Reactivity of $IrCl(PPh_3)_3$ with diphenylacetylene — A direct route to 1-iridaindene[1]

Joyanta Choudhury, Sanjay Pratihar, Arnab Kumar Maity, and Sujit Roy

Abstract: The 1-iridaindene complex, $Ir[C_8H_5(Ph\text{-}2)]Cl(PPh_3)_2$ (**2**), has been prepared from the reaction of $IrCl(PPh_3)_3$ with PhC≡CPh by a novel direct cycloiridation reaction. A plausible mechanistic pathway has been suggested involving π-coordination assisted *ortho*- C–H activation and subsequent alkyne hydroiridation reaction to provide the five-member iridacycle.

Key words: iridium, diphenylacetylene, C–H activation, cyclometallation, metallacycle.

Résumé : On a préparé le complexe du 1-iridaindène, $Ir[C_8H_5(ph\text{-}2)]Cl(PPh_3)_2$ (**2**), par réaction du $IrCl(PPh_3)_3$ avec le PhC≡CPh par une nouvelle réaction de cycloiridation directe. On propose une voie mécanistique plausible impliquant une activation du C–H en *ortho* qui serait assistée par une coordination π et qui serait suivie par une réaction d'hydroiridation de l'alcyne conduisant à la formation de l'iridacycle à cinq chaînons.

Mots-clés : iridium, diphénylacétylène, activation d'une liaison C–H, cyclométallation, métallacycle.

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Introduction

Metallacycles are important synthons as well as intermediates in many catalytic organic and organometallic reactions (1–12). Iridaindene motifs can be viewed as metallacyclopentadienes that are intermediates in metal-mediated [2+2+2] cyclotrimerization of alkynes to provide aromatic six-membered rings (13–18). There are also examples of [2+2+1] cyclotrimerization reactions with the intermediacy of metallacyclopentadienes (19–25). Moreover, the metallacyclopentadiene complexes are utilized for the synthesis of metallabenzenes, which are interesting structural units, compared with simple aromatics (26–28). To our knowledge, a direct and unassisted route for the preparation of such metallacycles by the activation of organic precursors with appropriate metal complexes is hitherto unknown. The more common routes involve (*i*) an indirect transmetallation method, which commonly uses organomercury compounds and (*ii*) carbon monoxide assisted cyclocarbonylation using alkynes or allenes leading to metallacyclopentadienones.

With specific reference to iridium, an iridaindene complex $Ir[C_8H_5(Ph\text{-}2)](C_5H_5)(P^iPr_3)$ was prepared earlier from $Ir(PhC{\equiv}CPh)(C_5H_5)(P^iPr_3)$ via the formation of a vinyl complex $Ir(PhC{=}CHPh)(OCOCF_3)(C_5H_5)(P^iPr_3)$ by CF_3COOH and subsequent reaction with NH_4PF_6 in methanol (29). Recently, Wright and co-workers (30) reported a transmetallation route for the synthesis of a substituted 1-iridaindene $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (**1**) from the corresponding organomercury compound $Hg(CH{=}CPh_2)_2$ and $IrHCl_2(PPh_3)_3$ (Scheme 1*a*). Earlier, they isolated **1** as a side product from the reaction of $Hg(CH{=}CPh_2)_2$ and $IrCl(CS)(PPh_3)_2$ in only 20% yield (Scheme 1*b*) (31).

Our recent interest in iridium chemistry, particularly on the activation and coupling of organic functionalities (32–37) led us to investigate the activation of alkynes. Herein we report the first example of a direct cycloiridation from the reaction of $IrCl(PPh_3)_3$ with PhC≡CPh, leading to a new air-stable 1-iridaindene complex, $Ir[C_8H_5(Ph\text{-}2)]Cl(PPh_3)_2$ (**2**). We also describe the structural characterization of **2** by single crystal X-ray diffraction and propose a plausible mechanism involving C–H activation followed by ring closure.

At this point it should be noted that our result is quite interesting because the 16-electron iridium(I) complex $IrCl(PPh_3)_3$ was reported earlier to react with various alkynes. With terminal alkynes, the oxidative addition products resulted (38). But in the case of diphenylacetylene, the π-complex, $IrCl(PhC{\equiv}CPh)(PPh_3)_2$ (**3**), was reported to be formed (vide ^1H NMR and IR) with the substitution of one phosphine ligand (Scheme 2*a*) (38). The complex **3** was also synthesized as yellow crystals by the reaction of $IrCl(N_2)(PPh_3)_2$ with diphenylacetylene (Scheme 2*b*) (39).

