Synthesis, Structures, and Reactivity of Single and Double Cyclometalated Complexes Formed by Reactions of \([\text{Cp}^*\text{MCl}_2]_2\) (\(\text{M} = \text{Ir} \text{ and Rh} \)) with Dinaphthyl Phosphines

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Supporting Information

ABSTRACT: Reactions of two dinaphthyl phosphines with \([\text{Cp}^*\text{IrCl}_2]_2\) have been carried out. In the case of di((\(\alpha\)-naphthyl)diphenylphosphine (1a), a simple P-coordinated neutral adduct 2a is obtained. However, tert-butyl(di(\(\alpha\)-naphthyl)diphenylphosphine (1b) is cyclometalated to form \([\text{Cp}^*\text{IrCl}(\text{P}^\text{N})])\) (3b). Complexes 2a and 3a undergo further cyclometalation to give the corresponding double cyclometalated complexes \([\text{Cp}^*\text{Ir}(\text{C}^\text{P}^\text{N})^\text{c}])\) (4a,b) upon heating. In the presence of sodium acetate, reactions of 1a,b with \([\text{Cp}^*\text{IrCl}_2]_2\) directly afford the final double cyclometalated complexes (4a,b). In the absence of acetate, \([\text{Cp}^*\text{RhCl}_2]_2\), shows no reaction with 1a,b, whereas with acetate, the reactions form the corresponding single cyclometalated complexes \([\text{Cp}^*\text{RhCl}(\text{P}^\text{N})])\) (5a,b), which react with BuOK to form the corresponding rhodium hydride complexes (6a,b). Treatment of 4a with CuCl or I₂ leads to opening of two Ir–C σ bonds to yield the corresponding P-coordinated iridium dihalide (7 or 8) by means of an intramolecular C–C coupling reaction. A new chiral phosphine (11) is formed by the ligand-exchange reaction of 8 with PMe₃. Reactions of the single cycloiridated complex 3b with terminal aromatic alkynes result in the corresponding five- and six-membered doubly cycloiridated complex 12 and/or \(\eta^2\)-alkene coordinated complexes 13–15; the latter discloses that the electronic effect of terminal alkynes affects the regioselectivity. While the single cycloiridated complex 5b reacts with terminal aromatic alkynes to form the corresponding six-membered cyclometalated complexes 16a–c by vinylidene rearrangement/1,1-insertion. Plausible pathways for formation of insertion products 13–16 were proposed. Molecular structures of twelve new complexes were determined by X-ray diffraction.

INTRODUCTION

To date, cyclometalation reactions are the most actively investigated reactions in the field of organometallic chemistry, which have been carried out with the most transition metal coordination five-membered ring compounds, and only few of them afford six-membered ring products.¹,¹¹,¹⁵,¹⁶ To date, there is less study on phosphine ligands involved cyclometalation with \([\text{Cp}^*\text{MCl}_2]_2\) (\(\text{M} = \text{Rh} \text{ and Ir} \)) to when compared to that of N-containing ligands. Recently, we reported the cyclometalation of phosphines and phosphinates with \([\text{Cp}^*\text{MCl}_2]_2\) (\(\text{M} = \text{Rh} \text{ and Ir} \)) and \([\{\text{p-cymene}\}\text{RuCl}_2]_2\) in methanol in the presence of sodium acetate, and the resulting five-membered cyclometalated products showed interesting and diverse chemical reactivity. To increase the diversity of donor ligands and further understand the reactivity of cyclometalated products, herein we report an investigation of cyclometalation of two dinaphthyl phosphate ligands with \([\text{Cp}^*\text{MCl}_2]_2\) (\(\text{M} = \text{Rh} \text{ and Ir} \)) and discuss the structures and reactivity of the resulting single and double cyclometalated complexes.

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Scheme 1. Reaction of \([\text{Cp}^*\text{IrCl}_2]_2\) with \(\text{Di}(\alpha\text{-naphthyl})\text{phenylphosphine} (1a)\) or \(\text{tert-Butyldi}(\alpha\text{-naphthyl})\text{phenylphosphine} (1b)\).

The structure of \(2a\) is shown in Figure 1, which reveals a classic three-legged piano stool geometry with the iridium(III) center coordinated by a \(\eta^1\) \(\text{Cp}^*\), one phosphorus atom \(P(1)\), and two chlorine atoms \(\text{Cl}(1)\) and \(\text{Cl}(2)\). The \(\text{Ir}(1)\)–\(\text{P}(1)\) bond distance \([2.349(3) \text{ Å}]\) is slightly longer than that \([2.324(3) \text{ Å}]\) in \(\text{Cp}^*\text{IrCl}_2\) \((\text{PPh}_3)\), which is probably due to the larger steric bulk of \(\text{di}(\alpha\text{-naphthyl})\text{phenylphosphine}\) compared to that of \(\text{PPh}_3\).

