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C–H activation on a diphosphine and hydrido-bridged diiridium complex: generation and detection of an active Ir^{II} – Ir^{II} species $[(Cp*Ir)_2(\mu$ -dmpm)(μ -H)]⁺[†]

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Reaction of $[Cp*Ir(\mu-H)]_2$ (5) $(Cp* = \eta^5-C_5Me_5)$ with bis(dimethylphosphino)methane (dmpm) gives a new neutral diiridium complex $[(Cp*Ir)_2(\mu-dmpm)(\mu-H)_2]$ (3). Treatment of 3 with methyl triflate at $-30 \degree C$ results in the formation of $[(Cp*Ir)(H)(\mu-dmpm)(\mu-H)(Me)(IrCp*)][OTf]$ (6). Warming a solution of 6 above 0 °C brings about predominant generation of $32e^- Ir^{II}-Ir^{II}$ species $[(Cp*Ir)(\mu-dmpm)(\mu-H)(IrCp*)][OTf]$ (7). Further heating of the solution of 7 up to 30 °C for 14 h leads to quantitative formation of a new complex $[(Cp*Ir)(H)(\mu-Me_2PCH_2PMeCH_2)(\mu-H)(IrCp*)][OTf]$ (8), which is formed by intramolecular oxidative addition of the methyl C–H bond of the dmpm ligand. Intermolecular C–H bond activation reactions with 7 are also examined. Reactions of 7 with aromatic molecules (benzene, toluene, furan, and pyridine) at room temperature result in the smooth sp² C–H activation to give $[(Cp*Ir)(H)(\mu-dmpm)(\mu-H)(Ar)(IrCp*)][OTf]$ (Ar = Ph (9); Ar = *m*-Tol (10a) or *p*-Tol (10b); Ar = 2-Fur (11)) and $[(Cp*Ir)(H)(\mu-dmpm)(\mu-C_5H_4N)(H)(IrCp*)][OTf]$ (12), respectively. Complex 7 also reacts with cyclopentene at 0 °C to give $[(Cp*Ir)(H)(\mu-dmpm)(\mu-H)(1$ cyclopentenyl)(IrCp*)][OTf] (13). Structures of 3, 8 and 12 have been confirmed by X-ray analysis.

Introduction

The study on C–H bond activation of hydrocarbons has been attracting much attention in organometallic chemistry,¹ since they are becoming increasingly important as elemental reactions in the functionalization of the inert but abundant organic molecules.² During recent decades, it has been revealed that a number of transition metal complexes are capable of activating C–H bonds. As for iridium complexes, $(C_3R_5)Ir(L)$ [R = Me (Cp*), H (Cp)] complexes are well known to be capable of such activation,³ and catalytic applications have been also reported.⁴

Meanwhile, much attention has been paid to the activation of organic molecules on multinuclear complexes in expectation of the synergetic effect of the multi-metal centers,⁵ and various multimetallic systems capable of C–H activation have been disclosed.⁶ In the course of our studies on the synthesis and reactivity of diphosphine- and dihydridobridged *dicationic* diiridium complexes [(Cp*Ir)₂(μ -diphos)(μ -H)₂]²⁺ [diphos = bis(dimethylphosphino)methane (dmpm) (1) as well as bis(diphenylphosphino)methane (dppm) (2)],⁷ we reported that the reaction of 1 and 2 with base resulted in the activation of aromatic C–H bonds.^{7c} The active species in these reactions was assumed to be a 32e⁻ Ir^{II}–Ir^{II} species, [(Cp*Ir)₂(μ -diphos)(μ - H)]⁺, which would be generated by base-induced nucleophilic deprotonation of **1** and **2**. Although intermediacy of $Ir^{II}-Ir^{II}$ (or mixed-valent $Ir^{I}-Ir^{III}$) species in C–H activation by diiridium complexes has been proposed by Bergman *et al.*^{8a} and Oro *et al.*,^{8b} direct detection of such species has never been reported.⁹

In this article, we report the synthesis and reactivity of a new *neutral* diiridium complex $[(Cp*Ir)_2(\mu-dmpm)(\mu-H)_2]$ (3): (1) treatment of 3 with methyl triflate results in the net abstraction of hydride to successfully afford the proposed 32e⁻ intermediate, (2) this 32e⁻ complex can be detected for the first time by NMR spectroscopy, and (3) it becomes evident that the detected active species readily brings about intramolecular sp³ and intermolecular sp² C–H bond activation.



