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Base-Promoted, Remote C−H Activation at a Cationic (η^5-C_5Me_5)Ir(III) Center Involving Reversible C−C Bond Formation of Bound C_5Me_5

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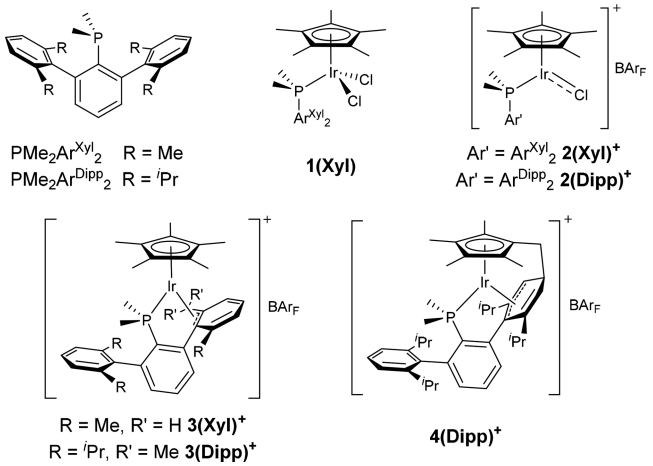
Supporting Information

ABSTRACT: C−H bond activation at cationic [(η^5-C_5Me_5)Ir(PMe_2Ar')] centers is described, where PMe_2Ar' are the terphenyl phosphine ligands $PMe_2Ar^{Xyl}{}_2$ and $PMe_2Ar^{Dipp}{}_2$. Different pathways are defined for the conversion of the five-coordinate complexes [(η^5-C_5Me_5)IrCl(PMe_2Ar')]$^+$, **2(Xyl)**$^+$ and **2(Dipp)**$^+$, into the corresponding pseudoallyls **3(Xyl)**$^+$ and **3(Dipp)**$^+$. In the absence of an external Brønsted base, electrophilic, remote ζ C−H activation takes place, for which the participation of dicationic species, [(η^5-C_5Me_5)Ir(PMe_2Ar')]$^{2+}$, is proposed. When NEt_3 is present, the $PMe_2Ar^{Dipp}{}_2$ system is shown to proceed via **4(Dipp)**$^+$ as an intermediate en route to the thermodynamic, isomeric product **3(Dipp)**$^+$. This complex interconversion involves a non-innocent C_5Me_5 ligand, which participates in C−H and C−C bond formation and cleavage. Remarkably, the conversion of **4(Dipp)**$^+$ to **3(Dipp)**$^+$ also proceeds in the solid state.

Cyclopentadienyls, C_5R_5, and tertiary phosphines, PR_3, are unquestionably two of the most important classes of ligands in organometallic chemistry and catalysis.[1] Although in most cases C_5R_5 and PR_3 behave strictly as spectators, in some reactions they can also directly participate. As PR_3 and C_5R_5 continue to be increasingly employed in homogeneous catalysis, knowledge of these unforeseen reactions is crucial because they might strongly influence catalytic outcomes[2] or lead to catalyst deactivation.[3] Certain aryl phosphines undergo facile cyclometalation,[4,5] and recently, nickel- and palladium-mediated dearomatization of dialkylbiaryl phosphines has been reported.[2,6] With cyclopentadienyl ligands, in particular C_5Me_5, ring methyl activation implying either deprotonation or hydride abstraction,[7,8] as well as metal-to-ring hydride transfer,[9,10] have all been documented.

