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# Cationic Ir(III) Alkylidenes Are Key Intermediates in C−H Bond Activation and C−C Bond-Forming Reactions

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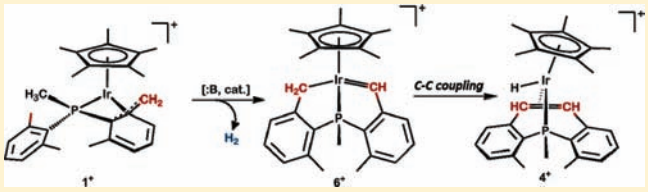
Supporting Information

**ABSTRACT:** This work describes the chemical reactivity of a cationic ($\eta^5$-$C_5Me_5$)Ir(III) complex that contains a bis(aryl) phosphine ligand, whose metalation determines its unusual coordination in a $\kappa^4$-*P,C,C′,C″* fashion. The complex ($\mathbf{1}^+$ in this paper) undergoes very facile intramolecular C−H bond activation of all benzylic sites, in all likelihood through an Ir(V) hydride intermediate. But most importantly, it transforms into a hydride phosphepine species $\mathbf{4}^+$ by means of an also facile, base-catalyzed, intramolecular dehydrogenative C−C coupling reaction. Mechanistic studies demonstrate the participation as a key intermediate of an electrophilic cationic Ir(III) alkylidene, which has been characterized by low-temperature NMR spectroscopy and by isolation of its trimethylphosphonium ylide. DFT calculations provide theoretical support for these results.




## INTRODUCTION

The efficient functionalization of the C−H bonds of alkanes and other common organic molecules remains a difficult and elusive research objective despite its important practical implications in many industrial and laboratory syntheses.[1] Transition metal compounds that are able to promote C−H bond activation with subsequent C−C (or C−X) bond formation (X = O, N, S or other element) hold promise for converting simple and generally available raw materials into complex, elaborated molecules such as pharmaceutical and natural products. Indeed, today many selective methods that combine C−H bond activation with C−C or C−X bond formation are available.[2,3]

Following the pioneering work of Bergman and co-workers on electrophilic Ir(III) complexes such as [($\eta^5$-$C_5Me_5$)Ir(Me)($PMe_3$)($ClCH_2Cl$)]$^+$ and related species,[4] many studies based on neutral or cationic Rh and Ir complexes that are constructed around Cp*M fragments have been performed, under both stoichiometric and catalytic conditions.[5−9] Somewhat surprisingly, the analogous rhodium cation [($\eta^5$-$C_5Me_5$)Rh(Me)($PMe_3$)($ClCH_2Cl$)]$^+$ is less reactive toward C−H bonds,[8c] and similarly, the closely related iridium molecule that contains $P(OMe)_3$ instead of $PMe_3$, i.e., [($\eta^5$-$C_5Me_5$)Ir(Me)($P(OMe)_3$)($ClCH_2Cl$)]$^+$, also shows diminished reactivity, as a consequence of lower electron density at the metal center.[8a] The carbonyl derivative, [Cp*Ir(Me)(CO)($ClCH_2Cl$)]$^+$, was likewise found to be unreactive toward the activation of the C−H bonds of benzene.[10]

With the above results in mind, we have recently undertaken a study of Cp*M compounds of the above kind in which the steric and electronic properties of the metal center are modified by the use of a phosphine ligand that is prone to cyclometalation to yield a five-membered metallacyclic structure.[11] For the sake of simplicity and to prevent undesirable $\beta$-H elimination reactions, the bis(aryl)phosphine $PMeXyl_2$ (Xyl = 2,6-$Me_2C_6H_3$) and other similar phosphines have been chosen for this study.

Transition metal cyclometalated complexes[12,13] have received a great deal of attention in recent decades due to their applications in many catalytic syntheses,[14] in bioorganometallic chemistry, including the development of anticancer drugs,[15] and in material science.[16]

Following the straightforward synthesis[17] of the chloride complex precursor **1-Cl**, we describe herein the generation of the cationic dichloromethane adduct $\mathbf{1\text{-}CH_2Cl_2}^+$ (Scheme 1), along with the study of its chemical reactivity. At variance with Bergman's complex [(Cp*)Ir(Me)($PMe_3$)($ClCH_2Cl$)]$^+$, the metalated benzylic unit of $\mathbf{1\text{-}CH_2Cl_2}^+$ permits stabilization of a solvent-free cation ($\mathbf{1}^+$ in Scheme 1), in which the metalated phosphine behaves as a tridentate, five-electron donor ligand (using the covalent formalism), by means of an unusual $\kappa^4$-*P,C,C′,C″* coordination mode, that consists of phosphine and pseudoallylic $\eta^3$-benzylic binding motifs. Whereas no intermolecular C−H bond activation chemistry has been disclosed for $\mathbf{1}^+$, the complex undergoes a very facile $\kappa^4$-to-$\kappa^2$ rearrangement of the metalated ligand, most probably through species **A** of Scheme 1 that, according to DFT calculations, features a very weak C−H···Ir interaction involving one of the Me groups of the non-metalated phosphine xylyl substituents. This provides the molecules of $\mathbf{1}^+$ with a unique chemical reactivity that in a base-catalyzed process allows access to a highly electrophilic cationic Ir(III) alkylidene ($\mathbf{6}^+$ in Scheme 1), which undergoes C−C coupling with formation of the hydride phosphepine

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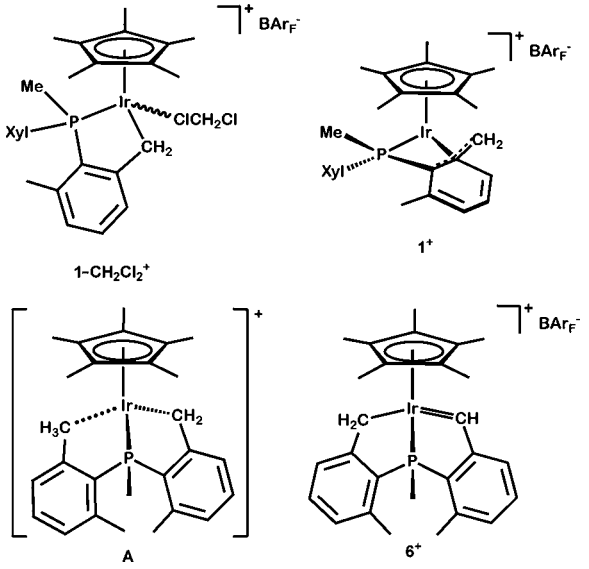
**Scheme 1. Some of the Cationic Complexes Investigated in This Work**[a]




[a]Species A is a proposed, readily accessible intermediate (according to DFT calculations).

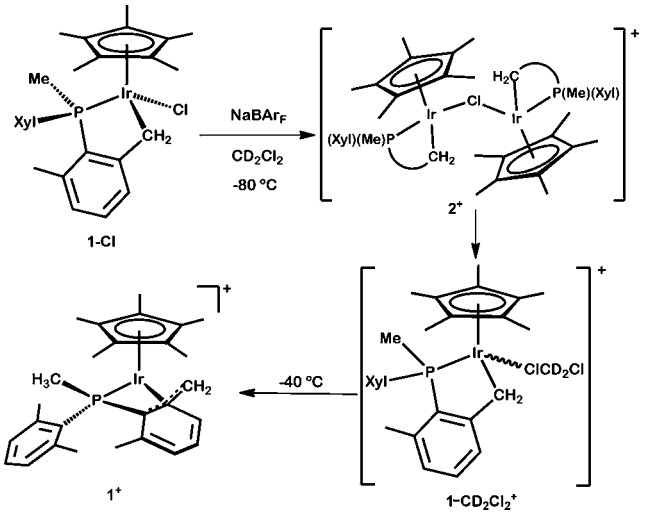
complex **4**$^+$ (*vide infra*). Alkylidene **6**$^+$ has been fully characterized by solution NMR studies and by isolation of its $PMe_3$ phosphonium ylide. The rhodium analogue of **1**$^+$ is a stable molecule that features interesting catalytic properties.[18]

## RESULTS AND DISCUSSION

**1. Cationic Ir(III) Complexes Generated by Chloride Abstraction from 1-Cl.** Reaction of the neutral compound **1-Cl** with 1 equiv of $NaBAr_F$ ($BAr_F$ = $[B(3,5\text{-}C_6H_3(CF_3)_2)_4]$), in $CH_2Cl_2$ as the solvent, led to complex **1**$^+$ isolated as the $BAr_F$ salt (see Scheme 2). However, low-temperature $^1H$ and $^{31}P\{^1H\}$ NMR monitoring of the reaction permitted observation of two intermediates, **2**$^+$ and **1-CH$_2$Cl$_2$**$^+$, which at room temperature converted cleanly into **1-BAr$_F$**. The interaction of **1-Cl** with $NaBAr_F$ is slow at −80 °C. In accordance with observations that are discussed in detail in the Supporting Information (SI), the reaction proceeds as represented in Scheme 2. The first species that forms is a dinuclear chloride-bridged cation **2**$^+$ that results, most probably, from the interaction of still unreacted **1-Cl** with the already formed **1-CH$_2$Cl$_2$**$^+$. Related complexes that contain a halide ligand bridging two metal units have been produced in similar halide abstraction reactions. Heinekey et al. recently reported[10] the formation of the binuclear cation $[\{Cp^*Ir(Me)(CO)\}_2(\mu\text{-}Cl)]BAr_F$, as the product of the reaction of $Cp^*Ir(Me)(Cl)(CO)$ with $[Li(OEt_2)_{2.5}]BAr_F$. Unlike this system that does not progress further to give the desired mononuclear dichloromethane adduct, $[Cp^*Ir(Me)(CO)(CH_2Cl_2)]^+$, even if 2.5 equiv of the abstracting lithium salt is utilized, complex **2**$^+$ converts cleanly into **1-CH$_2$Cl$_2$**$^+$ upon reaction with additional amounts of $NaBAr_F$. The **1-CH$_2$Cl$_2$**$^+$ cation is clearly analogous to Bergman's complex, $[Cp^*Ir(Me)(PMe_3)(CH_2Cl_2)]^+$, that is known to undergo very facile C−H activation reactivity at low temperatures but decomposes at room temperature in the absence of a trapping reagent.[4] In contrast, **1-CH$_2$Cl$_2$**$^+$ evolves, even at low temperatures, to form the stable cationic complex **1**$^+$, in which the coordinated molecule of $CH_2Cl_2$ has been replaced by the metalated phosphine, thanks to a change in coordination from $\kappa^2$-*P,C* to $\kappa^4$-*P,C,C′,C″*. The chelating nature of the phosphine−benzyl ligand of **1**$^+$ and the accessibility of its $\kappa^4$-coordination mode are probably the reasons for its reduced reactivity toward C−H bond activation of different substrates ($C_6H_6$, tetrahydrofuran, $Et_2O$, etc.).

