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Article

C−H Bond Activation and Subsequent C(sp^2)−C(sp^3) Bond Formation: Coupling of Bromomethyl and Triphenylphosphine in an Iridium Complex

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Treatment of $HC{\equiv}CCH(OH)CH{=}CH_2$ with $[IrHCl(CO)(PPh_3)_3]BF_4$ at room temperature afforded an iridacyclohexadiene, $[Ir(CH{=}C(PPh_3)CH{=}CHCH_2)Cl(CO)(PPh_3)_2]BF_4$ (**1**). The reactivity of complex **1** had been investigated. Reaction of **1** with 1 equiv of bromine produced an iridacyclopentadiene, $[Ir(CH{=}C(PPh_3)CH{=}C(CH_2Br))Cl(CO)(PPh_3)_2]BF_4$ (**2**). When excess bromine was used, iridacyclopentadiene **2** underwent subsequent intramolecular C(sp^2)−C(sp^3) coupling between the exocyclic $-CH_2Br$ group and a phenyl of the PPh_3 ligand, leading to the formation of a fused iridacycle complex, $[Ir(CH{=}C(PPh_3)C(Br){=}C(\overline{CHBr))(P(C_6H_4)Ph_2)}Cl(CO)PPh_3]Br_3$ (**3**). A mechanism for the formation of complex **3** starting from **1** was proposed, in which the process involved a triple C−H activation as well as a rare C(sp^2)−C(sp^3) reductive elimination.

Introduction

The formation of carbon−carbon bonds is at the heart of the synthesis of organic compounds. Activation of a C−H bond and subsequent C−C bond formation mediated by transition-metal complexes are extremely significant topics and have attracted increasing attention recently.[1,2] Among various strategies to C−H bond activation and C−C bond-forming, chelation assistance utilizing cyclometalation is considered to be one of the most promising ways.[3]

First- and second-row transition-metal complexes of group VIII have been widely used as catalysts for the C−C bond formation involving cyclometalation. However, progress with third-row transition-metal complexes as catalysts lags far behind.[4] This is probably due to the difficulty of C−C reductive elimination from a third-row transition-metal center, which is expected to be the critical bond-forming step in coupling reactions, since the metal−carbon bond in a third-row transition-metal complex is believed to be thermodynamically more stable than that in a first- or second-row transition-metal complex.[5,6] Thus, for example, for third-row transition-metal complexes, iridium-mediated catalytic and even stoichiometric C−C bond-forming reactions are much less common than the related chemistry of nickel, palladium, and rhodium.[6−9] However, iridium complexes have been used as valuable models for understanding the mechanisms of catalytic reactions.[4,10] Therefore, iridium-catalyzed and iridium-mediated stoichiometric C−C bond formation became attractive subjects and have made impressive progress in recent years.[11]

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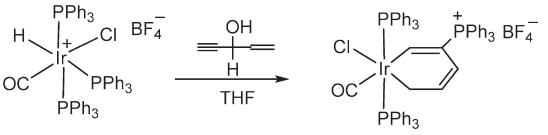
Scheme 1. Preparation of Iridacyclohexadiene 1



1

In our recent work, we have developed a convenient route to prepare some interesting third-row transition-metal-containing metallacycles,[12−15] including metallabenzenes,[12] ring-fused metallabenzenoids,[13] metallafurans,[12c,14] and bridged metallacycles[15] starting from the reactions between transition-metal-containing complexes and alkynes. As an outgrowth of our longstanding interest in such reactions, we have studied the reaction of HC≡CCH(OH)CH=CH_2[16] with $[IrH(CO)Cl(PPh_3)_3]BF_4$.[17] The reaction led to the formation of an iridacyclohexadiene, $[Ir(CH{=}C(PPh_3)CH{=}CHCH_2)Cl(CO)(PPh_3)_2]BF_4$ (**1**). During our investigation of the reactivity of **1**, we found that it is reactive toward bromine to produce first iridacyclopentadiene **2**, which can undergo intramolecular $C(sp^2)-C(sp^3)$ coupling promoted by the iridium center in the presence of excess bromine to give the fused iridacycle complex **3**. Triple C−H activation utilizing cyclometalation and C−C reductive elimination is proposed as the key step for the formation of complex **3** starting from **1** in the mechanism.

Results and Discussion

Preparation of Iridacyclohexadiene $[Ir(CH{=}C(PPh_3)CH{=}CHCH_2)Cl(CO)(PPh_3)_2]BF_4$ (1). Treatment of $[IrHCl(CO)(PPh_3)_3]BF_4$ with HC≡CCH(OH)CH=CH_2 in THF at room temperature led to the precipitation of a white solid with poor solubility, which could be isolated in 56% yield and was identified to be an iridacyclohexadiene, $[Ir(CH{=}C(PPh_3)CH{=}CHCH_2)Cl(CO)(PPh_3)_2]BF_4$ (**1**) (Scheme 1).