The structure of \(4a\) is shown in Figure 2, the dinaphthylphenylphosphine is acting as a tridentate ligand, which is coordinated to the iridium(III) center through one phosphorus atom \(P(1)\) and two metalated carbon atoms \(C(11)\) and \(C(21)\), both come from naphthyl groups. Two five-membered rings fused together sharing two adjacent atoms \(\text{Ir}(1)\) and \(P(1)\), which constitute the main molecular frame.

**RESULTS AND DISCUSSION**

**Reaction of \([\text{Cp}^*\text{IrCl}_2]_2\) with \(\text{Di}(\alpha\text{-naphthyl})\text{phenylphosphine} (1a)\) or \(\text{tert-Butyldi}(\alpha\text{-naphthyl})\text{phenylphosphine} (1b)\).** Compounds \(1a\) and \(1b\) were chosen as ligands for two reasons: first, two \(\alpha\text{-naphthyl}\) groups could provide two \(\text{C}(\text{sp}^2)\)–\(\text{H}\) bonds at the appropriate positions for potential \(\text{C}–\text{H}\) bond activation by the metal center; and second, phenyl and \(\text{tert-butyl}\) groups represent two typical groups with different steric effects, which might lead to different reactivity. By analogy to our previous work with similar substrates,\(^{25}\) phosphine \(1a\) was reacted with \([\text{Cp}^*\text{IrCl}_2]_2\) in methanol at room temperature, producing the corresponding phosphine-substituted iridium dichloride \(2a\) in good yield (Scheme 1). The similar complex \(\text{Cp}^*\text{Ir}(\text{PPh}_3)\text{Cl}_2\) has been reported as early as 1969,\(^{27}\) which was synthesized similarly by \([\text{Cp}^*\text{IrCl}_2]_2\) and \(\text{PPh}_3\), in hot ethanol. However, when phosphine \(1b\) reacted with \([\text{Cp}^*\text{IrCl}_2]_2\) under the same conditions, a five-membered cyclometalated complex \(3b\) was formed. Obviously, the formation of complexes \(3b\) goes through an intramolecular activation of the \(\text{C}(\text{sp}^2)\)–\(\text{H}\) bond on the adjacent \(\alpha\) position of naphthyl ring. Davies et al. have concluded that hydrogen bonding between the \(\text{C}–\text{H}\) bond and acetate are two key factors for successful cyclometalation,\(^{24}\) and here we consider that larger steric demand of phosphine ligand \(1b\) may also contribute to the implementation of cyclometalation, because cyclometalation could relieve the strain in the molecular structure. Thus, in the absence of acetate, the cyclometalation reaction still occurred in this case. When the above two reactions were carried out under heating conditions, the final products \(4a, b\) were obtained, which contain two five-membered metalated rings in their respective structures. Apparently, two \(\text{C}(\text{sp}^2)\)–\(\text{H}\) bonds from two naphthyl rings were activated by the metal center; \(2a\) is red solid, \(3b\) is orange solid, and \(4a, b\) are light yellow solid. All of them were fully characterized by spectroscopic analysis, in which the structures of \(2a\) and \(4a\) were confirmed by X-ray diffraction analysis.

The structure of \(2a\) is shown in Figure 1, which reveals a classic three-legged piano stool geometry with the iridium(III) center coordinated by a \(\eta^1\) \(\text{Cp}^*\), one phosphorus atom \(P(1)\), and two chlorine atoms \(\text{Cl}(1)\) and \(\text{Cl}(2)\). The \(\text{Ir}(1)\)–\(\text{P}(1)\) bond distance \([2.349(3) \text{ Å}]\) is significantly shorter than that \([2.324(3) \text{ Å}]\) in \(\text{Cp}^*\text{IrCl}_2\) \((\text{PPh}_3)\), which indicates that cyclometalation would help ease the strain in the molecular structure. Carmona has reported a structurally similar iridium complex \(\text{Cp}^*\text{Ir}(\text{PMe}(\eta^1\text{Xyl}))_2\)\(^{20}\) the formation of which went through intramolecular activation of two \(\text{C}(\text{sp}^2)\)–\(\text{H}\) bonds. Its \(\text{Ir}–\text{P}\) bond distance is \(2.205(2) \text{ Å}\), consistent with the value in \(4a\).

Davies et al. have reported that acetate could assist \(\text{C}–\text{H}\) bond activation and promote the cyclometalation in the reactions of 2-substituted pyridines with \([\text{Cp}^*\text{MCl}_2]_2\) \((\text{M} = \text{Ir}, \text{Rh})\). For comparison, similar reactions of \([\text{Cp}^*\text{IrCl}_2]_2\) with phosphines \(1a, b\) in the presence of sodium acetate were performed at room temperature, which resulted in corresponding doubly five-membered cyclometalated complexes \(4a, b\) in good yields (Scheme 2). It is quite clear that acetate also promotes the cyclometalation in our cases. The use of iridium complex \([\text{Cp}^*\text{IrCl}_2]_2\) as precursor in cyclometalation reactions with a large variety of nitrogen-containing and phosphine ligands has been widely reported, however, the similar cyclometalation reactions based on two \(\text{C}–\text{H}\) bonds activation
metalation reaction compared to C(sp^3)–H bond activation in the case of phosphine PMe(Xyl)$_2$.

