

Synthesis and Reactivity Studies of Cationic Ir(III) Alkylidines. α -Hydride Abstraction Reactions

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*In memory of Professor Roberto Sánchez Delgado, dear friend and outstanding
leader and scientist.*

Abstract

The chemistry of late transition metal alkylidenes $[M=CR_2]$, where R is H or a hydrocarbyl group, have attracted widespread attention although mainly with reference to complexes of metals in low oxidation state. We focus in this paper on reactions based on electrophilic attacks by Ph_3C^+ that allow either isolation of stable cationic Ir(III) alkylidenes, considerably more attractive than well-known Ir(I) counterparts, or the generation of very reactive variants that experience fast migratory insertion into existing Ir-C and Ir-H sigma bonds. The present studies are based on $(\eta^5-C_5Me_5)Ir(III)$ complexes that bear a cyclometalated $PMeXyl_2$ ligand ($Xyl = 2,6-Me_2C_6H_3$). The contribution of different monoanionic ligands (chloride, alkyl or hydride) to either stabilize the $Ir=CR_2$ linkage or provide facile reactivity routes has been investigated, including the use of various deuterium isotopologues of the iridium complex precursors.

Introduction

Carbenes have been widely utilized as spectator ligands since the development of N-heterocyclic carbenes (NHCs)¹ and more recently of the related cyclic (alkyl)(amino)carbenes (CAACs),² owing to their synthetic availability, the facility of modulating their steric and electronic properties and not least the kinetic and thermodynamic stability they confer to transition metal complexes. Together with cyclopentadienyls, tertiary phosphines and related P-donors, carbenes have become ubiquitous in transition metal chemistry including applications in homogeneous

catalysis.¹ Besides, the rich reactivity of the M=C bond places metal carbenes in a prominent position in organometallic chemistry.

Carbocyclic³ and heteroatom-stabilized carbenes (CRX; X = OR', NR'₂ and other groups)^{4,5} have been amply investigated and their reactivity comprehensively analyzed.^{6,7} A highly attractive and important group of carbenes are the so-called alkylidenes, examples of which are discussed in this article. With an ever growing number of carbene complexes of diverse reactivity, some confusion about their nomenclature has arisen. It is, therefore, pertinent to clarify that in accordance with IUPAC nomenclature, alkylidene complexes contain a M=CRR' bond where R, R' are hydrogen, alkyl, aryl and the like.⁸ At variance with Fischer carbenes, that hold one or two heteroatoms bonded to the carbene atom, metal alkylidenes cannot be classified in a general manner as electrophilic or nucleophilic, for M=CRR' termini of the two types exist depending on the metal, the carbene ligand and the other ligands of the complex. The capacity of metal alkylidenes to exhibit Fischer- (electrophilic) or Schrock-type (nucleophilic) reactivity has been widely exploited in homogeneous catalysis, most notably in an ample variety of olefin metathesis reactions.⁹

Although metal alkylidenes of late transition elements including iridium are typically stabilized by low oxidation states,^{10,11} over the years, our group studied the chemistry of Ir(III) complexes of hydrotris(pyrazolyl)borate ligands with carbenes of both the :CRR' and :CRX types.^{4a,b} The Ir-carbene unit was in many cases generated by double C-H bond activation reactions and we further authenticated unusual alkene-to-alkylidene reversible rearrangements involving reversible α - and β -hydrogen elimination reactions.¹² Ir(III) alkylidenes, particularly cationic variants, are highly electrophilic¹³ and have been proposed as reactive intermediates for several relevant transformations,¹⁴ including the cleavage of carbon-fluorine¹⁵ and carbon-carbon¹⁶ bonds.

Pursuing these studies further and following the pioneer work of Bergman and coworkers in the use of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{Me})(\text{PMe}_3)(\text{S})]^+$ for the selective activation of C-H bonds¹⁷ (S = solvent), we recently showed that $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{III})$ complexes of dialkylxylyl phosphines, $\text{PR}_2(\text{Xyl})$ (R = *i*Pr, Cy; Xyl = 2,6-Me₂C₆H₃),¹⁸ allowed isolation of stable cationic Ir(III) alkylidenes (structure **A** in Figure 1) in reactions that required the activation of two benzylic C-H bonds.¹⁹ Under similar conditions the related PMeXyl_2 ligand afforded the cyclometalated structure **B** (Figure 1) with uncommon $\eta^4\text{-P}$ -pseudoallyl coordination of the metalated ligand.²⁰ Further reactivity resulted in bicyclic complex **C** from which α -hydride abstraction by Ph_3C^+ led first to the

alkyl-alkylidene **D** and ultimately to an intriguing hydride phosphepine complex (not shown in Figure 1) by migratory insertion of the alkylidene into the iridium alkyl bond.²⁰ Related Ph_3C^+ promoted C-C bond forming reactions have been disclosed recently by our group.²¹

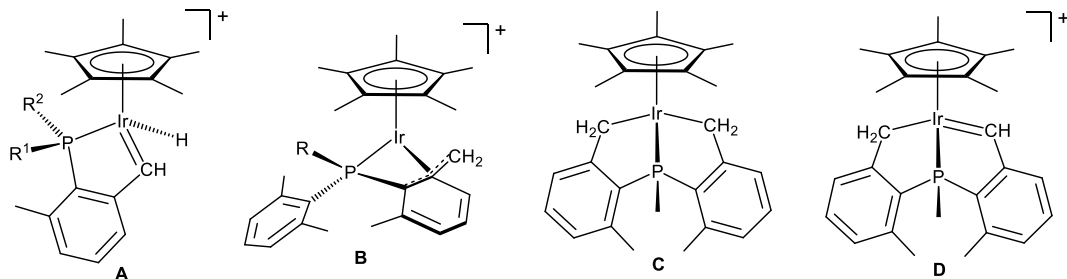


Figure 1. Previous examples from our group of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(III)}$ structures containing cyclometallated xylyl phosphine ligands.

Such electrophilic attacks to carbon-based ligands are important reactions that occur often without cleavage of the metal-carbon bond.^{22,23} Specifically, action of Ph_3C^+ on a metal-alkyl bond is known to yield a metal-carbene in a process thought to occur with initial electron transfer from the metal to Ph_3C^+ , followed by $\alpha\text{-H}$ atom transfer.²⁴ We thought of interest to broaden further recent related reactivity studies on platinum²⁵ and iridium^{10e} complexes, and in this paper we have extended these investigations, concentrating attention on the four $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(III)}$ complexes shown in Figure 2. As discussed later, some stable cationic Ir(III) alkylidenes have been isolated, along with somewhat related hydride alkene complexes. In addition, other C-C bond coupling reactions implicating transient carbenes derived from diazo compounds²⁶ have been investigated.

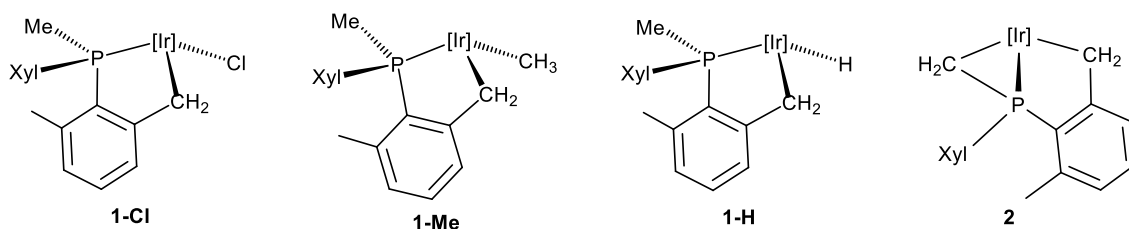


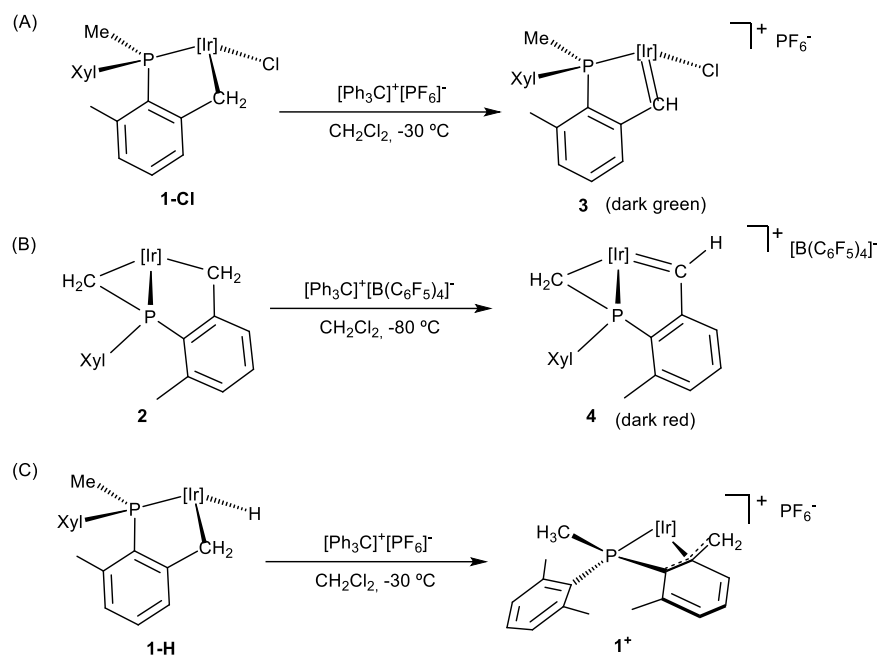
Figure 2. Ir(III) metalacycles studied in this work ($[\text{Ir}] = (\eta^5\text{-C}_5\text{Me}_5)\text{Ir}$)

