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Cyclometalated Iridium Complexes of Bis(Aryl) Phosphine Ligands: Catalytic C−H/C−D Exchanges and C−C Coupling Reactions

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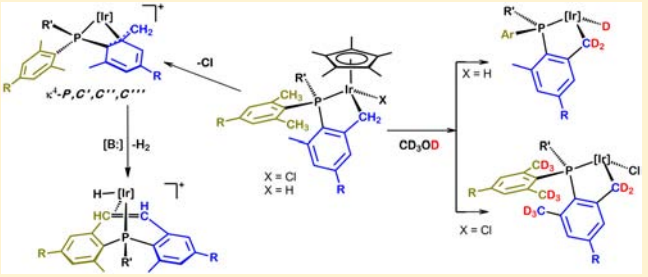
Supporting Information

ABSTRACT: This work details the synthesis and structural identification of a series of complexes of the (η^5-C_5Me_5)Ir(III) unit coordinated to cyclometalated bis(aryl)phosphine ligands, PR′(Ar)$_2$, for R′ = Me and Ar = 2,4,6-$Me_3C_6H_2$, **1b**; 2,6-Me_2-4-OMe-C_6H_2, **1c**; 2,6-Me_2-4-F-C_6H_2, **1d**; R′ = Et, Ar = 2,6-$Me_2C_6H_3$, **1e**. Both chloride- and hydride-containing compounds, **2b−2e** and **3b−3e**, respectively, are described. Reactions of chlorides **2** with $NaBAr_F$ (BAr_F = B(3,5-$C_6H_3(CF_3)_2)_4$) in the presence of CO form cationic carbonyl complexes, **4**$^+$, with ν(CO) values in the narrow interval 2030−2040 cm^{-1}, indicating similar π-basicity of the Ir(III) center of these complexes. In the absence of CO, $NaBAr_F$ forces κ^4-*P,C,C′,C″* coordination of the metalated arm (studied for the selected complexes **5b**, **5d**, and **5e**), a binding mode so far encountered only when the phosphine contains two benzylic groups. A base-catalyzed intramolecular, dehydrogenative, C−C coupling reaction converts the κ^4 species **5d** and **5e** into the corresponding hydrido phosphepine complexes **6d** and **6e**. Using CD_3OD as the source of deuterium, the chlorides **2** undergo deuteration of their 11 benzylic positions whereas hydrides **3** experience only D incorporation into the Ir−H and Ir−CH_2 sites. Mechanistic schemes that explain this diversity have come to light thanks to experimental and theoretical DFT studies that are also reported.



INTRODUCTION

The cationic Ir(III) complex [(η^5-C_5Me_5)Ir(Me)(PMe_3)($ClCH_2Cl$)]$^+$ of Bergman and co-workers (Scheme 1)[1] has served for many years as a model for studies on C−H bond activation reactions,[2] due to its ability to promote this transformation in a range of organic molecules, including methane and other hydrocarbons.[1] Somewhat surprisingly, the rhodium analog is more stable thermally and considerably less reactive.[3] Related Ir(III) complexes supported also by the η^5-C_5Me_5 ancillary group, but containing different phosphorus donor[4] and N-heterocyclic carbene[5] ligands, have been investigated too.

We have recently developed a series of rhodium and iridium complexes in which the phosphine and alkyl functionalities are constituents of an aryl phosphine ligand which has undergone metalation at one of its benzylic positions (see Scheme 1).[6] Transition metal metallacycles are an important family of coordination and organometallic complexes. Comprehensive studies on these compounds over the past decades[7,8] have discovered plentiful applications in different areas of research, encompassing catalysis,[9] medicinal chemistry,[10] and material science.[11] In particular, some iridium complexes of this type exhibit outstanding catalytic properties. Thus, iridacycles constructed around pincer ligands[12] feature an exceptional capacity to promote alkane dehydrogenation[9a,12c,13] and hydrogen release from aminoboranes.[14] Moreover, they also display great potential as light-emitting diodes.[15]

Complexes of the [(η^5-C_5Me_5)Ir] metal unit stabilized by coordination to cyclometalated phosphines (see general formulation **B** in Scheme 1) are known,[16] and some members of this series induce C−H activation at higher rates than nonmetalated analogs.[16c,e] As briefly mentioned, we have reported lately a set of cyclometalated rhodium and iridium complexes of the type shown in Scheme 1 (structure **C**) that stem from a bis(*o*-xylyl) phosphine, $PMeXyl_2$ (Xyl = 2,6-$Me_2C_6H_3$), which possesses 12 benzylic positions.[6] Cyclometalation of $PMeXyl_2$ is a facile reaction that occurs under mild conditions yielding a five-membered ring structure which is stable toward β-H elimination. Because of the existence of two xylyl groups in the phosphine, the cationic unsaturated species that form upon abstraction of the halide ligand in **C** (and the Rh analog)[6] undergoes facile exchange of the metalated and nonmetalated xylyl units. This key structural feature confers to these complexes valuable and unusual reactivity properties.[6,17] Furthermore, it also appears to be responsible for the uncommon binding of the metalated phosphine arm, which coordinates as a κ^4-*P,C,C′,C″* five-electron donor ligand.[6a,d,17]

As an extension of this work, we now report the preparation of iridium complexes like **C** but derived from bis(aryl) PR′Ar_2 phosphines (R′ = Me, Et; see Scheme 2) in which the xylyl

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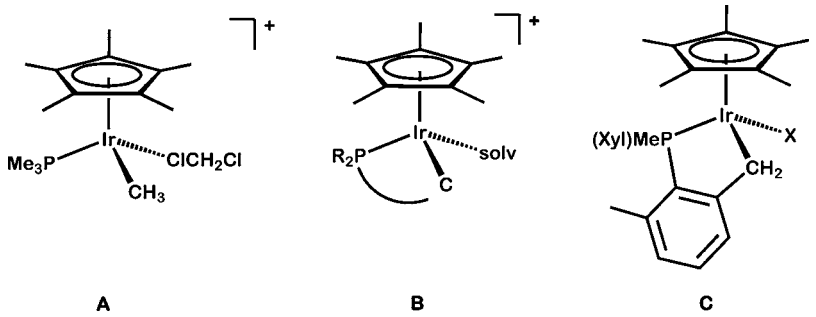
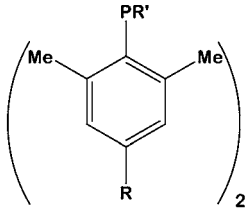
Scheme 1. Some (η^5-C_5Me_5)Ir(III) Structures Relevant to the Present Work



A B C

Bergman

Scheme 2. Alkyl Bis(aryl) Phosphine Ligands Employed in This Work (1b−1e) and Studied Previously (1a)[6]



R' = Me; R = H, 1a; Me, 1b; OMe, 1c and F, 1d
R' = Et; R = H, 1e

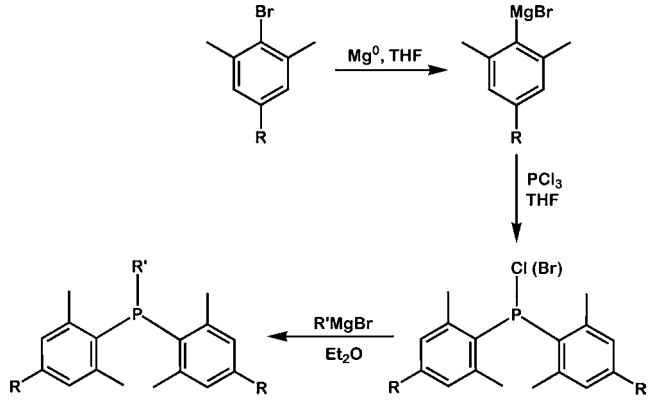
groups have been modified to accommodate a third R substituent (R = Me, OMe, F; **1b−1d**) in the 4-position of the aromatic ring. The analogous complex of the ethyl phosphine, $PEtXyl_2$, **1e**, has been studied too. Besides ascertaining possible electronic effects created by the R subtituent in the donor properties of the cyclometalated phosphine, the main objective of this work was to confirm that the unsual reactivity exhibited by these complexes is in fact due to the existence of two phosphine aryl rings with benzylic subtituents prone to cyclometalation. Adding to current interest in hydrogen isotope exchange reactions,[6,17] we also address in this contribution the diverse catalytic C−H/C−D exchanges shown by chloride and hydride complexes of type **C**, albeit resulting from the metalation of phosphines **1b−1e**, and provide a full mechanistic picture substantiated by experimental and computational studies. In addition, choosing as a representative example the cyclometalated iridium complexes that originate from the fluorophosphine **1d**, we describe a dehydrogenative C−C coupling reaction[6d] that generates a hybrid olefin-phosphine (phosphepine) ligand, which adds to other ligands of this kind already known mostly because of their numerous applications in catalysis.[19]

RESULTS AND DISCUSION

Synthesis of Bis(aryl)phosphines, PR′Ar_2, 1. Phosphine ligands have played a pivotal role in organometallic chemistry.[20] They generally behave as spectator ligands and are capable of stabilizing a range of oxidation states and a diversity of organometallic functionalities and structures. In recent years, bulky phosphines have proved irreplaceable in preparing molecules of biological interest as well as in promoting challenging chemical transformations,[21] particularly when combined with a suitable source of Pd(0).

