Isomerization of a cationic (η^5 -C₅Me₅)Ir(III) complex involving remote C–C and C–H bond formation

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This article is dedicated to the memory of our highly respected colleague and friend Professor Malcom L. H. Green

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ABSTRACT

The reactivity of an unsaturated, cationic (C₅Me₅)Ir(III) complex (**2**(Xyl)⁺) bearing the xylyl-substituted terphenyl phosphine PMe₂Ar^{Xyl2} (Ar^{Xyl2} = C₆H₃-2,6-(C₆H₃-2,6-Me₂)₂) towards triethylamine (NEt₃) is studied and compared to our previous investigations based on the related complex **2**(Dipp)⁺ containing the bulkier phosphine PMe₂Ar^{Dipp2} (Ar^{Dipp2} = C₆H₃-2,6-(C₆H₃-2,6-ⁱPr₂)₂). Low-temperature multinuclear NMR studies support the formation of a C–C bond between the deprotonated C₅Me₅ ligand and a flanking xylyl ring of the phosphine, which becomes dearomatized (complex **4**(Xyl)⁺). Interestingly, this complex presents divergent reactivity relative to the bulkier diisopropylphenyl counterpart, undergoing formal addition of HCl to yield complex **5**(Xyl)⁺, isomeric to the starting complex **2**(Xyl)⁺. These transformations are rationalized by means of Density Functional Theory (DFT) calculations.

1. Introduction

In the majority of the reactions promoted by transition metal complexes containing coordinated phosphine and cyclopentadienyl-type ligands, these groups behave as spectators and provide thermal or kinetic stability, inhibiting decomposition or other side reactions [1]. The protective role they exert is, in fact, a main reason justifying their widespread utilization. In some instances, however, these commonly used ligands have been found to participate actively in the chemistry taking place at the metal complex. For instance, it has already been shown that they may affect catalytic outcomes [2] and even lead to catalyst deactivation [3]. Therefore, gaining a deeper knowledge of these unpredictable reactions is of paramount importance.

Perhaps the best-known example of phosphine non-innocent behavior is their facile cyclometalation upon coordination to late transition metals [4]. More recently, startling examples describing the nickel- and palladium-mediated dearomatization of dialkylbiaryl phosphines have been reported (Fig. 1A) [2a,b,5]. For cyclopentadienyl ligands, in particular C₅Me₅, the activation of one of the methyl groups has been known for decades. This activation typically implies either

deprotonation [6] or hydride abstraction [7], although direct hydride migration from a CH₃ fragment to the metal has been reported as well [8]. Metal-to-ring proton transfer [9] processes have also been documented for late transition metal complexes, with important implications in catalysis. For instance, Miller [9d] proposed that the cyclopentadienyl ligand in [(η^5 -C₅Me₅)Rh(bpy)Cl] (bpy = 2,2'-bipyridine; see Fig. 1B, right) could be responsible for catalytic hydride transfer to NAD⁺ (NAD = Nicotinamide Adenine Dinucleotide), while Peters disclosed that protonated decamethylcobaltocenium, [(C₅Me₅)Co(η^4 -C₅Me₅H)]⁺, could act as a potent proton coupled electron transfer (PCET) reagent in the catalytic conversion of dinitrogen into ammonia [10]. Overall, these findings suggest that the non-innocent behavior of the C₅Me₅ ligand could be extended from anecdotal stoichiometric reactions to the development of effective catalytic cycles.

Though a rare transformation, the concerted activation of both a tertiary phosphine and a cyclopentadienyl ligand has also been documented, (Fig. 1C, left) [6e]. More recently, our group reported such a chemical change in compound [(η^5 -C₅Me₅)Ir(Cl)(PMe₂Ar^{Dipp2})]⁺ (**2**(Dipp)⁺), where Ar^{Dipp2} = C₆H₃-2,6-(C₆H₃-2,6-ⁱPr₂)₂, in the presence of triethylamine as a base. These studies evinced that the pentamethyl

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cyclopentadienyl unit can partake in reversible C–C bond formation to yield compound **4(Dipp)**⁺ (Fig. 1C, middle) and even mediate the activation of a C–H bond at a remote position from the metal center [11]. To extend our preliminary investigations in this area, herein we analyze the effect of steric hindrance on the concerted activation of C₅Me₅ and terphenylphosphine ligands by focusing on complexes of the xylyl-substituted terphenylphosphine $\text{PMe}_2\text{Ar}^{\text{Xyl}2}$, of reduced steric properties in comparison with $\text{PMe}_2\text{Ar}^{\text{Dipp}2}$ [12].