Results and Discussion

Ph_3C^+ promoted hydride abstraction reactions

The four Ir(III) complexes selected for this work (Figure 2) contain a five-member phosphine-alkyl metalacycle that results from metalation of a δ benzylic bond of a PMeXyl_2 ligand.¹⁸ Chloride **1-Cl** was the parent complex within this family, whereas **1-H** and **1-Me** are the corresponding hydride and methyl derivatives. Compound **2**, that resulted from the reaction of **1-Cl** with LiBu^n ,^{18a} is an unusual bis(iridacycle) that besides the common five member iridacycle holds an unusual three member $\text{Ir-CH}_2\text{-P}$ moiety that stems from the metalation of the P-Me bond. Clearly, as the four possess an Ir-CH₂ bond within the five member ring they are prone to undergo α -H abstraction. But in addition, **1-Me** and **2** bear another iridium-alkyl bond that could compete with the Ir-CH₂ metalacyclic bond for electrophilic attack by Ph_3C^+ . Moreover, complex **1-H** may also experience α -hydride abstraction at the Ir-H bond, which is a common reaction of metal hydrides^{22,23} that appears to imply a single-step hydride transfer.²⁷

Scheme 1 summarizes the outcome of the low-temperature reactions of complexes **1-Cl** (A), **2** (B) and **1-H** (C), with trityl salts, $[\text{Ph}_3\text{C}]^+[\text{X}]^-$ ($\text{X} = \text{PF}_6$ or $\text{B}(\text{C}_6\text{F}_5)_4$). In all cases a single reaction product was obtained though, as discussed later, formation of complex **1⁺** from **1-H** is more complex than may be inferred from Scheme 1C. At variance with these observations, the analogous reaction of **1-Me** (Scheme 2) gives a mixture of products and will be analyzed separately.



Scheme 1. α -Hydride abstraction from neutral compounds **1-Cl**, **1-H** and **2**.

Compounds **1-Cl** and **2** underwent formal α -hydride abstraction at the Ir-CH₂ bond of their five member metalacycle forming the cationic alkylidene complexes **3** and **4**, respectively. No reaction of the P-bonded methylene group of **2** was detected at -80 °C or at room temperature despite literature precedent for such reactivity.²⁸ Regarding the formation of the pseudo-allylic complex **1⁺** as in Scheme 1C, it is consistent with either direct Ir-H transfer to Ph₃C⁺, or formation of an unobserved hydride alkylidene related to complex **3**, followed by hydride attack to the highly electrophilic alkylidene carbon atom.^{20b} Migratory insertion reactivity could also be expected for the cationic alkylidene complex **4**. Indeed the somewhat related alkylidene **D** of Figure 1 was found to undergo facile C-C bond coupling with formation of an unusual hydride phosphine complex.^{20b,c} It appears that the analogous C-C coupling in **4** is thwarted by the rigidity of its three-membered alkyl unit that would require an energetically prohibited transition state.

Solutions of compounds **3** and **4** exhibit characteristic intense green and red colors, respectively, reminiscent of our previously synthesized Ir(III) alkylidene species **A** and **D** (Scheme 1).^{15,16b} The thermal stability of compounds **3** and **4** is remarkable when considering prior examples of late transition metal electrophilic alkylidenes. Compounds **3** and **4** are stable under inert atmosphere in the solid state for long periods of time, and in dichloromethane solutions exhibit $t_{1/2}$ of several days at 25 °C. The two compounds are characterized (Figure 3) by a deshielded ¹H NMR alkylidene signal at 16.61 (**3**, d, ³J_{HP} = 0.9 Hz) and 14.9 ppm (**4**, s), respectively, which are shifted by *ca.* 11 – 13 ppm with respect to the peaks due to the diastereotopic Ir-CH₂ protons of **1-Cl** and **2**. The corresponding ¹³C{¹H} signals are found at 262.4 and 243.7 (²J_{CP} = 28 Hz) ppm, respectively, with the former featuring a one-bond C-H coupling constant of 153 Hz, in agreement with the alkylidene formulation. A marked variation in the ³¹P{¹H} spectrum of **4** (-13.1 ppm) when compared to **2** (-41.6 ppm) is observed that is more significant than for the chloride compounds (from 11.3 in **1-Cl** to 20.8 ppm in **3**). Other spectroscopic data matched those of our related and previously synthesized complexes (see Experimental Section).

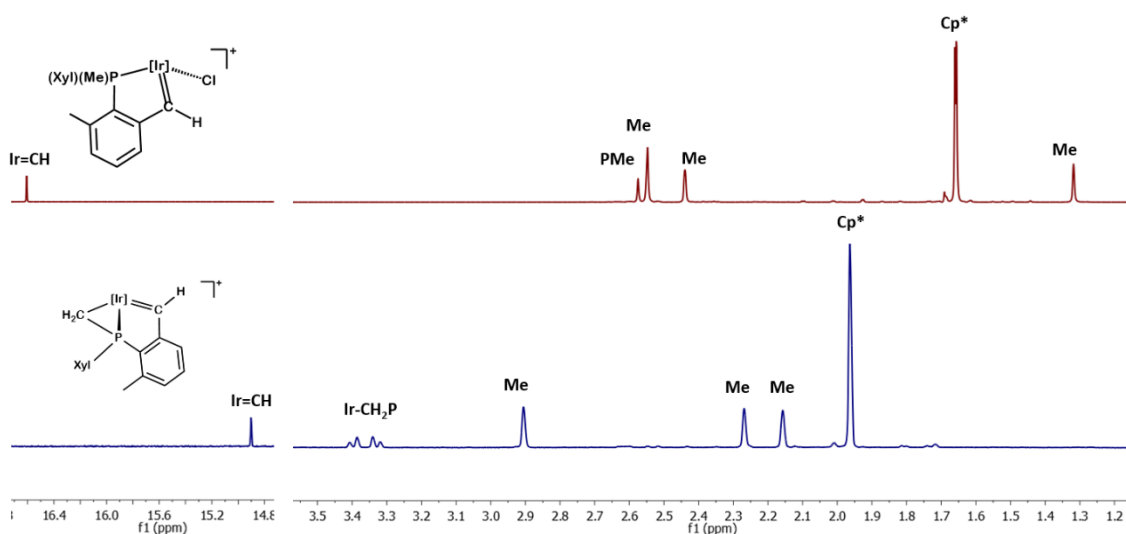


Figure 3. ^1H NMR (500 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) spectra of cationic alkylidenes **3** and **4**.

Single crystals of **3** and **4** suitable for X-ray studies were obtained by slow diffusion of pentane into dichloromethane solutions of the complexes at -20 $^\circ\text{C}$. A characteristically short Ir1–C17 bond distance was measured for both compounds (1.899(5) Å, (**3**); 1.905(4) Å, (**4**)), that compares well to the analogous distance in compounds of type **A** in Figure 1 (1.896(5) and 1.907(2) Å),¹⁹ whereas the average Ir–C distance in our previously reported neutral and cationic alkyl complexes of similar structures is significantly longer (*ca.* 2.12 Å)^{18b,20b,c}. As shown in Figure 4, X-ray crystallography unequivocally confirms that hydride abstraction from **2** occurred from the Ir–CH₂ methylene group within the five-membered ring, whereas the metallated P–Me group remained unaltered. The P1–C27 bond distance (1.750(4) Å) is slightly shorter than the other two P1–C bonds (*ca.* 1.80 Å), most likely due to the partial double-bond character of the P1–C27 unit.²⁹ The strain within the three-membered metallacycle is clearly reflected by the acute P1–Ir1–C27 angle of 46.84°, less than half the value that would correspond to a tetrahedral environment around the P1 atom.

