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Mild Oxidative Addition of C–H Bonds to a Hydrido-Bridged Dinuclear Complex of Iridium(II) Induced by the Coordination of Heteroatomic Ligands

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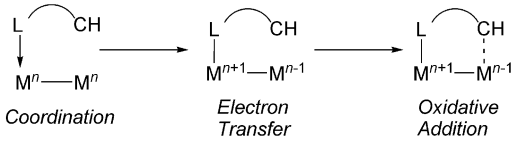
Keywords: Cooperative effects / Iridium / C–H activation / P ligands / S ligands

The oxidative addition of C–H bonds to a dinuclear complex of divalent iridium, $[Cp^*Ir(\mu\text{-}H)]_2$ (**1**), has been investigated. Reactions of **1** with phosphorus compounds containing a phenyl ring (PR^1R^2Ph) at ambient temperature gave novel five-membered diiridacyclic $[(Cp^*IrH)_2(\mu\text{-}H)(\mu\text{-}R^1R^2PC_6H_4)]$ [$R^1 = R^2 = Me$ (**2a**); $R^1 = Me$, $R^2 = Ph$ (**2b**); $R^1 = R^2 = Ph$ (**2c**); $R^1 = R^2 = OEt$ (**2d**); and $R^1 = OEt$, $R^2 = Ph$ (**2e**)] complexes through *ortho*-C–H activation of the phenyl ring bound to the phosphorus atom. The reaction of **1** with tripropylphosphane gave a new four-membered diiridacyclic $[(Cp^*IrH)_2(\mu\text{-}H)(\mu\text{-}Pr_2PCHCH_2CH_3)]$ (**3**) complex in a similar manner. On the other hand, the reaction of **1** with triethyl phosphite gave a Cp^*-metalated product, $[Ir(H)(P(OEt)_3)(\mu,\eta^5,\eta^1\text{-}C_5Me_4CH_2)\text{-}(\mu\text{-}H)Ir(H)(Cp^*)]$ (**4**), through C–H activation of a methyl group on one of the Cp^* ligands. Furthermore, similar mild C–H activation reactions of **1** with sulfoxides have also been revealed. Thus, reactions of **1** with dimethyl sulfoxide and a couple of sulfoxides containing phenyl groups brought about the activation of the C–H bonds of a methyl group and a phenyl group to give $[(Cp^*IrH)_2(\mu\text{-}H)(\mu\text{-}MeS(=O)CH_2)]$ (**5**) and $[(Cp^*IrH)_2(\mu\text{-}H)(\mu\text{-}RS(=O)C_6H_4)]$ [R = Me (**6a**) and R = Ph (**6b**)], respectively. The structures of **2a**, **4**, **5**, and **6a** have been confirmed by X-ray analysis. A plausible reaction pathway for these C–H activation reactions has been proposed.

Introduction

Recently, much attention has been paid to bond cleavage reactions on multimetallic complexes because these are expected to outperform monometallic complexes.[1] The proximity of multiple metal centers can generate unique functions based on their cooperativity.[2,3] To date, several interesting reports on the cooperative reactivity of multimetallic complexes bridged by carbonyls or hydrides have appeared. For example, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ exhibited high capabilities for the bond activation reactions of organic molecules.[4] The bond cleavage and reconstruction of small organic molecules on polyhydrido ruthenium clusters have also been reported.[5] While a number of bond activation processes on transition metal clusters including *ortho* metallation have been reported, the activation of carbon–hydrogen (C–H) bonds in organic molecules by transition metal complexes is still one of the most attractive areas of study in organometallic chemistry[6] since the activation and subsequent transformation of inert and abundant hydrocarbon molecules is an ideal synthetic tool from the viewpoint of efficiency and economy.



Scheme 1.

We previously reported on the synthesis and reactivity of diphosphane- and dihydrido-bridged diiridium(III) complexes[7] and disclosed the capability of the diiridium complexes to conduct facile C–H activation.[7c] We have found that treatment of a dihydrido-bridged complex of divalent iridium(II), $[Cp^*Ir(\mu\text{-}H)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**), with monophosphane brings about smooth C–H bond activation at the *ortho* position of the phenyl ring bound to the phosphorus atom at ambient temperature. It should be noted that in this reaction the phosphorus atom is coordinated to one of the iridium centers, while the C–H activation occurs on the other iridium center, which suggests that coordination of the ligand to the metal center might lead to enhancement of the reactivity of the adjacent metal center towards oxidative addition. Thus, it would be provable that coordination of a donor ligand to one of the metal centers gives rise to electron transfer to the other metal center to afford a mixed-valent intermediate and induce the facile oxidative

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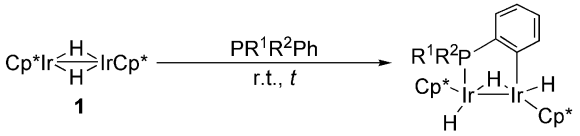
addition of C–H bonds on the lower valent metal center (Scheme 1). Herein, we report the mild C–H bond activation on the diiridium core in **1** induced by the coordination of a series of phosphorus compounds and sulfoxides.

Results and Discussion

Reactions of 1 with Phosphorus Ligands: Oxidative Addition of the C–H Bond of Phosphorus Ligands

The reaction of a slight excess (1.1 equiv.) of dimethyl(phenyl)phosphane with **1** in benzene at room temperature for 16 h afforded a new complex, **2a**, quantitatively (98% isolated yield). The complex **2a** was formed by coordination of the phosphorus atom to one of the iridium centers and C–H activation of the *ortho* position of the phenyl ring on the other iridium center [Equation (1)]. The κ-P,C bridging structure of **2a** was determined by NMR spectroscopy, elemental analysis, and X-ray crystallography. In the ^{1}H NMR of **2a** at room temperature, two nonequivalent signals due to the two Cp* ligands were observed at δ = 1.92 and 1.90 ppm. Three hydrides were observed at δ = –17.71 ppm as a broad singlet at room temperature, which indicates rapid interchange of the three hydrides on the NMR time scale because the signals due to the hydrides split into a singlet (δ = –14.87 ppm) and two doublets [δ = –17.73 (J_{PH} = 32 Hz) and –20.88 (J_{PH} = 10 Hz) ppm] at –90 °C. The singlet resonance would be due to a terminal hydride bound to the iridium without the phosphorus ligand. The doublet resonance with the larger J_{PH} would be due to a terminal hydride bound to the iridium coordinated by a phosphorus ligand, and the doublet resonance with the smaller J_{PH} would be due to a bridging hydride. In the ^{13}C{^{1}H} NMR, a signal due to the aromatic carbon bound to iridium was observed at δ = 150.5 ppm as a doublet ($^2J_{PC}$ = 30 Hz). A signal due to the carbon bound to phosphorus was observed at δ = 160.8 ppm as a doublet with a large coupling constant ($^1J_{PC}$ = 76 Hz).[8] Finally, an X-ray diffraction study of **2a** confirmed its structure. The molecular geometry and atom-numbering system are shown in Figure 1. It is apparent that the two iridium centers are bridged by an $Me_2PC_6H_4$ moiety in a κ-P,C fashion. The iridium–iridium distance is 2.9782(4) Å, which is the standard length for monohydrido-bridged diiridium complexes.[9,10] Although the positions of the three hydrides could not be determined from Fourier difference maps, the *transoid* configuration of the two Cp* ligands strongly suggests that two of the three hydrides are located at the terminal positions and another one at the bridging position,[9] consistent with the observation in the ^{1}H NMR analysis at –90 °C. There have been a few reports on the reactions of hydrido-bridged dinuclear complexes, $[(Cp^*Ru)(\mu\text{-}H)_2]_2$,[11] $[(C_6Me_6Ru)_2(\mu\text{-}H)_3]^+$,[12] $[Cp^*Ir(\mu\text{-}H)Cl]_2$,[13] and $[Cp^*Ir(\mu\text{-}H)_3RuCp^*]$,[14] with phosphorus ligands, in which P–C bond activation took place to give phosphide-bridged complexes. In contrast to these reports, it is noteworthy that selective C–H bond activation has occurred in the present study, and no P–C cleavage has been observed.



