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Inorganica Chimica Acta 357 (2004) 3064–3070
Inorganica Chimica Acta
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Phosphorus–carbon bond formation via reactions of triphenylphosphine with acetylene and pentamethylcyclopentadienyl coordinated to iridium(III) ☆

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Received 31 December 2003; accepted 6 January 2004
Available online 6 February 2004

Abstract

Phosphorus–carbon bond is formed via: (i) the apparent HC≡CH insertion into Ir–P bond to produce Ir–CH=CH–PPh_3 group and (ii) the activation of the ring-methyl group of the coordinated Cp^* ($C_5Me_5^-$) to produce Ir(η^5-$C_5Me_4CH_2$–PPh_3) group from reactions of iridium(III)–Cp^* complexes, $[Cp^*IrL_3]^{n+}$ ($n = 1, 2$); $Cp^* = C_5Me_5^-$; $L_3 = Cl(PPh_3)_2$ (**3**), $(CH_3CN)_3$ (**5**). The following new P–C bond containing iridium(III) complexes have been prepared: $[Cp^*Ir(–CH=CH–PPh_3)Cl(PPh_3)]^+$ (**4**) from **3** with HC≡CH; $[Ir(\eta^5\text{-}C_5Me_4CH_2–PPh_3)(H)(PPh_3)_2]^{2+}$ (**6**) from **5** with PPh_3; $[Cp^*Ir(–CH=CH–PPh_3)_2(PPh_3)]^{2+}$ (**7**) from **5** with HC≡CH and PPh_3; $[Ir(\eta^5\text{-}C_5Me_4CH_2–PPh_3)(–CH=CH–PPh_3)Cl(PPh_3)]^{2+}$ (**8**) from $[Ir(\eta^5\text{-}C_5Me_4CH_2–PPh_3)(Cl)(PPh_3)_2]^{2+}$ (**6-Cl**) with HC≡CH; $[Ir(\eta^5\text{-}C_5Me_3(1,3\text{-}CH_2–PPh_3)_2(H)(PPh_3)_2)]^{3+}$ (**10**) from $[Ir(\eta^5\text{-}C_5Me_4CH_2–PPh_3)(NCCH_3)_2(PPh_3)]^{3+}$ (**9**) with PPh_3; $[Ir(\eta^5\text{-}C_5Me_4CH_2–PPh_3)(–CH=CH–PPh_3)_2(PPh_3)]^{3+}$ (**11**) from **9** with HC≡CH and PPh_3.

Keywords: P–C bond formation; Phosphorous ylides; Alkyne insertion into Ir–P bond; Activation of the ring-methyl group of Cp^* ($Cp^* = C_5Me_5^-$); Iridium(III)

1. Introduction

Transition metal mediated phosphorus–carbon bond formation reactions could be more useful ones in synthetic organic chemistry than those in the absence of designed organometallic complexes since enhanced stereo- and regio-selectivity could be obtained from reactions mediated by those metal complexes. Reactions of PPh_3 and hydrocarbyl groups coordinated to metal have been known to form P–C bond to give saturated and unsaturated phosphorus ylides C–PPh_3 [1,2].

Activation of the ring-methyl group of Cp^* ($Cp^* = C_5Me_5^-$) coordinated to metal has been investigated to introduce various functional groups to Cp^* so that one can use these functionalized Cp^* ligands to prepare sterically and electronically more diverse metal complexes [3]. A variety of groups have been successfully introduced to replace the hydrogen of the ring-methyl of Cp^* coordinated to metal [3,4]. No report, to the best of our knowledge, has been made on P–C bond formation between the ring-methyl carbon of the coordinated Cp^* and phosphine to give phosphorus ylides ($C_5Me_4CH_2$–PR_3) via direct reaction of tertiary phosphine with coordinated Cp^* while Ru(η^5-C_5Me_4-CH_2–PPh_3) was prepared from reaction of Ru(η^5-$C_5Me_4CH_2Cl$) with PPh_3/PF_6^- [5].

During our investigation on carbon-carbon bond formation via reactions of alkynes with iridium, we found that phosphorus–carbon bond is readily obtained by the apparent insertion of alkynes into the Ir–PR_3 bond to produce phosphorus ylide C–PR_3, which actually occurs by the attack of PR_3 on the coordinated alkynes [2]. We recently reported carbon-hetero atom

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.01.001.