Compound **1-BAr$_F$** was obtained as a yellow microcrystalline solid by crystallization from $CH_2Cl_2$:$C_5H_{12}$ solvent mixtures and was characterized by microanalysis and variable-temperature 1D and 2D NMR spectroscopy. Crystals suitable for X-ray studies could not be obtained. However, at −60 °C, its $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra ($CD_2Cl_2$ solutions) resemble closely those of the X-ray-characterized rhodium analogue.[18] Thus, the Ir−$CH_2$ protons appear as the AB portion of an ABX spin system (X = $^{31}P$), with $\delta$ 2.98 ($H_A$, t; $^2J_{HH}$ = $^3J_{HP}$ = 4.8 Hz) and 1.15 ($H_B$, dd, $^2J_{HH}$ = 4.8, $^3J_{HP}$ = 15.6 Hz) ppm (see Experimental Section for additional data and Figure 1 for the atom labeling scheme employed). The

**Scheme 2. Chloride Abstraction from 1-Cl by NaBAr$_F$, Leading to 1$^+$ Isolated as 1-BAr$_F$**



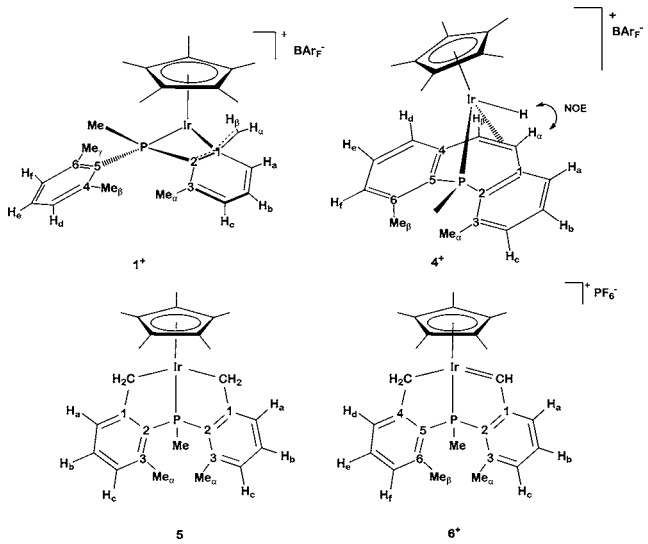




**Figure 1.** Labeling scheme for species **1**$^+$, **4**$^+$, **5**, and **6**$^+$ used for the assignment of $^1H$ and $^{13}C$ NMR signals. The labeling criteria for **1**$^+$ are also employed for the cationic derivatives **1-L**$^+$, **3**$^+$, **6**$^+$, and **7**$^+$.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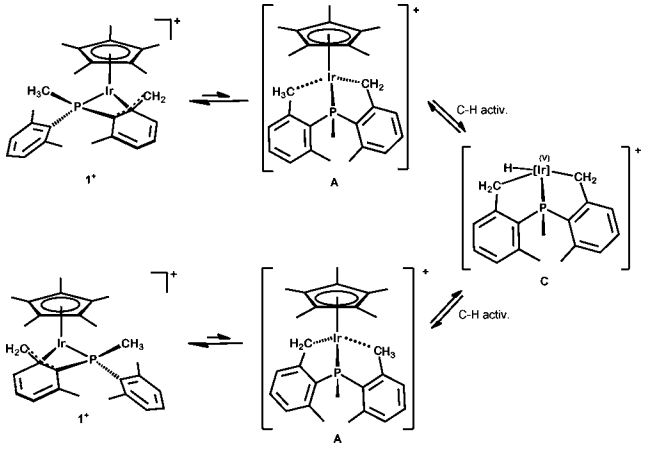
corresponding $^{13}C$ resonance appears at $\delta$ 27.0 and exhibits negligible coupling to $^{31}P$ and a one-bond, $^{1}J_{CH}$ coupling constant of 163 Hz. A distinct, strongly shielded $^{31}P\{^{1}H\}$ resonance for $\mathbf{1}^+$ is recorded at −44.9 ppm. However, at room temperature, all $^{1}H$ NMR signals are broad with the exception of those due to the $C_5Me_5$ and P−Me protons, which appear as two doublets, with $\delta$ 1.63 ($^{4}J_{HP}$ = 1.8 Hz) and 2.20 ($^{2}J_{HP}$ = 12.8 Hz) ppm, respectively. The low-temperature (−60 °C) $^{1}H$ NMR resonances of the methyl groups of the phosphine xylyl substituents detected at 2.50, 2.44, and 2.09 ppm and those of the iridium-bonded methylene protons coalesce to a broad signal centered at ca. 2.4 ppm. Resonances due to the aromatic protons are also broad and can be found at 7.4 (2H) and 2.3 (4H) ppm. Clearly, these observations are indicative of a dynamic behavior in solution of $\mathbf{1}^+$ that implies exchange of its metalated and non-metalated xylyl units, thereby including all methylene and methyl protons of the phosphine ligand.

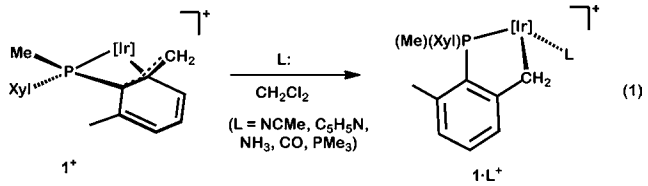
To clarify the mechanism of this exchange, a detailed NMR analysis, complemented by computational studies, was carried out. 2D EXSY NMR experiments demonstrated the absence of magnetization transfer at −60 °C, whereas at −45 °C transfer from the methylene protons ($\delta$ 1.14 and 2.98) to $Me_\beta$ ($\delta$ 2.09; see Figure S1) was seen. Weak magnetization effects between $Me_\gamma$ (2.50 ppm) and $Me_\beta$ were detected too, denoting rotation of the non-metalated xylyl ring around the P−C bond. Moreover, NOE cross peaks connected the two methylene protons at this temperature. At −35 °C, EXSY spectroscopy demonstrated involvement of all $CH_3$ and $CH_2$ protons in the chemical exchange. Rate constants for the site exchange between the $CH_2$ and $CH_3$ positions were estimated by full relaxation matrix analysis of the intensities of the EXSY peaks. A rate constant of 0.9 $s^{-1}$ was measured at this temperature for the exchange of $Me_\beta$ and $H_\alpha$. An Eyring study in the temperature interval from −45 to −25 °C yielded values of the activation parameters $\Delta H^{\ddagger}$ = 19.2 ± 0.8 kcal $mol^{-1}$ and $\Delta S^{\ddagger}$ = 20 ± 3 cal $mol^{-1}$ $K^{-1}$, with $\Delta G^{\ddagger}_{298K}$ = 13 ± 2 kcal $mol^{-1}$. Evaluation of the other $CH_2/CH_3$ exchanges gave similar results.

Scheme 3 presents a plausible mechanism for this exchange. The approach of one of the methyl C−H bonds of the non-metalated xylyl group to the iridium center, to form intermediate **A**, causes a change in the coordination of the metalated benzylic unit from $\eta^3$ to $\eta^1$. This is followed by C−H activation that could occur in a concerted manner, by a $\sigma$-complex-assisted metathesis mechanism,[19] or alternatively through a cationic doubly metalated Ir(V) hydride intermediate (**C**), resulting from oxidative cleavage of a C−H bond. This species would give back $\mathbf{1}^+$ by reductive coupling of the hydride with either of the Ir−$CH_2$ bonds, accompanied by $\kappa^4$-coordination of the metalated ligand fragment. In either case, the roles of the two xylyl rings are exchanged, the metalated becoming non-metalated and *vice versa*. Theoretical calculations (see SI, Figure S10) support the latter reaction pathway and reveal that access to the Ir(V) intermediate, which lies only 7.2 kcal $mol^{-1}$ above $\mathbf{1}^+$, needs to overcome a barrier of ca. $\Delta G^{\ddagger}$ = 14 kcal $mol^{-1}$, in good agreement with the NMR measurements described above.

**Scheme 3. Proposed Mechanism To Account for the Solution Dynamic Behavior of $\mathbf{1}^+$**




**2. Reactivity Studies of Complex 1-$BAr_F$.** *2.1. Reactions with Classical Lewis Bases.* As expected, addition of a Lewis base (NCMe, $C_5H_5N$, $NH_3$, CO, and $PMe_3$) to $CH_2Cl_2$ solutions of **1-$BAr_F$** resulted in the instantaneous formation of the corresponding adducts **1-$L^+$**, which were isolated in nearly quantitative yields (eq 1). $^{31}P\{^{1}H\}$ NMR monitoring of the

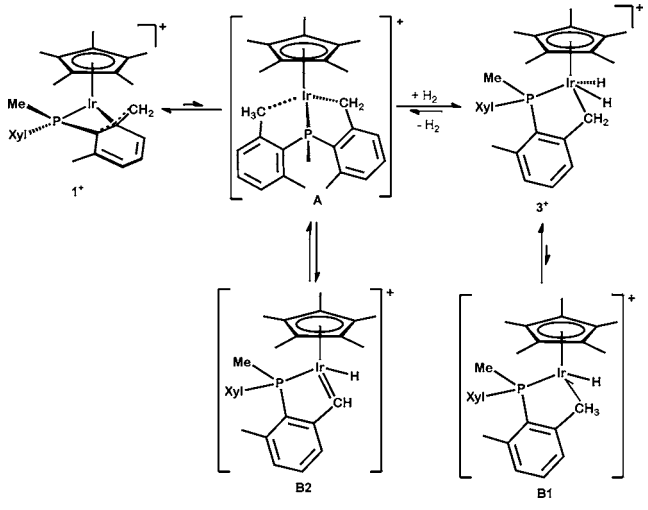



(1)

reactions revealed a marked shift of the resonance from the characteristic −44.9 ppm value of $\mathbf{1}^+$ to positive chemical shifts for **1-$L^+$**, in the interval 1.0−11.4 ppm. The NMR data collected for these compounds in the Experimental Section and the SI are in agreement with the proposed formulation. The solid-state structures of the $BAr_F^-$ salts of **1-$NCMe^+$** and **1-$PMe_3^+$** were determined by X-ray crystallography (Figures S4 and S5).