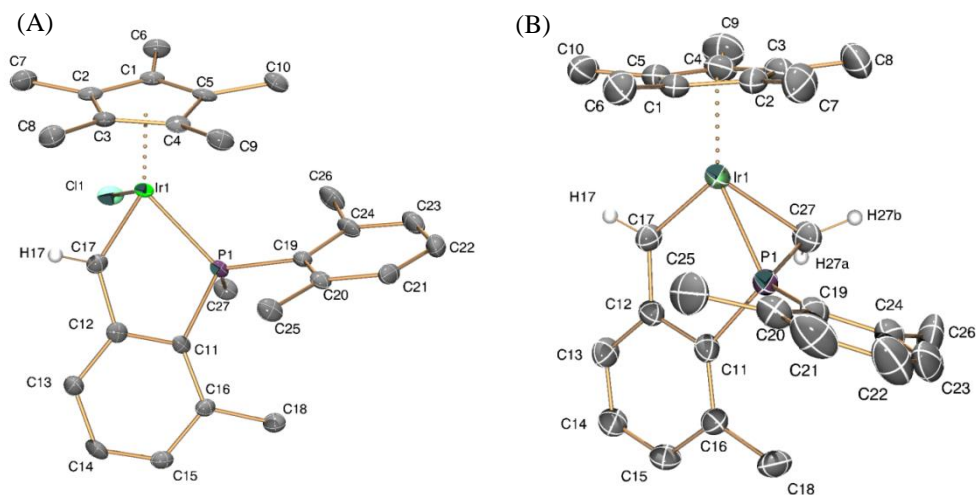
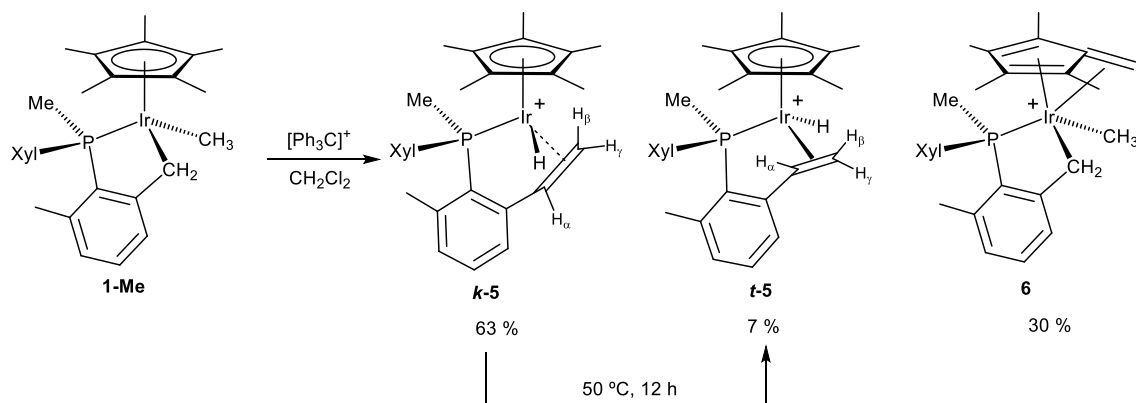


Figure 4. ORTEP diagrams for complexes **3** (A) and **4** (B). Thermal ellipsoids are drawn at the 50 % probability. Most hydrogen atoms and counterions have been omitted for clarity.

As noted briefly, the reaction of complex **1-Me** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ yielded a variety of products (Scheme 2). Two of them were diastereomeric hydride alkene complexes stemming from Ph_3C^+ -promoted C-C bond forming reactions (notice the existence of three stereogenic centers in the molecules of **5**, which are chiral at Ir, P and the CH carbon of the coordinated olefin). The third product, rather oddly unobserved in the reactions of the other complexes investigated (Scheme 1), resulted from β -hydride abstraction from one of the C_5Me_5 methyl groups and afforded the permethylated fulvene complex **6**.³⁰ The reaction of Scheme 2 was started at 0°C, and after stirring at room temperature for 30 minutes afforded a kinetic mixture of isomers *k*-**5**, *t*-**5** and **6** in a *ca.* 63:7:30 proportion. Since further stirring at room temperature did not change the *k*-**5**:*t*-**5** ratio, it can be concluded that they form along independent, competitive reaction paths. As discussed later, complex *k*-**5** derived from electrophilic attack at the Ir-CH₃ bond, while *t*-**5** resulted from an α -H abstraction reaction involving the Ir-CH₂ unit. This kinetic mixture of diastereomers **5** converted into the thermodynamic isomer *t*-**5** upon heating at 50 °C for 12 h. ³¹P{¹H} NMR monitoring at 40 °C gave a first order rate constant of $1.4 \cdot 10^{-5} \text{ s}^{-1}$ (see Figure S1), from which a ΔG^\ddagger value of $25.3 \pm 0.1 \text{ kcal} \cdot \text{mol}^{-1}$ was deduced. Related isomerization reactions of Ir(III) hydride alkene complexes have been extensively studied by our group³¹ and accordingly the present system was not further investigated.



Scheme 2. Reaction of **1-Me** with $[\text{Ph}_3\text{C}]^+$ and isomerization of **5**.

Compounds **t-5** and **k-5** are characterized by ^1H NMR signals at -15.77 (d, $^2J_{\text{HP}} = 30.1$ Hz) and -14.31 (d, $^2J_{\text{HP}} = 28.5$ Hz) ppm, respectively, due to the iridium hydride group. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra peaks at -0.1 and -9.8 ppm appear due to the thermodynamic and kinetic isomers, respectively. For the former, the olefin moiety features three ^1H NMR signals at 4.27 (dd), 2.83 (dt) and 2.64 (dd) ppm, due to H_α , H_γ and H_β , respectively. Coupling constants are in agreement with the formulation depicted in Scheme 2, with values of 10.5 and 8.6 Hz for the three-bond H–H coupling of *trans* ($\text{H}_\alpha\text{-H}_\gamma$) and *cis* ($\text{H}_\alpha\text{-H}_\beta$) protons, whereas the geminal $^2J_{\text{HH}}$ coupling between H_β and H_γ amounts 2.4 Hz. No coupling to the phosphorous nucleus is observed, except for H_γ , which exhibits a three-bond coupling of *ca.* 2.4 Hz. Corresponding $^{13}\text{C}\{^1\text{H}\}$ NMR signals appear strongly deshielded with respect to **1-Me** (which exhibits resonances at 16.9 and -22.9 ppm for Ir-CH_2 and Ir-CH_3 , respectively), with values of 62.7 (CH_α) and 34.1 ($\text{CH}_\beta\text{H}_\gamma$) ppm, as expected for olefinic C^{13} nuclei. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signals due to the kinetic isomer are similar to those of the thermodynamic one. The formulation depicted in Scheme 2 for the two diastereomers was tentatively inferred from 2D-NOE experiments. Compound **t-5** exhibits an intense NOE cross-peak between Ir-H and P-Me , thus suggesting that both groups lie in a *syn* conformation. However, this cross-peak is absent in **k-5**, which might suggest an *anti* arrangement of both functionalities. As represented in Figure 5, the structures suggested for isomers **5** were further confirmed by X-ray crystallography. These studies evidenced not only the formation of the new C–C double bond ($1.470(13)$ and $1.473(10)$ Å for **k-5** and **t-5**, respectively), but also the *syn* (**k-5**) vs *anti* (**t-5**) orientation of the Ir-H and P-Me units, without any other discernible structural differences. Other geometrical parameters are in agreement with previously discussed molecular structures of related compounds.¹⁸⁻²⁰

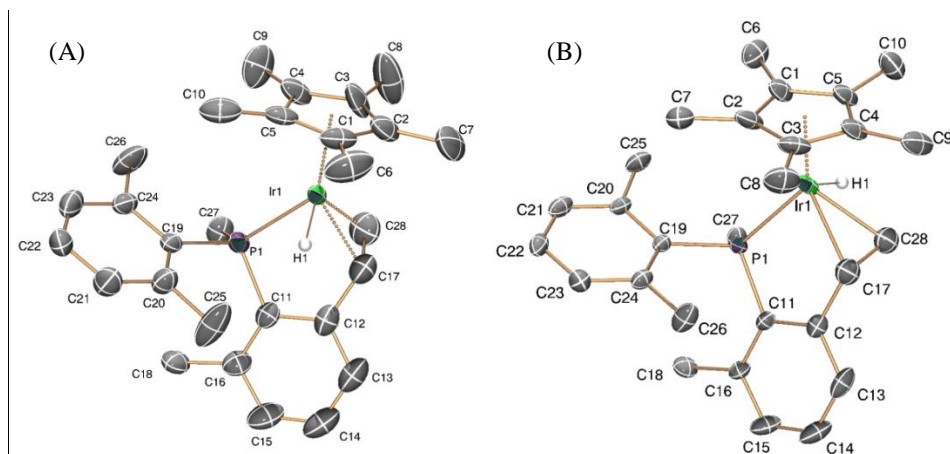


Figure 5. ORTEP diagrams for complexes for the two diastereomers of compound **5**: (A) kinetic isomer *k-5*; (B) thermodynamic isomer *t-5*. Thermal ellipsoids are drawn at the 50 % probability. Hydrogen atoms (except Ir–H) and counterions have been omitted for clarity.

