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# C–H Activation and C=C Double Bond Formation Reactions in Iridium *ortho*-Methyl Arylphosphane Complexes

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**Abstract:** The Vaska-type iridium(I) complex $[IrCl(CO)\{PPh_2(2\text{-}MeC_6H_4)\}_2]$ (**1**), characterized by an X-ray diffraction study, was obtained from iridium(III) chloride hydrate and $PPh_2(2,6\text{-}MeRC_6H_3)$ with R = H in DMF, whereas for R = Me, activation of two *ortho*-methyl groups resulted in the biscyclometalated iridium(III) compound $[IrCl(CO)\{PPh_2(2,6\text{-}CH_2MeC_6H_3)\}_2]$ (**2**). Conversely, for R = Me the iridium(I) compound $[IrCl(CO)\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$ (**3**) can be obtained by treatment of $[IrCl(COE)_2]_2$ (COE = cyclooctene) with carbon monoxide and the phosphane in acetonitrile. Compound **3** in $CH_2Cl_2$ undergoes intramolecular C–H oxidative addition, affording the cyclometalated hydride iridium(III) species $[IrHCl(CO)\{PPh_2(2,6\text{-}CH_2MeC_6H_3)\}\{PPh_2(2,6\text{-}Me_2C_6H_3)\}]$ (**4**). Treatment of **2** with $Na[BAr^f_4]$ ($Ar^f = 3,5\text{-}C_6H_3(CF_3)_2$) gives the fluxional cationic 16-electron complex $[Ir(CO)\{PPh_2(2,6\text{-}CH_2MeC_6H_3)\}_2][BAr^f_4]$ (**5**), which reversibly reacts with dihydrogen to afford the δ-agostic complex $[IrH(CO)\{PPh_2(2,6\text{-}CH_2MeC_6H_3)\}\{PPh_2(2,6\text{-}Me_2C_6H_3)\}][BAr^f_4]$ (**6**), through cleavage of an Ir–C bond. This species can also be formed by treatment of **4** with $Na[BAr^f_4]$ or of **2** with $Na[BAr^f_4]$ through C–H oxidative addition of one *ortho*-methyl group, via a transient 14-electron iridium(I) complex. Heating of the coordinatively unsaturated biscyclometalated species **5** in toluene gives the *trans*-dihydride iridium(III) complex $[IrH_2(CO)\{PPh_2(2,6\text{-}MeC_6H_3CH{=}CHC_6H_3Me\text{-}2,6)PPh_2\}][BAr^f_4]$ (**7**), containing a *trans*-stilbene-type terdentate ligand, as result of a dehydrogenative carbon–carbon double bond coupling reaction, possibly through an iridium carbene species.

**Keywords:** C–C coupling · C–H activation · hydrides · iridium · phosphanes

## Introduction

A central topic of organometallic chemistry is the activation of inert C–H bonds, induced by coordinatively unsaturated metal complexes, which represents the preliminary step for the stoichiometric and catalytic functionalization of organic molecules.[1] Cyclometalation reactions have been widely investigated and may be regarded as models for the intermolecular C–H bond activation processes.[2] With regard to phosphorus ligands, bulky phosphanes, such as triarylphosphanes containing methyl substituents in the *ortho* positions of the phenyl rings, have been successfully used for the preparation of cyclometalated transition metal complexes through methyl C–H bond cleavage.[3] Recently, by employment of the dimethyl-substituted phosphane $PR_2(2,6\text{-}Me_2C_6H_3)$ (R = Ph, Cy) we have isolated rare examples of 14-electron complexes of $d^6$ ruthenium[4] and $d^8$ platinum,[5] stabilized through δ-agostic interactions of the *ortho*-methyl groups (nonclassical $M\cdots\eta^3\text{–}H_2C$ interaction mode) (Figure 1).[6]

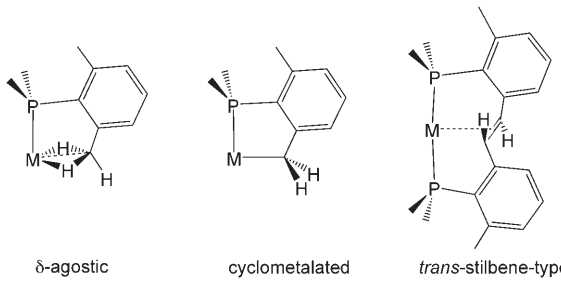


Figure 1. Types of arrangements observed with $PPh_2(2,6\text{-}Me_2C_6H_3)$.

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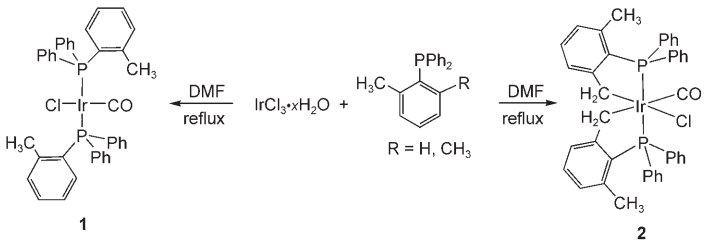
Agostic complexes, which feature M···$H_nC$ bonding between the metal of an unsaturated complex and a dangling $CH_n$ moiety, can be regarded as model intermediates on the reaction pathway for C–H activation (i.e., oxidative addition) reactions.[7] With $PPh_2(2,6\text{-}Me_2C_6H_3)$, cyclometalation reactions occur readily with platinum,[5] ruthenium,[8] and osmium,[9] producing stable compounds, each containing a carbon-metal σ bond. Interestingly, with the last of these metals a tridentate *trans*-stilbene-type ligand (Figure 1) is formed through a dehydrogenative carbon–carbon coupling of two phosphane methyl groups, which represents an intriguing mode for the functionalization of hydrocarbon groups mediated by metal centers.[8] A similar transformation has previously been reported for *ortho*-tolyl phosphanes $PPh_n(2\text{-}MeC_6H_4)_{3-n}$ ($n=0$–2) with $RhCl_3$[10] and with the azide $N_3$-(Mes) and $IrMes_3$ (Mes = 2,4,6-$Me_3C_6H_2$),[11] affording poor yields of products of dehydrogenative C–C coupling. It may be pointed out that iridium complexes have been shown to mediate a range of catalytic transformations[12] and have proven to be advantageous systems for alkane C–H activation,[13] a reaction extensively studied with PCP pincer complexes.[14]

In an effort to acquire better insight into the role of the metal center in C–H cleavage and C–C bond-formation reactions, we have extended our investigations into the coordination chemistry of $PPh_2(2,6\text{-}Me_2C_6H_3)$ to other transition metals. We now report that the individual steric properties of this phosphane allow the easy formation of neutral and cationic mono- and biscyclometalated $Ir^{III}$ complexes. Particularly interesting is the biscyclometalated 16-electron $Ir^{III}$ species $[Ir(CO)\{PPh_2(2,6\text{-}CH_2MeC_6H_3)\}_2]^+$, which reversibly reacts with dihydrogen, affording a cationic hydride $Ir^{III}$ complex stabilized by a δ-agostic interaction. This complex also undergoes thermal C–H activation of two alkyls, to afford a complex containing the *trans*-stilbene-type ligand (Figure 1). The role of three-coordinate 14-electron $Ir^{I}$ species $[Ir(CO)\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]^+$ in the C–H oxidative addition process is also discussed. For purposes of comparison, the coordination of the mono-*ortho*-tolyl phosphane $PPh_2(2\text{-}MeC_6H_4)$ has also been investigated, and the structure of the corresponding Vaska-type iridium(I) complex is reported.