2. Results and discussion.

2.1. Synthesis and characterization

As stated in our prior work, the complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2(\text{P-Me}_2\text{Ar}^{\text{Xyl}2})]$, (**1(Xyl)**), was prepared by reacting $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$ with $\text{PMe}_2\text{Ar}^{\text{Xyl}2}$ in CH_2Cl_2 [11]. The phosphorus atom of complex **1(Xyl)** resonates as a sharp singlet at -29.9 ppm in the $^{31}\text{P}\{^1\text{H}\}$ spectrum. In the ^1H NMR spectrum, slow rotation around the P–*ipso*-C₆H₃ bond is responsible for the observation of two distinct sets of signals corresponding to the benzylic and *meta* protons of the flanking xylyl rings, which undergo dynamical exchange as shown by EXSY experiments. The same experiments also revealed chemical exchange between coordinated and free $\text{PMe}_2\text{Ar}^{\text{Xyl}2}$, proving that the Ir–P bond is labile in this species. The structure proposed for complex **1(Xyl)** from solution NMR studies has now been confirmed by means of X-Ray crystallography (Fig. 2). At variance with prior results from our group using related systems based on bis(aryl) phosphines [13], **1(Xyl)** did not undergo

Fig. 2. ORTEP diagram of complex **1(Xyl)**. Hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 50 % probability.

Fig. 1. Representative examples of a) phosphine dearomatization, b) C₅Me₅ activation and non-innocence and c) C–C coupling between C₅Me₅ and phosphine ligands.

cyclometalation even in the presence of organic bases.

Treatment of **1(Xyl)** with one equivalent of the sodium salt of the weakly coordinating BAR_F anion ($\text{BAR}_\text{F} = [\{3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3\}_4\text{B}]^-$) at -20°C yielded the cationic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl(PMe}_2\text{Ar}^{\text{Xyl}2})]^+$ (**2(Xyl)**⁺). The analogous complex **2(Dipp)**⁺ was prepared directly by mixing 0.5 equivalents of $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}_2]_2$ with 1 equivalent of both $\text{PMe}_2\text{Ar}^{\text{Dipp}2}$ and NaBAR_F .¹¹ Although for most biaryl and terphenyl phosphine complexes metal unsaturation is often compensated by means of so-called secondary π -arene interactions [14], the flanking aryl rings of the terphenyl phosphine ligand in type **2**⁺ complexes appear equivalent in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, suggesting either fast exchange or a symmetrical disposition. Both situations are incompatible with the existence of strong metal-arene bonding interactions. The intense dark coloration of these complexes and above all X-ray crystallography studies of single crystals of **2(Dipp)**⁺ (Fig. 3) and **2(Xyl)**⁺ [11] support the absence of significant arene-metal bonding. For complex **2(Xyl)**⁺, the closest Ir–C_{aryl} distances found were ca. 3.92 (C_{ortho}) and 4.04 (C_{ipso}) Å.¹¹ For the **2(Dipp)**⁺ analog, somewhat shorter contacts of ca. 3.12 (C_{ortho}) and 3.16 (C_{ipso}) Å have now been found. They are, however, too long to imply any meaningful Ir–C_{aryl} bonding interaction. The large Ir–C distances and principally the reduced Ir–Cl bond lengths found in **2(Xyl)**⁺ and **2(Dipp)**⁺ of 2.278(1) [11] and 2.347(1) Å, respectively, suggest that in the solid-state the chloride ligand might be acting as a π -donor to the cationic Ir(III) center. For comparison, in the neutral **1(Xyl)** complex (Fig. 2), the Ir–Cl distances are of approximately 2.40 Å. A similar shortening of the metal-chloride bond length was reported for the ruthenium complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{Cl})(\text{P}^i\text{Pr}_3)]$ [15]. Caulton and coworkers also proposed π -stabilisation in $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{X})(\text{PR}_3)$ and related compounds [16].

Low-temperature ^1H NMR studies were carried out to ascertain the solution behavior of complex **2(Dipp)**⁺. The above-mentioned metrical parameters (Ir–Cl and Ir–C_{arene} distances) suggested the possibility of detecting for this species a metal-arene-bonded conformer that might be concealed at room temperature. Upon lowering the temperature to -30°C , the slow exchange regime was attained for the rotation around the P–*ipso*-C₆H₃ bond ($\Delta G^\ddagger = 12.8\text{ kcal}\cdot\text{mol}^{-1}$, determined by means of line-shape analysis), splitting the signals corresponding to the $i\text{Pr}$ methine protons and the aromatic *m*-Dipp protons in two sets (see SI). Further cooling to -80°C did not increase the complexity of the spectrum with additional signal splitting. The observed low-temperature pattern is similar to that of complex **1(Xyl)**, and implies the existence of a pseudo symmetry plane containing the P, Ir and Cl atoms, which rules out the existence of a firm metal-arene interaction in this complex. Despite these observations, metal-arene bonding indeed plays a key role

in the reactivity of the system [11].