Transition metal mediated C−H bond activation is a very important transformation with great potential for the functionalization of hydrocarbons. Decisive mechanistic advances have been made with the investigation of electrophilic C−H bond activation at (η^5-C_5Me_5)Ir(III) centers,[11] revealing, among other details, the influence of coligands, in particular their ability to act as a base to accept the generated proton.[12] Here, we targeted the synthesis of cationic (η^5-C_5Me_5)Ir(III) complexes of the terphenyl phosphines[13] $PMe_2Ar^{Xyl}{}_2$ and $PMe_2Ar^{Dipp}{}_2$ (Scheme 1). In particular, we report that the five-coordinate complexes [(η^5-C_5Me_5)IrCl(PR_2Ar')]$^+$, **2(Xyl)**$^+$ and **2(Dipp)**$^+$, promote facile electrophilic C−H activation at remote ζ C−H bonds of the phosphine ligand to form **3(Xyl)**$^+$ and **3(Dipp)**$^+$. Moreover, for **2(Dipp)**$^+$, the observed ζ C−H activation in the presence of NEt_3 occurs through a complex mechanism that implies reversible η^5-C_5Me_5 deprotonation and reversible C−C bond formation between the resulting tetramethylfulvene terminal methylene group, and one of the flanking Dipp rings of the phosphine, that itself undergoes dearomatization.[2,6] The resulting intermediate, **4(Dipp)**$^+$, contains a 10-membered phospha-iridacycle. Intriguingly, this complex transforms

Scheme 1. Dimethyl Terphenyl Phosphines and Corresponding Iridium(III) Cyclopentadienyl Complexes Reported in This Work



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readily into the isomeric ζ C−H activation species, **3(Dipp)**$^+$, not only in solution, but also in the solid state.

Treatment of $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ with $PMe_2Ar^{Xyl}{}_2$ in CH_2Cl_2 yielded the expected $[(\eta^5\text{-}C_5Me_5)IrCl_2(PMe_2Ar^{Xyl}{}_2)]$ product, **1(Xyl)**, in high yields (~90%). Chloride abstraction by $NaBAr_F$ was also straightforward and allowed isolation of the cationic complex $[(\eta^5\text{-}C_5Me_5)IrCl(PMe_2Ar^{Xyl}{}_2)]^+$ (**2(Xyl)**$^+$, Scheme 1) as its BAr_F salt, which appeared as a very dark red crystalline solid. Because of the high solution reactivity of this low-coordinate complex under ambient conditions, its synthesis and characterization were performed at −20 °C. Microanalytical and spectroscopic data (see the Supporting Information (SI)) were in agreement with the formulation indicated in Scheme 1, which was subsequently confirmed by X-ray crystallography (Figure 1, left). The short

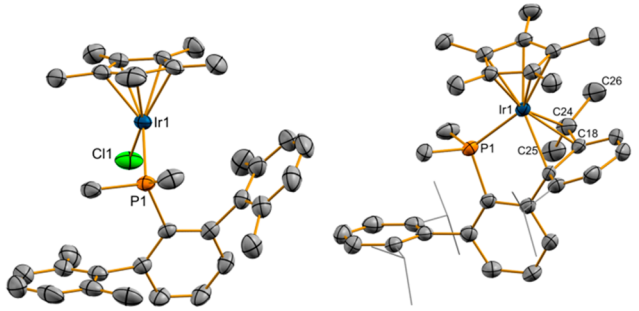


Figure 1. ORTEPs of the cations of complex **[2(Xyl)]BAr$_F$** and **[3(Dipp)]BAr$_F$**. Hydrogen atoms are excluded for clarity, and thermal ellipsoids are set at 50% probability. Gray lines represent Dipp ^{i}Pr substituents.

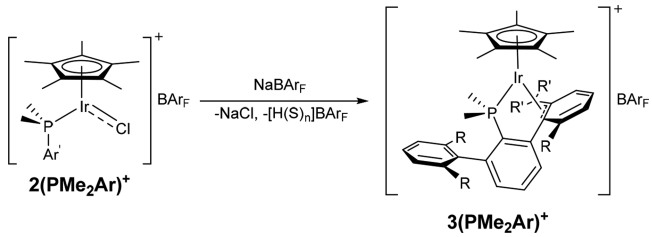
Ir−Cl bond length of 2.2785(9) Å (cf. the 2.396(1) Å average distance in **1(Xyl)**), coupled with the distinct, intense dark color,[14−16] suggests chloride acts as a π-donor in this formally 16e complex; similar Ru−Cl shortening was also reported in $[(\eta^5\text{-}C_5Me_5)RuCl(P^iPr_3)]$.[17]

