Reactions of Phosphine Ligands with Iridium Complexes Leading to C(sp^3)−H Bond Activation

Cristina Tejel,*,† Miguel A. Ciriano,† Sonia Jiménez,† Luis A. Oro,†,§ Claudia Graiff,‡ and Antonio Tiripicchio‡

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, E-50009 Zaragoza, Spain, Instituto Universitario de Catálisis Homogénea, Universidad de Zaragoza, E-50009 Zaragoza, Spain, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17/A, I-43100 Parma, Italy

Received November 8, 2004

Treatment of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (coe = cyclooctene) with the short-bite bifunctional N,P-donor ligand 1-benzyl-2-imidazolyldiphenylphosphine (Ph_2PBnIm) resulted in the oxidative addition of the C(sp^3)−H bond from the benzyl group to the metal to give $[IrHCl\{Ph_2P(CHPh)Im\}(Ph_2PBnIm)]$ (**1**), fully characterized by an X-ray study. The related ligand 2-pyridyldiphenylphosphine (Ph_2PPy) reacted with $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ to give the mononuclear iridium(I) complex $[IrCl(Ph_2PPy)_2]$ (**2**), which showed P,N-chelating and P-coordinated ligands. Addition of Ph_2PBnIm to **2** produced the replacement of the P-coordinated Ph_2PPy ligand along with the benzyl C−H bond addition to iridium to give $[IrHCl\{Ph_2P(CHPh)Im\}(Ph_2PPy)]$. This result indicates that mononuclear complexes of the type $[IrCl(Ph_2PBnIm)(L)]$ (L = P,N-chelating ligand) are the active species undergoing the C−H bond activation reaction. A related C−H bond activation process of the methylene group of dppm occurs in the reaction of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ with dppm in toluene to give the hydrido complex with one deprotonated dppm ligand $[IrHCl(Ph_2PCHPPh_2)(dppm)]$ (**4**). On the other hand, the hydride migrates to the methanide carbon in **4** on dissolving the complex in CD_2Cl_2 to establish an equilibrium with $[IrCl(dppm)_2]$ without H/D exchange. Protonating agents such as $HBF_4{\cdot}Et_2O$ and water reacted with complex **4** easily to give $[IrHCl(dppm)_2]X$ (X = BF_4, OH). The mononuclear complex **2** was found to be highly reactive. Reactions of **2** with O_2, H_2, and dichloromethane gave the complexes $[IrCl(O_2)(Ph_2PPy)_2]$, $[IrCl(H)_2(Ph_2PPy)_2]$, and $[IrCl_2(CH_2Cl)(Ph_2PPy)_2]$, respectively.

Introduction

Recent work in late transition metal complexes containing bifunctional P−C−N ligands have demonstrated the utility of such ligands in building homo- and heterodinuclear complexes for which a rich chemistry has been developed.[1−3] C−H bond activation reactions have also been reported for this type of ligand. As representative examples, Tani et al. have described that P−N heterochelate hybrid ligands undergo reversible C(sp^3)−H activation reactions.[4,5] Andersson et al. have also shown that related benzylic activations occur within hemilabile tertiary phosphines (P,O-donor ligands).[6−8] Considering the potential importance of these processes in homogeneous catalysis, a development of new functionalized tertiary phosphines able to form metallacycles from C−H activation reactions could be of importance in this area. In fact, the very active catalyst for allylic amination and etherification processes described by Hartwig resulted to be a cyclometalated phosphoramidite complex.[9] In this context, we have been studying the reactivity of the bifunctional P−C−N ligand (1-benzyl-2-imidazolyl)diphenylphosphine (Ph_2PBnIm). The ligand was found to be suitable for the construction of homo- and hetero-dinuclear complexes.[1] In the course of these investigations, we have observed a reversible C(sp^2)−H activation process, which resulted in the formation of the Ir(I)/Ir(III) compound $[IrCl(cod)\{\mu\text{-}PPh(C_6H_4)BnIm\}IrHCl(cod)]$.[10] Here we report on the C(sp^3)−H activation process of the benzyl group of the Ph_2PBnIm ligand by iridium along with an unusual C−H bond activation of the methylene group of dppm and related reactions.

* To whom correspondence should be addressed. E-mail: ctejel@unizar.es.
† Instituto de Ciencia de Materiales de Aragón.
§ Instituto Universitario de Catálisis Homogénea.
‡ Università di Parma.

(1) Tejel, C.; Ciriano, M. A.; Bravi, R.; Oro, L. A.; Graiff, C.; Galassi, R.; Burini, A. *Inorg. Chim. Acta* **2003**, *347*, 129, and references therein.
(2) Franciò, G.; Scopelliti, R.; Arena, C. G.; Bruno, G.; Drommi, D.; Faraone, F. *Organometallics* **1998**, *17*, 338.
(3) Zhang, Z.-Z.; Cheng, H. *Coord. Chem. Rev.* **1996**, *147*, 1.
(4) Katoaka, Y.; Imanishi, M.; Yamagata, T.; Tani, K. *Organometallics* **1999**, *18*, 3563.
(5) Katoaka, Y.; Shizuma, K.; Yamagata, T.; Tani, K. *Chem. Lett.* **2001**, 300.
(6) Sjövall, S.; Andersson, C.; Wendt, O. F. *Organometallics* **2001**, *20*, 4919.
(7) Sjövall, S.; Svensson, P. H.; Andersson, C. *Organometallics* **1999**, *18*, 5412.
(8) Sjövall, S.; Johansson, M.; Andersson, C. *Organometallics* **1999**, *18*, 2198.
(9) Kiener, C. A.; Shu, C.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 14272.
(10) Tejel, C.; Bravi, R.; Ciriano, M. A.; Oro, L. A.; Bordonaba, M.; Graiff, C.; Tiripicchio, A.; Burini, A. *Organometallics* **2000**, *19*, 3115.

10.1021/om049142i CCC: $30.25
Publication on Web 02/11/2005

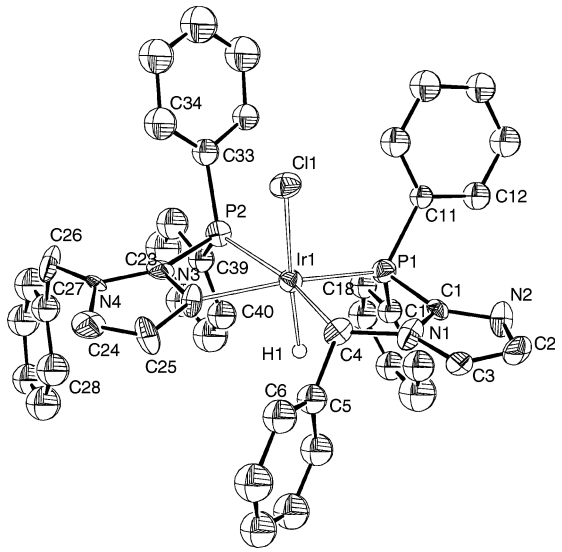


Figure 1. View of the structure of the compound **1** together with the atomic numbering system.