Attempts to isolate pure complex **6** were unsuccessful. The proposed formulation is therefore tentative although finds strong support on NMR data recorded for its mixtures with isomer *t-5*. Figure 6 shows the ^1H NMR spectrum in the region *ca.* 3 – 0.5 ppm for a *ca.* 6:4 mixture of complexes *t-5* and **6** that resulted from several attempts of fractional crystallization. The appearance of some distinctive signals due to the presence of a 1,2,3,4-tetramethylfulvene moiety provides strong support to the proposed formulation. In particular, olefinic resonances at 5.30 (d, $^4J_{\text{HP}} = 4.2$ Hz) and 4.54 ppm attributed to the CH_2 terminus, and at 1.80, 1.75, 1.57 and 0.76 ppm due to inequivalent methyl groups, each with the expected relative intensity and moreover exhibiting four-bond coupling to the ^{31}P nucleus (1.4 - 2.8 Hz), are conclusive and comparable to literature precedents.³⁰

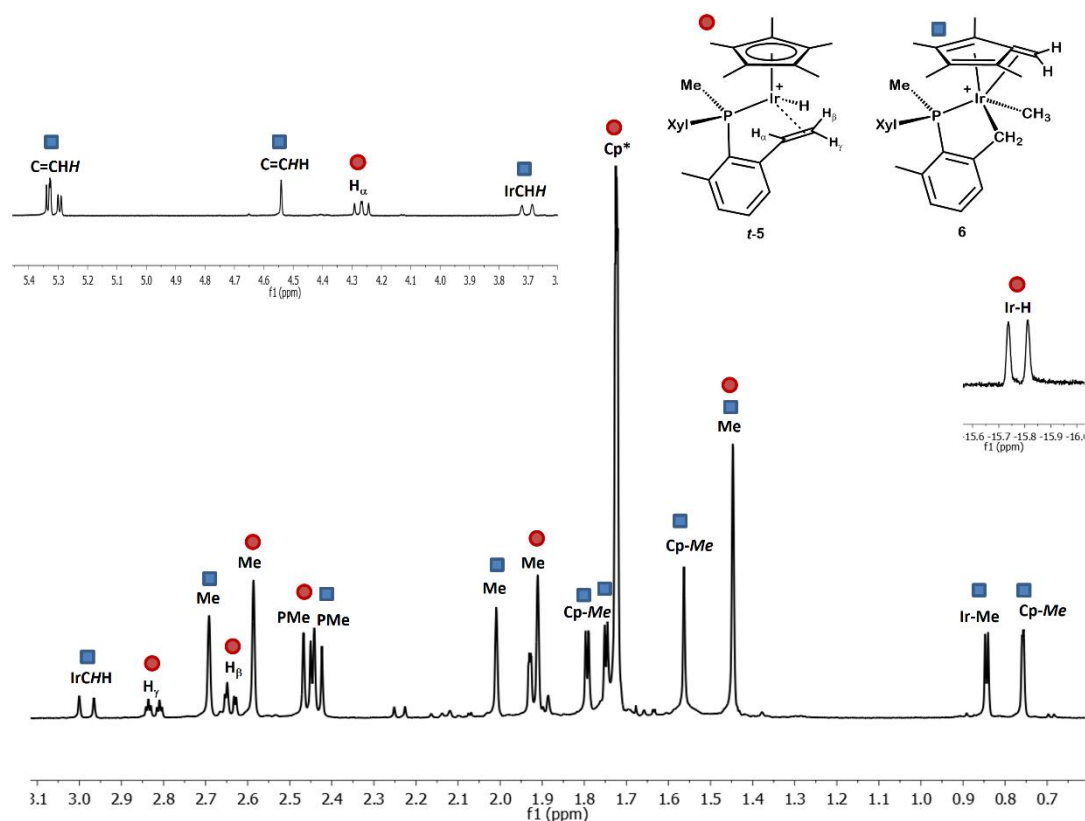


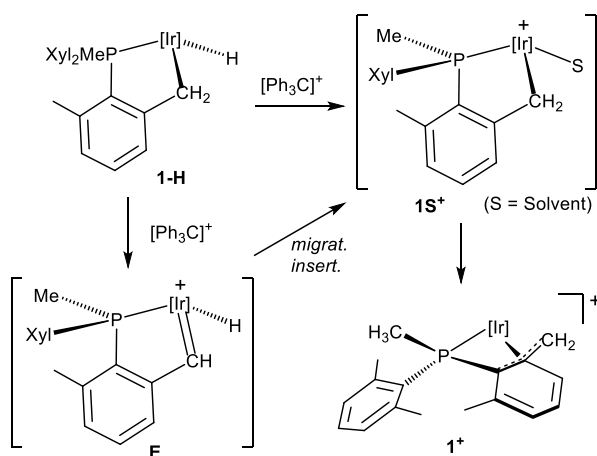
Figure 6. ^1H NMR (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) spectrum of a mixture of *t*-**5** and **6** (ca. 6:4).

Mechanistic considerations. Deuterium labeling studies.

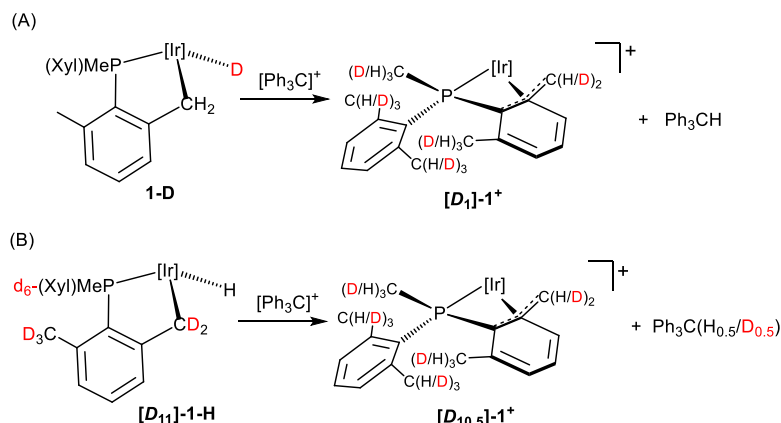
As pointed out earlier, electrophilic attack by Ph_3C^+ to either of the neutral molecules of **1-H** and **1-Me** could occur at two different bonds. For hydride **1-H** these are the Ir-H and one of the Ir- CH_2 sites, while for the methyl analog **1-Me**, α -H abstraction could occur at the Ir- CH_3 and Ir- CH_2 locations. To gain mechanistic insights, additional experiments were undertaken using different isotopologues of the two complexes.

Hydrogen abstraction from **1-H** through either the Ir-H or the Ir- CH_2 sites would clearly proceed through conspicuously different reaction routes, that would nonetheless turn into the same reaction outcome, namely complex **1** $^+$ (Scheme 1). As illustrated in Scheme 3, Ir-H abstraction would form a cationic solvento species **1S** $^+$, known to rearrange immediately²⁰ to the η^4 -*P*,benzylic complex **1** $^+$. Similarly, the Ir- CH_2 path would also produce **1** $^+$ albeit with initial generation of a highly electrophilic hydrido alkylidene **E**, followed by a 1,2-H shift from Ir to the carbene. Isotopologues **1-D** and **[D₁₁]-1-H**, selectively deuterated at the hydride and all benzylic positions of the cyclometalated phosphine, respectively, were assayed (Scheme 4). The first was prepared from **1-Cl** and LiAlD_4 ¹⁸ whereas the second emanated from H/D exchange

between **1-Cl** and $\text{CD}_3\text{OD}^{18}$ and subsequent reaction with LiAlH_4 . As delineated in Scheme 4, treatment of **1-D** with 1 equiv of Ph_3C^+ resulted in the exclusive formation of Ph_3CH , hinting faster Ir- CH_2 over Ir-D reactivity. Nevertheless, the analogous experiment performed with isotopologue $[\text{D}_{11}]\text{-1-H}$ led to $\text{Ph}_3\text{CH(D)}$ with *ca.* 50% deuterium incorporation, with protio scrambling over all benzylic positions (*ca.* 5%). These results indicate that the two reactions have comparable rates, with H-abstraction from Ir- CH_2 being somewhat faster than abstraction from the metal hydride site. Primary kinetic isotope effects mostly associated with the Ir- $\text{CH}_2/\text{Ir-CD}_2$ linkages are probably responsible for the above results.



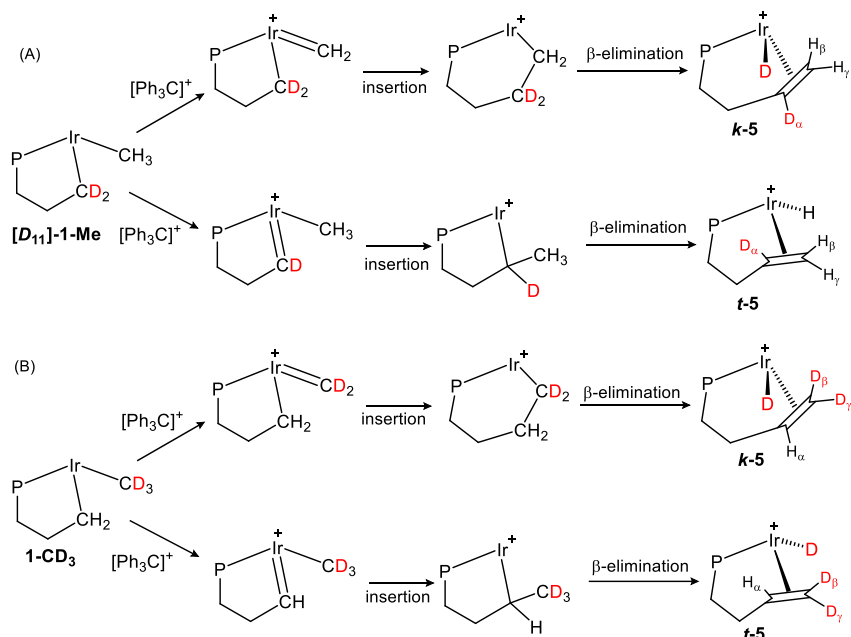
Scheme 3. Possible routes for hydride abstraction from **1-H** to give 1^+ .



Scheme 4. Hydride abstraction by $[\text{Ph}_3\text{C}]^+$ from **1-D** and $[\text{D}_{11}]\text{-1-H}$ isotopologues.

