27}H_{54}N_5SF_3Ir_2O_3P_2$: C 31.42, H 5.27, N 6.78, S 3.11; found: C 31.46, H 5.28, N 6.66, S 2.95.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(Cl)(NCMe)(P*i*Pr$_3$)$_2$] (9): *Method 1*: A solution of **4** (110.0 mg, 0.10 mmol) in methanol (5 mL) was treated with an excess of NaCl (ca. 200 mg) and stirred for 2 h at room temperature. The resulting suspension was taken to dryness and the residue was extracted with CH_2Cl_2 (5 mL) and filtered through Celite. The resulting colorless solution was dried and the residue treated with hexane to give a white solid, which was separated by decantation, washed with hexane, and dried in vacuo (71.1 mg, 77 %).

Method 2: A solution of **1** (110.9 mg, 0.13 mmol) in CH_2Cl_2 (4 mL) was treated with 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate (31.0 mg, 0.13 mmol) and stirred for 15 min at room temperature. The resulting orange solution was taken to dryness, and the residue was extracted with diethyl ether (20 mL) and filtered through Celite. The solution was dried and the residue treated with hexane to give a white solid. The solid was separated by decantation, washed with hexane, and dried in vacuo (76.8 mg, 67 %). ^{1}H NMR (CD_2Cl_2, 293 K): $\delta = -26.62$ (dd, J(H,P) = 21.3, J(H,H) = 2.8 Hz, 1H; IrH), −22.42 (dddd, J(H,P) = 14.4, 4.5, J(H,H) = 3.6, 2.8 Hz, 1H; IrHIr), −20.66 (dd, J(H,P) = 20.1, J(H,H) = 3.6 Hz, 1H; IrH), 1.07 (dd, J(H,P) = 13.2, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.16 (dd, J(H,P) = 12.9, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.25, 1.28 (2×dd, J(H,P) = 13.2, J(H,H) = 7.2 Hz, 9H each; PCHCH_3), 2.21, 2.27 (2×m, 3H each; PCHCH$_3$), 2.37 (s, 3H; NCCH$_3$), 5.80 (td, J(H,H) = 2.1, J(H,P) = 1.2 Hz, 1H; CH), 6.00 (dt, J(H,H) = 1.8, J(H,P) = 1.5 Hz, 1H; CH), 6.94 (d, J(H,H) = 1.8 Hz, 1H; CH), 7.32 (d, J(H,H) = 2.1 Hz, 1H; CH), 7.36 (d, J(H,H) = 1.8 Hz, 1H; CH), 7.50 (d, J(H,H) = 2.1 Hz, 1H; CH); ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K): $\delta = 10.27$, 16.86 (2×s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K): $\delta = 3.75$ (s; NCCH$_3$), 18.33, 19.02, 19.33, 19.44 (all s; PCHCH$_3$), 23.21 (d, J(C,P) = 29.9 Hz; PCHCH$_3$), 26.72 (d, J(C,P) = 30.9 Hz; PCHCH$_3$), 103.87 (d, J(C,P) = 3.7 Hz; CH), 104.56 (d, J(C,P) = 2.7 Hz; CH), 117.40 (s; NCCH$_3$), 134.47 (d, J(C,P) = 4.2 Hz; CH), 136.35 (d, J(C,P) = 4.1 