



# Activation of C–H and H–H bonds by dinuclear iridium complexes. Oxidative addition to highly active unsaturated $32e^-$ diiridium species

Ken-ichi Fujita<sup>a,b,\*</sup>, Yoshinori Takahashi<sup>a</sup>, Hirohide Nakaguma<sup>a</sup>, Taro Hamada<sup>a</sup>, Ryohei Yamaguchi<sup>a,\*</sup>

<sup>a</sup> Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

<sup>b</sup> Graduate School of Global Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

## ARTICLE INFO

### Article history:

Received 9 February 2008

Received in revised form 24 July 2008

Accepted 29 July 2008

Available online 5 August 2008

### Keywords:

Dinuclear complex

Iridium

C–H activation

Oxidative addition

Cooperative reactivity

## ABSTRACT

Reactions of  $[(Cp^*Ir)_2(\mu-dmpm)(\mu-H)_2][OTf]_2$  (**1**) with  $NaO^tBu$  in aromatic solvent at room temperature give  $[(Cp^*Ir)(H)(\mu-dmpm)(\mu-H)(Cp^*Ir)(Ar)][OTf]$  [Ar = Ph (**3**), *p*-Tol (**4a**), *m*-Tol (**4b**), 2-furyl (**5a**), 3-furyl (**5b**)] via intermolecular aromatic C–H activation. Treatment of  $[(Cp^*Ir)_2(\mu-dppm)(\mu-H)_2][OTf]_2$  (**2**) with weak base ( $Et_3NH$ ) results in intramolecular C–H activation of a phenyl group in the dppm ligand to give  $[(Cp^*Ir)(H)(\mu-PPh(C_6H_4)CH_2PPh_2)(\mu-H)(Cp^*Ir)][OTf]$  (**6**). Reaction of **1** with  $NaO^tBu$  in tetrahydrofuran under  $H_2$  (1 atm) results in activation of the H–H bond to give  $\{[(Cp^*Ir)(H)]_2(\mu-dmpm)(\mu-H)\}[OTf]$  (**7**). Reaction of **1** with  $NaO^tBu$  in dichloromethane under carbon monoxide (1 atm) gives a carbonyl-bridged  $Ir^{II}$ – $Ir^{II}$  complex,  $[(Cp^*Ir)_2(\mu-dmpm)(\mu-H)(\mu-CO)][OTf]$  (**8-OTf**). These results strongly suggest that the active species in C–H and H–H bond activation starting with **1** and **2** would be unsaturated  $32e^-$  diiridium species. The structures of **3**, **5a**, **6**, **7**, and **8-BPh<sub>4</sub>** have been determined by X-ray diffraction methods.

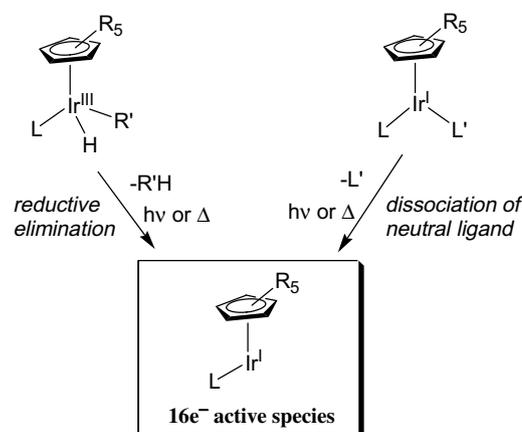
© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

The studies on the activation of inert C–H bonds in organic molecules by transition metal complexes have been attracting great interest in organometallic chemistry because of their significance in the functionalization of hydrocarbons [1]. A number of transition metal systems capable for the C–H activation have been discovered in the past decades, and some of them have been developed as catalysts for organic synthesis [2,3]. Since the first reports on the C–H activation with  $(\eta^5-C_5R_5)Ir$  [R = Me (Cp<sup>\*</sup>); R = H (Cp)] complexes by Bergman [4a] and Graham [5a], their capability for the activation of alkanes, arenes, and other inert C–H bonds has been vigorously investigated [4–8]. Up to date, the investigations on C–H activation by  $Cp^*Ir$  and  $CpIr$  complexes have been carried out with mononuclear complexes in many cases. The true active species in the oxidative addition of the C–H bond to these complexes is supposed to be an unsaturated  $16e^-$   $(\eta^5-C_5R_5)Ir^I(L)$  fragment, which is generated by the reductive elimination of hydrogen or hydrocarbon from  $(\eta^5-C_5R_5)Ir^{III}(R')(H)(L)$  ( $R' = H$  [4a,4b,5c], alkyl [4c,4d], or alkenyl [6c]), or by the dissociation of neutral ligand

from  $(\eta^5-C_5R_5)Ir^I(L)(L')$  ( $L' = CO$  [5a,5b],  $C_2H_4$  [6a–c], or  $\eta^2$ -nitrile [7]) under photo-irradiative or thermal conditions (Scheme 1).

In the mean time, growing interests have been focused on the activation of organic molecules on multinuclear metal complexes. The proximity of the metal centers can lead to the exhibition of unique functionality based on “cooperative reactivity” [9]. Actually, a number of interesting reactions on multinuclear metal complexes involving activation of inert bond in organic molecules have been appeared in recent years. For example, some dinuclear iridium

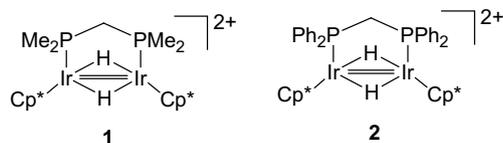


Scheme 1.

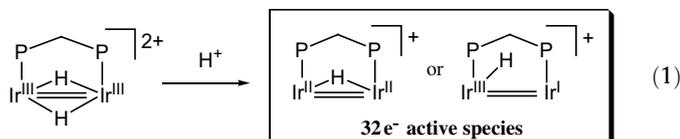
\* Corresponding authors. Address: Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan. Tel.: +81 75 753 6827; fax: +81 75 753 6634 (K.-i. Fujita).

E-mail addresses: fujitak@kagaku.mbox.media.kyoto-u.ac.jp (K.-i. Fujita), yama@kagaku.mbox.media.kyoto-u.ac.jp (R. Yamaguchi).

complexes are known to exhibit high capability for the activation of C–H and H–H bonds. Bergman reported the oxidative addition of C–H and H–H bonds to an Ir<sup>II</sup>–Ir<sup>III</sup> species [(Cp<sup>\*</sup>Ir)(η<sup>1</sup>,η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)(Cp<sup>\*</sup>Ir)] generated by the reductive elimination of benzene from an Ir<sup>III</sup>–Ir<sup>III</sup> complex [(Cp<sup>\*</sup>Ir)(Ph)(η<sup>1</sup>,η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)(μ-H)(Cp<sup>\*</sup>Ir)] [10]. Oro reported the activation of olefinic C–H bonds on an Ir<sup>II</sup>–Ir<sup>III</sup> species generated by the oxidation of Ir<sup>I</sup>–Ir<sup>I</sup> complexes [Ir<sub>2</sub>(μ-1,8-(NH)<sub>2</sub>naphth)(η<sup>2</sup>-RHC=CHR)<sub>2</sub>(P<sup>t</sup>Pr<sub>3</sub>)<sub>2</sub>] [11]. Heinekey reported the activation of hydrogen on a hydrido-bridged Ir<sup>II</sup>–Ir<sup>III</sup> species generated by the protonation of Ir<sup>I</sup>–Ir<sup>I</sup> complex [Cp<sup>\*</sup>Ir(μ-CO)]<sub>2</sub> [12]. In these examples, unsaturated Ir<sup>III</sup>–Ir<sup>I</sup> species or electronically unbalanced Ir<sup>III</sup>–Ir<sup>I</sup> species must be key intermediates in the bond activation.



We have previously reported the preparation and some reactivities of novel Ir<sup>III</sup>–Ir<sup>III</sup> complexes having a bridging diphosphine and multiple hydrido ligands, [(Cp<sup>\*</sup>Ir)<sub>2</sub>(μ-diphos)(μ-H)]<sub>2</sub>[OTf]<sub>2</sub> [diphos = bis(dimethylphosphino)methane (dmpm) (**1**) and bis(diphenylphosphino)methane (dpmm) (**2**)] [13,14]. Having these dinuclear complexes **1** and **2** in hand, we have anticipated that these complexes could generate unsaturated 32e<sup>-</sup> Ir<sup>II</sup>–Ir<sup>II</sup> (or Ir<sup>III</sup>–Ir<sup>I</sup>) species by the abstraction of one of the bridging hydrides as a proton, which might exhibit a high performance in the activation of inert molecules (Eq. (1)). Bond activation by hydrido-bridged 32e<sup>-</sup> diiridium species would be advantageous in view of further development of the reaction system, because such activation could give rise to a 34e<sup>-</sup> Ir<sup>III</sup>–Ir<sup>III</sup> complex as a product, which can be still regarded as unsaturated.