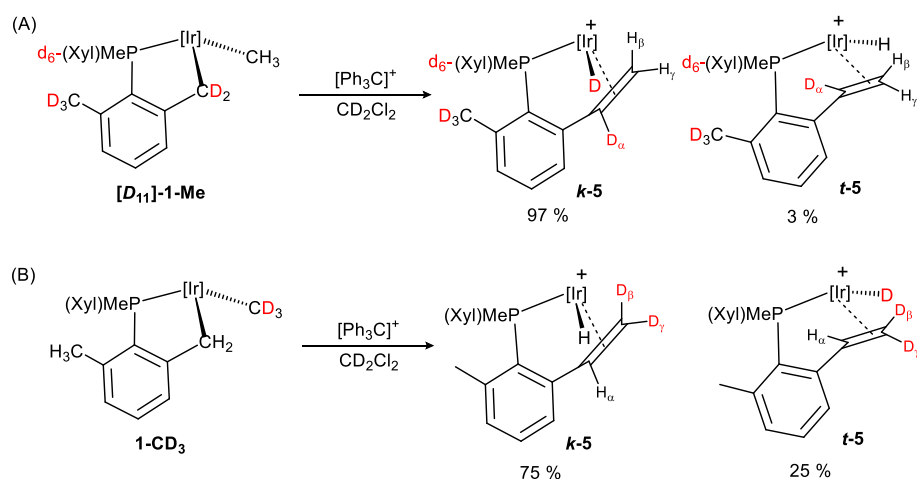
Scheme 5 shows the labeled products expected from the deuterated complexes $[\text{D}_{11}]\text{-1-Me}$ and **1-CD₃** after hydride abstraction from either the Ir- CH_3 (*A-top* and *B-top*) or Ir- CH_2 (*A-bottom* and *B-bottom*) sites. An important aspect to keep in mind is the fact that hydride abstraction from the Ir- CH_3 group would lead to a transient methyldiene ($\text{Ir}=\text{CH}_2$) that after insertion of the alkyl fragment and subsequent β -H elimination would yield the kinetic isomer of the final product **k-5**. In contrast, the analogous

rearrangement starting with H-abstraction from the Ir-CH₂ terminus would produce the diastereomer *t*-**5**.



Scheme 5. Expected deuteration patterns of the products (**5**) resulting from Ir-CH₃ or Ir-CH₂ hydride abstraction of isotopologues **[D₁₁]-1-Me** (A) and **1-CD₃** (B). Molecular structures have been simplified for clarity.

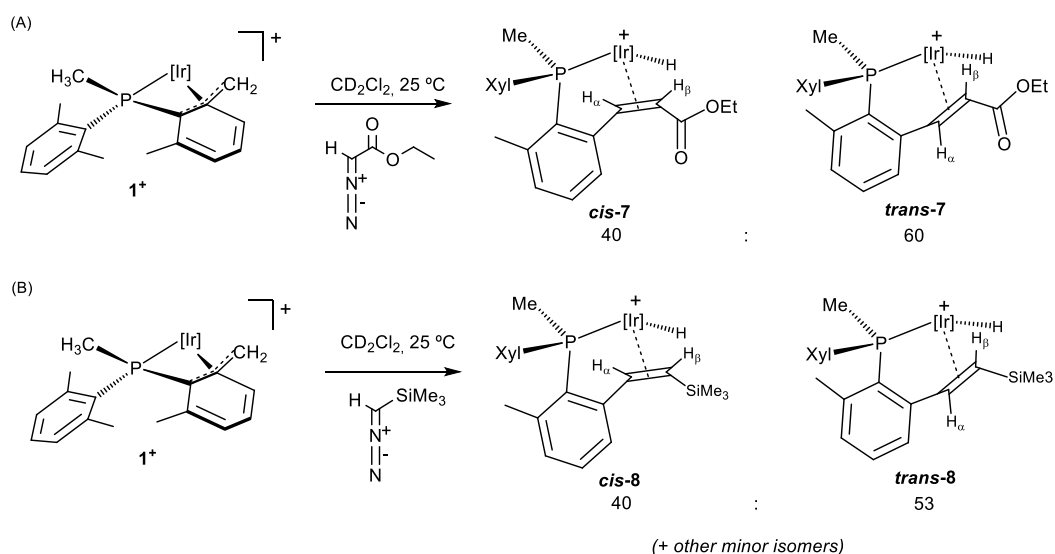
The distribution of the deuterium labels depicted in Scheme 6 was inferred from ¹H NMR spectroscopic analysis based on the expected isotopic distribution shown in Scheme 5. These results confirmed that not unreasonably, there is a competition between abstraction of the hydride from the two alkyl positions, Ir-CH₂ and Ir-CH₃, with the latter, that leads to the kinetic isomer *k*-**5**, being preferred. The reactions were carried out at 25 °C and spectroscopic analysis was acquired immediately to prevent H/D scrambling due to isomerization reactions. Primary kinetic isotopic effects were noticeable in these experiments: hydride abstraction from the protio isotopologue, **1-Me** (Scheme 2) yielded a 90:10 mixture of *k*-**5**:*t*-**5** (70% overall yield), whereas the use of **[D₁₁]-1-Me** increased the ratio of the *k*-isomer (abstraction from Ir-CH₃) at the expense of the *t*-isomer (abstraction from Ir-CD₂), with a *k*:*t* proportion of *ca.* 97:3. The opposite effect was found when **1-CD₃** underwent hydrogen abstraction (*k*:*t* ≈ 75:25).



Scheme 6. Reaction of trityl cation with deuterated compounds $[D_{11}]-1-Me$ (A) and $1-CD_3$ (B).

Reaction of 1^+ with Diazocompounds

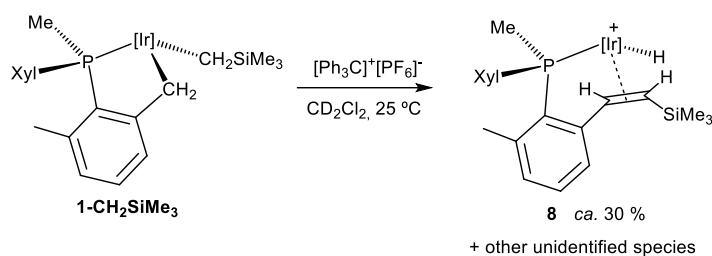
As an extension of these studies we investigated the reaction of 1^+ with two diazocompounds (Scheme 7) as carbene transfer reagents, with the aim of disclosing other C-C coupling reactions between alkyl and carbene fragments. Indeed, addition of either EDA (EDA = ethyldiazoacetate, $N_2CHCOOEt$) or (trimethylsilyl)diazomethane ($N_2CHSiMe_3$) resulted in the expected C-C coupling reaction that led to complexes **7** and **8**, respectively. These transformations could be regarded as models for related catalytic C-C coupling processes such as the C1 polymerization of diazocompounds³² and other relevant transformations that involve the formation of new C-C bonds.³³ The new compounds were obtained as mixtures of *cis* and *trans* isomers of the newly formed olefinic ligand. The identification of geometric isomers was achieved with the aid of 2D-COSY and NOESY NMR experiments. A slight preference for the *trans* isomer was found in the formation of both **7** and **8**. In fact, the proportion of *trans-7* increased to *ca.* 75 % when the reaction of 1^+ with EDA was effected at $-80\text{ }^\circ\text{C}$, and then the mixture allowed to reach slowly room temperature. No intermediates were detected by low-temperature ^1H NMR monitoring, but in view of the chemistry already discussed and our prior studies on related systems, the reaction involved, in all probability, highly reactive cationic alkylidene species resulting from carbene transfer from the diazocompound to the vacant site of 1^+ following a change in the coordination of the benzylic terminus^{20b} from η^3 to η^1 . The resulting metal carbene subsequently rearranged by migratory insertion of the Ir- CH_2 fragment and β -H elimination elementary steps.³⁴



Scheme 7. Reaction of **1**⁺ with diazocompounds EDA (A) and N₂CHSiMe₃ (B).

Compounds **7** and **8** exhibit strongly deshielded, highly characteristic ¹H NMR doublets between -15 and -17 ppm due to the iridium hydride ligands, with a two-bond coupling to the phosphorous nucleus of around 29 Hz. Their corresponding infrared bands appear between 2150 and 2175 cm⁻¹. Two doublets at 4.73 and 3.72 ppm in the ¹H NMR spectrum of *trans*-**7** are due to olefinic protons H_α and H_β, respectively, and exhibit a three-bond coupling constant of 9.3 Hz. The corresponding ¹³C{¹H} NMR signals for CH_α and CH_β appear at 59.5 and 40.9 ppm, respectively, the former presenting a small coupling to phosphorous of 4 Hz. The methylene protons of the ethoxy group (OCH₂CH₃) are diastereotopic and give two multiplets at 4.29 and 4.14 ppm, whereas the methyl group appears as a triplet (³J_{HH} = 7.1 Hz) at 1.32 ppm. ¹H and ¹³C{¹H} NMR data due to *cis*-**7** are not dissimilar to those of the *trans* isomer (see Experimental Section for details). Similar resonances are measured for compounds **8**. The olefinic protons of *cis*-**8** exhibit ¹H NMR doublets at 4.85 (H_α) and 2.38 (H_β) ppm, with a three-bond coupling constant of 11.7 Hz. The corresponding ¹³C{¹H} peaks appear at 71.6 (d, ²J_{CP} = 4 Hz) and 44.4 (s) due to CH_α and CH_β, respectively. The trimethylsilyl group is responsible for a singlet in the ¹H NMR spectrum at 0.13 ppm and comparable data are found for the related *trans* isomer. Two-dimensional homonuclear and heteronuclear NMR experiments further support the formulations depicted in Scheme 8 for compounds **7** and **8**.