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doi:10.1016/j.ica.2004.01.001

bond formation via reactions of an η^5-Cp* ($C_5Me_5^-$) complex of iridium(III) (Eq. (1)) [2c] while somewhat extensive studies for C–P bond formation have been done with iridium complexes containing $(PPh_3)_2(CO)$ unit [2a,2b,2d,2e]. We now wish to report new P–C bond formed via reactions of iridium complexes of η^5-Cp*, i.e., reactions of PPh_3 with HC≡CH and the CH_3 groups of Cp* coordinated to iridium(III).

$$[\underset{\mathbf{1}}{\text{LnIr–NCCH}_3}]^+ \overset{\text{HC}\equiv\text{CH,B}}{\underset{-\text{CH}_3\text{CN}}{\rightarrow}} [\underset{\mathbf{2}}{\text{LnIr–CH}{=}\text{CH–B}}]^+ \quad (1)$$

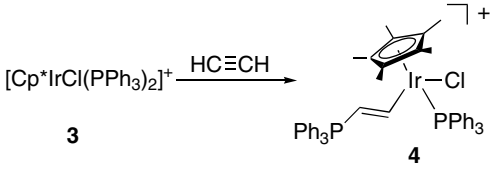
where Ln = (η^3-$CH_2CHCHPh$)(η^5-Cp*); B = NEt_3 (**a**), PPh_3 (**b**), $AsPPh_3$ (**c**).

2. Results and discussion

Reactions of $Cp^*Ir^{III}L_3$ ($L_3 = Cl(PPh_3)_2$, $(CH_3CN)_3$, etc.) complexes with PPh_3 in the absence and presence of HC≡CH produce new compounds with newly formed P–C (Ph_3***P–C***) bonds. The formation of **6** (Eq. (3)) is somewhat surprising while that of **4** (Eq. (2)) is not so unusual since we recently reported the related complexes, **2** (see Eq. (1)) [2] but the attack of a tertiary phosphine on the ring-methyl carbon of coordinated Cp* to form *C–P*Ph_3 bond (Eq. (3)) has not been previously reported.

The apparent insertion of HC≡CH into Ir–P bond (Eq. (2)) is understood, as previously suggested [2,6], by the following steps: (i) initial dissociation of one PPh_3 from **3** to provide a vacant site, (ii) coordination of HC≡CH to the vacant site and (iii) attack of PPh_3 on the carbon of the coordinated HC≡CH to form the Ir–CH=CH–PPh_3 moiety. The reaction (Eq. (2)) is significantly retarded by the excess of PPh_3.

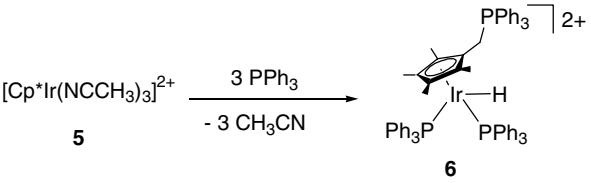
Metal complexes of Cp* undergo a variety of reactions in the presence of strong bases for the substitution of the hydrogen of the ring-methyl group to produce η^5-$C_5Me_4CH_2$–A (A = PR_2, NR_2, R, OR, CHO, X and, etc.) [3–5]. Metal complexes of η^4- and η^6-tetramethylfulvene ($C_5Me_4{=}CH_2$) have been observed and suggested as the intermediates produced by deprotonation of the ring-methyl group of Cp* in the presence of strong bases [3–7].



3 **4** (2)

The activation of the ring-methyl group of Cp* in **3** (Eq. (3)) does not occur from the reaction of **3** with excess PPh_3 in the presence or absence of HC≡CH. Replacing the three ligands, $Cl(PPh_3)_2$ of **3** with $(CH_3CN)_3$ makes the ring-methyl group of Cp*in **5** reactive with PPh_3. The lability of CH_3CN ligand of **5** seems to make the transfer of the ring-methyl hydrogen to the metal to provide a vacant site for the hydrogen to form the Ir–H bond.

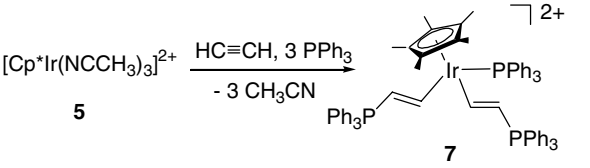
The hydrogen transfer from the ring-methyl group of Cp* to Ir (Eq. (3)) may occur in the intra-molecular fashion as shown in Scheme 1 as it is not likely to occur for the proton once dissociated from the methyl group to transfer to iridium(III) in its higher oxidation state while the deprotonation of the Cp* to give the tetramethylfulvene Ir($C_5Me_4{=}CH_2$) intermediate could not be completely excluded. The presumably weak interaction between the metal and one of the methyl hydrogen would become stronger by the nucleophilic attack of PPh_3 on the methyl carbon and the C–H bond would be eventually cleaved to give *Ir–H* and *C–P*Ph_3 bonds in **6** (Scheme 1).



5 **6** (3)

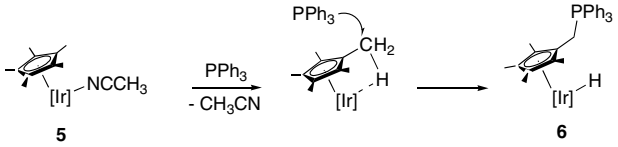
The hydride ligand of **6** is readily replaced with chloro ligand to give **6-Cl** [($C_5Me_4(CH_2$–$PPh_3)$)$Ir(Cl)(PPh_3)_2]^{2+}$ (see Fig. 1 for the crystal structure of **6-Cl**) in chlorinated solvents such as $CHCl_3$ and $PhCH_2Cl$.