Results and discussion

Preparation of a neutral dmpm and dihydrido-bridged dinuclear iridium complex 3

As reported earlier, we have demonstrated that treatment of diphosphine and dihydrido-bridged *dicationic* diiridium complex 1 and 2 with base induced the C–H bond activation and proposed that the $32e^{-1}$ Ir^{II}–Ir^{II} species might play an important role at the

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critical stage of the activation.^{7c} However, such C–H activation reactions were relatively sluggish (20 h at room temperature) probably because of the low solubility of the starting dicationic complexes and base (NaO'Bu), making it very difficult to carry out further investigations and direct detection of the true active 32e⁻ Ir^{II} – Ir^{II} species. Thus, we have designed a new *neutral* diiridium complex bridged by dmpm and dihydrides, [(Cp*Ir)₂(µ-dmpm)(µ-H)₂] (3), anticipating that 3 would be more soluble and could be converted into the active species by the abstraction of one of the bridging hydride as a form of hydride (H⁻).¹⁰



Treatment of $[(Cp*Ir)_2(\mu-H)_3]^+$ (4) with KO'Bu followed by an addition of dmpm to a solution of resulting $[Cp^*Ir(\mu-H)]_2^{11}$ (5) in benzene gave $[(Cp*Ir)_2(\mu-dmpm)(\mu-H)_2]$ (3) in high yield (eqn 1). The complex 3 was highly soluble in non-polar solvent as expected, and was isolated by the extraction with hexane in 93% yield. The NMR spectra of **3** indicated $C_{2\nu}$ symmetry in solution. In the ¹H NMR spectrum of 3, signals due to two Cp* ligands (δ 2.15) and four methyl groups of the dmpm ligand (δ 1.47) were observed equivalently as well as the signals due to two hydrides ($\delta - 17.76$). In the ³¹P{¹H} NMR, a singlet resonance was found at δ –46.7. All NMR data for 3 are consistent with the proposed structure. If the bridging hydride is regarded as a two-electron ligand, 3 would be a 34e⁻ complex. Cooling the hexane solution of **3** gave the brown single crystals suitable for X-ray diffraction study. An ORTEP drawing of 3 is shown in Fig. 1. The iridium-iridium distance (2.7618(3) Å) is slightly longer than that of the dicationic complex 1 (2.7237(3) Å),^{7a} reflecting the difference between the $34e^{-}$ (3) and the $32e^{-}$ (1) characters. Although a large torsion angle of P(1)-Ir(2)-P(2) was inconsistent with the higher symmetry observed in the NMR analysis, it would be rationalized by the fast ring flip of the Ir₂P₂C framework at room temperature in solution.

Abstraction of a hydride from the neutral complex 3 by the reaction with methyl triflate: generation and detection of a highly active $Ir^{II}-Ir^{II}$ species $[(Cp*Ir)_2(\mu-dmpm)(\mu-H)]^+$ (7)

At first, we attempted several reactions of **3** using the reagents for abstraction of hydride such as $(Ph_3C)^+$ in order to generate a $32e^-$ active species directly from **3**, but these reactions gave complicated mixtures.¹² Then, we anticipated that the reaction of **3** with methyl cation would give a methyl dihydrido intermediate $[(Cp*Ir)(H)(\mu-dmpm)(\mu-H)(Me)(IrCp*)]^+$ (**6**), from which reductive elimination of methane could occur to generate the desired $32e^-$ active species



Fig. 1 ORTEP drawing of the neutral complex 3 with 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (°), and a torsion angle (°): Ir(1)-Ir(2) = 2.7618(3); Ir(1)-P(1) = 2.200(2); Ir(2)-P(2) = 2.193(2); Ir(2)-Ir(1)-P(1) = 86.75(5); Ir(1)-Ir(2)-P(2) = 84.94(5); P(1)-Ir(1)-Ir(2)-P(2) = 43.96(8).

 $[(Cp*Ir)(\mu-dmpm)(\mu-H)(IrCp*)]^+$ (7) (Scheme 1). It should be noted that a net abstraction of a hydride can be achieved by these successive reactions.