Table 1. Selected Bond Distances (Å) and Angles (deg) in 1

Ir(1)−Cl(1)	2.503(4)	Ir(1)−H(1)	1.71(12)
Ir(1)−P(1)	2.212(5)	Ir(1)−P(2)	2.349(5)
Ir(1)−C(4)	2.120(15)	Ir(1)−N(3)	2.176(13)
P(1)−C(1)	1.799(17)	P(2)−C(23)	1.813(18)
N(1)−C(1)	1.35(2)	N(3)−C(23)	1.34(2)
N(1)−C(3)	1.36(2)	N(3)−C(25)	1.40(2)
C(2)−C(3)	1.41(2)	C(24)−C(25)	1.36(2)
N(2)−C(2)	1.35(2)	N(4)−C(24)	1.40(2)
N(2)−C(1)	1.34(2)	N(4)−C(23)	1.39(2)
N(1)−C(4)	1.49(2)	N(4)−C(26)	1.44(2)
C(4)−C(5)	1.49(2)	C(26)−C(27)	1.52(2)
C(4)−Ir(1)−N(3)	97.4(6)	C(4)−Ir(1)−P(1)	86.7(5)
N(3)−Ir(1)−P(2)	68.2(4)	P(1)−Ir(1)−P(2)	107.83(17)
C(4)−Ir(1)−Cl(1)	86.4(5)	N(3)−Ir(1)−Cl(1)	86.2(4)
P(1)−Ir(1)−Cl(1)	102.86(16)	P(2)−Ir(1)−Cl(1)	90.45(15)
C(4)−Ir(1)−H(1)	82(4)	N(3)−Ir(1)−H(1)	94(4)
P(1)−Ir(1)−H(1)	78(4)	P(2)−Ir(1)−H(1)	101(5)
C(1)−P(1)−Ir(1)	102.7(6)	C(23)−P(2)−Ir(1)	83.0(6)
N(1)−C(1)−P(1)	115.0(13)	N(3)−C(23)−P(2)	106.5(13)
C(1)−N(1)−C(4)	124.1(15)	C(23)−N(3)−Ir(1)	102.3(11)
N(1)−C(4)−Ir(1)	111.5(10)		

Results and Discussion

Reaction of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ with 4 molar equiv of 1-benzyl-2-imidazolyldiphenylphosphine (Ph_2PBnIm) in acetone caused the immediate formation of a red solution, from which a crystalline white material (**1**), analyzed as $[IrCl(Ph_2PBnIm)_2]$, precipitated. Interestingly, this reaction involves a C(sp^3)−H bond activation process under smooth conditions, since **1** displays a doublet of doublets for a hydride ligand along with a singlet of intensity 1H for the proton of one benzyl group bonded to iridium in the ^{1}H NMR spectrum. The complete characterization of **1** as the mononuclear complex [IrHCl{Ph_2P(CHPh)Im}(Ph_2PBnIm)] (**1**) was obtained by an X-ray diffraction study. The molecular structure of **1** is shown in Figure 1 together with the atomic numbering system. The most important bond distances and angles are listed in Table 1. The iridium atom exhibits octahedral coordination as expected for Ir(III) complexes. One Ph_2PBnIm ligand is coordinated to iridium through P2 and N3 atoms, forming a four-membered chelating ring in which the Ir1−P2 and Ir−N3 bond distances are 2.349(5) and 2.176(13) Å, respectively. The other ligand Ph_2P(CHPh)Im, obtained upon an oxidative addition of Ph_2PBnIm, chelates the metal center through P1 and C4 atoms, forming a five-membered chelating ring, in which the Ir1−P1 and Ir1−C4 bond distances are 2.212(5) and 2.120(15) Å, respectively. As expected the Ir−P bond involving the P atom in trans position with respect to the carbon atom is longer than that involving the P atom trans to the nitrogen atom. The octahedral coordination is completed by a Cl atom and by a hydride, in the apical positions.

According to the structure found in the solid state, the $^{31}P\{^1H\}$ NMR of **1** showed two doublets; that at $\delta = -4.1$ ppm was assigned to the phosphorus of the metalated phosphine, labeled P^b in Scheme 1. The other, shifted at high field ($\delta = -25.0$ ppm), corresponded to the phosphorus atom involved in the four-membered P−C−N−Ir ring (P^a in Scheme 1). The mutually cis-arrangement of both phosphorus atoms was indicated by the J_{P-P} coupling constant value (12 Hz).

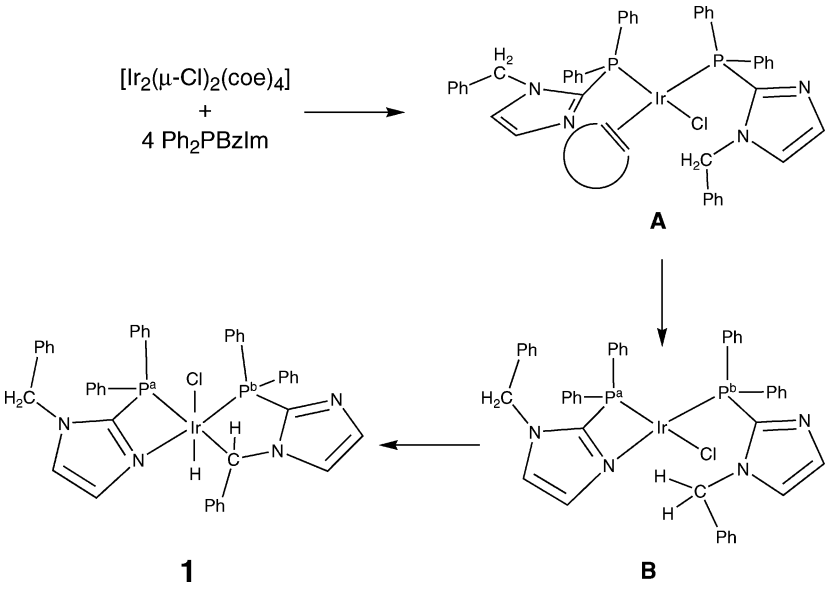
To find the active species leading to **1**, the reaction was monitored by NMR spectroscopy at −40 °C in CD_2Cl_2. Two intermediates for this process could be identified. The major compound detected just after mixing was the mononuclear species [IrCl(coe)(PPh_2-$BnIm)_2$] (**A**, Scheme 1), which showed coordinated coe in the ^{1}H NMR spectrum and two monodentate P-coordinated Ph_2PBnIm ligands, with phosphorus resonances at δ 4.1 and 1.1 ppm (J_{P-P} = 13 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The reaction mixture evolved to the complex [IrCl($PPh_2BnIm)_2$] (**B**, Scheme 1) and free coe in 30 min at low temperature. Complex **B** showed P-monodentate and P,N-chelating PPh_2BnIm ligands, as deduced from the two signals at δ -4.0 and −21.0 ppm (J_{P-P} = 25 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Finally, complex **B** transformed cleanly into **1** in 30 min at 25 °C. With this experimental information in mind, we hypothesized that the mononuclear complex [IrCl($PPh_2BnIm)_2$] (**B**), with a monodentate phosphine ligand, would be the active species undergoing the C(sp^3)−H activation process.