Recently, we have uncovered unusual reactivity modes in Rh, Ir, and Pt complexes stabilized by coordination to bulky mono- and bis-xylyl phosphine ligands.[6,17,22] In a related approach, we concentrate attention now on cyclometalated Ir(III) complexes of some bis(aryl)phosphines (Scheme 2). The synthesis of these ligands was effected utilizing the general, classical procedure depicted in Scheme 3. Reaction of the corresponding

Scheme 3. General Synthesis of the Phosphine Ligands 1



R' = Me; R = H, 1a; Me, 1b; OMe, 1c and F, 1d
R' = Et; R = H, 1e

Mg(Ar)Br with PCl_3 in a 2:1 molar ratio yielded the expected bis(aryl)halophosphine as a mixture of the chloro and bromo derivatives $PXAr_2$, which converted into the desired $PMeAr_2$ (**1b−1d**) upon reaction with Mg(Me)Br. The synthesis of $PEtXyl_2$, **1e**, was accomplished similarly, employing Mg(Et)Br. Derivatives **1a−1e** were isolated as white solids in yields around 80% (see Experimental Section).

Neutral Cyclometalated Ir(III) Chloride and Hydride Compounds. The new cyclometalated iridium chloride complexes **2b−2e** were generated with the procedure already reported[6b,d] for the $PMeXyl_2$ analog, **2a**. As summarized in Scheme 4, the room temperature reaction of $\{[(\eta^5\text{-}C_5Me_5)\text{-}IrCl_2]_2\}$ with 1 equiv of the phosphine in the presence of 2,2,6,6-tetramethylpyperidine (TMPP) allowed isolating complexes **2b−2e** as crystalline yellow solids in *ca.* 70% yield. Under these conditions, all compounds except the OMe substituted **2c** formed as the single stereomers shown in Scheme 4, for which steric pressure is relieved thanks to the *syn* distribution of the Ir−Cl and P−R (R = Me, Et) units. This proposal was conclusively demonstrated for **2a**[6b,c] and has now been additionally inferred from NOESY studies carried out with the hydride analogs, **3** (*vide infra*). However, it is difficult to explain the appearance for **2c** of a 60:40 diastereomer mixture, which remained unchanged upon prolonged heating at 40 °C in

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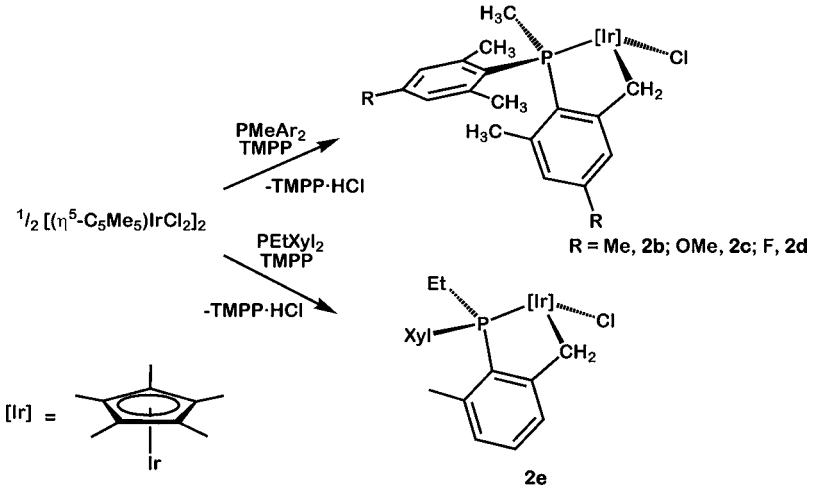
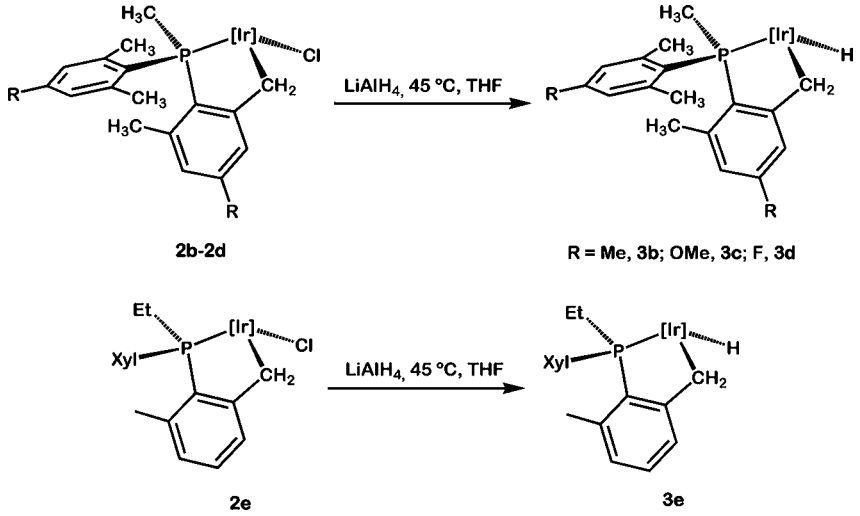
Scheme 4. Synthesis of the Cyclometalated Iridium Chloride Complexes, 2b−2e



Scheme 5. Synthesis of Ir(III) Hydride Compounds, 3b−3e



a 1:1 mixture of CH_2Cl_2 and CH_3OH. Since under the latter conditions, the kinetic 70:30 mixture of the *syn* and *anti* stereomers of **2a** converted into the *syn* structure by partial dissociation of the chloride ligand,[6b,c] it seems plausible that the chloride dissociation from compound **2c** finds a higher kinetic barrier that prevents its isomerization. This assumption is also in agreement with the observation of nearly one stereomer of hydride **3c** (90:10 mixture) upon reaction of **2c** with $LiAlH_4$ (vide infra).

The solution molecular structure of compounds **2** was unequivocally inferred from their NMR properties. Since they are similar to those described for the X-ray characterized **2a**, only some selected data will be analyzed here, while comprehensive lists of the NMR parameters are provided in the Experimental Section and in the Supporting Information (SI). For all compounds, a noticeable doublet is found for the C_5Me_5 protons between 1.4 and 1.6 ppm, with a $^4J_{HP}$ value of about 1.6 Hz. The diastereotopic hydrogen atoms of their metallacyclic moieties give rise to two multiplets between δ 3.5 and 3.8, as expected for ABX spin systems where X is ^{31}P. $^{31}P\{^1H\}$ resonances appear in the range 3−10 ppm for **2b−2d** (11.3 ppm for **2a**) and at a somewhat higher frequency for **2e** (22.8 ppm).

Chloride complexes **2b−2e** converted into their related hydrides, **3b−3e**, upon reaction with $LiAlH_4$ in THF at 45 °C for *ca.* 2 h (Scheme 5). Once more, we observed only the *syn* Ir−H/P−R stereomers for **3b**, **3d**, and **3e** but a 90:10 *syn*/*anti* mixture for isolated samples of **3c**. All hydrides feature a weak Ir−H stretching vibration in the IR spectrum between 2075 and 2125 cm^{-1} and a salient, strongly shielded ^1H NMR doublet resonance at *ca.* −17 ppm ($^2J_{HP}$ ∼ 35 Hz). Corresponding $^{31}P\{^1H\}$ resonances are only slightly shifted with respect to the chloride precursors (between 3 and 6 ppm for **3b−3d** and at 28.5 ppm for the $PEtXyl_2$ derivative **3e**). The proposed *syn* structure was deduced from NOESY studies (Experimental Section) carried out for **3c**, which revealed that the major stereoisomer has a *syn* structure.