**Reaction of [Cp*RhCl$_2$]$_2$ with 1a or 1b.** For comparison, reactions of phosphines 1a,b and [Cp*RhCl$_2$]$_2$ have been carried out in methanol; however, neither C–H activation product nor simple phosphine coordination product was observed even at elevated temperatures. The decreased reactivity of rhodium compared to iridium indicates that the former is less electrophilic, a similar argument has been made by Jones in discussion of the reactions of [Cp*MCl$_2$]$_2$ (M = Ir and Rh) with 2-benzylpyridine.\(^{11}\) When the same reactions were performed in the presence of sodium acetate, the corresponding five-membered cyclometalated rhodium complexes 5a,b were successfully produced (Scheme 3). It is worth noting that above reactions did not give the doubly metalated products even under heating conditions, which are different with the cases of iridium. We considered that doubly metalated rhodium compounds may not be the thermodynamically stable products, contrary to the iridium analogues 4a,b. To obtain the doubly metalated rhodium compounds, a reaction of 5a or 5b with an excess of BuOK in methanol was carried out at room temperature; however, no expected doubly metalated product was observed, but a light-yellow solid was precipitated in the bottom of flask. The solvent methanol was carefully removed and replaced with CD$_2$OD for further NMR characterization. In the $^1$H NMR spectra of 6a,b, a distinct triplet at high field (δ = −12.09 ppm for 6a and −12.72 ppm for 6b) was observed indicating the existence of Rh–H proton. Combined with other NMR spectra analysis, 6a,b were assigned as the cyclometalated rhodium hydride (Scheme 3). When above reactions were performed in CD$_3$OD, the corresponding products 6a–d$_1$ and 6b–d$_1$ were obtained. It is very clear that the hydride ligand in 6a or 6b comes from methanol. A similar Cl/D exchange reaction was observed in the reaction of Cp*RhCl[PMe(Xyl)]($^3$Xyl)] with NaOCD$_2$.\(^{20a}\) In the process of purification of 6a,b by column chromatography in air, serious decomposition was observed. Besides, we also tried the reaction of 5a with 1$^3$BuLi or MeLi in THF for further cyclometalation; however, no product was obtained except the starting material 5a.

Complexes 4a,b are structurally novel products, iridium(III) center is coordinated by one phosphorus atom and two sp$^3$ hybridized carbon atoms, and two fused five-membered rings constitute the main molecular framework. We are curious about the chemical reactivity of this type of complexes. To develop a general understanding of the reactivity of the complexes containing two metalated five-membered rings, we have chosen 4a as a representative and explored the reactions of 4a with anhydrous CuCl$_2$ and I$_2$.

**Reaction of 4a with CuCl$_2$.** Anhydrous CuCl$_2$ is a well-known oxidant, which is generally used for inducing oxidative coupling in organometallic reactions. Jones et al. have reported the insertion reactions of dimethylacetylenedicarboxylate with

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**Figure 2.** Thermal ellipsoid drawing of 4a showing the labeling scheme and 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ir(1)–P(1) 2.232(11), Ir(1)–C(11) 2.269(4), Ir(1)–C(21) 2.281(5), Ir(1)–Cp(centroid) 1.911, ∠C(11)–Ir(1)–C(21) 84.68(18), ∠C(11)–Ir(1)–P(1) 82.36(13), ∠C(21)–Ir(1)–P(1) 80.93(12).

**Scheme 2.** Reactions of [Cp*IrCl$_2$]$_2$ with 1a,b in the Presence of NaOAc

**Scheme 3.** Reactions of [Cp*RhCl$_2$]$_2$ with 1a,b
cyclometalated rhodium compounds, and then, the demetallization of the insertion compounds was achieved by oxidative coupling with CuCl₂ to form the novel isoquinoline salts. Here, a similar treatment of 4a with 2 equiv of anhydrous CuCl₂ in CH₂Cl₂ at room temperature was performed, which produced the phosphine-substituted iridium dichloride 7 (Scheme 4). Obviously, oxidative coupling of two metal-bound naphthyl groups occurred in the presence of CuCl₂ to form a binaphthyl unit, which was accompanied by the opening of two five-membered metallacycles. However, the phosphorus atom is still coordinated to metal center, which may due to the strong bonding between metal and phosphine ligand. When the same reaction was performed on 4a with only 1 equiv of CuCl₂, a mixture of the starting complex 4a and the product 7 was obtained, indicating that a full 2 equiv of CuCl₂ is required to complete the oxidative-coupling reaction. A plausible pathway was proposed in Scheme 5 to show how 2 equiv of CuCl₂ is required in the reaction. Complex 4a was also treated with excess Cu(OAc)₂, but no reaction was observed at room temperature. Complex 7 was fully characterized by spectroscopic analysis, and its structure was further confirmed by X-ray diffraction analysis.