## Results and Discussion

**Reactions between iridium(III) chloride hydrate and *ortho*-methyl arylphosphanes**: Treatment of $IrCl_3{\cdot}x\,H_2O$ ($x=3$) with $PPh_2(2\text{-}MeC_6H_4)$ in dimethylformamide at reflux affords the Vaska-type complex[15] $[IrCl(CO)\{PPh_2(2\text{-}MeC_6H_4)\}_2]$ (**1**), isolated in high yield (Scheme 1).

X-ray structural determination of the 16-electron square planar $d^8$ complex **1** shows a relatively long distance between the *ortho*-methyl groups and the metal center (C···Ir distance 3.97(1) Å) with small difference for the Ir-P-C bond angles, thus excluding the presence of agostic interactions (Figure 2 and Table 1).[16]




Scheme 1. Synthesis of complexes **1** and **2**.

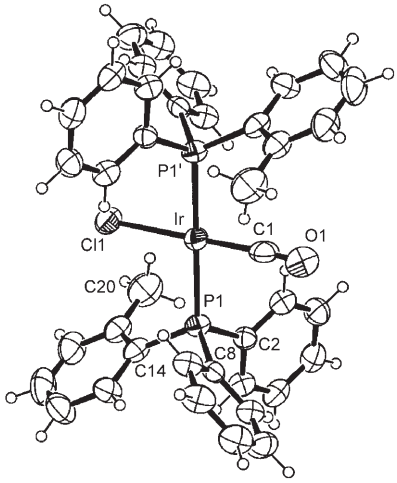



Figure 2. Molecular structure of **1** (ORTEP drawing, thermal ellipsoids at 40% probability level).

Table 1. Selected bond lengths [Å] and angles [°] in **1**·2 $CH_2Cl_2$.

| | | | |
|---|---|---|---|
| Ir–C1 | 1.839(12) | Ir–Cl1 | 2.433(8) |
| Ir–P1 | 2.3224(17) | C1–O1 | 1.100(17) |
| C1-Ir-P1 | 86.0(6) | C8-P1-Ir | 109.8(2) |
| C1-Ir-P1′ | 94.0(6) | C2-P1-Ir | 115.9(2) |
| C1-Ir-Cl1 | 177.9(9) | C14-P1-Ir | 116.6(2) |
| P1-Ir-Cl1 | 93.9(3) | O1-C1-Ir | 172(4) |
| P1-Ir-Cl1′ | 86.1(3) | | |

Primed atom at $-x$, $-y+1$, $-z+1$.

It may be noted that in the analogous derivative $[IrCl(CO)\{P(2\text{-}MeC_6H_4)_3\}_2]$, bearing a tri-(*ortho*-tolyl)phosphane unit, one methyl group was observed significantly closer to the metal center (3.55 Å).[17] In the $^1H$ NMR spectrum ($CD_2Cl_2$) the signal of the two methyl groups of **1** appears as a singlet at $\delta=2.62$ ppm, whereas in the $^{13}C$ NMR spectrum the resonance for the methyls is at $\delta=23.7$ ppm, which are values close to those of the free phosphane, in agreement with the lack of any agostic interaction. Complex **1** is stable in dichloromethane for many hours at room temperature and no cyclometalation has been observed. In contrast with the Vaska complex,[18] **1** is inert toward dioxygen, as inferred from $^{31}P$ NMR spectroscopy, and this can be ascribed to the steric influence of the *ortho*-methyl groups, which impede access of $O_2$ along the apical position and

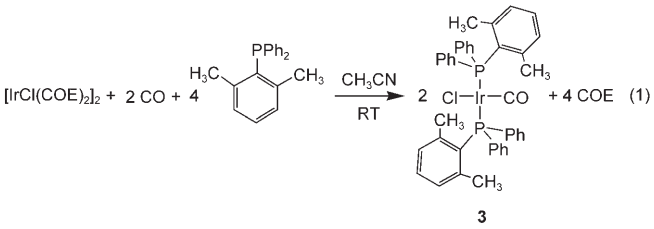
  

hinder coordination, as has also been described for the tri-(*ortho*-tolyl)phosphane iridium(I) derivative.[17] On the other hand, and similarly to the Vaska complex, compound **1** reacts slowly with dihydrogen (1 atm), to afford the expected product of oxidative addition—*cis*,*cis*,*trans*-$[IrH_2Cl(CO)\{PPh_2(2\text{-}MeC_6H_4)\}_2]$—through the folding back of the *trans*-Cl(CO) set of ligands of **1**.[19] The $^{31}P$ NMR spectrum of **1** in $CD_2Cl_2$ under $H_2$ thus shows one singlet at $\delta = 6.1$ ppm, whereas in the $^1H$ NMR spectrum the two hydride signals are at $\delta = -7.5$ and $-18.9$ ppm, showing $^2J(H,H) = 4.6$ Hz, with $^2J(H,P) = 17.8$ and 15.2 Hz, respectively, values close to those reported for the related $PPh_3$ complex.[20]