Although the purported six-coordinate neutral complex **1(Dipp)**, i.e. the analog of **1(Xyl)**, could not be accessed, a formally hexacoordinated complex was isolated by treating **2(Dipp)**⁺ with CO (1 bar, Scheme 1). This reaction occurred readily both in solution and in the solid-state. In the latter case, dark crystals of **2(Dipp)**⁺ immediately turned bright yellow upon exposure to CO. The solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2(Dipp)**⁺ underwent a remarkable chemical shift change of nearly 40 ppm for the $^{31}\text{P}\{^1\text{H}\}$ resonance upon CO addition (from 6.6 to -33.2 ppm), attributed to the formation of the CO adduct. The fluxional behavior of complex **2(Dipp)**⁺·CO was noticed thanks to the presence of broad signals in the room temperature ^1H NMR spectrum. Upon cooling at -20°C , these signals sharpened, giving rise to four different resonances corresponding to the inequivalent methine protons of the *iPr* groups, in agreement with the lack of symmetry expected for this chiral molecule. Exchange peaks in the EXSY experiment suggested that the rotation around the P–*ipso*-C₆H₃ bond, responsible for the observed fluxionality, is not completely hindered at this temperature. In the $^{13}\text{C}\{^1\text{H}\}$ spectrum, a doublet was detected within the characteristic region for metal carbonyls, at 167.9 ppm, $^2J_{\text{CP}} = 19\text{ Hz}$, which was unambiguously assigned to the incorporated CO ligand. A band at 2059 cm^{-1} in the IR spectrum (Nujol) of **[2(Dipp)·CO]BAR_F** can be assigned to the CO stretching frequency, further confirming the formation of the carbon monoxide adduct.

The $\text{PMe}_2\text{Ar}^{\text{Xyl}2}$ and $\text{PMe}_2\text{Ar}^{\text{Dipp}2}$ complexes of type **2**⁺ exhibit evident structural resemblances. Notwithstanding these similarities, the outcome of the reaction of complex **2(Xyl)**⁺ with NEt_3 diverged significantly from that found for **2(Dipp)**⁺. For the latter,¹¹ the low-temperature (-20°C) reaction allowed for the isolation and identification by NMR and X-ray crystallography of an unforeseen, unusual cationic complex, **4(Dipp)**⁺ (Fig. 1C, middle). This species possesses a ten-membered ring generated by deprotonation of one of the C₅Me₅ methyl substituents, with the resulting tetramethylfulvene unit attacking the *para* carbon atom of the proximal flanking Dipp ring, which loses aromaticity. The resulting **4(Dipp)**⁺ intermediate eventually evolved into the pseudoallylic complex **3(Dipp)**⁺ after reversible C–C bond cleavage and remote ζ –C–H bond activation (Scheme 2) [11].

By contrast, addition of an equimolar amount of NEt_3 to **2(Xyl)**⁺ at 25°C yielded a complex mixture of products that included only trace amounts of the pseudoallylic complex **3(Xyl)**⁺, as revealed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. As shown in Scheme 2, this species was prepared independently by reaction of **2(Xyl)**⁺ with NaBAR_F [11]. X-ray diffraction studies (Fig. 4) confirmed the ζ –C–H bond activation of a benzylic position of a flanking xylyl group, which adopts a pseudoallylic coordination to the metal with Ir–C bond distances of ca. 2.21 Å. Nonetheless, low temperature NMR monitoring of the reaction between NEt_3 and **2(Xyl)**⁺ revealed the immediate formation of **4(Xyl)**⁺, also featuring a new C–C bond between a deprotonated methyl group of the C₅Me₅ ligand and the *para* carbon atom of a xylyl ring, which becomes dearomatized. Complex **4(Xyl)**⁺ was characterized by a singlet at -2.5 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -30°C (CD_2Cl_2). For comparison, **4(Dipp)**⁺ resonates at -3.9 ppm under the same conditions. At -50°C , two clearly distinguishable exchanging ^1H NMR singlets were located at 6.09 and 4.85 ppm, once more reminiscent of the allylic and alkenic protons identified for **4(Dipp)**⁺ (6.17 and 4.97 ppm in CD_2Cl_2 , see SI). The exchange rate for the interconversion between the two equivalent pseudoallylic structures was faster for the xylyl system, with an associated barrier of $\Delta G^\ddagger = 10.7\text{ kcal}\cdot\text{mol}^{-1}$, as calculated by line shape analysis (cf. the $12.9\text{ kcal}\cdot\text{mol}^{-1}$ found for **4(Dipp)**⁺). Although compound **4(Xyl)**⁺ could not be isolated in a pure form and fully characterized, both its $^{31}\text{P}\{^1\text{H}\}$ and ^1H signature chemical resonances and the observed dynamic solution behavior support an analogous formulation to that elucidated for **4(Dipp)**⁺.

As stated above, the formation of **4(Xyl)**⁺ in the reaction of **2(Xyl)**⁺ and NEt_3 is a complex transformation and yielded in addition equimolar quantities of the neutral dichloride complex $[(\eta^5\text{-C}_5\text{Me}_5)$

Fig. 3. ORTEP diagram of the cation of complex **2(Dipp)**⁺. Hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 50 % probability.

Scheme 1. Reactivity of $2(\text{Dipp})^+$ towards CO. Scheme 2. Reactivity of type 2^+ complexes towards NEt_3 and NaBARF .