To confirm this hypothesis, we studied the reaction of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ with the related ligand 2-pyridyldiphenylphosphine (Ph_2PPy), which lacks the active benzyl group. The product of this reaction at room temperature was the mononuclear complex [IrCl(Ph_2-$PPy)_2$] (**2**), possessing a structure similar to **B** (Scheme 1), which was isolated as a highly air-sensitive red microcrystalline solid. The P-monodentate (P^b, Scheme 2) and P,N-chelating (P^a, Scheme 2) coordination modes of the two Ph_2PPy ligands in **2** were evidenced by the chemical shifts of the signals (δ = 16.7 (P^b) and −42.9 ppm (P^a)) in the $^{31}P\{^1H\}$ NMR spectrum, which were found to be similar to those described for the related cationic complex $[PtCl(Ph_2PPy)_2]^+$ characterized crystallographically.[11] The cis-arrangement of the phosphorus atoms is consistent with the coupling constant J_{P-P} (23 Hz).

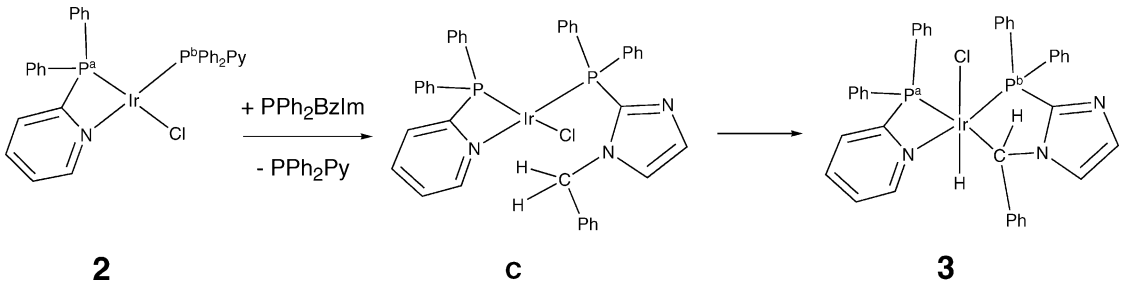
A further reaction of **2** with Ph_2PBnIm caused the replacement of one of the Ph_2PPy ligands along with the expected C(sp^3)−H bond activation of the benzyl group of the Ph_2PBnIm ligand to give [IrHCl{Ph_2P-(CHPh)Im}(Ph_2PPy)] (**3**, Scheme 2), which was isolated

(11) Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.

Scheme 1



Scheme 2



in moderate yield after recrystallization. Complex **3** was characterized according to the analytical and spectroscopic data. Thus, the hydride ligand was found to be cis to both phosphorus atoms to give a doublet of doublets in the ^{1}H NMR spectrum, while the remaining benzyl proton (Ir−C*H*Ph) gave a doublet (J_{H-P} = 6.7 Hz), which became a singlet in the selective ^{1}H{^{31}P} NMR spectrum. The coordination modes and the cis disposition of the phosphine ligands proposed for **3** (Scheme 2) are consistent with the chemical shifts and coupling constant of the two signals observed in the ^{31}P{^{1}H} NMR spectrum, at δ −6.4 and −39.9 ppm (J_{P-P} = 13 Hz). These chemical shifts are similar to those found for the metalated phosphine Ph_2P(CHPh)Im in **1** and the chelating Ph_2PPy in **2**, respectively.

Although the proposed intermediate in this reaction (**C**, Scheme 2) was not observed, the related rhodium complex [RhCl(dppe)(Ph_2PBnIm)] (**4**) with a monodentate P-coordinated Ph_2PBnIm ligand was isolated from the reaction of [$Rh_2(\mu$-Cl)$_2$(dppe)$_2$] with 2 molar equiv of Ph_2PBnIm. The rhodium complex **4**, however, did not undergo C(sp^3)−H nor C(sp^2)−H activation reactions even on heating **4** in toluene at reflux for 6 h. In addition, no C−H activation processes were detected in the reactions of Ph_2PBnIm with the rhodium complexes [$Rh_2(\mu$-Cl)$_2$(coe)$_4$] and [$Rh_2(\mu$-Cl)$_2$(C_2H_4)$_4$], which gave complicated mixtures without hydride signals in the ^{1}H NMR spectra of the products.

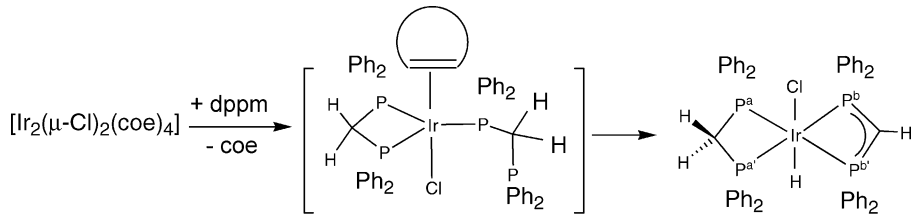
According to these results, it is reasonable to propose that the active species that undergo the C(sp^3)−H activation reaction are the complexes [IrCl(Ph_2PR)(Ph_2PBnIm)] (R = Py, BnIm) with the phosphine Ph_2PBnIm coordinated as monodentate ligand and both phosphorus in a cis disposition.

Indeed, the C−H activation reaction occurs on the benzyl group from the monodentate phosphine Ph_2PBnIm, which can be placed in close proximity to the metal atom. Moreover, the cis disposition of the benzylic carbon and the hydride ligand found in **1** and **3** is consistent with a concerted oxidative addition reaction of the C−H bond. Furthermore, the coordination of the phosphorus from the phosphine Ph_2PBnIm seems to be a prerequisite for the C−H activation reaction, since an intermolecular C−H activation reaction does not occur on treatment of [IrCl(Ph_2PPy)$_2$] (**2**) with 1-benzylimidazole. Therefore, the key factor for these mild C(sp^3)−H bond activation reactions seems to be the preactivation of the benzylic C−H bond by coordination of the P atom from Ph_2PBnIm to the Ir(I) center, which has been termed "remote activation".[12]

Attempts to produce the C−H bond activation reaction by heating the complex [IrCl(Ph_2PBnIm)(cod)] at 70 °C in C_6D_6 failed. This lack of reaction agrees with the reluctance of related neutral complexes of formula [IrCl(L)(cod)] (L = P,O ligand) to undergo C−H oxidative addition.[8] These results indicate that the P−C−N-chelated ligand in the active species [IrCl(Ph_2PR)(Ph_2PBnIm)] (R = Py, BnIm) does not have the role of a simple spectator; on the contrary, it provides to the

(12) Oh, M.; Yu, K.; Li, H.; Watson, E. J.; Carpenter, G. B.; Sweigart, D. A. *Adv. Synth. Catal.* **2003**, *345*, 1053.