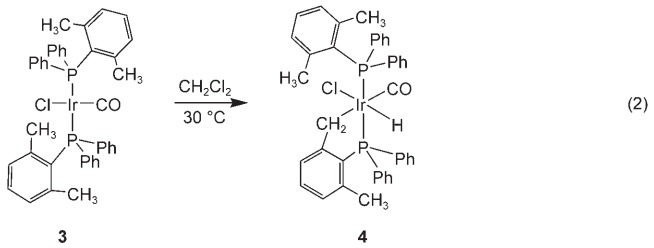
When the 2,6-dimethyl-substituted arylphosphane $PPh_2(2,6\text{-}Me_2C_6H_3)$ is employed instead of $PPh_2(2\text{-}MeC_6H_4)$ in the reaction with iridium chloride under identical experimental conditions, the colorless diamagnetic iridium(III) complex **2** is quantitatively formed through double C–H cleavage in two *ortho*-methyl groups (Scheme 1). The carbonyl stretching of **2** appears at 2006 $cm^{-1}$, shifted to higher wavenumbers than in **1** (1947 $cm^{-1}$), in agreement with the higher oxidation state of iridium. The $^{31}P$ NMR spectrum displays two doublets at $\delta = 29.6$ and 17.4 ppm with $^2J(P,P) = 349$ Hz, typical for iridium(III) species bearing two *trans* phosphanes.[21] In the $^1H$ NMR spectrum the two cyclometalated $CH_2$ moieties appear as four signals in the $\delta = 2.55$–2.04 ppm range for nonequivalent protons coupled with H and P atoms, whereas the singlets at $\delta = 1.85$ and 1.76 ppm are for the two methyl groups. The two $CH_2$ groups give $^{13}C$ NMR signals at $\delta = 34.3$ and 11.8 ppm, *trans* to the CO and the Cl ligands, respectively, while the two methyl groups are at $\delta = 22.9$ and 22.4 ppm, close to the value for the free phosphane. These data are therefore consistent with a geometry for **2** with two *trans* phosphanes and a *cis* arrangement of the alkyl ligands, which display a high *trans* influence. It should be noted that the arrangement of **2** resembles that of the *cis* dihydrido iridium(III) species obtained by oxidative addition of $H_2$ to **1** and the Vaska-type complexes. Recently, a biscyclometalated $Ir^{III}$ complex bearing heterocyclic carbenes has been reported by Nolan and co-workers.[22] Interestingly, compound **2**, in which the two Ir–C bonds show a *cis* arrangement, is thermally stable in DMF at reflux for many hours and does not undergo carbon–carbon bond-forming or reductive elimination reactions.[23]

With regard to $PPh_2(2,6\text{-}Me_2C_6H_3)$, it is worth noting that the presence of two *ortho*-methyl groups in the same phenyl unit, in addition to the bulky *gem*-phenyls, which enhance ring closure,[24] allows easy cyclometalation. This result should be compared with those obtained with the mono-*ortho*-tolyl phosphane and also with the more sterically hindered tri-(*ortho*-tolyl)phosphane, which do not give cyclometalation, resulting in the reduction of the $Ir^{III}$ chloride precursor to $Ir^I$ species, namely complex **1** and $[IrCl(CO)\{P(2\text{-}MeC_6H_4)_3\}_2]$.[17] The easy cyclometalation of $PPh_2(2,6\text{-}Me_2C_6H_3)$ should thus be ascribed not only to its relatively high bulkiness,[25] but also to the favorable geometrical features: that is, the presence in one phenyl group of two *ortho*-methyls, which are forced to come into proximity to the metal center.

**Synthesis and cyclometalation of 3**: The Vaska iridium(I) complex $[IrCl(CO)\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$ (**3**), bearing (2,6-dimethylphenyl)diphenylphosphane moieties, has previously been described by Walton and co-workers.[26] A modified procedure starting from $[IrCl(COE)_2]_2$[27] (COE = cyclooctene) [Eq. (1)] is reported here.




Treatment of $[IrCl(COE)_2]_2$ with CO (1 atm) in acetonitrile at room temperature gives a soluble $[IrCl(CO)_2]_2$ species, strongly solvated by $CH_3CN$,[27] which promptly reacts with $PPh_2(2,6\text{-}Me_2C_6H_3)$, affording **3** as a yellow precipitate in quantitative yield. This complex shows only one signal at $\delta = 2.24$ ppm for the protons of the four *ortho*-methyl groups, indicating that at room temperature the rotation of the xylyl groups about the C–P bond has a low energy barrier. Furthermore, the value of the methyl carbon resonance at 25.8 ppm suggests that, as observed for **1**, no agostic interaction occurs along the fifth coordination position. In contrast with **1**, which is thermally stable, when **3** is dissolved in dichloromethane the yellow solution slowly turns colorless at 30 °C, the iridium(III) derivative **4** being produced as a result of an intramolecular C–H oxidative addition [Eq. (2)].

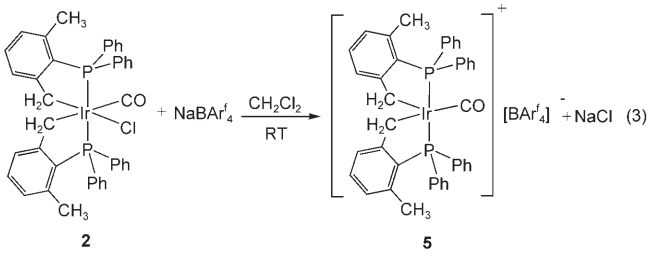



The $^{31}P$ NMR spectrum of **4** shows two doublets ($\delta = 32.3$ and 4.9 ppm) with $^2J(P,P) = 342$ Hz, consistent with a *trans* arrangement of the phosphanes, while in the $^1H$ NMR spectrum the hydride resonance appears as a double of doublets at $\delta = -17.5$ ppm with $^2J(H,P) = 12.7$ and 15.3 Hz. The carbonyl stretching absorption is at 2016 $cm^{-1}$, a value close to that in **2**, while the Ir–H band is at 2180 $cm^{-1}$, in agreement with literature data for iridium(III) complexes.[28] Comparison of the hydride $^1H$ NMR and the IR $\nu_{CO}$ spectroscopic

data for **4** with those for the analogous complexes of general formula $IrCl(H)(R)(phosphane)_2$ are consistent with a *trans*-H-Ir-Cl arrangement,[29] with respect to the *trans* H-Ir-CO one.[30] Interestingly, compound **3** is thermally stable in toluene and no conversion into **4** had been observed after 1 h at 70 °C. This suggests that the intramolecular C–H oxidative addition may occur through dissociation of the chloride in polar solvents, namely through the transient 14-electron $Ir^I$ species $[Ir(CO)\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]^+$. Although a few 14-electron rhodium(I) species have been isolated,[31] three-coordinate iridium(I) complexes are still elusive and are considered to be highly reactive intermediates capable of promoting C–H and N–H oxidative addition reactions.[32] Comparison of the stabilities of **1** and **3** indicates that the presence of two methyl groups in one phenyl unit strongly facilitates the C–H activation leading to oxidative addition to iridium(III). Because the mono- and dimethyl arylphosphanes have similar basic character, the easier metalation of the $Ir^I$ complex containing the latter phosphane may be ascribed to the presence of four methyl groups instead of two, as well as to the more suitable geometric features of the ligand, which favor the formation of 14-electron species.