The structure of **1** established by X-ray diffraction is shown in Figure 1. It confirms that complex **1** contains an almost planar six-membered ring, as reflected by the deviation of 0.0457 Å from the rms planes of the best fit. The coordination around the iridium atom can be rationalized as an octahedron with the phosphorus atoms of PPh_3 ligands occupying *trans* positions (P(1)−Ir(1)−P(2) = 176.5(1)°), while one chloride atom and one carbonyl ligand are *cis* to each other (Cl(1)−Ir(1)−C(6) = 98.9(1)°). As expected, there is a clear alternation in the C−C bond lengths around the six-membered ring; C(1)−C(2) and C(3)−C(4) are 1.335(6) and 1.330(6) Å, respectively, which are typical C=C double-bond lengths, while C(2)−C(3) and C(4)−C(5) are 1.473(6) and 1.501(7) Å, respectively, consistent with the value of C−C single bonds.[18] The Ir(1)−C(1) (2.061(4) Å) and Ir(1)−C(5) (2.131(4) Å) bonds compare well with those of reported iridacyclohexadiene $Ir(CH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3(H)$ (Ir(1)−C(1) 2.085(6) Å and Ir(1)−C(5) 2.189(6) Å).[19a] All these parameters strongly support a cyclohexadiene moiety in complex **1**.

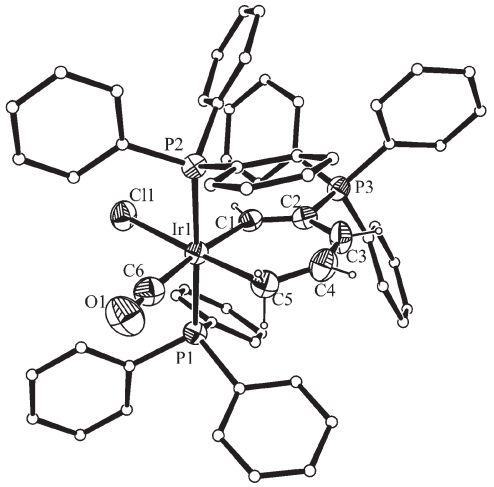


Figure 1. Molecular structure of complex **1** (50% probability thermal ellipsoids). Counteranion and the solvent molecules as well as some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Ir(1)−C(1) = 2.061(4), Ir(1)−C(5) = 2.131(4), C(1)−C(2) = 1.335(6), C(2)−C(3) = 1.473(6), C(3)−C(4) = 1.330(6), C(4)−C(5) = 1.501(7), O(1)−C(6) = 1.112(6), Ir(1)−C(6) = 1.938(5), Ir(1)−P(2) = 2.377(1), Ir(1)−P(1) = 2.381(1), C(1)−Ir(1)−C(5) = 91.2(2), C(2)−C(1)−Ir(1) = 129.0(3), C(1)−C(2)−C(3) = 125.2(4), C(4)−C(3)−C(2) = 124.6(4), C(3)−C(4)−C(5) = 130.6(4), C(4)−C(5)−Ir(1) = 118.5(3), P(2)−Ir(1)−P(1) = 176.5(1), C(5)−Ir(1)−Cl(1) = 177.7(1), Cl(1)−Ir(1)−C(6) = 98.9(1).

The NMR spectroscopic data of **1** are consistent with the structure shown in Figure 1. In the ^1H NMR spectrum, the characteristic IrC*H* resonance appeared at δ = 9.4 ppm and the signals of the two protons bonded to C5 were observed at δ = 1.9 ppm as a triplet. The signals of protons on C3 and C4 were at δ = 5.8 and 4.9 ppm, respectively, which are typical for olefinic compounds. The $^{31}P\{^1H\}$ NMR spectrum showed a triplet at δ = 18.9 ppm attributed to C*P*Ph_3, and the signals for Ir*P*Ph_3 were observed at δ = −3.1 ppm as a doublet, with a P−P coupling constant of 6.5 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the metallacycle carbon signals were observed at δ = 175.1 (C1), 111.0 (C2), 124.4 (C3), 131.9 (C4), and 3.4 (C5) ppm, respectively.

The formation of **1** involves nucleophilic attack of PPh_3 on the coordinated alkyne, as is the case in our previous reactions,[12a] which is then followed by hydride insertion to give cyclometalated intermediate **C**. Apparently, dehydration occurred to form the iridacyclohexadiene **1** (Scheme 2).

Although metallacyclohexadienes have been proposed as key intermediates in many reactions,[20] the strategies employed to construct stable metallacyclohexadienes of general structure related to **1** are still rare.[19,21−25] The first isolable example of metallacyclohexadiene complex

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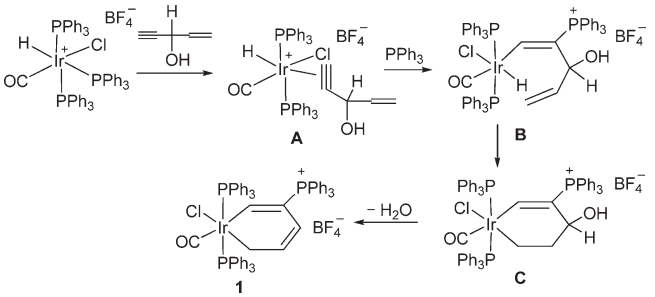
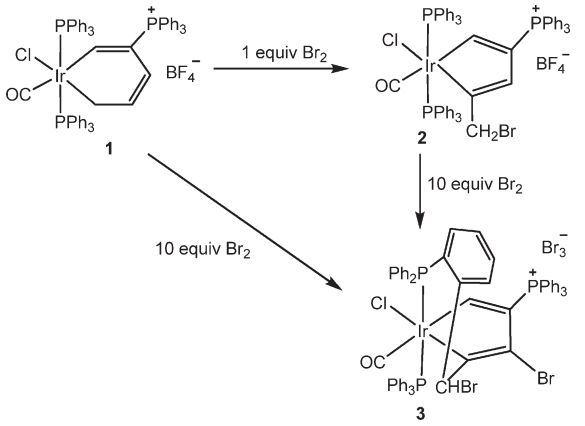
Scheme 2. Possible Mechanism for the Formation of Iridacyclohexadiene 1