At room temperature, dichloromethane solutions of **2(Xyl)**$^+$ underwent further chemical changes, as evidenced by a color change from the initial dark red to yellow-red. This process was accelerated by the presence of water and product crystallization from CH_2Cl_2/Et_2O solvent yielded mixtures of a new iridium complex, **3(Xyl)**$^+$, along with $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ and $[HPMe_2Ar^{Xyl}{}_2]BAr_F$. **3(Xyl)**$^+$ was unequivocally characterized as a pseudoallylic species formed via remote ζ C−H activation of a benzylic C−H bond of one of the Xyl substituents. It thus appears that the HCl released in the formation of **3(Xyl)**$^+$ decomposed unreacted **2(Xyl)**$^+$ to yield the above-mentioned side products.

Given that increased coligand steric demands often confer enhanced kinetic stability and hinder undesirable side reactions, $(\eta^5\text{-}C_5Me_5)Ir(III)$ complexes of the bulkier phosphine $PMe_2Ar^{Dipp}{}_2$ (Scheme 1) were considered. Although the dichloride analogue of **1(Xyl)** could not be generated, possibly because of steric hindrance, cationic **2(Dipp)**$^+$ formed rapidly when $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ and $PMe_2Ar^{Dipp}{}_2$ were allowed to react in the presence of $NaBAr_F$. The similar properties of the two **2(PMe$_2$Ar′)**$^+$ complexes, including the observation for **2(Dipp)**$^+$ of a $^{31}P\{^1H\}$ NMR singlet with a $\Delta(\delta)$ shift relative to free $PMe_2Ar^{Dipp}{}_2$ practically identical to the corresponding value for **2(Xyl)**$^+$, strongly supported a five-coordinate structure analogous to that of **2(Xyl)**$^+$. Notwithstanding the structural similarity, **2(Dipp)**$^+$ possesses much superior solution stability.

As the formation of cationic pseudoallyls, **3(PMe$_2$Ar′)**$^+$, from the corresponding chlorides, **2(PMe$_2$Ar′)**$^+$, implies electrophilic C−H activation and elimination of HCl, we considered it of interest to study (i) the generation of dicationic $[(\eta^5\text{-}C_5Me_5)Ir(PR_2Ar')]^{2+}$ species by chloride abstraction from **2(PMe$_2$Ar′)**$^+$ with $NaBAr_F$ and (ii) the use of an external Brønsted base such as NEt_3 to facilitate HCl elimination. The first approach actually constitutes the best procedure for the high yield synthesis of complexes **3(Xyl)**$^+$ and **3(Dipp)**$^+$ (see Scheme 2). Focusing on the $PMe_2Ar^{Dipp}{}_2$

Scheme 2. Electrophilic ζ C−H Activation in Complexes 2$^+$ To Give the Pseudoallylic Species 3$^+$; S Represents a Solvent Molecule



analogues for additional solution reaction studies, it was found that the formation of **3(Dipp)**$^+$ promoted by $NaBAr_F$ was very slow at room temperature, probably due to the absence of an effective base. Consistent with this hypothesis, reaction of $PMe_2Ar^{Dipp}{}_2$ with $[(\eta^5\text{-}C_5Me_5)Ir(H_2O)_3](SO_4)$[18] proceeded rapidly to afford **3(Dipp)**$^+$.