Under the atmosphere of HC≡CH, complex **5** surprisingly undergoes the apparent HC≡CH insertion into two Ir–PPh_3 bonds to give complex **7** (Eq. (4)). The formation of **7** (Eq. (4)) is also attributed to the lability of the CH_3CN ligand of **5** being readily substituted by HC≡CH and the nucleophilicity of PR_3 attacking on the coordinated HC≡CH. Varying amounts of PPh_3 in the reaction mixture of **5** and PPh_3 under 1 atm of HC≡CH does not give any other product than **7**.



5 **7** (4)

While the reaction of the hydrido complex **6** with HC≡CH gives unidentified complex(es), the chloro



5 **6**

[Ir] = $[IrL_2]^{2+}$ (L = CH_3CN (**5**), PPh_3 (**6**))

Scheme 1.

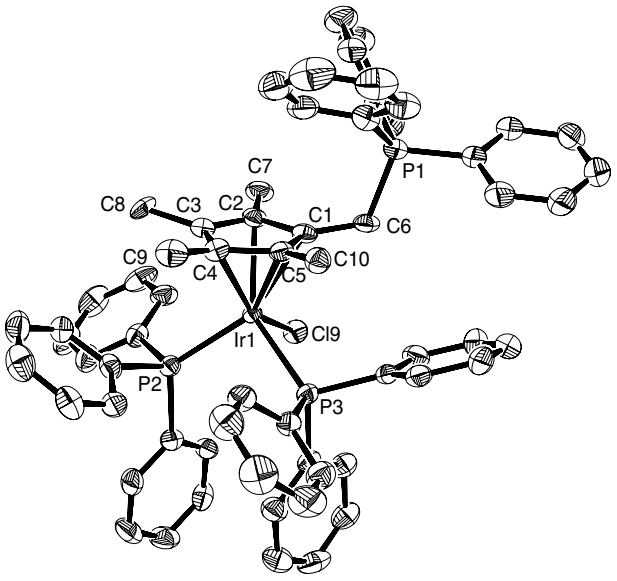
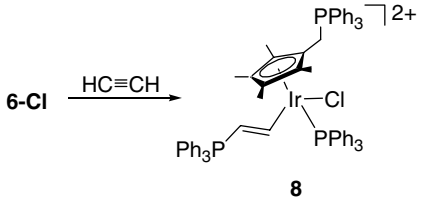


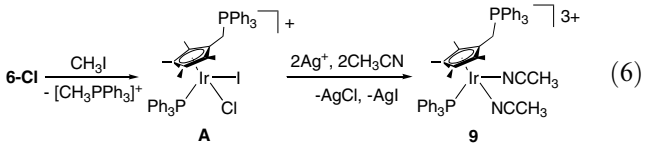
Fig. 1. ORTEP drawing of $[(\eta^5\text{-}C_4Me_4CH_2PPh_3)IrCl(PPh_3)_2](OTf)_2$ (**6**-Cl) with 50% thermal ellipsoids probability. Counter-anion (OTf) and hydrogen atoms are omitted for clarity. Selected bond distances (Å): $Ir_1–C_1 = 2.226(10)$; $Ir_1–C_2 = 2.278(10)$; $Ir_1–C_3 = 2.289(11)$; $Ir_1–C_4 = 2.258(11)$; $Ir_1–C_5 = 2.245(10)$; $C_1–C_2 = 1.471(14)$; $C_2–C_3 = 1.409(15)$; $C_3–C_4 = 1.429(16)$; $C_4–C_5 = 1.443(15)$; $C_1–C_5 = 1.423(14)$; $C_1–C_6 = 1.479(15)$; $C_2–C_7 = 1.494(15)$; $C_3–C_8 = 1.509(15)$; $C_4–C_9 = 1.494(16)$; $C_5–C_{10} = 1.511(14)$; $P_1–C_6 = 1.839(10)$. Selected bond angles (deg): $C_1C_6P_1 = 116.3(7)$; $C_6–C_1–Ir_1 = 127.9(7)$; $C_7–C_2–Ir_1 = 128.2(7)$; $C_8–C_3–Ir_1 = 133.6(8)$; $C_9–C_4–Ir_1 = 135.0(8)$; $C_{10}–C_5–Ir_1 = 132.0(7)$.

complex **6-Cl** ($[(C_5Me_4(CH_2–PPh_3))Ir(Cl)(PPh_3)_2]^{2+}$) reacts with HC≡CH to produce **8** which has both saturated ($–CH_2–PPh_3$) and unsaturated ($=CH–PPh_3$) phosphorus ylide groups (Eq. (5)). The formation of **8** (Eq. (5)) is significantly retarded by the presence of excess PPh_3 in the reaction mixture, which suggests the dissociation of PPh_3 from **6-Cl** occurring prior to the coordination of HC≡CH which is then attacked by PPh_3.