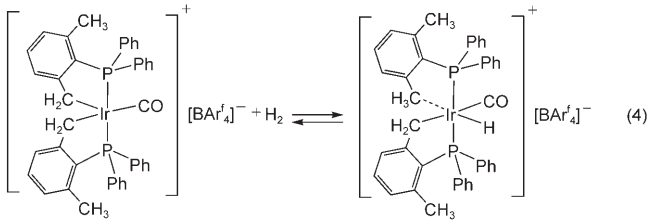
**Synthesis of the cationic 16-electron $Ir^{III}$ complex 5**: Treatment of **2** with one equivalent of $Na[BAr^f_4]$ in dichloromethane at room temperature affords the five-coordinate cationic complex **5** in 93 % yield, by displacement of the chloride [Eq. (3)].




2 5

The $^{31}P$ NMR spectrum of **5** at 20 °C in $CD_2Cl_2$ exhibits two doublets at $\delta = 33.5$ and 24.2 ppm with $^2J(P,P) = 313$ Hz for two nonequivalent *trans* phosphorus atoms. In the proton spectrum, one cyclometalated $CH_2$ moiety appears as two doublets of doublets at $\delta = 2.70$ and 2.58 ppm, with $^2J(H,H) = 14.8$ and $J(H,P) = 3.7$ Hz, while the second $CH_2$ group gives a broad resonance at $\delta = 2.37$. The $^1H$ NMR spectra significantly change at lower temperature, suggesting that the five-coordinate complex **5** displays fluxional behavior in solution, as would be expected for 16-electron species. The $^{13}C$ NMR spectrum at 20 °C shows a pseudo triplet at $\delta = 176.3$ ppm for the coordinated CO with $^2J(C,P) = 6.7$ Hz. The broad resonance at $\delta = 35.8$ ppm corresponds to the cyclometalated $CH_2$ group *trans* to CO, while apparently no signal is observed for the other $CH_2$ group, and the two close doublets at 22.3 ppm ($J(C,P) = 3.5$ Hz) and 22.2 ppm ($J(C,P) = 3.6$ Hz) correspond to the two methyls. A $^{13}C$ NMR of **5** carried out in $CDCl_3$ at 20 °C reveals two broad signals for the cyclometalated $CH_2$ groups at $\delta = 35.8$ and 5.3 ppm, the latter value for the carbon *trans* to the vacant site, suggesting that complex **5** in dichloromethane is involved in a dynamic process. Finally, the high $\nu_{CO}$ value (2022 $cm^{-1}$) is in agreement with a cationic iridium(III) species. Five-coordinate iridium(III) complexes containing two σ Ir–C metal bonds are relatively rare: namely those containing $sp^2$ C atoms bound to the metal, such as $Ir(R)(Ph)(PPh_3)_3^+$,[33] $Ir(C{-}X)(R)(PPh_3)_2^+$ (X = N, O),[34] and $Ir(biphenyl\text{-}2,2'\text{-}diyl)_2Cl(PPh_3)_2$.[35] Interestingly, the X-ray structure of the last of these systems shows a distorted Y geometry, involving two carbon atoms and the chloride, while calculations show a relatively flat potential between the Y and T geometry.[35b] The presence in **5** of two *cis* alkyl ligands and a vacant site makes this complex attractive for possible C–C coupling reactions.

**Reversible dihydrogen splitting promoted by 5 and formation of the δ-agostic hydride $Ir^{III}$ complex 6**: When a solution of complex **5** in $CD_2Cl_2$ is treated with $H_2$ (1 atm) at room temperature, almost quantitative formation of the monohydride **6** is observed within a few minutes, as inferred from NMR measurements [Eq. (4)].




5 6

The $^{31}P\{^1H\}$ NMR spectrum of **6** at 20 °C shows two doublets at $\delta = 35.0$ and 16.7 ppm with a $^2J(P,P)$ value of 278 Hz, whereas in the $^1H$ NMR spectrum the hydride resonance appears as a pseudo triplet at $\delta = -23.28$ ppm with a $^2J(H,P)$ coupling constant of 10.9 Hz. The diasterotopic protons of the cyclometalated $CH_2$ group are at $\delta = 2.94$ and 2.61 ppm with $J(H,H) = 17.6$ Hz, while the *ortho*-methyl groups give three signals at $\delta = 2.01$, 1.81, and 1.17 ppm (broad), indicating that the rotation of the xylyl group about the P–C bond is relatively slow with respect to the NMR timescale. Upon cooling, the last of these peaks progressively shifts upfield to $\delta = 0.40$ ppm (at −20 °C) and 0.28 ppm (at −80 °C) and can be assigned to the methyl involved in the δ-agostic interaction. The hydride signal, which is *trans* to the agostic methyl, is shifted to $\delta = -22.35$ ppm at −80 °C, whereas the other resonances are only slightly affected by the temperature. In the $^{13}C$ NMR spectrum at −80 °C the signal at $\delta =$ 26.1 ppm corresponds to the $CH_2$ moiety, while the three *ortho*-methyl groups are observed at $\delta = 23.2$, 21.2, and 11.7 ppm. The high-field shift of the latter signal is in agree-

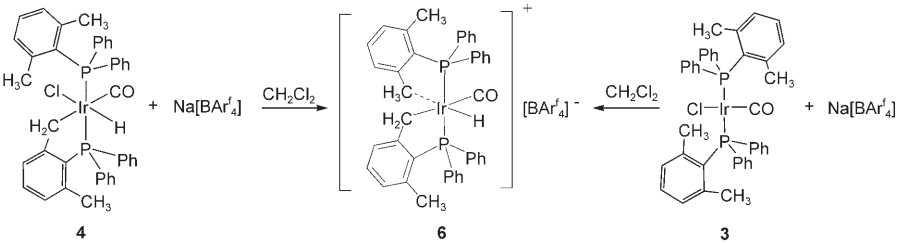
ment with the presence of a δ-agostic interaction as described for the 14-electron $Ru^{II}$ and $Pt^{II}$ complexes bearing $PPh_2(2,6\text{-}Me_2C_6H_3)$ systems.[4,5] A related coordinatively unsaturated alkyl-hydride $Ir^{III}$ complex with an $IrHRP_2^+$ core has been reported by Milstein,[36] whereas $IrH_2P_2^+$ species stabilized by two γ-agostic interactions have been described by Caulton et al.[37] When a solution of **6** is gently heated (35 °C) or the dihydrogen pressure is reduced, formation of the biscyclometalated **5** species through reversible elimination of $H_2$ is observed. Similar behavior has been reported for the related 14-electron species $[PtH\{PR_2(2,6\text{-}Me_2C_6H_3)\}]^+$ (R = Ph, Cy)[5] and iridium(III) derivatives bearing 2,6-diarylpyridine systems.[38] Because the strengths of the M–H bonds are in general significantly greater than those of M–C bonds,[39] the equilibrium between **5** and **6** may arise through a favorable chelate effect involving **5**. In the formation of **6** it is likely that the presence of a vacant site in **5** is fundamental for the coordination of $H_2$, which subsequently undergoes a heterolytic dihydrogen splitting with concomitant Ir–C cleavage. The resulting transient species, bearing a hydride *trans* to the alkyl ligand, should follow a subsequent rearrangement, due to the strong *trans* influence of these ligands,[40] affording the complex **6** with the hydride *trans* to the agostic *ortho*-methyl group. In the reverse reaction, the activation of the agostic methyl C–H bond is likely to be assisted by the hydride ligand.