The BAr_F salts of the two pseudoallyl complexes **3(Xyl)**$^+$ and **3(Dipp)**$^+$ were fully characterized by microanalysis and multinuclear NMR spectroscopy. For **3(Xyl)**$^+$ distinct ^1H NMR resonances corresponding to the *anti* and *syn* pseudoallylic protons are seen as multiplets at 3.14 and 1.04 ppm, with $^2J_{HH}$ = 3.9 and $^3J_{HP}$ = 1 and 14 Hz, respectively. The corresponding carbon atom gives a $^{13}C\{^1H\}$ signal at 26.3 ppm ($^2J_{CP}$ = 4 Hz), whereas the C_{ortho} and C_{ipso} involved in the η^3-bonded unit appear at 89.1 and 83.2 ppm, respectively. Single-crystals of **[3(Dipp)]BAr$_F$** were also investigated by X-ray crystallography (Figure 1, right) that confirms that a Dipp ring in **2(Dipp)**$^+$ has undergone ζ C−H activation to give a pseudoallylic product (Ir−CMe_2 = 2.224(3), Ir−C_{ortho} = 2.197(3) and Ir−C_{ipso} = 2.257(3) Å).

The mechanism of the C−H bond activation to form the **3(PMe$_2$Ar′)**$^+$ complexes was also investigated by DFT methods.[19] The most accessible pathway involves initial Cl^- dissociation to afford an ion-pair comprising dicationic $[(\eta^5\text{-}C_5Me_5)Ir(PMe_2Ar')]^{2+}$, in which the phosphine is bound in a κ-P, η^3-C_{arene} fashion (Figure S1), and Cl^-, which resides in the outer coordination sphere. For **2(Xyl)**$^+$, this process entails a barrier of 18.4 kcal/mol and gives a species at +16.5 kcal/mol. Facile rearrangement then forms ζ C−H agostic intermediate at +19.3 kcal/mol (Scheme 3). The acidity of the agostic proton in this dicationic species promotes its facile abstraction by the Cl^- ion via a transition state at +22.0 kcal/mol, this representing the overall barrier to the C−H activation process.[20] In contrast, chloride-mediated deprotonation in **2(Dipp)**$^+$ does not occur at the agostic complex, but requires an additional C−H oxidative cleavage step to form an Ir(V) hydride, which is then deprotonated by Cl^-. The overall barrier

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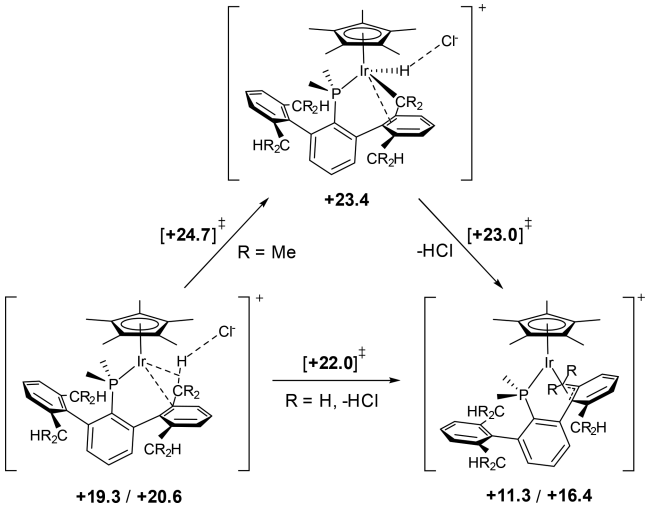
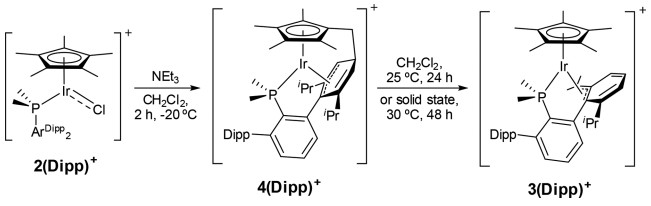
Scheme 3. Proposed Mechanism for the Electrophilic C−H Activation in 2(PMe$_2$Ar′)$^+$ Complexes (ΔG_{50}°, kcal/mol, R = H, Me)



in this case is 24.7 kcal/mol, 2.7 kcal/mol higher than that in **2(Xyl)**$^+$ and so consistent with the observed enhanced solution stability of the former (see the SI for details). The formation of [HPMe$_2$Ar′]BAr$_F$ and [(η^5-C$_5$Me$_5$)IrCl$_2$]$_2$ from **2**$^+$ and HCl seems to be the driving force of the reaction in both systems.