$\text{IrCl}_2(\text{PMe}_2\text{Ar}^{\text{Xyl}2})$, $1(\text{Xyl})$, and $[\text{HNEt}_3]\text{BARF}$ (Scheme 2, bottom center). This complexity is probably an important reason behind our failure to isolate $4(\text{Xyl})^+$ in a pure form. In all likelihood, the $[\text{HNEt}_3]\text{Cl}$ generated during the NEt_3 -mediated transformation of $[2(\text{Xyl})]\text{BARF}$ into $[4(\text{Xyl})]\text{BARF}$ reacted with still unaltered $[2(\text{Xyl})]\text{BARF}$ by chloride transfer, affording the neutral dichloride $1(\text{Xyl})$ and $[\text{HNEt}_3]\text{BARF}$. In this respect, it is worth remarking that the said reactivity is exclusive of the $\text{Ir}/\text{PMe}_2\text{Ar}^{\text{Xyl}2}$ system, because for the bulkier $\text{Ir}/\text{PMe}_2\text{Ar}^{\text{Dipp}2}$ analog the alleged neutral dichloride was not detected [11].

The $1(\text{Xyl})$ -plus- $[\text{HNEt}_3]\text{BARF}$ mixture is proposed to exist in equilibrium with $[2(\text{Xyl})]\text{BARF}$ -plus- $[\text{HNEt}_3]\text{Cl}$ (Scheme 2), allowing $[4(\text{Xyl})]\text{BARF}$ to react with $[\text{HNEt}_3]\text{Cl}$. The chemical transformation occurs at -30°C by formal HCl addition to the iridium cation $4(\text{Xyl})^+$ leading to the new complex $5(\text{Xyl})^+$ which is, in fact, an isomer of $2(\text{Xyl})^+$. Low-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the overall reaction (Fig. 5) furnished key information for a planned synthesis of $[5(\text{Xyl})]\text{BARF}$ that permitted its isolation as a yellow crystalline solid. The

cationic complex $5(\text{Xyl})^+$ exhibits a $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at 9.7 ppm, and becomes the only observable organometallic product if sufficient time is given for the transformation to take place (12 h at -30°C). It is important to notice that although stable in solution in pure form, at room temperature $5(\text{Xyl})^+$ decomposes in the presence of NEt_3 , giving rise to an unidentified mixture of products.

The molecular complexity of $5(\text{Xyl})^+$ was originally inferred from multinuclear NMR spectroscopy and further confirmed by X-ray diffraction studies. Its ^1H NMR spectrum presents unequivocal evidence for the dearomatization of a xylyl ring due to the formation of a C–C bond with the cyclopentadienyl ligand. Nonetheless, at variance with compounds 4^+ no fluxionality was detected by solution ^1H NMR. ^1H resonances for only six protons can be found in the aromatic region, whereas multiplets recorded at somewhat lower frequencies (5.44 and 3.01 ppm) can confidently be assigned to the alkenic *m*-CHXyl' and allylic *p*-Xyl' protons, respectively. A resonance at 2.06 ppm is attributed to a methylene group arising from protonation of one of the *meta*

Fig. 4. ORTEP diagram of the cation of complex **3(Xyl)**⁺. Hydrogen atoms are omitted for clarity and thermal ellipsoids are set at 50 % probability.

positions of the dearomatized xylyl ring. The methyl groups of the C₅Me₄ moiety give rise to four distinct ¹H signals (1.97, 1.83, 1.54 and 1.11 ppm), while the C₅Me₄CH₂ protons resonate at 2.00 ppm. Lastly, the methyl groups of the dearomatized xylyl ring resonate at 1.57 and 1.14 ppm, whereas corresponding signals for the non-coordinated ring appear at 2.07 and 1.89 ppm. The proposed η², alkene-type coordination of the dearomatized xylyl ring is also supported by the corresponding ¹³C chemical shifts. The non-coordinated, originally *ortho* carbon resonates at 136.6 ppm in the ¹³C{¹H} spectrum, cf. the bound *ipso* and *ortho* carbon atoms (84.0 and 82.8 ppm, respectively). The alkene meta carbon appears at 126.3 ppm, whereas the *sp*³-hybridized methylene counterpart resonates at 38.5 ppm. Similarly, the also *sp*³-hybridized carbon atom bonded to the C₅Me₄CH₂ moiety is responsible for the signal recorded at 31.9 ppm.

As previously indicated, the molecular structure of complex **5(Xyl)**⁺ was authenticated by X-ray crystallography (Fig. 6). The solid-state structural investigation further confirmed the formation of a C–C bond, with length of 1.551(9) Å, between the C₅Me₄CH₂ fulvene moiety derived from the cyclopentadienyl ligand and the *para* carbon atom of

one of the flanking xylyl rings. The η²-coordination of the resulting cyclohexadiene unit is characterized by Ir–C bond distances of 2.273(6) and 2.257(5) Å for the *ortho* and *ipso* carbon atoms, respectively, whereas the non-coordinated *ortho* carbon was located far from the metal center at 3.151(6) Å. Despite the cationic character of complex **5(Xyl)**⁺, the Ir–Cl bond distance (2.384(1) Å) is similar to that found for **1(Xyl)**, and both are significantly longer than those featured by complexes **2**⁺ (**2(Xyl)**⁺ = 2.278(1), **2(Dipp)**⁺ = 2.347(1) Å), once more reinforcing the hypothesis that the chloride ligand may act as a σ and π donor in the latter unsaturated species.