Cationic Complexes Generated by Chloride Abstraction from Compounds 2. To determine if the structural variations introduced by the R and R′ substituents in the phosphine ligands **1a−1e** of Scheme 2 have any detectable effect in the electronic properties of the iridium center of the cyclometalated complexes studied in this work, we prepared the cationic carbonyl species **4b**$^+$**−4e**$^+$ by treatment of the corresponding chloro derivatives **2** with $NaBAr_F$ (BAr_F = $[B(3,5\text{-}C_6H_3(CF_3)_2)_4]$) in the presence of 1.5 bar of CO

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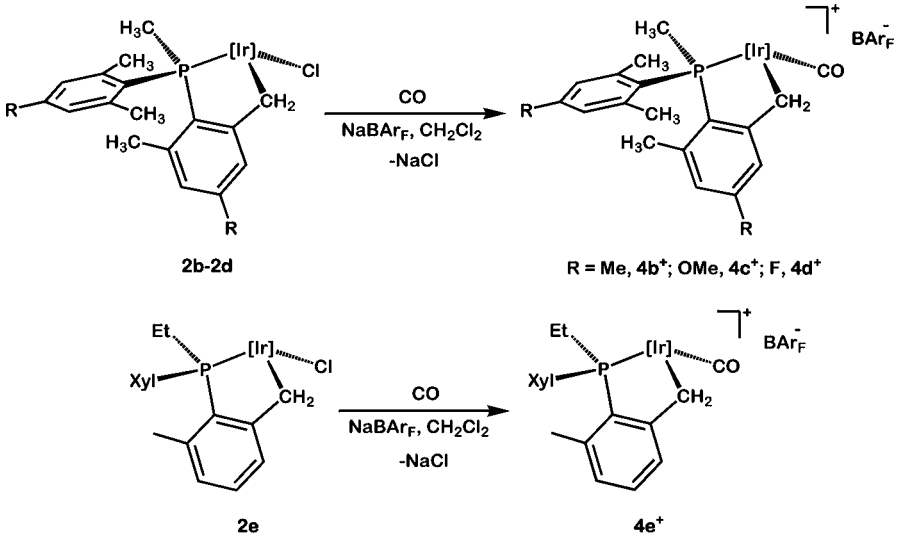
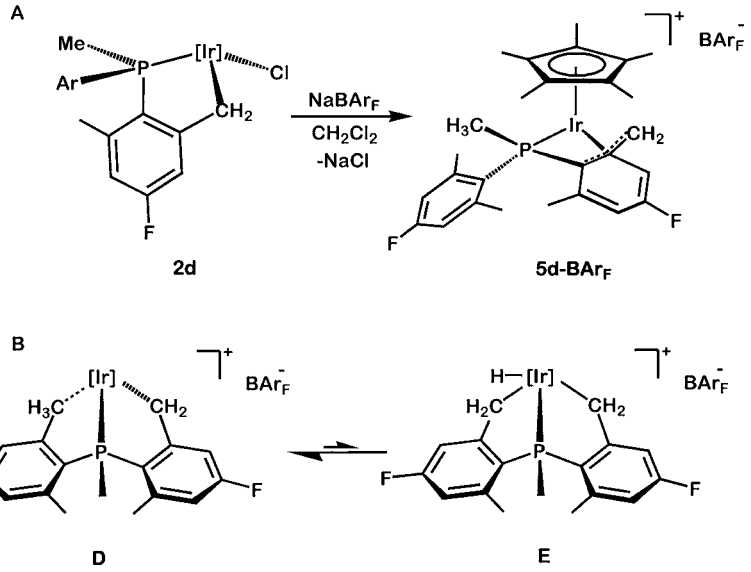
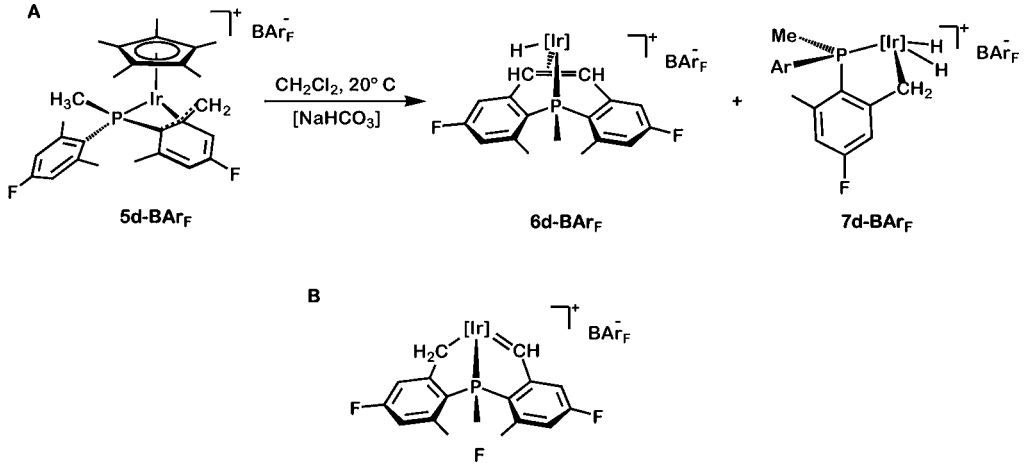
Scheme 6. Synthesis of Cationic Carbonyl Complexes, $4b^+-4e^+$



Scheme 7. Formation of Complex 5d-BAr_F with κ^4-*P,C,C′,C″* Coordination of the Cyclometalated Phosphine (A) and Suggested Intermediates, D and E, to Explain the Facile Solution Exchange of Its Aryl Groups (B)



Scheme 8. (A) Brönsted–Lowry Base-Catalyzed Rearrangement of Complex 5d-BAr_F and (B) Key Cationic Alkyl–Alkylidene Intermediate F in the Generation of the Hydride-Phosphepine Complex 6d-BAr_F



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(Scheme 6). We found that with the exception of the fluoro-substituted cation, **4d**$^+$, which features ν(CO) at a slightly higher wavenumber (2040 cm^{-1}), all other compounds, including **4a**$^+$, present this IR band in the narrow interval 2030−2035 cm^{-1}. The solid-state molecular structure of **4e-BAr$_F$** has been determined by X-ray crystallography (Figure S6 in SI).

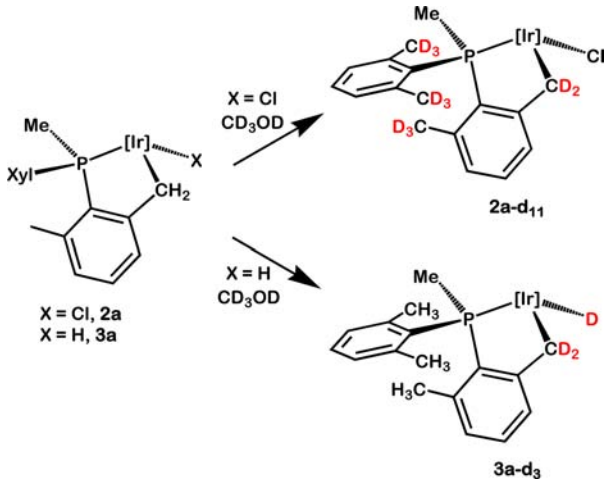
Effecting the above reaction of **2d** in the absence of CO yielded the new compound **5d-BAr$_F$** (Scheme 7A, the analogous complex **5e-BAr$_F$** was obtained similarly). Unequivocal analogies between the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra and those recorded for **5a-BAr$_F$**,[6d] as well as for the rhodium complex analog,[6a] evidenced the reorganization of the electronic structure of the cyclometalated phosphine ligand that leads to the κ^4-*P,C,C′,C″* coordination mode. As stated earlier, achieving this unusual binding appears to necessitate a second aryl unit in the phosphine ligand. Besides, the existence of the two aryls permits the facile intramolecular exchange of two degenerate ground-state structures through the low-energy intermediates **D** and **E** shown in Scheme 7B for the fluoro-containing compound **5d**.[6d] Similarly to **5a-BAr$_F$**, in the room temperature ^{1}H NMR spectrum of **5d**$^+$ only the signals due to the η^5-C_5Me_5 and P-Me fragments can be discerned clearly (δ 1.85, $^2J_{HP}$ = 2.0 and 2.31 ppm, $^2J_{HP}$ = 12.7, respectively). The benzylic protons of the two aryl fragments give a broad peak at 2.43 ppm, but upon cooling at −60 °C the aryl methyl groups resonate at 2.45 (6H) and 2.05 (3H) ppm, whereas the diastereotopic Ir−CH_2 protons yield two multiplets at 3.01 (t, $^2J_{HH}$ = $^3J_{HP}$ = 4.7 Hz) and 1.21 ppm (dd, $^3J_{HP}$ = 16.2 Hz).