Scheme 3. Reaction of Iridacyclohexadiene 1 with Bromine



$[PtC(Ph)=C(Ph)C(Ph)=CHCH_2](PPh_3)_2$ was obtained by Hughes from the ring-opening reactions of 3-vinyl-1-cyclopropenes with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$.[22a] The approach has also been extended to the synthesis of iridacyclohexadiene[22b] and rhodacyclohexadiene.[22c] Bleeke et al. have provided a different route utilizing pentadienide as the source of ring carbon atoms for synthesis of iridacyclohexadiene species,[19] which can be converted to the first examples of iridabenzenes.[23] An unprecedented method for iridacyclohexadienes derived from the [2+2+1] cyclotrimerization between alkynes was also reported.[24] A nucleophilic aromatic addition reaction of iridabenzenes or the hydrogenation of the iridacycloheptatrienes can also lead to iridacyclohexadienes.[25] We documented here another convenient route to construct iridacyclohexadiene. It is also worth noting that complex **1** shows excellent air and thermal stability, in view of the fact that the solid sample remains almost unchanged when heated at 100 °C under air for 5 h.

Reaction of Iridacyclohexadiene 1 with Bromine. With the intent of exploring the reactivity of the available iridacyclohexadiene, we have tried the reactions of complex **1** with many reagents such as HBF_4, Cs_2CO_3, and PMe_3; no obvious conversion was observed at room temperature. However, the reaction of complex **1** with 1 equiv of bromine afforded the iridacyclopentadiene **2**, which could subsequently undergo intramolecular $C(sp^2)-C(sp^3)$ coupling to give the fused iridacycle complex **3** in the presence of excess bromine.

A solution containing **1** and bromine in CH_2Cl_2 with a 1:1 molar ratio was stirred at room temperature for 6 h to give a light yellow solution, from which the iridacyclopentadiene $[Ir(CH=C(PPh_3)CH=C(CH_2Br))Cl(CO)(PPh_3)_2]BF_4$ (**2**) could be isolated in 65% yield. (Scheme 3).

An X-ray single-crystal diffraction experiment has clarified the structure of **2**. As shown in Figure 2, the geometry of the iridium center can be viewed as an octahedron in which the six coordination sites are occupied by C1 and C4, one chloride atom, one carbon atom of carbonyl ligand, and two phosphorus atoms of the phosphine ligands. The distances of Ir(1)−C(1) (2.070(8) Å) and Ir(1)−C(4) (2.068(7) Å) agree with the average for 318 recorded observation for Ir−C(vinyl) bonds (2.052 with a SD of 0.048 Å).[26] The C(1)−C(2) and C(3)−C(4) bonds length of 1.342(10) and 1.380(11) Å, respectively, indicate a C−C double bond, while the C(2)−C(3) bond length is 1.462(11) Å, supporting a C−C single bond.[18]

The solution NMR spectroscopic data of **2** are consistent with its solid-state structure. Particularly, the ^1H NMR spectrum of **2** showed the characteristic proton IrC*H* signal at $\delta = 9.1$ ppm, and the proton signal on C3 was at $\delta = 6.6$ ppm. The two protons of the exocyclic $-CH_2Br$ group were observed at $\delta = 2.6$ ppm as a broad peak. The $^{31}P\{^1H\}$ NMR spectrum showed a doublet at $\delta = -10.5$ ppm ($^4J(PP) = 4.8$ Hz, Ir*P*Ph_3) for the two equivalent phosphine ligands and a triplet at $\delta = 12.0$ ppm ($^4J(PP) = 4.8$ Hz, C*P*Ph_3) attributed to the phosphonium group on the ring structure. The NMR data seem to implicate the presence of a resonance contributor **2A** to the structure of **2** shown in Scheme 4.[27]

In fact, metallacyclopentadienes have always been invoked as key intermediates for cyclotrimerization of alkynes, and their reactions toward alkynes have been studied extensively.[28] Especially, various organic compounds obtained from metallacyclopentadienes have been widely studied.[24,29] Iridacyclopentadiene **2** with an exocyclic $-CH_2Br$ group

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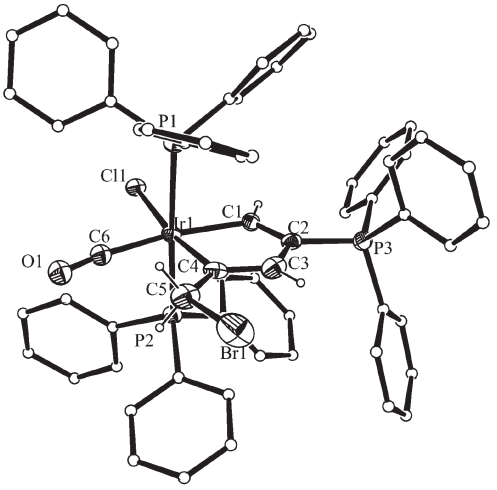
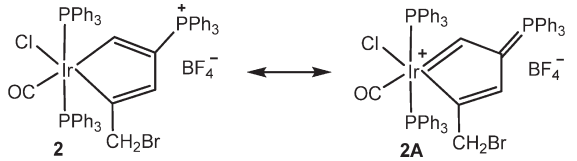