The structure of 7 is shown in Figure 3, which reveals a classic three-legged piano stool geometry with the iridium(III) center coordinated by a η⁵ Cᵖ*, one phosphorus atom P(1), and two chlorine atoms Cl(1) and Cl(2). It is noteworthy that two naphthyl groups from phosphine ligand are bonded by two adjacent α carbon atoms to constitute a seven-membered ring. The Ir(1)−P(1) bond distance is 2.3159(12) Å, which is in good agreement with the value [2.324(3) Å] in CᵖIrCl₂(PPh₃)₂ and slightly shorter than that [2.349(3) Å] in 2a, which is probably due to the less steric bulk of two bonded naphthyl groups compared to two normal naphthyl ones. The C(19)−C(21) bond distance is 1.494(6) Å, close to the normal value of C−C single bond, which means the absence of conjugation between two naphthyl rings.

**Reaction of 4a with I₂.** It is well-known that the M−C σ bond of the cyclometalated complex readily undergoes the oxidative addition of I₂ to give the ring-opening product. Treatment of 4a with an excess of I₂ in CH₂Cl₂ afforded the phosphine-substituted iridium diiodide 8, the analogue of 7 (Scheme 6). Generally speaking, oxidative addition of I₂ on two Ir−C bonds should similarly give the expected product 9 (Scheme 6). However, compound 9 has never been observed either by TLC monitoring or by column chromatography. We considered that the final product 8 was generated from the further cross-coupling of two iodonaphthalene units of the intermediate 9. The crystal structure of 8 is provided in the Supporting Information, which exhibits structure similar to that of 7.

**New Type of Chiral Phosphine Formed by the Ligand-Exchange Reaction.** The phosphine-substituted iridium diiodide 8 readily underwent the ligand-exchange reaction in the presence of excess PMe₃ in toluene at room temperature to free a new phosphine 11, as well as PMe₃-substituted iridium diiodide 10 (Scheme 7). Compound 11 is an air-stable white

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**Scheme 4. Reaction of 4a with CuCl₂**

![Scheme 4](image)

**Scheme 5. Plausible Pathway for Formation of 7**

![Scheme 5](image)

**Scheme 6. Reaction of 4a with I₂**

![Scheme 6](image)

**Figure 3. Thermal ellipsoid drawing of 7 showing the labeling scheme and 50% probability ellipsoids; hydrogens are omitted for clarity.**

Selected bond lengths [Å] and angles [°] are Ir(1)−P(1) 2.3159(12), Ir(1)−Cl(1) 2.4164(11), Ir(1)−Cl(2) 2.4119(10), C(19)−C(21) 1.494(6), Ir(1)−Cp(centroid) 1.825, ∠C(11)−P(1)−C(23) 113.0(2), ∠C(11)−P(1)−C(31) 100.05(19), and ∠C(23)−P(1)−C(31) 98.95(19).
Vinylidene rearrangement. Hence, considering the interest including 1,2-insertion and 1,1-insertion after the initial complexes. We observed different alkyne-insertion reactions into M.

Chiral catalyst or as an additive in stereoselective catalytic reactions may have potential application as ligands for construction of a bond (1.54 Å). This chiral phosphine is [1.516(3), 1.817(2), P(1)−C(13) 107.82(11), ∠C(1)−P(1)−C(13) 107.82(11), ∠C(1)−P(1)−C(21) 101.60(10), and ∠C(13)−P(1)−C(21) 100.76(10)].

Recently, we reported a series of results concentrated on the ve- and six-membered N- or P-containing cyclometalated complexes below, whose structure was determined by X-ray diffraction. Although complex 13 did not form crystal of high quality that is suitable for X-ray diffraction, its structure was supported by the consistent ¹H NMR data with the anion-exchanged complex 15e described below, whose structure was determined by X-ray diffraction.

The structure of 12 is shown in Figure 5 with selected bond lengths and angles, which shows that the iridium(III) center is exactly in the same plane. The dihedral angle between two naphthyl rings is 43.7°, so there should be no distinct conjugation between two naphthyl rings. This is also supported by the long C(9)−C(11) bond distance [1.516(3) Å], which is quite close to the value of normal C−C single bond (1.54 Å). This chiral phosphine is first reported, which may have potential application as ligands for construction of a chiral catalyst or as an additive in stereoselective catalytic reactions.

While in the case of p-MeOC₆H₄C≡CH, the reaction resulted in the only product 14 (Scheme 9), which is similar to 13, but the regioselectivity of alkyne insertion is opposite to that in 13. Complexes 12−14 were fully characterized by spectroscopic analysis, and the structures of 12 and 14 were further confirmed by X-ray crystallography. Although complex 13 did not form crystal of high quality that is suitable for X-ray diffraction, its structure was supported by the consistent ¹H NMR data with the anion-exchanged complex 15e described below, whose structure was determined by X-ray diffraction.

The structure of 12 is shown in Figure 5 with selected bond lengths and angles, which shows that the iridium(III) center is exactly in the same plane. The dihedral angle between two naphthyl rings is 43.7°, so there should be no distinct conjugation between two naphthyl rings. This is also supported by the long C(9)−C(11) bond distance [1.516(3) Å], which is quite close to the value of normal C−C single bond (1.54 Å). This chiral phosphine is first reported, which may have potential application as ligands for construction of a chiral catalyst or as an additive in stereoselective catalytic reactions.