2.2. Computational study of the formation of **5(Xyl)**⁺

To unveil the reasons behind the stark differences in the reactivity of complexes **2(Xyl)**⁺ and **2(Dipp)**⁺ against NEt₃, we conducted DFT calculations for the former system, under the same basis as previously performed for the latter.¹¹ We previously proposed that triethylamine acts as a base to deprotonate one of the methyl groups of the C₅Me₅ ring leading to a neutral fulvene intermediate (**A-Dipp** in Fig. 7). We considered C–C bond formation between a flanking Dipp ring and the

Fig. 6. ORTEP diagram of the cation of complex **5(Xyl)**⁺. Non-relevant hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 50 % probability.

Fig. 5. Low temperature ³¹P{¹H} NMR monitoring of the reaction of equimolar quantities of **2(Xyl)**⁺ (bottom) and NEt₃.

Fig. 7. Neutral and cationic fulvene complexes proposed for the Dipp system.

fulvene to occur from its cationic derivative, formed after chloride dissociation (**B-Dipp**). Here, we have also considered C–C bond formation to occur at the neutral fulvene complex, which has a comparable energy barrier ($\Delta G_{50}^\ddagger = 20.2$ kcal/mol for the cationic pathway and 20.4 kcal/mol for the C–C bond formation event taking place at the neutral fulvene, Fig. S1).

The profile for the base-promoted conversion of **2(Xyl)**⁺ into **3(Xyl)**⁺ (Fig. 8), for which only trace amounts are observed experimentally, is qualitatively similar to that disclosed previously for the Dipp system.¹¹ Calculations based on the xylyl phosphine supports that, after deprotonation of the C₅Me₅ ligand, the carbon–carbon bond formation step occurs through the analogous Ir(I) neutral fulvene **A Xyl** via **TS**_{AXyl–4XylCl} (17.5 kcal/mol), which is considerably more favourable than with the bulkier Dipp phosphine. Then, dissociation of the chloride

ligand (8.3 kcal/mol, **TS**_{4XylCl–4Xyl+}) from the Ir(III) species **4(Xyl)Cl** (0.8 kcal/mol) followed by facile η^1 -to- η^3 isomerisation gives the observed intermediate, **4(Xyl)**⁺, at –0.4 kcal/mol. At variance, C–C bond formation from the cationic fulvene **B Xyl** (Fig. S2) requires surmounting a barrier of 21.9 kcal/mol (**TS**_{A–BXyl}), that is, 4.4 kcal/mol higher than **TS**_{AXyl–4XylCl}.

Although for the xylyl complex the formation of the pseudoallylic complex **3(Xyl)**⁺ is thermodynamically more favourable (–16.6 instead of –11.5 kcal/mol), a noticeable increase was found for the barrier associated to the fulvene attack to the benzylic C–H atom (26.8 kcal/mol relative to **4(Xyl)**⁺, cf. the 21.5 kcal/mol found for the Dipp system) to yield intermediate **C Xyl**, that displays η^3 -coordination of the allylic moiety (instead of the η^1 mode found for **C Dipp**).¹¹ The higher barrier constitutes the rate limiting step for the xylyl system and seems to be responsible for the dissimilar reactivity exhibited by the two phosphines. Thus, the less accessible C–H deprotonation step permits other alternative pathways to compete and lead to a different reaction outcome, precluding the formation of **3(Xyl)**⁺ in the presence of NEt₃ (Scheme 2).

The aforementioned findings prompted us to computationally study the formal addition of HCl (from the [HNEt₃]Cl salt present in the reaction medium) to **4(Xyl)**⁺. This species, at –0.4 kcal/mol relative to **2(Xyl)**⁺, readily incorporates a chloride anion via **TS**_{4Xyl+–4XylCl} (8.3 kcal/mol, Fig. 9) to give the neutral complex **4(Xyl)Cl** at 0.8 kcal/mol. Protonation of the formerly *meta* carbon atom closer to the chloride ligand was found to be accessible through **TS**_{4XylCl–5Xyl+} at 11.3 kcal/mol, yielding complex **5(Xyl)**⁺ at –4.0 kcal/mol (cf. **3(Xyl)**⁺ at –16.2

Fig. 8. ΔG_{50}° profile for the NEt₃-promoted conversion of **2(Xyl)**⁺ into **3(Xyl)**⁺ via **4(Xyl)**⁺.

Fig. 9. ΔG_{50}° profile for the formal incorporation of HCl to $4(\text{Xyl})^+$ to yield complex $5(\text{Xyl})^+$.

kcal/mol [17]. In agreement with our experimental findings, it may be concluded that $5(\text{Xyl})^+$ is the kinetic product of a complex base-promoted isomerisation of $2(\text{Xyl})^+$, which indeed contrasts with the formation of $3(\text{Xyl})^+$ in the absence of external base (Scheme 2).¹¹ It is therefore evident that the present work has disclosed an interesting case of a base-dependent competing isomerisation path involving C–H bond activation along with C–C bond formation.