2a PMe_2Ph t = 16 h (98%)
2b $PMePh_2$ t = 16 h (84%)
2c PPh_3 t = 3 d (51%)
2d $P(OEt)_2Ph$ t = 16 h (56%)
2e $P(OEt)Ph_2$ t = 16 h (61%) (1)

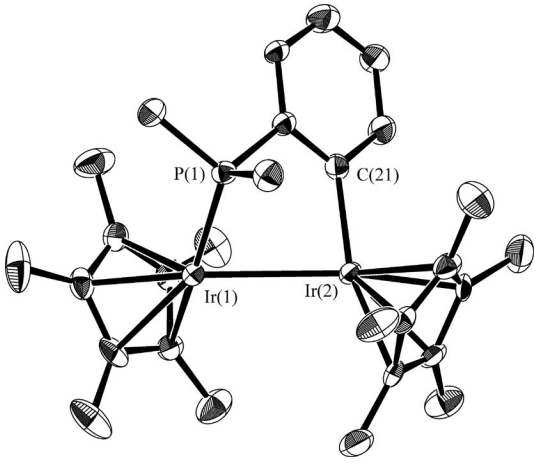
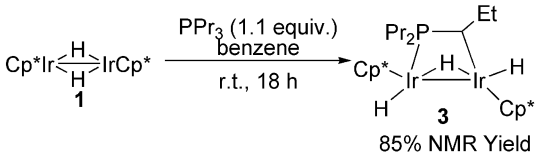


Figure 1. ORTEP drawing of complex **2a** with 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–Ir(2) 2.9782(4), Ir(1)–P(1) 2.214(2), Ir(2)–C(21) 2.052(8), Ir(2)–Ir(1)–P(1) 76.83(5), Ir(1)–Ir(2)–C(21) 84.7(2).

Next, we investigated the C–H activation process with a series of phosphorus ligands containing phenyl rings. The results are summarized in Equation (1). The structures of complexes **2b**–**2e** were determined by NMR spectroscopy and elemental analysis, and these provided support for the κ-P,C bridging structures. These reactions proceeded almost quantitatively, however the isolated yields were moderate in some cases because of the instability of the products. The reaction of **1** with triphenylphosphane (cone angle = 145°) [15] was obviously much slower than the reactions with less sterically hindered dimethyl(phenyl)phosphane (cone angle = 122°) and diethyl phenylphosphonite (cone angle = 116°), which indicates that the reaction rate is dependent on the steric bulkiness of the phosphorus ligands rather than their electronic nature.[16]

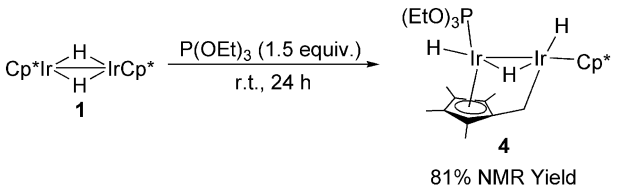
Then, we turned our attention to the reaction with phosphorus compounds containing no aromatic rings. The reaction of **1** with tripropylphosphane resulted in C–H activation of the α-methylene group on the phosphorus atom

to give the four-membered κ-P,C bridging complex, **3** [Equation (2)]. Characterization of **3** was carried out by NMR spectroscopy, and the yield was determined by NMR because of difficulties in isolating **3**. In the ^{1}H NMR of **3**, two nonequivalent signals due to the two Cp* ligands were observed at δ = 2.06 and 1.98 ppm, and broad signals due to the three hydrides were observed at δ = –16.77, –17.56, and –22.08 ppm. Three triplets due to the methyl protons of the propyl groups were observed at δ = 1.24, 1.05, and 1.00 ppm. A signal due to the methine proton was observed at δ = 1.41 ppm overlapped with signals due to the methylene protons. In the ^{13}C{^{1}H} NMR, a characteristic signal for the methine carbon bound to iridium was observed at δ = –19.0 ppm as a doublet (J = 18 Hz). A correlation between the methine carbon (δ = –19.0 ppm) and the methine proton (δ = 1.41 ppm) was confirmed in a ^{13}C{^{1}H}–^{1}H COSY spectrum. All NMR spectroscopic data (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) of **3** were consistent with the proposed structure.



(2)

On the other hand, the reaction of **1** with triethyl phosphite brought about the C–H activation of a methyl group on one of the Cp* ligands to give rise to **4** [Equation (3)]. The structure of **4** was determined by NMR spectroscopy and X-ray crystallography. In the ^{1}H NMR of **4**, a signal due to one of the Cp* ligands was observed at δ = 2.08 ppm with an integration value of 15 H as well as signals due to the four methyl groups on the activated Cp* ligand at δ = 2.15, 1.89, 1.67, and 1.37 ppm (an integration value of 3 H was assigned to each of the signals). Signals due to the protons of the methylene group bound to iridium were found at δ = 3.33 and 2.75 ppm. In the ^{13}C{^{1}H} NMR, a characteristic signal due to the methylene carbon was observed at δ = –25.3 ppm as a singlet. The structure of **4** was unequivocally confirmed by an X-ray diffraction study. The molecular geometry and atom-numbering system are shown in Figure 2. It is clear that the phosphorus atom binds to one of the iridium centers and that a methyl groups on one of the Cp* ligands is activated by the other iridium center.



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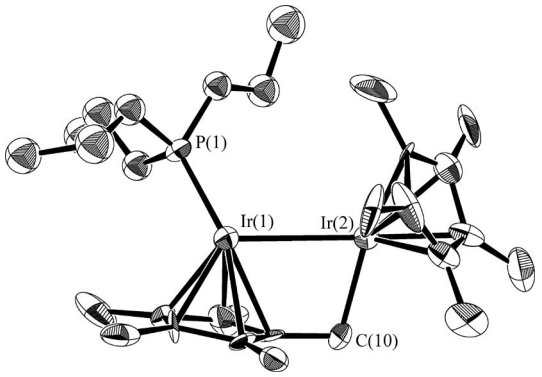
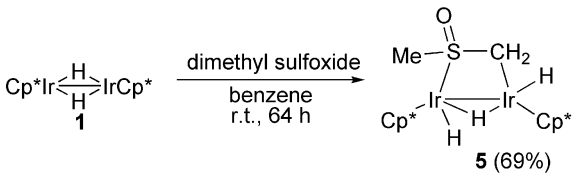


Figure 2. ORTEP drawing of complex **4** with 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–Ir(2) 2.9315(19), Ir(1)–P(1) 2.179(7), Ir(2)–C(10) 2.14(2), Ir(2)–Ir(1)–P(1) 113.5(7), Ir(1)–Ir(2)–C(1) 76.2(10).

Reactions of 1 with Sulfoxides: Oxidative Addition of the C–H Bond of Sulfoxides

The results shown above prompted us to investigate the activation of other donor molecules, and we found that one of the methyl groups of dimethyl sulfoxide was subject to oxidative addition of a C–H bond on ligation to **1**. Thus, dimethyl sulfoxide reacted with **1** in benzene at room temperature for 64 h to induce the C–H activation of one of the methyl groups on the sulfur atom to give **5** in 69% yield [Equation (4)]. Complex **5** was characterized by NMR spectroscopy and X-ray crystallography. Since the NMR spectra of **5** showed broad, unresolved resonances at room temperature, they were measured at –80 °C. In the ^{1}H NMR of **5**, three nonequivalent hydrides were observed at δ = –13.38, –17.24, and –20.68 ppm together with signals for the two Cp* ligands (δ = 1.98 and 1.87 ppm). A signal due to the methyl groups of dimethyl sulfoxide was observed at δ = 3.12 ppm, and two nonequivalent signals due to the protons of the methylene group bound to iridium were observed at δ = 4.61 and 2.56 ppm. In the ^{13}C{^{1}H} NMR spectrum, a signal due to the methylene carbon was observed at δ = 12.0 ppm, and a signal for the methyl carbon on the sulfur atom was observed at δ = 42.9 ppm, which was slightly shifted to a lower field than that for free dimethyl sulfoxide (δ = 40.2 ppm in CD_2Cl_2 at –80 °C). Single crystals suitable for X-ray crystallography were obtained by recrystallization from hexane solution. The results of the X-ray diffraction study of **5** are shown in Figure 3. It is apparent that the complex contains a four-membered ring consisting of the two iridium atoms, the sulfur atom, and the carbon atom of the methylene group. The length of the iridium–carbon bond is 2.112(9) Å, which is the standard length for an iridium–sp^3 carbon bond.[17] No interaction is observed between the oxygen atom and the iridium centers.