Hz; CH), 141.09 (d, J(C,P) = 5.1 Hz; CH), 141.63 (d, J(C,P) = 3.2 Hz; CH); IR (KBr): $\tilde{\nu} = 2206$ (Ir-H), 1761 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 918 (22) [M^+]; elemental analysis calcd (%) for $C_{26}H_{54}N_5ClIr_2P_2$: C 34.00, H 5.93, N 7.62; found: C 34.21, H 5.99, N 7.60. The crystals used in the X-ray diffraction experiment were obtained by slow diffusion of hexane into a saturated solution of **9** in CH_2Cl_2 at 253 K.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(NCMe)(OCHPh)(P*i*Pr$_3$)$_2$]BF$_4$ (10): The compound was prepared as detailed for **5**, using **4** (128.8 mg, 0.11 mmol) and benzaldehyde (34.0 μL, 0.33 mmol): yield 104.0 mg (87 %). ^{1}H NMR ($CDCl_3$, 293 K): $\delta = -21.81$ (dd, J(H,P) = 19.2, J(H,H) = 3.6 Hz, 1H; IrH), −21.37 (dddd, J(H,P) = 12.9, 3.6, J(H,H) = 3.6, 3.6 Hz, 1H; IrHIr), −20.70 (dd, J(H,P) = 19.8, J(H,H) = 3.6 Hz, 1H; IrH), 0.87, 1.07, 1.16 (all dd, J(H,P) = 13.8, J(H,H) = 6.9 Hz, 9H each; PCHCH_3), 1.25 (dd, J(H,P) = 13.5, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 2.11, 2.22 (2×m, 3H each; PCHCH$_3$), 2.60 (s, 3H; NCCH$_3$), 5.70 (dt, J(H,P) = J(H,H) = 1.8 Hz, 1H; CH), 6.00 (dt, J(H,P) = J(H,H) = 1.6 Hz, 1H; CH), 6.70 (m, 1H; CH), 7.19 (m, 2H; CH), 7.49 (d, J(H,H) = 1.6 Hz, 1H; CH), 7.51 (dd, J(H,H) = 8.1, 6.9 Hz, 2H; CH), 7.67, 7.70 (2×d, J(H,H) = 1.8 Hz, 1H each; CH), 7.21 (t, J(H,H) = 8.1 Hz, 1H; CH), 10.25 (s, 1H; OCH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): $\delta = 11.85$, 17.23 (2×s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): $\delta = 3.11$ (s; NCCH$_3$), 18.12, 18.25, 18.88, 18.95 (all s; PCHCH$_3$), 23.37, 26.46 (2×d, J(C,P) = 30.0 Hz; PCHCH$_3$), 105.48 (d, J(C,P) = 3.2 Hz; CH), 105.70 (d, J(C,P) = 2.8 Hz; CH), 118.86 (s; NCCH$_3$), 128.61, 128.95, 129.67 (all s; CH), 131.21 (d, J(C,P) = 4.7 Hz; CH), 134.34 (s; C), 135.16 (d, J(C,P) = 3.7 Hz; CH), 138.13 (d, J(C,P) = 6.0 Hz; CH), 141.88 (d, J(C,P) = 5.0 Hz; CH), 208.33 (s; OCH); IR (KBr): $\tilde{\nu} = 2183$ (Ir-H), 1757 (Ir-H-Ir), 1612 cm^{-1}(C=O); MS (FAB+): m/z (%): 988 (17) [M^+]; elemental analysis calcd (%) for $C_{33}H_{60}N_5BF_4Ir_2OP_2$: C 36.83, H 5.62, N 6.50. Found: C 36.55, H 5.52, N 6.54.