The addition of a slight excess of NEt$_3$ to solutions of **2(Dipp)**$^+$ highlighted the remarkable chemical and structural changes that occur en route to **3(Dipp)**$^+$. The latter formed quantitatively by ^{1}H NMR after stirring at room temperature for about 24 h. However, following the reaction by NMR demonstrated the formation of an intermediate, **4(Dipp)**$^+$, responsible for a ^{31}P{^{1}H} singlet resonance at −4.4 ppm, clearly distinguishable from those of **2(Dipp)**$^+$ and **3(Dipp)**$^+$ at 6.6 and 9.8 ppm, respectively. After careful NMR analysis of reaction temperature and time, we found that intermediate **4(Dipp)**$^+$ formed as the only observable product when **2(Dipp)**$^+$ and NEt$_3$ were allowed to react at −20 °C for 2 h (Scheme 4).

Scheme 4. NEt$_3$-Assisted Formation of Complex 4(Dipp)$^+$ from 2(Dipp)$^+$, and Solution and Solid-State Isomerization of 4(Dipp)$^+$ to 3(Dipp)$^+$[a]



[a] BAr$_F$ anions omitted for clarity.

Although **3(Dipp)**$^+$ and **4(Dipp)**$^+$ are isomers, the latter exhibits a very different chemical constitution, for it contains a 10-membered metallacyclic unit resulting from deprotonation of the C$_5$Me$_5$ ring,[7] followed by nucleophilic attack[7a,b] at the *para* carbon atom of the coordinated Dipp ring, which is dearomatized.[2,6] Unequivocal structural evidence was gained from variable temperature multinuclear NMR and X-ray studies (Figure 2). In solution, two degenerate pseudoallylic structures undergo fast exchange at room temperature, but

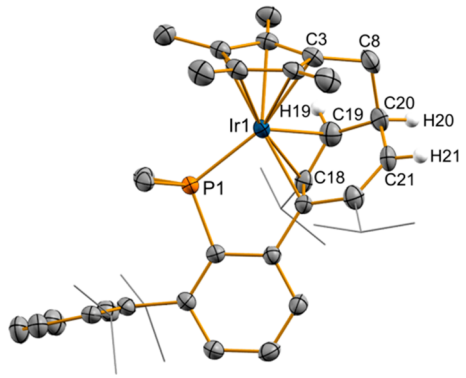


Figure 2. ORTEP of the cation of complex [**4(Dipp)**]BAr$_F$. Hydrogen atoms are excluded for clarity, and thermal ellipsoids are set at 50% probability. Gray lines represent Dipp ^{i}Pr substituents.

reach the slow-exchange regime at −30 °C. At this temperature, the diastereotopic C$_5$Me$_4$C*H*$_2$ protons resonate as doublets of doublets centered at 3.27 and 2.46 ppm, as a consequence of additional coupling to the adjacent *para* C*H* nucleus. The X-ray structure in Figure 2 reveals that, beyond the η^5 coordination of the C$_5$Me$_4$CH$_2$ moiety, the now activated phosphine ligand binds to iridium through the phosphorus atom and three adjacent carbon atoms of the dearomatized ring (Ir−C bond distances of 2.166(4) (to C$_{ipso}$), 2.178(4) (C$_{ortho}$), and 2.255(5) Å (C$_{meta}$)), whereas the newly formed C−C bond has a length of 1.560(6) Å.