Scheme 3



5

iridium atom the electronic and steric conditions allowing the observed C(sp^3)−H activation reactions.

As the active complexes [IrCl(Ph_2PR)(Ph_2PBnIm)] (R = Py, BnIm) contain a chelating P−C−N ligand not involved directly in the C−H bond activation, we speculated if related complexes with ancillary chelating P-donor ligands could also be suitable for this reaction. This prompted us to prepare complexes of the type [$Ir_2(\mu$-Cl)$_2$(diphos)$_2$] (diphos = bis(diphenylphosphino)-methane (dppm), bis(diphenylphosphino)ethane (dppe)) to be used further in C−H activation reactions. However, these preparations met with variable success and led to uncovering an unexpected C−H bond activation reaction of dppm.

Thus, reaction of [$Ir_2(\mu$-Cl)$_2$(coe)$_4$] with 4 molar equiv of dppm in toluene gave a red solution for a few seconds, which became pale yellow and rendered a pale yellow solid (**5**) in good yield after working up. Indeed, the reaction requires 2 molar equiv of dppm per iridium; otherwise mixtures of [$Ir_2(\mu$-Cl)$_2$(coe)$_4$] and **5** result if the phosphine is in defect. The solid was identified as the hydride complex [IrHCl($Ph_2PCHPPh_2$)(dppm)] (**5**) coming from the activation of a methylene proton from one of the dppm ligands. According to the structure depicted in Scheme 3, the hydride is cis to the four phosphorus atoms, since complex **5** exhibits the hydride resonance as the X part of a AA′BB′X system with similar couplings to the two phosphorus ligands (J_{H-P} = 10.5, 14.2 Hz) in the ^{1}H NMR spectrum (Figure 2). Moreover, the hydride gave a singlet while the methanide proton and carbon from the deprotonated dppm gave a singlet and a triplet of triplets (J_{C-P} = 66 and 5 Hz) in the ^{1}H{^{31}P} and ^{13}C{^{1}H} NMR spectra, respectively. The planar disposition of the metal and the four phosphorus atoms from the diphosphine ligands produces a AA′BB′ spin system in the ^{31}P{^{1}H} NMR spectrum of **5** (Figure 2), which is in accordance with the presence of a symmetry plane that relates two equivalent halves of the molecule.

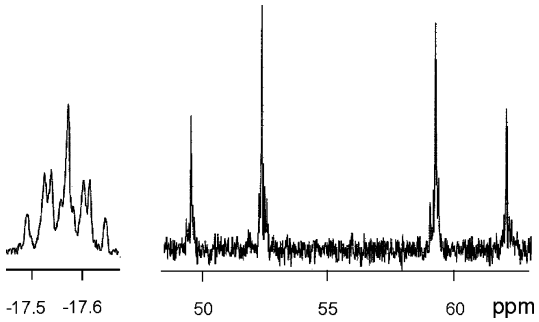


Figure 2. Signal for the hydride in the ^{1}H NMR spectrum and ^{31}P{^{1}H} NMR spectrum of complex **5** in CD_2Cl_2.

Protonation of complex **5** with HBF_4·Et_2O gave the cationic hydride complex [IrHCl(dppm)$_2$]BF_4, which shows the expected methylene signals for the coordinated dppm ligands and the hydride resonance as a quintet in the ^{1}H NMR spectrum. However, deprotonation of [IrHCl(dppm)$_2$]BF_4 does not occur on treatment with triethylamine.

We were most surprised because an apparently similar reaction of [$Ir_2(\mu$-Cl)$_2$(coe)$_4$] with dppm (in a 1:4 molar ratio) in benzene has been reported to give the Ir(I) complex [IrCl(dppm)$_2$].[13] The unique difference between our procedure and that reported for [IrCl-(dppm)$_2$] is that dichloromethane was further used to recrystallize this complex. This prompted us to investigate the fate of complex **5** in dichloromethane.

Pale yellow crystals of **5** deposited from a concentrated and cold solution in dry CH_2Cl_2 kept under −25 °C. In a separate NMR experiment, a freshly prepared solution containing initially **5** in dry CD_2Cl_2 evolved to a mixture of **5** and [IrCl(dppm)$_2$] in relative proportions 20:80, respectively, in 20 min at room temperature. This proportion remains unaltered for days, due to a chemical equilibrium between these species. The interconversion of the compounds **5** and [IrCl(dppm)$_2$] was confirmed by the observation of cross-peaks of the methanide and methylene signals of both compounds in the EXCSY spectrum. In consequence, the C−H bond activation of dppm above-described is reversed in dichloromethane at room temperature to reach an equilibrium of **5** with [IrCl(dppm)$_2$], in which the reported complex is the major species.[14] This equilibrium could proceed easily through a square-planar complex easily accessible from both sides by a migration of the hydride to the methanide carbon in **5** and by the dissociation of one end of dppm followed by the C−H bond activation of the methylene group (Scheme 4).

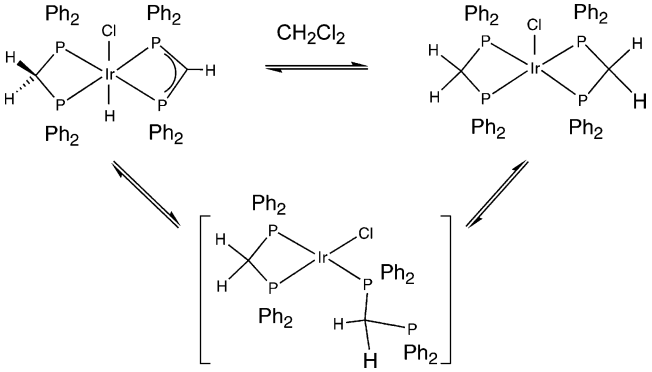
Nonetheless, complex **5** is very moisture sensitive and reacts irreversibly with water to give the complex [IrHCl(dppm)$_2$]$^+$ as the result of the abstraction of a proton from water, which may compound the results. Thus, a mixture of [IrCl(dppm)$_2$], [IrHCl(dppm)$_2$]$^+$, and **5** in relative proportions 40:50:10 resulted on leaving a solution of **5** in a NMR tube overnight, because of the adventitious entrance of air into the reaction medium. As this reaction proceeded, a signal due to hydroxide at δ 1.842 grew up steadily in the ^{1}H NMR spectrum of the sample.

As the above-mentioned equilibrium found in dichloromethane raises the question of whether the C−H

(13) Hitts, R. H.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 1297.

(14) We observed a singlet at δ −37.6 ppm in the ^{31}P{^{1}H} NMR spectrum for [IrCl(dppm)$_2$] instead of the reported value δ −56 ppm.