Figure 2. Molecular structure of complex **2** (50% probability thermal ellipsoids). Counteranion and the solvent molecules as well as some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Ir(1)−C(1) = 2.070(8), Ir(1)−C(4) = 2.068(7), C(1)−C(2) = 1.342(10), C(2)−C(3) = 1.462(11), C(3)−C(4) = 1.380(11), C(4)−C(5) = 1.477(12), O(1)−C(6) = 1.140(9), Ir(1)−P(2) = 2.368(2), Ir(1)−P(1) = 2.378(2), Br(1)−C(5) = 1.916(8), C(1)−Ir(1)−C(4) = 79.4(3), C(2)−C(1)−Ir(1) = 115.4(6), C(1)−C(2)−C(3) = 115.4(7), C(4)−C(3)−C(2) = 116.0(7), C(3)−C(4)−Ir(1) = 113.7(6), P(2)−Ir(1)−P(1) = 173.6(1).

Scheme 4. Resonance Structures of 2



might be used as a potential starting material for the synthesis of organic species.

Interestingly, the reaction of iridacyclohexadiene **1** with an excess (10 equiv) of bromine at room temperature afforded the fused iridacycle complex [Ir(CH=C(PPh$_3$)C(Br)=C(CHBr))(P(C$_6$H$_4$)Ph$_2$)Cl(CO)PPh$_3$]Br$_3$ (**3**) in an isolated yield of 81%. Treatment of isolated iridacyclopentadiene **2** with an excess of bromine also led to the formation of **3**.

As shown in Figure 3, complex **3** contains an iridacyclopentadiene moiety that is similar to that of complex **2**. However, the coupling between a phenyl of a PPh$_3$ ligand and the exocyclic −CH$_2$Br group occurred to construct a six-membered ring, which is fused with cyclopentadiene. The single-bond distance for Br(2)−C(5) (1.895(14) Å) is comparable with that of Br(1)−C(5) (1.916(8) Å) in complex **2**. The bond length of Br(1)−C(3) (1.942(12) Å) clearly indicates that bromination has occurred at C(3). The C(136)−C(5) bond distance of 1.55(2) Å is a typical C−C single bond.[18]

The ^{1}H NMR spectrum of **3** in CD$_2$Cl$_2$ showed the characteristic IrC*H* proton signal at δ = 9.7 ppm. The proton signal on C5 was at δ = 7.0 ppm according to ^{1}H−^{13}C HMQC. In the ^{31}P{^{1}H} NMR spectrum, the signal at δ = 16.6 (dd, ^4J(PP) = 6.0 Hz, ^4J(PP) = 2.8 Hz, C*P*Ph$_3$) ppm was attributed to the phosphonium group on the ring structure. The two phosphine ligand signals appeared at δ = 1.6 and −17.1 ppm, respectively, with a large P−P coupling