When methyl triflate (1.0 equiv.) was added to a dichloromethane solution of **3** at -30 °C and the solution was stirred for 2 h, we found that methyl dihydride complex **6** was formed quantitatively (Scheme 1). The structure of complex **6** was identified by NMR spectroscopy below -30 °C because of its thermal instability. In the ¹H NMR spectrum, a signal due to the iridium-bound methyl group was observed at δ 0.51 as a doublet. In the ¹³C{¹H} NMR spectrum, a characteristic signal due to the iridium-bound methyl carbon was observed at δ -32.7 as a doublet coupled to one of the phosphorus atoms. Signal patterns of Cp* and dmpm in ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR were similar to those of C–H activated complexes so far reported by us.^{7c}

Then, we traced the reaction of **6** by variable-temperature NMR spectroscopy by raising the temperature from -30 to 30 °C. ¹H NMR spectra of the hydride region and a possible reaction pathway are summarized in Fig. 2 and Scheme 1. Upon warming the solution of complex **6**, the signals of hydrides (δ –16.86 for terminal and δ –25.25 for bridging) and the methyl group bound to iridium (δ 0.51) of **6** disappeared. Instead, a new triplet signal of a species **7** appeared at δ –20.23 with an integration value corresponding to 1H, which was predominantly observed around the temperature range of 0 to 20 °C. ¹³C{¹H} and ³¹P{¹H} spectra of **7** were also measured at –10 °C in addition to ¹H NMR. In the ¹H and ¹³C{¹H} NMR, signals due to two Cp* ligands were equivalently observed at δ 1.77 (¹H) and δ 11.5 (¹³C), respectively, indicating the high symmetrical structure of **7**. Signals due to the four methyl groups of dmpm were also observed equivalently





Fig. 2 Monitoring of the reaction of 6 in dichloromethane-d₂ by ¹H NMR analysis from -30 to 30 °C. Signals due to the iridium hydrides are shown.

at δ 1.75 (¹H) and δ 20.2 (¹³C). In the ³¹P{¹H} NMR, only one signal was observed at δ 10.6, also supporting the proposed symmetrical structure of 7. From these NMR analyses, the structure of 7 was confirmed to be 32e⁻ Ir^{II}–Ir^{II}, [(Cp*Ir)₂(µ-dmpm)(µ-H)]⁺, as illustrated in Scheme 1.¹³ Further heating of the solution of 7 up to 30 °C for 14 h resulted in the quantitative formation of the complex **8**, formed by intramolecular oxidative addition of the methyl C–H bond of dmpm ligand to the diiridium core (*vide infra*).

The above successful generation and detection of the true active Ir^{II} - Ir^{II} intermediate 7 prompted us to investigate the scope of C-H activation. The brown solid of **6** was converted to the purple solid of **7** by the simple procedures, which consisted of the generation of **6** followed by the removal of volatiles *in vacuo* at -30 °C and warming to room temperature (see the Experimental section for details). Using the desired purple solid **7**, we have performed the C-H activation reactions with several organic molecules as shown below.¹⁴

Intramolecular activation of sp3 C-H bond in dmpm ligand

When a solution of 7 in dichloromethane was kept at 40 °C for 24 h, the complex 8 was formed quantitatively (eqn 2).¹⁵ The structure of 8 was determined by spectroscopic analysis and X-ray crystallography. The ¹H NMR spectrum of 8 showed signals due to two hydrides at δ –16.78 (terminal) and –24.47 (bridging) and signals due to non-equivalent methylene protons of the activated methyl group at δ 2.84 and 0.85. In the ¹³C{¹H} NMR spectrum, the methylene carbon bound to the iridium center was observed at δ –8.2 as a doublet. The structure of 8 was finally confirmed by X-ray diffraction study. The molecular geometry is shown in Fig. 3. The iridium–iridium distance (3.0189(4) Å) is 0.17 Å shorter than that of phenyl complex 9 (3.190(1) Å).^{7c} The iridium–carbon bond length (2.154(8) Å) is a typical value compared to those in sp³ carbon–iridium bonds.¹⁶





Fig. 3 ORTEP drawing of the cationic part of 8 with 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir(1)-Ir(2) = 3.0189(4); Ir(1)-P(1) = 2.257(2); Ir(2)-P(2) = 2.235(2); Ir(1)-C(25) = 2.154(8); P(1)-Ir(1)-P(26) = 80.3(2); P(1)-Ir(1)-Ir(2) = 89.38(6); Ir(1)-Ir(2)-P(2) = 66.10(5).