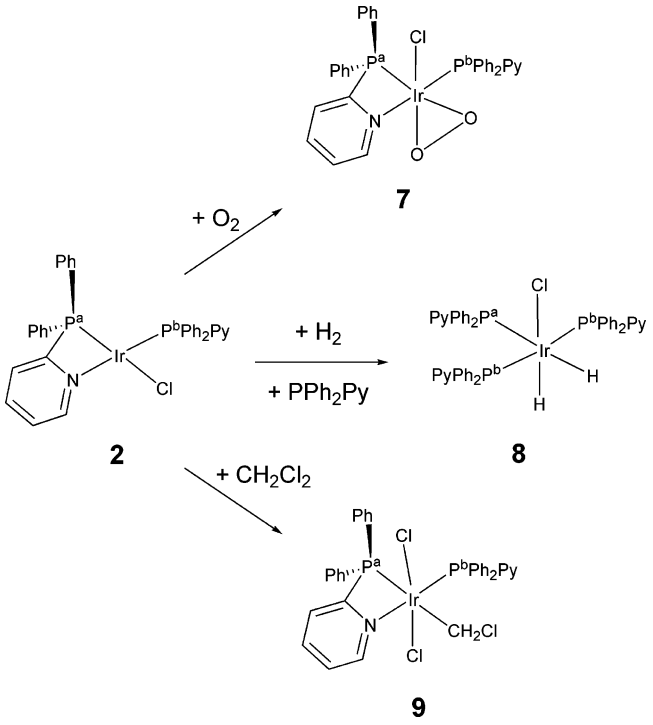
Scheme 4



bond activation of dppm depends on the solvent, a mixture of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ and dppm (in 1:4 molar ratio) was dissolved in CD_2Cl_2 in a separate NMR experiment. The resulting dichroic (green by reflection and red by transparence) solution showed a main broad signal in the $^{31}P\{^1H\}$ NMR spectrum at δ −38 ppm and the spin system corresponding to complex **5**. The broad signal at room temperature was resolved at −60 °C in several multiplets, which corresponded to $[IrCl(dppm)_2]$ and two species containing coe, and monodentate and chelating dppm in equilibrium. Moreover, the coe present in the mixture produces this equilibrium, since the methylene protons of coordinated dppm and the olefinic protons of coordinated coe gave broad signals in the ^1H NMR spectrum at room temperature. The presence of **5** and $[IrCl(dppm)_2]$ in the complex mixture resulting from the reaction of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ with dppm in dichloromethane evidences that the activation of the methylene proton of dppm also occurs in dichloromethane at room temperature, although the equilibrium is shifted to $[IrCl(dppm)_2]$ in this solvent. In contrast, the C−H activation reaction to give **5** takes place cleanly in benzene and toluene, in the NMR tube and in a preparative scale, in which the product can be easily purified because it crystallizes out in these solvents.[15]

It is well known that deprotonation of free and coordinated dppm occurs by reaction with strong bases such as BuLi or KOH.[16] Deprotonation reactions of dppm occur also by hydrogen transfer to a coordinated imido ligand[17] and by hydrogen abstraction by a free radical,[18] but the sole precedent of a C−H activation of dppm in a tris(pyrazolyl)borate iridium complex has been recently reported by Heinekey.[19] A unique example of methyne C−H activation of the related ligand 2-pyridylbis(diphenylphosphino)methane by platinum and iridium complexes has also appeared recently,[20] but the possible mechanisms for these reactions have not been proposed. The equilibrium between the activated complex **5** and $[IrCl(dppm)_2]$ observed in dichloromethane is evidence of the reversibility of this C−H activation reaction. Noteworthy, although the $^{31}P\{^1H\}$ NMR spectrum of $[IrCl(dppm)_2]$ in the slow-exchange region could not be observed at low temperature, this compound should be fluxional not only because it is a pentacoordinated Ir(I) complex but because of the dissociation of one end of a dppm to give a square-planar species. In fact, the reactions of this compound with metal fragments to give dinuclear complexes with bridging dppm described by Cowie evidence the easy dissociation of one P-donor atom of dppm.[13] Moreover, the chemical shift of the singlet in the $^{31}P\{^1H\}$ NMR spectrum is between that of chelating and monodentate dppm. Seen in this light, we believe the activation of the CH_2 group occurs on the monodentate dppm, which allows the transfer of the proton of the methylene group to the metal center, as shown in Scheme 4.

Scheme 5



In favor of this proposal, the reaction of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ with dppe gave the very stable square-planar $[Ir(dppe)_2]^+$ cation independently of the molar ratio used, in which the chelating mode of the dppe ligands prevents any C−H bond activation process. Using a 1:4 molar ratio the previously reported complex $[Ir(dppe)_2]Cl$ was isolated,[21] while using a 1:2 molar ratio the ionic $[Ir(dppe)_2][IrCl_2(coe)_2]$ (**6**) compound crystallized as an orange solid. Analytical and spectroscopic data of **6** (see Experimental Section) agreed with the proposed formula and ionic nature. A further reaction of PPh_2BnIm with **6** led to an equimolar mixture of $[Ir(dppe)_2]Cl$ and complex **1**. Moreover, no reaction was observed between $[Ir(dppe)_2]Cl$ and PPh_2BnIm even under toluene at reflux. Therefore, the high stability of the $[Ir(dppe)_2]^+$ cation prevented the replacement reaction of even one dppe ligand by PPh_2BnIm.

Complex **2** was found to be a very reactive species (Scheme 5). Thus, the simple air exposure of red solutions of **2** in acetone caused the formation of a yellow precipitate corresponding to the dioxygen complex

(15) Complex **5** has been observed to crystallize from a concentrated mixture of $[Ir_2(\mu\text{-}Cl)_2(cod)_2]$ and dppm in 1:4 molar ratio in deuterobenzene. Pérez-Torrente, J. J. Personal communication.

(16) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.
(17) Ye, C.; Sharp, P. R. *Inorg. Chem.* **1995**, *34*, 55, and references therein.
(18) Torkelson, J. R.; Oke, O.; Muritu, J.; McDonald, R.; Cowie, M. *Organometallics* **2000**, *19*, 854.
(19) Wiley, J. S.; Heinekey, D. M. *Inorg. Chem.* **2002**, *41*, 4961.
(20) Mague, J. T.; Krinsky, J. L. *Inorg. Chem.* **2001**, *40*, 1962.
(21) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324.

$[Ir(O_2)Cl(Ph_2PPy)_2]$ (**7**). However, the reaction of **2** with neat O_2 (see Experimental Section) was required to obtain pure analytical samples of **7**, which showed an IR band ν(O−O) at 844 cm^{-1}. In solution, complex **7** was found to be fluxional, as indicated by the broad signal at $\delta = -20.0$ ppm along with a doublet at $\delta = -67.0$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. Scheme 5 shows one of the possible isomers for this complex.