For the sake of comparison, we decided to computationally explore the potential formation of $5(\text{Dipp})^+$, derived from the bulkier $\text{PMe}_2\text{Ar}^{\text{Dipp}2}$ phosphine (Fig. 10), which was not observed experimentally. As anticipated, energy barriers are higher than for the Xyl system as a consequence of the steric hindrance exerted by the isopropyl groups around the coordination environment of the metal center. Considering that these barriers are comparable to those found for the formation of $3(\text{Dipp})^+$ [11], we postulate that the selectivity towards the latter is due to thermodynamic reasons, that is, formation of $5(\text{Dipp})^+$ from $4(\text{Dipp})^+$ and $[\text{HNEt}_3]\text{Cl}$ is not exergonic.

3. Experimental section

3.1. General considerations

All manipulations were carried out using standard Schlenk techniques, under high purity nitrogen. Solvents were rigorously dried and distilled under nitrogen prior to use. *n*-Pentane (C_5H_{12}) and *n*-hexane (C_6H_{14}) were distilled over sodium. Diethyl ether was distilled over sodium/benzophenone. CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2 . $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}(\text{PMe}_2\text{Ar}^{\text{Xyl}2})][\text{BAR}_f]$ (complex $2(\text{Xyl})^+$) was prepared according to our previous report.¹¹ NEt_3 was commercially available and used as received. Solution NMR spectra were recorded on Bruker DRX-400 and DRX-500 spectrometers. Spectra were referenced to external

SiMe_4 (δ : 0 ppm) using the residual proton solvent peaks as internal standards (^1H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments), while ^{31}P was referenced to H_3PO_4 . Spectral assignments were made by routine one- and two-dimensional NMR experiments (^1H , $^1\text{H}\{^{31}\text{P}\}$, $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, COSY, NOESY, HSQC and HMBC) where appropriate. Single crystals were grown from saturated hexane/dichloromethane solutions. For elemental analyses a LECO TruSpec CHN elementary analyzer was utilized.

3.2. Complex $2(\text{Dipp})^+\cdot\text{CO}$

A CH_2Cl_2 solution (5 mL) of complex $[2(\text{Dipp})]\text{BAR}_f$ (40.0 mg, 0.024 mmol) was charged with CO (1 bar). The solution was stirred for 5 min and the solvent was removed under reduced pressure, quantitatively affording the BAR_f salt of complex $2(\text{Dipp})^+\cdot\text{CO}$ as a yellow solid. Crystalline starting material permitted to carry out the reaction in the solid–gas interphase. The NMR characterisation was carried out in acetone- d_6 due to the limited solubility of this complex in CD_2Cl_2 at -20°C . **Anal. Calcd.** for $\text{C}_{75}\text{H}_{70}\text{BClF}_{24}\text{IrOP}$: C, 52.59; H, 4.12. **Found:** C, 52.25; H, 4.50. **^1H NMR** (400 MHz, $(\text{CD}_3)_2\text{CO}$, -20°C) δ : 7.81 (m, 8H, *o*-Ar), 7.72 (s, 4H, *p*-Ar), 7.68 (td, $^3J_{\text{HH}} = 7.6$ Hz, $^5J_{\text{HP}} = 2.5$ Hz, 1H, *p*- C_6H_3), 7.47 (t, $^3J_{\text{HH}} \approx 7.6$ Hz, 2H, *p*-Dipp), 7.45 (m, 1H, *m*-Dipp), 7.39 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 0.9$ Hz, 1H, *m*-Dipp), 7.33 (ddd, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HP}} = 3.9$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 1H, *m*- C_6H_3), 7.26 (m, 3H, *m*-Dipp), 7.23 (m, 1H, *m*- C_6H_3), 3.30 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 1H, $(\text{CHMe}_2)_{\text{Dipp}}$), 3.19 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 1H, $(\text{CHMe}_2)_{\text{Dipp}}$), 2.65 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 1H, $(\text{CHMe}_2)_{\text{Dipp}}$), 2.52 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 1H, $(\text{CHMe}_2)_{\text{Dipp}}$), 2.12 (d, $^2J_{\text{HP}} = 10.8$ Hz, 3H, *PM*Me), 1.91 (d, $^4J_{\text{HP}} = 2.2$ Hz, 15H, C_5Me_5), 1.57 (d, $^2J_{\text{HP}} = 11.3$ Hz, 3H, *PM*Me), 1.35 (d, $^3J_{\text{HH}} \approx 6.7$ Hz, 3H, Me_{Dipp}), 1.33 (d, $^3J_{\text{HH}} \approx 6.7$ Hz, 3H, Me_{Dipp}), 1.31 (d, $^3J_{\text{HH}} = 6.6$ Hz, 3H, Me_{Dipp}), 1.27 (d, $^3J_{\text{HH}} = 6.7$ Hz, 3H, Me_{Dipp}), 1.18 (d, $^3J_{\text{HH}} = 6.7$ Hz, 3H, Me_{Dipp}), 1.15

Fig. 10. ΔG_{50° profile for the formal incorporation of HCl to $4(\text{Dipp})^+$ to yield complex $5(\text{Dipp})^+$.