*2.2. Reaction with $H_2$.* Exposure of a dichloromethane solution of $\mathbf{1}^+$ to 1 bar of $H_2$ at 20 °C allowed the formation of the cationic bis(hydride) complex $\mathbf{3}^+$ in quantitative yield by $^{1}H$ NMR (Scheme 4). Formation of $\mathbf{3}^+$ was found to be reversible, and removal of $H_2$ under vacuum regenerated cleanly the

**Scheme 4. Reversible Reaction of $\mathbf{1}^+$ with $H_2$ To Yield $\mathbf{3}^+$, and Possible Intermediates, B1 and B2, for the Dynamic Behavior of $\mathbf{3}^+$**





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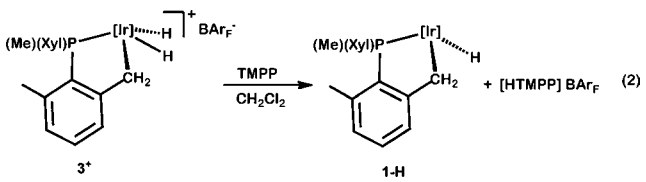
starting compound $1^+$. A classical dihydride structure is proposed for $3^+$, in agreement with the observation of two deshielded $^1$H NMR resonances (500 MHz, $CD_2Cl_2$, −80 °C) at $\delta$ −12.79 (s, 1H) and −13.37 (d, $^2J_{HP}$ = 17.5 Hz, 1H) ppm, with a spin−lattice relaxation time $T_1$ = 261 ms (average value for the two hydride resonances at the above temperature).

Generation of $3^+$ in the reaction of $1^+$ with $H_2$ contrasts with results reported for the similar reaction of the analogous rhodium compound.[18a] In the latter case, an agostic hydride like **B1** in Scheme 4, detected only at low temperatures (around −70 to −90 °C), was observed as the minor constituent of an equilibrium dominated by the $\kappa^4$-rhodium cation. These differences are most likely dictated by the higher propensity of Ir, in comparison with Rh, to attain the higher oxidation state, M(V). Many Ir(V) hydrides have been reported in the literature and their role as catalysts for different transformations demonstrated.[20−22]

At −80 °C, **3-BAr$_F$** is stable in solution toward loss of $H_2$. In addition to the two $^1$H NMR hydride signals, cation $3^+$ features two doublets at 3.93 and 3.38 ppm ($^2J_{HH}$ = 14.2 Hz), each with a relative intensity corresponding to one hydrogen atom, attributable to the diastereotopic Ir−$CH_2$ protons. Upon warming to −60 °C, the two Ir−H and the two Ir−$CH_2$ resonances broaden and coalesce into the baseline. Exchange between the two hydride hydrogen atoms can occur through an Ir($\eta^2$-$H_2$) species. However, for the additional exchange that implicates also the Ir−$CH_2$ hydrogen atoms, the situation is not clear-cut, and two possible pathways involving intermediates **B1** and **B2** of Scheme 4 may be foreseen. Present data do not permit to distinguish unambiguously between these two routes. Accordingly, we defer a definite proposal on this matter until the results of work being presently developed in our laboratory on related complexes become available. At room temperature, the corresponding four low-temperature resonances are replaced by a broad singlet at −4.6 ppm that integrates for four hydrogen atoms. This chemical shift matches closely the average of the resonances due to the four individual protons (ca. −4.7 ppm). Line-shape analysis of these resonances at different temperatures, in conjunction with an Eyring study of the observed rate constants, yields the following activation parameters for the overall process: $\Delta H^{\ddagger}$ = 12.6 ± 0.4 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = 6 ± 2 cal mol$^{-1}$ K$^{-1}$, and $\Delta G^{\ddagger}_{300K}$ = 11 ± 1 kcal mol$^{-1}$.

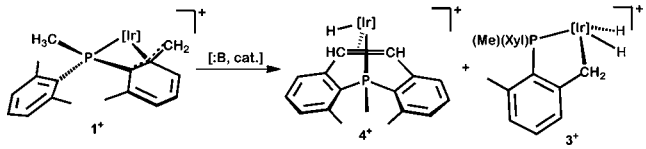
The Brönsted−Lowry acidity of the cationic Ir(V) bis(hydride) complex $3^+$ finds ample literature precedent, not only for electrophilic transition metal hydrides but also for related dihydrogen complexes.[23] Indeed, treatment of $3^+$ with $NEt_3$ or with 2,2,6,6-tetramethylpiperidine (TMPP) afforded the known[17b] neutral hydride **1-H** (eq 2).




*2.3. Base-Catalyzed Intramolecular Dehydrogenative C−C Coupling in $1^+$ Leading to the Hydride Phosphepine Cation $4^+$.* Although compound **1-BAr$_F$** seems to be stable in solution and in the solid state for long periods of time, in some of its preparations, and also during unsuccessful attempts to grow single crystals (which required several manipulations, use of different solvents, etc.), small amounts of a new hydride complex that featured $^1$H and $^{31}$P{$^1$H} NMR resonances at $\delta$ −13.03 (d, $^2J_{HP}$ = 25.5 Hz) and 8.9 ppm, respectively, were observed. Small quantities of bis(hydride) $3^+$ were detected too. It was soon realized that generation of these complexes was due to the presence of adventitious water that performed a Brönsted−Lowry base catalytic role. Trace amounts of water acting as an acid catalyst have been reported recently by the groups of Milstein and Brookhart to facilitate the hydrogenation step of reactions of $H_2$ with Ir complexes of pincer ligands.[24]

Following the screening of different base reagents and solvents, optimal experimental conditions for the formation of $4^+$ were determined to involve the reaction of **1-Cl** with $NaBAr_F$ in dichloromethane, in the presence of catalytic amounts of a saturated aqueous solution of $NaHCO_3$ (ca. 30 mol %, 20 °C, 16 h). A buffer solution of piperidinium/piperidine can also be used. The already discussed cationic bis(hydride) complex $3^+$ was observed as a side product of this rearrangement. In fact, when the above reaction was effected in a sealed NMR tube, a 1:1 mixture of $4^+$ and $3^+$ was cleanly generated (Scheme 5). In order to isolate **4-BAr$_F$** in high yields

**Scheme 5. Base-Catalyzed Dehydrogenative C−C Coupling of $1^+$ Leading to the Hydride Phosphepine Cation $4^+$**




(ca. 90%, see Experimental Section), the above catalyzed reaction was performed for a period of about 16 h, with intermittent vacuum−argon cycles to remove the $H_2$ generated in the C−C coupling reaction. In accord with these observations, strong base catalysts like NaOH also gave rise to the neutral hydride **1-H** as a result of fast deprotonation of $3^+$ by the base.

Compound **4-BAr$_F$** was isolated as a crystalline solid with low reactivity toward oxygen and water. Its Ir−H linkage features an IR absorption at 2135 cm$^{-1}$ and a $^1$H NMR resonance at $\delta$ −13.03 (d, $^2J_{HP}$ = 28.5 Hz), whereas the alkene part of the chelating ligand is characterized by $^1$H NMR resonances at 4.97 (dd, $^3J_{HH}$ = 8.6 Hz, $^2J_{HP}$ = 2.8 Hz) and 4.51 (d, $^3J_{HH}$ = 8.6 Hz) ppm. Corresponding $^{13}$C{$^1$H} signals are found at $\delta$ 56.1 (d, $^2J_{CP}$ = 8 Hz) and 63.3 (d, $^2J_{CP}$ = 4 Hz) ppm and exhibit one-bond $^{13}$C−$^1$H couplings of 168 and 160 Hz, respectively. Cation $4^+$ was also characterized by a single-crystal X-ray study of its $BAr_F^-$ salt, with the results represented in Figure 2 (see SI for details). The structure clearly shows that the new ligand is coordinated to iridium in a bidentate fashion through the phosphorus atom and the C=C bond, with an Ir1−P1 bond distance of 2.268(3) Å and Ir1−C17 and Ir1−C25 bond distances of 2.186(13) and 2.161(13) Å, respectively. The coordinated carbon−carbon double bond has a length of 1.45(2) Å and forms an iridium-centered angle with the P1 atom of $C_{centr.}$−Ir1−P1 = 77.06°. These bond parameters are comparable to those found in the literature for somewhat related complexes.[13a,c,26c,g,h] The two aromatic rings that are part of the chelating phosphepine ligand feature an almost perpendicular distribution, as they form a dihedral angle of 81.3°, while the plane that contains the coordinated atoms P1,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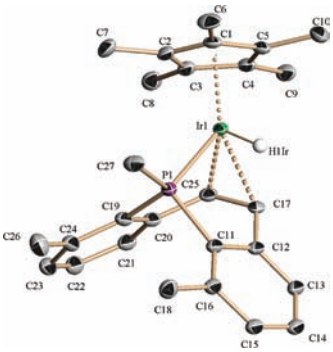


**Figure 2.** X-ray molecular structure of $4^+$, with H atoms and $BAr_F$ anion omitted for clarity.

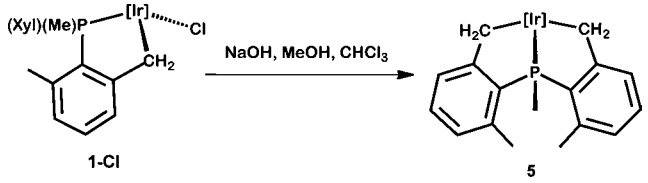
C17, and C25 forms a dihedral angle of ca. 23.7° with the Cp* ring.

Hybrid phosphine−olefin ligands find ample use in homogeneous catalysis. Transition metal compounds of tridentate diphosphine−olefin ligands generated by intramolecular C−C coupling reactions analogous to that described in this paper were reported previously by Bennet[25] and later by Baratta.[13a,c] In addition, different research groups have employed chiral and non-chiral phosphine−olefin ligands for different catalytic applications.[26] Clearly, a mechanistic understanding of the reaction pathway leading to cation $4^+$ was desirable. Accordingly, some experimental studies toward this aim were performed and are described in the following paragraphs.