Solutions of complex **2** reacted with dihydrogen leading to a mixture of several dihydride complexes from which the complex $[Ir(H)_2Cl(Ph_2PPy)_3]$ (**8**) could be identified as the main product. According to the formulation, complex **8** was obtained in good yield by carrying out the above-described reaction in the presence of 1 molar equiv of Ph_2Ppy. A clean synthesis of **8** consists in the reaction of $[Ir_2(\mu\text{-}Cl)_2(cod)_2]$ with dihydrogen in the presence of 6 molar equiv of Ph_2PPy. Complex **8** was easily identified as the isomer depicted in Scheme 5 from the spectroscopic data (see Experimental Section).

A slow reaction with the solvent was observed on dissolving complex **2** in dichloromethane. The product was found to be the compound $[IrCl_2(\eta^1\text{-}CH_2Cl)(Ph_2PPy)_2]$ (**9**) (Scheme 5), as the result of the oxidative addition of one C−Cl bond from the dichloromethane to iridium. The most relevant spectroscopic feature of **9** related to its structure was an AB spin system in the $^1H\{^{31}P\}$ NMR spectrum corresponding to the diastereotopic protons of the chloromethyl Ir−CH_2Cl group, which appeared as two doublets of doublets in the ^1H NMR spectrum ($J_{H-P} = 2.3$ and 7.4 Hz for the A and B protons, respectively) due to the coupling with the phosphorus atom in trans position, labeled P^a in Scheme 5. In addition the presence of terminal and chelated phosphine ligands was deduced from the distinctive chemical shifts in the $^{31}P\{^1H\}$ NMR spectrum.

In conclusion, easy C(sp^3)−H bond activation reactions from a "CH_2Ph" group can take place under smooth conditions in mononuclear iridium complexes of the type $[IrCl(L_2)(Ph_2PBnIm)]$ (L_2 = Ph_2PPy, Ph_2-PBnIm). The key for these activation reactions was found to be the remote preactivation of the benzyl group by coordination of the P-end of the substrate to iridium. The related unusual C−H bond activation of a methylene group of dppm in $[IrCl(dppm)_2]$ occurs probably through a proton transfer to the metal from a monodentate dppm ligand.

Experimental Section

All the reactions were carried out under argon using standard Schlenk techniques. $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$,[22] $[Ir_2(\mu\text{-}Cl)_2(cod)_2]$,[23] and 1-benzyl-2-imidazolyldiphenylphosphine (PPh_2-BnIm)[24] were prepared according to literature methods, while 2-pyridyldiphenylphosphine was purchased from Aldrich. Solvents were dried and distilled under argon before use by standard methods. Carbon, hydrogen, and nitrogen analyses were performed with a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded with a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as matrix. Molecular weights were determined with a Knauer osmometer using chloroform solutions. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX 300 and on a Varian UNITY 300 spectrometer operating at 300.13 and 299.95 MHz for ^1H, respectively. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the residual signal of the deuterated solvent as reference and 85% phosphoric acid, respectively.

[IrHCl{Ph_2P(CHPh)Im}(Ph_2PBnIm)] (1). The addition of solid Ph_2PBnIm (137.0 mg, 0.40 mmol) to a solution of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (89.6 mg, 0.10 mmol) in acetone (10 mL) caused the immediate formation of a red solution, which evolved to yellow in 20 min. After stirring for 3 h, the precipitation of a white solid took place. The solid was filtered, washed with cold acetone (2 × 3 mL), and vacuum-dried. Yield: 162 mg (89%). Anal. Calcd for $C_{44}H_{38}N_4ClP_2Ir$: C, 57.92; H, 4.20; N, 6.14. Found: C, 57.06; H, 4.06; N, 6.01. ^1H NMR (25 °C, CD_2Cl_2): δ multiplets from 7.66 to 6.52 (34H, Ph), 6.46 (d, $J_{H-P} = 7.2$, 1H, Ir−CH), 4.89 (δ_A, 1H) and 4.82 (δ_B, $J_{A-B} = 15.0$ Hz, 1H) (PCH_2), −20.42 (dd, $J_{H-P} = 21.9$ and 10.4 Hz, 1H, Ir−H). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): δ −4.1 (d, $J_{P-P} = 12$ Hz), −25.0 (d, $J_{P-P} = 12$ Hz). MS (FAB^+): 912 (65%, M^+), 875 (100%, M − Cl^+). MW Calcd for $C_{44}H_{38}N_4ClP_2Ir$: 912. Found: 1010.

[IrCl($Ph_2PPy)_2$] (2). The addition of solid Ph_2PPy (117.5 mg, 0.45 mmol) to a suspension of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (100.0 mg, 0.11 mmol) in acetone (5 mL) caused the formation of a red solution in 10 min. The solution was concentrated to ca. 2 mL, and the slow addition of hexane (20 mL) gave a red microcrystalline solid that was filtered off under argon, washed with hexane (2 × 5 mL), and vacuum-dried. Yield: 130 mg (77%). Anal. Calcd for $C_{34}H_{28}N_2ClP_2Ir$: C, 54.14; H, 3.74; N, 3.71. Found: C, 53.98; H, 3.76; N, 3.93. ^1H NMR (25 °C, CD_2Cl_2): δ 9.04 (br s, 1H); 8.19 (d, $J = 4$ Hz, 1H); multiplets from 7.90 to 6.97 (26H). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): δ 16.7 (d, $J_{P-P} = 23$ Hz, P^b), −42.9 (d, $J_{P-P} = 23$ Hz, P^a). MS (FAB^+): 754 (30%, M^+), 719 (100%, M − Cl^+).

[IrHCl{Ph_2P(CHPh)Im}(Ph_2PPy)] (3). Solid Ph_2PBnIm (72.6 mg, 0.21 mmol) was added to a suspension of $[IrCl(Ph_2PPy)_2]$ (**2**) (160.0 mg, 0.21 mmol) in acetone (5 mL). After stirring for 4 h an orange precipitate was formed. The suspension was concentrated to ca. 2 mL, and hexane (10 mL) was added to complete the precipitation. The solid was filtered, washed with hexane, and vacuum-dried. The ^1H NMR of the crude product (184.0 mg) showed a mixture of the title compound (60%), complex **1** (20%), and another unidentified minor species. This crude was recrystallized twice from dichloromethane/hexane to render orange microcrystals corresponding to **3**. Yield: 71 mg (40%). Anal. Calcd for $C_{39}H_{33}N_3ClP_2Ir$: C, 56.21; H, 3.99; N, 5.04. Found: C, 56.32; H, 3.86; N, 4.93. ^1H NMR (25 °C, $CDCl_3$): δ multiplets from 7.84 to 7.04 (30H), 6.88 (s, 1H, Im), 6.35 (d, $J_{H-P}a = 6.7$ Hz, 1H, Ir−CHPh), −19.40 (dd, $J_{H-P}b = 15.0$ Hz, $J_{H-P}b = 9.0$ Hz, 1H, Ir−H). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$): δ −6.4 (d, $J_{P-P} = 13$ Hz, P^b), −39.9 (d, $J_{P-P} = 13$ Hz, P^a).