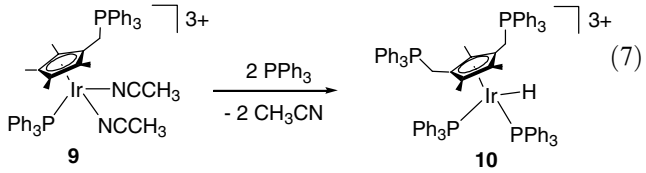


(5)

We have seen above that introducing labile ligand such as CH_3CN in place of non-labile ligand such as Cl^- and PPh_3 enhances the reactivity of these iridium complexes investigated in this study especially toward phosphines and HC≡CH to form new P–C bonds. In order to see further new P–C bond formation, complex **9** containing two CH_3CN ligands has been prepared from reaction of **6-Cl** according to Eq. (6).



(6)

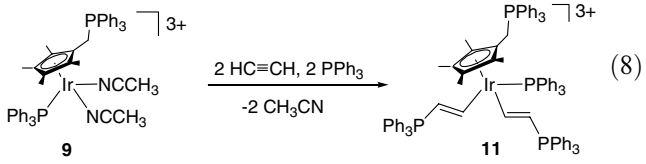


(7)

Another ring-methyl group of the coordinated η^5-$C_5Me_4(CH_2–PPh_3)$ in **9** is activated in the reaction of **9** with PPh_3 (in the absence of HC≡CH) to give the *hydrido*-1,3-di-ring-methyl group substituted Cp* complex **10** (Eq. (7)). Two different products have been reported from the double C–H activation of the ring-methyl group of Cp* coordinated to metal [8–10]. While the double C–H bond activation occurs at the 1 and 3 ring-methyl groups of Cp* in the reaction of $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ with $(C_6F_5)_2PCH_2CH_2–P(C_6F_5)_2$ to give $[\{\eta^5\text{-}C_5Me_4CH_2\text{-}C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}RhBr]^+$ [8], the double ring-metalation at the two neighboring methyl groups of Cp* has been reported for the reaction of Cp^*TaCl_4 with sodium amalgam in the presence of PMe_3 to give the 1,2-di-methyl group substituted Cp*complex, $\{\eta^5\text{-}C_5Me_3\text{-}1,2\text{-}(CH_2)_2\}Ta(H)_2(PMe_3)_2$ [9]. Both 1,2- and 1,3-ring-methyl group activation has been also observed for the Cp* in $[Cp^*RhCl(Ph_2PCH{=}CH_2)_2]^+$ from the reaction with potassium *tert*-butoxide to give $[\{\eta^5\text{-}C_5Me_3\text{-}1,2\text{-}[CH_2CH_2CH_2P(C_6H_5)_2]_2\}RhCl]^+$ and $[\{\eta^5\text{-}C_5Me_3\text{-}1,2\text{-}[CH_2CH_2CH_2P(C_6H_5)_2]_2\}RhCl]^+$ [10].

Again, the hydride (*Ir–H*) of **10** may come from the ring-methyl group of $C_5Me_4(CH_2–PPh_3)$ of **9** as suggested above for the formation of **6** (see Scheme 1).

Complex **9** undergoes the apparent HC≡CH insertion reaction into two $Ir–PPh_3$ bonds under the atmosphere of HC≡CH in the presence of PPh_3 to give **11** (Eq. (8)) that has three C–P bonds (one $Ir–CH{=}C–PPh_3$ and two $Ir(C_5Me_4–CH_2–PPh_3)$).



(8)

We have not been successful to prepare complexes containing more than three $C–PPh_3$ bonds probably due to the bulkiness of PPh_3.

New complexes, **4**, **6**–**11** have been unambiguously characterized by ^1H-, ^{13}C-, ^{31}P NMR, ^1H, ^{13}C-2D HECTOR, IR spectral and elemental analysis data analysis (see Section 3 for detailed assignments and Supplementary material), and also by X-ray diffraction

data analysis for the crystal structure of **6-Cl**. Spectral data analyses are mostly straightforward by comparing with those of related compounds from our recent studies as well as others [1,2].

These newly prepared complexes **4**, **6**–**11** in study are soluble in polar solvents such as $CHCl_2$, $CHCl_3$and CH_3COCH_3, stable in the solid state in air and in solution under N_2.

3. Experimental

3.1. General information

A standard vacuum system and Schlenk type glassware were used in handling metal complexes under N_2 although most of metal complexes seem to be stable.

The NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer for ^1H and 75 or 126 MHz for ^{13}C, and 81 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205. Elemental analysis was carried with a Carlo Erba EA1108 at the Organic Chemistry Center, Sogang University.