Intermolecular activation of sp² C-H bonds by complex 7

We next investigated intermolecular aromatic C-H bond activation reactions of benzene, toluene, and hetero aromatics. As soon as benzene was added to pre-formed 7 at room temperature, the purple solid of 7 was dissolved and turned into a red-orange solution. After stirring for 75 min, [(Cp*Ir)(H)(µ-dmpm)(µ-H)(Ph)(IrCp*)]⁺ (9) was produced in 89% yield (eqn 3). The spectral data of 9 were identical to those we have previously reported.7c This C-H activation reaction of benzene apparently proceeded much faster compared to the reaction starting with the dicationic complex 1 (20 h, 44% isolated yield), and the yield of 9 was also higher. Using similar procedures, the C-H activation reactions of toluene and furan were also accomplished to give 10 (45%) and 11 (89%), respectively (eqn 3). While the activation of toluene gave a mixture of the meta- and para-activated products in a ratio of $1: 1.6^{17}$ comparable to those of our earlier report (1: 2)^{7c} and others,^{3g,18} the activation of furan gave the 2-furyl product 11 as a single product in high yield (89%) and the 3-furyl product was not detected.



We further examined the C-H activation of a hetero aromatic compound. The similar activation of pyridine by pre-formed 7 gave $[(Cp*Ir)(H)(\mu-dmpm)(\mu-C_5H_4N)(IrCp*)(H)]^+$ (12) in 74% yield (eqn 4). In the ¹H NMR spectra of **12**, signals due to two non-equivalent hydrides were observed in the terminal hydride region (δ -14.92 and -14.99). It was deduced from the signal pattern of aromatic protons that the C-H bond at the 2-position of the pyridine ring was selectively cleaved.¹⁹ The structure of 12 was unequivocally confirmed by X-ray diffraction. The molecular geometry and atom-numbering system are shown in Fig. 4. It is apparent that the two iridium centers are bridged by the pyridine ring at the nitrogen and the carbon at the orthoposition. The iridium-iridium distance is 4.0287(4) Å, indicating the absence of a bonding interaction between the two iridium centers. The lengths of the iridium-carbon bond (2.054(8) Å) and the iridium-nitrogen bond (2.159(8) Å) are typical of iridiumaromatic carbon single bonds and iridium-pyridine dative bonds. respectively.²⁰ Formation of this 36e⁻ complex 12 indicates that other C-H activated 34e⁻ complexes (8-11) could be potentially coordinatively unsaturated.



Fig. 4 ORTEP drawing of the cationic part of 12 with 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected (bond) distances (Å) and angles (°): Ir(1)-Ir(2) = 4.0287(4); Ir(1)-P(1) = 2.240(2); Ir(2)-P(2) = 2.247(2); Ir(1)-C(26) = 2.054(8); Ir(2)-N(1) = 2.159(8); P(1)-Ir(1)-C(26) = 84.1(2); P(2)-Ir(2)-N(1) = 94.23(19).

By the C-H activation methodology using the neutral complex **3** as a precursor, the activation of olefinic C-H bonds was

next examined. A large excess of cyclopentene was added to the dichloromethane solution of 7 at -30 °C and the solution was stirred at 0 °C for 18 h. These procedures brought about the activation of the olefinic C–H bonds of cyclopentene to give[(Cp*Ir)(H)(μ -dmpm)(μ -H)(1-cyclopentenyl)(IrCp*)]⁺ (13) in 56% yield (eqn 5).¹⁹ Complex 13 was relatively unstable and its structure was elucidated by NMR analysis. In the ¹H NMR spectrum of 13, signals due to hydrides were observed at δ –17.20 (terminal) and –25.80 (bridging). In the ¹³C{¹H} NMR spectrum, characteristic signals due to olefinic carbons were observed at δ 131.4 and 130.2 and the latter signal at δ 130.2 (d, J = 14 Hz) was coupled to one of the phosphorus atoms in the dmpm ligand. All NMR data were consistent with the proposed structure.



Conclusions

We have accomplished the synthesis of electronically neutral dmpm and dihydrido-bridged diiridium(II) complex **3** and disclosed that treatment of **3** with methyl triflate results in a net abstraction of a hydride from **3**, leading to successful generation of a highly reactive $32e^{-1}$ Ir^{II}–Ir^{II} species **7** that can be detected for the first time by means of variable-temperature NMR analysis. Using pre-formed **7** derived from the neutral complex **3** as a precursor, rapid activation of aromatic and olefinic C–H bonds can be achieved under very mild conditions.