Alternatively, complex **6** can be prepared by treatment of **4** with a molar amount of $Na[BAr^f_4]$ in dichloromethane under argon, through displacement of the chloride ligand (Scheme 2).

This reaction is straightforward and provides **6** as the main product at room temperature in a few minutes, together with traces of **5** due to the loss of $H_2$, as in the aforementioned equilibrium reaction [Eq. (4)]. It is noteworthy that **6** can also be obtained from the iridium(I) complex **3** by treatment with one equivalent of $Na[BAr^f_4]$ in dichloromethane at room temperature, the reaction being complete after a few minutes (Scheme 2). As a matter of fact, the abstraction of the chloride produces the transient cationic 14-electron species $[Ir(CO)\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2][BAr^f_4]$, which promptly undergoes cyclometalation of one *ortho*-methyl group. Comparison of the rate of the C–H cleavage occurring in the **3**/$Na[BAr^f_4]$ system vs. **3**, which requires one day, is in agreement with a cyclometalation involving a δ-agostic *ortho*-methyl group of the three-coordinate 14-electron iridium(I) transient species.

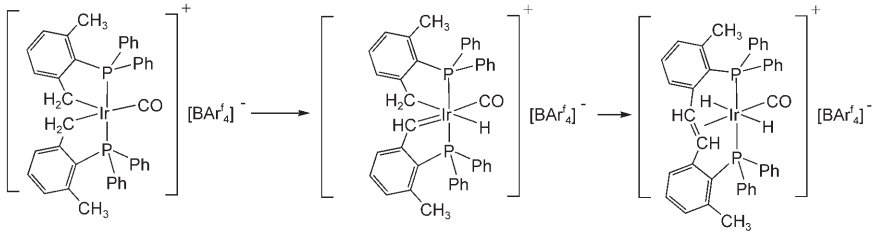
**Synthesis of 7 by a carbon–carbon double bond formation reaction**: The presence of coordinative unsaturation in the biscyclometalated complex **5** could be the origin of another interesting reaction that occurs at higher temperature. When a toluene solution of **5** is heated at 70 °C for 2 h the complex **7**, containing a terdentate *trans*-stilbene diphosphane ligand, is formed quantitatively and has been isolated as a pale yellow solid in 93 % yield (Scheme 3).

Alternatively, **7** can be prepared in situ by treatment of the derivative **2** with one molar amount of $Na[BAr^f_4]$ in toluene, elimination of NaCl, and heating the solution as for **5**. Formation of the olefinic ligand was inferred on the basis of NMR data, which are similar to those obtained for the osmium complex, characterized by a solid-state study. The $^{31}P$ NMR spectrum of **7** in $[D_8]$toluene exhibits two doublets at $\delta = 16.4$ and 10.9 ppm with $^2J(P,P) = 273$ Hz. The olefinic CH resonances appear as two doublets at $\delta = 5.56$ and 5.19 ppm (d, $J(H,H) = 11.2$ Hz), while the two methyl signals give resonances at $\delta = 1.41$ and 1.39 ppm. The triplet at $\delta = -9.17$ ppm is for two hydrides with $^2J(H,P) = 13.1$ Hz, in agreement with related *trans*-dihydride iridium(III) complexes.[41] In the $^{13}C$ NMR spectrum the olefinic =CH groups appear as two doublets at $\delta = 88.3$ ppm ($J(C,P) = 3.6$ Hz) and 86.4 ppm ($J(C,P) = 3.6$ Hz), close to the values reported for the *trans*-stilbene-type ligand coordinated to osmium,[9] while the two methyls are at $\delta = 25.3$ and 25.1 ppm. Complex **7** displays a carbonyl band at relatively high wavelength (2058 $cm^{-1}$), whereas the weaker absorption at 2152 $cm^{-1}$ corresponds to the Ir–H stretching, in agreement with other hydride $Ir^{III}$ complexes.[28] The absorption at 935 $cm^{-1}$, which is not present in the precursor **5**, corresponds to the olefinic CH bending, shifted to lower wavenumbers in relation to the related free ligand *trans*-2,2′-bis(diphenylphosphane)stilbene (955 $cm^{-1}$) and in the same range as other $Rh^I$ and $Ir^I$




4 6 3

Scheme 2. Formation of cationic complex **6**.




5 A 7

Scheme 3. Synthesis of complex **7** through dehydrogenative C–C coupling.

complexes.[42] The quantitative conversion of the coordinatively unsaturated **5** into 18-electron **7** is due to the formation of a strongly chelating terdentate ligand[43] in addition to two Ir–H bonds.

With regard to the mechanism of the formation of the C–C double bond, it is likely that the reaction occurs through an activation of one cyclometalated C–H bond in the coordinatively unsaturated complex **5**, affording the six-coordinate carbene-hydride species **A** through α-hydride elimination (Scheme 3). Coupling of the carbene ligand with the alkyl carbon, a key step invoked in the Fischer–Tropsch synthesis,[44] produces a five-coordinate alkyl-hydride species, which converts into the olefinic-dihydride complex **7** through β-hydride elimination. Although the α-hydride elimination reaction[45] has been less studied than the β-hydride elimination,[39a,46] due to the higher reactivity of the resulting carbene vs. alkene species, reversible formation of a carbene-hydride iridium species from five-coordinate iridium(III) alkyl complexes has been reported for IrH(C–N)$(PPh_3)_2^+$ and $Tp^{Me_2}$Ir(Ph)(R) species.[47] The inertness of the six-coordinate complex **2** in relation to the five-coordinate **5** indicates that the generation of a *cis* vacant site is a prerequisite in the dehydrogenative carbon–carbon bond formation. A direct $sp^3$ C–$sp^3$ C coupling and reductive elimination followed by dehydrogenation of the -$CH_2$-$CH_2$- diphosphane backbone seems to be less likely. As a matter of fact, attempts to dehydrogenate *o*-$Ph_2PC_6H_4$-$(CH_2)_2C_6H_4PPh_2$-*o* with iridium complexes failed, affording stable cyclometalated hydride species,[28b,42] in contrast to rhodium derivatives.[48] Interestingly, the dehydrogenation of the diphosphane backbone of $tBu_2P(CH_2)_5PtBu_2$ results in the formation of an iridium carbene complex, as reported by Shaw.[49] Therefore, the C=C coupling reaction observed in **5** could reasonably occur through an α-C–H bond activation of an alkyl $CH_2$ moiety on a cationic coordinatively unsaturated iridium(III) complex. The isolation of the biscyclometalated iridium(III) species **2**, and in particular **5**, may shed new light on the intriguing way in which dangling *ortho*-methyl groups can afford olefinic ligands through mediation by transition metal centers (i.e., Os, Rh, Ir).[9–11]