Figure 4. Thermal ellipsoid drawing of 11 showing the labeling scheme and 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are P(1)−C(1) 1.813(2), P(1)−C(13) 1.817(2), P(1)−C(21) 1.841(2), C(9)−C(11) 1.516(3), ∠C(1)−P(1)−C(13) 107.82(11), ∠C(1)−P(1)−C(21) 101.60(10), and ∠C(13)−P(1)−C(21) 100.76(10).

Scheme 7. Reaction of 8 with PMe₃

Scheme 8. Reaction of 3b with p-FC₆H₄C≡CH

Scheme 9. Reaction of 3b with p-MeOC₆H₄C≡CH
framework: one is a five-membered ring, and the other is a six-membered one; they share two adjacent atoms Ir(1) and C(35). For the five-membered ring, all five atoms in the ring are almost in the same plane. The corresponding bond lengths and angles in 12 are almost equal to those of its analogue obtained from the phenylacetylene insertion reaction of the five-membered cycloiridated complex Cp*IrClPh₄(η₂-C₆H₄H₂). In our previous work.⁵

The structure of 14 is shown in Figure 6 with selected bond lengths and angles. The iridium cationic center is coordinated by a η²-C₆H₄ bond, η¹-C₆H₄ double bond, one phosphorus atom P(1), and one metalated carbon atom C(36). The five-membered ring (Ir(1)−P(1)−C(34)−C(35)−C(36)) adopts a nonplanar “puckered” conformation. The Ir(1)−C(36) bond distance is 2.077(12) Å, which is shorter than two almost equal length ones 2.204(12) and 2.208(10) Å in Ir(1)(η²-C(18)=C(19)) unit and also shorter than those [2.269(4) and 2.281(5) Å] in double five-membered cycloiridated complex 4a. The Ir(1)−P(1) bond distance [2.286(3) Å] is shorter than [2.349(3) Å] in Cp*IrCl₂PPh₂(Naph)₂ (2a) but longer than that [2.2232(11) Å] in 4a. The η²-coordinated disubstituted alkene adopts a stable cis configuration, which might be ascribed to the steric factor.

Recently, some alkyne insertion reactions of five-membered cycloiridated complexes were studied in the presence of NaBAR₄, which presented 1,2-insertion mode or 1,1-insertion mode after the initial vinylidene rearrangement.⁶⁵ Thus, we have further investigated the reactivity of 3b with terminal aryl acetylenes and NaBAR₄. When a mixture of 3b with p-RC₆H₄C≡CH (R = H, MeO, or F) and NaBAR₄ in CH₂Cl₂ was stirred at room temperature for 30 min, a yellow-green crystal was obtained by recrystallization. X-ray diffraction studies disclosed the structures of 15a–c (Scheme 10). For PhC≡CH or p-MeOC₆H₄C≡CH, similar products (15a,b) were obtained with the same regioselectivity of alkyne insertion; however, for p-FC₆H₄C≡CH, the product 15c was formed with the opposite regioselectivity of alkyne insertion. The ¹H NMR spectra of 15b and 15c show the consistent peaks with those of 14 and 13, respectively, except the extra peaks for the protons on BAR₄ anion. The X-ray structure of 15c is depicted in Figure 7, and the crystal structures and crystallographic data for 15a and 15b are provided in the Supporting Information.

In the structure of 15c, the iridium cationic center is coordinated by a η²-C₆H₄ bond, η¹-C₆H₄ double bond, one phosphorus atom P(1), and one metalated carbon atom C(36). The Ir(1)−C(36) bond distance is 2.139(8) Å, slightly longer than the similar Ir(1)−C(36) bond distance [2.077(12) Å] in 14. Unlike those in 14, Ir(1)−C(35) and Ir(1)−C(42) bond distances [2.289(9) and 2.121(9) Å] in Ir(1)(η²-C(35)=C(42)) unit are not even, which might be due to the different steric effect on two carbon atoms, C(42) is bonded with two H atoms, whereas C(35) is bonded with two bulky aromatic groups. The Ir(1)−P(1) bond distance [2.286(2) Å] is almost equal to that [2.286(3) Å] in 14.