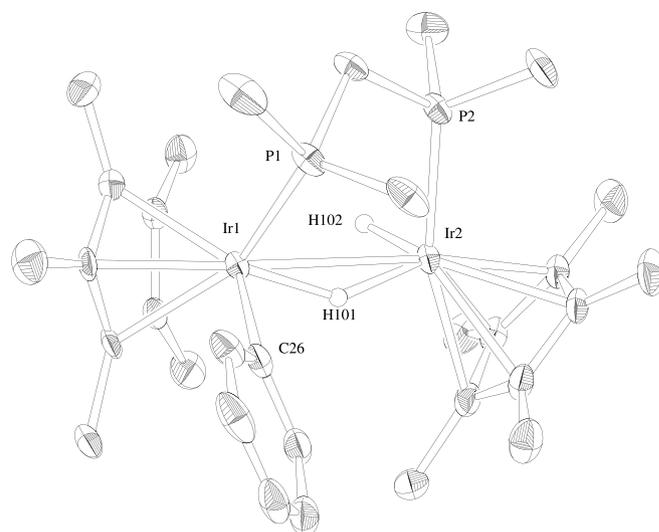


In this paper, we report the inter- and intra-molecular activation of aromatic C–H bonds and hydrogen induced by the deprotonation of **1** and **2** [15]. Mechanistic aspects of these activation reactions are also demonstrated.

## 2. Results and discussion

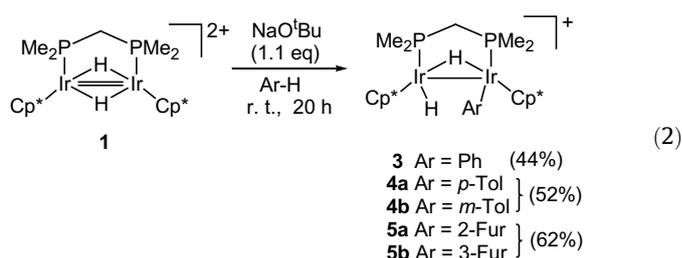
### 2.1. Intermolecular activation of aromatic sp<sup>2</sup> C–H bonds by dicationic complex **1**

Treatment of **1** with 1.1 equiv. of NaO<sup>t</sup>Bu in benzene at room temperature for 20 h gave [(Cp<sup>\*</sup>Ir)(H)(μ-dmpm)(μ-H)(Cp<sup>\*</sup>Ir)(Ph)][OTf] (**3**) in 44% yield via intermolecular C–H activation of benzene (Eq. (2)) [16]. In the <sup>1</sup>H NMR spectrum of **3**, two signals for non-equivalent Cp<sup>\*</sup> were found at δ 2.12 and 1.85. Signals for hydrides were observed at δ –17.02 (terminal) and –25.39 (bridge). Signals due to aromatic protons were found at δ 7.50, 6.94, and 6.88. In the <sup>13</sup>C{<sup>1</sup>H} NMR, a signal due to the carbon at ipso position of phenyl ring was found at δ 132.8 as a doublet (*J* = 13 Hz) coupling to a phosphorus. In the <sup>31</sup>P{<sup>1</sup>H} NMR, two distinct signals were observed at δ –25.3 and –37.6 as doublets coupling to each other. All NMR data (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H}) of **3** were consistent with the proposed structure. The structure of **3** was confirmed by X-ray diffraction study. The molecular geometry of **3** is shown in Fig. 1. It is apparent that the phenyl ring bonds to

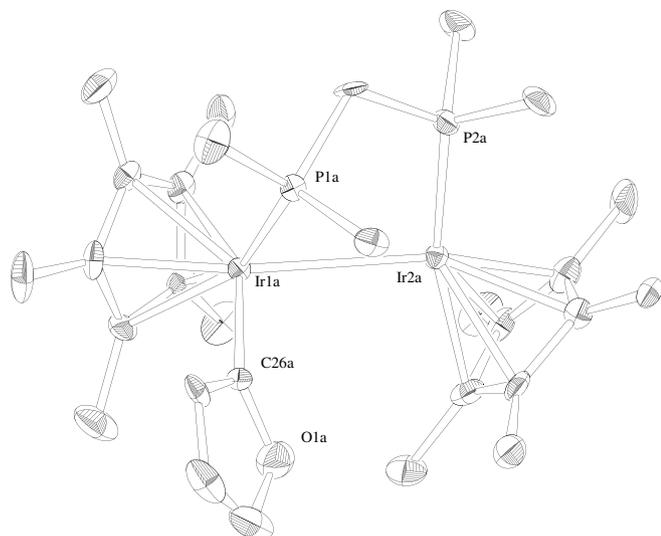


**Fig. 1.** ORTEP drawing of the cationic part of **3** with 30% thermal probability ellipsoids. Hydrogen atoms (except hydride) are omitted for clarity. Selected (bond) distances (Å): Ir(1)–Ir(2) = 3.190(1); Ir(1)–P(1) = 2.250(2); Ir(2)–P(2) = 2.259(2); Ir(1)–C(26) = 2.073(6); Ir(1)–H(101) = 1.62; Ir(2)–H(101)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

one of the iridium atoms with an Ir–C distance of 2.073(6) Å, showing no interaction with another iridium center. The hydrides are located in the difference Fourier maps. One of the hydrides is found at bridging position and the other at terminal position, which is coincident with the <sup>1</sup>H NMR analysis. The iridium–iridium distance is 3.190(1) Å, which is relatively larger than general monohydrido-bridged iridium–iridium bond, reflecting the steric hindrance around iridium centers by two Cp<sup>\*</sup> ligands and phenyl ring. The complex **3** would be a 34e<sup>-</sup> one, if the bridging hydride is regarded as a two-electron ligand.



The C–H activation of toluene starting with **1** gave a mixture of the products [(Cp<sup>\*</sup>Ir)(H)(μ-dmpm)(μ-H)(Cp<sup>\*</sup>Ir)(*p*-Tol)][OTf] (**4a**) and [(Cp<sup>\*</sup>Ir)(H)(μ-dmpm)(μ-H)(Cp<sup>\*</sup>Ir)(*m*-Tol)][OTf] (**4b**) in 1:2 ratio (Eq. (2)), which were deduced to be *p*-tolyl and *m*-tolyl isomers, respectively, according to the NMR signal patterns of aromatic ring. No *o*-tolyl or benzyl metallated product was observed. There have been several publications describing the regioselectivity of the C–H activation of toluene by transition metal complexes [17], which demonstrates that the cleavage of para and meta C–H bonds are thermodynamically much favored compared to ortho and benzylic ones. In some of these publications, the ratios of the para- and meta-activated products are reported to be 1:2 similar to the present study [17a,17d,17e]. The C–H activation of furan also gave two products [(Cp<sup>\*</sup>Ir)(H)(μ-dmpm)(μ-H)(Cp<sup>\*</sup>Ir)(2-Fur)][OTf] (**5a**) and [(Cp<sup>\*</sup>Ir)(H)(μ-dmpm)(μ-H)(Cp<sup>\*</sup>Ir)(3-Fur)][OTf] (**5b**) in 5:2 ratio (Eq. (2)). In this reaction, the yield of the products was slightly higher than those of the activation of benzene and toluene. In the most of previous reports on the activation of furan, selective cleavages of the C–H bond at 2-position have been observed [18].