**3. Isolation of Key Intermediates along the Reaction Pathway Leading to $4^+$.** On the basis of the chemical reactivity already discussed for complex $1^+$ and taking additionally into consideration the molecular complexity of the phosphepine ligand of $4^+$, the mechanistic hypothesis presented in Scheme 6 can be suggested for the base-catalyzed conversion of the former into the latter. As argued previously, the low-energy intermediates **A** and **C** are responsible for the facile exchange of the metalated and non-metalated xylyl groups of $1^+$. Similarly to the cationic bis(hydride) $3^+$, species **C**, resulting from oxidative cleavage of a C−H bond of **A**, should be acidic. Hence, its deprotonation by the base catalyst B would give the neutral dimetallacycle complex **5**, together with $HB^+$, which in a subsequent step, that consists of hydride abstraction from **5** promoted by $HB^+$, could produce the cationic benzyl benzylidene structure $6^+$ plus $H_2$. Fast reaction between the latter two molecules would lead back to **C**, in all likelihood in an irreversible manner, thereby making the process unproductive until irreversible migratory insertion of the Ir−$CH_2$ bond of $6^+$ onto the Ir=CH− unit becomes competitive with hydrogenation. The hydrido phosphepine cation $4^+$ would thus form, along with equimolar quantities of $H_2$ that could combine with $1^+$ (or **A**) to yield $3^+$, the other product of this rearrangement. Employing a concentration of 5 mol % of TMPP as the base catalyst, a half-life $t_{1/2}$ = 47 min was measured at 298 K for the overall conversion of $1^+$ into a mixture of the final products, $3^+$ and $4^+$. As discussed later, the bis(hydride) $3^+$ can be obtained by reaction of $6^+$ with an excess of $H_2$ under appropriate conditions.

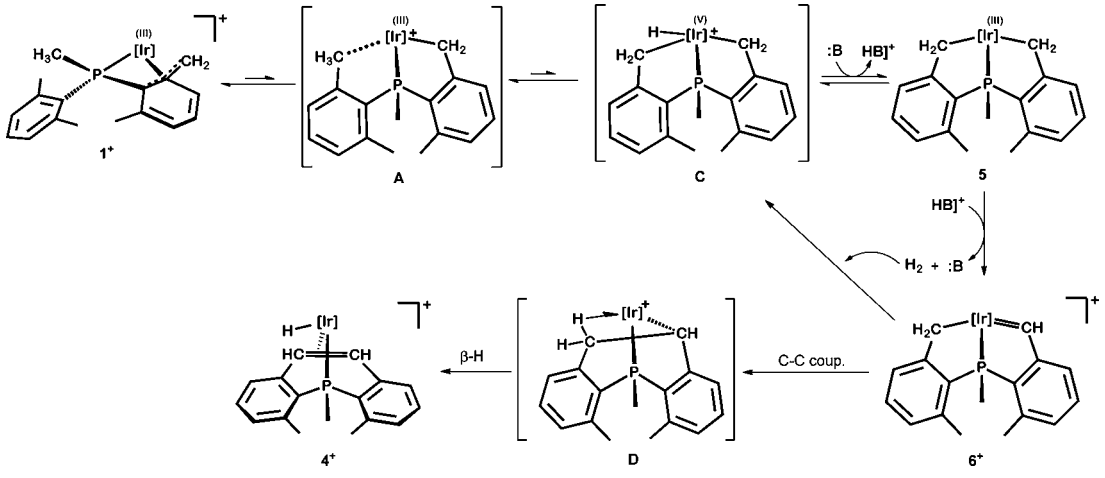
*3.1. Synthesis and Characterization of Neutral, Doubly Metalated Complex* ***5****.* Treatment of **1-Cl** with an excess of NaMeO (generated *in situ* from NaOH and MeOH) yielded hydride **1-H** as the main reaction product, accompanied by minor amounts of the desired dimetallacycle **5** (ca. 9:1 ratio). Since it is known that **1-H** rapidly regenerates **1-Cl** in the presence of $CHCl_3$, an efficient, high-yield synthesis of **5** was developed by performing the above reaction in a 1:1 solvent mixture of MeOH and $CHCl_3$ (Scheme 7).

**Scheme 7. Synthesis of the Doubly Metalated Complex 5**




Although in the solid state the two metalated xylyl groups of **5** are distinctly different (see below), in solution average resonances for two equivalent rings are observed down to −80 °C, due to a dynamic process that exchanges the conformation of the two rings. Thus, only one set of resonances (two doublets at 3.19 and 2.79 ppm, with $^2J_{HH}$ = 14.6 Hz) is observed for the Ir−$CH_2$ protons and only one signal (2.35 ppm) for the Me groups of the xylyl substituents. In the $^{13}C\{^1H\}$ NMR spectrum, the Ir−$CH_2$ groups give rise to a

**Scheme 6. Proposed Mechanism for the Dehydrogenative C−C Bond Formation That Leads to Complex $4^+$**





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doublet at 11.7 ppm ($^2J_{CP}$ = 1.8 Hz). As a consequence of the metalation of the second Xyl group, the $^{31}P\{^1H\}$ resonance of **5**, with $\delta$ 34.5, appears deshielded by more than 20 ppm from those of **1-Cl** and **1-H**.

Single crystals of **5** suitable for X-ray studies were collected by crystallization from its concentrated solutions in pentane at −20 °C. As shown in Figure 3, the phosphepine ligand of this

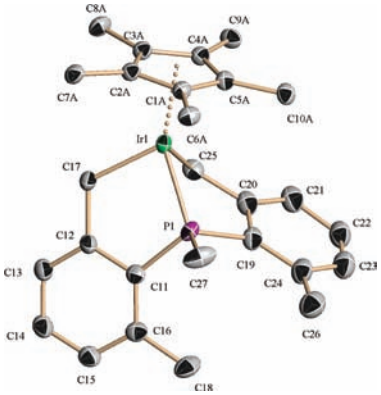
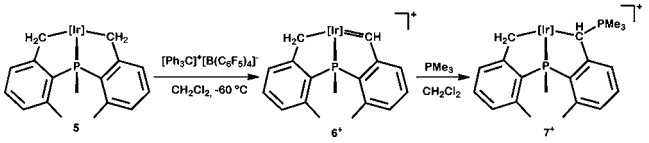



**Figure 3.** X-ray molecular structure of **5**, with H atoms omitted for clarity.

complex is acting as tridentate and is coordinated to iridium through the phosphorus atom P1 and the metalated carbon atoms C17 and C25, one from each of the original xylyl groups, making the overall geometry a distorted octahedron. In the solid-state structure these rings have a mutual spatial distribution that approaches perpendicularity (dihedral angle 76.2°), and since one of them is almost perpendicular to the $C_5Me_5$ ring (80.4°), the other is nearly parallel (dihedral angle 17.8°). The two Ir−C bond distances are almost identical (2.093(7) and 2.123(8) Å), and the Ir−P bond has a normal length of 2.205(2) Å. The double metalation undergone by the ligand to become tridentate does not appear to introduce much coordination strain, as the iridium-centered angles C17−Ir1−C25, C17−Ir1−P1, and C25−Ir1−P1 have values of 86.3(3), 83.1(2), and 75.8(2)°, respectively, close to the ideal 90° value corresponding to octahedral coordination.

*3.2. Synthesis and Characterization of the Cationic Alkylidene* $6^+$. The cationic intermediate $6^+$ responsible for the C−C coupling reaction was successfully generated (Scheme 8) by the low-temperature (−60 °C) reaction of **5** and

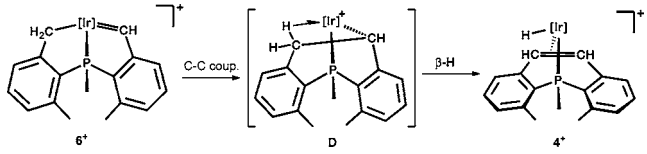
**Scheme 8. Synthesis of Iridium Alkylidene $6^+$ and Its Phosphonium Ylide $7^+$**




$[Ph_3C][BF_4]$ in $CH_2Cl_2$ solution, as demonstrated by NMR spectroscopy. Hydride abstraction was instantaneous at this temperature. In agreement with the proposed benzyl (Ir−$CH_2$−)/benzylidene (Ir=CH−) formulation, widely separated resonances were recorded for the Ir−$CH_2$ (two doublets with $\delta$ 3.70 and 2.70 ppm and $^2J_{HH}$ = 14.2 Hz) and Ir=CH protons (singlet at $\delta$ 15.91 ppm). Corresponding signals were found in the $^{13}C\{^1H\}$ NMR spectrum at $\delta$ 10.8 (d, $^1J_{CP}$ = 39 Hz) and 258.3 ppm.

Only a few species of this type have been reported for iridium. They are rarely isolable or even observable,[27] in particular those of Ir(III). Indeed, upon warming to room temperature a freshly prepared solution of $6^+$ in $CD_2Cl_2$ at −60 °C, the hydride phosphepine $4^+$ was formed in essentially quantitative yield (by NMR) in less than 1 h (Scheme 9). The

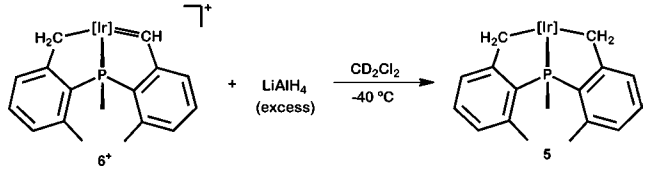
**Scheme 9. C−C Bond Coupling from Alkylidene $6^+$**




rate of formation of $4^+$ according to Scheme 9 was measured by $^{31}P\{^1H\}$ NMR spectroscopy at 0 °C, using $CD_2Cl_2$ solutions of $4^+$ generated *in situ* at −60 °C from **5** and $[Ph_3C]^+[PF_6]^-$. A first-order dependence on the concentration of $4^+$ was disclosed (Figure S9), with a calculated rate constant of $2.2 \times 10^{-4}$ $s^{-1}$ and an associated energy barrier, $\Delta G^{\ddagger}$ = 20.5 kcal $mol^{-1}$. The alkyl/alkylidene C−C coupling reaction that leads to $4^+$ may be viewed as a model for the key step of several catalytic processes, including C1 polymerization of diazo compounds.[28]

The hydride abstraction reaction that converts compound **5** into the metallacyclic alkylidene $6^+$ can actually be reversed. As depicted in Scheme 10, treatment of $CD_2Cl_2$ solutions of $6^+$ with $LiAlH_4$ at −40 °C produces cleanly the neutral dimetallacycle **5**.