We further examined the C–H activation reactions of other sulfoxides such as methyl phenyl sulfoxide and diphenyl sulfoxide [Equation (5)]. In the reaction of **1** with methyl phenyl sulfoxide, selective C–H activation at the *ortho* position of the phenyl ring occurred to give **6a**. Com-



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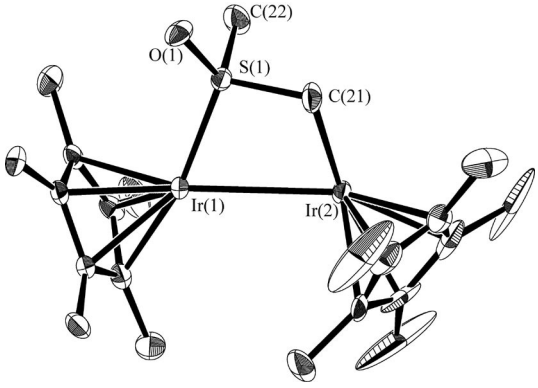
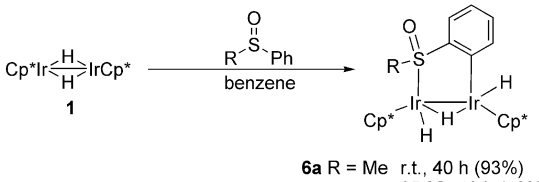


Figure 3. ORTEP drawing of complex **5** with 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–Ir(2) 2.9414(4), Ir(1)–S(1) 2.2097(19), Ir(2)–C(21) 2.112(9), S(1)–C(21) 1.739(10), S(1)–C(22) 1.797(9), S(1)–O(1) 1.485(6), Ir(2)–Ir(1)–S(1) 71.26(5), Ir(1)–Ir(2)–C(21) 74.0(2).

plex **6a** was characterized by NMR spectroscopy and X-ray structural analysis. In the ^1H NMR spectrum of **6a**, two nonequivalent signals due to the two Cp* ligands (δ = 1.88 and 1.81 ppm) and broad signals due to hydrides [δ = –15.27 (2 H) and –19.57 (1 H) ppm] were observed. In the $^{13}C\{^1H\}$ NMR spectrum, a signal for the aromatic carbon bound to an iridium center was observed at δ = 144.2 ppm. The results of the X-ray diffraction study of **6a** are shown in Figure 4. The crystal structure of **6a** is very similar to that of **2a** derived from dimethyl(phenyl)phosphane with respect to the iridium–iridium distance [2.9836(2) Å in **6a** vs. 2.9782(4) Å in **2a**], the iridium–sulfur distance [2.2034(15) Å in **6a** vs. an iridium–phosphorus distance of 2.214(2) Å in **2a**], and the iridium–carbon distance [2.055(5) Å in **6a** vs. 2.052(8) Å in **2a**]. The *ortho* C–H activation of the phenyl ring of diphenyl sulfoxide with **1** also proceeded to give **6b** [Equation (5)]. The structure of **6b** was characterized by NMR spectroscopy and elemental analysis. Thus, it has been found that not only phosphorus compounds, but also sulfoxides, are coordinating molecules that can be effectively subjected to the oxidative addition of C–H bonds to the dinuclear complex of divalent iridium, **1**.[18]



(5)

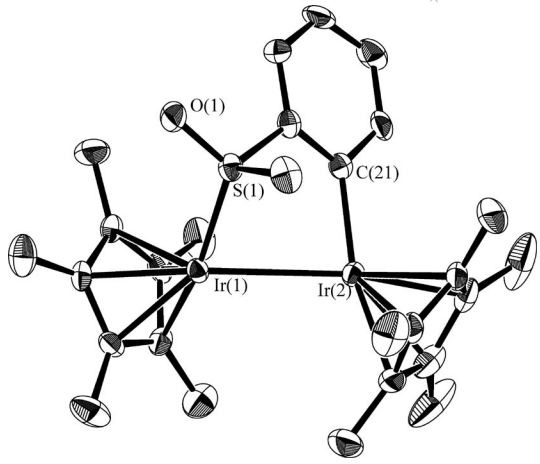
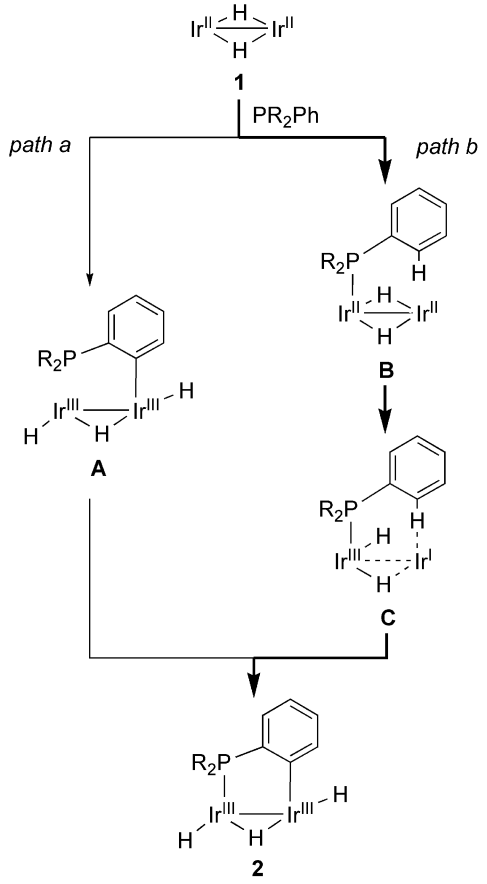


Figure 4. ORTEP drawing of complex **6a** with 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–Ir(2) 2.9836(2), Ir(1)–S(1) 2.2034(15), Ir(2)–C(21) 2.055(5), S(1)–C(22) 1.790(6), S(1)–O(1) 1.485(4), Ir(2)–Ir(1)–S(1) 80.08(3), Ir(1)–Ir(2)–C(21) 83.98(13).

Mechanistic Considerations

Two plausible pathways for the present oxidative addition of C–H bonds induced by coordination of a heteroatomic ligand to dinuclear complex **1** are shown in Scheme 2. At first, we considered that direct oxidative addition of a C–H bond to **1** to produce **A** followed by coordination of the heteroatom could occur to give stable product **2** (path *a*), because H/D scrambling reactions of the hydrides in **1**-d_2 with dihydrogen or methanol have been previously reported by Hou et al.[19] Another plausible pathway starts with initial coordination of the heteroatom to one of the iridium centers (Ir^{II}–Ir^{II}) to afford **B**, which could be transformed to a mixed-valent (Ir^{III}–Ir^{I}) intermediate **C** by electron transfer between the two iridium centers with concomitant migration of a bridging hydride into a terminal position. The successive oxidative addition of a C–H bond to the highly reactive Ir^{I} center should then occur very smoothly to give product **2** (path *b*).

To examine the possibility of path *a*, an H/D scrambling experiment of **1** with C_6D_6 was attempted; however, no detectable H/D scrambling of the hydrides and the Cp* methyl protons was observed (e.g., complex **1** remained unchanged), which suggests that the direct oxidative addition of a C–H bond to **1** to produce **A** (path *a*) is improbable. Additionally, the reaction of **1** with triethyl phosphite to afford **4** through the C–H activation of a Cp* methyl group strongly supports a pathway whereby coordination of donor molecules to one of the iridium centers induces the activation of the adjacent metal center for the subsequent oxidative addition. Thus, we propose that the present oxidative addition reactions of C–H bonds proceed through pathway *b*, and that the reactivity of **1** in the C–H activation reactions with donor ligands can be attributed to the cooperative reactivity of the dinuclear complex of divalent iridium, **1**.