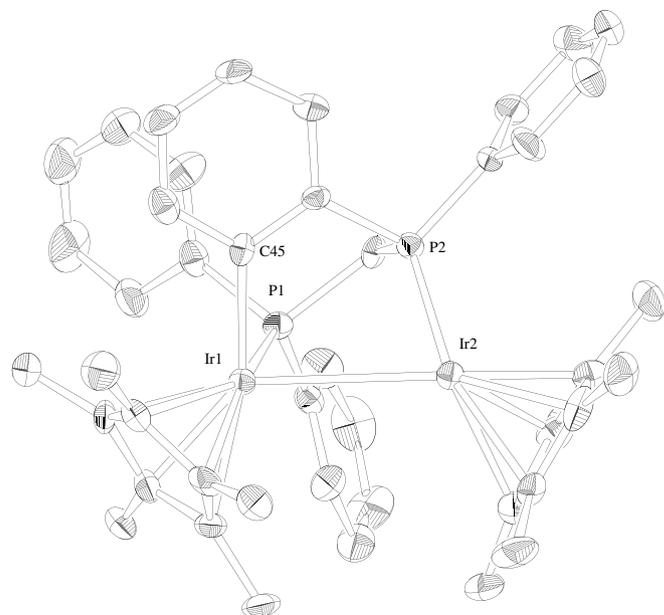
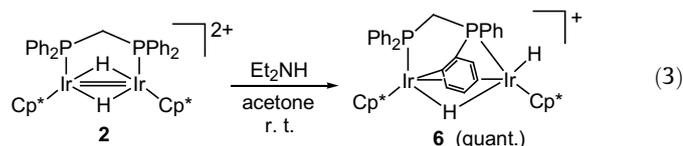


**Fig. 2.** ORTEP drawing of the cationic part of **5a** with 30% thermal probability ellipsoids (molecule A). Hydrogen atoms are omitted for clarity. In the unit cell there are two independent molecules A and B, which are very similar to each other. Selected (bond) distances (Å): Ir(1)–Ir(2) = 3.0938(8), 3.1370(8); Ir(1)–P(1) = 2.253(3), 2.250(3); Ir(2)–P(2) = 2.249(3), 2.261(3); Ir(1)–C(26) = 2.05(1), 2.05(1); C(26)–O(1) = 1.38(1), 1.39(1).

Very recently, however, Parkin reported that the activation of furan by a molybdenocene complex resulted in the C–H cleavage at both 2- and 3-position, like the results in the present study [19]. X-ray diffraction study of **5a** was performed to confirm its structure. The molecular geometry of **5a** is shown in Fig. 2. The crystal structure of **5a** is very similar to that of **3** except for the aryl group. No interaction is observed between oxygen atom of the furan ring and the iridium center (inter-atomic distance were 4.253 Å for molecule A and 4.015 Å for molecule B), indicating that **5a** would also be a  $34e^-$  structure.

## 2.2. Intramolecular activation of aromatic $sp^2$ C–H bonds by dicationic complex **2**

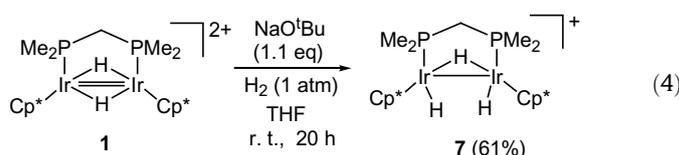
In contrast to the intermolecular C–H activation by the dmpm bridged diiridium complex **1**, reaction of the dppm bridged diiridium complex **2** with weak base ( $\text{Et}_2\text{NH}$ ) at room temperature for 1 h resulted in intramolecular C–H activation of phenyl group of dppm ligand to give  $[(\text{Cp}^*\text{Ir})(\text{H})\{\mu\text{-PPh}(\text{C}_6\text{H}_4)\text{CH}_2\text{PPh}_2\}(\mu\text{-H})(\text{Cp}^*\text{Ir})][\text{OTf}]$  (**6**) in quantitative yield (Eq. (3)). In the  $^1\text{H}$  NMR spectrum of **6**, two signals due to  $\text{Cp}^*$  were found at  $\delta$  1.90 and 1.70. Signals due to hydrides were observed at  $\delta$  –15.63 (terminal) and –24.37 (bridge). In the  $^{31}\text{P}\{^1\text{H}\}$  NMR, two signals were observed at  $\delta$  –2.6 and –7.1 as doublets coupling to each other. All NMR data ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$ ) of **6** are consistent with the proposed structure. The structure of **6** was confirmed by X-ray diffraction study. The molecular geometry of **6** is shown in Fig. 3. One of the ortho carbons of phenyl group in dppm ligand is attached to one of the iridium centers with an Ir–C distance of 2.10(2) Å. The iridium–iridium distance [3.235(2) Å] is larger than that in **3** [3.190(1) Å], possibly due to the steric hindrance of much bulky dppm ligand in addition to two  $\text{Cp}^*$  ligands.

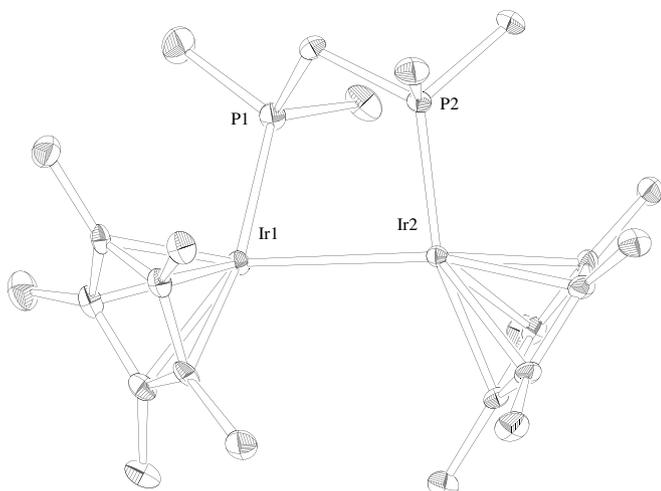


**Fig. 3.** ORTEP drawing of the cationic part of **6** with 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected (bond) distances (Å): Ir(1)–Ir(2) = 3.235(2); Ir(1)–P(1) = 2.285(4); Ir(2)–P(2) = 2.224(4); Ir(1)–C(45) = 2.10(2).

## 2.3. Activation of hydrogen ( $\text{H}_2$ ) by dicationic complex **1**

The reaction of **1** with 1.1 equiv. of  $\text{NaO}^t\text{Bu}$  in tetrahydrofuran under  $\text{H}_2$  (1 atm) at room temperature for 20 h resulted in the activation of  $\text{H}_2$  to give  $[(\text{Cp}^*\text{Ir}(\text{H}))_2(\mu\text{-dmpm})(\mu\text{-H})][\text{OTf}]$  (**7**) in 61% yield (Eq. (4)). In the  $^1\text{H}$  NMR spectrum of **7**, signals due to two  $\text{Cp}^*$  ligands were observed equivalently at  $\delta$  2.05 together with those for methylene ( $\delta$  3.63) and methyl ( $\delta$  1.72) of the dmpm ligand. The signal due to three hydrides was found equivalently at  $\delta$  –18.79 as a triplet ( $J = 13$  Hz) coupling to the two phosphorus atoms, indicating rapid interchange of three hydrides on the NMR time scale. Upon cooling the sample to  $-80^\circ\text{C}$ , the resonances due to the hydrides as well as the methylene protons in dmpm ligand broadened, but well-resolved spectrum could not be obtained at this temperature. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR at room temperature, a single resonance was observed at  $\delta$  –40.7. Considering that the most of  $\text{Cp}^*\text{Ir}^{\text{III}}$  complexes possess a 6-coordination mode, the static structure of **7** must include two terminal hydrides and one bridging hydride, i.e.  $(\text{IrH})_2(\mu\text{-H})$  fashion as illustrated in Eq. (4). X-ray diffraction study of **7** was performed to confirm its structure, which also supports the proposed  $(\text{IrH})_2(\mu\text{-H})$  fashion. The molecular geometry of **7** is shown in Fig. 4. The iridium–iridium distance in **7** is 3.0248(5) Å, which is ca. 0.3 Å larger than the double bond in the mother complex **1** [14], reflecting the single bond character in **7**. Although three hydrides could not be located in the difference Fourier maps, existence of one bridging hydride and two terminal hydrides on each iridium center could be anticipated considering the geometry around the iridium centers. Closely related iso-electronic complexes,  $[(\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H}))_2(\mu\text{-H})]^+$  and  $[(\text{Cp}^*\text{Ir}(\text{CO})(\text{H}))_2(\mu\text{-H})]^+$  are known [12,20], and their structures have been elucidated to be  $(\text{IrH})_2(\mu\text{-H})$  fashion.