We performed an additional experiment to corroborate the proposed nature of compounds **7** and **8** and in support of our mechanistic suggestion of alkyl migratory insertion into an alkyldiene functionality as the key C-C coupling step. Thus, we attempted the synthesis of the trimethylsilyl-substituted alkene complex **8** by α -hydride abstraction by Ph_3C^+ from alkyl compound **1-CH₂SiMe₃** (Scheme 8), earlier reported by our group.^{18b} The reaction proved to be more complex than foreseen and led to a mixture of compounds encompassing several iridium hydrides. Among the latter, the main species (*ca.* 30% overall yield by NMR) was, however, the expected complex **8** (Scheme 8), therefore corroborating the advanced hypothesis regarding the participation of reactive iridium alkyldienes in the formation of complexes **7** and **8** as in Scheme 7.



Scheme 8. Reaction of **1-CH₂SiMe₃** with $[\text{Ph}_3\text{C}]^+[\text{PF}_6]^-$.

Conclusions

Five-membered iridacycles that contain the bulky phosphine $\text{PMe}(\text{Xyl})_2$ metalated at one of its benzylic γ -CH bonds and further stabilized by metal coordination to η^5 - C_5Me_5 , readily generate uncommon cationic Ir(III) alkyldienes by electrophilic attack of Ph_3C^+ . Hampering participation of the resulting iridium-carbene bond in migratory insertion reactions permitted isolation of cationic Ir(III) metalacyclic alkyldienes **3** and **4** of remarkable thermal stability, while on the contrary, the presence of an additional hydride or methyl ligand promoted further reactivity, in the latter case with formation of a new C-C bond. From these studies, which are summarized in Schemes 1 and 2, and from deuterium labeling experiments collected in Schemes 4-6, it can be concluded that Ph_3C^+ is capable to effect electrophilic attack at α and β positions of carbon-based ligands in our complex precursors, as well as at Ir-H sites.

Acknowledgments

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Experimental Section

General considerations. All preparations and manipulations were carried out under oxygen free argon or nitrogen, using conventional Schlenk techniques and, when specified, at low temperature. Solvents were rigorously dried and degassed before use. 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. Solution NMR spectra were recorded on Bruker Avance DPX-300, Avance DRX-400, Avance DRX-500, and 400 Ascend/R spectrometers. The ^1H and ^{13}C resonances of the solvent were used as the internal standard and the chemical shifts are reported relative to TMS, while ^{31}P was referenced to external H_3PO_4 . All aromatic couplings in the ^1H NMR spectra are of *ca.* 7.5 Hz. The crystal structures were determined in a Bruker-Nonius, X8Kappa diffractometer. **1-H**, **1-Cl**, **1-Me** and **1-CH₂SiMe₃** were prepared according to literature methods.¹⁸ Other chemicals were commercially available and used as received. CCDC nos. 1498592-1498595 contain the crystallographic data for compounds **3**, **4**, *k-5* and *t-5*. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

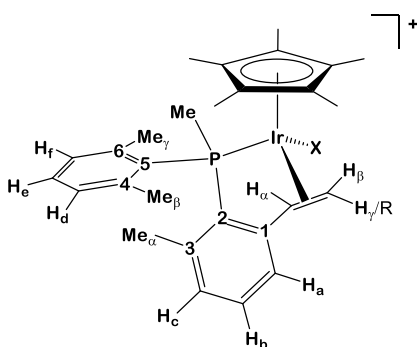


Figure 7. Labeling scheme used for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR assignments.

Compound 1-CD₃. It was synthesized by a modified procedure from that employed for the preparation of **1-Me**,¹⁸ consisting in the addition of a diethyl ether solution of $\text{Mg}(\text{CD}_3)\text{I}$ (1M, 50 μL) to a CH_2Cl_2 solution of **1⁺** (50 mg, 0.035 mmol). The reaction mixture was stirred at room temperature for 15 min, then the volatiles were removed under vacuum and the residue extracted with pentane. The solvent was evaporated to

dryness to give compound **1-CD₃** as a pale yellow powder (13 mg, 62 %). Spectroscopic data matched those of **1-Me** except for the ¹H NMR resonance due to Ir-CH₃ that was absent in the case of **1-CD₃**.

Compound 3. A solid mixture of **1-Cl** (50 mg, 0.08 mmol) and [Ph₃C]⁺[PF₆]⁻ (32 mg, 0.08 mmol) was dissolved in CH₂Cl₂ (3 mL) at -20 °C and stirred at room temperature for 5 minutes, resulting in a dark green solution. Addition of pentane (10 mL) led to the precipitation of a green solid which was washed with diethyl ether to yield complex **3** as a dark green powder (54 mg, 87 %). Suitable crystals for X-ray analysis were obtained by slow diffusion of pentane into a dichloromethane solution of the compound. Elemental analysis calcd. for C₂₇H₃₉ClF₆IrP₂: C, 42.27; H, 5.12; found: C, 42.3; H, 4.8. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ: 16.61 (d, 1 H, ³J_{HP} = 0.9 Hz, Ir=CH), 8.18 (d, 1 H, H_a), 7.87 (dd, 1 H, ⁴J_{HP} = 3.4 Hz, H_c), 7.61 (td, 1 H, ⁵J_{HP} = 2.4 Hz, H_b), 7.40 (td, 1 H, ⁵J_{HP} = 2.1 Hz, H_e), 7.33, 7.06 (m, 1 H each, H_d, H_f), 2.56 (d, 3 H, ²J_{HP} = 11.0 Hz, PMe), 2.55, 1.32 (s, 3 H each, Me_β, Me_γ), 2.44 (s, 3 H, Me_α), 1.66 (d, 15 H, ⁴J_{HP} = 1.8 Hz, C₅Me₅). ¹³C NMR (100 MHz, CD₂Cl₂, 25 °C) δ: 262.4 (¹J_{CH} = 153 Hz, Ir=CH), 165.2 (d, ²J_{CP} = 29 Hz, C₁), 145.6 (C₃), 143.8 (d, ¹J_{CP} = 61 Hz, C₂), 142.4 (d, ²J_{CP} = 11 Hz, C_{4/6}), 140.9 (d, ²J_{CP} = 8 Hz, C_{4/6}), 139.1 (d, ³J_{CP} = 8 Hz, CH_c), 135.2 (CH_b), 132.5 (d, ⁴J_{CP} = 2 Hz, CH_e), 131.9, 131.0 (d, ³J_{CP} = 10 Hz, CH_d, CH_f), 131.4 (d, ³J_{CP} = 13 Hz, CH_a), 121.0 (d, ¹J_{CP} = 54 Hz, C₅), 108.7 (C₅Me₅), 25.6, 24.0 (d, ³J_{CP} = 6 Hz, Me_β, Me_γ), 20.4 (d, ³J_{CP} = 2 Hz, Me_α), 14.5 (d, ¹J_{CP} = 42 Hz, PMe), 8.8 (C₅Me₅). ³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 25 °C) δ: 20.8.

Compound 4. A solution of [Ph₃C]⁺[B(C₆F₅)₄]⁻ (40 mg, 0.04) in dichloromethane (0.5 mL) was added under argon over a solution of **2** (25 mg, 0.04) in the same solvent at -60 °C. The solution turned dark-red immediately and, after addition of pentane, compound **4** precipitated as a red powder. Washing with pentane and drying under vacuum gave alkylidene **4** in 60 % yield (31 mg). Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated dichloromethane solution of the complex, however, due to its instability toward moisture and oxygen, reliable microanalytical data could not be obtained. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ: 14.9 (s, 1 H, Ir=CH), 7.76 (d, 1 H, H_a), 7.55 (m, 2 H, H_c, H_e), 7.40, 7.25 (m, 1 H each, H_d, H_f), 7.35 (m, 1 H, H_b), 3.40 (d, 1 H, ²J_{HH} = 8.6 Hz, IrCHH), 3.33 (d, 1 H, ²J_{HH} = 8.6 Hz, IrCHH), 2.91, 2.16 (s, 3 H each, Me_β, Me_γ), 2.27 (s, 3 H, Me_α), 1.96 (d, 15 H, ⁴J_{HP} = 1.8 Hz, C₅Me₅). ¹³C NMR (125 MHz, CD₂Cl₂, -60 °C) δ: 243.7 (d, ²J_{CP} = 28 Hz,

Ir=CH), 162.4 (d, $^2J_{\text{CP}} = 27$ Hz, C₁), 144.8 (d, $^2J_{\text{CP}} = 4$ Hz, C₃), 143.9 (d, $^2J_{\text{CP}} = 16$ Hz, C_{4/6}), 141.5 (d, $^2J_{\text{CP}} = 6$ Hz, C_{4/6}), 134.4 (CH_b, overlapped with BAr₄⁻), 133.3 (d, $^3J_{\text{CP}} = 10$ Hz, CH_c), 129.8 (CH_e), 129.1, 128.4 (d, $^3J_{\text{CP}} = 11$ Hz, CH_d, CH_f), 127.2 (d, $^3J_{\text{CP}} = 17$ Hz, CH_a), 111.1 (d, $^1J_{\text{CP}} = 69$ Hz, C₅), 101.9 (C₅Me₅), 24.4, 19.2 (d, $^3J_{\text{CP}} = 6, 14$ Hz, Me_β, Me_γ), 19.0 (d, $^3J_{\text{CP}} = 5$ Hz, Me_α), 13.7 (d, $^1J_{\text{CP}} = 45$ Hz, IrCH₂), 8.5 (C₅Me₅). Signal corresponding to C₂ was not identified. $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD₂Cl₂, 25 °C) δ: -13.1.