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(NCMe)(NH$_2$Ph)(P*i*Pr$_3$)$_2$]BF$_4$ (11): The compound was prepared as detailed for **5**, using **4** (182.8 mg, 0.16 mmol) and aniline (43.2 μL, 0.48 mmol): yield 143.2 mg (85 %). ^{1}H NMR ($CDCl_3$, 293 K): $\delta = -23.77$ (dd, J(H,P) = 21.0, J(H,H) = 3.6 Hz, 1H; IrH), −22.34 (dddd, J(H,P) = 12.3, 3.6, J(H,H) = 3.6, 1.8 Hz, 1H; IrHIr), −20.52 (dd, J(H,P) = 20.1, J(H,H) = 1.8 Hz, 1H; IrH), 1.01 (dd, J(H,P) = 13.2, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.19 (dd, J(H,P) = 14.1, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.30, 1.32 (2×dd, J(H,P) = 13.5, J(H,H) = 6.9 Hz, 9H each; PCHCH_3), 2.01, 2.37 (2×m, 3H each; PCHCH$_3$), 2.56 (s, 3H; NCCH$_3$), 5.19, 5.48 (2×d, J(H,H) = 12.6 Hz, 1H each; NH), 5.73 (td, J(H,H) = 2.1, J(H,P) = 1.5 Hz, 1H; CH), 5.95 (td, J(H,H) = 2.1, J(H,P) = 1.4 Hz, 1H; CH), 6.85 (d, J(H,H) = 2.1 Hz, 1H; CH), 7.12 (m, 1H; CH), 7.22 (m, 2H; CH), 7.24 (d, J(H,H) = 2.1 Hz, 1H; CH), 7.31 (m, 2H; CH), 7.35 (m, 1H; CH), 7.54 (d, J(H,H) = 2.1 Hz, 1H; CH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): $\delta = 9.20$, 17.65 (2×s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): $\delta = 3.16$ (s; NCCH$_3$), 17.94, 18.65, 18.86, 19.27 (all s; PCHCH$_3$), 23.79 (d, J(C,P) = 30.0 Hz; PCHCH$_3$), 26.87 (d, J(C,P) = 30.9 Hz; PCHCH$_3$), 104.92, 105.16 (2×d, J(C,P) = 3.2 Hz; CH), 118.19 (s; NCCH$_3$), 122.88, 126.15, 128.66 (all s; CH), 134.69 (d, J(C,P) = 4.6 Hz; CH), 138.30 (d, J(C,P) = 2.8 Hz; CH), 141.01 (d, J(C,P) = 3.7 Hz; CH), 142.75 (d, J(C,P) = 3.6 Hz; CH), 144.50 (s; C); ^{19}F NMR ($CDCl_3$, 293 K): $\delta = -154.6$ (s); IR (KBr): $\tilde{\nu} = 3288$ (N-H), 2183 (Ir-H), 1742 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 975 (10) [M^+]; elemental analysis calcd (%) for $C_{32}H_{61}N_6BF_4Ir_2P_2$: C 36.15, H 5.78, N 7.90; found: C 36.22, H 5.42, N 7.87.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(OSO$_2$CF$_3$)(CO)(P*i*Pr$_3$)$_2$] (12): A solution of [Ir$_2$(μ-H)(μ-Pz)$_2$H$_3$(CO)(P*i*Pr$_3$)$_2$] (86.0 mg, 0.10 mmol) in toluene (5 mL) was treated with $MeOSO_2CF_3$ (11.2 μL, 0.10 mmol) and stirred for 2 h at 273 K. The resulting solution was filtered through Celite and taken to dryness. The residue was treated with hexane at 213 K to give a white solid, which was separated by decantation, washed with hexane and dried in vacuo (83.8 mg, 83 %). ^{1}H NMR ([D$_8$]toluene, 293 K): $\delta = -22.55$ (dd, J(H,P) = 21.2, J(H,H) = 2.2 Hz, 1H; IrH), −16.81 (dd, J(H,P) = 16.8,