## Conclusion

In summary, we have described a series of iridium complexes containing the phosphane $PPh_2(2,6\text{-}Me_2C_6H_3)$ unit, for which C–H and C–C coupling reactions involving agostic interactions have been observed. In the Vaska-type complex **3** the cyclometalation apparently occurs in polar solvent through dissociation of the chloride and subsequent activation of a δ-agostic *ortho*-methyl group in a 14-electron three-coordinate iridium(I) species. Displacement of the chloride in **2** with a noncoordinating anion allows the isolation of a cationic 16-electron biscyclometalated complex **5**, which can easily promote a reversible dihydrogen splitting. Upon heating, the coordinatively unsaturated complex **5** gives the dihydride iridium(III) species **7** containing a stilbene-type ligand, possibly through α-hydride elimination and carbene generation. The sequence of reactions reported here shows that one pendant $CH_3$ group can undergo a stepwise double C–H bond activation, resulting in the formation of a C=C double bond through a cationic 16-electron $Ir^{III}$ species. Comparison of the reactivities of the complexes containing the 2-methyl- and the 2,6-dimethyl-substituted arylphosphane shows the idiosyncrasy of the latter ligand, which displays a strong ability to promote coordinatively unsaturated species through δ-agostic interactions, as well as facile C–H bond activation reactions. Work to detect the intermediates involved in the C–C coupling formation and to extend this chemistry to other transition metals is in progress.

## Experimental Section

**General**: All reactions were carried out under argon with use of standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. Iridium trichloride hydrate and all other chemicals were purchased from Aldrich and were used without further purification, whereas $[Ir(COE)_2Cl]_2$ (COE = cyclooctene)[50] and the salt $Na[BAr^f_4]$[51] were prepared by literature procedures. NMR measurements were recorded with a Bruker AC 200 spectrometer and chemical shifts, in ppm, are relative to TMS for $^1H$ and $^{13}C\{^1H\}$, whereas 85% $H_3PO_4$ was used for $^{31}P\{^1H\}$. Infrared measurements were obtained with a Brucker Vector 22 FTIR spectrometer. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 elemental analyzer.

**Synthesis of 1**: $IrCl_3{\cdot}x\,H_2O$ (891.8 mg, $x=3$; 2.53 mmol) and (2-methylphenyl)diphenylphosphane (2.60 g, 9.41 mmol) were heated at reflux for 4 h in DMF (30 mL) under argon. The resulting solution was concentrated to half volume, and the product was precipitated by addition of methanol. After filtration the yellow product was recrystallized from dichloromethane/EtOH and dried under reduced pressure. Yield: 1.80 g (88%). $^1H$ NMR (200.1 MHz, $CD_2Cl_2$, 20°C): $\delta=7.92$–6.90 (m, 28H; aromatic protons), 2.62 ppm (s, 6H; $CH_3$); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CD_2Cl_2$, 20°C): $\delta=172.1$ (t, $^2J(C,P)=11.2$ Hz; CO), 142.3 (t, $^2J(C,P)=6.0$ Hz; $CCH_3$), 135.7–125.6 (m, aromatic carbons), 23.7 ppm (t, $J(C,P)=4.1$ Hz; $CH_3$); $^{31}P\{^1H\}$ NMR (81.0 MHz, $CD_2Cl_2$, 20°C): $\delta=21.4$ ppm (s); IR (Nujol): $\tilde{\nu}=1947\ cm^{-1}$ (CO); elemental analysis calcd (%) for $C_{39}H_{34}ClIrOP_2$: C 57.95, H 4.24; found: C 58.10, H 4.30.

**Synthesis of 2**: The preparation of **2** was carried out as described for **1**, with $IrCl_3{\cdot}x\,H_2O$ (1.00 g; $x=3$; 2.84 mmol) and (2,6-dimethylphenyl)diphenylphosphane (2.92 g, 10.1 mmol) in place of (2-methylphenyl)diphenylphosphane. Yield: 2.27 g (96%). $^1H$ NMR (200.1 MHz, $CD_2Cl_2$, 20°C): $\delta=7.90$–6.84 (m, 26H; aromatic protons), 2.55 (dd, $^2J(H,H)=16.4$, $^3J(H,P)=4.1$ Hz, 1H; $CH_2$), 2.35 (dd, $^2J(H,H)=15.8$, $^3J(H,P)=2.1$ Hz, 1H; $CH_2$), 2.20 (d, $^2J(H,H)=16.4$ Hz, 1H; $CH_2$), 2.04 (dd, $^2J(H,H)=15.8$, $^3J(H,P)=4.1$ Hz, 1H; $CH_2$), 1.85 (s, 3H; $CH_3$), 1.76 ppm (s, 3H; $CH_3$); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CD_2Cl_2$, 20°C): $\delta=175.1$ (t, $^2J(C,P)=6.7$ Hz; CO), 162.8 (dd, $^2J(C,P)=37.0$, $^3J(C,P)=8.9$ Hz; $CCH_2$), 162.6 (dd, $^2J(C,P)=32.1$, $^3J(C,P)=7.1$ Hz; $CCH_2$), 143.2 (t, $J(C,P)=1.6$ Hz; $CCH_3$), 143.1 (t, $J(C,P)=1.3$ Hz; $CCH_3$), 134.0–128.0 (aromatic carbons), 34.3 (dd, $^2J(C,P)=5.4$, $^2J(C,P)=2.9$ Hz; $CH_2$), 22.9 (d, $^3J(C,P)=3.1$ Hz; $CH_3$), 22.4 (d, $^3J(C,P)=3.0$ Hz; $CH_3$), 11.8 ppm (d, $^2J(C,P)=2.6$ Hz; $CH_2$); $^{31}P\{^1H\}$ NMR (81.0 MHz, $CD_2Cl_2$, 20°C): $\delta=29.6$ (d, $^2J(P,P)=349$ Hz), 17.4 ppm (d, $^2J(P,P)=349$ Hz); IR (Nujol): $\tilde{\nu}=2006\ cm^{-1}$ (CO); elemental analysis calcd (%) for $C_{41}H_{36}ClIrOP_2$: C 59.02, H 4.35; found: C 58.81, H 4.50.