**Scheme 10. Hydride Addition to Alkylidene Complex $6^+$**




Additional support for the structure proposed for cation $6^+$ was obtained with the generation of the phosphonium ylide $7^+$ that resulted when solutions of $PMe_3$ were added to $6^+$ at −60 °C. A dramatic shift of the methylidene proton from 15.91 ppm in $6^+$ to 3.72 ppm (d, $^2J_{HP}$ = 21 Hz) in $7^+$ was observed, accompanied by the appearance of a $^{13}C\{^1H\}$ doublet at 2.5 ppm ($^1J_{CP}$ = 26 Hz). Two doublets were detected in the $^{31}P\{^1H\}$ NMR spectrum at 33.3 (Ir−P) and 26.8 ppm ($PMe_3$, $^3J_{PP}$ = 3 Hz).

*3.3. Some Reactivity Studies of* **5** *and* $6^+$. To gain additional information on key steps of Scheme 6 that involves species **5** and $6^+$, some additional experiments were performed, involving hydrogenation of the latter and protonation of the former.

As discussed above, hydride abstraction from dimetallacycle **5** by $HB^+$ yields equimolar amounts of $6^+$ and $H_2$. The highly electrophilic character of the benzylidene terminus of $6^+$ is evidently responsible for the migratory insertion reaction that produces ultimately the hydride phosphepine cation $4^+$. Nonetheless, interaction of $6^+$ with $H_2$ to afford $1^+$ (through intermediates **C** and **A**), and subsequently $3^+$ if sufficient $H_2$ is available, is also expected to be a facile process.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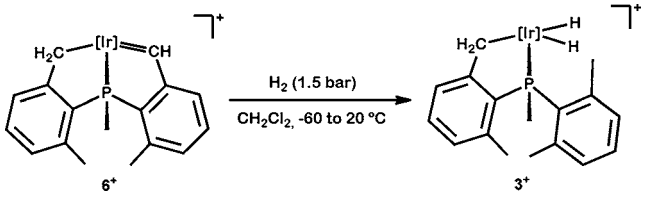
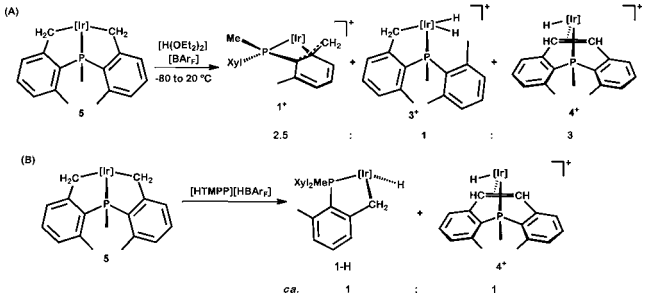
In agreement with this assumption, when a solution of $6^+$ (generated by the procedure of Scheme 8) was treated with a large excess of $H_2$ (1.5 bar) and the mixture allowed to reach slowly room temperature with intense stirring, clean quantitative transformation into $3^+$ was achieved (Scheme 11). Hence, under these conditions, alkylidene hydrogenation is much faster than benzyl−benzylidene coupling and subsequent $\beta$-H elimination. Not unexpectedly, an analogous NMR tube reaction afforded slightly different results, most probably due to slow diffusion of $H_2$. At −80 °C, ca. 5% of $3^+$ was observed, but its concentration remained unchanged until −40 °C, suggesting that inaccurate temperature control during the mixing of reagents permitted its formation. At −40 °C, both hydrogenation and C−C coupling are slow processes, as ca. 67% of the original alkylidene remained unreacted after 40 min. After this time the mixture of $1^+$ and $3^+$ accounted for ca. 29% of the product mixture and was complemented by 4% of hydrido phosphepine $4^+$. The NMR tube was then allowed to reach room temperature for a period of about 15 min, with frequent shaking to facilitate mixing of the reagents. Following this operation, a 1:4 mixture of $4^+$ and $3^+$ was ascertained by NMR. Clearly, the low solution concentration of $H_2$ retarded hydrogenation and allowed partial formation of the C−C coupling product.

**Scheme 11. Reaction of Alkylidene $6^+$ with an Excess of $H_2$**




With regard to protonation reactions, 1 equiv of $[H(OEt_2)_2][BAr_F]$ was added to a solution of **5** cooled at −80 °C. Under these conditions only minor amounts of $1^+$ were detected by NMR spectroscopy (ca. 7%, but varying between 3 and 8% from one experiment to another; once again we believe that this is due to a local temperature increase during the reagent mixing and solution process). Upon warming at −40 °C, the relative concentration of $1^+$ increased to ca. 15% and alkylidene $6^+$ also became detectable (ca. 15%), along with an unknown species (ca. 7%) characterized by a hydride signal at −17.4 ppm ($^2J_{HP}$ = 34.5 Hz; corresponding $^{31}P\{^1H\}$ resonance at 7 ppm). Even if the exact nature of this hydride remains undisclosed, it is tempting to formulate it as the cationic Ir(V) hydride **C** of Scheme 6. Regardless of this particular detail, upon further warming to room temperature all these species converted cleanly into a ca. 2.5:1:3 mixture of complexes $1^+$, $3^+$, and $4^+$ (Scheme 12A). A similar experiment employing 3 equiv of $[H(OEt_2)_2][BAr_F]$ gave analogous results. At −60 °C the protonation of **5** is slow (95% of **5** and 5% of the $\kappa^4$ complex $1^+$), but upon warming to −40 °C conversion into $1^+$, $3^+$, and alkylidene $6^+$ was readily observed. After 40 min at this temperature, the neutral dimetalated compound **5** reacted completely with the acid to furnish the $\kappa^4$ complex $1^+$ (65%), the bis(hydrido) $3^+$ (15%), and the cationic alkylidene $6^+$ (20%). Further warming to room temperature permitted conversion of alkylidene $6^+$ into the hydridophosphepine $4^+$, and a final $1^+$:$3^+$:$4^+$ product ratio of ca. 3:1:1 was identified. If one keeps in mind that under these acid conditions alkylidene $6^+$ is the only source of hydridophosphepine $4^+$, and that at

**Scheme 12. Protonation Reactions of 5 (See Text for Details)**

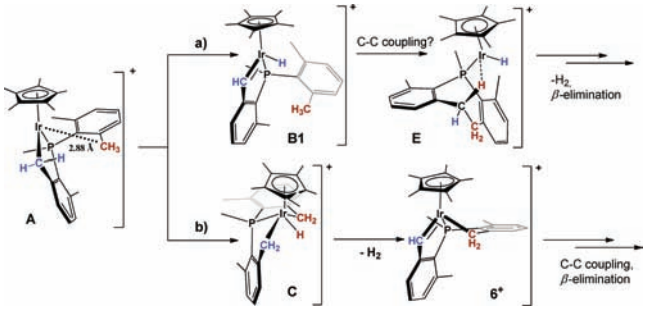



−40 °C the reaction of $6^+$ with the $H_2$ liberated in the conversion of **5** into $6^+$ is slow, these results may be taken as indicative that protonation of **5** occurs in both the **5** → **C** and the **5** → $6^+$ directions in Scheme 6, with the former being seemingly kinetically favored over the latter.

As a further test for this hypothesis, one last acid-promoted hydride abstraction reaction from **5** was effected utilizing 1 equiv of $[HTMPP][BAr_F]$ (HTMPP = 2,2,6,6-tetramethylpiperidinium). In terms of reactivity, this is similar to the base-catalyzed conversion of $1^+$ into a 1:1 mixture of $3^+$ and $4^+$. However, in this case 1 equiv of the base, rather than a catalytic amount, would be produced. Hence, a 1:1 mixture of the hydride−phosphepine compound $4^+$ and of the neutral hydride **1-H** should be expected (the latter resulting from deprotonation of $3^+$ according to Scheme 5), which is in excellent agreement with the experimental results shown in Scheme 12B.

**4. Computational Studies on the Formation of $4^+$.** DFT calculations at the M06/6-31G(d,p) and SDD level were carried out to gain insight into the mechanism for the formation of the hydride phosphepine $4^+$. The calculations were carried out using the real system in the gas phase and corrected for bulk solvent effects. Two mechanistic pathways were considered to account for the formation of the hydride phosphepine $4^+$. In the first route (Scheme 13A), $\alpha$-elimination

**Scheme 13. Initial Steps in the Two Mechanisms Considered for the C−C Bond Formation Reaction Leading to Hydride Phosphepine $4^+$**




in **A** yields the carbene hydride intermediate **B1**, and then C−C coupling followed by dihydrogen elimination gives the hydride phosphepine. The second route (Scheme 12B) requires elimination of two hydrogen atoms from the Ir(V) intermediate **C** prior to C−C coupling.

Both routes start from the cationic species $1^+$. Calculations support a $\kappa^4$-*P,C,C′,C″* structure for $1^+$ in equilibrium with a $\kappa^2$-*P,C* structure (**A**). This result is similar to that previously reported for the analogous Rh system.[18a] However, while the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Rh analogue of **A** features an agostic interaction with a $CH_3$ of the non-metalated xylyl fragment ($d_{Rh-H}$ = 2.07 Å), in this case the shortest Ir−$CH_3$ distance is 2.90 Å. Interestingly, the calculations predict that the formation of **A** in dichloromethane is endothermic by just 0.9 kcal mol$^{-1}$, with an energy barrier of 6.4 kcal mol$^{-1}$, but vibrational analysis yields a free energy variation of −4.0 kcal mol$^{-1}$ (i.e., the step is predicted to be exergonic). This result, which contrasts with the experimental data, suggests overestimation of the solvation effects ($\Delta E$ = 4.3 kcal mol$^{-1}$ in gas phase) or the entropic effects. As already discussed, intermediate **A** is instrumental in the dynamic behavior of $\mathbf{1}^+$ in solution, and it also plays a key role in the formation of the hydride phosphepine $\mathbf{4}^+$.

Route A in Scheme 13 begins with $\alpha$-elimination from **A** to yield an 18-electron hydride carbene (**B1**). This step is endothermic by 10.9 kcal mol$^{-1}$ and needs to overcome a moderate potential energy barrier of 16.8 kcal mol$^{-1}$. Reversible $\alpha$-elimination is well documented for related metal systems,[29] and formation of **B1** may compete with formation of **C** according to calculations (Figure 4). Even though formation of the hydride phosphepine $\mathbf{4}^+$ from the C−C coupling product **E** (see Figure S11) is facile, this route must be discarded since the energy barrier for the preceding C−C coupling step (i.e., from **B1** to **E**) exceeds 55 kcal mol$^{-1}$. Further details of this pathway are given in the SI.