The isomerization of **4(Dipp)**$^+$ to **3(Dipp)**$^+$ required neither base (NEt$_3$) nor acid (HNEt$_3^+$) catalysis. Instead, it occurred cleanly in CH$_2$Cl$_2$ solution (Scheme 4) following first-order kinetics ($t_{1/2} \approx 6$ h; see the SI for details). It was, however, most notable to find that the **4(Dipp)**$^+$ to **3(Dipp)**$^+$ isomerization occurred also easily in the solid state (2 days, 30 °C).[21,22] Periodical sampling and NMR monitoring disclosed no observable intermediates.

The conversion of **2(Dipp)**$^+$ into **3(Dipp)**$^+$ through **4(Dipp)**$^+$ was also studied computationally (Figure 3). Amine-mediated C$_5$Me$_5$ deprotonation (17.4 kcal/mol, **TS$_{2-A}$**) led to the formation of a neutral, Ir(I) fulvene complex (12.0 kcal/mol, **A**). The thus generated triethylammonium cation then facilitates chloride release (20.2 kcal/mol, **TS$_{A-B}$**) to yield intermediate **B** (1.0 kcal/mol). **B** is a cationic fulvene complex for which metal unsaturation is compensated by means of a π-arene interaction with one of the flanking aryl rings of the phosphine, and presents an appropriate geometry to undergo C−C bond formation via **TS$_{B-4}$** at 17.7 kcal/mol. We propose this ring dearomatization step proceeds with concomitant metal reoxidation to give Ir(III) complex **4(Dipp)**$^+$ at −2.1 kcal/mol. Isomerization of **4(Dipp)**$^+$ to **3(Dipp)**$^+$ involves the reversible formation of Ir(I) complex **B** via **TS$_{B-4}$**. Attack of the fulvene moiety in **B** at the C−H of an isopropyl group of the proximate aryl ring (19.4 kcal/mol, **TS$_{B-C}$**) reoxidizes the metal center to Ir(III) and gives the η^1-allyl complex **C** (see the SI) at 7.6 kcal/mol. Isomerization to the corresponding η^3-allyl occurs via **TS$_{C-3}$** (18.9 kcal/mol) and yields **3(Dipp)**$^+$ at −11.5 kcal/mol. It is striking that both the classically innocent ligands (C$_5$Me$_5$ and PR$_3$) play a fundamental role in these transformations (C−H activation and reversible C−C bond formation), whereas the metal center participates by means of the Ir(I)−Ir(III) redox cycle (see the SI for details).

