Reversible C−H Bond Activation of a Bifunctional Phosphine Bridging Ligand across Two Unbonded Metal Centers

Cristina Tejel,[†] Rita Bravi,[†] Miguel A. Ciriano,*[,†] Luis A. Oro,*[,†] Marta Bordonaba,[‡] Claudia Graiff,[‡] Antonio Tiripicchio,[‡] and Alfredo Burini[§]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, Parco Area delle Scienze 17A, I-43100 Parma, Italy, and Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, I-62032 Camerino, Italy

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Reaction of [{Ir(μ-Cl)(cod)}$_2$] with the short-bite bifunctional N,P-donor ligand (1-benzyl-2-imidazolyl)diphenylphosphine (Ph_2PBzIm) gives the yellow complex [IrCl(Ph_2PBzIm)(cod)] (**2**). A further addition of [{Ir(μ-Cl)(cod)}$_2$] to **2** results in the reversible metalation of a phenyl ring across two unbonded iridium centers to give orange crystals of [IrCl(cod){μ-PPh(C_6H_4)-BzIm}IrHCl(cod)] (**1**). Complex **1** is in equilibrium with the mononuclear complex [IrCl(Ph_2-PBzIm)(cod)] and the active species undergoing the sp^2-C−H activation, [{IrCl(cod)}$_2$(μ-Ph_2PBzIm)], in solution. Abstraction of one chloride ligand from **1** with $AgBF_4$ produces the deinsertion of the C−H bond yielding the cationic complex [{Ir(cod)}$_2$(μ-Ph_2PBzIm)(μ-Cl)]-BF_4, which regenerates **1** upon addition of a chloride-soluble salt. The cationic complex [{Ir-(cod)}$_2$(μ-Ph_2PBzIm)(μ-Cl)]BF_4 is inactive for the above-mentioned sp^2-C−H bond activation and can be prepared alternatively from the reaction of **2** with [Ir(cod)(CH_3CN)$_2$]BF_4. A related binuclear sp^2-C−H bond activation across two unbonded metals also occurs in the reaction of dppm with [{Ir(μ-Cl)(cod)}$_2$] in a 1:1 molar ratio. This reaction leads to a mixture in equilibrium of [{IrCl(cod)}$_2$(μ-dppm)] and the hydride complex [IrCl(cod){μ-PPh(C_6H_4)CH_2-PPh_2)}IrHCl(cod)] in a 1.5:1 molar ratio, respectively, in dichloromethane at 20 °C. The structure of the mixed-valence complex **1** was solved by X-ray diffraction studies.

Introduction

Short-bite bifunctional N,P ligands such as 2-(diphenylphosphino)pyridine (Ph_2PPy) have been the focus of much interest in building dinuclear complexes holding the metal atoms in close proximity, and a rich chemistry for them has been developed.[1] However, to the best of our knowledge, C−H bond activation of these ligands is very rare, despite the ability of phenyl and pyridyl groups to undergo ortho-metalation reactions.[2] Some examples of P−C bond activation in reactions with ruthenium clusters[3] and ortho metalation of a phenyl ring of Ph_2PPy across a multiple Re−Re bond have been previously reported.[4]

We report here on reversible C−H bond activation reactions of a hybrid P,N (phosphine−imidazolyl) ligand and of dppm in dinuclear complexes leading to the ortho metalation of a phenyl ring across two unbonded iridium centers, and we give evidence for both the assistance of the second metal center to enter in the binuclear sp^2-C−H activation and the active species undergoing this reaction.

Results and Discussion

Reaction of [{Ir(μ-Cl)(cod)}$_2$] with 1 molar equiv of 1-benzyl-2-imidazolyldiphenylphosphine (Ph_2PBzIm) in dichloromethane gives orange crystals analyzed as [{IrCl(cod)}$_2$(μ-Ph_2PBzIm)] after layering the reaction mixture with hexanes overnight. Interestingly, this reaction involves a C−H bond activation process under smooth conditions, indicated by the detection of a hydride ligand as a doublet at δ −12.90 ppm (J_{H-P} = 9.3 Hz) in the ^{1}H NMR spectrum of these crystals. As this spectrum is too complicated to establish unambiguously the source of the hydride ligand (Figure 1), the complete characterization of the orange crystals as [IrCl-(cod){μ-PPh(C_6H_4)BzIm}IrHCl(cod)] (**1**) was fully elucidated by a X-ray diffraction study.