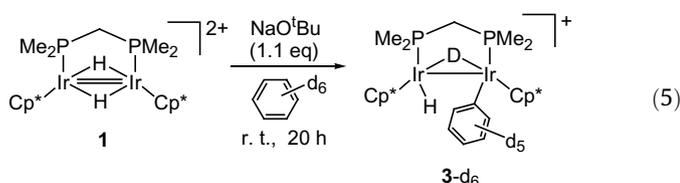


**Fig. 4.** ORTEP drawing of the cationic part of **7** with 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected (bond) distances (Å): Ir(1)–Ir(2) = 3.0248(5); Ir(1)–P(1) = 2.233(2); Ir(2)–P(2) = 2.257(2).

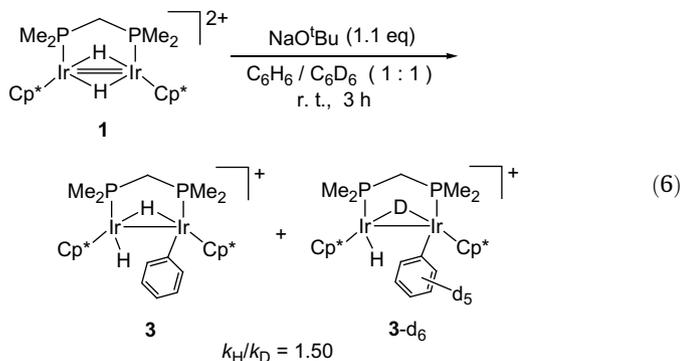
## 2.4. Mechanistic experiments

### 2.4.1. C–H activation of benzene-*d*<sub>6</sub> by **1**

When the C–H activation reaction by **1** was carried out in benzene-*d*<sub>6</sub>, D-incorporation was observed selectively in the bridging hydride position (Eq. (5)). This result indicates that the crucial step of the C–H activation involves the oxidative addition of a C–H bond to one of the iridium centers (vide infra). H/D scrambling between bridging and terminal hydrides in **3-d**<sub>6</sub> was slow; only a trace of scrambling (<10%) was observed after the NMR sample of **3-d**<sub>6</sub> was allowed to stand for 3 h.



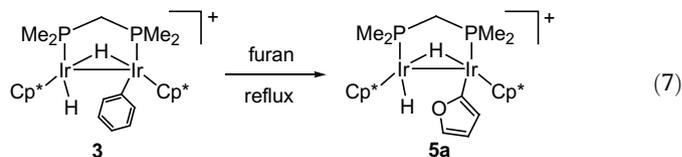
We also carried out the similar reaction of **1** with NaOtBu in an equimolar amount of benzene and benzene-*d*<sub>6</sub> (Eq. (6)). From the <sup>1</sup>H NMR analysis of a mixture of products, the value of kinetic isotope effect for the C–H activation of benzene by **1** was determined to be 1.50, which is comparable to those reported for the C–H activation by mononuclear Cp\*Ir complexes [4b,4d].



### 2.4.2. C–H activation of furan starting with the phenyl complex **3**

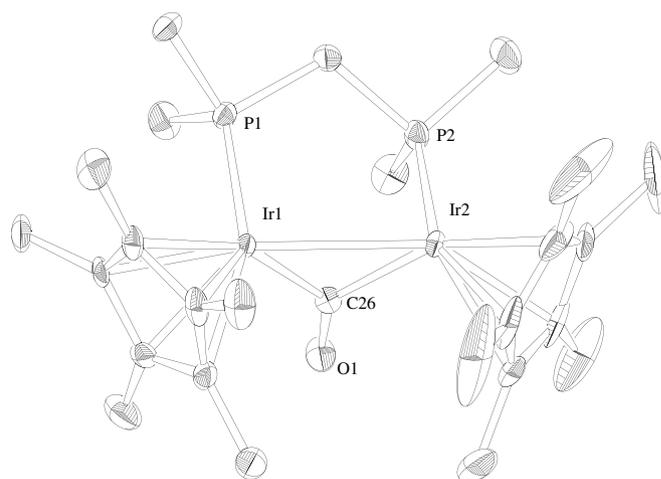
When the phenyl complex **3** was refluxed in furan for 20 h, complete conversion into the 2-furyl complex **5a** (**5b** was not

detected) was observed (Eq. (7)) [21]. This reaction would proceed via reductive elimination of benzene from **3** to generate an active intermediate at first, followed by C–H activation of furan. Additionally, when the solution of the mixture of **5a** and **5b** in furan was refluxed for 6 h, almost complete conversion into **5a** was observed, indicating that **5a** would be thermodynamically more stable than **5b**.

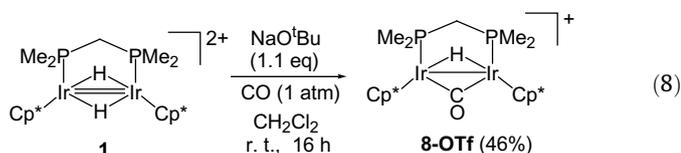


### 2.4.3. Reaction of the dicationic complex **1** with base under CO atmosphere

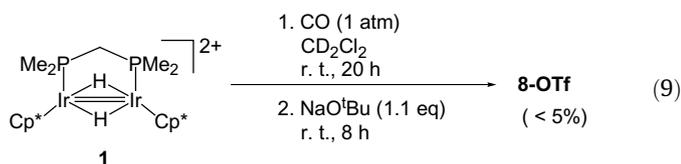
We next examined the reaction of **1** with CO in presence of base. The reaction of **1** with 1.1 equiv. of NaOtBu under an atmosphere of CO (1 atm) in dichloromethane gave an Ir<sup>II</sup>–Ir<sup>III</sup> complex, [(Cp\*Ir)<sub>2</sub>(μ-dmpm)(μ-H)(μ-CO)](OTf) (**8-OTf**) in 46% yield (Eq. (8)) [22]. In the <sup>1</sup>H NMR spectrum of **8-OTf**, signals due to two Cp\* were equivalently observed at δ 2.08. Signals due to two methylene protons of dmpm ligand were non-equivalently observed at δ 1.86 and 1.75, indicating a nonsymmetric character of this complex respective to the plane defined by two iridium and two phosphorus atoms. A signal for bridging hydride was found at δ –16.93 as a triplet. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, a characteristic triplet signal was found at δ 218.2, which is due to the bridging carbonyl ligand. In the IR spectrum of **8-OTf**, absorption due to CO stretch was observed at 1700 cm<sup>–1</sup> in the metal bridging carbonyl region [23]. These spectroscopic data support the structure of **8-OTf** as illustrated in Eq. (8). To confirm the structure of **8** by X-ray diffraction, attempts to obtain a single crystal were made. After some trials, single crystals of **8-BPh<sub>4</sub>** having tetraphenylborate as a counter anion were obtained by the recrystallization of **8-OTf** in the presence of three equivalents of NaBPh<sub>4</sub>. The NMR spectra of **8-OTf** and **8-BPh<sub>4</sub>** were essentially identical except for the signals due to anionic moiety. The result of the X-ray diffraction study of **8-BPh<sub>4</sub>** is shown in Fig. 5. It is apparent that CO bridges two iridium centers, and **8** can be regarded as Ir<sup>II</sup>–Ir<sup>III</sup> complex with 34e<sup>–</sup> structure.



**Fig. 5.** ORTEP drawing of the cationic part of **8-BPh<sub>4</sub>** with 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected (bond) distances (Å) and angles (°): Ir(1)–Ir(2) = 2.8727(5); Ir(1)–P(1) = 2.261(2); Ir(2)–P(2) = 2.253(2); Ir(1)–C(26) = 2.005(6); Ir(2)–C(26) = 2.015(6); C(26)–O(1) = 1.189(7); Ir(1)–C(26)–Ir(2) = 91.2(3); Ir(1)–C(26)–O(1) = 134.8(5); Ir(2)–C(26)–O(1) = 133.2(5).