[RhCl(dppe)(Ph_2PBnIm)] (**4**)**.** Solid Ph_2PBnIm (25.6 mg, 0.073 mmol) was added to a solution of $[Rh_2(\mu\text{-}Cl)_2(dppe)_2]$ (39.0 mg, 0.036 mmol) in dichloromethane (2 mL). After 10 min the solution was concentrated and layered with hexanes (15 mL) to render a crystalline yellow solid, which was separated by decantation, washed with hexane, and vacuum-dried. Yield: 61 mg (96%). Anal. Calcd for $C_{48}H_{43}N_2ClP_3Rh$: C, 65.58; H, 4.93; N, 3.19. Found: C, 65.50; H, 4.90; N, 3.36. ^1H NMR (25 °C, CD_2Cl_2) (assigned from the $^1H-^{31}P$ spectrum): δ 7.96 (t, $J_{P^b-H} = J_{H-H} = 9.2$ Hz, 4H, dppe), multiplets from 7.53 to 7.00 (32H, Ph+Im), 6.78 (s, 1H, Im), 5.36 (d, $J_{P^c-H} = 2.0$ Hz, CH_2Ph), 2.13, 2.05, 1.97, and 1.90 (m, 1H each, $Ph_2P^a(CH_2)_2P^b$-Ph_2). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): δ 74.1 (dt, $J_{P^a-P^b} = J_{P^a-P^c} = 34$ Hz, $J_{P^a-Rh} = 184$ Hz, $Ph_2P^a(CH_2)_2P^bPh_2$), 60.2 (ddd, $J_{P^b-P^c} = 352$ Hz, $J_{P^b-P^a} = 34$ Hz, $J_{P^b-Rh} = 143$ Hz, $Ph_2P^a(CH_2)_2P^b$-Ph_2), 13.3 (ddd, $J_{P^c-P^b} = 352$ Hz, $J_{P^c-P^a} = 34$ Hz, $J_{P^c-Rh} = 128$ Hz, Ph_2P^cBnIm). MS (FAB^+): 879 (6%, M^+), 843 (100%, M − Cl^+).

(22) Van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 91.
(23) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.
(24) Burini, A.; Pietroni, R. B.; Galassi, R.; Valle, G.; Caloggero, S. *Inorg. Chim. Acta* **1995**, *229*, 299.

[IrHCl(Ph$_2$PCHPPh$_2$)(dppm)] (5). Solid dppm (153.8 mg, 0.40 mmol) was added to a solution of [Ir$_2$(μ-Cl)$_2$(coe)$_4$] (89.6 mg, 0.10 mmol) in toluene (7 mL). The initial orange solution turned dark red and immediately evolved to a pale yellow solution. After stirring for 30 min the solution was evaporated to ca. 2 mL and carefully layered with hexane (20 mL) to render a pale yellow microcrystalline solid in 3 days at room temperature. The solid was filtered, washed with hexane, and vacuum-dried. Yield: 150 mg (75%). Anal. Calcd for the toluene solvate $C_{57}H_{52}ClP_4Ir$: C, 63.39; H, 4.81. Found: C, 63.05; H, 4.68. ^{1}H{^{31}P} NMR (25 °C, C_6D_6): δ 7.85−7.70 (m, 40H, Ph), 5.14 (δ_A, 1H) and 5.04 (δ_B, J_{A-B} = 14.4 Hz, 1H) (CH_2), 4.14 (s, 1H, CH), −17.58 (s, 1H, Ir−H). ^{31}P{^{1}H} NMR (25 °C, C_6D_6): δ −55.7 (m, corresponding to an AA′BB′ spin system, which appears as an apparent AB spin system: δ_A = −50.8, δ_B = −60.6 J_{A-B} = 338 Hz). ^{13}C{^{1}H}-apt NMR (25 °C, C_6D_6): δ 50.9 (t, J_{C-P} = 24 Hz, CH_2), 25.2 (tt, J_{C-P} = 66 and 5 Hz, CH). MS (FAB$^+$): 997 (100%, M + H$^+$), 961 (42%, M − Cl$^+$).

[IrHCl(dppm)$_2$]BF$_4$. To a suspension of **5** (48 mg, 0.048 mmol) in diethyl ether (4 mL) was added HBF_4·Et_2O (6.6 μL, 0.048 mmol) to give a white solid. The liquid was decanted, and the solid was washed with diethyl ether and vacuum-dried. Yield: 43 mg (83%). Anal. Calcd for $C_{50}H_{45}ClP_4IrBF_4$: C, 55.39; H, 4.18. Found: C, 55.37; H, 4.08. ^{1}H NMR (25 °C, HDA): δ 7.49 (m, 24H, Ph), 7.33 (m, 16H, Ph), 5.80 (m, 2H, CH_2P), 5.58 (m, 2H, CH_2P), −16.17 (quint, J_{H-P} = 12, 1 Hz, Ir−H). ^{31}P{^{1}H} NMR (25 °C, HDA): δ −54.6 (s).

[Ir(dppe)$_2$][IrCl$_2$(coe)$_2$] (6). To a solution of [Ir$_2$(μ-Cl)$_2$(coe)$_4$] (105.5 mg, 0.118 mmol) in 1,2-dimethoxyethane (4 mL) was slowly added via cannula a solution of dppe (96.7 mg, 0.24 mmol) in the same solvent. After 1 h stirring the orange solid was filtered, washed with diethyl ether, and vacuum-dried. Yield: 160 mg (96%). Anal. Calcd for $C_{68}H_{76}Cl_2P_4Ir_2$: C, 55.46; H, 5.20. Found: C, 55.51; H, 5.08. ^{1}H NMR (25 °C, HDA) (assigned from the ^{1}H,^{1}H-COSY spectrum): δ 7.37 (m, 20H, Ph), 2.29 (m, 4H, CH_2) (dppe); 5.12 (q, J_{H-H} = 12.2 Hz, 2H), 1.87 (dd, J_{H-H} = 13.9, 1.9 Hz, 2H), 1.48 (m, 6H) and 1.28 (m, 4H) (coe). ^{31}P{^{1}H} NMR (25 °C, HDA): δ 49.8 (s, dppe). MS (FAB$^+$): 989 (100%, M$^+$).

[Ir(O$_2$)Cl(Ph$_2$PPy)$_2$] (7). A solution of [IrCl(Ph$_2$PPy)$_2$] (**2**) (151.0 mg, 0.20 mmol) in acetone (10 mL) was maintained under an oxygen atmosphere for 30 min. The initial red solution turned pale yellow in a few minutes and a yellow solid precipitated. The solid was filtered, washed with cold acetone (2 × 5 mL), and vacuum-dried. Yield: 153 mg (97%). Anal. Calcd for $C_{34}H_{28}N_2ClO_2P_2Ir$: C, 51.94; H, 3.59; N, 3.56. Found: C, 51.91; H, 3.97; N, 3.21. IR (KBr, cm^{-1}): ν(O−O) 844. ^{1}H NMR (25 °C, $CDCl_3$): δ 9.07 (t, J = 4.0 Hz, 1H); from 7.88 to 6.92 (m, 27H). ^{31}P{^{1}H} NMR (25 °C, $CDCl_3$): δ −20.0 (br s, P^b), −67.0 (d, J_{P-P} = 22 Hz, P^a). MS (FAB$^+$): 787 (15%, M$^+$), 754 (100%, M − O_2^+).