By careful analysis of the crystal structures of 13–15, we proposed a plausible pathway for the formation of them in Scheme 11. First, the chloride of 3b dissocitates to free up a coordinate space for aromatic alkyne and then generate a η²-alkyne complex B, which undergoes 1,2-alkyne insertion to give the seven-membered metallacycle C or C’. The most noteworthy thing is the different regioselectivity of the alkyne insertion in this step. For the simple phenylacetylene or the arylacetylene containing an electron-donating substituent (p-OMe), the aryl group is found on the carbon atom adjacent to the metal iridium in C, and the regioselectivity is the same as that found by Jin in the reaction of PhC≡CH with the similar five-membered cycloiridated aryl imine complex,⁵ also the
same as that reported by Davies in the reaction of PhC≡CH with the five-membered cycloiridated phenylpyrazole or imine complex. For the arylacetylene containing an electron-withdraw substituent (p-F), the terminal carbon atom is bonded to the metal in C', and the regioselectivity similar to this case was rarely observed. The above results indicate the dominance of electronic effects on the regioselectivity. Subsequently, this is followed by an intramolecular activation of the C–H bond on the adjacent α position of the other naphthyl ring to build a new five-membered metallacycle (D or D'). In the last step, reductive reduction occurs to give a disubstituted alkene, which subsequently coordinates to the metal center in η² mode and affords the final products 15a, b or 15c. Apparently, 1,2-alkyne insertion into the Ir–C(naphthyl) bond was more favored in these reactions than vinylidene rearrangement of alkyne, while the opposite preference was observed in the reaction of PhC≡CH with the five-membered cycloiridated complex Cp*IrClPPh₂(η¹-C₁₀H₆) in our previous work, we considered that an appropriate and activable C–H bond provided by the other naphthyl group on phosphine ligand is crucial.

Finally, we have studied the reactions of terminal aryl acetylenes with five-membered cyclorhodated phosphine complex (5b). When a mixture of 5b with p-RC₆H₄C≡CH (R = H, MeO, or F) in methanol was stirred at room temperature for 1–2 h, the corresponding red crystals 16a–c were obtained by recrystallization (Scheme 12). X-ray diffraction studies disclosed the structures of 16b,c, which are the six-membered cyclorhodated phosphine complexes, so the formation of 16a–c should occur through the initial vinylidene rearrangement to the corresponding phenylvinylidene intermediate followed by the 1,1-insertion of vinylidene ligand into the Rh–C(naphthyl) bond and Cl recoordination to metal center. It is noteworthy that products 16a–c did not undergo

Scheme 10. Reaction of 3b with p-RC₆H₄C≡CH (R = H, MeO, or F) in the Presence of NaBAF₄

Figure 7. Thermal ellipsoid drawing of 15c showing the labeling scheme and 50% probability ellipsoids; anion and hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are Ir(1)–P(1) 2.288(2), Ir(1)–C(11) 2.139(8), Ir(1)–C(35) 2.289(9), Ir(1)–C(42) 2.121(9), C(35)–C(42) 1.449(14), C(33)–C(35) 1.541(14), Ir(1)–Cp(centroid) 1.928, ∠C(35)–Ir(1)–C(42) 38.1(4), ∠C(35)–Ir(1)–P(1) 86.4(2), ∠P(1)–Ir(1)–C(11) 74.2(3), ∠C(42)–C(35)–C(36) 119.0(8), ∠C(42)–C(35)–C(33) 115.7(9), and ∠C(11)–Ir(1)–P(1)–C(13) 36.9(9).

Scheme 11. Plausible Pathway for the Formation of 15a–c (Anion Cl⁻ or BAf⁴⁻ is Omitted for Clarity)
the further intramolecular activation of the C–H bond on the α position of the other naphthyl group to build the second metallacycle. Besides, this result is also different with the reaction of the similar five-membered cyclorhodated phosphine complex Cp*RhClPPh$_2$(η$^2$-C$_6$H$_4$) with PhC≡CH, which mainly produced the corresponding seven-membered cyclometalated complex by means of 1,2-alkyne insertion. This difference shows that the substituents on phosphine may affect the alkyne insertion modes.

The X-ray structure of 16b is depicted in Figure 8, which shows that the rhodium(III) center is coordinated by a η$^1$ Cp*, one phosphorus atom P(1), one chlorine atom Cl(1), and one carbon atom C(21), which come from p-MeOC$_6$H$_4$C≡CH. For the six-membered ring Rh(1)–P(1)–C(12)–C(11)–C(20)–C(21), the five nonmetal atoms are almost in one plane, whereas the metal atom Rh(1) is 1.2797 Å away from the plane. The bond lengths Rh(1)–P(1), Rh(1)–Cl(1), and Rh(1)–C(21) [2.2941(11), 2.4183(11), and 2.064 Å] are in good agreement with those [2.2776(7), 2.4007(7), and 2.079(2) Å] in a five-membered cyclorhodated phosphine analogue Cp*RhClP(η$^1$-Xyl) reported by Carmona. Two aryl groups on alkene C(21)≡C(22) unit adopt a cis conformation, which is reflected by the minor torsion angle [2C(20)–C(21)–C(22)–C(23) = 9.4(7)°]. The crystal structure of 16c is similar to that of 16b, and the crystallographic data of 16c is provided in the Supporting Information.