**Synthesis of 3**: $[IrCl(COE)_2]_2$ (100 mg, 0.103 mmol) was added to $CH_3CN$ (15 mL) and the suspension was stirred for 15 minutes. On replacement of argon with CO (1 atm) an orange solution was immediately obtained. After 5 minutes, (2,6-dimethylphenyl)diphenylphosphane (130 mg,

0.448 mmol) was added, quickly affording a yellow precipitate, which was filtered, washed with *n*-hexane, and dried under reduced pressure. Yield: 164 mg (95%). $^1$H NMR (200.1 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 8.05–6.95 (m, 26H; aromatic protons), 2.24 ppm (s, 12H; $CH_3$); $^{13}$C{$^1$H} NMR (50.3 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 172.6 (s; CO), 143.4 (t, $J$(C,P) = 4.7 Hz; $C$CH$_3$), 136.0–128.5 (aromatic carbons), 25.8 ppm (s; $CH_3$); $^{31}$P{$^1$H} NMR (81.0 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 18.5 ppm (s); IR (Nujol): $\tilde{\nu}$ = 1954 cm$^{-1}$ (CO); elemental analysis calcd (%) for $C_{41}H_{38}ClIrOP_2$: C 58.88, H 4.58; found: C 58.50, H 4.62.

**Synthesis of 4**: Complex **3** (105 mg, 0.126 mmol) was dissolved in dichloromethane (15 mL) and the solution was stirred at 30°C for 24 h. The solution was concentrated, and addition of *n*-hexane afforded a colorless precipitate that was filtered and dried under reduced pressure. Yield: 102 mg (97%). $^1$H NMR (200.1 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 8.05–6.88 (m, 26H; aromatic protons), 3.10–2.75 (m, 2H; $CH_2$), 1.92 (s, 6H; $CH_3$), 1.74 (s, 3H; $CH_3$), −17.5 ppm (dd, $^2J$(H,P) = 15.3, $^2J$(H,P) = 12.7 Hz, 1H; IrH); $^{13}$C{$^1$H} NMR (50.3 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 174.4 (pseudo t, $^2J$(C,P) = 7.1 Hz; CO), 163.7 (dd, $J$(C,P) = 34.9, $J$(C,P) = 7.1 Hz; $C$CH$_2$), 143.4 (d, $J$(C,P) = 8.0 Hz; $C$CH$_3$), 142.4 (dd, $J$(C,P) = 2.5, $J$(C,P) = 1.7 Hz; $C$CH$_3$), 137.0–127.2 (aromatic carbons), 25.3 (d, $^3J$(C,P) = 5.6 Hz; $CH_3$), 23.1 (dd, $J$(C,P) = 5.2, $J$(C,P) = 2.4 Hz; $CH_2$), 21.8 ppm (d; $J$(C,P) = 3.3 Hz; $CH_3$); $^{31}$P{$^1$H} NMR (81.0 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 32.3 (d, $^2J$(P,P) = 342 Hz), 4.9 ppm (d, $^2J$(P,P) = 342 Hz); IR (Nujol): $\tilde{\nu}$ = 2180 (Ir–H), 2016 cm$^{-1}$ (CO); elemental analysis calcd (%) for $C_{41}H_{38}ClIrOP_2$: C 58.88, H 4.58; found: C 58.50, H 4.69.

**Synthesis of 5**: Complex **2** (218 mg, 0.261 mmol) was dissolved in dichloromethane (10 mL), and Na[BAr$^f_4$] (231 mg, 0.261 mmol) was added. The mixture was stirred for 2 h at room temperature and, after filtration of NaCl, the solution was evaporated to dryness. The light yellow solid was washed with hexane (3 × 10 mL) and, after elimination of the solvent, the product was dried under reduced pressure. Yield: 402 mg (93%). $^1$H NMR (200.1 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 7.80–6.95 (m, 38H; aromatic protons), 2.70 (dd, $^2J$(H,H) = 14.8, $J$(H,P) = 3.7 Hz, 1H; $CH_2$), 2.58 (dd, $^2J$(H,H) = 14.8, $J$(H,P) = 3.7 Hz, 1H; $CH_2$), 2.37 (m, 2H; $CH_2$), 1.86 ppm (s, 6H; $CH_3$); $^{13}$C{$^1$H} NMR (50.3 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 176.3 (pseudo t, $^2J$(C,P) = 6.7 Hz; CO), 162.3 (q, $^1J$(CB) = 49.8 Hz; CB), 143.9 (dd, $^3J$(C,P) = 2.4, $J$(C,P) = 1.4 Hz; $C$CH$_3$), 143.3 (dd, $^3J$(C,P) = 2.0 Hz, $J$(C,P) = 1.4 Hz; $C$CH$_3$), 135.4–126.2 (aromatic carbons), 125.2 (q, $^1J$(C,F) = 272.3 Hz; $CF_3$), 118.1 (aromatic carbons), 35.8 (br s; $CH_2$), 22.3 (d, $J$(C,P) = 3.5 Hz; $CH_3$), 22.2 ppm (d, $J$(C,P) = 3.6; $CH_3$); $^{31}$P{$^1$H} NMR (81.0 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 33.5 (d, $^2J$(P,P) = 313 Hz), 24.2 ppm (d, $^2J$(P,P) = 313 Hz); IR (Nujol): $\tilde{\nu}$ = 2022 cm$^{-1}$ (CO); elemental analysis calcd (%) for $C_{73}H_{48}BF_{24}IrOP_2$: C 52.75, H 2.91; found: C 52.41, H 3.01.