[Ir(H)$_2$Cl(Ph$_2$PPy)$_3$] (8). The addition of solid Ph$_2$PPy (164.7 mg, 0.62 mmol) to a suspension of [Ir$_2$(μ-Cl)$_2$(cod)$_2$] (70.0 mg, 0.10 mmol) in acetone (7 mL) caused the immediate formation of an orange solution. The solution was maintained for 1 h under a hydrogen atmosphere, leading to a pale yellow solution, which was concentrated to ca. 2 mL. Addition of hexane (10 mL) under vigorous stirring gave a pale yellow solid that was filtered, washed with hexane (2 × 5 mL), and vacuum-dried. Yield: 195 mg (92%). Anal. Calcd for $C_{51}H_{44}N_3ClP_3Ir$: C, 60.08; H, 4.35; N, 4.12. Found: C, 59.95; H, 4.30; N, 3.93. ^{1}H NMR (25 °C, C_6D_6): δ 8.36−6.13 (42H), −9.54 (dtd, $J_{H-P}a$ = 129.6 Hz, $J_{H-P}b$ = 19.8 Hz, J_{H-H} = 5.1 Hz, 1H, H^a−Ir), −20.27 (qd, J_{H-P^b} = 13.5 Hz, J_{H-H} = 5.1 Hz, 1H, H^b−Ir). ^{31}P{^{1}H} NMR (25 °C, C_6D_6): δ 14.3 (d, J_{P-P} = 15 Hz, 2P, P^b), 1.94 (t, J_{P-P} = 15 Hz, 1P, P^a). MS (FAB$^+$): 984 (43%, M − Cl$^+$), 719 (100%, Ir(Ph$_2$PPy)$_2^+$)

[IrCl$_2$(η^1-CH$_2$Cl)(Ph$_2$PPy)$_2$] (9). To a suspension of [Ir$_2$(μ-Cl)$_2$(coe)$_4$] (100.0 mg, 0.11 mmol) in dichloromethane (5 mL) was added Ph$_2$PPy (117.5 mg, 0.45 mmol). The resulting red solution was stirred at 35 °C for 2 h to give a pale orange solution. The solution was concentrated to ca. 2 mL and layered with diethyl ether (15 mL) to render an off-white solid overnight. The mother liquors were decanted, and the solid was washed with diethyl ether (2 × 5 mL) and vacuum-dried. Yield: 133 mg (71%). Anal. Calcd for $C_{35}H_{30}N_2Cl_3P_2Ir$: C, 50.10; H, 3.60; N, 3.34. Found: C, 50.34; H, 3.52; N, 3.17. ^{1}H{^{31}P} NMR (25 °C, $CDCl_3$) (assigned from the ^{1}H,^{1}H−COSY spectrum): δ 9.97 (d, J = 5.9 Hz, 1H, PyP^a), 9.10 (d, J = 5.2 Hz, 1H, PyP^b), 8.29 (t, J = 7.7 Hz, 1H, PyP^a), 8.14 (m, 4H, PyP^a+PyP^b+Ph^{o}P^b), 7.95 (d, J = 7.8 Hz, 2H, Ph′^{o}P^a), 7.94 (t, J = 5.5 Hz, 1H, PyP^b), 7.60 (m, 2H, PyP^a+Ph^{p}P^b), 7.53 (m, 3H, Ph^{m}P^b+Ph′^{p}P^a), 7.40 (m, 5H, PyP^b+Ph^{p}P^a+Ph′^{m}P^a+Ph′^{p}P^b), 7.23 (m, 4H, Ph^{m}P^a+Ph′^{m}P^b), 7.12 (d, J = 7.1 Hz, 2H, Ph′^{o}P^b), 6.24 (d, J = 7.7 Hz, 2H, Ph^{o}P^a), 6.18 (δ_A, 1H) and 5.37 (δ_B, J_{A-B} = 12.1 Hz, 1H) (Ir−CH_2Cl). ^{31}P{^{1}H} NMR (25 °C, $CDCl_3$): δ 8.3 (d, J(PP) = 15 Hz, P^b), −60.7 (d, J(PP) = 15 Hz, P^a). ^{13}C{^{1}H} NMR (25 °C, $CDCl_3$): δ 44.7 (br s, Ir−CH_2Cl). MS (FAB$^+$): 803 (100%, M − Cl$^+$).

Table 2. Crystal Data and Structure Refinement for 1

formula	Cl Ir P_2 N_4 C_{44} H_{38}
fw	912.37
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	10.284(4)
b, Å	23.343(5)
c, Å	16.066(3)
β, deg	97.56(3)
V, Å^3	3823(2)
Z	4
D_{calcd}, g cm^{-3}	1.585
F(000)	1816
μ, cm^{-1}	36.83
no. of reflns collected and unique	4265, 4092 [R(int) = 0.0894]
no. of obsd reflns [I>2σ(I)]	1965
no. of params	302
final R indices [I > 2σ(I)][a]	R1 = 0.0370, wR2 = 0.0822
R indices (all data)[a]	R1 = 0.1371, wR2 = 0.1413

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Crystal Structure Determination of Complex 1. The crystals of **1** were rather small in size and of poor quality and diffracted weakly. The intensity data of **1** were collected at room temperature on a Philips PW1100 single-crystal diffractometer using graphite-monochromated Mo Kα radiation. Crystallographic and experimental details for the structure are summarized in Table 2. A correction for absorption was made [maximum and minimum value for the transmission coefficient was 1.000 and 0.775].[25] The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97)[26] first with isotropic and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms except the carbon atoms of the phenyl rings. The hydrogen atoms were introduced into geometrically calculated positions and refined riding on the corresponding parent atoms except the hydride H1, which was localized in the ΔF map.

Acknowledgment. The financial support from Ministerio de Ciencia y Tecnología (MCyT(DGI)/FEDER) Projects BQU2002-0074 and BQU2003-05412 is gratefully acknowledged. S.J. thanks Diputacion General de Aragón (DGA) for a fellowship.

Supporting Information Available: An X-ray crystallographic file, in CIF format, containing full details of the structural analyses of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049142I

(25) (a) Walker N.; Stuart D. *Acta Crystallogr*. **1983**, *A39*, 158. (b) Ugozzoli F. *Comput. Chem*. **1987**, *11*, 109.

(26) Sheldrick, G. M. *SHELX-97*. Programs for Crystal Structure Analysis (Release 97-2); Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.