The molecular structure of the Ir(I)−Ir(III) complex [IrCl(cod)[{μ-PPh(C_6H_4)BzIm}IrHCl(cod)] (**1**) is shown in Figure 2 together with the atomic numbering system. Selected bond distances and angles are given in Table 1. The two iridium atoms, separated by 4.475(3) Å, are bridged by the PPh(C_6H_4)BzIm ligand (through the N(1)

[†] Universidad de Zaragoza-CSIC.
[‡] Università di Parma.
[§] Università degli Studi di Camerino.

(1) Zhang, Z.-Z.; Cheng, H. *Coord. Chem. Rev.* **1996**, *147*, 1.
(2) For a review see: Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879 and references therein.
(3) (a) Deeming, A. J.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1993**, 2041. (b) Lugan, N.; Lavigne, G.; Bonnet, J. J. *Inorg. Chem.* **1987**, *26*, 585.
(4) Barder, T. J.; Tetrick, S. M.; Walton, R. A.; Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 4090.

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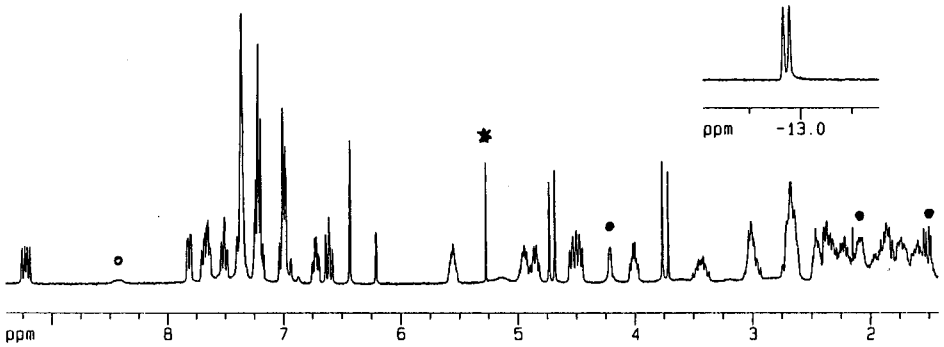


Figure 1. ^{1}H NMR spectrum of crystals of **1** in $CDCl_3$ showing the resonances of **1**, [{Ir(μ-Cl)(cod)}$_2$] (●), [IrCl(Ph_2PBzIm)(cod)], and [{IrCl(cod)}$_2$(μ-Ph_2PBzIm)] (○). The asterisk (*) denotes the CH_2Cl_2 of crystallization.

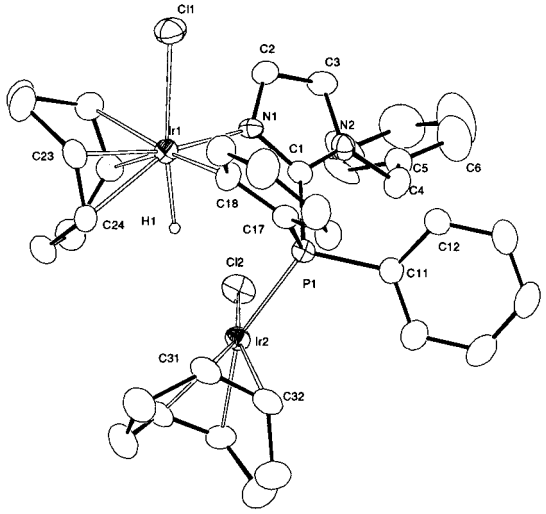


Figure 2. View of the structure of compound **1** together with the atomic numbering system.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 1[a]