The stirring of a dichloromethane solution of **5d-BAr$_F$** at 20 °C, in the presence of a catalytic amount of aqueous $NaHCO_3$, led to the formation of two new compounds (Scheme 8A) identified as **6d-BAr$_F$** and **7d-BAr$_F$** on the basis of their IR and NMR spectra. By analogy with the previously studied[6d] reaction that originated **6a-BAr$_F$**, the C−C coupling that gives rise to the phosphepine ligand implied, most probably, an irreversible migratory insertion of the Ir−CH_2 linkage of intermediate **F** in Scheme 8B onto the Ir═CH functionality. Diagnostic spectroscopic data for **6d**$^+$ are (i) an Ir−H IR stretching at 2140 cm^{-1} and a corresponding ^{1}H NMR signal at −12.93 ppm (d, $^2J_{HP}$ = 28 Hz) and (ii) olefinic ^{1}H and ^{13}C{^{1}H} NMR resonances recorded respectively at 4.89 and 4.42 ppm (^{1}H) and 61.4 and 54.8 ppm (^{13}C), which exhibit the expected couplings to other magnetically active nuclei. The analogous complexes **6e-BAr$_F$** and **7e-BAr$_F$** have also been investigated (see SI).

Under ordinary conditions, cation **7d**$^+$ was the minor product of the reaction represented in Scheme 8A. Moreover, upon prolonged stirring at 20 °C of the **6d**$^+$ plus **7d**$^+$ mixture, **7d**$^+$ converted into **6d**$^+$ in a process that became accelerated by removing volatile materials under a vacuum. However, performing the reaction in a sealed NMR tube furnished a 1:1 mixture of the two cations.[6d] These observations, along with its characteristic spectroscopic data (see below), support the formulation of **7d**$^+$ as the bis(hydride)Ir(V) species represented in Scheme 8A. Hence, in the reaction depicted in Scheme 8A, complex **7d**$^+$ resulted from the fast reaction of the H_2 liberated in the C−C coupling leading to **6d**$^+$ with the still unreacted **5d**$^+$. Indeed, in the presence of H_2, **5d**$^+$ yielded cleanly **7d**$^+$. Like **7a**$^+$, the new complex **7d**$^+$ undergoes at room temperature the exchange of the Ir-$(H)_2$ and Ir-CH_2 protons, which results in the observation of a broad, average signal centered at −4.55 ppm. At −80 °C, four individual resonances appear at 3.90, 3.32 (Ir-CH_2; d, $^2J_{HH}$ = 14.4 Hz), −12.77 (s), and −13.10 ppm (d, $^2J_{HP}$ = 16 Hz).

C−H/C−D Exchanges in Chloride (2) and Hydride (3) Complexes. We reported previously that the parent chloride and hydride complexes **2a** and **3a**, respectively, undergo facile C−H/C−D exchanges using CD_3OD as a deuterium source.[6c] As recalled in Scheme 9, the exchange affected all benzylic sites

Scheme 9. C−H/C−D Reactions Reported for Complexes 2a and 3a[6c]



of chloride **2a** with the same rate, but only the Ir−H and Ir−CH_2 positions (simultaneously too) of hydride **3a**. Furthermore, whereas deuteration of **2a** was almost imperceptibly influenced by Brönsted−Lowry acids, a remarkable acid catalysis ensued for **3a**. In the first instance, experimental data supported the participation of a cationic methanol adduct generated by momentary chloride dissociation, but for the second we could only speculate with the possible participation of a cationic alkylidene species, and a clear mechanistic picture did not emerge. To settle this question, we have performed analogous deuteration experiments with the new compounds **2b−2e** and **3b−3e**, as well as additional assays with the parent chloride **2a**. A simple, general mechanistic scenario that explains the diverse deuteration of the two sets of compounds has come to light. This mechanism finds theoretical support in DFT calculations that are reported. However, contrary to our initial suggestion,[6c] the new results do not back the participation of iridium alkylidenes in the C−H/C−D exchanges in complexes **3**.

C−H/C−D exchange reactions of the parent **2a** and the new chlorides **2b−2d** occurred with comparable rates for the four compounds ($t_{1/2}$ *ca.* 500−600 min at room temperature), again with no observable differences among the 11 benzylic sites (Scheme 10). Nevertheless, the deuteration of the $PEtXyl_2$ derivative **2e** was appreciably faster, with a half-life of *ca.* 25 min. For solubility reasons, CD_2Cl_2/CD_3OD solvent mixtures were employed, with the rate of deuteration increasing with the concentration of CD_3OD ($t_{1/2}$ of *ca.* 490 min for 1:1 mixtures and of about 900 min for 3:1 mixtures). For a cationic NCMe adduct derived from **2a** by chloride elimination (by action of $NaBAr_F$) in the presence of acetonitrile,[6d] the half-life of the exchange in 1:1 CD_2Cl_2/CD_3OD mixtures was of only 30 min, reflecting the need for Cl^- dissociation. These data complement those already described[6c] and support the mechanistic exchange represented in Scheme 11, whose key step is D^+

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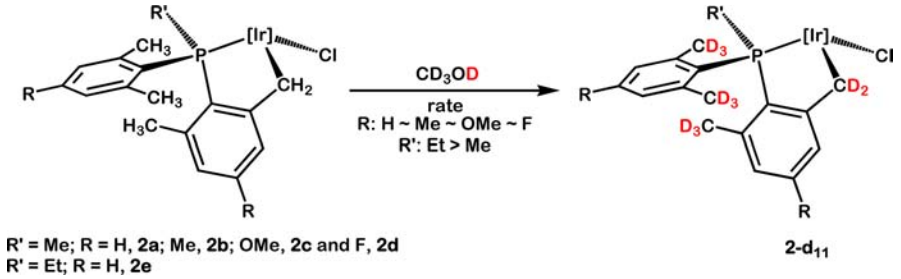
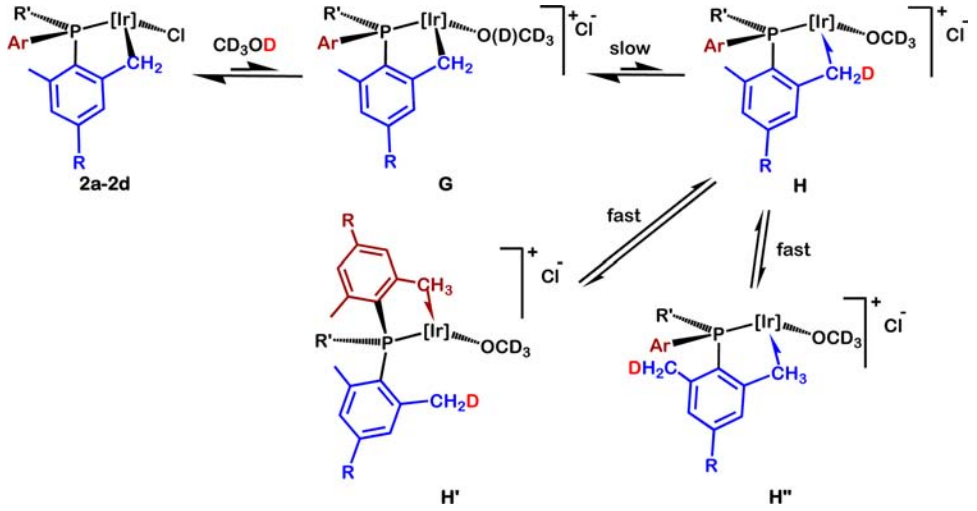
Scheme 10. H/D Exchange Reactions for Compounds 2a−2e



Scheme 11. Proposed Mechanism for C−H/C−D Exchange in Iridium(III) Chloride Complexes