Scheme 2. Plausible reaction pathways for the oxidative addition of a C–H bond to **1** induced by the coordination of a phosphorus ligand.

Conclusions

We have disclosed that mild oxidative additions of C–H bonds in phosphorus, Cp*, and sulfoxide ligands take place at ambient temperature by reaction with the dinuclear iridium complex, **1**. Heteroatomic ligands containing phenyl rings or α-C–H bonds to the heteroatom resulted in the C–H activation of the *ortho*-C–H bond or the α-C–H bond, while heteroatomic ligands containing neither phenyl ring nor α-C–H bond led to the C–H activation of a Cp* ligand. These C–H bond activation reactions are induced by coordination of heteroatomic ligands, such as phosphorus compounds and sulfoxides, to produce novel κ-P,C and κ-S,C bridging complexes. The proximity of the two iridium centers together with the characteristic electron configuration (Ir^{II}–Ir^{II}) of **1** provides these simple but unique reactivities based on synergetic and cooperative effects.

Experimental Section

General Procedures: All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques or in an N_2 dry-box. Melting points were determined on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were measured with JEOL EX-270 and JEOL A-500 spectrometers. $^{31}P\{^1H\}$ NMR spectra were referenced to an 85% H_3PO_4 external standard. Solvents were dried by using standard procedures and distilled prior to use. $[Cp^*Ir(\mu\text{-}H)]_2$ (**1**) [19] and $P(OEt)_2Ph$[20] were prepared by literature methods. Other reagents were used as obtained from commercial sources.

Reaction of $[Cp^*Ir(\mu\text{-}H)]_2$ (1) with PMe_2Ph To Give 2a: A two-necked 30 mL flask was charged with **1** (157 mg, 0.239 mmol) in benzene (0.7 mL). Dimethyl(phenyl)phosphane (36.1 mg, 0.261 mmol) was added to the reaction mixture, and this was stirred at room temperature for 16 h. After removal of the volatiles in vacuo, the residue was extracted with hexane. Evaporation of the solvent gave **2a** as a yellow-brown powder (185 mg, 0.233 mmol, 98%). Single crystals suitable for X-ray analysis were obtained by cooling of a hexane solution of **2a**. ^1H NMR (500.00 MHz, C_6D_6, r.t.): δ = 7.97–7.95 (m, 1 H, aromatic), 7.03 (t, J = 8 Hz, 1 H, aromatic), 6.97 (t, J = 8 Hz, 1 H, aromatic), 6.75–6.71 (m, 1 H, aromatic), 1.92 (s, 15 H, Cp*), 1.90 (s, 15 H, Cp*), 1.65 (d, J = 10 Hz, 6 H, P*Me*), –17.71 (br. s, 3 H, Ir-H) ppm. ^1H NMR (500.00 MHz, CD_2Cl_2, –90 °C): δ = 7.37 (d, J = 6 Hz, 1 H, aromatic), 6.63 (m, 2 H, aromatic), 6.53 (m, 1 H, aromatic), 1.88 (s, 15 H, Cp*), 1.81 (s, 15 H, Cp*), 1.59 (d, J = 9 Hz, 3 H, P*Me*), 1.46 (d, J = 10 Hz, 3 H, P*Me*), –14.87 (s, 1 H, terminal Ir-H), –17.73 (d, J = 32 Hz, 1 H, terminal Ir-H), –20.88 (d, J = 10 Hz, 1 H, bridging Ir-H-Ir) ppm. $^{13}C\{^1H\}$ NMR (125.65 MHz, C_6D_6, r.t.): δ = 160.8 (d, J = 76 Hz, P-C), 150.5 (d, J = 30 Hz, Ir-C), 143.3 (d, J = 19 Hz, aromatic), 126.8 (d, J = 3 Hz, aromatic), 126.6 (d, J = 10 Hz, aromatic), 119.5 (d, J = 9 Hz, aromatic), 93.3 (d, J = 3 Hz, C_5Me_5), 89.6 (s, C_5Me_5), 22.7 (d, J = 28 Hz, P*Me*), 11.4 (s, C_5Me_5), 10.7 (s, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR (202.35 MHz, C_6D_6, r.t.): δ = –46.8 (s) ppm. M.p. 137 °C (dec.). $C_{28}H_{43}Ir_2P$ (795.05): calcd. C 42.30, H 5.45; found C 42.34, H 5.39.

Reaction of 1 with Other Phosphorus Ligands To Give 2b–2e, 3, and 4: These reactions were carried out in a similar manner as described above.

A similar reaction of **1** (104 mg, 0.158 mmol) with methyldiphenylphosphane (35.9 mg, 0.179 mmol) gave **2b** as a brown powder (113 mg, 0.132 mmol, 84%). ^1H NMR (500.00 MHz, C_6D_6, r.t.): δ = 8.04 (d, J = 7 Hz, 1 H, aromatic), 7.53–7.50 (m, 2 H, aromatic), 7.10 (t, J = 8 Hz, 1 H, aromatic), 7.06–7.04 (m, 3 H, aromatic), 6.97 (t, J = 8 Hz, 1 H, aromatic), 6.85 (t, J = 8 Hz, 1 H, aromatic), 1.92 (s, 15 H, Cp*), 1.68 (s, 15 H, Cp*), 1.63 (d, J = 9 Hz, 3 H, P*Me*), –17.33 (br. s, 3 H, Ir-H) ppm. ^1H NMR (500.00 MHz, CD_2Cl_2, –90 °C): δ = 7.48 (m, 2 H, aromatic), 7.16 (m, 2 H, aromatic), 7.09 (m, 2 H, aromatic), 6.74 (m, 2 H, aromatic), 6.63 (m, 1 H, aromatic), 2.04 (s, 15 H, Cp*), 1.59 (d, J = 9 Hz, 3 H, PMe), 1.46 (s, 15 H, Cp*), –15.24 (s, 1 H, Ir-H), –17.39 (d, J = 32 Hz, 1 H, Ir-H), –18.98 (d, J = 6 Hz, 1 H, Ir-H-Ir) ppm. $^{13}C\{^1H\}$ NMR (125.65 MHz, C_6D_6, r.t.): δ = 158.3 (d, J = 80 Hz, P-C), 153.3 (d, J = 31 Hz, Ir-C), 145.2 (d, J = 59 Hz, aromatic), 143.6 (d, J = 19 Hz, aromatic), 131.2 (d, J = 10 Hz, aromatic), 129.3 (d, J = 10 Hz, aromatic), 128.8 (d, J = 2 Hz, aromatic), 127.6 (d, J = 10 Hz, aromatic), 127.4 (d, J = 2 Hz, aromatic), 119.7 (d, J = 9 Hz, aromatic), 93.6 (d, J = 3 Hz, C_5Me_5), 89.9 (s, C_5Me_5), 21.0 (d, J = 31 Hz, P*Me*), 11.3 (s, C_5Me_5), 10.2 (s, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR (202.35 MHz, C_6D_6, r.t.): δ = –25.1 (s) ppm. M.p. 50.0–51.4 °C. $C_{33}H_{45}Ir_2P$ (857.12): calcd. C 46.24, H 5.29; found C 46.20, H 5.31.