Experimental

General

All reactions and manipulations were carried out under an atmosphere of argon by means of standard Schlenk techniques. ¹H, ¹³C{¹H}, ¹⁹F, and ³¹P{¹H} NMR spectra were recorded using a JEOL A-500 and EX-270 spectrometers. ³¹P{¹H} NMR were referenced to an 85% H₃PO₄ external standard. ¹⁹F NMR were referenced to a CF₃CO₂Et external standard. Melting points were determined using a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University.

Materials

Solvents were subjected to freeze-thaw-degas cycles three times after being dried by using standard procedures and were distilled prior to use. $[(Cp*Ir)_2(\mu-H)_3]Cl$ (4) was prepared following the literature method.²¹ Dmpm, methyl triflate and potassium *tert*-butoxide were used as obtained from commercial sources. Other reagents were used after distillation.

Preparation of [(Cp*Ir)₂(µ-dmpm)(µ-H)₂] (3)

In a 10 mL Schlenk tube, $[(Cp*Ir)_2(\mu-H)_3](Cl)$ (4) (692 mg, 0.998 mmol) and potassium *tert*-butoxide (133 mg, 1.19 mmol)

were placed. After addition of benzene (6 mL), the mixture was stirred for 2 hours at room temperature. The color of the solution turned brown. Dmpm (150 mg, 1.10 mmol) was added, and the mixture was further stirred for 24 hours at room temperature. After evaporation of the volatiles, the residue was extracted with hexane. Removal of hexane *in vacuo* afforded a brown solid **3** (735 mg, 0.927 mmol, 93%). Single crystals suitable for X-ray diffraction were obtained by recrystallization from a hot hexane solution of **3**. ¹H NMR (500 MHz, C₆D₆): δ 2.61 (2H, t, *J* = 10 Hz, PCH₂P), 2.15 (30H, s, Cp*), 1.47 (12H, br s, PMe), -17.76 (2H, t, *J* = 17 Hz, Ir–*H*–Ir). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 90.6 (s, C₅Me₅), 56.6 (t, *J* = 36 Hz, PCH₂P), 16.0 (s, PMe), 12.40 (s, C₅Me₅). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ -46.7 (s). M.p. 173.3–175.0 °C. Anal. Calcd for C₂₆H₄₆Ir₂P₂: H, 5.85; C, 37.86. Found: H, 5.82; C, 37.96.

Generation and detection of 6 and 7 by the reaction of 3 with MeOTf using low-temperature and variable-temperature NMR analysis

A two-necked 30 mL flask was charged with **3** (242 mg, 0.305 mmol) and dichloromethane (12 mL) at -30 °C. Methyl triflate (49.8 mg, 0.303 mmol) was added to the solution, and the reaction mixture was stirred for 2 h at -30 °C. After removal of the solvent *in vacuo* at -30 °C, CD₂Cl₂ (1.0 mL) was added. The solution was transferred into an NMR tube at -40 °C, and the tube was flame sealed. The tube was kept below -80 °C before being placed in a pre-cooled (-80 °C) NMR probe. The probe temperature was elevated by 10 °C every 30 min from -50 to 30 °C.

6: ¹H NMR (500 MHz, CD₂Cl₂, at -40 °C): δ 4.60 (1H, m, PCHHP), 2.10 (1H, m, PCHHP), 1.92 (15H, s, Cp*), 1.76 (15H, s, Cp*), 1.64 (3H, d, J = 10 Hz, PMe), 1.55 (3H, d, J = 9 Hz, PMe), 1.39 (3H, d, J = 10 Hz, PMe), 1.38 (3H, d, J = 10 Hz, PMe), 0.51 (3H, d, J = 6 Hz, IrMe), -16.86 (1H, dd, J = 37 Hz, 2 Hz, IrH,), -25.25 (1H, m, Ir-H-Ir). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, at -40 °C): δ 120.5 (q, J = 321 Hz, CF₃), 94.2 (d, J = 2 Hz, C₅Me₅), 94.0 (d, J = 3 Hz, C₅Me₅), 25.5 (d, J = 44 Hz, PCH₂P), 17.3 (d, J = 34 Hz, PMe), 14.8 (d, J = 43 Hz, PMe), 11.8 (d, J = 35 Hz, PMe), 11.7 (d, J = 35 Hz, PMe), 10.6 (s, C₅Me₅), 9.8 (s, C₅Me₅), -32.7 (d, J = 9 Hz, IrMe). ³¹P{¹H</sup> NMR (202 MHz, CD₂Cl₂, at -40 °C): δ -30.9 (d, J = 42 Hz), -40.5 (d, J = 42 Hz).