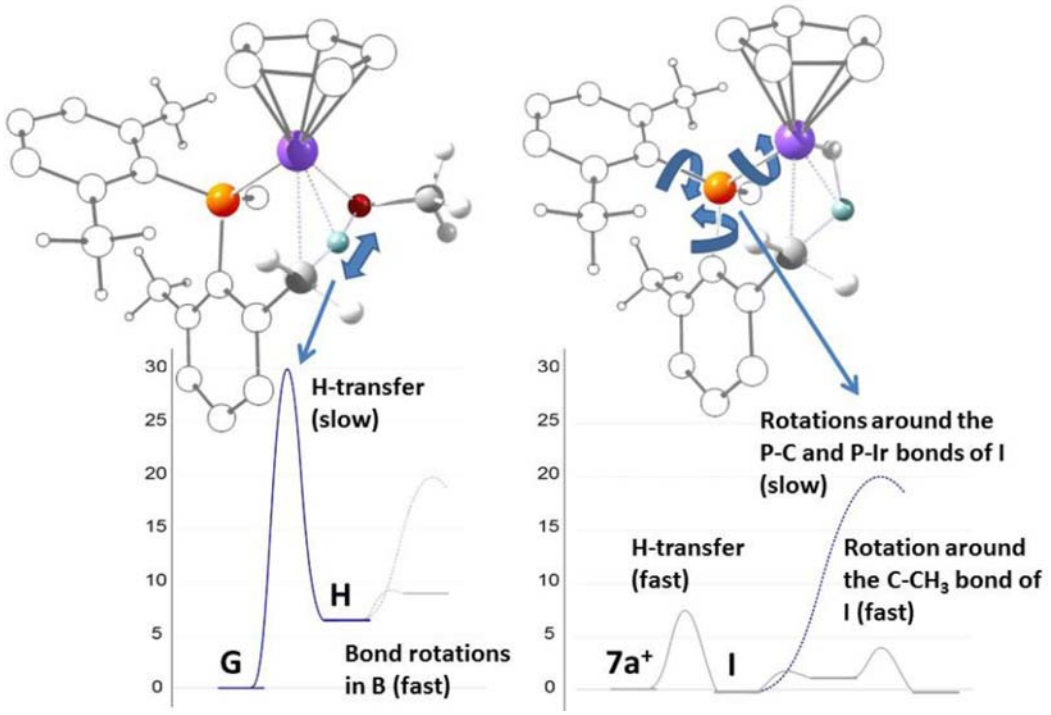


Figure 1. DFT-calculated potential energy profiles (ΔE, kcal·mol^{-1}) for H/D exchange in the chloride **2a** (**G**) and hydride **3a** (**7a**$^{+}$) complexes and DFT-optimized geometries (most hydrogens are omitted) of the transition states for the corresponding H transfer steps. This step is rate limiting for the reaction with **2a**, whereas it is fast for the reaction with **3a**.

transfer from the coordinated CD_3OD in cationic intermediate **G** to the Ir−CH_2 bond. The faster deuteration of the $PEtXyl_2$ derivative **2e** results probably from the larger steric requirements of the P-Et substituent in comparison with the P-Me

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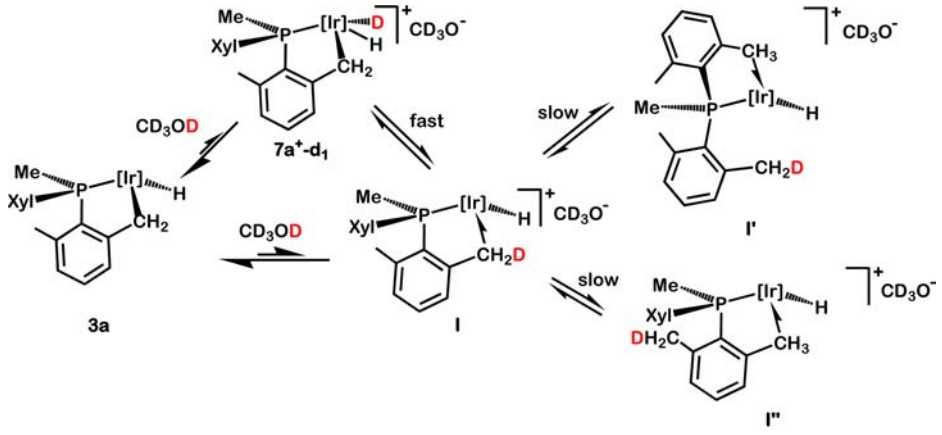
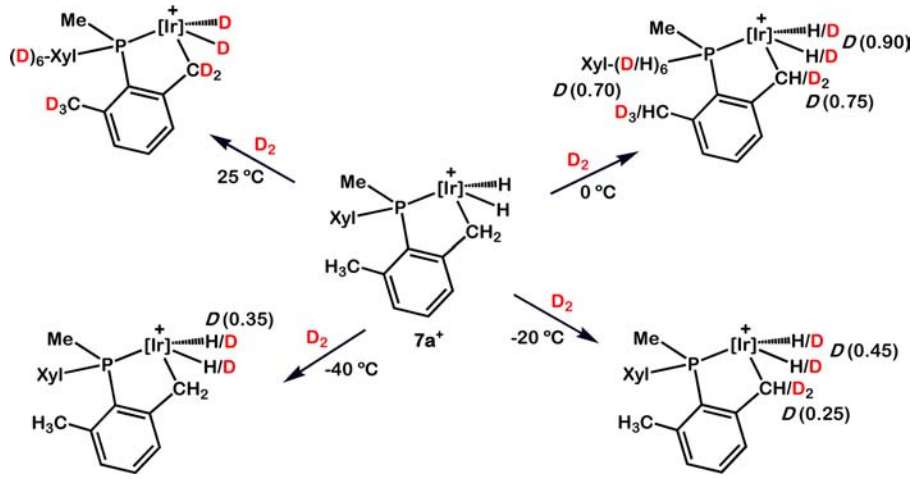
Scheme 12. Proposed Mechanism for the CD_3OD Deuteration of 3a



Scheme 13. H/D Exchange Reactions of $7a^+$ with D_2 at Variable Temperature, with a Reaction Time of 45 min



analogs of **2a**–**2d**. Electronic effects, although not manifested in the ν(CO) values of the cationic carbonyls $\mathbf{4}^+$, would also play into the same direction. The DFT calculations we have now developed for **2a** provided theoretical reinforcement of this proposal (Figure 1) and disclosed that the above D^+ transfer reaction needs to surmount a barrier of *ca.* 30 kcal·mol^{-1}. The resulting agostic structure **H** could experience C–H (or C–D) activation at all benzylic sites, following C_{Ar}–CH_3 and P–C_{Ar} bond rotations, along with the exchange of the aryl units. No transition states were located for C_{Ar}–CH_3, P–C_{Ar}, and Ir–P bond rotations. Accordingly, corresponding barriers (all below 20 kcal·mol^{-1}) were estimated by relaxed coordinate Potential Energy Surface (PES) scans.

All hydride compounds **3a**–**3e** underwent H/D exchanges with similar rates (CD_2Cl_2/CD_3OD mixtures, 20 °C; $t_{1/2}$ between 120 and 150 min) to give the corresponding d_3 isotopologues with specific deuterium incorporation at the Ir–H and Ir–CH_2 positions. The exchange was inhibited by added bases (NaOH or NaOMe) but was significantly enhanced by catalytic amounts of *p*-toluensulfonic acid or acetic acid, to the point that suffiently large H^+ concentrations (5×10^{-3} M, against 2.5×10^{-2} M of **2a**) led to immediate deuteration of all benzylic sites. Interestingly, an intermediate situation is observed when using lower concentrations of *p*-TsOH, which results in full deuteration of the hydride and methylene positions and only partial exchange at the non-metalated benzylic sites (i.e., with 1.5×10^{-3} M or 2×10^{-3} M of *p*-TsOH deuteration of Ir–H and Ir–CH_2 was immediate, whereas the half-life for *o*-CH_3 was around 650 and 150 min, respectively).