3.2. Synthesis

$Cp^*IrCl(PPh_3)_2$ (**3**) [3] and $[Cp^*Ir(NCMe)_3](OTf)_2$ (**5**) [11] were prepared by the literature methods.

3.2.1. Synthesis of $[Cp^*Ir(–CH{=}CH–P_aPh_3)Cl(P_b\text{-}Ph_3)]OTf$ (**4**)

A solution of **3** (0.10 g, 0.11 mmol) in CH_3COCH_3 (20 ml) was stirred under HC≡CH (1 atm) for 10 hours at 25 °C before diethyl ether (30 ml) was added to precipitate beige microcrystals, which were collected, washed with diethyl ether (3 × 10 ml) and dried in vacuum. The yield was 0.10 g and 98% based on **4**. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.3 (s, 15H, $C_5(CH_3)_5$), 6.9 (ddd, 1H, $J(H,P_a) = 34.0$ Hz, $J(H,H) = 17.0$ Hz, $J(H,P_b) = 1.5$ Hz, Ir–CH=C*H*–PPh_3), 9.9 (ddd, 1H, $J(H,P_a) = 29.0$ Hz, $J(H,H) = 17.0$ Hz, $J(H,P_b) = 8.0$ Hz, Ir–C*H*=CH–PPh_3). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 8.3 (s, $C_5(CH_3)_5$), 95.7 (s, $C_5(CH_3)_5$), 178.0 (dd, Ir–*C*H=CHPPh_3, $J(C,P_a) = 14.3$ Hz, $J(C,P_b) = 8.1$ Hz), 107.7 (d, Ir–CH=*C*HPPh_3, $J(C,P_a) = 71.0$ Hz). ^1H, ^{13}C-2D HETCOR (^1H (500 MHz) → ^{13}C (126 MHz)): δ 9.9 178.0; 6.9 → 107.7. ^{31}P NMR ($CDCl_3$, 81 MHz): δ 15.0 (d, $J(P_a,P_b) = 7.4$ Hz), 3.3 (d, $J(P_a,P_b) = 7.4$ Hz). IR (KBr, cm^{-1}): 1258, 1140 and 1026 (br. s, OTf). *Anal.* Calc. for $Ir_1P_2C_{49}H_{47}F_3O_3S_1Cl_1$: C, 62.74; H, 5.05; S, 3.42. Found: C, 62.65; H, 4.97; S, 3.34%.

3.2.2. Synthesis of $[Ir(\eta^5\text{-}C_5Me_4CH_2–P_aPh_3)(H)(P_bPh_3)_2](OTf)_2$ (**6**)

A reaction mixture of **5** (0.37 g, 0.50 mmol) and PPh_3 (0.52 g, 2.00 mmol) in CH_3CN (20 ml) was stirred under N_2 for 10 h at 25 °C and distilled under vacuum to obtain yellow solid which was recrystallized in chloroform/diethyl ether to obtain yellow microcrystals of **6**. The yield was 0.68 g and 97% based on **6**. ^1H NMR ($CDCl_3$, 500 MHz): δ −15.4 (td, 1H, $J(H,P_b) = 28.0$ Hz, $J(H,P_a) = 6.3$ Hz, Ir–*H*), 0.73 and 1.50 (both s, 12H, $C_5(CH_3)_4$), 3.70 (d, 2H, $J(H,P_a) = 11.0$ Hz, CH_2P_a). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 9.27 and 9.54 (s, $C_5(CH_3)_5$), 82.5, 101.6 and 104.7 (s, $C_5(CH_3)_5$), 23.0 (d, $J(C,P_a) = 47.0$ Hz, CH_2P_a). ^1H, ^{13}C-2D HETCOR (^1H (500 MHz) → ^{13}C (126 MHz)): δ 0.73 → 9.27; 1.50 → 9.54; 3.70 → 23.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 17.4 (t, P_a, $J(P_a,P_b) = 9.3$ Hz), 6.86 (d, P_b, $J(P_a,P_b) = 9.3$ Hz). IR (KBr, cm^{-1}): 1230, 1100 and 1039 (br s, OTf), 2172 (m, Ir–*H*). *Anal.* Calc. for $Ir_1P_3C_{66}H_{60}S_2F_6O_6$: C, 56.12; H, 4.28; S, 4.54. Found: C, 56.13; H, 4.43; S, 4.54%.