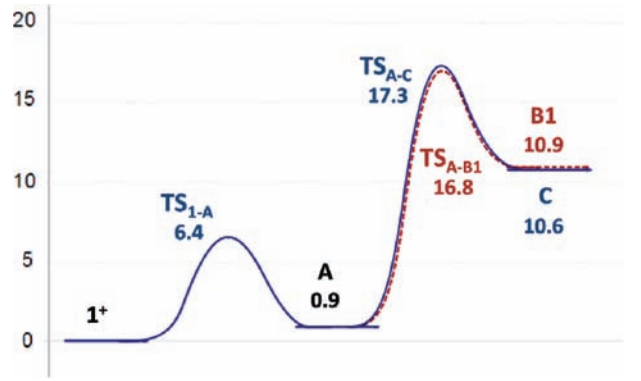


**Figure 4.** Potential energy profiles in dichloromethane (in kcal mol$^{-1}$) for the formation of the Ir(V) hydride **C** (blue solid line) and hydride carbene **B1** (red dashed line).

The second route considered is based on the mechanism which describes the dynamic behavior of $\mathbf{1}^+$ in solution (from this point the data discussed correspond to free energy in dichloromethane relative to $\mathbf{1}^+$ unless stated otherwise). The first elemental step is $CH_3$ oxidative addition in **A** to yield the Ir(V) intermediate **C**. Next, according to experimental data, elimination of two hydrogen atoms from **C** gives species $\mathbf{6}^+$. The calculations indicate that $\mathbf{6}^+$ + $H_2$ is less stable than the starting material by 10.7 kcal mol$^{-1}$, while **C** is predicted to lie 8.1 kcal mol$^{-1}$ higher in energy than $\mathbf{1}^+$. In this mechanism, C−C coupling from $\mathbf{6}^+$ remains the rate-limiting step, but the barrier to form the hydride phosphepine $\mathbf{4}^+$ from $\mathbf{6}^+$ is moderate (17.2 kcal mol$^{-1}$; 27.9 kcal mol$^{-1}$ when calculated from $\mathbf{1}^+$). This value is only ca. 3 kcal mol$^{-1}$ below that calculated from kinetic experiments (20.5 kcal mol$^{-1}$, see above), which is an acceptable difference. Interestingly, the resulting species (**F**), which is formally an unsaturated 16-electron complex, features a $\kappa^4$-*P,C,C′,C″* structure, showing a secondary interaction with the metalated xylyl ring analogous to that described for $\mathbf{1}^+$. Conformational changes in **F** yield two intermediates **G** and **H**, which are connected through low energy barriers. In the first of these conformers, **G**, the secondary interaction with the metalated xylyl is lost. However, this results only in a small destabilization of **G** relative to **F** by 3.1 kcal mol$^{-1}$ when the calculations are carried out in the gas phase. When the solvent effects are taken into account, **G** is stabilized by 1.2 kcal mol$^{-1}$ relative to **F**. The second conformer, **H**, is marginally more stable than **F** by 0.5 kcal mol$^{-1}$, likely due to the existence of an agostic interaction between the metal and one of the C−H bonds of the $\beta$-$CH_2$ carbon. $\beta$-Elimination from **H** is nearly barrier-less and yields the final product in an exoergic step with an energy return of 11.8 kcal mol$^{-1}$. The overall reaction from $\mathbf{6}^+$ and $\mathbf{1}^+$ is exoergic by 12.9 and 2.2 kcal mol$^{-1}$, respectively. These results are outlined in Figure 5.

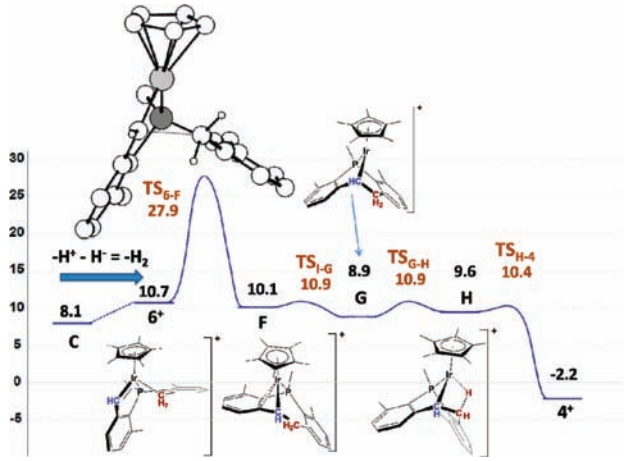


**Figure 5.** Free energy profile in dichloromethane (in kcal mol$^{-1}$) for the formation of the hydride phosphepine $\mathbf{4}^+$ from the alkyl alkylidene derivative $\mathbf{6}^+$ (note $\mathbf{1}^+$ is the origin of free energies). The inset shows the calculated geometry for $TS_{6\rightarrow F}$, indicating the forming C−C bond with a dotted line.

## SUMMARY

The Ir(III) cation $\mathbf{1}^+$ that contains a monometalated xylyl phosphine coordinated in a $\kappa^4$-*P,C,C′,C″* fashion through the phosphorus and three benzylic carbon atoms experiences a base-catalyzed C−C dehydrogenative coupling that results in equimolar mixtures of hydride phosphepine complex $\mathbf{4}^+$ and the cationic bis(hydride) Ir(V) derivative $\mathbf{3}^+$. The latter results from a fast reaction of the $H_2$ liberated in the C−C coupling leading to $\mathbf{4}^+$ with unconverted $\mathbf{1}^+$ (or **A** in Scheme 6), whereas $\mathbf{4}^+$ derives from a cationic alkyl−alkylidene intermediate $\mathbf{6}^+$, which experiences migration of the iridium−alkyl onto the iridium−alkylidene, accompanied by $\beta$-H elimination.

## EXPERIMENTAL SECTION

**General.** All operations were performed under an argon atmosphere using standard Schlenk techniques, employing dry solvents and glassware. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were recorded on a Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400, and DRX-300 spectrometers. Spectra were referenced to external $SiMe_4$ ($\delta$ 0 ppm) using the residual proton solvent peaks ($^1$H NMR


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experiments) or the characteristic resonances of the solvent nuclei ($^{13}$C NMR experiments) as internal standards, while $^{31}$P NMR was referenced to external $H_3PO_4$. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. The crystal structures were determined in a Bruker-Nonius, X8Kappa diffractometer. Dimer $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$,[30] $NaBAr_F$,[31] and $[H(OEt_2)_2][BAr_F]$[32] were prepared according to literature procedures. In the $^1$H NMR spectra all aromatic couplings were of ca. 7.5 Hz, and signals corresponding to the $BAr_F$ counterion were invariant for different complexes ($CD_2Cl_2$; $\delta$ 7.74 (s, 8H, $H_o$), 7.57 (s, 4H, $H_p$)).

**Computational Details.** DFT calculations were performed with the Gaussian 09 package[33] with Truhlar's hybrid meta-GGA functional M06.[34] The Ir atom was represented by the Stuttgart/Dresden effective core potential and the associated basis set[35] as implemented in Gaussian 09 (SDDALL). The remaining H, C, P, and Si atoms were represented by means of the 6-31G(d,p) basis set.[36−38] The geometries for all species described were optimized in the gas phase without symmetry restrictions. Frequency calculations were performed on the optimized structures at the same level of theory to characterize the stationary points, as well as for the calculation of gas-phase enthalpies ($H$), entropies ($S$), and Gibbs energies ($G$) at 298.15 K. The nature of the intermediates connected was determined by intrinsic reaction coordinate calculations or by perturbing the transition states along the TS coordinate and optimizing to a minimum. The solvent effects (dichloromethane $\varepsilon$ = 8.93) were modeled with the SMD continuum model[39] by single-point calculations on gas-phase-optimized geometries (test free optimizations in solution of some species gave analogous results). The relative free energies in solution were calculated according to $\Delta G^{solution} = \Delta E^{solution} + (\Delta G^{gas} - \Delta E^{gas})$, where $\Delta E^{solution}$ is the electronic energy plus the solvent entropy.[40]

**Synthesis of Compound 1$^+$.** To a solid mixture of **1-Cl** (100 mg, 0.16 mmol) and $NaBAr_F$ (143 mg, 0.16 mmol) was added 5 mL of $CH_2Cl_2$ under argon. The reaction mixture was stirred for 10 min at room temperature, after which the solution turned from orange to yellow. The mixture was filtered and the solvent evaporated under reduced pressure to obtain a yellow solid (220 mg, 95%). For further purification, the complex can be crystallized from a 1:2 mixture of $CH_2Cl_2$:pentane. Anal. Calcd for $C_{59}H_{47}BF_{24}IrP$: C, 49.01; H, 3.28. Found: C, 49.1; H, 3.7. $^1$H NMR (500 MHz, CD2Cl2, −60 °C): $\delta$ 7.36 (m, 1 H, $H_c$), 7.28 (t, 1 H, $H_b$), 7.24 (t, 1 H, $H_e$), 7.04, 6.94 (m, 1 H each, $H_d$, $H_f$), 6.73 (dd, 1 H, $^4J_{HP}$ = 3.7 Hz, $H_a$), 2.98 (t, 1 H, $^2J_{HH}$ = $^3J_{HP}$ = 4.8 Hz, IrC$H_\alpha$), 2.50 (s, 3 H, Me$_\gamma$), 2.44 (s, 3 H, Me$_\alpha$), 2.20 (d, 3 H, $^2J_{HP}$ = 12.8 Hz, PMe), 2.09 (s, 3 H, Me$_\beta$),1.63 (s, 15 H, $C_5Me_5$), 1.15 (dd, 1 H, $^2J_{HH}$ = 4.8, $^3J_{HP}$ = 15.6 Hz, IrC$H_\beta$). $^1$H NMR (300 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 7.36, (m, 2 H, $H_{a/b/c/d/e/f}$), 7.12 (br. s, 4 H, $H_{a/b/c/d/e/f}$), 2.44 (br. s, 11 H, Me$_\alpha$, Me$_\beta$, Me$_\gamma$, IrC$H_2$), 2.28 (d, 3 H, $^2J_{HP}$ = 12.8 Hz, PMe), 1.63 (d, 15 H, $^4J_{HP}$ = 1.8 Hz, $C_5Me_5$). $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$, −60 °C): $\delta$ 142.2, 141.4 (s, d, $^2J_{CP}$ = 16 Hz, $C_4$, $C_6$), 136.7 ($C_3$), 132.7 ($CH_b$), 132.1 ($CH_e$), 131.2 (d, $^3J_{CP}$ = 4 Hz, $CH_c$), 129.2, 128.7 (d, $^3J_{CP}$ = 10 Hz, $CH_d$, $CH_f$), 126.8 (d, $^3J_{CP}$ = 6 Hz, $CH_a$), 116.8 (d, $^1J_{CP}$ = 65 Hz, $C_5$), 95.6 (d, $^2J_{CP}$ = 15 Hz, $C_1$), 92.7 ($C_5Me_5$), 67.5 (d, $^1J_{CP}$ = 28 Hz, $C_2$), 27.0 (IrC$H_2$), 22.7 (Me$_\alpha$), 22.1, 21.9 (d, s, $^3J_{CP}$ = 16 Hz, 7 Hz, Me$_\beta$, Me$_\gamma$), 12.8 (d, $^1J_{CP}$ = 41 Hz, PMe), 8.5 ($C_5Me_5$). $^{31}$P{$^1$H} NMR (200 MHz, $CD_2Cl_2$, −60 °C): $\delta$ −44.9.