A plausible mechanism that explains these observations and is backed by the DFT calculations discussed below is shown in Scheme 12. The key assumption is that the protonation (deuteration) of **3a** by CD_3OD (to yield the hydride/deuteride species $\mathbf{7a}$–$\mathbf{d}^+$) as well as the formation of the cationic agostic hydride isotopomer **I** are fast, reversible processes, whereas the barriers for the exchange of the agostic and nonagostic methyl groups of the latter species (isotopomers **I**′ and **I**″, right-hand side of Scheme 12) are so large that they cannot be overcome at appreciable rates at very low concentrations of H^+/D^+ (pK_a of CH_3OH, 15.54), similarly to the results observed when using variable catalytic amounts of *p*-TsOH for the deuteration of **3a**. Indeed, DFT calculations disclose that protonation/deuteration of either the *Ir* or the Ir-*CH*$_2$ sites yields two fast-interconverting intermediates ($\mathbf{7a}^+$ and **I** in Scheme 12) with small and comparable forward and reverse barriers (*ca.* 7.6 and 7.9 kcal·mol^{-1} respectively). Then, whereas rotation around the C_{Ar}–CH_3 bond is facile (*ca.* 2.9 kcal·mol^{-1}), other rotations (P–C_{Ar} and Ir–P bonds) that would permit D incorporation into the remaining benzylic positions encounter significantly higher barriers (Figure 1).

To complete this isotopic exchange study, we analyzed the reactivity toward D_2 of the cationic bis(hydride) $\mathbf{7a}^+$, a key intermediate in the deuteration mechanistic path proposed in

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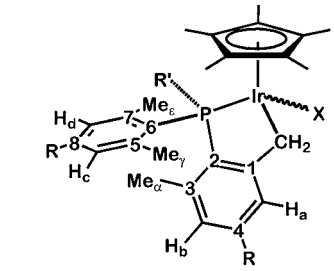
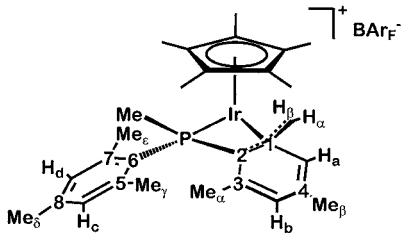
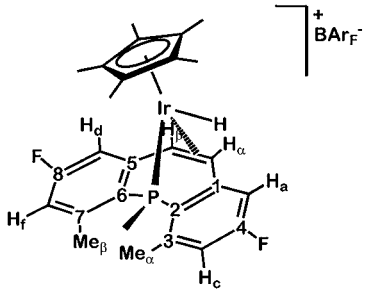
Scheme 14. Labeling Scheme for the ^{1}H and ^{13}C NMR Assignment of Compounds 2−7-BAr_F



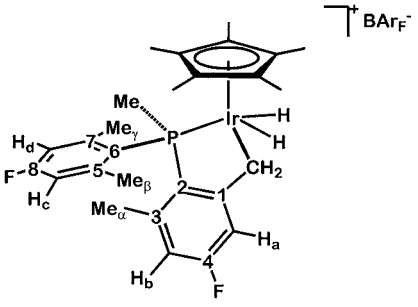
R' = Me; R = H, a; Me, b; OMe, c and F, d
R' = Et; R = H, e



5b-BAr_F



6d-BAr_F



7d-BAr_F

Scheme 12. As discussed earlier, $7a^+$, and the F-subtituted analog $7d^+$, undergo facile solution exchange by NMR of the two hydrides and the two Ir-CH_2 sites,[6d] with an energy barrier $\Delta G^{\ddagger} \approx 11$ kcal·mol^{-1} measured at 300 K (calculated $\Delta G^{\ddagger} \approx 10$ kcal·mol^{-1}). We set up four parallel experiments that were performed at temperatures of −40, −20, 0, and 25 °C. For each of them, $7a^+$ was generated by reacting a CD_2Cl_2 solution of $5a^+$ with H_2. Excess of the gas was eliminated by cooling with liquid N_2 and pumping under a vacuum, and the resulting solution of $7a^+$ was charged with 0.5 bar of D_2 and stirred for *ca.* 45 min at the desired temperature. Scheme 13 summarizes the results of this experiment, which induced deuterium incorporation only at the hydride position at −40 °C (no D-incorporation at all at −60 °C after stirring for 2 h) and at the hydride and methylene sites at −20 °C. Partial and complete C−H/C−D exchange at all benzylic positions took place at respectively 0 and 25 °C. These results are in excellent agreement with the mechanistic proposal of Scheme 12 regarding C−H/C−D exchanges in the hydride complexes **3**.

In summary, the use of the methyl- and ethyl-bis(aryl) phosphines $PR'Ar_2$, **1**, with differently substituted Ar groups does not seem to affect significantly the electronic properties of the Ir(III) complexes investigated. The existence of the two identical benzylic Ar units in the phosphine, one metalated and the other free, explains their facile solution exchange in the cationic, Lewis base-free complexes 5^+ and also seems responsible for the adoption of the rare κ^4-*P,C,C′,C″* binding mode of the metalated appendage. So far, this coordination mode remains unobserved in related complexes with only one benzylic Ar group. Additionally, these two substituents participate in an intramolecular, dehydrogenative, base-catalyzed C−C coupling reaction that culminates in the formation of a hybrid phosphine-olefin ligand.

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 $SiMe_4$ (δ 0 ppm) using the residual proton solvent peaks as internal standards (^{1}H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments), while $^{31}P\{^{1}H\}$ spectra were referenced to external H_3PO_4 [Scheme 14 gives the labeling scheme for the ^{1}H and ^{13}C NMR assignment of compounds **2**−7-BAr_F]. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. The dimer $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$,[23] $NaBAr_F$,[24] and 4-bromo-3,5-dimethylanisol[25] were prepared according to literature procedures, as well as complexes **2a**,[6b] **3a**,[6b] and **1**-H_2^+.[6d] In the ^{1}H NMR spectra, all aromatic couplings are of *ca.* 7.5 Hz, and signals corresponding to the BAr_F counterion were invariant for different complexes (CD_2Cl_2; δ 7.74 (s, 8 H, H_o), 7.57 (s, 4 H, H_p).

Synthetic procedures and characterization data for representative complexes are given below. Those for the remaining compounds studied can be found in the Supporting Information.

COMPUTATIONAL DETAILS

DFT calculations were performed with the Gaussian 09 package[26] and were carried out using Truhlar's hybrid meta-GGA functional M06.[27] The Ir atom was represented by the Stuttgart/Dresden Effective Core Potential and the associated basis set[28] 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.[29−31] 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

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Coordinate (IRC) calculations or by perturbing the transition states along the TS coordinate and optimizing to a minimum.

General Synthesis of Phosphine Ligands. Phosphine ligands were prepared according to the procedure depicted in Scheme 3. As a representative phosphine, the preparation of $PMe(Xyl)_2$ is described in detail in the SI. Other phosphines were prepared by the same procedure and isolated as white crystalline materials in yields of around 80%. In the case of $PEt(Xyl)_2$, a solution of EtMgBr was employed instead of the methyl Grignard reagent.