| CONCLUSIONS |
| [Cp*IrCl$_2$]$_2$ and [Cp*RhCl$_2$]$_2$ show different cyclometalation reactivity with dinaphthyl phosphines (1a,b). For the former, the reactions give the corresponding double cyclometalated complexes [Cp*Ir(C$^p$P$^c$C)] (4a,b), while for the latter, the reactions afford the single cyclometalated complexes [Cp*RhCl(P$^c$C)] (5a,b). An intramolecular C–C coupling reaction in 4a is induced by CuCl$_2$ or I$_2$ to form the simple P-coordinated iodinum dihalide (7 or 8). The double cyclometalated complexes 4a,b show no reaction with terminal or internal aromatic alkynes, whereas the single cyclometalated complexes 3b and 5b present novel and different reactivity with terminal aromatic alkynes. For the former, competition between vinylidene rearrangement/1,1-insertion and 1,2-alkyne insertion into the Ir–C is observed with p-FC$_6$H$_4$C≡CH; an appropriate C–H bond provided by the other naphthyl ring could be readily activated by metal center, which may contribute to the pathway of 1,2-alkyne insertion, because we did not observe the similar process in the reaction of the single cyclooctadienyl complex Cp*IrClPPh$_2$(η$^2$-C$_6$H$_4$) with PhC≡CH or PhC≡CPh. In the presence of NaBAR$_2$, only η$^2$-alkene coordinated complexes 15a–c are obtained by means of 1,2-alkyne insertion followed by the further intramolecular transformation. The regioselectivity of insertion of alkynes with different electronic effects has also been tentatively studied, and the regioselectivity was found to depend on the exact alkyne used; terminal alkyne with electron-rich aromatic ring favored insertion with the aromatic ring next to the meal, whereas terminal alkyne with electron-poor aromatic ring favored insertion with the aromatic ring next to the naphthyl phosphate. For the cyclometalated rhodium complex 5b, the six-membered cyclometalated complexes 16a–c are formed by vinylidene rearrangement/1,1-insertion. In summary, these results show that both the activity of transition metals and steric and electronic effect of substituents on phosphine would affect the alkyne insertion modes and the subsequent structural transformation. |

| EXPERIMENTAL SECTION |
| General Considerations. All reactions were carried out under nitrogen using standard Schlenk and vacuum line techniques; however, the workup was carried out in air unless stated otherwise. All solvents were distilled from appropriate drying agents under nitrogen prior to use. $^1$H (400 MHz), $^13$C (100 MHz), and $^{31}$P (162 MHz) NMR spectra were recorded on a Bruker AV400 instrument at room temperature with CDCl$_3$ as the solvent. Chemical shifts were recorded in ppm, referenced to residual $^1$H and $^{13}$C signals of the nondeuterated CDCl$_3$ (δ 7.26 and 77.16) as internal standards or to the $^{31}$P signal of PPh$_3$ (δ = 5.65) as an external standard. Elemental analyses were performed on a PerkinElmer 240C analyzer. The starting materials [Cp*MCl$_2$]$_2$ (M = Ir, Rh) and terminal aromatic alkynes p-RC$_6$H$_4$C≡CH (R = H, MeO, or F) were purchased from Strem without further purification; the ligand di(α-naphthyl)phenylphosphine (1a) was prepared by literature methods. |

**Synthesis of tert-ButylI(d(α-naphthyl)-phenylphosphine (1b).** A solution of 1-bromonaphthalene (1.04 g, 5.0 mmol) in diethyl ether (5 mL) was slowly added
over a period of 10 min to a solution of n-butyllithium (1.6 M solution in n-hexane) (3.2 mL, 5.0 mmol) in diethyl ether (5 mL) at -78 °C. After allowing the reaction mixture to stir for 30 min at room temperature, a solution of tert-butylchloro-
phosphine (0.40 g, 2.5 mmol) in diethyl ether (5 mL) was added dropwise to the above 1-naphthyl lithium solution. The resulting solution was heated under reflux for 3 h, then allowed to come to room temperature. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a mixture of petrol ether/ethyl acetate as the eluent.

**General Procedures for the Reactions of [CpIrCl2]** with Phosphines (1a,b) in the Absence of Sodium Acetate. A mixture of [Cp*IrCl2] (40 mg, 0.05 mmol) and phosphine (2.0 equiv) in methanol (10 mL) was stirred for 2 h at room temperature or under reflux. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with a mixture of petrol ether/ethyl acetate as the eluent. The products were recrystallized from n-hexane/CH2Cl2 (1:1) at -10 °C to afford 4a,b or 5a,b.

**Preparation of 7.** A solution of 4a (20 mg, 0.03 mmol) and anhydrous copper(II) chloride (2.0 equiv) in 5 mL of CH2Cl2 was stirred at RT for 2 h. After removal of the solvent, the residue was chromatographed on a silica gel column using petrol ether/ethyl acetate (1:1) as the eluent. The products were recrystallized from n-hexane/CH2Cl2 (1:1) at -10 °C to afford 4a,b or 5a,b.

**Synthesis of 6a,b.** A mixture of 5a or 5b (0.02 mmol) and excess BuOK in methanol (5 mL) was stirred for 5 min at room temperature. A light yellow precipitate was obtained, and then the solvent was removed and replaced with C6D6 for further NMR characterization.

**Preparation of 8.** A solution of 5a (30 mg, 0.11 mmol) and I2 (2.5 equiv) in 5 mL of CH2Cl2 was stirred at RT for 30 min. After removal of the solvent, the residue was chromatographed on a silica gel column using dichloromethane as the eluent. The product was recrystallized from n-hexane/CH2Cl2 at -10 °C to afford 7 as orange crystals (82%).