Ir(1)−Cl(1)	2.489(3)	Ir(1)−H(1)	1.60(6)
Ir(1)−N(1)	2.067(6)	Ir(1)−C(18)	2.034(8)
Ir(1)−M(1)	2.077(9)	Ir(1)−M(2)	2.195(9)
Ir(2)−P(1)	2.292(2)	Ir(2)−CI(2)	2.356(2)
Ir(2)−M(3)	2.010(9)	Ir(2)−M(4)	2.095(9)
N(1)−C(1)	1.329(10)	N(1)−C(2)	1.360(10)
N(2)−C(1)	1.353(10)	N(2)−C(3)	1.358(11)
N(2)−C(4)	1.487(11)		
C(18)−Ir(1)−N(1)	86.5(3)	C(18)−Ir(1)−Cl(1)	89.3(3)
N(1)−Ir(1)−Cl(1)	85.71(19)	P(1)−Ir(2)−Cl(2)	89.71(9)
C(1)−P(1)−Ir(2)	115.7(3)	C(1)−N(1)−Ir(1)	123.8(5)
N(1)−C(1)−P(1)	119.6(6)	N(2)−C(1)−P(1)	130.4(6)
N(I)−C(1)−N(2)	109.8(7)		

[a] M(1), M(2), M(3), and M(4) are the midpoints of the double bonds C(23)−C(24), C(27)−C(28), C(31)−C(32), and C(35)−C(36), respectively.

and P(1) atoms), which also interacts with Ir(1) through the C(18) atom from the ortho-metalated phenyl. The hydrogen atom H(1) coming from the C−H activation is terminally bound to the Ir(1) atom (Ir(1)−H(1) = 1.60(6) Å). If the midpoints of the double bonds of the cod ligands are considered as coordination sites, the Ir(1) and Ir(2) atoms exhibit octahedral and square-planar coordinations, respectively, as expected for Ir(III) and Ir(I) atoms.

The hydride ligand located in the solid state on the iridium atom coordinated at the N-donor end could be thought to bridge the two iridium atoms, since the coupling with the phosphorus nucleus is slightly smaller than the typical for a hydride cis to a phosphine in iridium complexes. However, X-ray data indicate that this bridge, if it exists, is very unsymmetrical (Ir(2)···H(1) = 2.59(7) Å). Therefore, the large coupling constant could arise from a large scalar coupling through four bonds due to the close proximity between these atoms in the molecule.

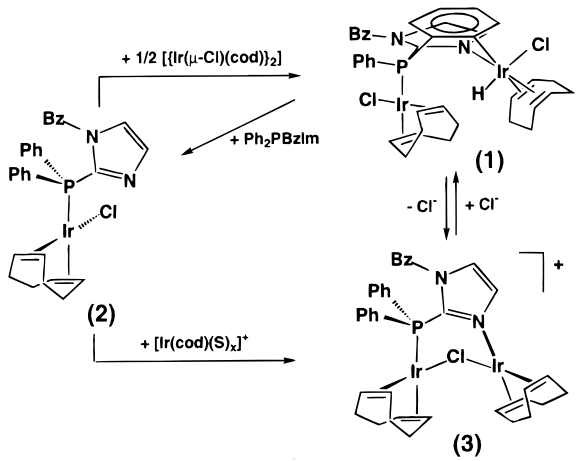
Solutions of **1** in $CDCl_3$ invariably show three P-containing species in a concentration-dependent equilibrium (with signals in the $^{31}P\{^1H\}$ NMR spectrum at δ 25.2, 10.8, and 7.0 ppm in a 75:10:15 molar ratio for a concentrated solution) and [{Ir(μ-Cl)(cod)$_2$]. The spectroscopic data for the main species including H,H-COSY and H,H-NOESY experiments are consistent with the hydrido complex **1**. A second species identified in the equilibrium is the yellow mononuclear complex [IrCl(Ph_2PBzIm)(cod)] (**2**) with the P atom bonded to the metal, which is easily prepared by reaction of [{Ir(μ-Cl)(cod)}$_2$] with 2 molar equiv of (1-benzyl-2-imidazolyl)-diphenylphosphine (Ph_2PBzIm) in dichloromethane. Finally, the broad singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 10.8 is attributed to [{IrCl(cod)}$_2$(μ-Ph_2PBzIm)] (**A**), which could not be isolated. These species are related by the equilibria

$$^1/_2[\{Ir(\mu\text{-Cl})(cod)\}_2] + [IrCl(Ph_2PBzIm)(cod)] \rightleftharpoons [\{IrCl(cod)\}_2(4\text{-}Ph_2PBzIm)] \rightleftharpoons \mathbf{1}$$

