Base-Promoted, Remote C–H Activation at a Cationic \((\eta^5\text{C}_5\text{Me}_5)\text{Ir(III)}\) Center Involving Reversible C–C Bond Formation of Bound \text{C}_5\text{Me}_5

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Supporting Information

ABSTRACT: C–H bond activation at cationic \([(\eta^5\text{C}_5\text{Me}_5)\text{Ir(PMe}_2\text{Ar}')]\) centers is described, where PMe2Ar are the terphenyl phosphine ligands PMe2Ar512 and PMe2ArDipp2. Different pathways are defined for the conversion of the five-coordinate complexes \([(\eta^5\text{C}_5\text{Me}_5)\text{IrCl(PMe}_2\text{Ar}')]\)\(^{\text{1a}}\), 2(Xyl)\(^{\text{1a}}\) and 2(Dipp)\(^{\text{1a}}\), into the corresponding pseudoallyls 3(Xyl)\(^{\text{1a}}\) and 3(Dipp)\(^{\text{1a}}\). In the absence of an external Brønsted base, electrophilic, remote \(\zeta\) C–H activation takes place, for which the participation of dicatonic species, \([(\eta^5\text{C}_5\text{Me}_5)\text{Ir-(PMe}_2\text{Ar}')\]\(^{2a}\)), is proposed. When NEt3 is present, the PMe2ArDipp2 system is shown to proceed via 4(Dipp)\(^{\text{1a}}\) as an intermediate en route to the thermodynamic, isomeric product 3(Dipp)\(^{\text{1a}}\). This complex interconversion involves a non-innocent C5Me5 ligand, which participates in C–H and C–C bond formation and cleavage. Remarkably, the conversion of 4(Dipp)\(^{\text{1a}}\) to 3(Dipp)\(^{\text{1a}}\) also proceeds in the solid state.

Cyclopentadienyls, C5R5, and tertiary phosphines, PR3, are unquestionably two of the most important classes of ligands in organometallic chemistry and catalysis. Although in most cases C5R5 and PR3 behave strictly as spectators, in some reactions they can also directly participate. As PR3 and C5R5 continue to be increasingly employed in homogeneous catalysis, knowledge of these unforeseen reactions is crucial because they might strongly influence catalytic outcomes or lead to catalyst deactivation. Certain aryl phosphines undergo facile cyclometalation, and recently, nickel- and palladium-mediated dearomatization of dialkylbiaryl phosphines has been reported. With cyclopentadienyl ligands, in particular C5Me5, ring methyl activation implying either deprotonation or hydride abstraction, as well as metal-to-ring hydride transfer, 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 \((\eta^5\text{C}_5\text{Me}_5)\text{Ir(III)}\) centers, revealing, among other details, the influence of coligands, in particular their ability to act as a base to accept the generated proton. Here, we targeted the synthesis of cationic \((\eta^5\text{C}_5\text{Me}_5)\text{Ir(III)}\) complexes of the terphenyl phosphines PMe2Ar512 and PMe2ArDipp2 (Scheme 1). In particular, we report that the five-coordinate complexes \([(\eta^5\text{C}_5\text{Me}_5)\text{IrCl-(PMe}_2\text{Ar}')]\), 2(Xyl)\(^{\text{1a}}\) and 2(Dipp)\(^{\text{1a}}\), promote facile electrophilic C–H activation at remote \(\zeta\) C–H bonds of the phosphine ligand to form 3(Xyl)\(^{\text{1a}}\) and 3(Dipp)\(^{\text{1a}}\). Moreover, for 2(Dipp)\(^{\text{1a}}\), the observed \(\zeta\) C–H activation in the presence of NEt3 occurs through a complex mechanism that implies reversible \(\eta^5\text{C}_5\text{Me}_5\) 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 deaomatization. The resulting intermediate, 4(Dipp)\(^{\text{1a}}\), contains a 10-membered phospha-iridacycle. Intriguingly, this complex transforms...
appears that the HCl released in the formation of 3(Xyl)+ of a benzylic C−H activation species, 3(Dipp)+, not only in solution, but also in the solid state.

Treatment of \([\{\eta^5-C_5Me_5\}IrCl_2]_2\) with PMe2ArXyl in CH2Cl2 yielded the expected \([\{\eta^5-C_5Me_5\}IrCl_2(PMe2ArXyl)_2]\) product, 1(Xyl), in high yields (~90%). Chloride abstraction by NaBArF was also straightforward and allowed isolation of the cationic complex \([\{\eta^5-C_5Me_5\}IrCl(PMe2ArXyl)_2]^{+}\) (2-(Xyl)+, Scheme 1) as its BArF 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

![](image)

Figure 1. ORTEPs of the cations of complex [2(Xyl)]BArF and [3(Dipp)]BArF. Hydrogen atoms are excluded for clarity, and thermal ellipsoids are set at 50% probability. Gray lines represent Dipp ‘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, suggests chloride acts as a π-donor in this formally 16e complex; similar Ru−Cl shortening was also reported in \([\{\eta^5-C_5Me_5\}RuCl(PPr3)]_2\).

