

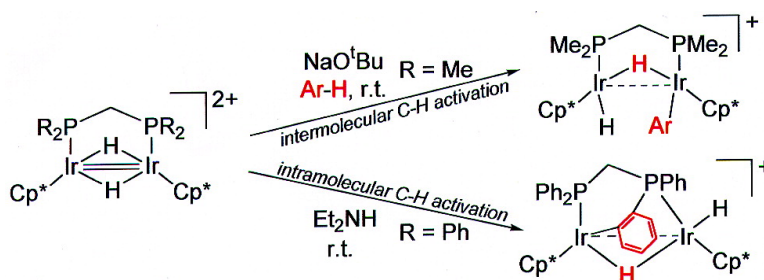
Communication

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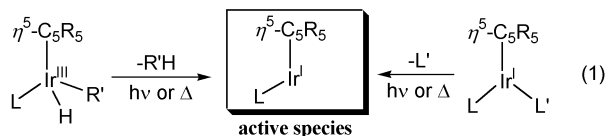
Inter- and Intramolecular Activation of Aromatic C–H Bonds by Diphosphine and Hydrido-Bridged Dinuclear Iridium Complexes

Ken-ichi Fujita,^{*,†,‡} Hirohide Nakaguma,[†] Taro Hamada,[†] and Ryohei Yamaguchi^{*,†}

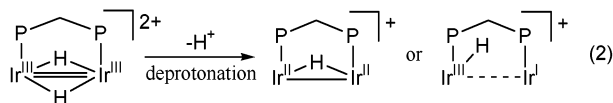
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The studies on C–H bond activation reactions of hydrocarbon molecules by transition metal complexes¹ have been one of the most attractive areas in organometallic chemistry because of their importance in functionalization of inert hydrocarbon molecules.² Among organometallic systems, (η^5 -C₅R₅)Ir [R = Me (Cp*); R = H (Cp)] complexes are the most promising for such activations, and their ability has been disclosed.^{3–7} The investigations on C–H activation by Cp*Ir and CpIr complexes have been mainly carried out with mononuclear complexes. The active species in the oxidative addition of the C–H bond of hydrocarbons to these complexes is believed to be an unsaturated 16e[−] (η^5 -C₅R₅)Ir^I(L) fragment,^{3–6} which is generated by reductive elimination of the hydrogen or hydrocarbon from (η^5 -C₅R₅)Ir^{III}(R')(H)(L) [R' = H,^{3a,b,4c} alkyl,^{3c,d} or alkenyl^{5c}], or by dissociation of the neutral ligand from (η^5 -C₅R₅)Ir^I(L)(L') [L' = CO,^{4a,b} C₂H₄,^{5a–c} or η^2 -nitrile⁶] (eq 1) under photoirradiation or thermal conditions.



On the other hand, much attention has been paid to the activation of organic molecules on multinuclear metal complexes, and several interesting results involving C–H activation have been reported in recent years.⁸ We have recently disclosed the synthesis and some reactivities of novel dinuclear Cp*Ir complexes containing multiple hydrido ligands, [(Cp*Ir)₂(μ -diphos)(μ -H)₂]²⁺ [diphos = bis(dimethylphosphino)methane (dmpm) (**1**)^{9a} or bis(diphenylphosphino)methane (dppm) (**2**)^{9b}]. Having these novel dinuclear complexes **1** and **2** in hand, we have anticipated that these complexes could generate unsaturated 32e[−] Ir^{II}–Ir^{II} (or Ir^{III}–Ir^I) species by deprotonation (eq 2). While C–H activation by dinuclear Ir^{II}–Ir^{II} complexes has been rare,¹⁰ it could give 34e[−] Ir^{III}–Ir^{III} products by oxidative addition of the C–H bond, the bridge splitting of which might again generate coordinatively unsaturated species desirable for further functionalization of the activated C–H bond. In this paper, we report the base-induced inter- and intramolecular activation of aromatic C–H bonds by **1** and **2** under extremely mild conditions without photochemical activation.¹¹



Treatment of **1** with 1.1 equiv of NaO^tBu in benzene at room temperature gave [(Cp*Ir)(H)(μ -dmpm)(μ -H)(Cp*Ir)(Ph)]⁺ (**3**) in 44% yield via intermolecular C–H activation of benzene (eq 3). In the ¹H NMR spectrum of **3**, two signals for nonequivalent Cp*