**Synthesis of Cationic Adducts 1-L$^+$ (L = NCMe, $C_5H_5N$, $NH_3$, CO, $PMe_3$).** To a solid mixture of **1-Cl** (50 mg, 0.08 mmol) and $NaBAr_F$ (72 mg, 0.08 mmol) placed in a Schlenk flask was added 5 mL of $CH_2Cl_2$. The reaction mixture was stirred for 5 min at room temperature under 1.5 bar of CO or $NH_3$ (a thick-wall vessel instead of a conventional Schlenk flask was employed in these cases), or alternatively treated with 100 $\mu$L of NCMe or pyridine (for corresponding NCMe or pyridine adducts, respectively) or with a toluene solution of $PMe_3$ (0.4 mL, 1 M) (for corresponding cationic $PMe_3$ complex). The solution was filtered, and the solvent was then evaporated under reduced pressure to obtain pale white (**Ir-NCMe$^+$**, **Ir-PMe$_3^+$**, **Ir-CO$^+$**) or yellow powders (**Ir-NC$_5$H$_5^+$**, **Ir-NH$_3^+$**) in ca. 95% yield. Complexes **Ir-NCMe$^+$** and **Ir-NH$_3^+$** were obtained as mixtures of diastereomers (88:12, L = NCMe; 94:6, L = $NH_3$). These complexes can be recrystallized from a 1:2 mixture of $CH_2Cl_2$:pentane.

**1-NCMe$^+$**: Anal. Calcd for $C_{61}H_{50}BF_{24}IrNP$: C, 49.27; H, 3.39; N, 0.94. Found: C, 49.4; H, 3.6; N, 1.4. IR (Nujol): $\nu$(CN) 2285 cm$^{-1}$. $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 7.44 (d, 1 H, $H_a$), 7.26, (m, 3 H each, $H_b$, $H_{d/f,}$ $H_e$), 6.98 (m, 1 H, $H_{d/f}$), 6.94 (dd, 1 H, $^4J_{HP}$ = 3.5 Hz, $H_c$) 3.52 (d, 1 H, $^2J_{HH}$ = 15.0 Hz, IrC$H$H), 3.32 (dd, 1 H, $^2J_{HH}$ = 15.0, $^2J_{HP}$ = 3.5 Hz, IrCH$H$), 2.65, 1.44 (s, 3 H each, Me$_\beta$, Me$_\gamma$), 2.55 (s, 3H, NCMe), 2.26 (d, 3 H, $^2J_{HP}$ = 9.9 Hz, PMe), 2.03 (s, 3H, Me$_a$), 1.55 (d, 15 H, $^4J_{HP}$ = 1.8 Hz, $C_5Me_5$). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 155.9 (d, $^2J_{CP}$ = 30 Hz, $C_1$), 142.0, 140.9 (d, $^2J_{CP}$ = 8 Hz, $C_4$, $C_6$), 140.8 ($C_3$), 139.4 (d, $^1J_{CP}$ = 63 Hz, $C_2$), 131.0, 130.3 ($CH_b$, $CH_e$), 130.9, 130.5 (d, $^3J_{CP}$ = 9 Hz, $CH_d$, $CH_f$), 127.4 (d, $^1J_{CP}$ = 51 Hz, $C_5$), 128.6 (d, $^3J_{CP}$ = 7 Hz, $CH_c$), 126.8 (d, $^3J_{CP}$ = 15 Hz, $CH_a$), 118.6 (NCMe), 95.0 (d, $^2J_{CP}$ = 2 Hz, $C_5Me_5$), 25.6, 23.2 (d, $^3J_{CP}$ = 6 Hz, $^3J_{CP}$ = 8 Hz, respectively, Me$_\beta$, Me$_\gamma$), 20.5 (d, $^3J_{CP}$ = 3 Hz, Me$_\alpha$), 19.4 (d, $^1J_{CP}$ = 39 Hz, PMe), 17.3 (IrC$H_2$), 8.2 ($C_5Me_5$), 4.4 (NC$Me$). $^{31}$P{$^1$H} NMR (160 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.9.

The minor diastereomer of compound **Ir-NCMe$^+$** is characterized by $^1$H NMR multiplets with $\delta$ 3.55 and 3.29 ppm, due to the IrC$H_2$ protons, which are partly overlapped with the signals corresponding to the IrC$H_2$ group of the major diastereomer. A doublet at 1.76 ppm is associated with the $C_5Me_5$ ligand. In the $^{31}$P{$^1$H} NMR spectrum a singlet is recorded with $\delta$ 5.8 ppm. Analytical and spectroscopic data for the other Lewis base adducts are reported in the SI.

**Synthesis of Bis(Hydride) 3$^+$.** To a solid mixture of **1-Cl** (100 mg, 0.16 mmol) and $NaBAr_F$ (143 mg, 0.16 mmol) placed in a thick-wall vessel was added 3 mL of $CH_2Cl_2$. The reaction mixture was stirred for 30 min at room temperature under 1 bar of $H_2$, after which the original solution with intense yellow color became almost colorless. Addition of pentane under hydrogen atmosphere caused precipitation of complex **3$^+$** as a fine, pale yellow powder in quantitative yield. Workup of the complex in the absence of hydrogen led to release of $H_2$ and formation of **1$^+$**. $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C, $H_2$ atmosphere): $\delta$ 7.39 (d, 1 H, $H_a$), 7.33−7.25 (m, 3 H, $H_b$, $H_{d/f,}$ $H_e$), 7.05 (dd, 1 H, $^4J_{HP}$ = 3.8 Hz, $H_{d/f}$), 6.98 (dd, 1 H, $^4J_{HP}$ = 4.7 Hz, $H_c$), 2.59, 1.50 (s, 3 H each, Me$_\beta$, Me$_\gamma$), 2.55 (d, 3H, $^2J_{HP}$ = 10.5 Hz, PMe), 2.00 (s, 3 H, Me$_\alpha$), 1.79 (d, 15 H, $^4J_{HP}$ = 1.1 Hz, $C_5Me_5$), −4.63 (br. s, 4 H, IrC$H_2$, Ir−$H_2$). $^1$H NMR (400 MHz, $CD_2Cl_2$, −80 °C, $H_2$ atmosphere): $\delta$ 7.31 (d, 1 H, $H_a$), 7.22−7.10 (m, 3 H, $H_b$, $H_{d/f,}$ $H_e$), 6.88 (m, 2 H, $H_c$, $H_{d/f}$), 3.93 (d, 1 H, $^2J_{HH}$ = 14.2 Hz, IrC$H$H), 3.38 (d, 1 H, $^2J_{HH}$ = 14.2, IrCH$H$), 2.45 (m, 6 H, Me$_{\beta/\gamma}$, PMe), 1.92 (s, 3 H, Me$_\alpha$), 1.60 (s, 15 H, $C_5Me_5$), 1.31 (s, Me$_{\beta/\gamma}$), −12.79 (s, 1 H, Ir$H$H), −13.37 (d, 1 H, $^2J_{HP}$ = 17.5 Hz, IrH$H$). $^{13}$C {$^1$H} NMR (125 MHz, $CD_2Cl_2$, 25 °C, $H_2$ atmosphere): $\delta$ 152.4 (d, $^2J_{CP}$ = 29 Hz, $C_1$), 141.6, 140.4 (d, $^2J_{CP}$ = 9 Hz, 8 Hz, $C_4$, $C_6$), 140.1 (d, $^2J_{CP}$ = 3 Hz, $C_3$), 136.4 (d, $^1J_{CP}$ = 62 Hz, $C_2$), 132.4, 132.1 ($CH_b$, $CH_e$), 131.3, 130.8 (d, $^3J_{CP}$ = 9 Hz, $CH_d$, $CH_f$), 129.9 (d, $^3J_{CP}$ = 8 Hz, $CH_c$), 126.4 (d, $^3J_{CP}$ = 17 Hz, $CH_a$), 124.9 (br. s, $C_5$), 104.2 ($C_5Me_5$), 29.6 (br. d, $^1J_{CP}$ = 57 Hz, PMe), 24.9, 23.4 (d, $^3J_{CP}$ = 5 Hz, 8 Hz, Me$_\beta$, Me$_\gamma$), 20.3 (Me$_\alpha$), 11.7 (br. s, IrC$H_2$), 8.8 ($C_5Me_5$). $^{31}$P{$^1$H} NMR (200 MHz, $CD_2Cl_2$, 25 °C, $H_2$ atmosphere): $\delta$ 3.7 (br. s).