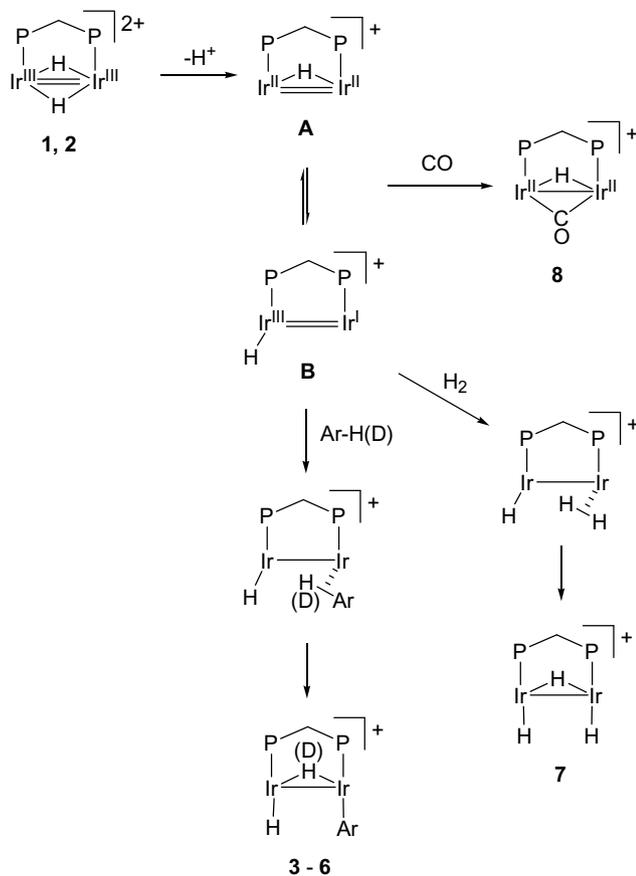


There are two possible paths for the formation of **8-OTf** by the reaction of **1** with CO in the presence of base (i.e. dissociative path and associative path). To clarify this point, we carried out the reaction of **1** with CO in the absence of base for 20 h, followed by the treatment with NaOtBu (Eq. (9)). This reaction gave relatively complicated mixture, and only a trace amount (<5%) of **8-OTf** was observed in  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR analyses. Thus, we conclude that the formation of **8-OTf** from **1** shown in Eq. (8) would proceed via a dissociative path through a  $32e^-$  diiridium intermediate  $[(\text{Cp}^*\text{Ir})_2(\mu\text{-diphos})(\mu\text{-H})]^+$ . These results strongly suggest that C–H and H–H activation reactions starting with **1** would proceed through the same  $32e^-$  intermediate (vide infra).



### 2.5. Possible mechanism for C–H and H–H activation reactions by dinuclear iridium complexes

A possible mechanism for the C–H and H–H activation reactions by **1** and **2** is summarized in Scheme 2. At the initial stage, one of



Scheme 2.

the bridging hydrides in **1** or **2** would be eliminated as a proton induced by the reaction with base, generating an unsaturated  $32e^-$   $\text{Ir}^{\text{II}}\text{-Ir}^{\text{II}}$  species **A**. This  $\text{Ir}^{\text{II}}\text{-Ir}^{\text{II}}$  species **A** would be in equilibrium with the electronically unbalanced  $\text{Ir}^{\text{III}}\text{-Ir}^{\text{I}}$  species **B** accompanied by the migration of the hydride between the bridging and terminal positions. When the reaction was carried out in CO atmosphere, coordination of CO to **A** or **B** would occur immediately to afford the CO-bridged complex **8**. The C–H or H–H bond would approach the  $\text{Ir}^{\text{I}}$  center in **B**, and the activation would occur to give the complexes **3–7**. This explanation means that crucial step of the bond activation would involve the oxidative addition of C–H or H–H bond to one of the iridium centers, which is supported by the experimental results of the activation of benzene- $d_6$  by **1** (vide supra).

### 3. Summary

We have described the inter- and intra-molecular activation of aromatic C–H bonds and hydrogen on diphosphine and hydrido-bridged dinuclear  $\text{Cp}^*\text{Ir}$  complexes induced by the treatment with base. From this work, three conclusions can be made. (1) Highly active  $32e^-$  diiridium species  $[(\text{Cp}^*\text{Ir})_2(\mu\text{-diphos})(\mu\text{-H})]^+$  can be generated by the treatment of dicationic  $[(\text{Cp}^*\text{Ir})_2(\mu\text{-diphos})(\mu\text{-H})]^{2+}$  with base, the bond activation readily occurs under ambient conditions. (2) The critical stage of the bond activation on  $32e^-$  species involves the electron transfer between two iridium centers to afford an electronically unbalanced  $\text{Ir}^{\text{III}}\text{-Ir}^{\text{I}}$  species. This phenomenon can be regarded as “cooperative reactivity” of dinuclear iridium complexes. (3) Activation of C–H or H–H bond on the  $32e^-$  species gives the  $34e^-$  complex as a product, which can be still regarded as unsaturated. In view of further development of the reaction system into the catalytic functionalization, the results presented in this work are suggestive.

### 4. Experimental

#### 4.1. General

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. Melting points were determined on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were measured with JEOL EX-270 and JEOL A-500 spectrometers. Solvents were dried by using standard procedures and distilled prior to use. The complexes  $[(\text{Cp}^*\text{Ir})_2(\mu\text{-dmpm})(\mu\text{-H})_2][\text{OTf}]_2$  (**1**) and  $[(\text{Cp}^*\text{Ir})_2(\mu\text{-dppm})(\mu\text{-H})_2][\text{OTf}]_2$  (**2**) were prepared by literature methods [13,14]. Other reagents were used as obtained from commercial sources.

#### 4.2. Reaction of $[(\text{Cp}^*\text{Ir})_2(\mu\text{-dmpm})(\mu\text{-H})_2][\text{OTf}]_2$ (**1**) with NaOtBu in benzene. C–H activation of benzene

To a mixture of  $[(\text{Cp}^*\text{Ir})_2(\mu\text{-dmpm})(\mu\text{-H})_2][\text{OTf}]_2$  (**1**) (0.099 g, 0.091 mmol) and NaOtBu (0.0095 g, 0.099 mmol) was added benzene (10 mL), and the mixture was stirred at room temperature for 20 h. After evaporation of the solvent (at this stage, formation of **3** was confirmed by  $^1\text{H}$  NMR analysis in  $\text{C}_6\text{D}_6$ ), the residue was chromatographed on Florisil. Elution with dichloromethane and methanol (30:1) followed by evaporation of the solvent gave **3** (0.041 g, 0.040 mmol, 44%) as an orange powder. Crystals of **3** suitable for an X-ray study were obtained by recrystallization from toluene solution at  $-25^\circ\text{C}$ . **3**: M.p.:  $100.0\text{--}102.0^\circ\text{C}$  (dec).  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  7.50 (d,  $J = 7$  Hz, 2H, *o*-Ph), 6.94 (t,  $J = 7$  Hz, 2H, *m*-Ph), 6.88 (t,  $J = 7$  Hz, 1H, *p*-Ph), 4.70 (m, 1H, PCHHP), 2.61 (m, 1H,

PCHHP), 2.12 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.89 (dd, *J* = 11, 2 Hz, 3H, PMe), 1.85 (d, *J* = 2 Hz, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.82 (d, *J* = 9 Hz, 3H, PMe), 1.75 (d, *J* = 10 Hz, 3H, PMe), 1.35 (d, *J* = 11 Hz, 3H, PMe), –17.02 (dd, *J* = 35, 5 Hz, 1H, Ir–H), –25.39 (ddd, *J* = 11, 5, 5 Hz, 1H, Ir–H–Ir). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 144.3 (s, Ph), 132.8 (d, *J* = 13 Hz, Ir–C), 128.5 (s, Ph), 123.3 (s, Ph), 122.4 (q, *J* = 321 Hz, CF<sub>3</sub>), 97.0 (d, *J* = 3 Hz, C<sub>5</sub>Me<sub>5</sub>), 95.9 (d, *J* = 3 Hz, C<sub>5</sub>Me<sub>5</sub>), 52.4 (dd, *J* = 36, 31 Hz, PCH<sub>2</sub>P), 24.2 (d, *J* = 41 Hz, PMe), 18.1 (d, *J* = 34 Hz, PMe), 17.0 (d, *J* = 44 Hz, PMe), 11.9 (dd, *J* = 29, 7 Hz, PMe), 11.2 (s, C<sub>5</sub>Me<sub>5</sub>), 10.6 (s, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ –25.3 (d, *J* = 37 Hz), –37.6 (d, *J* = 37 Hz). Anal. Calc. for C<sub>32</sub>H<sub>51</sub>F<sub>3</sub>O<sub>3</sub>P<sub>2</sub>SiR<sub>2</sub> · C<sub>7</sub>H<sub>8</sub>: C, 42.14; H, 5.35. Found: C, 42.04; H, 5.27%.