A similar reaction of **1** (61.4 mg, 0.0935 mmol) with triphenylphosphane (27.6 mg, 0.105 mmol) gave **2c** as an orange powder (44 mg, 0.047 mmol, 51%). ^1H NMR (500.00 MHz, C_6D_6, r.t.): δ = 8.10–

8.08 (m, 1 H, aromatic), 7.53–7.50 (m, 4 H, aromatic), 7.08 (m, 4 H, aromatic), 7.02–6.99 (m, 2 H, aromatic), 6.98–6.95 (m, 1 H, aromatic), 6.83–6.80 (m, 1 H, aromatic), 6.78–6.75 (m, 1 H, aromatic), 1.73 (s, 15 H, Cp*), 1.68 (d, J = 3 Hz, 15 H, Cp*), –16.29 (br., 3 H, Ir-H) ppm. ^{1}H NMR (500.00 MHz, CD_2Cl_2, –90 °C): δ = 7.59–7.17 (m, 10 H, aromatic), 6.79 (br., 1 H, aromatic), 6.66 (m, 1 H, aromatic), 6.59 (m, 1 H, aromatic), 6.36 (m, 1 H, aromatic), 1.65 (s, 15 H, Cp*), 1.46 (s, 15 H, Cp*), –15.26 (s, 1 H, Ir-H), –17.25 (d, J = 29 Hz, 1 H, Ir-H), –18.16 (br., 1 H, Ir-H) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, C_6D_6, r.t.): δ = 156.9 (d, J = 83 Hz, P-C), 152.8 (d, J = 34 Hz, Ir-C), 144.8 (d, J = 18 Hz, aromatic), 141.1 (d, J = 50 Hz, P-C), 134.2 (d, J = 20 Hz, aromatic), 134.0 (d, J = 10 Hz, aromatic), 133.9 (d, J = 10 Hz, aromatic), 128.8 (s, aromatic), 127.4 (d, J = 9 Hz, aromatic), 119.6 (d, J = 8 Hz, aromatic), 93.2 (d, J = 3 Hz, C_5Me_5), 90.9 (s, C_5Me_5), 10.9 (s, C_5Me_5), 10.5 (s, C_5Me_5) ppm. ^{31}P{^{1}H} NMR (202.35 MHz, C_6D_6, r.t.): δ = 4.9 (s) ppm. M.p. 148 °C (dec.). $C_{38}H_{47}Ir_2P$ (919.19): calcd. C 49.65, H 5.15; found C 49.50, H 5.21.

A similar reaction of **1** (110 mg, 0.167 mmol) with diethyl phenyl phosphonite (39.7 mg, 0.200 mmol) gave **2d** as a yellow-orange powder (80.1 mg, 0.0936 mmol, 56%). ^{1}H NMR (500.00 MHz, C_6D_6, r.t.): δ = 7.99 (m, 1 H, aromatic), 7.28 (t, J = 7 Hz, 1 H, aromatic), 7.11 (t, J = 7 Hz, 1 H, aromatic), 7.04 (m, 1 H, aromatic), 3.78 (td, J = 9, 7 Hz, 2 H, OCH_2CH$_3$), 3.46 (br. s, 2 H, OCH_2CH$_3$), 1.94 (s, 15 H, Cp*), 1.92 (d, J = 2 Hz, 15 H, Cp*), 1.16 (t, J = 7 Hz, 6 H, OCH$_2$CH_3), –17.41 (br. s, 3 H, Ir-H) ppm. ^{1}H NMR (500.00 MHz, CD_2Cl_2, –90 °C): δ = 7.39 (m, 1 H, aromatic), 6.77 (m, 2 H, aromatic), 6.69 (m, 1 H, aromatic), 3.75 (m, 1 H, OCH_2CH$_3$), 3.51 (m, 2 H, OCH_2CH$_3$), 2.73 (m, 1 H, OCH_2CH$_3$), 1.83 (s, 15 H, Cp*), 1.75 (d, J = 2 Hz, 15 H, Cp*), 1.33 (t, J = 7 Hz, 3 H, OCH$_2$CH_3), 1.03 (t, J = 7 Hz, 3 H, OCH$_2$CH_3), –15.06 (s, 1 H, Ir-H), –18.00 (d, J = 28 Hz, 1 H, Ir-H), –20.60 (d, J = 11 Hz, 1 H, Ir-H-Ir) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, C_6D_6, r.t.): δ = 160.7 (d, J = 102 Hz, P-C), 149.4 (d, J = 38 Hz, Ir-C), 142.8 (d, J = 22 Hz, aromatic), 129.4 (d, J = 8 Hz, aromatic), 128.1 (d, J = 2 Hz, aromatic), 119.2 (d, J = 9 Hz, aromatic), 94.6 (d, J = 4 Hz, C_5Me_5), 90.0 (s, C_5Me_5), 59.5 (d, J = 6 Hz, OCH$_2$CH$_3$), 15.9 (d, J = 8 Hz, OCH$_2$$CH_3$), 10.96 (s, C_5Me_5), 10.49 (s, C_5Me_5) ppm. ^{31}P{^{1}H} NMR (202.35, C_6D_6, r.t.): δ = 93.4 (s) ppm. M.p. 108 °C (dec.). $C_{30}H_{47}Ir_2O_2P$ (855.10): calcd. C 42.14, H 5.56; found C 42.05, H 5.54.

A similar reaction of **1** (84.0 mg, 0.128 mmol) with ethyl diphenyl phosphinite (33.8 mg, 0.147 mmol) gave **2e** as an orange powder (69.8 mg, 0.0787 mmol, 61%). ^{1}H NMR (500.00 MHz, C_6D_6, r.t.): δ = 7.95 (m, 1 H, aromatic), 7.70 (m, 2 H, aromatic), 7.46 (m, 1 H, aromatic), 7.16 (m, 2 H, aromatic), 7.05 (m, 2 H, aromatic), 6.96 (m, 1 H, aromatic), 3.58 (m, 1 H, OCHHCH$_3$), 3.17 (m, 1 H, OCHHCH$_3$), 1.97 (d, J = 2 Hz, 15 H, Cp*), 1.59 (s, 15 H, Cp*), 0.93 (t, J = 7 Hz, 3 H, OCH$_2$CH_3), –17.41 (br. s, 3 H, Ir-H) ppm. ^{1}H NMR (500.00 MHz, CD_2Cl_2, –90 °C): δ = 7.40 (m, 1 H, aromatic), 7.17 (m, 5 H, aromatic), 6.89–6.83 (m, 3 H, aromatic), 3.61 (m, 1 H, OCHHCH$_3$), 2.92 (m, 1 H, OCHHCH$_3$), 1.86 (s, 15 H, Cp*), 1.35 (s, 15 H, Cp*), 1.07 (m, 3 H, OCH$_2$CH_3), –15.06 (s, 1 H, Ir-H), –17.04 (d, J = 28 Hz, 1 H, Ir-H), –21.48 (d, J = 7 Hz, 1 H, Ir-H-Ir) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, C_6D_6, r.t.): δ = 159.6 (d, J = 100 Hz, P-C), 147.6 (d, J = 38 Hz, Ir-C), 143.0 (d, J = 21 Hz, aromatic), 141.5 (d, J = 60 Hz, aromatic), 132.0 (d, J = 10 Hz, aromatic), 130.8 (d, J = 8 Hz, aromatic), 129.8 (s, aromatic), 128.0 (s, aromatic), 127.5 (d, J = 10 Hz, aromatic), 119.9 (d, J = 9 Hz, aromatic), 95.0 (d, J = 3 Hz, C_5Me_5), 90.2 (s, C_5Me_5), 59.9 (d, J = 4 Hz, OCH$_2$CH$_3$), 16.0 (d, J = 8 Hz, OCH$_2$$CH_3$), 11.2 (s, C_5Me_5), 10.3 (s, C_5Me_5) ppm. ^{31}P{^{1}H} NMR (202.35, C_6D_6, r.t.): δ = 70.5 (s) ppm. M.p. 145 °C (dec.). $C_{34}H_{47}Ir_2O_2P$ (887.14): calcd. C 46.03, H 5.34; found C 45.79, H 5.32.