**NMR evidence of 6**: Complex **5** (25 mg, 0.015 mmol) was dissolved in $CD_2Cl_2$ (0.45 mL), and dihydrogen (1 atm) was bubbled into the solution, quantitatively affording **6** after a few minutes. $^1$H NMR (200.1 MHz, $CD_2Cl_2$, −80°C): $\delta$ = 8.00–6.80 (m, 38H; aromatic protons), 2.72 (dd, $^2J$(H,H) = 18.2, $^3J$(H,P) = 4.7 Hz, 1H; $CH_2$), 2.42 (dd, $^2J$(H,H) = 18.2, $^3J$(H,P) = 5.8 Hz, 1H; $CH_2$), 1.71 (s, 3H; $CH_3$), 1.64 (s, 3H; $CH_3$), 0.28 (s, 3H; agostic $CH_3$), −22.35 ppm (pseudo t, $J$(H,P) = 10.4 Hz, 1H; IrH); $^{13}$C{$^1$H} NMR (50.3 MHz, $CD_2Cl_2$, −80°C): $\delta$ = 174.1 (pseudo t, $^2J$(C,P) = 6.0 Hz; CO), 161.3 (q, $^1J$(CB) = 49.5 Hz; CB), 158.7 (dd, $^2J$(C,P) = 34.7, $^2J$(C,P) = 8.3 Hz; $C$CH$_2$), 145.6 (s; $C$CH$_3$), 142.7 (d, $J$(C,P) = 2.0 Hz, $C$CH$_3$), 140.3 (dd, $J$(C,P) = 20.6, $J$(C,P) = 1.8 Hz; $C$CH$_3$), 135.0–126.6 (aromatic carbons), 123.9 (q, $^1J$(C,F) = 272.5 Hz; $CF_3$), 117.1 (aromatic carbon), 26.1 (s; $CH_2$), 23.2 (d, $^3J$(C,P) = 4.2 Hz; $CH_3$), 21.2 (d, $^3J$(C,P) = 3.6 Hz; $CH_3$), 11.7 ppm (br d, $J$(C,P) = 6.3 Hz; agostic $CH_3$); $^{31}$P{$^1$H} NMR (81.0 MHz, $CD_2Cl_2$, 20°C): $\delta$ = 35.0 (d, $^2J$(P,P) = 278 Hz), 16.7 ppm (d, $^2J$(P,P) = 278 Hz).

**Synthesis of 7—Method 1**: Complex **5** (140 mg, 0.084 mmol) was dissolved in toluene (10 mL) and the solution was heated to 70°C for 2 h. After evaporation of the solvent, the pale yellow product was washed with *n*-hexane and dried under reduced pressure. Yield: 130 mg (93%). $^1$H NMR (200.1 MHz, [D$_8$]toluene, 20°C): $\delta$ = 8.35–6.60 (m, 38H; aromatic protons), 5.56 (d, $^3J$(H,H) = 11.2 Hz, 1H; CH=), 5.19 (d, $^3J$(H,H) = 11.2 Hz, 1H; CH=), 1.41 (s, 3H; $CH_3$), 1.39 (s, 3H; $CH_3$), −9.17 ppm (t, $^2J$(H,P) = 13.1 Hz, 2H; Ir–H); $^{13}$C{$^1$H} NMR (50.3 MHz, [D$_8$]toluene, 20°C): $\delta$ = 175.7 (t, $^2J$(C,P) = 5.8 Hz; CO), 166.4 (q, $^1J$(CB) = 49.8 Hz; CB), 152.6 (dd, $J$(C,P) = 22.3, $J$(C,P) = 4.2 Hz; $C$CH=), 151.7 (dd, $J$(C,P) = 24.0, $J$(C,P) = 5.2 Hz; $C$CH=), 148.9 (dd, $J$(C,P) = 2.3 Hz, $J$(C,P) = 1.2 Hz; $C$CH$_3$), 148.1 (m; $C$CH$_3$), 139.2–128.0 (aromatic carbons), 128.9 (q, $^1J$(C,F) = 272.3 Hz; $CF_3$), 121.7 (aromatic carbon), 88.3 (d, $J$(C,P) = 3.6 Hz; CH=), 86.4 (d, $J$(C,P) = 3.6 Hz; CH=), 25.3 (d; $J$(C,P) = 3.4 Hz; $CH_3$), 25.1 ppm (d; $J$(C,P) = 3.4 Hz; $CH_3$); $^{31}$P{$^1$H} NMR (81.0 MHz, [D$_8$]toluene, 20°C): $\delta$ = 16.4 (d, $^2J$(P,P) = 273 Hz), 10.9 ppm (d, $^2J$(P,P) = 273 Hz); IR (Nujol): $\tilde{\nu}$ = 2152 (Ir–H), 2058 (CO), 935 cm$^{-1}$ (olefinic CH bending); elemental analysis calcd (%) for $C_{73}H_{48}BF_{24}IrOP_2$: C 52.75, H 2.91; found: C 52.44, H 2.97.

**Method 2**: Complex **2** (115 mg, 0.138 mmol) was dissolved in toluene (10 mL), and Na[BAr$^f_4$] (122 mg, 0.138 mmol) was added. The mixture was stirred for 4 h at room temperature and, after removal of NaCl by filtration, the solution was heated to 70°C for 2 h. After evaporation of the solvent, the product was washed with *n*-hexane and dried under reduced pressure. Yield: 169 g (74%).

**X-ray crystal structure**: Diffraction data for **1** were collected at 200(2) K on a Nonius DIP-1030H system ($Mo_{K\alpha}$ radiation, graphite monochromatized). A total of 30 frames were collected, each with an exposure time of 20 min, over half of reciprocal space with a rotation of 5° about $\phi$, the detector being sited 80 mm from the crystal. Cell refinement, indexing, and scaling of the data set were carried out with the programs Denzo and Scalepack.[52] The structure was solved by Patterson and Fourier analyses and refined by the full-matrix, least-squares method based on $F^2$ with all observed reflections.[53] The complex is located on a center of symmetry with chloride and CO ligands statistically disordered with 0.50 occupancy factor each. A molecule of dichloromethane was detected in the $\Delta F$ map. All non-H atoms in the complex were refined with anisotropic temperature factors. The contribution of hydrogen atoms at calculated positions were included in final cycles of refinement. All the calculations were performed with the WinGX System, Ver 1.70.00.[54] Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 2.

CCDC-637 694 contains 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.

Table 2. Crystal data and structure refinement details for **1**·2 $CH_2Cl_2$.

| | |
|---|---|
| formula | $C_{41}H_{38}Cl_5IrOP_2$ |
| $M$ [g mol$^{-1}$] | 978.10 |
| crystal system | monoclinic |
| space group | $P2_1/c$ |
| $a$ [Å] | 11.991(3) |
| $b$ [Å] | 20.693(4) |
| $c$ [Å] | 8.091(3) |
| $\beta$ [°] | 95.92(2) |
| $V$ [Å$^3$] | 1996.9(10) |
| $Z$ | 2 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.627 |
| $\mu Mo_{K\alpha}$ [mm$^{-1}$] | 3.790 |
| $F$(000) | 968 |
| $\theta$ range [°] | 1.97–27.48 |
| reflns collected | 21 319 |
| unique reflections | 3910 |
| $R_{int}$ | 0.0560 |
| observed $I > 2\sigma(I)$ | 2134 |
| parameters | 241 |
| goodness-of-fit ($F^2$) | 0.853 |
| $R1$ ($I > 2\sigma(I)$)[a] | 0.0408 |
| $wR2$[a] | 00.0879 |
| residuals [e Å$^{-3}$] | 0.832, −0.670 |

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

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