#### 4.3. Reaction of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) with NaO<sup>t</sup>Bu in toluene. C–H activation of toluene

To a mixture of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) (0.070 g, 0.064 mmol) and NaO<sup>t</sup>Bu (0.0068 g, 0.071 mmol) was added toluene (10 mL), and the mixture was stirred at room temperature for 20 h. After evaporation of the solvent, the residue was chromatographed on Florisil. Elution with dichloromethane and methanol (30:1) followed by evaporation of the solvent gave a mixture of **4a** and **4b** (1:2; determined by NMR) (0.034 g, 0.033 mmol, 52%) as an oily brown powder. **4a**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.20 (d, *J* = 7 Hz, 2H, Tol), 6.74 (d, *J* = 7 Hz, 2H, Tol), 4.30 (m, 1H, PCHHP), 2.38 (m, 1H, PCHHP), 2.23 (s, 3H, Tol-Me), 2.02 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.74 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), –17.20 (dd, *J* = 34, 5 Hz, 1H, Ir–H), –25.59 (ddd, *J* = 11, 5, 5 Hz, 1H, Ir–H–Ir). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ –25.5 (d, *J* = 37 Hz), –37.7 (d, *J* = 37 Hz). **4b**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.22 (s, 1H, Tol), 7.08 (d, *J* = 7 Hz, 1H, Tol), 6.79 (t, *J* = 7 Hz, 1H, Tol), 6.69 (d, *J* = 7 Hz, 1H, Tol), 4.30 (m, 1H, PCHHP), 2.38 (m, 1H, PCHHP), 2.21 (s, 3H, Me), 2.02 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.74 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), –17.18 (dd, *J* = 34, 5 Hz, 1H, Ir–H), –25.53 (ddd, *J* = 11, 5, 5 Hz, 1H, Ir–H–Ir). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ –25.6 (d, *J* = 37 Hz), –37.8 (d, *J* = 37 Hz). Elemental analyses for **4a** and **4b** were unsatisfactory because of a small amount of contaminant.

#### 4.4. Reaction of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) with NaO<sup>t</sup>Bu in furan. C–H activation of furan

To a mixture of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) (0.062 g, 0.057 mmol) and NaO<sup>t</sup>Bu (0.0060 g, 0.062 mmol) was added furan (6 mL), and the mixture was stirred at room temperature for 20 h. After evaporation of the solvent, the residue was chromatographed on Florisil. Elution with dichloromethane and methanol (30:1) followed by evaporation of the solvent gave a mixture of **5a** and **5b** (5:2; determined by NMR) (0.035 g, 0.035 mmol, 62%) as an orange powder. Crystals of **5a** suitable for an X-ray study were obtained by recrystallization from toluene solution at –25 °C. **5a**: M.p.: 149.4–149.9 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 7.59 (d, *J* = 2 Hz, 1H, Fur), 6.27 (dd, *J* = 3, 2 Hz, 1H, Fur), 5.89 (d, *J* = 3 Hz, 1H, Fur), 4.95 (m, 1H, PCHHP), 2.54 (m, 1H, PCHHP), 2.14 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.94 (d, *J* = 3 Hz, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.84 (d, *J* = 10 Hz, 3H, PMe), 1.78 (d, *J* = 9 Hz, 3H, PMe), 1.77 (d, *J* = 9 Hz, 3H, PMe), 1.36 (d, *J* = 11 Hz, 3H, PMe), –16.38 (dd, *J* = 38, 3 Hz, 1H, Ir–H), –24.56 (ddd, *J* = 12, 5, 3 Hz, 1H, Ir–H–Ir). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 145.5 (s, Fur), 138.0 (d, *J* = 18 Hz, Ir–C), 122.4 (q, *J* = 322, CF<sub>3</sub>), 117.4 (s, Fur), 112.0 (s, Fur), 97.6 (d, *J* = 3, C<sub>5</sub>Me<sub>5</sub>), 96.1 (s, C<sub>5</sub>Me<sub>5</sub>), 52.8 (dd, *J* = 36, 31 Hz, PCH<sub>2</sub>P), 25.3 (m, PMe), 18.1 (d, *J* = 45 Hz, PMe), 17.8 (d, *J* = 35 Hz, PMe), 12.1 (dd, *J* = 36, 8 Hz, PMe), 10.9 (s, C<sub>5</sub>Me<sub>5</sub>), 10.8 (s, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ –26.0 (d, *J* = 39 Hz), –39.5 (d, *J* = 39 Hz). Anal. Calc. for C<sub>30</sub>H<sub>49</sub>F<sub>3</sub>O<sub>4</sub>P<sub>2</sub>SiR<sub>2</sub>: C, 35.70; H, 4.89. Found: C, 35.60; H, 4.81%. **5b**: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 7.36 (s, 1H, Fur), 6.12 (d, *J* = 6 Hz, 1H, Fur), 5.23 (d, *J* = 6 Hz, 1H, Fur), 5.07 (m, 1H, PCHHP), 2.39 (m, 1H, PCHHP), 2.11 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.93 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.86 (d, *J* = 6 Hz, 3H, PMe), 1.81 (d, *J* =

11 Hz, 3H, PMe), 1.68 (d, *J* = 10 Hz, 3H, PMe), 1.61 (d, *J* = 11 Hz, 3H, PMe), –16.84 (dd, *J* = 37, 3 Hz, 1H, Ir–H), –26.15 (br, 1H, Ir–H–Ir). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ –31.9 (d, *J* = 40 Hz), –40.3 (d, *J* = 40 Hz).

#### 4.5. Reaction of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**2**) with Et<sub>2</sub>NH. Intramolecular C–H activation of Ph group in dppm

To a solution of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**2**) (0.034 g, 0.020 mmol) in acetone (3 mL) was added Et<sub>2</sub>NH (0.014 g, 0.021 μL, 0.19 mmol), and the mixture was stirred at room temperature for 1 h. The color of the solution changed from dark green to orange. After evaporation of the solvent, the residue was solved in acetone. Slow diffusion of diethyl ether into this solution gave orange crystals of **6** in quantitative yield. **6**: M.p.: 142.1–143.1 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 7.78–6.37 (m, 19H, Ph), 5.05 (m, 1H, PCHHP), 3.10 (m, 1H, PCHHP), 1.90 (d, *J* = 2 Hz, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.70 (d, *J* = 2 Hz, 15H, C<sub>5</sub>Me<sub>5</sub>), –15.63 (d, *J* = 29 Hz, 1H, Ir–H), –24.37 (m, 1H, Ir–H–Ir). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 154.1–123.4 (Ph), 99.0 (s, C<sub>5</sub>Me<sub>5</sub>), 95.9 (d, *J* = 2 Hz, C<sub>5</sub>Me<sub>5</sub>), 44.7 (dd, *J* = 44, 31 Hz, PCH<sub>2</sub>P), 10.5 (brs, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ –2.6 (d, *J* = 41 Hz), –7.1 (d, *J* = 41 Hz). Anal. Calc. for C<sub>46</sub>H<sub>53</sub>F<sub>3</sub>O<sub>3</sub>P<sub>2</sub>SiR<sub>2</sub>: C, 46.45; H, 4.49. Found: C, 46.18; H, 4.65%.

#### 4.6. Reaction of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) with NaO<sup>t</sup>Bu under hydrogen atmosphere. Activation of H–H bond of hydrogen

To a mixture of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) (0.074 g, 0.068 mmol) and NaO<sup>t</sup>Bu (0.0072 g, 0.075 mmol) was added tetrahydrofuran (7 mL) under an atmosphere of H<sub>2</sub>, and the mixture was stirred at room temperature for 20 h. After evaporation of the solvent, the residue was chromatographed on Silica-gel. Elution with dichloromethane and methanol (30:1) followed by evaporation of the solvent gave **7** (0.039 g, 0.041 mmol, 61%) as an orange powder. **7**: M.p.: 145.0 °C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.63 (t, *J* = 11 Hz, 2H, PCH<sub>2</sub>P), 2.05 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 1.72 (m, 12H, PMe), –18.79 (t, *J* = 13 Hz, 3H, Ir–H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 120.9 (q, *J* = 319 Hz, CF<sub>3</sub>), 94.6 (s, C<sub>5</sub>Me<sub>5</sub>), 55.0 (t, *J* = 34 Hz, PCH<sub>2</sub>P), 20.9 (m, PMe), 11.1 (s, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ –40.7 (s). Anal. Calc. for C<sub>26</sub>H<sub>47</sub>Ir<sub>2</sub>O<sub>3</sub>P<sub>2</sub>SF<sub>3</sub>: C, 33.11; H, 5.02. Found: C, 32.81; H, 4.95%.