Reaction of 1-Me with [Ph₃C]⁺[B(C₆F₅)₄]⁻ (Compounds 5 and 6). A solution of [Ph₃C]⁺[B(C₆F₅)₄]⁻ (92 mg, 0.10 mmol) in CH₂Cl₂ (1 mL) was added at 0 °C under argon over a CH₂Cl₂ solution of **1-Me** (60 mg, 0.10 mmol) placed in a Schlenk flask. The reaction mixture was stirred at room temperature for 30 min and analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR, which showed complete conversion of the methyl complex **1-Me** into a *ca.* 63:7:30 mixture of compounds **k-5** : **t-5** : **6**. Heating the solution at 50 °C for 12 hours resulted in complete isomerization of **k-5** into **t-5**, while **6** remained unaltered. The solvent was removed under vacuum and the residue washed with diethyl ether. Compounds **5** and **6** were purified by crystallization from CH₂Cl₂/pentane to obtain a mixture of both isomers in 56 % overall yield (72 mg); however all attempts to isolate the individual complexes in a pure state were unsuccessful. Spectroscopic data obtained from mixtures of these isomers, are detailed below. Elemental analysis for the mixture of isomers calcd. for C₅₂H₄₂BF₂₀IrP: C, 48.76; H, 3.31. Found: C, 48.9; H, 3.5.

Compound t-5: ^1H NMR (500 MHz, CD₂Cl₂, 25 °C) δ: 7.47 (d, 1 H, H_a), 7.36 – 7.23 (m, 3 H, CH_{Xyl}), 7.07 – 6.98 (m, 2 H, CH_{Xyl}), 4.27 (dd, 1 H, $^3J_{\text{HH}} = 10.5$, $^3J_{\text{HH}} = 8.6$ Hz, H_a), 2.83 (dt, 1 H, $^3J_{\text{HH}} = 10.5$, $^2J_{\text{HH}} = ^3J_{\text{HP}} = 2.4$ Hz, H_γ), 2.64 (dd, 1 H, $^3J_{\text{HH}} = 8.6$, $^2J_{\text{HH}} = 2.4$ Hz, H_β), 2.59, 1.45 (s, 3 H each, Me_β, Me_γ), 2.46 (d, 3 H, $^2J_{\text{HP}} = 9.0$ Hz, PMe), 1.91 (s, 3 H, Me_α), 1.73 (d, 15 H, $^4J_{\text{HP}} = 1.7$ Hz, C₅Me₅), -15.77 (d, 1 H, $^2J_{\text{HP}} = 30.1$ Hz, IrH). ^{13}C NMR (125 MHz, CD₂Cl₂, 25 °C) δ: 146.9 (d, $^2J_{\text{CP}} = 23$ Hz, C₁), 141.8 (C₃), 141.6, 140.2 (d, $^2J_{\text{CP}} = 9$ Hz, C₄, C₆), 136.8 (d, $^1J_{\text{CP}} = 61$ Hz, C₂), 131.8, 131.5 (CH_b, CH_e), 131.1, 130.3 (d, $^3J_{\text{CP}} = 8$ Hz, CH_d, CH_f), 130.7 (d, $^3J_{\text{CP}} = 8$ Hz, CH_c), 127.0 (d, $^3J_{\text{CP}} = 16$ Hz, CH_a), 123.4 (d, $^1J_{\text{CP}} = 52$ Hz, C₅), 101.0 (C₅Me₅), 62.7 (d, $^2J_{\text{CP}} = 4$ Hz, CH_α), 34.1 (CH_βH_γ), 28.0 (d, $^1J_{\text{CP}} = 50$ Hz, PMe), 24.7, 22.8 (d, $^3J_{\text{CP}} = 7$ Hz, Me_β, Me_γ), 19.9 (d, $^3J_{\text{CP}} = 18$ Hz, Me_α), 8.4 (C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CD₂Cl₂, 25 °C) δ: -0.1. **Compound k-5:** ^1H NMR (500 MHz, CD₂Cl₂, 25 °C) δ: 7.40 (m, 1 H, H_a), 7.35 – 7.19 (m, 3 H, CH_{Xyl}), 7.08 – 6.96 (m, 2 H, CH_{Xyl}), 4.41 (t, 1 H, $^3J_{\text{HH}}$, $^3J_{\text{HH}} = 9.1$ Hz,

H_α), 2.67 (m, overlapped, H_γ), 2.65, 1.72 (s, 3 H each, Me_β, Me_γ), 2.24 (d, 3 H, ²J_{HP} = 10.2 Hz, PMe), 2.12 (t, 1 H, ³J_{HH} = ²J_{HH} = 9.1 Hz, H_γ), 1.93 (d, 15 H, ⁴J_{HP} = 1.8 Hz, C₅Me₅), 1.89 (s, 3 H, Me_α), -14.31 (d, 1 H, ²J_{HP} = 28.5 Hz, IrH). ³¹P{¹H} NMR (200 MHz, CD₂Cl₂, 25 °C) δ: -9.8. **Compound 6:** ¹H NMR (500 MHz, CD₂Cl₂, 25 °C) δ: 7.36 – 7.23 (m, 4 H, CH_{Xyl}), 7.07 – 6.98 (m, 2 H, CH_{Xyl}), 5.30 (d, 1 H, ⁴J_{HP} = 4.2 Hz, H_{αβ}), 4.54 (s, 1 H, H_{αβ}), 3.71 (d, 1 H, ²J_{HH} = 13.9 Hz, IrCHH), 2.99 (d, 1 H, ²J_{HH} = 13.9 Hz, IrCHH), 2.69, 1.45 (s, 3 H each, Me_β, Me_γ), 2.43 (d, 3 H, ²J_{HP} = 9.6 Hz, PMe), 2.01 (s, 3 H, Me_α), 1.80, 1.75 (d, 3 H each, ⁴J_{HP} = 2.8 Hz, 2 Cp-Me), 1.57 (s, 3 H, Cp-Me), 0.85 (d, 3 H, ³J_{HP} = 2.7 Hz, IrCH₃), 0.76 (d, 3 H, ⁴J_{HP} = 1.4 Hz, Cp-Me). ¹³C NMR (125 MHz, CD₂Cl₂, 25 °C) δ: 152.7 (d, ²J_{CP} = 27 Hz, C₁), 141.5, 140.1 (C_{4/6}), 140.2 (C₃), 134.8 (d, ¹J_{CP} = 65 Hz, C₂), 129.4 (d, ³J_{CP} = 9 Hz, CH_c), 132.1 (CH_b, CH_e), 131.2, 131.0 (d, ³J_{CP} = 9 Hz, CH_d, CH_f), 127.5 (d, ³J_{CP} = 16 Hz, CH_a), 124.8 (d, ¹J_{CP} = 53 Hz, C₅), 114.2, 111.8, 110.1, 109.4, 109.3 (C₅Me₄CH_αH_β), 68.6 (CH_αH_β), 29.6 (IrCH₂), 25.3, 24.7 (d, ³J_{CP} = 6 Hz, Me_β, Me_γ), 21.0 (d, ¹J_{CP} = 44 Hz, PMe), 20.1 (d, ³J_{CP} = 16 Hz, Me_α), 8.2, 7.8, 6.8, 4.7 (C₅Me₄CH_αH_β), -10.9 (d, ²J_{CP} = 3 Hz, IrCH₃). ³¹P{¹H} NMR (200 MHz, CD₂Cl₂, 25 °C) δ: 12.2.