(d, $^3J_{\text{HH}} = 6.7$ Hz, 3H, MeDipp), 0.83 (d, $^3J_{\text{HH}} = 6.7$ Hz, 3H, MeDipp), 0.69 (d, $^3J_{\text{HH}} = 6.6$ Hz, 3H, MeDipp). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$, -20°C) δ : 167.9 (d, $^2J_{\text{CP}} = 19$ Hz, CO), 162.3 (q, $^1J_{\text{CB}} = 50$ Hz, *ipso*-Ar), 149.3 (*o*-Dipp), 148.0 (*o*-Dipp), 147.2 (*o*-Dipp), 146.6 (*o*-Dipp), 146.2 (d, $^2J_{\text{CP}} = 6$ Hz, *o*-C₆H₃), 145.4 (d, $^2J_{\text{CP}} = 11$ Hz, *o*-C₆H₃), 140.8 (*ipso*-Dipp), 139.7 (*ipso*-Dipp), 136.2 (d, $^3J_{\text{CP}} = 10$ Hz, *m*-C₆H₃), 135.2 (*o*-Ar), 134.8 (d, $^3J_{\text{CP}} = 9$ Hz, *m*-C₆H₃), 130.7 (*p*-Dipp), 130.5 (*p*-C₆H₃), 130.1 (*p*-Dipp), 129.7 (q, $^2J_{\text{CF}} = 32$ Hz, *m*-Ar), 126.8 (*m*-Dipp), 125.4 (d, $^1J_{\text{CP}} = 54$ Hz, *ipso*-C₆H₃), 125.0 (q, $^1J_{\text{CF}} = 272$ Hz, CF₃), 124.7 (*m*-Dipp), 123.1 (*m*-Dipp), 122.9 (*m*-Dipp), 118.4 (m, *p*-Ar), 107.1 (C₅Me₅), 32.4 ((CHMe₂)Dipp), 31.6 ((CHMe₂)Dipp), 31.2 ((CHMe₂)Dipp), 30.8 ((CHMe₂)Dipp), 27.5 (MeDipp), 25.9 (MeDipp), 25.0 (MeDipp), 24.9 (MeDipp), 24.8 (MeDipp), 23.7 (MeDipp), 23.5 (d, $^1J_{\text{CP}} \approx 39$ Hz, PMeMe), 22.0 (MeDipp), 21.0 (MeDipp), 20.9 (d, $^1J_{\text{CP}} = 35$ Hz, PMeMe), 9.4 (C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, $(\text{CD}_3)_2\text{CO}$, 25°C) δ : -33.2 . IR (Nujol): $\nu(\text{IrCO})$ 2059 cm^{-1} .

Complex 5(Xyl)⁺ To a -35°C CH_2Cl_2 solution of complex $2(\text{Xyl})^+$ (40.0 mg, 0.025 mmol) was added NEt₃ (3.7 μL , 0.050 mmol). The solution was kept at -32°C for 12 h. The solvent was removed under reduced pressure and the yellow residue washed with pentane (10 mL) and extracted with Et₂O at -30°C (15 mL). The solvent was concentrated to approximately half the original volume and the same amount of

hexane was carefully added to form a bilayer. Crystallisation at -32°C afforded compound $5(\text{Xyl})^+$ as a yellow, crystalline solid with ca. 70 % yield. **Anal. Calcd.** for C₆₆H₅₄BClF₂₄IrP: C, 50.41, H, 3.46. **Found:** C, 50.34; H, 3.54. ^1H NMR (500 MHz, CD_2Cl_2 , 25°C) δ : 7.72 (s, 8H, *o*-Ar), 7.61 (td, $^3J_{\text{HH}} = 7.6$ Hz, $^5J_{\text{HP}} = 2.7$ Hz, 1H, *p*-C₆H₃), 7.56 (s, 4H, *p*-Ar), 7.27 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, *p*-Xyl), 7.21 (m, 2H, *m*-C₆H₃, *m*-Xyl), 7.12 (ddd, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HP}} = 3.9$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, *m*-C₆H₃), 7.10 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H, *m*-Xyl), 5.44 (m, 1H, *m*-CH_{Xyl}), 3.01 (m, 1H, *p*-Xyl), 2.08 to 2.05 (m, 2H, *m*-CH₂), 2.07 (s, 3H, Me_{Xyl}), 2.03 to 1.97 (m, 2H, C₅Me₄CH₂), 1.97 (d, $^4J_{\text{HP}} = 4.3$ Hz, 3H, C₅Me₄), 1.89 (s, 3H, Me_{Xyl}), 1.83 (d, $^4J_{\text{HP}} = 4.5$ Hz, 3H, C₅Me₄), 1.81 (d, $^2J_{\text{HP}} = 10.6$ Hz, 3H, PMeMe), 1.57 (m, 3H, Me_{Xyl}), 1.54 (s, 3H, C₅Me₄), 1.14 (d, $^2J_{\text{HP}} = 12.0$ Hz, 3H, PMeMe), 1.14 (s, 3H, Me_{Xyl}), 1.11 (s, 3H, C₅Me₄). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , -25°C) δ : 161.7 (q, $^1J_{\text{CB}} = 50$ Hz, *ipso*-Ar), 147.2 (d, $^2J_{\text{CP}} = 28$ Hz, *o*-C₆H₃), 144.8 (*o*-C₆H₃), 137.4 (m, *o*-Xyl, *ipso*-Xyl), 136.6 (*o*-Xyl), 136.0 (d, $^1J_{\text{CP}} = 60$ Hz, *ipso*-C₆H₃), 134.8 (*o*-Xyl), 134.7 (*o*-Ar), 133.9 (*p*-C₆H₃), 130.9 (d, $^3J_{\text{CP}} = 7$ Hz, *m*-C₆H₃), 128.8 (overlapped, *p*-Xyl), 128.6 (q, $^2J_{\text{CF}} = 31$ Hz, *m*-Ar), 127.9 (*m*-Xyl), 127.6 (d, $^4J_{\text{CP}} \approx 14$ Hz, *m*-C₆H₃), 127.5 (*m*-Xyl), 126.3 (*m*-CH_{Xyl}), 124.5 (q, $^1J_{\text{CF}} = 272$ Hz, CF₃), 1