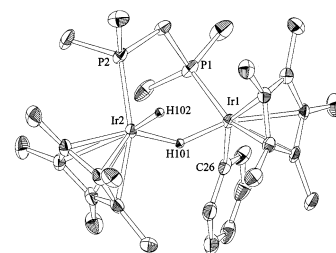
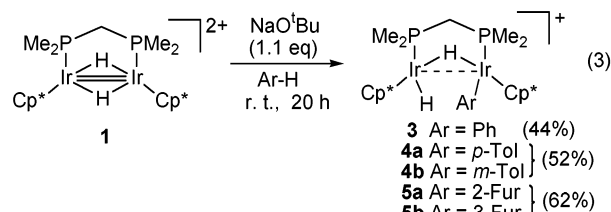


Figure 1. ORTEP drawing of the cation part of **3** with 30% thermal probability ellipsoids. Hydrogen atoms (except hydride) are omitted for clarity. Selected (bond) distances (Å): Ir(1)···Ir(2) = 3.190(1); Ir(1)–P(1) = 2.250(2); Ir(2)–P(2) = 2.259(2); Ir(1)–C(26) = 2.073(6); Ir(1)–H(101) = 1.62; Ir(2)–H(101) = 1.77; Ir(2)–H(102) = 1.39.

were found at δ 2.12 and 1.85. Signals for hydrides were observed at δ –17.02 (terminal) and –25.39 (bridge). Signals for the aromatic ring were found at δ 7.50, 6.94, and 6.88. In the ¹³C{¹H} NMR, a signal for the carbon at the ipso position of the aromatic ring was found at δ 132.8 as a doublet (J = 13 Hz) coupling to a phosphorus. All NMR data (¹H, ¹³C{¹H}, and ³¹P{¹H}) of **3** are consistent with the proposed structure. When the reaction was carried out in benzene-*d*₆, D-incorporation was observed in the bridging hydride position.¹² The structure of **3** was confirmed by an X-ray diffraction study. The molecular geometry and atom-numbering system of **3** are shown in Figure 1. It is apparent that the phenyl ring bonds to one of the iridium atoms with an Ir–C distance of 2.073(6) Å, showing no interaction with another iridium center. The hydrides were located in the difference Fourier maps. Complex **3** would be a 34e[−] one, if the bridging hydride is regarded as a two-electron ligand.



The C–H activation of toluene gave a mixture of the products [(Cp*Ir)(H)(μ -dmpm)(μ -H)(Cp*Ir)(*p*-Tol)]⁺ (**4a**) and [(Cp*Ir)(H)(μ -dmpm)(μ -H)(Cp*Ir)(*m*-Tol)]⁺ (**4b**) in a 1:2 ratio (eq 3), which were deduced to be *p*-tolyl and *m*-tolyl isomers, respectively, according to the NMR signal patterns of the aromatic ring (see Supporting Information). No *o*-tolyl or benzylmetallated product was observed. The C–H activation of furan also gave two products [(Cp*Ir)(H)(μ -dmpm)(μ -H)(Cp*Ir)(2-Fur)]⁺ (**5a**) and [(Cp*Ir)(H)(μ -dmpm)(μ -H)(Cp*Ir)(3-Fur)]⁺ (**5b**) in a 5:2 ratio (eq 3). An X-ray diffraction study of **5a** was performed (see Supporting Information). The structure of **5a** was very similar to that of **3** except for the aryl group.

When the phenyl complex **3** was refluxed in furan for 20 h, conversion of **3** into the 2-furyl complex **5a** was observed (eq 4).

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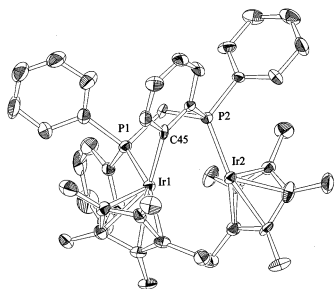
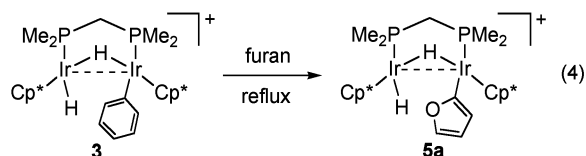
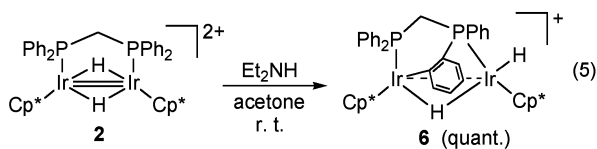


Figure 2. ORTEP drawing of the cation part of **6** with 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected (bond) distances (Å): Ir(1)⋯Ir(2) = 3.235(2); Ir(1)–P(1) = 2.285(4); Ir(2)–P(2) = 2.224(4); Ir(1)–C(45) = 2.10(2).