7: ¹H NMR (500 MHz, CD₂Cl₂, at 10 °C): δ 2.33 (2H, t, J = 10 Hz, PCH₂P), 1.77 (30H, s, Cp*), 1.75 (12H, br s, PMe₂), -20.23 (1H, t, J = 10 Hz, Ir-*H*-Ir). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, at -10 °C): δ 120.9 (q, J = 322 Hz, CF₃), 93.5 (s, C_5 Me₅), 36.7 (t, J = 35 Hz, PCH₂P), 20.2 (app. triplet, AA'X system, ΣJ_{PC} = 44 Hz, PMe), 11.5 (d, J = 4 Hz, C_5Me_5). ¹⁹F NMR (470 MHz, CD₂Cl₂, at 10 °C) δ -78.4 (s). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, at -10 °C): δ 10.6 (s).

General procedures for the C–H activation reactions: concise generation of $32e^-$ complex 7

A two-necked 30 mL flask was charged with 0.30 mmol of **3** and 12 mL of dichloromethane at -30 °C. Methyl triflate (0.30 mol, 1.0 equiv.) was added to the solution and the reaction mixture was stirred for 2 h at -30 °C. After removal of the volatiles *in vacuo* at -30 °C, the flask was warmed to room temperature, and the brown solid turned purple. NMR analyses of the purple solid

thus obtained confirmed quantitative formation of **7**. Then, C–H activation reactions were conducted as described below.

Intramolecular C-H bond activation to give 8

After the generation of 7 (from 0.190 mmol of 3), the purple solid was dissolved in dichloromethane (12 mL). Heating the solution at 40 °C for 24 h gave the C-H bond activated product 8. Extraction with toluene gave the brown oil 8 (173 mg, 0.184 mmol, 97%). Single crystals suitable for X-ray analysis were obtained by cooling the toluene solution of 8. ¹H NMR (500 MHz, CD_2Cl_2): δ 3.38 (1H, m, PCHHP), 2.84 (1H, m, PCHHIr), 2.03 (15H, s, Cp*), 2.01 (1H, m, PCHHP), 1.91 (15H, d, J = 3 Hz, Cp*), 1.73 (3H, d, J = 11 Hz, PMe), 1.60 (3H, d, J = 10 Hz, PMe), 1.52 (3H, d, J = 10 Hz, PMe), 0.85 (1H, m, PCHHIr), -16.78 (1H, d, J = 28 Hz, IrH,), -24.47 (1H, m, Ir-H-Ir). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 : δ 121.2 (q, J = 322 Hz, CF_3), 94.0 (d, J = 3 Hz, C_5Me_5), 93.2 (d, J = 3 Hz, C_5 Me₅), 36.4 (t, J = 38 Hz, PCH₂P), 21.0 (m, PMe), 19.8 (dd, J = 37 Hz, 4 Hz, PMe), 13.8 (dd, J = 36 Hz, 3 Hz, PMe), 11.1 (d, J = 4 Hz, $C_5 Me_5$), 10.1 (d, J = 4 Hz, $C_5 Me_5$), -8.2 (d, J = 37 Hz, PCH₂Ir). ¹⁹F NMR (470 MHz, CD₂Cl₂) δ -78.3 (s). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ -22.7 (d, J = 46 Hz), -43.6 (d, J = 46 Hz). M.p. 169 °C (decomp.). Anal. Calcd for C₂₆H₄₅F₃Ir₂O₃P₂S: C, 33.18; H, 4.82. Found: C, 33.47; H, 4.76.

General procedure for the C–H activation reaction of aromatic molecules to give 9–12

After the generation of 7, aromatic solvent was added to the purple solid of 7 and stirred for 75 min. The color of the solution turned from purple to orange–red within 10–15 min. After removal of the volatiles, complexes 9-12 were isolated. The spectral data of 9, 10 and 11 are identical to those we have previously reported.^{7c}

C-H activation reaction of benzene to give 9

After removal of benzene *in vacuo*, the residue was washed with benzene and hexane to give **9** as an orange powder (756 mg, 0.741 mmol, 89%).