#### 4.7. Reaction of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) with NaO<sup>t</sup>Bu under CO atmosphere

To a mixture of [(Cp\*Ir)<sub>2</sub>(μ-dppm)(μ-H)<sub>2</sub>][OTf]<sub>2</sub> (**1**) (0.100 g, 0.092 mmol) and NaO<sup>t</sup>Bu (0.0097 g, 0.101 mmol) was added dichloromethane (10 mL), and the mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was chromatographed on Florisil. Elution with dichloromethane and methanol (30:1) followed by evaporation of the solvent gave **8-OTf** (0.041 g, 0.042 mmol, 46%) as an orange powder. **8-OTf**: M.p.: 183.5–185.0 °C. IR (KBr): ν<sub>CO</sub> 1700 cm<sup>–1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 2.08 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 1.86 (m, 1H, PCHHP), 1.85 (m, 6H, PMe), 1.75 (m, 1H, PCHHP), 1.56 (m, 6H, PMe), –16.93 (t, *J* = 10 Hz, 1H, Ir–H–Ir). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 218.2 (t, *J* = 6.6 Hz, CO), 122.4 (q, *J* = 322 Hz, CF<sub>3</sub>), 98.4 (s, C<sub>5</sub>Me<sub>5</sub>), 30.8 (t, *J* = 35 Hz, PCH<sub>2</sub>P), 19.2 (dd, *J* = 22, 21 Hz, PMe), 14.8 (dd, *J* = 24, 22 Hz, PMe), 10.5 (s, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ –15.6 (s). Anal. Calc. for C<sub>27</sub>H<sub>45</sub>Ir<sub>2</sub>O<sub>4</sub>P<sub>2</sub>SF<sub>3</sub>: C, 33.46; H, 4.68. Found: C, 33.16; H, 4.64%. Crystals of **8-BPh<sub>4</sub>** suitable for an X-ray study were obtained by slow diffusion of diethyl ether to a solution of **8-OTf** in acetone in the presence of three equivalents of NaBPh<sub>4</sub>. **8-BPh<sub>4</sub>**: M.p.: 241.0–242.8 °C. IR (KBr): ν<sub>CO</sub> 1701 cm<sup>–1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 6.76–7.33 (m, 20H, Ph), 2.05 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 2.10 (m, 1H, PCHHP), 1.78 (m, 6H, PMe), 1.68 (m, 1H, PCHHP), 1.51 (m, 6H, PMe), –16.94 (t, *J* = 11 Hz, 1H, Ir–H–Ir). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-

**Table 1**  
Crystal data and structure refinement parameters for **3** · C<sub>7</sub>H<sub>8</sub>, **5a**, **6**, **7**, and **8-BPh<sub>4</sub>**

	<b>3</b> · C <sub>7</sub> H <sub>8</sub>	<b>5a</b>	<b>6</b>	<b>7</b>	<b>8-BPh<sub>4</sub></b>
Description of crystal					
Color, habit	Orange, cubic	Orange, block	Orange, prismatic	Yellow, plate	Orange-red, plate
Maximum crystal dimensions (mm)	0.30 × 0.30 × 0.30	0.35 × 0.35 × 0.30	0.25 × 0.25 × 0.25	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.10
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P1	P2 <sub>1</sub>	P2 <sub>1</sub>	P1	P1
a (Å)	13.702(3)	10.845(3)	11.459(8)	10.620(1)	13.741(2)
b (Å)	14.763(4)	19.462(4)	13.782(9)	15.200(2)	18.349(3)
c (Å)	11.466(5)	17.299(4)	14.696(5)	10.116(1)	9.586(2)
α (°)	112.75(3)	90	90	95.84(1)	94.71(1)
β (°)	97.02(3)	107.70(2)	107.89(3)	92.787(9)	105.16(1)
γ (°)	98.27(2)	90	90	79.61(1)	100.55(1)
V (Å <sup>3</sup> )	2076(1)	3478(2)	2209(2)	1597.1(3)	2271.7(7)
Z	2	4	2	2	2
Formula	C <sub>39</sub> H <sub>59</sub> F <sub>3</sub> O <sub>3</sub> P <sub>2</sub> Si <sub>2</sub>	C <sub>30</sub> H <sub>49</sub> F <sub>3</sub> O <sub>4</sub> P <sub>2</sub> Si <sub>2</sub>	C <sub>46</sub> H <sub>53</sub> F <sub>3</sub> O <sub>3</sub> P <sub>2</sub> Si <sub>2</sub>	C <sub>26</sub> H <sub>47</sub> F <sub>3</sub> O <sub>3</sub> P <sub>2</sub> Si <sub>2</sub>	C <sub>50</sub> H <sub>65</sub> BOP <sub>2</sub> Ir <sub>2</sub>
Formula weight	1111.34	1009.16	1189.37	943.10	1139.26
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.778	1.927	1.788	1.961	1.665
Data collection					
Radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
Temperature (K)	203	203	291	203	203
Scan technique	ω – 2θ	ω – 2θ	ω – 2θ	ω – 2θ	ω – 2θ
Scan width (°)	(1.05 + 0.30tan θ)	(1.05 + 0.30tan θ)	(1.10 + 0.30tan θ)	(1.21 + 0.30tan θ)	(1.26 + 0.30tan θ)
2θmax (°)	55.0	55.0	55.0	55.0	55.0
No. of reflections measured	9991	8472	5532	7710	11038
Structure determination					
No. of reflections used	6752	7324	4293	5894	7536
No. of parameters varied	451	756	493	334	505
Data/parameter ratio	14.97	9.69	8.71	17.65	14.92
Transmission factors	0.8394–0.9994	0.6656–1.0000	0.6895–1.0000	0.3679–1.0000	0.3924–1.0000
Goodness-of-fit (GOF)	1.30	1.18	1.21	1.75	1.53
R <sup>a</sup>	0.030	0.033	0.045	0.037	0.032
R <sub>w</sub> <sup>a</sup>	0.033	0.032	0.044	0.046	0.034

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}, w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}.$$

d<sub>6</sub>): δ 218.0 (t, J = 5.9 Hz, CO), 164.8 (q, J = 50 Hz, Ph), 136.9 (s, Ph), 125.9 (q, J = 3 Hz, Ph), 122.1 (s, Ph), 98.3 (s, C<sub>5</sub>Me<sub>5</sub>), 30.7 (t, J = 36 Hz, PCH<sub>2</sub>P), 18.9 (t, J = 21 Hz, PMe), 14.7 (t, J = 22 Hz, PMe), 10.4 (s, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-d<sub>6</sub>): δ –14.9 (s). Anal. Calc. for C<sub>50</sub>H<sub>65</sub>Ir<sub>2</sub>OP<sub>2</sub>B: C, 52.71; H, 5.75. Found: C, 52.98; H, 5.78%.

#### 4.8. X-ray structure analysis of **3** · C<sub>7</sub>H<sub>8</sub>, **5a**, **6**, **7**, and **8-BPh<sub>4</sub>**

Crystal data and experimental details for X-ray structure analysis are summarized in Table 1. Diffraction data were obtained with a Rigaku AFC-5S. The reflection intensities were monitored by three standard reflections every 150 measurements. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections were empirically applied (psi scans). Decay corrections were not applied. The structures were solved by heavy-atom Patterson methods [24,25], and refined anisotropically for non-hydrogen atoms by full-matrix least squares calculations, except for carbon and fluorine atoms of triflate anion in **6**, which were refined isotropically. Atomic scattering factors and anomalous dispersion terms were taken from the literature [26]. The hydrogen atoms were located on idealized positions except for metal hydrides in **3** · C<sub>7</sub>H<sub>8</sub>, which were defined on Fourier difference maps. Metal hydrides in **5a**, **6**, **7**, and **8-BPh<sub>4</sub>** were not located. In **5a**, there were two independent molecules A and B, which were very similar to each other, in the unit cell. In **5a** and **6**, the crystal chirality was tested by inverting all the coordinates and refining to convergence once again. The results indicated the original choice should be the correct one. The calculations were performed using the program system TEXSAN [27].