J(H,H) = 3.0 Hz, 1H; IrH), −9.39 (dddd, J(H,P) = 11.7, 3.0, J(H,H) = 3.0, 2.2 Hz, 1H; IrHIr), 0.65, 0.87 (2×dd, J(H,P) = 14.6, J(H,H) = 7.3 Hz, 9H each; PCHCH_3), 0.94 (dd, J(H,P) = 13.9, J(H,H) = 7.3 Hz, 9H; PCHCH_3), 1.00 (dd, J(H,P) = 13.2, J(H,H) = 7.3 Hz, 9H; PCHCH_3), 1.83, 1.94 (2×m, 3H each; PCHCH$_3$), 5.30 (td, J(H,H) = 2.2, J(H,P) = 1.5 Hz, 1H; CH), 5.74 (td, J(H,H) = 2.2, J(H,P) = 1.4 Hz, 1H; CH), 6.56, 6.89, 7.08, 7.92 (all d, J(H,H) = 2.2 Hz, 1H each; CH); ^{31}P{^{1}H} NMR ([D$_8$]toluene, 293 K): δ = 11.85, 22.68 (2×s); ^{13}C{^{1}H} NMR ([D$_8$]toluene, 293 K): δ = 17.29, 17.43, 18.38, 18.44 (all s; PCHCH_3), 22.78 (d, J(C,P) = 30.3 Hz; PCHCH$_3$), 26.50 (d, J(C,P) = 32.2 Hz; PCHCH$_3$), 104.60 (d, J(C,P) = 3.7 Hz; CH), 105.33 (d, J(C,P) = 2.8 Hz; CH), 116.08 (q, J(C,F) = 319.8 Hz; OSO_2CF_3), 138.55, 143.32 (2×br; CH), 144.32 (d, J(C,P) = 3.7 Hz; CH), 167.72 (d, J(C,P) = 9.2 Hz; IrCO); ^{19}F NMR ([D$_8$]toluene, 293 K): δ = −77.5 (s; OSO_2CF_3); IR (KBr): $\tilde{\nu}$ = 2192 (Ir-H), 2043 cm^{-1} (C≡O); MS (FAB+): m/z (%): 869 (75) [M^+−OSO_2CF_3]; elemental analysis calcd (%) for $C_{26}H_{51}N_4SF_3Ir_2O_4P_2$: C 30.64, H 5.04, N 5.49, S 3.15; found: C 30.75, H 5.27, N 5.47, S 3.13.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(OSO$_2$CF$_3$)(py)(P*i*Pr$_3$)$_2$] (13): The complex was prepared as described for **12** using [Ir$_2$(μ-H)(μ-Pz)$_2$H$_3$(py)(P*i*Pr$_3$)$_2$] (124.7 mg, 0.14 mmol) and $MeOSO_2CF_3$ (15.3 μL, 0.14 mmol); yield: 118.1 mg, 82%. ^{1}H NMR (C_6D_6, 293 K): δ = −24.00 (dd, J(H,P) = 21.2, J(H,H) = 2.2 Hz, 1H; IrH), −22.52 (dddd, J(H,P) = 14.6, 4.4, J(H,H) = 4.4, 2.2 Hz, 1H; IrHIr), −21.26 (dd, J(H,P) = 20.3, J(H,H) = 4.4 Hz, 1H; IrH), 0.85 (dd, J(H,P) = 13.2, J(H,H) = 7.3 Hz, 9H; PCHCH_3), 0.93 (dd, J(H,P) = 13.9, J(H,H) = 7.3 Hz, 9H; PCHCH_3), 1.08, 1.19 (2×dd, J(H,P) = 13.2, J(H,H) = 7.3 Hz, 9H each; PCHCH_3), 1.96, 2.03 (2×m, 3H each; PCHCH$_3$), 5.50 (td, J(H,H) = 2.2, J(H,P) = 1.5 Hz, 1H; CH), 5.90 (d, J(H,H) = 2.2 Hz, 1H; CH), 6.10 (td, J(H,H) = 2.2, J(H,P) = 1.5 Hz, 1H; CH), 6.19 (t,
J(H,H) = 7.3 Hz, 2H; CH), 6.84 (t, J(H,H) = 7.3 Hz, 1H; CH), 6.93, 7.49, 8.36 (all d, J(H,H) = 2.2 Hz, 1H each; CH), 8.74 (br, 2H; CH); ^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ = 11.04, 11.63 (2×s); ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ = 17.08 (d, J(C,P) = 2.2 Hz; PCHCH_3), 17.83, 18.76, 19.19 (all s; PCHCH_3), 22.88 (d, J(C,P) = 28.5 Hz; PCHCH$_3$), 25.99 (d, J(C,P) = 30.7 Hz; PCHCH$_3$), 103.96, 104.05 (2×d, J(C,P) = 2.9 Hz; CH), 116.20 (q, J(C,F) = 319.8 Hz; OSO_2CF_3), 123.91 (s; CH), 132.72 (d, J(C,P) = 3.7 Hz; CH), 135.11 (br; CH), 135.32 (s; CH), 141.98 (br; CH), 142.72 (s; CH), 143.45 (br; CH); IR (KBr): $\tilde{\nu}$ = 2176 (Ir-H), 1735 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 920 (38) [M^+−OSO_2CF_3]; elemental analysis calcd (%) for $C_{30}H_{56}N_5SF_3Ir_2O_3P_2$: C 33.67, H 5.27, N 6.54, S 3.00; found: C 33.89, H 5.01, N 6.39, S 2.98.