0.5 (m, *p*-Ar), 114.3 (C₅Me₄), 107.7 (C₅Me₄), 102.5 (C₅Me₄), 97.1 (d, $^2J_{\text{CP}} = 10$ Hz, C₅Me₄), 88.1 (C₅Me₄), 84.0 (*ipso*-Xyl), 82.8 (*o*-Xyl), 38.5

(*m*-CH₂), 31.9 (*p*-Xyl¹), 27.8 (Me¹_{Xyl}), 23.2 (Me_{Xyl}), 21.2 (Me_{Xyl}), 20.8 (Me_{Xyl}), 17.5 (d, ¹J_{CP} = 37 Hz, *PMeMe*), 14.9 (C₅Me₄CH₂), 10.2 (d, ¹J_{CP} ≈ 45 Hz, *PMeMe*), 10.0 (C₅Me₄), 9.8 (C₅Me₄), 7.4 (C₅Me₄), 4.9 (C₅Me₄). ³¹P{¹H} NMR (200 MHz, CD₂Cl₂, 25 °C) δ: 9.7.

Computational details. Calculations were performed at the DFT level with the Gaussian 09 (Revision D.01) program [18]. The hybrid functional PBE0 [19] was used throughout the computational study, and dispersion effects were accounted for at the optimisation step by using Grimme's D3 parameter set with Becke–Johnson (BJ) damping [20]. Geometry optimisations were carried out without geometry constraints, using the 6-31G(d,p) [21] basis set to represent the C, H, P, Cl and N atoms and the Stuttgart/Dresden Effective Core Potential and its associated basis set (SDD) [22] to describe the Ir atoms. Bulk solvent effects (dichloromethane) were included at the optimisation stage with the SMD continuum model [23]. The stationary points and their nature as minima or saddle points (TS) were characterized by vibrational analysis, which also produced enthalpy (H), entropy (S) and Gibbs energy (G) data at 298.15 K. The minima connected by a given transition state were determined by perturbing the transition states along the TS coordinate and optimizing to the nearest minimum. 50%-corrected free energy variations (ΔG₅₀), employed to account for translational entropy overestimation [24].

4. Conclusions

In summary, this work demonstrates that steric effects can impact the reactivity between unsaturated, cationic (C₅Me₅)Ir(III) complexes (2⁺) and triethylamine. For 2(Xyl)⁺, C–C bond formation between the deprotonated C₅Me₅ ligand and a xylyl ring from the phosphine, which becomes dearomatized, takes place via the Ir(III)/Ir(I) redox cycle, though at a remote distance from the metal center, in agreement with the reactivity of the previously reported system based on the bulkier *PMe₂Ar^{Dipp2}* phosphine. Interestingly, the lower steric protection offered by the xylyl-derived terphenyl phosphine allows solution equilibria and the formal addition of HCl to the iridium allyl species (4 (Xyl)⁺), yielding a saturated Ir(III) complex (5(Xyl)⁺) presenting η² coordination to a hexadiene ligand as the result of a unique base-mediated isomerisation of 2(Xyl)⁺. DFT calculations allow the overall rationalisation of the observed divergent reactivity and indicate that thermodynamic reasons preclude the observation of the HCl addition product with the bulkier, diisopropylphenyl-substituted system.

CCRediT authorship contribution statement

Juan José Moreno: Investigation, Formal analysis, Writing - original draft. **María F. Espada:** Investigation. **Celia Maya:** Investigation, Visualization. **Jesús Campos:** Conceptualization, Supervision, Writing - review & editing. **Joaquín López-Serrano:** Conceptualization, Formal analysis, Supervision, Writing - review & editing. **Stuart A. Macgregor:** Conceptualization, Formal analysis, Supervision, Writing - review & editing. **Ernesto Carmona:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC contains the supplementary crystallographic data for complexes 1(Xyl), 2(Dipp)BAr_F, 3(Xyl)BAr_F and 5(Xyl)BAr_F. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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