C-H activation reaction of toluene to give 10

After removal of toluene *in vacuo*, the residue was chromatographed on silica gel, and subsequent recrystallization from toluene gave a mixture of **10a** and **10b** as an orange powder (119 mg, 0.115 mmol, 45%). The ratio of products was determined by ¹H NMR.

C-H activation reaction of furan to give 11

After removal of furan *in vacuo*, the residue was washed with toluene and hexane to give **11** as a light yellow powder (832 mg, 0.824 mmol, 89%).

C-H activation reaction of pyridine to give 12

After removal of pyridine *in vacuo*, the residue was washed with toluene and extracted with dichloromethane to give the light yellow powder (219 mg, 0.215 mmol, 74%). ¹H NMR (500 MHz, acetone-d₆): δ 9.16 (1H, d, J = 8 Hz, aromatic), 7.59 (1H, d, J = 9 Hz, aromatic), 6.45 (1H, t, J = 9 Hz, aromatic), 6.45 (1H, t, t)

J = 7 Hz, aromatic), 2.66 (1H, m, PC*H*HP), 1.96 (3H, d, *J* = 10 Hz, P*Me*), 1.95 (15H, s, Cp^{*}), 1.90 (3H, d, *J* = 10 Hz, P*Me*), 1.85 (15H, s, Cp^{*}), 1.81 (3H, d, *J* = 11 Hz, P*Me*), 1.76 (1H, m, PCH*H*P), 1.32 (3H, d, *J* = 10 Hz, P*Me*), -14.92 (1H, d, *J* = 22 Hz, Ir–*H*), -14.99 (1H, s, Ir–*H*). ¹³C{¹H} NMR (126 MHz, acetone-d₆): δ 179.5 (d, *J* = 17 Hz, Ir–C), 163.7 (s, aromatic), 144.1 (s, aromatic), 132.5 (s, aromatic), 122.4 (q, *J* = 321 Hz, CF₃), 118.4 (s, aromatic), 96.6 (d, *J* = 3 Hz, C₅Me₅), 93.7 (d, *J* = 3 Hz, C₅Me₅), 29.9 (dd, *J* = 25 Hz, 31 Hz, PCH₂P), 26.7 (dd, *J* = 48 Hz, 7 Hz, P*Me*), 19.3 (d, *J* = 38 Hz, P*Me*), 17.0 (d, *J* = 39 Hz, 6 Hz, P*Me*), 10.9 (d, *J* = 34 Hz, P*Me*), 10.41 (s, C₅*Me*₅), 9.96 (s, C₅*Me*₅). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ -22.6 (d, *J* = 7 Hz), -25.8 (d, *J* = 7 Hz). M.p. 163 °C (decomp.). Anal. Calcd for C₃₁H₅₀F₃Ir₂NO₃P₂S: C, 36.50; H, 4.94; N, 1.37. Found: C, 36.30; H, 4.72; N, 1.31.

C-H activation reaction of cyclopentene to give 13

To the pre-formed 7 (0.209 mmol), cyclopentene (4 mL) and dichloromethane (2 mL) were added and the mixture was stirred for 18 h at 0 °C. After removal of the solvent *in vacuo*, the residue was washed with toluene and hexane to give **13** as an orange powder (119 mg, 0.118 mmol, 56%) with a small amount of contaminants probably because of the thermal decomposition of **13**. ¹H NMR (500 MHz, CD₂Cl₂): δ 5.12 (1H, s, CH₂CH=CIr),

 Table 1
 Crystal data and structure refinement parameters for 3, 8 and 12

4.10 (1H, m, PCH*H*P), 2.47 (1H, m, PC*H*HP), 2.31 (2H, m, =CHC*H*₂CH₂), 2.18 (2H, m, IrCC*H*₂CH₂), 1.97 (15H, d, *J* = 3 Hz, Cp*), 1.81 (15H, s, Cp*), 1.68 (3H, d, *J* = 10 Hz, P*Me*), 1.65 (3H, d, *J* = 10 Hz, P*Me*), 1.47 (3H, d, *J* = 11 Hz, P*Me*), -17.20 (1H, dd, *J* = 34 Hz, 5 Hz, Ir*H*), -25.80 (1H, m, Ir-*H*-Ir). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 131.4 (d, *J* = 4 Hz, IrC=*C*H-CH₂), 130.2 (d, *J* = 14 Hz, Ir-*C*=CH-CH₂), 121.3 (q, *J* = 320 Hz, CF₃), 96.3 (d, *J* = 3 Hz, C₅Me₅), 95.3 (d, *J* = 2 Hz, C₅Me₅), 52.3 (s, IrC-*C*H₂-CH₂), 26.3 (s, CH₂-*C*H₂-CH₂), 24.3 (dd, *J* = 44 Hz, 6 Hz, P*Me*), 13.1 (dd, *J* = 37 Hz, 7 Hz, P*Me*), 11.2 (s, C₅*Me*₅), 10.6 (s, C₅*Me*₅). ³¹P{¹H}</sup> NMR (202 MHz, CD₂Cl₂): δ -27.8 (d, *J* = 37 Hz), -38.6 (d, *J* = 37 Hz).