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 CH2Cl2/Et2O solvent yielded mixtures of a new iridium complex, 3(Xyl)+, along with \([\{\eta^5-C_5Me_5\}IrCl_2]_2\) and \([HPMe2ArXyl]_2BArF\). 3(Xyl)+ was unequivocally characterized as a pseudoallylic species formed via remote 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, \(\{\eta^5-C_5Me_5\}Ir(III)\) complexes of the bulkier phosphine PMe2ArDipp (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 \([\{\eta^5-C_5Me_5\}IrCl_2]_2\) and PMe2ArDipp2 were allowed to react in the presence of NaBArF. The similar properties of the two 2(PMe2Ar)+ complexes, including the observation for 2(Dipp)+ of a 31P{1H} NMR singlet with a Δ(δ) shift relative to free PMe2ArDipp2 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(PMe2Ar)+, from the corresponding chlorides, 2(PMe2Ar)+, implies electrophilic C−H activation and elimination of HCl, we considered it of interest to study (i) the generation of dicaticionic \([\{\eta^5-C_5Me_5\}Ir(PR2Ar)2]^{2+}\) species by chloride abstraction from 2(PMe2Ar)+ with NaBArF and (ii) the use of an external Brønsted base such as NEt3 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 PMe2ArDipp2 analogues for additional solution reaction studies, it was found that the formation of 3(Dipp)+ promoted by NaBArF was very slow at room temperature, probably due to the absence of an effective base. Consistent with this hypothesis, reaction of PMe2ArDipp2 with \([\{\eta^5-C_5Me_5\}Ir(H_2O)_3](SO_4)_{18}\) proceeded rapidly to afford 3(Dipp)+.

The BArF 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 3JHH = 3.9 and 3JHP = 1 and 14 Hz, respectively. The corresponding carbon atom gives a 13C{1H} signal at 26.3 ppm (JCP = 4 Hz), whereas the Cortho and Cipso involved in the η2-bonded unit appear at 89.1 and 83.2 ppm, respectively. Single-crystals of [3(Dipp)]BArF 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−CMe3 = 2.224(3), Ir−Cortho = 2.197(3) and Ir−Cipso = 2.257(3) Å).

The mechanism of the C−H bond activation to form the 3(PMe2Ar)+ complexes was also investigated by DFT methods. The most accessible pathway involves initial Cl− dissociation to afford an ion-pair comprising dicaticionic \([\{\eta^5-C_5Me_5\}Ir(PMe2Ar)2]^{2+}\), in which the phosphine is bound in a κ-P, η2-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 dicaticionic species promotes its facile abstraction by the Cl− ion via a transition state at +22.0 kcal/mol, representing the overall barrier to the C−H activation process. 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
Scheme 3. Proposed Mechanism for the Electrophilic C–H Activation in 2(PMe2Ar') Complexes (ΔG°, kcal/mol, R = H, Me)

Scheme 4. NEt3-Assisted Formation of Complex 4(Dipp)+ from 2(Dipp)+, and Solution and Solid-State Isomerization of 4(Dipp)+ to 3(Dipp)+

Although 3(Dipp)+ and 4(Dipp)+ are isomers, the latter exhibits a very different chemical constitution, for it contains a 10-membered metalacyclic unit resulting from deprotonation of the C₅Me₅ ring followed by nucleophilic attack at the para carbon atom of the coordinated Dipp ring, which is dearomatized. Unequivocal structural evidence was gained from variable temperature multinuclear NMR and X-ray studies (Figure 2). In solution, two degenerate pseudosymmetric structures undergo fast exchange at room temperature, but

reach the slow-exchange regime at −30 °C. At this temperature, the diastereotopic C₅Me₅CH₂ protons resonate as doublets of doublets centered at 3.27 and 2.46 ppm, as a consequence of additional coupling to the adjacent para CH nucleus. The X-ray structure in Figure 2 reveals that, beyond the η⁵ coordination of the C₅Me₅CH₂ 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 Cᵢ₆, 2.178(4) (Cᵢ₇₋₈), and 2.255(5) Å (Cᵢ₉₋₁₀)), 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 (NEt₃) nor acid (HNEt₃) catalysis. Instead, it occurred cleanly in CH₂Cl₂ solution (Scheme 4) following first-order kinetics (t₁/₂ ≈ 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). 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 C₅Me₅ deprotonation (17.4 kcal/mol, TSB−A) led to the formation of a neutral, Ir(1) fulvene complex (12.0 kcal/mol, A). The thus generated triethylammonium cation then facilitates chloride release (20.2 kcal/mol, TSA−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 TSB−A 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(1) complex B via TSB−A. Attack of the fulvene moiety in B at the C=H of an isopropyl group of the proximate aryl ring (19.4 kcal/mol, TSB−C) reoxidizes the metal center to Ir(III) and gives the η⁵-allyl complex C (see the SI) at 7.6 kcal/mol. Isomerization to the corresponding η⁶-allyl occurs via TSC−C (18.9 kcal/mol) and yields 3(Dipp)+ at −11.5 kcal/mol. It is striking that both the classically innocent ligands (C₅Me₅ and Pr₅) 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(1)→Ir(III) redox cycle (see the SI for details).
In conclusion, chloride abstraction from complexes 2-(PMe₂Ar′)(Ar′ = ArXyl₂, ArDipp₂) fosters electrophilic, remote C–H bond activation at dicationic intermediates [(η⁵-C₅Me₅)Ir(PMe₂Ar′)]⁺, to give the pseudoallyl products 3(PMe₂Ar′)⁺ shown in Scheme 2. In the presence of NEt₃, 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 C₅Me₅ 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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(19) Calculations were performed with the Gaussian 09 program employing the hybrid functional PBE0. Geometry optimizations were
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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involving 16e 2(Xyl)+, but these proved to be not competitive (see 
SI).

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