[Ir$_2$(μ-H)(μ-Pz)$_2$H$_2$(OSO$_2$CF$_3$)(η^2-C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (14): The complex was prepared as described for **12** using [Ir$_2$(μ-H)(μ-Pz)$_2$H$_3$(η^2-C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (93.5 mg, 0.11 mmol) and $MeOSO_2CF_3$ (12.2 μL, 0.11 mmol); yield: 91.2 mg, 83%. ^{1}H NMR ([D$_8$]toluene, 253 K): δ = −22.76 (d, J(H,P) = 21.6 Hz, 1H; IrH), −16.32 (d, J(H,P) = 17.5 Hz, 1H; IrH), −9.29 (d, J(H,P) = 13.4 Hz, 1H; IrHIr), 0.73, 1.03 (2×dd, J(H,P) = 13.5, J(H,H) = 6.8 Hz, 9H each; PCHCH_3), 1.20 (dd, J(H,P) = 13.2, J(H,H) = 6.5 Hz, 9H; PCHCH_3), 1.26 (dd, J(H,P) = 13.2, J(H,H) = 7.1 Hz, 9H; PCHCH_3), 1.74, 2.08 (2×m, 3H each; PCHCH$_3$), 3.16, 3.33 (2×br, 2H each; η^2-C$_2$H$_4$), 5.56, 6.07 (2×td, J(H,H) = 2.0, J(H,P) = 1.4 Hz, 1H each; CH), 6.45, 6.86, 7.54, 8.24 (all d, J(H,H) = 2.0 Hz, 1H each; CH); ^{31}P{^{1}H} NMR ([D$_8$]toluene, 253 K): δ = 1.47, 10.37 (2×s); ^{13}C{^{1}H} NMR ([D$_8$]toluene, 253 K): δ = 18.25, 18.52, 19.54, 19.82 (all s; PCHCH_3), 23.96 (d, J(C,P) = 29.5 Hz; PCHCH$_3$), 49.40 (s; η^2-C$_2$H$_4$), 104.95 (d, J(C,P) = 2.9 Hz; CH), 105.77 (d, J(C,P) = 1.5 Hz; CH), 117.10 (q, J(C,F) = 319.4 Hz; OSO_2CF_3), 128.93 (br; CH), 139.43 (d, J(C,P) = 2.8 Hz; CH), 144.01, 145.08 (2×br; CH); ^{19}F NMR ([D$_8$]toluene, 253 K): δ = −77.8 (s; OSO_2CF_3); IR (KBr): $\tilde{\nu}$ = 2191 (Ir-H), 1651 (C=C), 1633 cm^{-1} (Ir-H-Ir); MS (FAB+): m/z (%): 870 (48) [M^+−OSO_2CF_3]; elemental analysis calcd (%) for $C_{27}H_{55}N_4SF_3Ir_2O_3P_2$: C 31.82, H 5.44, N 5.50, S 3.15; found: C 32.03, H 5.35, N 5.49, S 3.08.