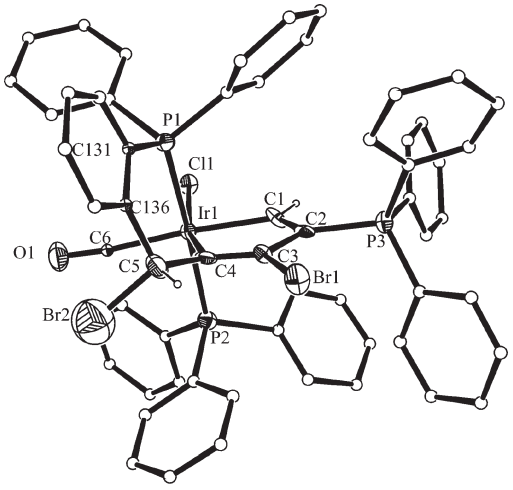


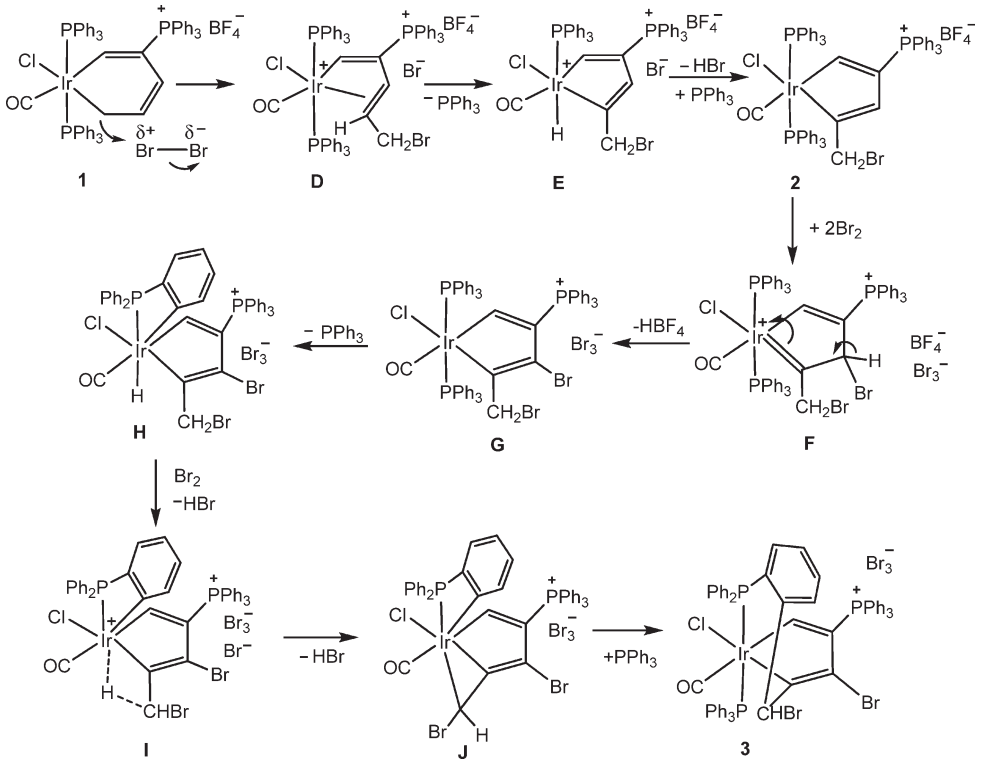
Figure 3. Molecular structure of complex **3** (50% probability thermal ellipsoids). Counteranion and the solvent molecules as well as some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Ir(1)−C(1) = 2.052(13), Ir(1)−C(4) = 2.082(14), C(1)−C(2) = 1.358(18), C(2)−C(3) = 1.448(18), C(3)−C(4) = 1.290(17), C(4)−C(5) = 1.485(19), O(1)−C(6) = 1.141(17), Ir(1)−C(6) = 1.920(18), Ir(1)−P(2) = 2.389(4), Ir(1)−P(1) = 2.335(4), Br(1)−C(3) = 1.942(12), Br(2)−C(5) = 1.895(14), C(5)−C(136) = 1.55(2), C(1)−Ir(1)−C(4) = 77.9(5), C(2)−C(1)−Ir(1) = 116.7(10), C(1)−C(2)−C(3) = 111.6-(12), C(4)−C(3)−C(2) = 120.1(12), C(3)−C(4)−Ir(1) = 113.6(10), P(2)−Ir(1)−P(1) = 176.5(2), C(4)−C(5)−C(136) = 114.2(12).

constant of 295.1 Hz. In the ^{13}C{^{1}H} NMR spectrum, the cyclopentadiene moiety resonances appeared at δ = 198.4 (C1), 122.3 (C2), 116.4 (C3), and 149.2 (C4) ppm, respectively. The *C*O resonance was observed at δ = 174.0 ppm.

A plausible mechanism for the formation of complexes **2** and **3** is proposed in Scheme 5. Electrophilic abstraction of the alkyl carbon (C5) of complex **1** by Br$_2$ followed by coordination of the double bond to the Ir center gives an η^2-olefin coordinated iridacycle **D**. Dissociation of a PPh$_3$ ligand and oxidative addition of the vinyl C−H bond produces a monophosphine metal-hydride intermediate **E**, which then undergoes deprotonation of the hydrido ligand and recoordination of a PPh$_3$ ligand to afford the iridacyclopentadiene **2**. Electrophilic substitution reaction of **2** with bromine could produce first intermediate **F** and then give bromine-substituted complex **G** by deprotonation. Dissociation of a PPh$_3$ ligand from **G** can provide a vacant site for the oxidative addition of the *ortho* phenyl C−H bond of the PPh$_3$ ligand on Ir to form the hydrido intermediate **H**. *Ortho*-metalation of the aryl ring of a phosphine attached to a metal is a widely occurring reaction, and this type of reaction is one of the earliest examples of metal activation of a C−H bond.[30] The hydride in **H** can be removed by the excess Br$_2$ in the form of HBr via an electrophilic subtraction. Again, the C−H bond of the exocyclic −CH$_2$Br group can be activated to give an agostic species **I**. Subsequent abstraction of the agostic proton by counterion Br$^-$ results in a seven-coordinated iridium species **J**. Eventually, reductive elimination of the two

(30) (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (b) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (c) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (d) Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974. (e) Huang, Y.-H.; Huang, W.-W.; Lin, Y.-C.; Huang, S.-L. *Organometallics* **2010**, *29*, 38.

Scheme 5. Plausible Mechanism for the Formation of Complexes 2 and 3



hydrocarbyl ligands from the Ir center and recoordination of a PPh_3 ligand afford the $C(sp^2)-C(sp^3)$ coupling product **3**.