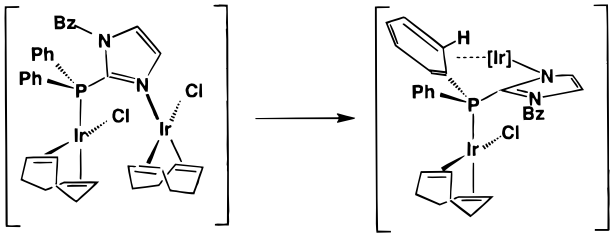
To identify the active species undergoing the C−H bond activation, the reaction was performed stepwise by the successive additions of the "Ir(cod)" moiety and chloride to **2**. Thus, reaction of **2** with [Ir(cod)(CH_3CN)$_2$]-BF_4 in dichloromethane gives the purple complex [{Ir(cod)$_2$(μ-Ph_2PBzIm)(μ-Cl)]BF_4 (**3**) (Scheme 1). The cationic compound **3**, in which the P,N ligand is coordinated to both iridium atoms, remains unaltered in solution for days. A further addition of the chloride-soluble salt PPNCl to **3** gives the mixture containing mainly the hydrido complex **1** in a few minutes (Scheme 1). Both steps are accomplished by the direct reaction of the mononuclear **2** with [{Ir(μ-Cl)(cod)$_2$] in a 1:0.5 molar ratio (Scheme 1). These experiments evidence that the active species which undergoes the sp^2-C−H activation reaction is the neutral complex [{IrCl(cod)}$_2$(μ-Ph_2-PBzIm)] (**A**; Scheme 2), while the related cationic complex **3** is inactive under identical conditions.

The key to this distinctive reactivity of **A** versus **3** probably relies on the ability of one phenyl ring on the Ph_2P−Ir(1) moiety to interact with the metal in the

Scheme 1



Scheme 2



other half of the complex, Ir(2)−N(BzIm). The close proximity of Ir and phenyl groups is allowed in complex **A** by a free rotation of half of the binuclear complex around the P−C(BzIm) bond (Scheme 2), while it is prevented in **3** by the bridging chloride ligand.

Molecular models show that this rotation in **A** allows the approach of the ortho CH of a phenyl group to the second iridium center, which is necessary to start the CH activation process. A frozen structure of such an intermediate with a bridging dppm between two platinum atoms in $(NBu_4)[(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pt(C_6F_5)_2]$ has just been described.[5] Moreover, the stereochemistry of **1**, in which the ortho carbon and hydride are *cis*, is consistent with a concerted oxidative addition of the C−H bond. The reaction leading to **1** represents a rare example of ortho metalation across two metal centers due to the assistance between the two metals, since the first iridium center coordinates the Ph_2P fragment while the second one undergoes the sp^2-C−H bond activation reaction giving **1**. No insertion of the hydride ligand into one of the olefinic bonds is observed, despite the right stereochemistry for this reaction in the molecular structure of **1**.

A further remarkable feature of the transformation of **3** into **1** by addition of chloride is that it is fully reversible. The abstraction of one chloride ligand from **1** by addition of $AgBF_4$ regenerates **3** quantitatively. This reversibility involves the corresponding formation and rupture of the C−H bond. Moreover, the formation of the C−H bond from the hydride and the ortho-metalated carbon is also achieved by addition of Ph_2-PBzIm to **1**, which regenerates **2** in quantitative yield.

The Ph_2PBzIm ligand is not particularly needed to reverse the reaction, since either of the two donor entities of the P,N hybrid ligand is enough to fulfill this process. Thus, complex **1** reacts with PPh_3 to render an equimolecular mixture of **2** and $[IrCl(PPh_3)(cod)]$ and with *N*-benzylimidazole to give **2** and [IrCl(*N*-benzylimidazole)(cod)].[6]

As this unusual assisted reaction and mechanism should not be restricted to this N,P ligand, we undertook the study of a similar reaction with the much used diphenylphosphine ligand (dppm).[7] Some examples of P−C and C−H bond activations of metal−metal bonds in the reactions of dppm with ruthenium and osmium clusters have been described,[8,9] and cyclometalation of a phenyl ring of dppm taking place at the same metal to which the phosphorus is bound has been observed in a heterodinuclear complex.[10] Supporting this idea, a binuclear sp^2-C−H bond activation across the two metals also occurs in the reaction of dppm with $[\{Ir(R\text{-}Cl)(cod)_2]$ in a 1:1 molar ratio in dichloromethane. After workup, an orange microcrystalline solid analyzed as $[\{IrCl(cod)\}_2(\mu\text{-dppm})]$ is isolated. Solutions of this solid in CD_2Cl_2 or d_6-benzene at 20 °C and those prepared from [IrCl(cod)(dppm)] and $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ in a 1:0.5 molar ratio in CD_2Cl_2 contain an equilibrium mixture of $[\{IrCl(cod)\}_2(\mu\text{-dppm})]$ and the hydride complex [IrCl-(cod){μ-PPh(C_6H_4)CH_2PPh_2)}IrHCl(cod)] **(4)** in a 1.5:1 molar ratio, respectively.