Kinetics: The transformation of **7** into **5** was studied at 253 K in CD_2Cl_2 solutions of initial concentration 3.0×10^{-2} mol L^{-1}, in the presence of 10, 30 and 60 equivalents of CD_3CN, respectively. Reaction rates were obtained from the least-squares fitting of the intensity decrease of the ^{31}P{^{1}H} NMR signals of **7** as a function of time, during the initial 10% of the reaction (zero-order conditions). The values obtained were: 2.05×10^{-6}, 2.05×10^{-6} and 2.11×10^{-6} mol L^{-1} s^{-1}, respectively.

Structural analysis of 5, 7 and 9: X-ray data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å) using ω scans (0.3°). Data were collected over the complete sphere by a combination of four sets, and corrected for absorption using a multi-scan method applied with SADABS program.[15] The structures were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 by using SHELXL97,[16] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen non-disordered atoms. Hydrogen atoms were included in calculated positions and refined either riding on carbon atoms with the thermal parameter related to bonded atoms or with very weak positional restrains. Particular details concerning the presence of solvent, static disorder and hydrogen refinement are given below. The highest electronic residuals were observed in close proximity of the Ir centers and make no chemical sense.

Crystal data for 5: $C_{28}H_{57}BF_4Ir_2N_6P_2\cdot CH_2Cl_2$, M = 1095.87; colorless plate, 0.30×0.30×0.04 mm^3; monoclinic, $P2(1)/n$; a = 15.5327(12), b = 13.5193(11), c = 19.3055(15) Å, β = 93.3190(10); Z = 4; V = 4047.2(6) Å^3; ρ_{calcd} = 1.799 g cm^{-3}; μ = 6.827 mm^{-1}, minimum and maximum transmission factors 0.2339 and 0.6719; $2\theta_{max}$ = 57.04°; T = 100.0(2) K; 47567 reflections collected, 9621 unique [R(int) = 0.0613]; number of data/restrains/parameters 9621/22/436; final GoF 0.927, $R1$ = 0.0384 [6960 reflections $I > 2\sigma(I)$], $wR2$ = 0.0879 for all data; largest difference peak 1.631 e Å^{-3}. The BF_4 anion was found to be disordered by rotation about a B–F bond. This anion was refined with retrains in the geometry and with isotropic displacement parameters for all atoms except the boron. A solvent molecule (dichloromethane) was also observed and refined freely. Hydride ligands H(01), H(02) and H(03) were observed and refined with fixed thermal parameters (10.05) and with weak positional restrains for H(01).

Crystal data for 7: $C_{26}H_{56}BF_4Ir_2N_5OP_2\cdot 0.38\ CH_2Cl_2$, M = 1019.77; colorless irregular block, 0.20×0.12×0.06 mm^3; monoclinic, $C2/c$; a = 33.923(3), b = 11.7074(11), c = 24.696(2) Å, β = 125.5620(10); Z = 8; V = 7978.9(13) Å^3; ρ_{calcd} = 1.697 g cm^{-3}; μ = 6.839 mm^{-1}, minimum and maximum transmission factors 0.342 and 0.684; $2\theta_{max}$ = 57.16°; temperature 100.0(2) K; 46205 reflections collected, 9561 unique [R(int) = 0.0689]; number of data/restrains/parameters 9561/12/423; final GoF 0.848, $R1$ = 0.0392 [5674 reflections $I > 2\sigma(I)$], $wR2$ = 0.0890 for all data; largest difference peak 2.070 e Å^{-3}. Two dichloromethane molecules were found disordered at the same crystal site, and were refined with restraints in the geometry and thermal parameters. Their final occupancy factors were estimated from the thermal parameters as 0.25 and 0.13, respectively. The hydrogen atoms of the water ligand, H(1A) and H(1B), were refined with weak positional and thermal parameters restraints (O(1)–H(1A) and O(1)–H(1B) 0.95(1) Å, 1.2 × U_{eq} O(1)). The hydride ligands were observed and refined as free isotropic atoms.

Crystal data for 9: $C_{26}H_{54}ClIr_2N_5P_2$, M = 918.53; pale yellow irregular block, 0.14×0.11×0.05 mm^3; monoclinic, $P2(1)/n$; a = 33.923(3), b = 103.414(2), c = 24.696(2) Å, β = 125.5620(10); Z = 8; V = 7978.9(13) Å^3; ρ_{calcd} = 1.837 g cm^{-3}; μ = 8.206 mm^{-1}, minimum and maximum transmission factors 0.393 and 0.684; $2\theta_{max}$ = 57.84°; T = 100.0(2) K; 40895 reflections collected, 8229 unique [R(int) = 0.0714]; number of data/restrains/parameters 8229/2/348; final GoF 0.821, $R1$ = 0.0413 [5049 reflections $I > 2\sigma(I)$], $wR2$ = 0.0740 for all data; largest difference peak 2.115 e Å^{-3}. Hydride ligands H(01), H(02) and H(03) were observed and refined with fixed thermal parameters (10.05) and weak positional restrains for H(01).

CCDC-285574 (**5**), -285575 (**7**) and -285576 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computation: The computational method used for geometry optimization of model compound **2′** was density functional theory in its B3LYP formulation,[17] using the Gaussian03[18] series of programs. The basis set used were the LanL2DZ effective core potential for iridium atoms, 6-31G** for atoms directly bonded to the metals, and 6-31G for the re-

maining atoms. Natural population analysis[19] was used for generation of natural charges.

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