In an attempt to get some insight into the mechanism for the formation of **3**, we have tried to monitor the reaction of **2** with different amounts of bromine by NMR. Upon treatment of **2** with 1 or 2 equiv of bromine at room temperature, no appreciable reaction could be observed even after 3 days. When the reaction of **2** with 3 equiv of bromine in $CDCl_3$ was monitored by $^{31}P\{^1H\}$ NMR, two sets of new ^{31}P signals at δ = 13.0(t), −14.3(d) ppm (J(PP) = 12.0 Hz) and δ = 11.8(t), −9.6(d) ppm (J(PP) = 4.5 Hz) started to appear simultaneously in 6 h, indicating the formation of a small amount of two new species with two equivalent phosphine ligands on metal centers, respectively. However, the reaction proceeded very slowly. As can be indicated by the *in situ* $^{31}P\{^1H\}$ NMR spectra, complex **2** was still the dominant species (~85%) in the solution when the reaction was almost suspended after 2 days. Although further increasing the ratio of bromine could speed up the reaction at the early stage, the two newly formed species could undergo further reaction to evolve to the final product **3** in the solution, and the $^{31}P\{^1H\}$ NMR spectra for the reaction process became even more complicated. Therefore, it is difficult to isolate and characterize the intermediates from the reaction. Nevertheless, the pattern of the $^{31}P\{^1H\}$ NMR signals for the two above-mentioned detectable intermediates supported that bromine substitution at C(3) of **2** should take place before the *ortho*-metalation of the PPh_3 ligand for the formation of **3**.

Transformation of **I** to **J** can be formally viewed as an electrophilic substitution, in which the positively charged metal center acts as the electrophile and the agostic proton is subtracted by the Br^- counterion. Similar roles played by Cl^-, which can abstract an agostic H in the electrophilic substitution mechanism, have already been postulated for the reaction of CH_4 with $(bpym)PtCl_2$,[31a−c] the cycloisomerizations of bromoallenyl ketones with $Au(PH_3)Cl$,[31d] as well as for the isomerization of intramolecularly coordinated η^2-allene complex $[Os\{CH{=}C(PPh_3)C(CH_3){=}\eta^2\text{-}C{=}CH_2\}(PhCN)_2(PPh_3)_2]Cl_2$ to osmabenzene $[Os\{CHC(PPh_3)C(CH_3)CHCH\}(PhCN)_2(PPh_3)_2]Cl_2$.[31e]

It is worthy to note that, in principle, both C−H and C−Br bonds in the $-CH_2Br$ group of **H** can be possibly activated. Apparently, only C−H activation occurred in our reaction, however. Selective C−H activation in the presence of C−X bonds has been reported for Pd, Rh, Au, and Ir system.[32−35] The reactions of the (PNP)Ir fragment with haloarenes

(31) (a) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2002**, *21*, 511. (b) Xu, X.; Kua, J.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2003**, *22*, 2057. (c) Xu, X.; Fu, G.; Goddard, W. A., III.; Periana, R. A. *Stud. Surf. Sci. Catal.* **2004**, *147*, 505. (d) Xia, Y.; Dudnik, A. S.; Gevorgyan, V.; Li, Y. *J. Am. Chem. Soc.* **2008**, *130*, 6940. (e) Gong, L.; Chen, Z.; Lin, Y.; He, X.; Wen, T. B.; Xu, X.; Xia, H. *Chem.—Eur. J.* **2009**, *15*, 6258.

(32) Selective C−H activation for Pd: (a) Zaitsev, V. G.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 4156. (b) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330.

(33) Selective C−H activation for Rh: (a) Gatard, S.; Celenligil-Cetin, R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 2808. (b) Gatard, S.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2007**, *26*, 6066.

(34) Selective C−H activation for Au: Fuchita, Y.; Utsunomiya, Y.; Yasutake, M. *J. Chem. Soc., Dalton Trans.* **2001**, *16*, 2330.

(35) Selective C−H activation for Ir: (a) Zhu, Y.; Fan, L.; Chen, C.-H.; Finnell, S. R.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2007**, *26*, 6701. (b) Fan, L.; Parkin, S.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 16772. (c) Chotana, G. A.; Rak, M. A.; Smith, M. R., III. *J. Am. Chem. Soc.* **2005**, *127*, 10539. (d) Ben-Ari, E.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 4714. (e) Tellers, D. M.; Yung, C. M.; Arndtsen, B. A.; Adamson, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 1400. (f) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (g) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III. *Science* **2002**, *295*, 305.

showed that C−H activation was favored kinetically, whereas the C−X (X = Cl, Br) activation was preferred thermodynamically.[35b] It has also been reported that C−H activation in haloarenes is more likely to be successful with Ir (5d metal) than Rh (4d metal).[33a]

It should also be mentioned that C−H activation and C−C reductive elimination through an Ir(V) intermediate have been recently supported both theoretically and experimentally.[36] In our case, the related process of C−H activation steps in the formation of complex **3** is probably promoted by the synergistic effects of iridium and bromine. Iridium can readily undergo cyclometalation and has proven effective in catalytic reactions involving C−H activation through chelation assistance.[37] Bromine is used as a strong oxidant and facilitates the abstraction of the hydrido ligand, which, in turn, is favorable for the subsequent electrophilic C−H activation. Additionally, previous reports of C−C reductive elimination from the iridium center usually involve vinyl−vinyl or vinyl−acyl to form a conjugated system, while $C(sp^2)-C(sp^3)$ reductive elimination reactions from iridium are still scarce.[6]