3.2.3. Synthesis of $[Ir(\eta^5\text{-}C_5Me_4CH_2–PPh_3)Cl(PPh_3)_2](OTf)_2$ (**6-Cl**)

A solution of **6** in $CHCl_3$ was stirred at 25 °C for 30 min under N_2 and distilled to obtain yellow microcrystals of **6-Cl**. ^1H NMR (CD_2Cl_2, 500 MHz): δ 0.62 and 1.11 (both s, 12H, $C_5(CH_3)_4$), 2.80 (d, 2H, $J(H,P) = 11.0$ Hz, CH_2P_a). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 11.6 (s, $C_5(CH_3)_5$), 82.5, 101.6 and 104.7 (s, $C_5(CH_3)_5$), 22.5 (d, $J(C,P_a) = 49.5$ Hz, CH_2P_a). ^1H, ^{13}C-2D HETCOR (^1H (500 MHz) → ^{13}C (126 MHz)): δ 0.62, 1.11 → 11.6; 2.80 → 22.5. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81 MHz): δ 18.3 (t, P_a, $J(P_a,P_b) = 11.6$ Hz), -11.7 (d, P_b, $J(P_a,P_b) = 11.6$ Hz). IR (KBr, cm^{-1}): 1230, 1100 and 1039 (br s, OTf). *Anal.* Calc. for $Ir_1P_3C_{66}H_{59}S_2F_6O_6Cl_1$: C, 54.79; H, 4.11; S, 4.43. Found: C, 54.53; H, 4.03; S, 4.63%.

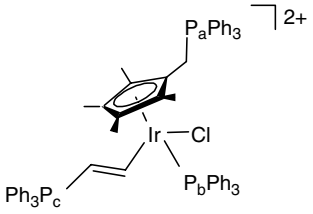
3.2.4. Synthesis of $[Cp^*Ir(–CH{=}CH–PPh_3)_2(PPh_3)](OTf)_2$ (**7**)

A 0.52 g (2.00 mmol) of $PPh_3$was added to a solution of **5** (0.37 g, 0.50 mmol) in CH_3COCH_3 (20 ml) under HC≡CH (1 atm) and the resulting solution was stirred for 10 h at 50 °C before diethyl ether (30 ml) was added to precipitate beige microcrystals which were collected, washed with diethyl ether (3 × 10 ml) and dried in vacuum. The yield was 0.71 g and 97% based on **7**. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.4 (s, 15H, $C_5(CH_3)_5$), 6.2 (dd, 2H, $J(H,P_a) = 29.5$ Hz, $J(H,H) = 17.7$ Hz, Ir–CH=C*H*PPh_3), 9.9 (ddd, 2H, $J(H,P_a) = 29.4$ Hz, $J(H,H) = 17.7$ Hz, $J(H,P_b) = 4.2$ Hz, Ir–C*H* = $CHPPh_3$). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 8.8 (s, $C_5(CH_3)_5$), 98.3 (s, $C_5(CH_3)_5$), 176.6 (dd, Ir–*C*H=$CHPPh_3$), 107.7 (d, Ir–CH=*C*HPPh_3, $J(C,P) = 72.4$ Hz). ^1H, ^{13}C-2D HETCOR (^1H (500 MHz) → ^{13}C (126 MHz)): δ 9.9 → 176.6; 6.2 → 107.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 23.0 (d, $J(P_a,P_b) = 2.0$ Hz, Ir–CH=CHP_aPh_3), 8.38 (t, $J(P_b,P_a) = 2.0$ Hz, Ir–P_bPh_3). IR (KBr, cm^{-1}): 1259, 1147 and 1026 (br. s, OTf). *Anal.* Calc. for

$Ir_1P_3C_{70}H_{64}F_6S_2O_6$: C, 57.41; H, 4.40; S, 4.38. Found: C, 57.53; H, 4.49; S, 4.41%.

3.3. Synthesis of $[Ir(\eta^5\text{-}C_5Me_4CH_2\text{–}PPh_3)(\text{–}CH{=}CH\text{–}PPh_3)Cl(PPh_3)](OTf)_2$ (**8**)

A solution of **6-Cl** (0.72 g, 0.50 mmol) in CH_3COCH_3 (20 ml) was stirred under HC≡CH (1 atm) for 10 h at 25 °C before diethyl ether (30 ml) was added to precipitate beige microcrystals, which were collected, washed with diethyl ether (3 × 10 ml) and dried in vacuum. The yield was 0.72 g and 98% based on **8**.