The characterization of **4** relies on spectroscopic data, and the compound seems to be similar to complex **1** (Figure 3a). In particular, the resonance for the hydride ligand appears as a multiplet at δ −15.39 ppm in the ^1H NMR spectrum, due to the coupling with the two phosphorus nuclei, one in a cis position and the other on the neighboring iridium atom. The close proximity of the hydride ligand with two olefinic protons of cod in cis positions is clearly indicated by the cross-peaks in the H,H-NOESY spectrum (Figure 3b), and therefore, cod and hydride occupy *fac* positions in the octahedral environment.

In separate experiments, the mononuclear [IrCl-(dppm)(cod)] (**5**) and the cationic $[Ir_2(\mu\text{-}Cl)(\mu\text{-dppm})(cod)_2]BF_4$ (**6**) complexes were isolated and characterized to discard their presence in the above-mentioned equilibrium. As for the hybrid P,N ligand, the cationic complex $[Ir_2(\mu\text{-}Cl)(\mu\text{-dppm})(cod)_2]BF_4$ (**5**) is inactive for the phenyl C−H activation, remaining unaltered for

(5) Casas, J. M.; Forniés, J.; Martinez, F.; Rueda, A. J.; Tomis, M.; Welch, A. J. *Inorg. Chem.* **1999**, *38*, 1529.

(6) Bonati, F.; Oro, L. A.; Pinillos, M. T.; Tejel, C.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1989**, *369*, 253.

(7) (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191. (c) Adams, R. D. In *The Chemistry of Metal Cluster Compounds*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: Weinheim, Germany, 1990; Chapter 3.

(8) (a) Lavigne, G.; de Bonneval, B. In *Catalysis by Di- and Polynuclear Metal Cluster Compounds*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998, Chapter 2, p 39. (b) Sappa, E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, U.K., 1995; Vol. 7, Chapter 14.

(9) (a) Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *Can. J. Chem.* **1995**, *73*, 3, 903. (b) Bruce, M. I.; Hinchliffe, J. R.; Surynt, R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *469*, 89. (c) Harding, M. M.; Kariuki, B.; Mathews, A. J.; Smith, A. K.; Braunstein, P. *J. Chem. Soc., Dalton Trans.* **1994**, 33. (d) Bruce, M. I.; Humphrey, P. A.; Miyamae, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *429*, 187.

(10) Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 1297.

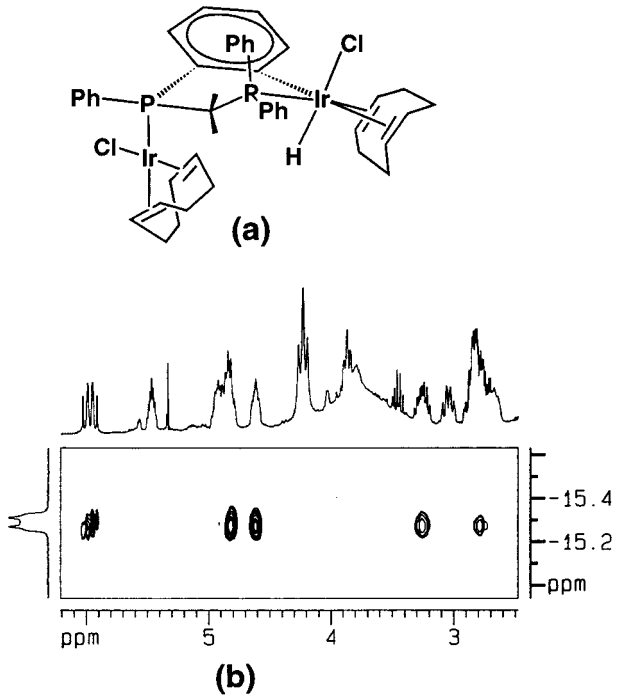


Figure 3. (a) Proposed structure for **4**. (b) Section of of the H,H-NOESY spectrum of **4** in CD_2Cl_2 at 27 °C, showing the positive cross-peaks due to proximity between the hydride and one diasterotopic proton (CH_2) of dppm, two olefinic protons of the cod in cis positions, and two olefinic protons of the other cod ligand.

days in solution, but addition of a soluble chloride drives the reaction to the equilibrium mixture.