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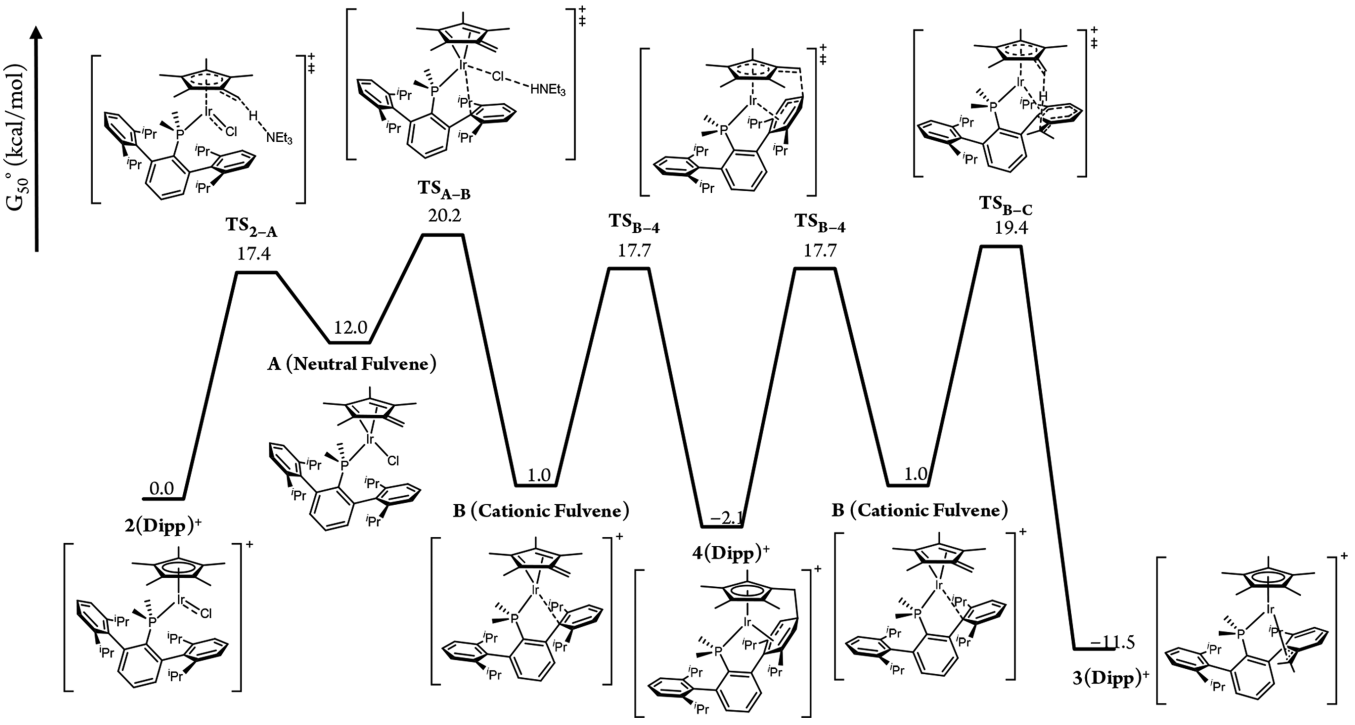

Figure 3. ΔG_{50}° profile for the conversion of **2(Dipp)**$^+$ into **3(Dipp)**$^+$ through **4(Dipp)**$^+$.

In conclusion, chloride abstraction from complexes **2-(PMe$_2$Ar′)**$^+$ (Ar′ = Ar$^{Xyl}{}_2$, Ar$^{Dipp}{}_2$) fosters electrophilic, remote C−H bond activation at dicationic intermediates $[(\eta^5\text{-}C_5Me_5)Ir(PMe_2Ar')]^{2+}$, to give the pseudoallyl products **3(PMe$_2$Ar′)**$^+$ shown in Scheme 2. In the presence of NEt$_3$, complex **2(Dipp)**$^+$ converts into the same C−H activation product **3(Dipp)**$^+$, though through an unforeseen intermediate, **4(Dipp)**$^+$. The latter participates in a complex reaction path involving a non-innocent C_5Me_5 ligand that undergoes reversible C−H and C−C bond formation and cleavage at one of the methyl termini. The **4(Dipp)**$^+$-to-**3(Dipp)**$^+$ conversion occurs both in solution and in the solid state. The latter observation represents, we believe, a valuable contribution to the field of solid state organometallic chemistry, which, despite its importance as a bridge between molecular and solid-state chemistry, and hence between homogeneous and heterogeneous catalysis, is still underdeveloped.[21a]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b11752.

All optimized geometries along with their SCF energies (electrophilic) (XYZ)

All optimized geometries along with their SCF energies (base promoted) (XYZ)

Crystallographic data for **2(Xyl)**$^+$ (CIF)

Crystallographic data for **3(Dipp)**$^+$ (CIF)

Crystallographic data for **4(Dipp)**$^+$ (CIF)

Experimental procedures, NMR spectra, full computational details and results and kinetic experiments (PDF)

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Notes

The authors declare no competing financial interest.

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carried out without geometry constraints and included solvent (dichloromethane) and dispersion effects (Grimme's D3 parameter set). 50%-corrected free energy variations (ΔG_{50}°) were employed to account for translational entropy overestimation.

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