Conclusion

The thermally stable iridacyclohexadiene [Ir(CH=C(PPh_3)CH=$CHCH_2$)Cl(CO)(PPh_3)$_2$]BF_4 (**1**) can be easily synthesized from the reaction of readily accessible HC≡CCH(OH)CH=CH_2 with [IrHCl(CO)(PPh_3)$_3$]BF_4. Reaction of complex **1** with 1 equiv of bromine leads to the formation of iridacyclopentadiene [Ir(CH=C(PPh_3)CH=C(CH_2Br))Cl(CO)(PPh_3)$_2$]BF_4 (**2**). When excess bromine is provided, iridacyclopentadiene **2** can subsequently undergo intramolecular $C(sp^2)-C(sp^3)$ coupling between the exocyclic $-CH_2Br$ group and a phenyl of a PPh_3 ligand at the iridium, which results in the formation of the fused iridacycle complex [Ir(CH=C(PPh_3)C(Br)=C(CHBr))(P(C_6H_4)Ph_2)Cl(CO)PPh_3]Br_3 (**3**). The proposed mechanism for the formation of complex **3** from **1** involves triple C−H activation as well as a rare $C(sp^2)-C(sp^3)$ reductive elimination.

Experimental Section

General Considerations. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (ether, tetrahydrofuran) or calcium hydride (dichloromethane). The starting material [IrHCl(CO)(PPh_3)$_3$]BF_4[17] and HC≡CCH(OH)CH=CH_2[16] were synthesized by literature procedures. All the NMR spectra were recorded with a Bruker AV300 (^{1}H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz) or a Bruker AV400 (^{1}H 400.1 MHz; ^{13}C 100.6 MHz; ^{31}P 162.0 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analyses data were obtained on an Elementar Analysensyetem GmbH Vario EL III instrument.

[Ir(CH=C(PPh_3)CH=$CHCH_2$)Cl(CO)(PPh_3)$_2$]BF_4 (1). A mixture of [IrHCl(CO)(PPh_3)$_3$]BF_4 (500 mg, 0.44 mmol) and HC≡CCH(OH)CH=CH_2 (37 mg, 0.45 mmol) in THF (10 mL) was stirred at room temperature for 3 days to give a white suspension. The solid was collected by filtration, washed with THF (2 × 2 mL) and Et_2O (10 mL), and then dried under vacuum (yield: 295 mg, 56%). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 9.4 (d, ^3J(PH) = 29.2 Hz, 1 H, IrC*H*), 6.8−7.8 (m, 45 H, PPh_3), 5.8 (dd, ^3J(PH) = 9.6 Hz, ^3J(HH) = 9.6 Hz, 1 H, IrCHCC*H*), 4.9 (m, 1 H, $IrCH_2CH$), 1.9 (t, ^3J(PH) = 11.6 Hz, 2 H, IrCH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 162.0 MHz): δ 18.9 (t, ^4J(PP) = 6.5 Hz, C*P*Ph_3), −3.1 (d, ^4J(PP) = 6.5 Hz, Ir*P*Ph_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 175.1 (td, ^2J(PC) = 11.5 Hz, ^2J(PC) = 3.5 Hz, Ir*C*CH), 174.6 (m, *C*O), 131.9 (d, ^3J(PC) = 11.8 Hz, IrCHC(PPh_3)CH*C*H), 124.4 (d, ^2J(PC) = 21.1 Hz, IrCHC*C*H), 111.0 (dt, ^1J(PC) = 71.7 Hz, ^3J(PC) = 4.7 Hz, IrCH*C*(PPh_3)), 3.4 (t, ^2J(PC) = 3.5 Hz, Ir*C*H_2), 110.0−136.0 (m, PPh_3) ppm. Anal. Calcd (%) for $C_{60}H_{50}ClOIrP_3BF_4$: C 60.33, H 4.22. Found: C 60.46, H 4.58.

[Ir(CH=C(PPh_3)CH=C(CH_2Br))Cl(CO)(PPh_3)$_2$]BF_4 (2). A mixture of [Ir(CH=C(PPh_3)CH=$CHCH_2$)Cl(CO)(PPh_3)$_2$]BF_4 (**1**) (500 mg, 0.42 mmol) and Br_2 (22 μL, 0.43 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 24 h to give a yellow suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone, 12:1) (yield: 345 mg, 65%). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 9.1 (d, ^3J(PH) = 20.4 Hz, 1 H, IrC*H*), 6.9−7.9 (m, 45 H, PPh_3), 6.6 (br, 1 H, IrCHC(PPh_3)C*H*), 2.6 (br, 2 H, CH_2Br) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 162.0 MHz): δ 12.0 (t, ^4J(PP) = 4.8 Hz, C*P*Ph_3), −10.5 (d, ^4J(PP) = 4.8 Hz, Ir*P*Ph_3). Anal. Calcd (%) for $C_{60}H_{49}IrOClBrP_3BF_4$: C 56.60, H 3.88. Found: C 57.02, H 4.24.