In conclusion, intramolecular reversible sp^2-C−H activation reactions of frequently used short-bite binucleating ligands across two unbonded metals can take place under smooth conditions in binuclear iridium complexes, and they involve the assistance of the second metal center. The key to these activations seems to be also related to the presence of a single bridging ligand that provides the flexibility needed for the initial approach of a phenyl group to the second metal center.

Experimental Section

General Considerations. All the reactions were carried out under argon using standard Schlenk techniques. Those with silver salts were protected from light with black photographic paper. The complex [{Ir(μ-Cl)(cod)}$_2$][11] and (1-benzyl-2-imidazolyl)diphenylphosphine[12] were prepared according to literature methods. Solvents were dried and distilled under argon before use by standard methods. Carbon, hydrogen, and nitrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at ca. 30 kV; 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 Bruker ARX 300 and Varian UNITY 300 spectrometers 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 and 85% phosphoric acid as references, respectively. The phase-sensitive H,H-NOESY experiments were carried out on the Bruker spectrometer using the pulse program NOESYST with 512 FID's and a mixing time of 1000 ms. Conductivities were measured in (4−5) × 10^{-4} M acetone solutions using a Philips PW 9501/01 conductimeter.

[IrCl(cod){μ-PPh(C_6H_4)BzIm}IrHCl(cod)] (1). Solid [IrCl(Ph$_2$PBzIm)(cod)] (**2**; 135.6 mg, 0.20 mmol) was added to a solution of [{Ir(μ-Cl)(cod)}$_2$] (67.1 mg, 0.10 mmol) in dichloromethane (10 mL) to give a red solution. This solution was concentrated to ca. 2 mL and layered with hexanes. During the diffusion, the initial red solution became orange and orange monocrystals, suitable for X-ray diffraction studies, were deposited. The crystals were washed with hexane and vacuum-dried. Yield: 182.4 mg (90%). Anal. Calcd for $C_{38}H_{43}N_2Cl_2PIr_2$: C, 45.01; H, 4.27; N, 2.76. Found: C, 45.91; H, 3.88; N, 2.57. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$): δ 25.2 (74%, corresponding to **1**); 10.8 (12%, attributed to [{IrCl(cod)$_2$}(4-Ph$_2$PBzIm)] (**A**), and 7.0 (14%, corresponding to **2**). Molecular weight in $CHCl_3$: calcd 1014, found 1005.

[IrCl(Ph$_2$PBzIm)(cod)] (2). Solid [{Ir(μ-Cl)(cod)}$_2$] (134.2 mg, 0.20 mmol) was added to a solution of Ph$_2$PBzIm (137.2 mg, 0.40 mmol) in dichloromethane (10 mL). After it was stirred for 1 h, the orange solution was concentrated to ca. 1 mL and layered with hexanes (20 mL) to give orange microcrystals overnight. The solution was decanted, and the crystals were washed with hexane and vacuum-dried. Yield: 250 mg (92%). Anal. Calcd for $C_{30}H_{31}N_2ClPIr_2$: C, 53.13; H, 4.61; N, 4.13. Found: C, 52.84; H, 4.30; N, 3.96. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$): δ 7.0. ^1H NMR (room temperature, $CDCl_3$): δ 7.673 (m, 4H, H^o*Ph*$_2$PBzIm); 7.358 (br, 12H, *Ph*$_2$-PCH$_2$*PhIm*); 6.938 (s, 1H, Ph$_2$PCH$_2$Ph*Im*); 6.214 (s, 2H, Ph$_2$P*CH*$_2$PhIm); 5.191 (br, 2H) and 2.790 (br, 2H) (HC═ cod), 2.094 (br, 4H) and 1.578 (br, 4H) (CH_2 cod).