**Synthesis of Hydride−Phosphepine 4$^+$.** A solid mixture of **1-Cl** (100 mg, 0.16 mmol) and $NaBAr_F$ (145 mg, 0.16 mmol) placed in a Schlenk flask was suspended in $CH_2Cl_2$ (5 mL) under argon. A saturated aqueous solution of $NaHCO_3$ (5 $\mu$L) was added to the reaction mixture, which was stirred for 16 h with intermittent vacuum−argon cycles to pump out the produced molecular hydrogen. The yellow solution was filtered and the solvent evaporated under reduced pressure to obtain a pale yellow solid, which was washed with pentane to yield compound **4$^+$** (210 mg, 90%). For further purification **4$^+$** can be recrystallized from a 1:1 mixture of $CH_2Cl_2$:pentane. Anal. Calcd for $C_{59}H_{45}BF_{24}IrP$: C, 49.08; H, 3.14. Found: C, 48.7; H, 3.1. IR (Nujol): $\nu$(Ir−H) 2135 cm$^{-1}$. EM (ES) $m/z$ calcd for M$^+$: 581.19. Expt.: 581.2. $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 7.34 (m, 2 H, $H_a$, $H_d$), 7.16 (m, 2 H, $H_b$, $H_e$), 6.95, 6.92 (dd, 1H, $^4J_{HP}$ = 3.9 Hz $H_c$, $H_f$), 4.97 (dd, 1 H, $^3J_{HH}$ = 8.6, $^4J_{HP}$ = 2.8 Hz, $CH_\alpha$), 4.51 (d, 1 H, $^3J_{HH}$ = 8.6 Hz, $CH_\beta$), 2.58 (d, 3 H, $^2J_{HP}$ = 13.2 Hz, PMe), 2.52, 2.50 (s, 3 H each, Me$_\alpha$, Me$_\beta$), 1.97 (d, 15 H, $^4J_{HP}$ = 1.0 Hz, $C_5Me_5$), −13.03 (d, 1 H, $^2J_{HP}$ = 28.5 Hz, Ir$H$). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 148.2 (d, $^2J_{CP}$ = 17 Hz, $C_4$), 143.6 (d, $^2J_{CP}$ = 23 Hz, $C_1$), 139.2, 138.8, 137.1, 136.0 ($C_2$, $C_3$, $C_5$, $C_6$), 131.3, 131.2, 131.1, 130.5 ($CH_b$, $CH_c$,


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$CH_e$, $CH_f$), 126.6, 124.8 (d, $^3J_{CP}$ = 15, 10 Hz, $CH_a$, $CH_d$), 100.2 (s, $C_5Me_5$), 63.3 (d, $^2J_{CP}$ = 4, $CH_\beta$), 56.1 (d, $^2J_{CP}$ = 8 Hz, $CH_\alpha$), 22.1, 21.6 (d, $^3J_{CP}$ = 3 Hz, $Me_\alpha$, $Me_\beta$), 12.6 (d, $^1J_{CP}$ = 36 Hz, PMe), 8.9 (s, $C_5Me_5$). $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.9.

**Synthesis of Compound 5.** A solution of NaOH in MeOH (6 mL, 0.5M) was added to a solution of **1-Cl** (100 mg, 0.16 mmol) in $CHCl_3$ (6 mL) under nitrogen. The reaction mixture was stirred at room temperature for 15 h, after which the suspension turned bright yellow. The solution was filtered and the solvent removed under vacuum. The residue was extracted with $Et_2O$, filtered through a pad of Celite and the solution evaporated to dryness. Complex **5** was obtained as a fine yellow powder (78 mg, 0.13 mmol, 84%). Anal. Calcd for $C_{27}H_{34}IrP$: C, 55.74; H, 5.89. Found: C, 55.3; H, 5.4. $^1H$ NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ 7.29 (d, 2 H, $H_a$), 6.90 (td, 2 H, $^5J_{HP}$ = 1.4 Hz, $H_b$), 6.61 (dd, 2 H, $^4J_{HP}$ = 2.4 Hz, $H_c$), 3.19 (d, 2 H, $^2J_{HH}$ = 14.6 Hz, IrC*H*H), 2.79 (d, 2 H, $^2J_{HH}$ = 14.6, IrCH*H*), 2.35 (s, 6 H, $Me_\alpha$), 1.94 (d, 3 H, $^2J_{HP}$ = 10.9 Hz, PMe), 1.67 (d, 15 H, $^4J_{HP}$ = 1.3 Hz, $C_5Me_5$). $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$, 25 °C): $\delta$ 162.1 (d, $^2J_{CP}$ = 32 Hz, $C_1$), 140.1 (d, $^1J_{CP}$ = 54 Hz, $C_2$), 137.7 (d, $^2J_{CP}$ = 3 Hz, $C_3$), 128.9 (d, $^4J_{CP}$ = 2.2 Hz, $CH_b$), 126.8 (d, $^3J_{CP}$ = 6 Hz, $CH_c$), 126.7 (d, $^3J_{CP}$ = 14 Hz, $CH_a$), 90.5 ($C_5Me_5$), 21.4 (d, $^3J_{CP}$ = 2.4 Hz, $Me_\alpha$), 14.0 (d, $^1J_{CP}$ = 29 Hz, PMe), 11.7 (d, $^2J_{CP}$ = 1.8 Hz, $IrCH_2$), 8.7 ($C_5Me_5$). $^{31}P\{^1H\}$ NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ 34.5.

**Synthesis of Alkylidene 6$^+$.** To a solid mixture of **1-Cl** (30 mg, 0.05 mmol) and $[Ph_3C]^+[PF_6]^-$ (18 mg, 0.05 mmol) placed in a screw-cap NMR tube was added 0.6 mL of $CD_2Cl_2$ at −60 °C under argon. The tube was rapidly shaken and the resulting orange solution analyzed by $^1H$, $^{31}P$ and $^{13}C$ NMR spectroscopy at −60 °C. $^1H$ NMR (400 MHz, $CD_2Cl_2$, −60 °C): $\delta$ 15.91 (s, 1 H, Ir=CH−), 7.82 (d, 1 H, $H_a$), 7.61 (m, 1 H, $H_c$), 7.41 (t, 1 H, $H_b$), 7.30 (m, 1 H, $H_{d/e/f}$, overlapped with $Ph_3CH$), 6.94 (m, 2 H, $H_{d/e/f}$), 3.70 (d, 1 H, $^2J_{HH}$ = 14.2 Hz, IrC*H*H), 2.70 (d, 1 H, $^2J_{HH}$ = 14.2, IrCH*H*), 2.61 (s, 3 H, $Me_\alpha$), 2.55 (s, 3 H, $Me_\beta$), 2.24 (d, 3 H, $^2J_{HP}$ = 11.7 Hz, PMe), 1.87 (s, 15 H, $C_5Me_5$). $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$, −60 °C): $\delta$ 258.3 (Ir=CH−), 162.5 (d, $^2J_{CP}$ = 29 Hz, $C_1$), 157.0 (d, $^2J_{CP}$ = 27 Hz, $C_4$), 144.5 ($C_3$), 144.0 ($C_5$), 140.8 ($C_2$), 140.5 ($C_6$), 135.2, 135.1 ($CH_b$, $CH_c$), 130.4, 126.2, 128.1 ($CH_d$, $CH_e$, $CH_f$), 128.5 ($CH_a$), 104.2 ($C_5Me_5$), 22.5 ($Me_\alpha$), 20.5 ($Me_\beta$), 11.3 ($IrCH_2$), 10.8 (d, $^1J_{CP}$ = 39 Hz, PMe), 9.3 ($C_5Me_5$). $^{31}P\{^1H\}$ NMR (160 MHz, $CD_2Cl_2$, −60 °C): $\delta$ 47.3.

**Synthesis of Phosphonium Ylide 7$^+$.** To a solid mixture of **5** (50 mg, 0.09 mmol) and $[Ph_3C]^+[PF_6]^-$ (33 mg, 0.09 mmol) placed in a Schlenk flask was added 5 mL of $CH_2Cl_2$ at −80 °C to give a dark orange solution. The reaction mixture was allowed to warm to −60 °C and additionally stirred for 15 min at this temperature. Next $PMe_3$ (1 M in toluene, 140 $\mu$L, 0.14 mmol) was added at the same temperature, and the solution turned pale yellow in a few seconds. The solvent was removed under vacuum and the crude washed with $Et_2O$ to yield complex 7$^+$ as a yellow solid (61 mg, 88%). Anal. Calcd for $C_{30}H_{42}F_6IrP$: C, 44.94; H, 5.28. Found: C, 44.8; H, 5.3. $^1H$ NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 7.38 (d, 1 H, $H_d$), 7.17−7.07 (m, 3 H, $H_a$, $H_b$, $H_e$), 7.01 (m, 1 H, $H_c$), 6.87 (dd, $^4J_{HP}$ = 2.8 Hz, 1 H, $H_f$), 3.72 (d, 1 H, $^2J_{HP}$ = 21 Hz, IrCHP), 3.54 (d, 1 H, $^2J_{HH}$ = 16.0 Hz, IrC*H*H), 2.88 (dd, 1 H, $^2J_{HH}$ = 16.0, $^3J_{HP}$ = 4.2 Hz, IrCH*H*), 2.72 (s, 3 H, $Me_\alpha$), 2.50 (s, 3 H, $Me_\beta$), 2.22 (d, 3 H, $^2J_{HP}$ = 11.2 Hz, PMe), 1.71 (d, 15 H, $^4J_{HP}$ = 1.7 Hz, $C_5Me_5$), 1.13 (d, 9 H, $^2J_{HP}$ = 12.6 Hz, $PMe_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 160.6 (d, $^2J_{CP}$ = 30 Hz, $C_4$), 152.3 (d, $^2J_{CP}$ = 31 Hz, $C_1$), 144.0 ($C_3$), 142.2 (dd, $^1J_{CP}$ = 52, $^3J_{CP}$ = 6 Hz, $C_2$), 141.3 (d, $^1J_{CP}$ = 57 Hz, $C_5$), 140.3 ($C_6$), 131.3 ($CH_c$), 131.0, 130.0 ($CH_b$, $CH_e$), 128.1 (d, $^3J_{CP}$ = 7 Hz, $CH_f$), 127.6 (d, $^3J_{CP}$ = 14 Hz, $CH_d$), 127.3 (dd, $^3J_{CP}$ = 13, $^3J_{CP}$ = 5 Hz, $CH_a$), 92.6 ($C_5Me_5$), 22.7 ($Me_\alpha$), 21.1 ($Me_\beta$), 14.4 (d, $^1J_{CP}$ = 33 Hz, PMe), 11.4 (d, $^1J_{CP}$ = 53 Hz, $PMe_3$), 8.4 ($C_5Me_5$), 7.0 ($IrCH_2$), 2.5 (d, $^1J_{CP}$ = 26 Hz, IrCHP$Me_3$). $^{31}P\{^1H\}$ NMR (200 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 33.3 (d, $^3J_{PP}$ = 3 Hz, IrP), 26.8 (d, $^3J_{PP}$ = 3 Hz, $PMe_3$).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details for the reaction of **1-Cl** with $NaBAr_F$; analytical and spectroscopic data for adducts **1-L**$^+$; dynamic NMR studies; $T_1$ measurements; X-ray and computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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