X-Ray structure analyses of 3, 8, and 12

Crystal data and structure refinement parameters for **3**, **8** and **12** are summarized in Table 1. Diffraction data were obtained using a Rigaku AFC-5S. The reflection intensities were monitored by three standard reflections every 150 measurements. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom

	3	8	12
Description of crystal			
Color, habit	Orange, block	Orange, block	Orange, block
Max dimensions/mm	$0.60 \times 0.50 \times 0.30$	$0.60 \times 0.30 \times 0.30$	$0.40 \times 0.35 \times 0.35$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (#14)	P1 (#2)	$P2_1/a$ (#14)
a/Å	8.505(6)	9.771(3)	17.7878(14)
b/Å	16.341(7)	10.880(3)	12.3618(17)
c/Å	20.088(4)	15 431(3)	18 402(2)
$a/^{\circ}$	90	80.24(2)	90
$\beta/^{\circ}$	96.95(3)	83.09(2)	117.595(7)
v/°	90	86.91(3)	90
$V/Å^3$	2771.2(23)	1604.0(8)	3586.1(7)
Z	4	2	4
Formula	$C_{25}H_{46}P_2Ir_2$	$C_{26}H_{45}O_3F_3P_2SIr_2$	$C_{31}H_{50}NO_3F_3P_2SIr_2$
$M_{ m w}$	793.03	941.08	1020.18
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.901	1.948	1.889
Data collection			
Radiation $\lambda/\text{\AA}$	MoK α ($\lambda = 0.71069$ Å)	MoK α ($\lambda = 0.71069$ Å)	MoK α ($\lambda = 0.71069$ Å)
T/K	203	296	293
Scan technique	ω -2 θ	ω -2 θ	ω -2 θ
Scan width/°	$(1.26 + 0.30 \tan\theta)$	$(1.31 + 0.30 \tan\theta)$	$(1.15 + 0.30 \tan\theta)$
$2\theta_{\rm max}/^{\circ}$	55.0	55.0	55.0
Reflections collected	6744	7637	8475
Structure determination			
Observed reflections $(I > 3.00\sigma(I))$	5326	5063	5785
No. of variables	306	377	436
Reflection/parameter ratio	17.41	13.43	13.27
Transmission factor	0.023-0.054	0.063–0.078	0.042-0.069
R _{int}	0.0638	0.0197	0.0230
$R(I > 3.00\sigma(I))^a$	0.0447	0.0375	0.0426
$R_{\rm w} \left(I > 3.00\sigma(I)\right)^a$	0.0738	0.0498^{c}	0.0598
wR_2 (all data) ^e	0.1518	0.1111	0.1352
Goodness of fit indicator	1.004	1.020	1.007
${}^{a}R = \Sigma F_{o} - F_{c} /\Sigma F_{o} , R_{w} = [\Sigma w($	$(F_{o} - F_{c})^{2} / \Sigma w F_{o}^{2}]^{1/2}$. ^b w = 1/[0	$.0048F_{o}^{2} + 1.0000\sigma(F_{o}^{2})].^{c}w = 1/[0.0000\sigma(F_{o}^{2})].^{c}w$	$0016F_0^2 + 1.0000\sigma(F_0^2)].^d w =$

 $1/[0.0025F_{o}^{2} + 1.0000\sigma(F_{o}^{2})] \cdot wR_{2} = \{\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2}.$

Patterson methods²² and expanded using Fourier techniques.²³ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Atomic scattering factors, anomalous dispersion terms and the values for the mass attenuation coefficients were taken from the literature.²⁴ The hydrogen atoms were located on idealized positions except for metal hydrides. Metal hydrides in **3**, **8**, and **12** were not located. All calculations were performed using the CrystalStructure^{25,26} crystallographic software package.

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