Results and discussion

The reaction of $IrCl(PPh_3)_3$ with diphenylacetylene in refluxing benzene was accompanied by a gradual color change from yellow to red, which is noticeable to the naked eye within 4–6 h. Ex-situ UV–vis monitoring of the solution in benzene showed the appearance of a new peak at 510 nm. After reflux for 18 h, evaporation of the solvent in vacuum and subsequent recrystallization of the resulting solid resi-

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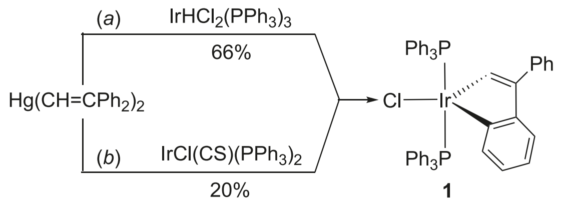
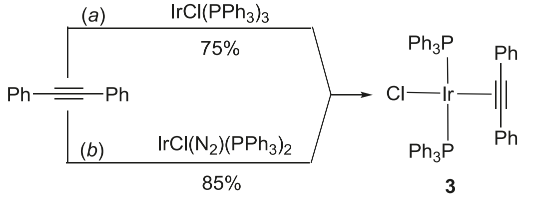
Scheme 1.



Scheme 2.



Scheme 3.

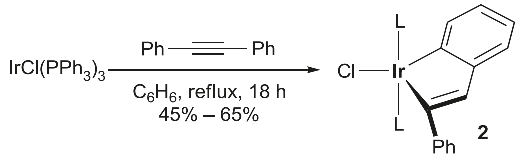
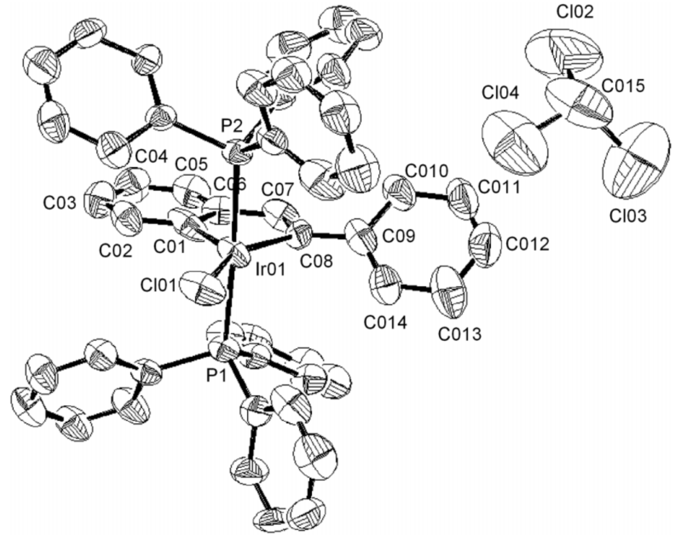


Fig. 1. ORTEP representation for the molecular structure of **$2\cdot CHCl_3$** (50% thermal ellipsoids). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(01)–P(1), 2.349(4); Ir(01)–P(2), 2.341(4); Ir(01)–Cl(01), 2.411(4); Ir(01)–C(01), 2.00(2); Ir(01)–C(08), 2.035(15); C(06)–C(07), 1.42(3); C(01)–C(06), 1.40(2); C(07)–C(08), 1.36(3); ∠P(1)-Ir(01)-P(2), 176.73(16); ∠Cl(01)-Ir(01)-C(01), 133.1(5); ∠Cl(01)-Ir(01)-C(08), 149.6(6); ∠C(01)-Ir(01)-C(08), 77.3(8).



due from chloroform/ethanol or dichloromethane/ethanol afforded **2** as deep red block-like air-stable crystals, the 1st crop yield being 45%–65% (Scheme 3).