A similar reaction of **1** (105 mg, 0.160 mmol) with tripropylphosphane (28.4 mg, 0.177 mmol) gave **3** as a brown oil (85%, determined by ^{31}P{^{1}H} NMR). ^{1}H NMR (500.00 MHz, C_6D_6, r.t.): δ = 2.06 (s, 15 H, Cp*), 1.98 (s, 15 H, Cp*), 1.66–1.41 (m, PCH_2, CHCH_2CH$_3$, and Ir-CH), 1.24 (t, J = 7 Hz, 3 H, CH$_2$CH_3), 1.05 (t, J = 7 Hz, 3 H, CH$_2$CH_3), 1.00 (t, J = 7 Hz, 3 H, CH$_2$CH_3), –16.77 (br. s, 1 H, Ir-H), –17.56 (br. s, 1 H, Ir-H), –22.08 (br. s, 1 H, Ir-H) ppm. ^{1}H NMR (500.00 MHz, CD_2Cl_2, –10 °C): δ = 2.04 (s, 15 H, Cp*), 1.87 (s, 15 H, Cp*), 1.49–1.18 (m, PCH_2, CHCH_2CH$_3$, and Ir-CH), 0.95 (m, 6 H, CH$_2$CH_3), 0.82 (t, J = 7 Hz, 3 H, CH$_2$CH_3), –17.23 (s, 1 H, terminal Ir-H), –17.66 (d, J = 28 Hz, 1 H, terminal Ir-H), –22.42 (d, J = 13 Hz, 1 H, bridging Ir-H-Ir) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, C_6D_6, r.t.): δ = 92.1 (d, J = 3 Hz, C_5Me_5), 88.3 (s, C_5Me_5), 36.3 (d, J = 34 Hz, CH_2), 33.3 (s, CH_2), 29.0 (d, J = 10 Hz, CH_2), 19.1 (s, CH_2), 18.8 (d, J = 15 Hz, Me), 18.2 (d, J = 3 Hz, CH_2), 16.0 (d, J = 3 Hz, Me), 15.9 (s, Me), 11.7 (s, C_5Me_5), 11.1 (s, C_5Me_5), –19.0 (d, J = 18 Hz, Ir-CH) ppm. ^{31}P{^{1}H} NMR (202.35 MHz, C_6D_6, r.t.): δ = –52.1 (s) ppm. $C_{34}H_{47}Ir_2O_2P$ (903.16): calcd. C 42.63, H 6.54; found C 43.22, H 6.54.

A similar reaction of **1** (80.2 mg, 0.122 mmol) with triethyl phosphite (28.0 mg, 0.169 mmol) gave **4** as yellow crystals (81%, determined by ^{31}P{^{1}H} NMR). ^{1}H NMR (500.00 MHz, C_6D_6, r.t.): δ = 4.03–3.86 (m, 6 H, OCH_2CH$_3$), 3.33–3.32 (m, 1 H, $C_5Me_4CH_2$Ir), 2.75 (d, J = 7 Hz, 1 H, $C_5Me_4CH_2$Ir), 2.15 (m, 3 H, $C_5Me_4CH_2$Ir), 2.08 (s, 15 H, Cp*), 1.89 (m, 3 H, $C_5Me_4CH_2$Ir), 1.67 (m, 3 H, $C_5Me_4CH_2$Ir), 1.37 (m, 3 H, $C_5Me_4CH_2$Ir), 1.18 (t, J = 8 Hz, 6 H, OCH$_2$$CH_3$), –17.07 (d, J = 37 Hz, 1 H, Ir-H), –18.13 (d, J = 25 Hz, 1 H, Ir-H), –19.87 (s, 1 H, Ir-H) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, C_6D_6, r.t.): δ = 88.2 (s, C_5Me_5), 60.6 (s, OCH$_2$CH$_3$), 16.2 (d, J = 7 Hz, OCH$_2$$CH_3$), 11.8 (s, $C_5Me_4CH_2$Ir), 11.1 (s, C_5Me_5), 10.5 (d, J = 3 Hz, $C_5Me_4CH_2$Ir), 10.2 (s, $C_5Me_4CH_2$Ir), 8.1 (s, $C_5Me_4CH_2$Ir), –25.3 (s, $C_5Me_4CH_2$Ir) ppm. ^{31}P{^{1}H} NMR (202.35, C_6D_6, r.t.): δ = 70.5 (s) ppm. $C_{26}H_{47}Ir_2O_3P$ (823.06): calcd. C 37.94, H 5.76; found C 37.94, H 5.47.

Reaction of 1 with Dimethyl Sulfoxide To Give 5: A two-necked 30 mL flask was charged with **1** (552 mg, 0.839 mmol) in benzene (3.0 mL). Dimethyl sulfoxide (326 mg, 4.17 mmol) was added to the reaction mixture, and this was stirred for 64 h. After removal of the volatiles in vacuo, the residue was extracted with benzene to give **5** as a brown powder (428 mg, 0.582 mmol, 69%). Single crystals suitable for X-ray analysis were obtained by cooling of a hexane solution of **5**. ^{1}H NMR (500.00 MHz, CD_2Cl_2, –80 °C): δ = 4.61 (d, J = 9 Hz, 1 H, Ir-CHH), 3.12 (s, 3 H, SMe), 2.56 (s, 1 H, Ir-CHH), 1.98 (s, 15 H, Cp*), 1.87 (s, 15 H, Cp*), –13.38 (s, 1 H, Ir-H), –17.24 (s, 1 H, Ir-H), –20.68 (s, 1 H, Ir-H) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, CD_2Cl_2, –80 °C): δ = 92.0 (s, C_5Me_5), 89.2 (s, C_5Me_5), 42.9 (s, SMe), 12.0 (s, S-CH$_2$-Ir), 10.4 (s, C_5Me_5), 10.3 (s, C_5Me_5) ppm. M.p. 121 °C (dec.). $C_{22}H_{38}Ir_2OS$ (735.04): calcd. C 35.95, H 5.21; found C 35.53, H 4.91.

Reaction of 1 with Methyl Phenyl Sulfoxide To Give 6a: A two-necked 30 mL flask was charged with **1** (443 mg, 0.674 mmol) in benzene (2.0 mL). Methyl phenyl sulfoxide (287 mg, 2.05 mmol) was added to the reaction mixture, and this was stirred for 40 h. After removal of the volatiles in vacuo, the residue was washed with hexane then extracted with benzene to give **6a** as a yellow-brown powder (501 mg, 0.629 mmol, 93%). Single crystals suitable for X-ray analysis were obtained from a hot hexane solution of **6a**. ^{1}H NMR (500.00 MHz, C_6D_6, r.t.): δ = 7.82 (d, J = 7 Hz, 1 H, aromatic), 7.65 (d, J = 7 Hz, 1 H, aromatic), 6.98 (m, 2 H, aro-

matic), 3.47 (s, 3 H, Me), 1.88 (s, 15 H, Cp*), 1.81 (s, 15 H, Cp*), –15.27 (br., 2 H, Ir-H), –19.57 (br., 1 H, Ir-H) ppm. ^{1}H NMR (500.00 MHz, CD_2Cl_2, –90 °C): δ = 7.37 (d, J = 7 Hz, 1 H, aromatic), 6.85 (d, J = 7 Hz, 1 H, aromatic), 6.80 (t, J = 7 Hz, 1 H, aromatic), 6.74 (t, J = 7 Hz, aromatic), 3.27 (s, 3 H, Me), 1.86 (s, 15 H, Cp*), 1.82 (s, 15 H, Cp*), –14.93 (s, 1 H, Ir-H), –15.83 (s, 1 H, Ir-H), –19.57 (s, 1 H, Ir-H) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, C_6D_6, r.t.): δ = 169.1 (s, aromatic), 144.2 (s, aromatic), 139.5 (s, aromatic), 128.4 (s, aromatic), 124.4 (s, aromatic), 120.6 (s, aromatic), 94.9 (s, C_5Me_5), 90.3 (s, C_5Me_5), 59.9 (s, SMe), 10.6 (s, C_5Me_5), 10.5 (s, C_5Me_5) ppm. M.p. 155 °C (dec.). $C_{27}H_{40}Ir_2OS$ (797.10): calcd. C 40.68, H 5.06; found C 40.89, H 4.81.