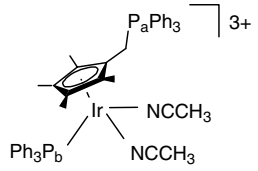


8

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.48 (d, 3H, J(H,P) = 2.5 Hz, $C_5(CH_3)_4$), 0.77 (d, 3H, J(H,P) = 2.0 Hz, $C_5(CH_3)_4$), 1.57 (d, 3H, J(H,P) = 3.5 Hz, $C_5(CH_3)_4$), 1.67 (s, 3H, J(H,P) = 2.5 Hz, $C_5(CH_3)_4$), 3.2 (dd, 1H, J(H,H′) = 15.5 Hz, J(H,P_a) = 12.0 Hz, CHH′P_a), 3.6 (dd, 1H, J(H,H′) = 15.5 Hz, J(H′,P_a) = 12.0 Hz, CH$H'P_a$) 6.9 (ddd, 1H, J(H,P_c) = 32.0 Hz, J(H,H) = 17.0 Hz, J(H,P_b) = 1.0 Hz, Ir–CH=C$H$$P_a$$Ph_3$), 10.1 (ddd, 1H, J(H,P) = 28.0 Hz, J(H,H) = 17.0 Hz, J(H,P_b) = 6.5 Hz, Ir–CH=CHPPh_3).^{13}C NMR ($CDCl_3$, 126 MHz): δ 7.81, 8.42, 8.51 and 8.80 (s, $C_5(CH_3)_5$), 75.2, 98.0, 102.1 and 122 (s, $C_5(CH_3)_5$), 22.0 (d, J(C,P_a) = 46.0 Hz, CH_2P_a), 109.5 (d, Ir–CH=CH$P_c$$Ph_3$, J(C,P_c) = 68.0 Hz), 174.1 (dd, J(C,P_c) = 11.0 Hz, J(C,P_b) = 9.0 Hz, Ir–CH=CH$P_c$$Ph_3$). ^{1}H, ^{13}C-2D HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 0.48 → 8.51; 0.77 → 8.80; 1.57 → 7.81; 1.67 8.42; 3.2, 3.6 → 22.0; 6.9 → 109.5; 10.1 → 174.1. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ 16.2 (d, J(P_a,P_b) = 4.3 Hz), 14.5 (d, J(P_c,P_b) = 6.7 Hz), 2.1 (dd, J(P_c,P_b) = 6.7 Hz, J(P_a,P_b) = 4.3 Hz). *Anal.* Calc. for $Ir_1P_3C_{68}H_{61}F_6S_2O_6Cl_1$: C, 55.45; H, 4.17; S, 4.35. Found: C, 55.40; H, 4.01; S, 4.26%.

3.3.1. Synthesis of $[Ir(\eta^5\text{-}C_5Me_4CH_2\text{–}PPh_3)(PPh_3)(NCCH_3)_2](OTf)_3$ (**9**)

A reaction mixture of **6-Cl** (0.72 g, 0.50 mmol) and CH_3I (0.041 ml, 0.66 mmol) in CH_3COCH_3 (20 ml) was stirred for 20 h under N_2 at 25 °C before the solvent was distilled under vacuum to dryness to obtain red solid. The solid was dissolved in CH_3CN (20 ml) of AgOTf (0.26 g, 1.0 mmol) and the reaction mixture was stirred for 15 min at 25 °C before white AgCl was removed by filtration. The yellow filtrate was distilled under vacuum to dryness. The yield was 0.66 g and 95% based on **9**.

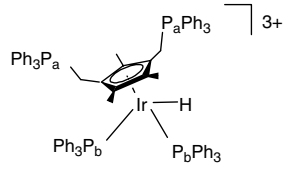


9

^{1}H NMR (CD_3COCD_3, 300 MHz): δ 1.2 (d, 6H, J(H,P_a) = 2.2 Hz, $C_5(CH_3)_4$), 1.5 (d, 6H, J(H,P_a) = 2.0 Hz, $C_5(CH_3)_4$), 2.7 (s, 6H, CH_3CN), 4.7 (d, 2H, J(H,P_a) = 14.2 Hz, CH_2P_a). ^{31}P{^{1}H} NMR (CD_3COCD_3, 81 MHz): δ 18.9 (d, J(P_a,P_b) = 0.18 Hz), 7.9 (d, J(P_a,P_b) = 0.18 Hz). IR (KBr, cm^{-1}): 1230, 1100 and 1039 (br s, OTf). *Anal.* Calc. for $Ir_1P_2C_{53}H_{50}N_2S_3F_9O_9$: C, 46.12; H, 3.65; S, 6.97. Found: C, 46.52; H, 3.74; S, 6.89%.

3.3.2. Synthesis of $[C_5(CH_3)_3(CH_2PPh_3)_2Ir(H)(PPh_3)_2](OTf)_3$ (**10**)

A reaction mixture of **9** (0.69 g, 0.50 mmol) and PPh_3 (0.52 g, 2.0 mmol) in CH_3COCH_3 (20 ml) was stirred for 1 day under N_2 at 25 °C. The filtrate was distilled under vacuum to obtain pale yellow powders, which were recrystallized in CH_3Cl/diethyl ether to obtain pale yellow microcrystals. The yellow filtrate was distilled under vacuum to dryness. The yield was 0.86 g and 94% based on **10**.