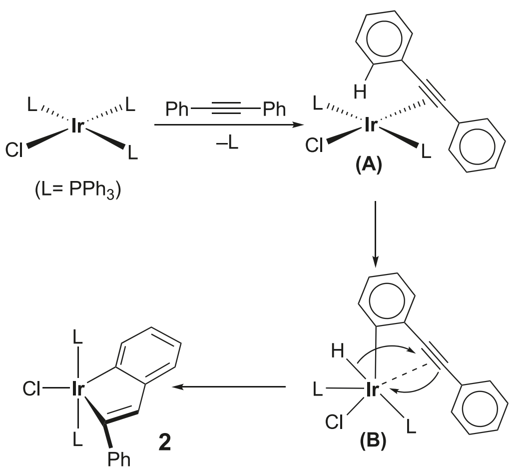
The IR spectrum of **2** in KBr discs shows no characteristic peak for coordinated alkyne. The $\nu_{C\equiv C}$ frequency in IR of the known η^2-alkyne complex **3** appears within 1850–1865 cm^{-1} (31, 32). In the ^1H NMR spectrum of **2**, there is a clean signature for the resonances of the iridaindene fragment. The sharp singlet at 5.65 ppm is assigned to the resonance of the C*H* of the five-membered iridacycle. The remaining four protons of the iridaindene six-membered ring resonate as an unresolved doublet of doublet at 5.99 ppm ($J_{H\text{-}H}$= 7.2, 7.6 Hz), a doublet at 6.10 ppm ($J_{H\text{-}H}$ = 7.2 Hz), an apparent triplet at 6.43 ppm (formally doublet of doublet, $J_{H\text{-}H}$ = 7.2, 7.2 Hz), and a doublet at 6.91 ppm ($J_{H\text{-}H}$ = 7.6 Hz), respectively. In the ^{13}C NMR spectrum, the signals of two carbon atoms bonded to iridium, viz., vinyl-*C*(Ph)Ir and aryl-*C*Ir appear as unresolved triplets at 133.9 and 145.9 ppm, respectively. The assignment is made according to a literature comparison (31). The carbon atoms of the iridaindene six-membered ring and phenyl substituent of iridaindene resonate separately as singlets between 120.1 and 133.0 ppm. The ^{31}P NMR signal appears at 22.78 ppm.

A single crystal of **2** suitable for an X-ray diffraction study was obtained by slow diffusion of ethanol into a chloroform solution of the compound at room temperature. The solid-state molecular structure of **2** is illustrated in Fig. 1. The structure contains a $CHCl_3$ molecule as solvent of crystallization. The geometry around the iridium atom is trigonal bipyramidal with axial phosphines (∠P1-Ir01-P2 = 176.73(16)°), while the equatorial plane is occupied by the chlorine atom and the two carbon atoms (∠Cl01-Ir01-C01 = 133.1(5)°, ∠Cl01-Ir01-C08 = 149.6(6)°, ∠C01-Ir01-C08 = 77.3(8)°). The iridaindene ring is found to be planar, while the phenyl group at the 2 position is slightly tilted away from the plane. In the five-membered iridacycle, the two Ir–C bond lengths are 2.00(2) and 2.035(15) Å, which signify some degree of multiple bond nature instead of single bond character. The other three C–C bond lengths within this ring are 1.42(3) Å (C06–C07), 1.40(2) Å (C01–C06), and 1.36(3) Å (C07–C08), indicating little delocalization within the ring. The two triphenylphosphine ligands are mutually trans with Ir–P distances of 2.349(4) and 2.341(4) Å. The Ir–Cl distance is 2.411(4) Å.

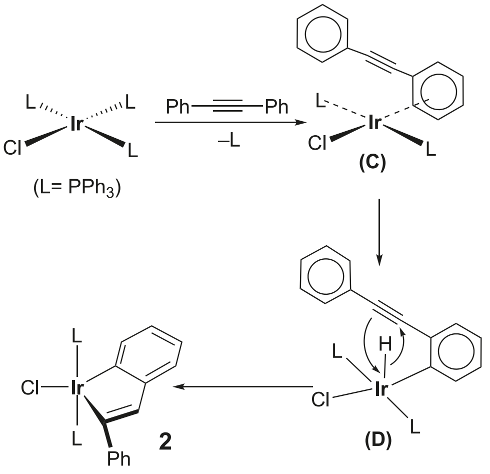
To gain some insight into the plausible mechanistic pathway of this cycloiridation process, the aliquots from a 1:1 reaction mixture of $IrCl(PPh_3)_3$ and $PhC\equiv CPh$ in C_6D_6 at 30, 60, and 90 °C (oil-bath temperature) were subjected to ^1H NMR spectral analysis. The formation of complex **2** was observed only under reflux conditions, as revealed from the appearance of new and characteristic peaks at 5.50, 5.84, 5.98, 6.25, and 6.37 ppm due to the iridaindene fragment. These characteristic peaks were observed at slightly downfield region in $CDCl_3$ solution of **2** (see the Experimental section). The temperature effect suggests that sufficient thermal energy was required for the C–H activation–cycloiridation to take place.