**Preparation of 9.** A solution of 8 (30 mg, 0.11 mmol) and PMe3 (5.0 equiv) in toluene (10 mL) was refluxed...
overnight. After removal of the solvent, the residue was chromatographed on a silica gel column using petrol ether and petrol ether/ethyl acetate (1:1) as the eluent. The first band (colorless) afforded 11 as a white solid (9% yield). The second band (yellow) gave product 10 as an orange solid (90% yield). The product 11 was recrystallized from n-hexane/CH2Cl2 at −10 °C to afford 15a–c as yellow-green crystals. 15a, (80% yield). 1H NMR: δ 8.03 (t, J = 7.4 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.70 (s, 8H), 7.64 (d, J = 10.3 Hz, 2H), 7.58–7.54 (m, 2H), 7.51 (s, 4H), 7.40–7.32 (m, 3H), 7.16 (t, J = 8.1 Hz, 1H), 6.82 (dd, J = 16.2, 8.2 Hz, 2H), 6.47 (t, J = 7.9 Hz, 2H), 5.84 (t, J = 6.8 Hz, 3H), 5.10 (d, J = 10.7 Hz, 1H), 4.45 (d, J = 10.6 Hz, 1H), 1.41 (s, 15H, Cp*), 1.17 (d, J = 16.4 Hz, 9H, CH3). 13C NMR: δ 132.6, 132.1, 131.8 (overlap), 131.6, 131.4, 131.2, 130.6, 129.6, 129.4, 129.0, 128.8, 128.7, 128.4, 106.5, 104.4, 32.1, 29.9, 8.9. 31P NMR: δ 48.6. Anal. Calcd for C26H26BF4IrP: C, 54.9; H, 3.39. Found: C, 54.55; H, 3.34.
15b, (82% yield). 1H NMR: δ 8.02 (t, J = 7.4 Hz, 1H), 7.87 (dd, J = 8.2, 1.6 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.71 (s, 8H), 7.66 (dd, J = 7.6, 3.7 Hz, 2H), 7.59–7.54 (m, 1H), 7.52 (s, 4H), 7.42–7.30 (m, 2H), 7.18–7.11 (m, 1H), 6.86 (t, J = 7.7 Hz, 1H), 6.42 (dd, J = 12.3, 6.9 Hz, 1H), 6.02 (d, J = 8.9 Hz, 2H), 5.84 (d, J = 7.4 Hz, 1H), 5.77 (d, J = 8.4 Hz, 2H), 5.04 (d, J = 10.8 Hz, 1H), 4.48 (d, J = 10.8 Hz, 1H), 3.50 (s, 3H, CH3), 1.41 (d, J = 1.2 Hz, 15H, Cp*), 1.17 (d, J = 16.4 Hz, 9H, CH3).
13C NMR: δ 162.6, 162.1, 161.6, 161.1, 159.1, 146.5, 146.3, 138.6, 135.0, 134.2, 133.4, 133.6, 133.4 (overlap), 133.3, 133.2, 132.7, 132.6, 132.1, 131.9, 131.1, 130.5, 131.2, 129.4, 129.2 (overlap), 128.9 (overlap), 128.8, 128.4, 110.3, 101.4, 58.5, 38.0, 37.7, 29.8, 8.6. 31P NMR: δ 48.2. Anal. Calcd for C26H26BF4IrP: C, 54.13; H, 3.45. Found: C, 53.96; H, 3.33.
15c, (87% yield). 1H NMR: δ 8.03 (t, J = 7.7 Hz, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.1 Hz, 1H), 7.70 (s, 8H), 7.65 (d, J = 7.5 Hz, 2H), 7.51 (s, 4H), 7.39–7.34 (m, 2H), 7.19–7.14 (m, 1H), 6.87 (t, J = 7.7 Hz, 1H), 6.42 (dd, J = 12.2, 7.3 Hz, 1H), 6.17 (t, J = 8.6 Hz, 2H), 5.88–5.77 (m, 3H), 5.06 (d, J = 10.8 Hz, 1H), 4.40 (d, J = 10.7 Hz, 1H), 1.40 (d, J = 1.2 Hz, 15H, Cp*), 1.16 (d, J = 16.5 Hz, 9H, CH3). 31P NMR: δ 48.5. Anal. Calcd for C26H26BF4IrP: C, 53.80; H, 3.29. Found: C, 53.62; H, 3.57.

General Procedures for the Insertion Reactions of Alkynes into the Ir–C Bond of 3b. A mixture of 3b (15 mg, 0.02 mmol) and alkyne (4.0 equiv) in methanol (5 mL) was stirred for 1 h at room temperature. The solvent was then removed under vacuum, and the residue was chromatographed on a silica gel column with petrol ether or methanol as the eluent. The products were recrystallized from n-hexane/CH2Cl2 at −10 °C to afford 15a–c as yellow-green crystals.
The authors declare no competing financial interest.

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