#### Acknowledgement

This work was partially supported by a Grant-in-Aid for Young Scientists (B) Nos. 14750666 and 17750052 from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

#### Appendix A. Supplementary material

CCDC 223707, 223708, 223709, 675851 and 675852 contains the supplementary crystallographic data for **3** · C<sub>7</sub>H<sub>8</sub>, **5a**, **6**, **7** and **8-BPh<sub>4</sub>**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.07.032](https://doi.org/10.1016/j.jorganchem.2008.07.032).

#### References

- [1] (a) A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879. and references cited therein;  
(b) J.A. Labinger, J.E. Bercaw, Nature 417 (2002) 507. and references cited therein.
- [2] For example (a) W. Xu, G.P. Rosini, M. Gupta, C.M. Jensen, W.C. Kaska, K. Krogh-Jespersen, A.S. Goldman, Chem. Commun. (1997) 2273;  
(b) H. Chen, S. Schlecht, T.C. Semple, J.F. Hartwig, Science 287 (2000) 1995;  
(c) T. Matsumoto, D.J. Taube, R.A. Periana, H. Taube, H. Yoshida, J. Am. Chem. Soc. 122 (2000) 7414;  
(d) J.-Y. Cho, M.K. Tse, D. Holmes, R.E. Maleczka Jr., M.R. Smith III, Science 295 (2002) 305;  
(e) T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N.R. Anastasi, J.F. Hartwig, J. Am. Chem. Soc. 124 (2002) 390.
- [3] K. Godula, D. Sames, Science 312 (2006) 67. and references cited therein.
- [4] (a) A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352;  
(b) A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 3929;  
(c) J.M. Buchanan, J.M. Stryker, R.G. Bergman, J. Am. Chem. Soc. 108 (1986) 1537;  
(d) P.O. Stoutland, R.G. Bergman, J. Am. Chem. Soc. 110 (1988) 5732.
- [5] (a) J.K. Hoyano, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3723;  
(b) J.K. Hoyano, A.D. McMaster, W.A.G. Graham, J. Am. Chem. Soc. 105 (1983) 7190;  
(c) P.E. Bloyce, A.J. Rest, I. Whitwell, W.A.G. Graham, R. Holmes-Smith, J. Chem. Soc., Chem. Commun. (1988) 846.
- [6] (a) D.M. Haddleton, R.N. Perutz, J. Chem. Soc., Chem. Commun. (1986) 1734;  
(b) T.W. Bell, D.M. Haddleton, A. McCamley, M.G. Partridge, R.N. Perutz, H. Willner, J. Am. Chem. Soc. 112 (1990) 9212;  
(c) T.W. Bell, S.-A. Brough, M.G. Partridge, R.N. Perutz, A.D. Rooney, Organometallics 12 (1993) 2933.
- [7] P.A. Chetcuti, C.B. Knobler, M.F. Hawthorne, Organometallics 7 (1988) 650.

- [8] In addition to C–H activations by Cp<sup>+</sup>Ir<sup>I</sup> species, C–H activations by cationic Cp<sup>+</sup>Ir<sup>III</sup> species have been known. (a) P. Burger, R.G. Bergman, *J. Am. Chem. Soc.* 115 (1993) 10462; (b) B.A. Arndtsen, R.G. Bergman, *Science* 270 (1995) 1970; (c) D.M. Tellers, C.M. Yung, B.A. Arndtsen, D.R. Adamson, R.G. Bergman, *J. Am. Chem. Soc.* 124 (2002) 1400.
- [9] (a) H. Suzuki, *Eur. J. Inorg. Chem.* (2002) 1009, and references cited therein; (b) Y. Yuan, M.V. Jiménez, E. Sola, F.J. Lahoz, L.A. Oro, *J. Am. Chem. Soc.* 124 (2002) 752; (c) J.R. Torkelson, F.H. Antwi-Nsiah, R. McDonald, M. Cowie, J.G. Pruis, K.J. Jalkanen, R.L. DeKock, *J. Am. Chem. Soc.* 121 (1999) 3666; (d) D.A. Vacic, W.D. Jones, *Organometallics* 18 (1999) 134.
- [10] (a) W.D. McGhee, R.G. Bergman, *J. Am. Chem. Soc.* 108 (1986) 5621; (b) W.D. McGhee, F.J. Hollander, R.G. Bergman, *J. Am. Chem. Soc.* 110 (1988) 8428.
- [11] M.V. Jiménez, E. Sola, J. Caballero, F.J. Lahoz, L.A. Oro, *Angew. Chem., Int. Ed.* 41 (2002) 1208.
- [12] D.M. Heinekey, D.A. Fine, D. Barnhart, *Organometallics* 16 (1997) 2530.
- [13] K. Fujita, T. Hamada, R. Yamaguchi, *J. Chem. Soc., Dalton Trans.* (2000) 1931.
- [14] K. Fujita, H. Nakaguma, F. Hanasaka, R. Yamaguchi, *Organometallics* 21 (2002) 3749.
- [15] A part of this paper has been preliminarily reported. For a preliminary communication, see: K. Fujita, H. Nakaguma, T. Hamada, R. Yamaguchi, *J. Am. Chem. Soc.* 125 (2003) 12368.
- [16] Strong base such as NaO<sup>t</sup>Bu was required for the intermolecular C–H activation starting with **1**. Use of weaker base such as Et<sub>2</sub>NH resulted in no reaction.
- [17] (a) W.D. Jones, F.J. Feher, *J. Am. Chem. Soc.* 106 (1984) 1650; (b) M.D. Fryzuk, P.A. MacNeil, N.T. McManus, *Organometallics* 6 (1987) 882; (c) W.D. Jones, E.T. Hessel, *J. Am. Chem. Soc.* 115 (1993) 554; (d) P. Diversi, S. Iacoponi, G. Ingrassio, F. Laschi, A. Lucherini, C. Pinzino, G. Uccello-Barretta, P. Zanella, *Organometallics* 14 (1995) 3275; (e) M. Kanzelberger, B. Singh, M. Czerw, K. Krogh-Jespersen, A.S. Goldman, *J. Am. Chem. Soc.* 122 (2000) 11017.
- [18] (a) H.E. Selnau, J.S. Merola, *Organometallics* 12 (1993) 1583; (b) W.D. Jones, L. Dong, A.W. Myers, *Organometallics* 14 (1995) 855; (c) T. Morikita, M. Hirano, A. Sasaki, S. Komiya, *Inorg. Chim. Acta* 291 (1999) 341; (d) K.A. Pittard, J.P. Lee, T.R. Cundari, T.B. Gunnoe, J.L. Petersen, *Organometallics* 23 (2004) 5514.
- [19] D.G. Churchill, B.M. Bridgewater, G. Zhu, K. Pang, G. Parkin, *Polyhedron* 25 (2006) 499.
- [20] T.M. Gilbert, R.G. Bergman, *J. Am. Chem. Soc.* 107 (1985) 3502.
- [21] We also carried out the reaction of **3-d<sub>6</sub>** in furan under reflux for 20 h, which gave **5a** with no deuterium.
- [22] We also examined the reaction of **2** with base under CO atmosphere. However, this reaction gave a complicated mixture, and we could not characterize the product.
- [23] (a) B.R. Sutherland, M. Cowie, *Inorg. Chem.* 23 (1984) 2324; (b) R.G. Ball, W.A.G. Graham, D.M. Heinekey, J.K. Hoyano, A.D. McMaster, B.M. Mattson, S.T. Michel, *Inorg. Chem.* 29 (1990) 2023; (c) R. McDonald, M. Cowie, *Inorg. Chem.* 32 (1993) 1671.
- [24] PATTY: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
- [25] DIRDIF94, P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1994.
- [26] (a) D.T. Cromer, G.T. Waber, *International Tables for X-ray Crystallography*, vol. IV, Kynoch, Birmingham, UK, 1974; (b) J.A. Ibers, W.C. Hamilton, *Acta Crystallogr.* 17 (1964) 781; (c) D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (Ed.), *International Tables for X-ray Crystallography*, vol. C, Kluwer Academic publishers, Boston, MA, 1992; (d) D.C. Creagh, J.H. Hubbell, in: A.J.C. Wilson (Ed.), *International Tables for X-ray Crystallography*, vol. C, Kluwer Academic publishers, Boston, MA, 1992.
- [27] TEXSAN for Windows, Crystal Structure Analysis Package, Molecular Structure Corporation, 1997.