[{Ir(cod)}$_2$(μ-Ph$_2$PBzIm)(μ-Cl)]BF_4 (3). Solid [IrCl(Ph$_2$-PBzIm)(cod)] (**2**; 67.8 mg, 0.10 mmol) was added to a solution of [Ir(cod)(CH_3CN)$_2$]BF_4 (46.9 mg, 0.10 mmol) in dichloromethane (10 mL). The color of the solution changed inmediately from yellow to dark red. After evaporation of the dichloromethane to ca. 1 mL the solution was carefully layered with diethyl ether (15 mL) to render dark red microcrystals overnight. The solution was decanted and the solid washed with diethyl ether and vacuum-dried. Yield: 89.0 mg (91%). Anal. Calcd for $C_{38}H_{43}N_2ClPIr_2BF_4$: C, 42.84; H, 4.07; N, 2.63. Found: C, 42.73; H, 4.27; N, 1.78. $^{31}P\{^1H\}$ NMR (223 K, d_6-acetone): δ 11.1. $^1H\{^{31}P\}$ NMR (223 K, HDA): δ 8.020 (d, 1.50 Hz, 1H) and 7.585 (d, 1.50 Hz, 1H) (Ph$_2$PBz*Im*); 7.859 (d, 7.23 Hz, 2H, H^o), 7.790 (d, 7.07 Hz, 2H, H$^{o'}$), 7.723 (m, 3H, H$^{m'+p'}$) and 7.587 (m, 3H, H^{m+p}) (*Ph*$_2$PBzIm); 7.171 (t, 7.29 Hz, 1H, H^p), 7.062 (t, 7.29 Hz, 2H, H^m), and 6.284 (d, 7.29 Hz, 2H, H^o) (Ph$_2$P*Bz*Im); 4.976 (d, 15.28 Hz, 1H) and 4.715 (d, 15.28 Hz, 1H) (Ph$_2$P*CH*$_2$PhIm); 5.402 (m, 1H), 4.964 (m, 1H), 4.387 (m, 1H), 4.365 (m, 1H), 4.071 (m, 2H), 3.857 (m, 1H), and 3.142 (m, 1H) (HC═ cod); 2.635 (m, 3H), 2.198 (m, 9H), 1.644 (m, 1H), and 1.429 (m, 3H) (CH_2 cod). Λ_M (4.9 × 10^{-4} M in acetone) = 102 S cm^2 mol^{-1}.

[IrCl(cod){μ-PPh(C_6H_4)CH_2PPh_2)}IrHCl(cod)] (4) was prepared as for **1**, starting from [IrCl(dppm)(cod)] (**5**; 72.0 mg, 0.10 mmol) and [{Ir(μ-Cl)(cod)}$_2$] (33.6 mg, 0.050 mmol) in dichloromethane to yield an orange solid after layering with hexanes. A second crop was obtained from the mother liquor after concentration. Overall yield: 90 mg (82%). Anal. Calcd for $C_{41}H_{46}Cl_2P_2Ir_2$: C, 46.63; H, 4.39. Found: C, 46.69; H, 4.63. $^{31}P\{^1H\}$ NMR (room temperature, CD_2Cl_2): δ 20.7 (d, J_{P-P} = 12 Hz), −17.1 (d, J_{P-P} = 12 Hz) (40%, **4**), 13.6 (br s, 60%, attributed to [{IrCl(cod)}$_2$(μ-dppm)]).

[IrCl(dppm)(cod)] (5). Addition of solid [{Ir(μ-Cl)(cod)}$_2$] (150 mg, 0.22 mmol) to a solution of dppm (171.6 mg, 0.44 mmol) in dichloromethane (10 mL) gives a yellow solution in a few minutes. Evaporation of this solution under vacuum to ca. 1 mL followed by layering with hexanes (10 mL) yields a

(11) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.
(12) Burini, A.; Pietroni, R. B.; Galassi, R.; Valle, G.; Calogero, S. *Inorg. Chim. Acta* **1995**, *229*, 299.

microcrystalline yellow solid. The solution was decanted, and the solid was washed with hexanes and dried under vacuum. Yield: 279 mg (87%). Anal. Calcd for $C_{33}H_{34}ClP_2Ir$: C, 55.03; H, 4.76. Found: C, 54.42; H, 4.93. $^{31}P\{^1H\}$ NMR (room temperature, CD_2Cl_2): δ −54.9. ^1H NMR (room temperature, CD_2Cl_2): δ 7.46 (m, 8H), 7.36 (m, 12H) ($Ph_2PCH_2PPh_2$); 4.835 (m, 2H, $Ph_2PCH_2PPh_2$); 3.999 (br s, 4H, HC═ cod); 2.36 (m, 4H) and 1.94 (m, 4H) (CH_2 cod). Molecular weight in $CHCl_3$: calcd 720, found 745.