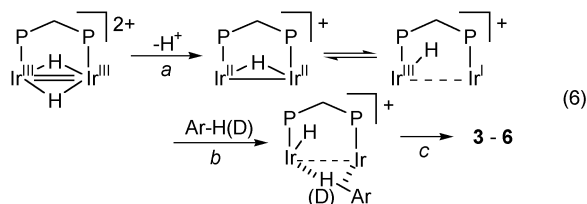
This reaction could be explained by reductive elimination of benzene to generate an active Ir^{II}–Ir^{II} (or Ir^{III}–Ir^I) intermediate at first, followed by C–H activation of furan.¹³



In contrast to the intermolecular C–H activation by the dmpm bridged diiridium complex **1**, reaction of the dppm bridged diiridium complex **2** with weak base (Et₂NH) resulted in intramolecular C–H activation of the phenyl group of the dppm ligand to give [(Cp*Ir)–(H){μ-PPh(C₆H₄)CH₂PPh₂}(μ-H)(Cp*Ir)]⁺ (**6**) in quantitative yield (eq 5).¹⁴ The structure of **6** was confirmed by an X-ray diffraction study. The molecular geometry and atom-numbering system of **6** are shown in Figure 2. One of the ortho carbons of the phenyl group in the dppm ligand is attached to one of the iridium centers with an Ir–C distance of 2.10(2) Å.



A possible mechanism for the present C–H activation by dinuclear iridium complexes is as follows (eq 6). First, one of the



bridging hydrides in **1** or **2** would be eliminated as a proton by the reaction with base to generate a monocationic Ir^{II}–Ir^{II} species (step a).¹⁵ This Ir^{II}–Ir^{II} species would be in equilibrium with the Ir^{III}–Ir^I species accompanied by migration of the hydride between the bridging and terminal positions.¹⁶ The C–H bond of the aromatic solvent or the phenyl ring in the dppm ligand would then approach the Ir^I center (step b), and activation of the C–H bond would occur to give complexes **3–6** (step c). This mechanism is supported by the result of the C–H activation of benzene-*d*₆, showing a selective D-incorporation at the bridging position in the product (vide supra).

In summary, we have demonstrated the novel base-induced inter- and intramolecular activation of aromatic C–H bonds by diphosphine and hydrido-bridged dinuclear iridium complexes under extremely mild conditions. It should be noted that the present C–H activation reactions by diiridium complexes give hydrido-bridged

34e[−] complexes, which might generate coordinatively unsaturated species by bridge-splitting transformation.

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Supporting Information Available: Experimental details for **3–6**, crystallographic data of **3**, **5a**, and **6** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) H/D scrambling between bridging and terminal hydride positions was very slow. Only a trace of scrambling (<10%) was observed after the NMR sample of **3-d₆** was allowed to stand for 3 h.
- (13) When the furan solution of the mixture of **5a** and **5b** was refluxed for 6 h, almost complete conversion into **5a** was observed, indicating that **5a** would be thermodynamically more stable than **5b**.
- (14) The complexes **1** and **2** contain triflate (OTf[−]) as counteranions. The C–H activation similarly proceeded in the reaction of [(Cp*Ir)₂(μ-dppm)(μ-H)₂][BPh₄]₂ with Et₂NH to give [(Cp*Ir)(H){μ-PPh(C₆H₄)CH₂PPh₂}(μ-H)(Cp*Ir)]⁺[BPh₄].
- (15) Formation of isoelectronic Ir^{II}–Ir^I complex, [(Cp*Ir)₂(CO)₂(μ-H)]⁺, from [(Cp*Ir)₂(CO)₂(μ-H)₂]²⁺ by deprotonation has been reported (ref 10b).
- (16) One of the referees argued the possibility that the cleavage of the Ir–Ir bond in the intermediate could occur to produce two separated 16e[−] Ir centers. We cannot rule out this possibility completely; however, we have recently observed that, when **1** was treated with NaO^tBu in THF under CO atmosphere, a carbonyl-bridged Ir^{III}–Ir^{III} complex, [(Cp*Ir)₂(μ-dmpm)(μ-CO)(μ-H)]⁺ (Ir–Ir 2.8727 Å), was obtained. This result suggests that two Ir centers in the intermediate would be kept in close proximity. The details of this reaction will be discussed in due course.

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