A plausible route for the formation of **2** is suggested in Scheme 4, invoking prior dissociation of a phosphine ligand from $IrCl(PPh_3)_3$ in solution, followed by the π coordination of the alkyne ligand forming the complex **A**. This proximal π-alkyne coordination in **A** adopts one of the alkyne phenyl rings, such that the iridium center can access the *ortho* C–H bond for the purpose of orthometallation. Though alkyne is less well-known to serve such a role of tethering for orthometallation, compared with other donor groups such as carbonyl, halide, or amine (40, 41), recently Hill et al. (42)

Scheme 4.



Scheme 5.



proposed such a phenomenon during the formation of a ruthenaindenone complex. Accordingly, in our proposal the iridium-hydride intermediate **B** resulting from the *ortho* C–H activation then undergoes alkyne hydroiridation to generate the iridacycle **2**. At this stage we cannot rule out another alternative mechanism (Scheme 5), involving the η^2 alkyne as dead-end, with the coordination of iridium to phenyl group leading to the hypothetical intermediate **C**. The latter, upon *ortho* C–H insertion, would produce intermediate **D**, which subsequently converts to the iridacycle **2**. Complexes featuring the binding of a phenyl group of diphenylacetylene to the metal in a η^2- or η^6-fashion (as in intermediate **C**, vide Scheme 5) have precedents in the literature. Examples from late transition metal complexes include $[Os(NH_3)_5(\eta^2\text{-}C_6H_5C{\equiv}CPh)](OTf)_2$ (43) and $[CpRu(\eta^6\text{-}C_6H_5C{\equiv}CPh)](OTf)$ (44). Two examples of η^6-bound diphenylacetylene complexes of early transition metals are $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}CPh)]$ (45) and $[(CO)_3Mo(\eta^6\text{-}C_6H_5C{\equiv}CPh)]$ (46). Recently, Legzdins and co-workers reported the formation of tungsten complexes of the type **D** having a pendent dead η^2-alkyne moiety (40). The observation of selective *ortho* C–H activation may be due to the driving force of the subsequent ring-closure reaction to a stable product, whereas the insertion into *meta* or *para* C–H bonds would be reversible.

The possibility of catalysis in the presence of traces of acid impurity (29) in our reaction mixture was also considered. We ruled out this possibility because even in the presence of 1 equiv. of Na_2CO_3, the reaction of $IrCl(PPh_3)_3$ with diphenylacetylene proceeded well, leading to the formation of the desired iridacycle **2**.

In summary, we have demonstrated here a direct cycloiridation reaction leading to an iridaindene molecule that is poised towards further functionalization of the activated indene moiety to useful organic end-product(s). A plausible mechanistic pathway has also been suggested involving π-coordination assisted *ortho* C–H activation and subsequent alkyne hydroiridation reaction to provide the five-membered iridacycle. Work is underway to explore the generality of the reaction, the reactivity of the iridacycle, and deducing the mechanism.

Experimental

General

All preparations and manipulations have been performed under a dry, oxygen-free argon atmosphere using standard vacuum lines and Schlenk techniques. All solvents have been dried and distilled by standard methods and previously deoxygenated in the vacuum line. ^1H (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on Bruker Avance II 400 MHz spectrometer at 300 K. Tetramethylsilane was used as internal reference for ^1H and ^{13}C, while H_3PO_4 was used as external reference for ^{31}P NMR. FT-IR (4000-500 cm^{-1}; using KBr pellets) spectra were obtained using a PerkinElmer FTIR Spectrometer (Spectrum RX-I). UV–vis spectra were recorded in a Chemito Spectroscan UV 2600 spectrophotometer using HPLC-grade benzene. Elemental analyses were performed on PerkinElmer Instruments 2400 Series II CHNS/O Analyzer. $IrCl(PPh_3)_3$ was prepared according to literature procedure (47). Diphenylacetylene (Lancaster, 99%) either used directly or after recrystallization from ethanol, yielded identical results. All other chemicals were obtained commercially and used without further purification.