Reaction of 1 with Diphenyl Sulfoxide to Give 6b: A two-necked 30 mL flask was charged with **1** (142 mg, 0.216 mmol) in benzene (0.6 mL). Diphenyl sulfoxide (45.2 mg, 0.223 mmol) was added to the reaction mixture, and this was stirred for 48 h at 35 °C. After removal of the volatiles in vacuo, the residue was washed with hexane and extracted with benzene to give **6b** as a brown powder (79 g, 0.091 mmol, 42%). ^{1}H NMR (500.00 MHz, C_6D_6, r.t.): δ = 7.90 (m, 1 H, aromatic), 7.68 (m, 1 H, aromatic), 7.55 (m, 2 H, aromatic), 7.03–6.99 (m, 2 H, aromatic), 6.95–6.88 (m, 2 H, aromatic), 6.83 (m, 1 H, aromatic), 1.95 (s, 15 H, Cp*), 1.63 (s, 15 H, Cp*), –15.89 (s, 3 H, Ir-H) ppm. ^{1}H NMR (500.00 MHz, CD_2Cl_2, –90 °C): δ = 7.44 (m, 1 H, aromatic), 7.26 (m, 3 H, aromatic), 7.07 (m, 2 H, aromatic), 6.86 (m, 3 H, aromatic), 2.02 (s, 15 H, Cp*), 1.47 (s, 15 H, Cp*), –15.39 (s, 1 H, Ir-H), –16.03 (s, 1 H, Ir-H), –16.83 (s, 1 H, Ir-H) ppm. ^{13}C{^{1}H} NMR (125.65 MHz, C_6D_6, r.t.): δ = 165.3 (s, aromatic), 157.5 (s, aromatic), 144.5 (s, aromatic), 142.2 (s, aromatic), 130.0 (s, aromatic), 129.1 (s, aromatic), 128.5 (s, aromatic), 126.2 (s, aromatic), 127.6 (s, aromatic), 120.6 (s, aromatic), 95.3 (s, C_5Me_5), 90.7 (s, C_5Me_5), 10.6 (s, C_5Me_5), 10.4 (s, C_5Me_5) ppm. M.p. 109 °C (dec.). $C_{32}H_{42}Ir_2OS$ (859.17): calcd. C 44.73, H 4.93; found C 45.03, H 4.87.

X-ray Structure Analyses of 2a, 4, 5, and 6a: The crystallographic data and experimental details for **2a**, **4**, **5**, and **6a** are summarized in Table 1. Diffraction data for **2a**, **4**, **5**, and **6a** were obtained with a Rigaku RAXIS RAPID instrument. Reflection data for **2a**, **4**, **5**, and **6a** were corrected for Lorentz and polarization effects. Numer-

Table 1. Crystallographic data and structure refinement parameters for **2a**, **4**, **5**, and **6a**.

	2a	**4**	**5**	**6a**
Description of Crystal				
Color, habit	orange, block	yellow, platelet	yellow, block	orange, block
Max. crystal dim. [mm]	0.10 × 0.10 × 0.07	0.13 × 0.13 × 0.04	0.26 × 0.14 × 0.12	0.23 × 0.16 × 0.14
Crystallographic system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1/n$ (#14)
a [Å]	9.2907(18)	8.6369(5)	15.7174(3)	8.53486(15)
b [Å]	10.801(2)	11.1296(7)	8.9219(3)	17.6525(3)
c [Å]	13.642(3)	16.8625(9)	17.2809(4)	17.3759(3)
α [°]	90.862(6)	73.4397(19)	90	90
β [°]	92.084(8)	76.9323(16)	104.3353(7)	93.1088(7)
γ [°]	99.095(7)	66.349(2)	90	90
V [Å^3]	1350.5(5)	1411.61(14)	2347.84(9)	2614.03(8)
Z	2	2	4	4
Formula	$C_{28}H_{43}Ir_2P$	$C_{26}H_{47}Ir_2O_3P$	$C_{22}H_{38}Ir_2SO$	$C_{27}H_{40}Ir_2SO$
FW [g mol^{-1}]	795.06	823.07	735.04	797.11
D_{calc} [g cm^{-3}]	1.955	1.936	2.079	2.025
Data Collection				
Radiation (λ [Å])	Mo-K_α (λ = 0.71075 Å)	Mo-K_α (λ = 0.71075 Å)	Mo-K_α (λ = 0.71075 Å)	Mo-K_α (λ = 0.71075 Å)
Temperature [K]	173	173	173	173
No. of data images	110	110	110	110
ω oscillation range (χ = 45.0, ϕ = 0.0) [°]	130.0–190.0	130.0–190.0	130.0–190.0	130.0–190.0
Exposure rate [s deg^{-1}]	300	300	300	300
ω oscillation range (χ = 45.0, ϕ = 180.0) [°]	0.0–160.0	0.0–160.0	0.0–160.0	0.0–160.0
Exposure rate (s/deg)	300	300	300	300
Detector position [mm]	127.40	127.40	127.40	127.40
Pixel size [mm]	0.100	0.100	0.100	0.100
$2\theta_{max}$ [°]	55.0	55.0	54.9	54.9
No. of reflections measured	total: 13254 unique: 6122 (R_{int} = 0.060)	total: 13999 unique: 6459 (R_{int} = 0.092)	total: 22344 unique: 5363 (R_{int} = 0.054)	total: 25410 unique: 5958 (R_{int} = 0.076)
Structure Determination				
No. of observations	4249	2969	4268	5061
No. of variables	320	288	270	317
Reflection/paramater ratio	13.28	10.31	15.81	15.97
Absorbance correction	multiscan	multiscan	numerical	numerical
Transmission factor	0.392–0.499	0.146–0.683	0.211–0.253	0.234–0.237
R [$I > 3.00\sigma(I)$][a]	0.0335	0.0622	0.0339	0.0325
R_w [$I > 3.00\sigma(I)$][a]	0.0428[b]	0.0985[c]	0.0527[d]	0.0470[e]
Goodness of fit indicator	0.992	1.002	1.010	1.008

[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] $1/[1.0000\sigma(F_o^2)]$. [c] $1/[0.0054F_o^2 + 1.0000\sigma(F_o^2)]$. [d] $1/[0.0011F_o^2 + 1.0000\sigma(F_o^2)]$. [e] $1/[0.0002F_o^2 + 1.0000\sigma(F_o^2)]$.

ical or empirical absorption corrections were applied. The structures of **2a**, **4**, **5**, and **6a** were solved by the heavy-atom Patterson method,[21,22] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations, except for the carbon and oxygen atoms in the triethyl phosphite ligand of **4** which were refined isotropically. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[23] The location of the metal hydrides could not be determined. Other hydrogen atoms were located on the idealized positions. Calculations were performed using the program system CrystalStructure.[24,25]

CCDC-686348 (for **2a**), -686349 (for **4**), -686350 (for **5**), and -686351 (for **6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] a) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 4th ed., John Wiley & Sons, Inc., New Jersey, **2005**, ch. 13; b) R. D. Adams in *Comprehensive Organometallic Chemistry II* (Eds: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, New York, **1995**, vol. 10; c) J. Halpern, *Inorg. Chim. Acta* **1982**, *62*, 31–37; d) H. Suzuki, *Eur. J. Inorg. Chem.* **2002**, 1009–1023.

[2] a) M. E. Broussard, B. Juma, S. G. Train, W.-J. Peng, S. A. Laneman, G. G. Stanley, *Science* **1993**, *260*, 1784–1788; b) H. Suzuki, H. Omori, D. H. Lee, Y. Yoshida, M. Fukushima, M. Tanaka, Y. Moro-oka, *Organometallics* **1994**, *13*, 1129–1146; 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.* **1999**, *121*, 3666–3683; d) A. F. Heyduk, D. G. Nocera, *Science* **2001**, *293*, 1639–1641; e) H. Kondo, K. Matsubara, H. Nagashima, *J. Am. Chem. Soc.* **2002**, *124*, 534–535; f) T. Hattori, S. Matsukawa, S. Kuwata, Y. Ishii, M. Hidai, *Chem. Commun.* **2003**, 510–511; g) Y. Ohki, N. Matsuura, T. Marumoto, H. Kawaguchi, K. Tatsumi, *J. Am. Chem. Soc.* **2003**, *125*, 7978–7988; h) S. Tsutsuminai, N. Komine, M. Hirano, S. Komiya, *Organometallics* **2004**, *23*, 44–53; i) S. Tanaka, C. Dubs, A. Inagaki, M. Akita, *Organometallics* **2005**, *24*, 163–184; j) R. D. Adams, B. Captain, L. Zhu, *J. Am. Chem. Soc.* **2006**, *128*, 13672–13673.