Compound 7. 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 were added 5 mL of CH₂Cl₂. The reaction mixture was stirred for 5 min at room temperature and ethyldiazoacetate (10 μL, 0.096 mmol) was added. The solution was filtered and the volatiles were evaporated under reduced pressure to obtain **7** (102 mg, 86 %) as a pale yellow powder mixture of isomers in a ratio of *ca.* 60:40. Tentative isomer assignment for each set of signals is based on 2D-NOESY analysis, since NOE cross-peaks can be found between H_α and H_β only for the *cis* isomer, whereas the *trans* isomer presents a NOE cross-peak between H_α and H_α, which cannot be detected in the former case. The two isomers were jointly recrystallized from a 1:2 mixture of CH₂Cl₂:pentane. Elemental analysis for the mixture of isomers calcd. for C₆₃H₅₃BF₂₄IrO₂P: C, 49.39; H, 3.49, found: C, 49.0; H, 3.0. **Trans-7 (60%):** IR (Nujol): ν(IrH) 2175, ν(CO) 1710 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ: 7.57 (d, 1 H, H_α), 7.37, 7.30, 7.08 (m, H_{b-f}, overlapped with analogous signals of the minor isomer), 4.73 (d, 1 H, ³J_{HH} = 9.3 Hz, CH_α), 4.29 (m, 1 H, OCHHCH₃), 4.14 (m, 1 H, OCHHCH₃), 3.72 (d, 1 H, ³J_{HH} = 9.3 Hz, CH_β), 2.61, 1.46 (s, 3 H each, Me_β, Me_γ), 2.56 (d, 3 H, ²J_{HP} = 10.0 Hz, PMe), 1.95 (s, 3 H, Me_α), 1.73 (d, 15 H, ⁴J_{HP} = 1.7 Hz, C₅Me₅), 1.32 (t, 3 H, ³J_{HH} = 7.1 Hz, OCH₂CH₃), -15.35 (d, 1 H, ²J_{HP} = 27.8 Hz, IrH). ¹³C NMR

(100 MHz, CD₂Cl₂, 25 °C) δ : 170.0 (CO), 147.6 (d, $^2J_{CP} = 26$ Hz, C₁), 142.3, 141.7, 141.5, 141.1 (C₂, C₃, C₄, C₆), 132.7 (CH_b), 132.2 (d, $^4J_{CP} = 2$ Hz, CH_e), 131.5 (CH_{d/f}), 131.4 (CH_c), 131.0 (d, $^3J_{CP} = 6$ Hz, CH_{d/f}), 127.1 (d, $^3J_{CP} = 16$ Hz, CH_a), 122.7 (d, $^1J_{CP} = 56$ Hz, C₅), 103.1 (C₅Me₅), 61.7 (OCH₂CH₃), 59.5 (d, $^2J_{CP} = 4$ Hz, CH_a), 40.9 (CH _{β}), 26.5 (d, $^1J_{CP} = 47$ Hz, PMe), 25.0, 23.7 (d, $^3J_{CP} = 6$ Hz, Me _{β} , Me _{γ}), 20.3 (d, $^3J_{CP} = 6$ Hz, Me _{α}), 14.5 (OCH₂CH₃), 8.8 (C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD₂Cl₂, 25 °C) δ : 1.0. **Cis-7 (40 %)**: IR (Nujol): $\nu(\text{IrH})$ 2150, $\nu(\text{CO})$ 1650 cm⁻¹. ^1H NMR (400 MHz, CD₂Cl₂, 25 °C) δ : 7.46 (d, 1 H, H_a), 7.37, 7.30, 7.08 (m, H_{b-f}, overlapped with analogous signals of the major isomer), 4.67 (d, 1 H, $^3J_{\text{HH}} = 9.1$ Hz, CH_a), 4.02 (m, 1 H, OCH₂CH₃), 3.96 (m, 1 H, OCH₂CH₃), 3.49 (d, 1 H, $^3J_{\text{HH}} = 9.1$ Hz, CH _{β}), 2.61, 1.53 (s, 3 H each, Me _{β} , Me _{γ}), 2.50 (d, 3 H, $^2J_{\text{HP}} = 11.1$ Hz, PMe), 1.92 (s, 3 H, Me _{α}), 1.75 (d, 15 H, $^4J_{\text{HP}} = 1.6$ Hz, C₅Me₅), 1.16 (t, 3 H, $^3J_{\text{HH}} = 7.1$ Hz, OCH₂CH₃), -16.39 (d, 1 H, $^2J_{\text{HP}} = 27.8$ Hz, IrH). ^{13}C NMR (100 MHz, CD₂Cl₂, 25 °C) δ : 172.5 (CO), 146.4 (d, $^2J_{CP} = 23$ Hz, C₁), 142.2, 141.5, 141.4, 141.0 (C₂, C₃, C₄, C₆), 132.4 (d, $^4J_{CP} = 2$ Hz, CH_e), 132.0 (CH_b), 131.6 (CH_{d/f}), 131.3 (CH_c), 130.9 (d, $^3J_{CP} = 6$ Hz, CH_{d/f}), 126.8 (d, $^3J_{CP} = 17$ Hz, CH_a), 124.7 (C₅), 103.1 (C₅Me₅), 63.9 (d, $^2J_{CP} = 3$ Hz, CH_a), 61.4 (OCH₂CH₃), 40.3 (CH _{β}), 25.7 (d, $^1J_{CP} = 47$ Hz, PMe), 25.6, 23.4 (d, $^3J_{CP} = 5$ Hz, 8 Hz, Me _{β} , Me _{γ}), 20.1 (d, $^3J_{CP} = 6$ Hz, Me _{α}), 14.0 (OCH₂CH₃), 8.8 (C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD₂Cl₂, 25 °C) δ : 3.1.

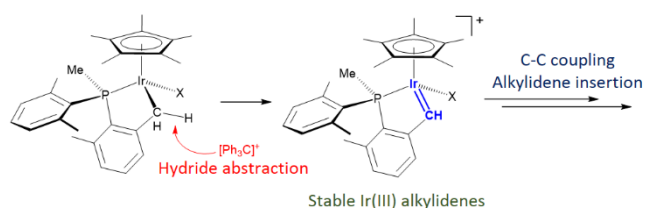
Compound 8. To a solid mixture of **1-Cl** (50 mg, 0.081 mmol) and NaBAr_F (72 mg, 0.081 mmol) placed in a Schlenk flask 3 mL of CH₂Cl₂ were added at -20 °C. After stirring for 10 min, a solution of N₂CHSiMe₃ (2M in hexanes, 50 μL) was added at this temperature and the reaction allowed to warm up to 25 °C and additionally stirred for 1 hour. The solution was filtered and the volatiles were removed under vacuum to give a pale yellow foam which was washed with pentane. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic analysis of the crude showed four different products in a ratio of *ca.* 53:40:4:3, all of which exhibited characteristic Ir–H resonances in the ^1H NMR spectrum. The two major species were identified as the *trans* (53 %) and *cis* (40 %) isomers. However, only **cis-8** was isolated as a single species by crystallization from Et₂O/pentane (1:1) in 30 % yield (38 mg). **Cis-8 (40 %)**: IR (Nujol): $\nu(\text{IrH})$ 2160 cm⁻¹. Elemental analysis calcd. for C₆₃H₅₇BF₂₄IrPSi: C, 49.39; H, 3.75, found: C, 49.3; H, 3.6. ^1H NMR (500 MHz, CD₂Cl₂, 25 °C) δ : 7.41 (d, 1 H, H_a), 7.34 (m, 2 H, H_b, H_c), 7.26, 7.01 (dd, 1 H each, $^4J_{\text{HP}} = 4.2$ Hz, H_d, H_f), 7.05 (dd, 1 H, $^4J_{\text{HP}} = 4.1$ Hz, H_c), 4.85 (d, 1 H, $^3J_{\text{HH}} = 11.7$ Hz, CH_a),

2.62, 1.53 (s, 3 H each, Me_β, Me_γ), 2.52 (d, 3 H, ²J_{HP} = 10.5 Hz, PMe), 2.38 (d, 1 H, ³J_{HH} = 11.7 Hz, CH_β), 1.89 (s, 3 H, Me_α), 1.70 (d, 15 H, ⁴J_{HP} = 1.6 Hz, C₅Me₅), 0.13 (s, 9 H, SiMe₃), -15.85 (d, 1 H, ²J_{HP} = 30.7 Hz, IrH). ¹³C NMR (125 MHz, CD₂Cl₂, 25 °C) δ: 147.2 (d, ²J_{CP} = 27 Hz, C₁), 142.2, 140.5 (d, ²J_{CP} = 10, 8 Hz, C₄, C₆), 141.6 (C₃), 132.3, 131.6 (CH_b, CH_e), 131.3 (d, ³J_{CP} = 10 Hz, CH_{d/f}), 130.9 (m, CH_c, CH_{d/f}), 128.8 (C₂, overlapped with BAr_F), 127.3 (d, ³J_{CP} = 17 Hz, CH_a), 124.4 (d, ¹J_{CP} = 49 Hz, C₅), 101.0 (C₅Me₅), 71.6 (d, ²J_{CP} = 4 Hz, CH_α), 44.4 (CH_β), 28.4 (d, ¹J_{CP} = 48 Hz, PMe), 25.8, 22.5 (d, ³J_{CP} = 5, 8 Hz, Me_β, Me_γ), 19.8 (d, ³J_{CP} = 4 Hz, Me_α), 8.6 (C₅Me₅), 0.0 (SiMe₃). ³¹P{¹H} NMR (200 MHz, CD₂Cl₂, 25 °C) δ: -7.6. **Trans-8 (53%)**: It could not be isolated in pure form, but representative spectroscopic data include: ¹H NMR (500 MHz, CD₂Cl₂, 25 °C) 4.36 (d, ³J_{HH} = 12.7 Hz, CH_α), 2.27 (PMe and CH_β), 1.94 (C₅Me₅), 0.26 (SiMe₃) and -16.84 (d, ²J_{CP} = 30.7 Hz, Ir-H) ppm. ³¹P{¹H} NMR (200 MHz, CD₂Cl₂, 25 °C) δ: 0.9 ppm.

Associated Content

Supporting Information: kinetic studies on the isomerization of compound **5** and X-ray crystallographic studies.

Graphical Abstract



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