[Ir(CH=C(PPh_3)C(Br)=C(CHBr))(P(C_6H_4)Ph_2)Cl(CO)PPh_3]Br_3 (3). Method A: A mixture of [Ir(CH=C(PPh_3)CH=$CHCH_2$)Cl(CO)(PPh_3)$_2$]BF_4 (**1**) (500 mg, 0.42 mmol) and Br_2 (215 μL, 4.20 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 3 days to give a yellow suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum (yield: 509 mg, 81%). **Method B:** A mixture of [Ir(CH=C(PPh_3)CH=C(CH_2Br))Cl(CO)(PPh_3)$_2$]BF_4 (**2**) (500 mg, 0.39 mmol) and Br_2 (200 μL, 3.90 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 3 days to give a yellow suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum (yield: 492 mg, 83%). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ 9.7 (dd, ^3J(PH) = 20.2 Hz, ^3J(PH) = 3.0 Hz, 1 H, IrC*H*), 7.0 (1 H, C*H*Br, obscured by the phenyl signals and confirmed by ^{1}H−^{13}C HMQC), 6.6−7.9 (m, 44 H, PPh_3) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 16.6 (dd, ^4J(PP) = 6.0 Hz, ^4J(PP) = 2.8 Hz, C*P*Ph_3), 1.6 (dd, ^2J(PP) = 295.1 Hz, ^4J(PP) = 2.8 Hz, Ir*P*Ph_3), −17.1 (dd, ^2J(PP) = 295.1 Hz, ^4J(PP) = 6.0 Hz, Ir*P*Ph_3). ^{13}C{^{1}H} NMR plus HMQC (CD_2Cl_2, 75.5 MHz): δ 198.4 (d, ^2J(PC) = 10.1 Hz, IrCHC(PPh_3)), 174.0 (m, *C*O), 149.2 (d, ^2J(PC) = 11.9 Hz, Ir*C*C(Br)), 122.3 (d, ^1J(PC) = 61.1 Hz, *C*PPh_3), 116.4 (d, ^3J(PC) = 22.8 Hz, IrCHC(PPh_3)*C*(Br)), 60.7 (s, *C*HBr), 124.7−139.7 (m, PPh_3) ppm. Anal. Calcd (%) for $C_{60}H_{46}IrOBr_5ClP_3$: C 47.94, H 3.08. Found: C 48.14, H 2.68.

X-ray Crystal Structures Determination of 1, 2, and 3. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 or

(36) (a) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816, and references therein. (b) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125*, 16114. (c) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2005**, *24*, 4367. (d) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L. *Organometallics* **1996**, *15*, 823.

(37) Li, X.; Chen, P.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2005**, *24*, 4810, and references therein.

Table 1. Crystal Data and Structure Refinement for 1, 2, and 3

	1·CH_2Cl_2	**2**·0.25CH_2Cl_2	**3**·0.5CH_2Cl_2
empirical formula	$C_{60}H_{50}ClIrP_3O\cdot BF_4\cdot CH_2Cl_2$	$C_{60}H_{49}ClBrIrP_3O\cdot BF_4\cdot 0.25CH_2Cl_2$	$C_{60}H_{46}ClBr_2IrP_3O\cdot Br_3\cdot 0.5CH_2Cl_2$
fw	1194.43	1273.33	1503.12
temperature, K	223(2)	123(2)	173(2)
radiation (Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	14.099(3)	12.1921(7)	11.8828(9)
b, Å	14.656(2)	14.7377(10)	15.1966(13)
c, Å	14.670(2)	15.8268(8)	17.9860(14)
α, deg	105.785(12)	91.655(5)	107.820(7)
β, deg	96.294(13)	91.188(4)	106.346(7)
γ, deg	104.262(15)	99.375(5)	97.560(7)
V, Å^3	2775.9(8)	2803.7(3)	2881.6(4)
Z	2	2	2
d_{calcd}, g cm^{-3}	1.531	1.533	1.781
F(000)	1280	1285	1498
cryst size, mm	0.40 × 0.25 × 0.20	0.40 × 0.24 × 0.10	0.20 × 0.14 × 0.10
θ range, deg	2.21−26.00	2.74−25.00	2.05−25.00
reflns collected	26 060	33 339	24 357
indep reflns	10 859	9859	10 132
data/restraints/params	10 859/0/667	9859/16/661	10 132/9/652
goodness-of-fit on F^2	0.998	1.005	1.039
final R ($I > 2\sigma(I)$)	$R_1 = 0.0331$, $wR_2 = 0.0769$	$R_1 = 0.0456$, $wR_2 = 0.1167$	$R_1 = 0.0695$, $wR_2 = 0.1707$
R indices (all data)	$R_1 = 0.0499$, $wR_2 = 0.0828$	$R_1 = 0.0631$, $wR_2 = 0.1270$	$R_1 = 0.1169$, $wR_2 = 0.1816$

$CHCl_3$ solutions layered with ether or hexane for all complexes. Selected crystals were mounted on top of a glass fiber and transferred into a cold stream of nitrogen. Data collections were performed on an Oxford Gemini S Ultra CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Multiscan or empirical absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL-97 program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. The disordered CH_2Cl_2 solvent in **2** was refined isotropically using fixed C−Cl distances and Cl−C−Cl angle restraints with site occupancy of 0.25. The hemisolvating CH_2Cl_2 molecule in **3** was refined with isotropic thermal parameters using fixed C−Cl distances and Cl−C−Cl angle restraints. CCDC-761743 (**1**), 761744 (**2**), and 761745 (**3**) contain the supplementary crystallographic data for this paper. Details on crystal data, data collection, and refinements are summarized in Table 1.

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Supporting Information Available: X-ray crystallographic files (CIF). ORTEP views of the whole structure of **1**, **2**, and **3**, including the anions and the solvent molecules. These materials are available free of charge via the Internet at http://pubs.acs.org.