Synthesis of Chloride Complexes, 2. $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (1g, 1.25 mmol) was dissolved in dry CH_2Cl_2 (30 mL) in a Schlenk flask provided with a stir bar. The solution was cooled to 0 °C and the phosphine (2.5 mmol) dissolved in CH_2Cl_2 (10 mL) was added, followed by the addition of 2,2,6,6-tetramethyl piperidine (425 μL, 2.5 mmol). The reaction mixture was allowed to warm to room temperature and additionally stirred for 2 h. The solvent was then removed in vacuo and the product extracted with toluene in the air. The solution was evaporated to dryness and the solid washed with pentane to yield a bright yellow powder in *ca.* 70% yield. Complex **2c** was obtained as a mixture of two isomers (60:40). Crystallization from CH_2Cl_2/pentane (1:2) provided analytically pure samples of the desired products. **Compound 2b**. Anal. Calcd. for $C_{29}H_{39}ClIrP$: C, 53.9; H, 6.1. Found: C, 53.8; H, 6.2. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.12 (s, 1H, H_a), 6.91 (s, 1H, H_d), 6.66 (s, 1H, H_c), 6.57 (s, 1H, H_b), 3.64 (d, 1H, $^2J_{HH}$ = 14.9 Hz, IrC*H*H), 3.47 (dd, 1H, $^2J_{HH}$ = 14.7, $^3J_{HP}$ = 4.1 Hz, IrCH*H*), 2.56 (s, 3H, Me_ε), 2.25 (s, 3H, Me_δ), 2.23 (s, 3H, Me_β), 2.20 (d, 3H, $^2J_{HP}$ = 10.3 Hz, PMe), 1.91 (s, 3H, Me_α), 1.43 (d, 15H, $^4J_{HP}$ = 1.5 Hz, C_5Me_5), 1.42 (s, 3H, Me_γ). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C): δ 157.7 (d, $^2J_{CP}$ = 31 Hz, C_1), 141.5 (d, $^2J_{CP}$ = 9 Hz, C_5), 139.8 (d, $^2J_{CP}$ = 8 Hz, C_7), 139.5 (d, $^4J_{CP}$ = 2 Hz, C_4), 138.9 (d, $^4J_{CP}$ = 3 Hz, C_8), 138.8 (d, $^2J_{CP}$ = 3 Hz, C_3), 137.1 (d, $^1J_{CP}$ = 62 Hz, C_2), 130.6 (d, $^3J_{CP}$ = 8 Hz, CH_d), 130.3 (d, $^3J_{CP}$ = 8 Hz, CH_c), 128.2 (d, $^3J_{CP}$ = 7 Hz, CH_a), 128.0 (d, $^3J_{CP}$ = 15 Hz, CH_b), 127.6 (d, $^1J_{CP}$ = 48 Hz, C_6), 91.7 (d, $^2J_{CP}$ = 3 Hz, C_5Me_5), 25.2 (d, $^3J_{CP}$ = 5 Hz, Me_ε), 22.6 (d, $^3J_{CP}$ = 8 Hz, Me_γ), 20.7 (Me_δ), 20.6 (Me_β), 20.5 (IrCH_2), 20.3 (d, $^3J_{CP}$ = 3 Hz Me_α), 18.0 (d, $^1J_{CP}$ = 40 Hz, PMe), 8.0 (C_5Me_5). ^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ 9.2.

Synthesis of Hydride Complexes, 3. The corresponding chloride precursor **2b**−**2e** (0.153 mmol) was dissolved in THF (5 mL), and a solution of $LiAlH_4$ in THF (1M, 0.49 mL) was added under argon. The reaction mixture was heated at 45 °C for 2 h and quenched with H_2O (40 μL). The solvent was removed under a vacuum and the residue extracted with pentane and then evaporated to dryness, to provide the product as a pale yellow powder. Recrystallization from pentane yielded the product as pale yellow crystals. Complexes **3b**−**3d** were obtained in *ca.* 40% yield, whereas **3e** was isolated in *ca.* 70% yield. **Compound 3b**. Anal. Calcd. for $C_{29}H_{40}IrP$: C, 56.9; H, 6.6. Found: C, 56.4; H, 6.4. IR (Nujol): 2080 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.07 (s, 1H, H_a), 6.92 (s, 1H, H_d), 6.69 (s, 1H, H_c), 6.57 (s, 1H, H_b), 3.35 (dt, 1H, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = $^3J_{HP}$ = 2.9 Hz, IrC*H*H), 2.80 (d, 1H, $^2J_{HH}$ = 15.2 Hz, IrCH*H*), 2.55 (s, 3H, Me_ε), 2.28 (s, 3H, Me_δ), 2.27 (s, 3H, Me_β), 2.23 (d, 3H, $^2J_{HP}$ = 9.9 Hz, PMe), 1.90 (s, 3H, Me_α), 1.70 (s, 15H, C_5Me_5), 1.43 (s, 3H, Me_γ), −17.81 (d, 1H, $^2J_{HP}$ = 34.4 Hz, Ir-*H*). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C): δ 160.3 (d, $^2J_{CP}$ = 31 Hz, C_1), 142.0 (d, $^2J_{CP}$ = 9 Hz, C_5), 141.3 (d, $^1J_{CP}$ = 62 Hz, C_2), 139.7 (d, $^2J_{CP}$ = 8 Hz, C_7), 139.4 (C_3), 139.3 (C_8), 138.6 (C_4), 130.8 (d, $^3J_{CP}$ = 8 Hz, CH_d, CH_c), 129.5 (d, $^1J_{CP}$ = 41 Hz, C_6), 128.3 (d, $^3J_{CP}$ = 7 Hz, CH_b), 127.7 (d, $^3J_{CP}$ = 14 Hz, CH_a), 92.1 (d, $^2J_{CP}$ = 3 Hz, C_5Me_5), 31.4 (d, $^1J_{CP}$ = 45 Hz, PMe), 25.5 (d, $^3J_{CP}$ = 4 Hz, Me_ε), 21.8 (d, $^3J_{CP}$ = 9 Hz, Me_γ), 21.2 (Me_β, Me_δ), 20.9 (Me_α), 9.8 (C_5Me_5), 3.8 (IrCH_2). ^{31}P{^{1}H} NMR (160 MHz, C_6D_6, 25 °C): δ 6.1.

Synthesis of 4b$^+$−4e$^+$. To a solid mixture of the corresponding chloride precursor **2b**−**2e** (0.08 mmol) and $NaBAr_F$ (0.08 mmol) placed in a thick-wall vessel was added 5 mL of CH_2Cl_2. The reaction mixture was stirred for 10 min at room temperature under 1.5 bar of CO. The solution was filtered, and the solvent was then evaporated under reduced pressure to obtain pale white (**4e-BAr$_F$**) or yellow powders in ca. 95% yield. These complexes can be recrystallized from a 1:2 mixture of CH_2CL_2/pentane. **Compound 4b$^+$**. HRMS (FAB), *m*/*z* calcd. for $C_{30}H_{39}IrOP$: 639.2365. Found: 639.2368. IR (Nujol): 2032 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.26, 7.14, 6.93, 6.90 (br. s., 1H each, $H_{a/b/c/d}$), 3.68 (dd, 1H, $^2J_{HH}$ = 14.1, $^3J_{HP}$ = 2.7 Hz, IrC*H*H), 3.15 (d, 1H, $^2J_{HH}$ = 14.0, IrCH*H*), 2.60 (d, 3H, $^2J_{HP}$ = 10.0 Hz, PMe), 2.55, 2.39, 2.36, 2.06, 1.48 (s, 3H each, $Me_{\alpha/\beta/\gamma/\delta/\varepsilon}$), 1.80 (d, 15H, $^4J_{HP}$ = 2.0 Hz, C_5Me_5). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ 167.2 (d, $^2J_{CP}$ = 11 Hz, CO), 153.4 (d, $^2J_{CP}$ = 27 Hz, C_1), 142.9, 142.8 (d, $^4J_{CP}$ = 3 Hz, $C_{4/8}$), 141.8 (d, $^2J_{CP}$ = 10 Hz, $C_{5/7}$), 140.6 (d, $^2J_{CP}$ = 10 Hz, $C_{5/7}$), 139.9 (d, $^2J_{CP}$ = 4 Hz, C_3), 133.3 (d, $^1J_{CP}$ = 68 Hz, C_2), 131.8, 131.6, 130.8 (d, $^3J_{CP}$ = 9 Hz, $CH_{b/c/d}$), 127.1 (d, $^3J_{CP}$ = 15 Hz, CH_a), 120.3 (d, $^1J_{CP}$ = 54 Hz, C_6), 102.4 (d, $^2J_{CP}$ = 2 Hz, C_5Me_5), 25.1 (d, $^3J_{CP}$ = 6 Hz, $Me_{\gamma/\varepsilon}$), 25.0 (d, $^1J_{CP}$ = 47 Hz, PMe), 22.9 (d, $^3J_{CP}$ = 8 Hz, $Me_{\gamma/\varepsilon}$), 20.5 ($Me_{\alpha/\delta}$), 20.0 (d, $^4J_{CP}$ = 4 Hz, Me_β), 10.3 (IrCH_2), 8.1 (C_5Me_5). ^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ 0.18.