[$Ir_2(\mu$-Cl)(μ-dppm)(cod)$_2$]BF_4 (6) was prepared as described for **3**, starting from [IrCl(dppm)(cod)] (140.0 mg, 0.20 mmol) and [Ir(cod)$(CH_3CN)_2$]BF_4 (93.8 mg, 0.20 mmol), to render orange microcrystals. Yield: 197.0 mg (89%). Anal. Calcd for $C_{41}H_{46}ClP_2Ir_2BF_4$: C, 44.47; H, 4.19. Found: C, 43.91; H, 3.93. $^{31}P\{^1H\}$ NMR (223 K, CD_2Cl_2): δ 19.4. ^1H NMR (223 K, CD_2Cl_2): δ 7.571 (br s, 20H, $Ph_2PCH_2PPh_2$); 3.750 (t, J_{H-P} = 9.30 Hz, 2H, $Ph_2PCH_2PPh_2$); 4.565 (br s, 4H) and 2.567 (br s, 4H) (HC═ cod); 1.763 (m, 12H) and 1.349 (m, 3H) (CH_2 cod). Λ_M (5.0×10^{-4} M in acetone) = 102 S cm^2 mol^{-1}.

Crystal Structure Determination of Complex 1·$^1/_4CH_2Cl_2$. The intensity data of **1**·$^1/_4CH_2Cl_2$ were collected at room temperature (293(2) K) on a Siemens AED single-crystal diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and the $\theta/2\theta$ scan technique. Crystallographic and experimental details are summarized in Table 2. A correction for absorption was made for the complex (maximum and minimum values for the transmission coefficient were 1.0000 and 0.716).[13] The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms, except the atoms of the CH_2Cl_2 solvent, which were found disordered in two positions around the center of inversion. All hydrogen atoms were placed at their geometrically calculated positions and refined riding on their parent atoms, except for the hydride, which was localized in the final ΔF map and refined isotropically. The weighting scheme $w = 1/[(\sigma^2(F_o^2) + (0.0817\,P)^2]$ was used in the last cycles of refinement, where $P = (F_o^2 + 2F_c^2)/3$. All calculations were carried out on the DIGITAL Alpha Station 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-97 systems of crystallographic computer programs.[14]

(13) (a) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158. (b) Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 1099.

(14) Sheldrick, G. M. SHELX-97 Program for the Solution and the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

Table 2. Crystal Data and Data Collection and Refinement for Complex 1

chem formula	$C_{38}H_{43}Cl_2Ir_2N_2P\cdot0.25CH_2Cl_2$
fw	1035.25
cryst size, mm	0.23 × 0.20 × 0.30
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	26.335(5)
b, Å	13.860(4)
c, Å	9.961(3)
β, deg	91.93(6)
V, Å^3	2670.5(14)
Z	4
D_{calcd}, g cm^{-3}	1.891
μ(Mo Kα), cm^{-1}	75.69
temp, °C	20
scan type	$\theta/2\theta$
scan speed, deg/min	3−10
0 range, deg	5−30
no. of measd rflns	11 162
no. of unique rflns	10620 ($I > 2\sigma(I)$) (R_{int} = 0.0946)
R1[a]	0.0427 (0.1045, all data)
wR2[b]	0.1102 (0.1439, all data)
GOF[c]	0.942

[a] $R1(F^2) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $GOF = \{[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

The details of the crystal structure investigation have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-146826. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. code + 44(1223)336-033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Listings of full experimental details of the structure determination, atomic coordinates, thermal parameters, hydrogen coordinates, and bond distances and angles for **1**·$^1/_4CH_2Cl_2$ and a section of the H,H-NOESY spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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