[3] a) W. D. McGhee, R. G. Bergman, *J. Am. Chem. Soc.* **1986**, *108*, 5621–5622; b) W. D. McGhee, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc.* **1988**, *110*, 8428–8443; c) D. M. Heinekey, D. A. Fine, D. Barnhart, *Organometallics* **1997**, *16*, 2530–2538; d) M. V. Jiménez, E. Sola, J. A. Lopéz, F. J. Lahoz, L. A. Oro, *Chem. Eur. J.* **1998**, *4*, 1398–1410; e) D. A. Vicic, W. D. Jones, *Organometallics* **1999**, *18*, 134–138; f) A. F. Heyduk, D. G. Nocera, *J. Am. Chem. Soc.* **2000**, *122*, 9415–9426; g) M. V. Jiménez, E. Sola, J. Caballero, F. J. Lahoz, L. A. Oro, *Angew. Chem. Int. Ed.* **2002**, *41*, 1208–1211; h) T. G. Gray, A. S. Veige, D. G. Nocera, *J. Am. Chem. Soc.* **2004**, *126*, 9760–9768.

[4] a) C. W. Bradford, R. S. Nyholm, *J. Chem. Soc., Chem. Commun.* **1972**, 87–89; b) A. J. Deeming, M. Underhill, *J. Chem. Soc., Dalton Trans.* **1973**, 2727–2730; c) D. Himmelreich, G. Müller, *J. Organomet. Chem.* **1985**, *297*, 341–348; d) A. J. Deeming, S. E. Kabir, N. I. Powell, P. A. Bates, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1987**, 1529–1534; e) J. A. Cabeza, I. del Río, L. Martínez-Méndez, D. Miguel, *Chem. Eur. J.* **2006**, *12*, 1529–1538.

[5] a) K. Matsubara, R. Okamura, M. Tanaka, H. Suzuki, *J. Am. Chem. Soc.* **1998**, *120*, 1108–1109; b) A. Inagaki, D. G. Musaev, T. Takemori, H. Suzuki, K. Morokuma, *Organometallics* **2003**, *22*, 1718–1727; c) T. Kawashima, T. Takao, H. Suzuki, *J. Am. Chem. Soc.* **2007**, *129*, 11006–11007.

[6] a) A. H. Janowicz, R. G. Bergman, *J. Am. Chem. Soc.* **1982**, *104*, 352–354; b) J. K. Hoyano, W. A. G. Graham, *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725; c) A. H. Janowicz, R. G. Bergman, *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939; d) D. M. Haddleton, R. N. Perutz, *J. Chem. Soc., Chem. Commun.* **1986**, 1734–1736; e) P. A. Chetcuti, C. B. Knobler, M. F. Hawthorne, *Organometallics* **1988**, *7*, 650–660; f) T. W. Bell, S.-A. Brough, M. G. Partridge, R. N. Perutz, A. D. Rooney, *Organometallics* **1993**, *12*, 2933–2941; g) P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 10462–10463; h) B. A. Arndtsen, R. G. Bergman, *Science* **1995**, *270*, 1970–1972.

[7] a) K. Fujita, T. Hamada, R. Yamaguchi, *J. Chem. Soc., Dalton Trans.* **2000**, 1931–1936; b) K. Fujita, H. Nakaguma, F. Hanasaka, R. Yamaguchi, *Organometallics* **2002**, *21*, 3749–3757; c) K. Fujita, H. Nakaguma, T. Hamada, R. Yamaguchi, *J. Am. Chem. Soc.* **2003**, *125*, 12368–12369.

[8] These coupling constants had larger values compared to those in free dimethyl(phenyl)phosphane ($^1J_{PC}$ = 16 Hz and $^2J_{PC}$ = 18 Hz). Although the increase of the P–C coupling constant in phosphorus ligands resulting from their coordination to transition metal centers is generally known, an abnormally large $^1J_{PC}$ was observed in the cases of complexes **2a**–**e**. We suppose that the delocalization of electrons in the diiridacycle of **2a**–**e** might give rise to "ylidic" character of the P–C bond, which would cause this increase in the coupling constants.

[9] T. M. Gilbert, R. G. Bergman, *J. Am. Chem. Soc.* **1985**, *107*, 3502–3507.

[10] There are many examples of 34 e^- bimetallic system with bridging hydrides. For example: a) E. Sola, V. I. Bakhmutov, F. Torres, A. Elduque, J. A. López, F. J. Lahoz, H. Werner, L. A. Oro, *Organometallics* **1998**, *17*, 683–696; b) Y. Gao, M. C. Jennings, R. J. Puddephatt, *Dalton Trans.* **2003**, 261–265. See also ref.[7]

[11] H. Omori, H. Suzuki, Y. Take, Y. Moro-oka, *Organometallics* **1989**, *8*, 2270–2272.

[12] M. J.-L. Tschan, F. Chérioux, L. Karmazin-Brelot, G. Süss-Fink, *Organometallics* **2005**, *24*, 1974–1981.

[13] V. V. Grushin, A. B. Vymenits, A. I. Yanovsky, Y. T. Struchkov, M. E. Vol'pin, *Organometallics* **1991**, *10*, 48–49.

[14] T. Shima, H. Suzuki, *Organometallics* **2005**, *24*, 1703–1708.

[15] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.

[16] The electron-donating nature of phosphorus ligands decreases in the following order: PMe_2Ph ($\Sigma\chi i = 9.5$) > PPh_3 ($\Sigma\chi i = 12.9$) > $P(OEt)_2Ph$ ($\Sigma\chi i = 17.9$). $\Sigma\chi i$ values are cited in ref.[15]

[17] a) J. M. Buchanan, J. M. Stryker, R. G. Bergman, *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550; b) C. A. Kiener, C. Shu, C. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 14272–14273; c) R. W. Hilts, O. Oke, M. J. Ferguson, R. McDonald, M. Cowie, *Organometallics* **2005**, *24*, 4393–4405; d) C. Tejel, M. A. Ciriano, S. Jiménez, L. A. Oro, C. Graiff, A. Tiripicchi, *Organometallics* **2005**, *24*, 1105–1111; e) T. Hara, T. Yamagata, K. Mashima, Y. Kataoka, *Organometallics* **2007**, *26*, 110–118.

[18] We have also examined the reactions using other donor molecules such as amines (aniline and pyridine), N-heterocyclic carbenes, and sulfides. However these reactions resulted in the quantitative recovery of complex **1** or the formation of complicated mixtures.

[19] Z. Hou, T. Koizumi, A. Fujita, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **2001**, *123*, 5812–5813.

[20] D. J. Collins, P. F. Drygala, J. M. Swan, *Aust. J. Chem.* **1983**, *36*, 2095–2110.

[21] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *PATTY*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1992**.

[22] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1999**.

[23] a) D. T. Cromer, G. T. Waber, *International Table for X-ray Crystallography*, Kynoch, Birmingham, UK, **1974**, vol. IV; b) J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781–782; c) D. C. Creagh, W. J. McAuley in *International Tables for X-ray Crystallography* (Ed.: A. J. C. Wilson), Kluwer Academic

Publishers, Boston, MA, **1992**; vol. C, Table 4.2.6.8, pp. 219–222; d) D. C. Creagh, J. H. Hubbel in *International Tables for X-ray Crystallography* (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Boston, MA, **1992**; vol. C, Table 4.2.4.3, pp. 200–206.
[24] *CrystalStructure 3.8*, Crystal Structure Analysis Package, Rigaku and Rigaku/Molecular Structure Corp., **2000**–**2006**.
[25] J. R.Carruthers, J. S. Rollett, P. W. Betteridge, D. Kinna, L. Pearce, A. Larsen, E. Gabe, *CRYSTALS Issue 11*, Chemical Crystallography Laboratory, Oxford, UK, **1999**.

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