Synthesis of 5d-BAr$_F$. To a mixture of **2d** (100 mg, 0.15 mmol) and $NaBAr_F$ (133 mg, 0.15 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 resulting suspension was filtered and the solvent evaporated under reduced pressure to obtain compounds **5-BAr$_F$** as yellow solids in *ca.* 95% yield. For further purification, the complexes can be crystallized from a 1:2 mixture of CH_2Cl_2/pentane. **Compound 5d-BAr$_F$**. ^{1}H NMR (400 MHz, CD_2Cl_2, −60 °C): δ 7.23 (d, 1H, $^3J_{HF}$ = 7.9 Hz, H_a), 6.76 (d, 1H, $^3J_{HF}$ = 6.8 Hz, $H_{c/d}$), 6.68 (d, 1H, $^3J_{HF}$ = 7.9 Hz, $H_{c/d}$), 6.45 (d, 1H, $^3J_{HF}$ = 8.7 Hz, H_b), 3.01 (t, 1H, $^2J_{HH}$ = $^3J_{HP}$ = 4.7 Hz, IrCH_α), 2.45 (s, 6H, Me_α, Me_γ), 2.18 (d, 3H, $^2J_{HP}$ = 12.6 Hz, PMe), 2.05 (s, 3H, Me_β), 1.66 (s, 15H, C_5Me_5), 1.21 (dd, 1H, $^2J_{HH}$ = 5.5, $^3J_{HP}$ = 16.2 Hz, IrCH_β). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 6.94 (m, 4H, $H_{a/b/c/d}$), 2.43 (br. s, 11H, Me_α, Me_β, Me_γ, IrCH_2), 2.31 (d, 3H, $^2J_{HP}$ = 12.7 Hz, PMe), 1.85 (d, 15H, $^4J_{HP}$ = 2.0 Hz, C_5Me_5). ^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ −44.2 (br. s). ^{19}F{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ −104.8 (br. s).

Synthesis of 6d-BAr$_F$. A mixture of **2d** (100 mg, 0.15 mmol) and $NaBAr_F$ (133 mg, 0.15 mmol) placed in a Schlenk flask was suspended in CH_2Cl_2 (5 mL) under argon. A saturated aqueous solution of $NaHCO_3$ (5 μL) 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 **6d-BAr$_F$** in 90% yield. For further purification, **6-BAr$_F$** can be recrystallized from a 1:1 mixture of CH_2Cl_2/pentane. **Compound 6d-BAr$_F$**. IR (Nujol): 2140 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.12 (m, 2H, H_a, H_d), 6.76, 6.69 (d, 1H each, $^3J_{HF}$ = 9.2 Hz, H_b, H_c), 4.89 (dd, 1H, $^3J_{HH}$ = 8.7 Hz, $^4J_{HP}$ = 4.1 Hz, CH_α), 4.42 (d, 1H, $^3J_{HH}$ = 8.5 Hz, CH_β), 2.59 (d, 3H, $^2J_{HP}$ = 13.2 Hz, PMe), 2.53, 2.50 (s, 3H each, Me_α, Me_β), 2.01 (s, 15H, C_5Me_5), −12.93 (d, 1H, $^2J_{HP}$ = 27.9 Hz, Ir*H*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ 164.1 (d, $^1J_{CF}$ = 251 Hz, $C_{4/8}$), 163.3 (d, $^1J_{CF}$ = 257 Hz, $C_{4/8}$), 150.8 (C_5), 146.6 (C_1), 139.3, 138.4, 135.4, 134.8 (C_2, C_3, C_6, C_7), 117.7, 117.0 (dd, $^2J_{CF}$ = 21, $^3J_{CP}$ = 11 Hz, CH_b, CH_c), 114.0 (dd, $^2J_{CF}$ = 23, $^3J_{CP}$ = 16 Hz, $CH_{a/d}$), 112.3 (dd, $^2J_{CF}$ = 22, $^3J_{CP}$ = 11 Hz, $CH_{a/d}$), 100.7 (C_5Me_5), 61.4 (t, $^4J_{CF}$ = $^2J_{CP}$ = 3 Hz, CH_β), 54.8 (dd, $^2J_{CP}$ = 8, $^4J_{CF}$ = 2 Hz, CH_α), 22.2, 21.7 (Me_α, Me_β), 12.3 (d, $^1J_{CP}$ = 37 Hz, PMe), 9.1 (C_5Me_5). ^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ 6.3. ^{19}F{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ −34.2, −34.9.

Synthesis of 7d-BAr$_F$. To a mixture of **2d** (100 mg, 0.15 mmol) and $NaBAr_F$ (142 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. Workup of the reaction in the absence of hydrogen led to the release of H_2 and formation of **5d-BAr$_F$**. Thus, characterization of **7d-BAr$_F$** by 1D- and 2D-NMR spectroscopy was carried out in a Young NMR tube under a H_2 atmosphere. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, H_2 atmosphere): δ 7.12 (dt, 1H, $^4J_{HP}$ = 1.8, $^3J_{HF}$ = 8.9 Hz, H_a), 7.06 (dt, 1H, $^4J_{HP}$ = 2.9, $^3J_{HF}$ = 9.0 Hz, $H_{c/d}$), 6.91 − 6.79 (m, 2H, H_b, $H_{c/d}$), 2.61 (s, 3H, $Me_{\beta/\gamma}$), 2.57 (d, 3H, $^2J_{HP}$ = 10.4 Hz, PMe), 2.01 (s, 3H, Me_α), 1.84 (d,

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15H, $^4J_{HP}$ = 1.7 Hz, C_5Me_5), 1.55 (s, 3H, $Me_{\beta/\gamma}$), −4.55 (br. s, 4H, $IrCH_2$, Ir−H_2). ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C, H_2 atmosphere): δ 7.02 (d, 1H, H_a), 6.91 (d, 1H, $H_{c/d}$), 6.67 − 6.63 (m, 2H, H_b, $H_{c/d}$), 3.90 (d, 1H, $^2J_{HH}$ = 14.4 Hz, IrC*H*H), 3.32 (d, 1H, $^2J_{HH}$ = 14.4 Hz, IrCH*H*), 2.47 (m, 6H, $Me_{\beta/\gamma}$, PMe), 1.91 (s, 3H, Me_α), 1.66 (s, 15H, C_5Me_5), 1.35 (s, 3H, $Me_{\beta/\gamma}$), −12.77 (s, 1H, Ir*H*H), −13.10 (d, 1H, $^2J_{HP}$ = 16.1 Hz, IrCH*H*). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C, H_2 atmosphere): δ 165.3 (d, $^1J_{CF}$ = 254 Hz, C_4), 163.9 (d, $^1J_{CF}$ = 255 Hz, C_8), 155.4 (dd, $^2J_{CP}$ = 32, $^4J_{CF}$ = 9 Hz, C_1), 144.4 (dd, $^2J_{CP}$ = 9, $^3J_{CF}$ = 11 Hz, $C_{7/5}$), 143.4 (t, $^2J_{CP}$ = $^3J_{CF}$ = 10 Hz, $C_{7/5}$), 141.8 (dd, $^2J_{CP}$ = 5, $^3J_{CF}$ = 9 Hz, C_3), 131.7 (dd, $^1J_{CP}$ = 68, $^4J_{CF}$ = 2 Hz, C_2), 119.0 (br. d, $^1J_{CP}$ = 46 Hz, C_6), 117.9, 117.4, 116.8 (dd, $^3J_{CP}$ = 10, $^2J_{CF}$ = 21 Hz, CH_c, CH_d, CH_b), 112.6 (dd, $^3J_{CP}$ = 18, $^2J_{CF}$ = 21 Hz, CH_a), 104.0 (C_5Me_5), 29.5 (br. d, $^1J_{CP}$ = 65 Hz, PMe), 24.7 (d, $^3J_{CP}$ = 5 Hz, $Me_{\beta/\gamma}$), 23.3 (d, $^3J_{CP}$ = 7 Hz, $Me_{\beta/\gamma}$), 20.2 (d, $^3J_{CP}$ = 3 Hz, Me_α), 9.9 (br. s, $IrCH_2$), 8.5 (C_5Me_5). ^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ 0.9 (br. s). ^{19}F{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ −108.8 (br. s).

■ ASSOCIATED CONTENT

Supporting Information

General synthesis, analytical, and spectroscopic data of phosphine ligands; analytical and spectroscopic data of complexes **2c**−**2e**, **3c**−**3e**, **4c**$^+$−**4e**$^+$, **5d**$^+$, **5e**$^+$, and **6d**$^+$; hydrogen/deuteration exchange reactions; X-ray structure analysis of **4e**$^+$; tables of the optimized geometries (Cartesian coordinates, in Ångstroms) for the calculated species. 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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■ DEDICATION

Dedicated to Professor Antonio Laguna on the occasion of his 65th birthday.

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