Synthesis and characterization details of 2[3]

In a typical example, $IrCl(PPh_3)_3$ (0.1 mmol, 101 mg) and diphenylacetylene (0.3 mmol, 54 mg) were placed in a Schlenk flask under argon. Following dissolution in dry benzene (3 ml), the solution was refluxed for 18 h. The color of the solution gradually changed from yellow to deep red. After this period, the solvent was removed under vacuum at 300 K, and the resulting solid residue was recrystallized

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[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3810. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 652721 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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from chloroform/ethanol to give iridaindene **2** as deep red block-like crystals (68 mg, 65%), mp 282–284 °C (dec).

UV–vis (benzene) λ_{max} (nm) (ε (mol/L)$^{-1}$cm^{-1})): 364 (10 000), 510 (640). IR (KBr, cm^{-1}): 694 (s), 743(s), 1094(s), 1435(s), 1483(s). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.10–7.57 (m, $P(C_6H_5)_3$, and 3H′s of C_6H_5, 33H), 6.96–7.02 (m, 2H′s of C_6H_5, 2H), 6.91 (d, $J_{H\text{-}H}$= 7.6 Hz, *H*05, 1H), 6.43 (dd, $J_{H\text{-}H}$= 7.2, 7.2 Hz, *H*03, 1H), 6.10 (d, $J_{H\text{-}H}$= 7.2 Hz, *H*02, 1H), 5.99 (dd, $J_{H\text{-}H}$= 7.2, 7.6 Hz, *H*04, 1H), 5.65 (s, *H*07, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ: 127.4 (t, $^{2,4}J_{CP}$= 5.1 Hz, *o*-C_6H_5P), 129.3–129.8 (m, *i*-C_6H_5P and *p*-C_6H_5P), 134.9 (t, $^{3,5}J_{CP}$= 5.1 Hz, *m*-C_6H_5P), 120.1, 121.8, 122.1, 126.4, 127.1, 127.8, 133.0 (all singlet signals are for *C*H of iridaindene six-membered ring and Ph substituent of iridaindene); 133.9 (unresolved t, $^{2}J_{CP}$= 7.9 Hz, iridaindene *C*2Ph), 139.5 (s, iridaindene *C*3H), 144.5 (s, quat. C), 145.9 (unresolved t, $^{2}J_{CP}$= 6.9 Hz, iridaindene *C*Ir), 160.3 (s, quat. C). N.B. in ^{1}H and ^{13}C NMR spectra, peaks due to the solvated $CHCl_3$ appeared at 7.27 and 77.0 ppm, respectively. ^{31}P NMR (162 MHz, $CDCl_3$, ppm) δ: 22.78. Anal. calcd. for $C_{50}H_{40}ClP_2Ir.CHCl_3$: C 58.35, H 3.94; found: C 57.82, H 4.36.

X-ray structure determination of 2·CHCl$_3$

Single crystals of **2** suitable for X-ray diffraction study were obtained from slow diffusion of ethanol into a solution of **2** in chloroform or dichloromethane at room temperature. A suitable deep-red blocklike crystal of the complex **2** obtained from $CHCl_3$/EtOH solution was subjected to an Enraf Nonius Turbo CAD4 diffractometer with Graphite monochromated Mo Kα (λ= 0.710 73 Å). Unit cell parameters were obtained from a least-square refinement of 25 reflections. The structure was solved by SHELXS-97 and refined by full-matrix least squares on F^2 with SHELXL-97 methods (48, 49). The non-hydrogen atoms were refined anisotropically. All calculations were performed using WinGX crystallographic software package (50). Crystallographic data as well as structure solution and refinement details for **2**: $C_{50}H_{40}Cl_1P_2Ir_1.CHCl_3$; triclinic, P-1; a = 10.3295(15) Å, b = 12.4243(19) Å, c = 17.544(3) Å; α = 94.005(11)°, β = 98.539(13)°, γ = 98.581(12)°; V = 2191.9(6) Å^3; Z = 2; T = 293(2) K; λ (Mo K α) = 0.710 73 Å; D_{calc} = 1.591 mg/m^3; μ = 3.398 mm^{-1}; F(000) = 1044; Θ (min–max) = 1.18–25.00°; independent reflection = 6440; R_{int} = 0.0201; T (min, max) = 0.6124, 0.7727; data, restraints, parameters = 6440, 0, 524; final R indices ($I>2\sigma(I)$) R_1 = 0.0711, wR_2 = 0.1693; R indices (all data) R_1 = 0.1339, wR_2 = 0.2386; GOF on F^2 = 1.137.

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