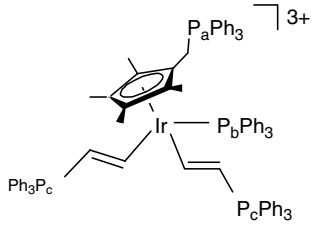


10

^{1}H NMR ($CDCl_3$, 500 MHz): δ −15.8 (tt, 1H, J(H,P_b) = 28.0 Hz, J(H,P_a) = 6.30 Hz, Ir–H), 0.56 (s, 3H, 2-CH_3 of $C_5(CH_3)_3$), 1.01 (s, 6H, 4- and 5-CH_3 of $C_5(CH_3)_3$), 3.60 (t, 2H, J(H,P_a) = 14.6 Hz, J(H,H′) = 14.6 Hz, CHH′P_a), 3.90 (t, 2H, J(H′,P_a) = 14.6 Hz, J(H,H′) = 14.6 Hz, CH$H'P_a$). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 9.60 (s, 4- and 5-CH_3 of $C_5(CH_3)_3$), 10.3 (s, 2-CH_3 of $C_5(CH_3)_3$), 88.5 and 104.5 (s, $C_5(CH_3)_5$), 23.9 (d, J(C,P_a) = 48.4 Hz, CH_2P_a). ^{1}H, ^{13}C-2D HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 0.56 10.3; 1.01 → 9.60; 3.6 and 3.9 → 23.9. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ 17.7 (t, J(P_a,P_b) = 5.2 Hz), 2.8 (t, J(P_a,P_b) = 5.2 Hz). IR (KBr, cm^{-1}): 1230, 1100 and 1039 (br s, OTf), 2172 (m, Ir–H). *Anal.* Calc. for $Ir_1P_4C_{85}H_{74}F_9S_3O_9$: C, 56.01; H, 4.09; S, 5.28. Found: C, 56.11; H, 4.12; S, 5.20%.

3.4. Synthesis of $[C_5(CH_3)_4CH_2PPh_3Ir(CH{=}CHPPh_3)_2(PPh_3)](OTf)_3$ (**11**)

A solution of **9** (0.69 g, 0.50 mmol) and PPh_3 (0.52 g, 2.0 mmol) in CH_3COCH_3 was stirred for 10 h under HC≡CH (1 atm) at 25 °C. The filtrate was distilled under vacuum to obtain pale yellow powders which were recrystallized in CH_3Cl/diethyl ether to obtain yellow microcrystals. The yield was 0.87 g and 93% based on **11**.



11

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.8 (d, 6H, $J(H,P_a) = 2.2$ Hz, $C_5(CH_3)_4$), 1.4 (d, 6H, $J(H,P_a) = 2.0$ Hz, $C_5(CH_3)_4$), 3.9 (d, 2H, $J(H,P_a) = 11.8$ Hz, CH_2P_a), 6.7 (ddd, 2H, $J(H,P_c) = 30.2$ Hz, $J(H,H) = 17.0$ Hz, $J(H,P_b) = 1.0$ Hz, Ir–CH=C*H*P$_c$Ph$_3$), 9.7 (ddd, 2H, $J(H,P_c) = 30.2$ Hz, $J(H,H) = 17.0$ Hz, $J(H,P_b) = 4.6$ Hz, Ir–C*H*=CHP$_c$Ph$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 18.2 (d, $J(P,P) = 7.3$ Hz), 16.7 (d, $J(P,P) = 5.6$ Hz), 7.1 (dd, $J(P,P) = 7.3$ Hz, $J(P,P) = 5.6$ Hz). IR (KBr, cm^{-1}): 1230, 1100 and 1039 (br s, OTf). *Anal.* Calc. for $Ir_1P_4C_{89}H_{78}O_9S_3F_9$: C, 57.01; H, 4.19; S, 5.13. Found: C, 57.13; H, 4.18; S, 5.14%.

3.4.1. X-ray structure determination of $[Ir(\eta^5\text{-}C_5Me_4CH_2{-}PPh_3)Cl(PPh_3)_2](OTf)_2$ (**6-Cl**)

Crystals of **6-Cl** were grown by slow evaporation from CH_2Cl_2/*n*-hexane solution. The crystal evaluation and data collection were performed on a Bruker CCD diffactometer with radiation Mo Kα ($\lambda = 0.71073$). Preliminary orientation matrix and cell constants were determined from three series of ω-scan at different starting angles. Each series consisted of 10 frames collected at intervals of 0.3° ω-scans with the exposure time 10 s per frame. The structure of this compound was solved by direct methods from the E-map (SHELXS-TL). Non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. Non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Details of crystallographic data collection are listed in Table 1. Bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters have been included in CIF format of Supplementary material.

Table 1
Details of crystallographic data collection for **6**-Cl

Chemical formula	$C_{66}H_{59}ClF_6IrO_6P_3S_2$
Formula weight	1354.06
Temperature (K)	293(2)
Crystal dimensions (mm)	$0.46 \times 0.44 \times 0.20$
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.483(2)
b (Å)	14.963(3)
c (Å)	23.657(5)
α (°)	85.964(3)
β (°)	86.241(3)
γ (°)	84.281(3)
V (Å^3)	4027.3(14)
Z (Mg/m^3)	3
ρ (calc) (g/cm^{-1})	1.802
μ (mm^{-1})	3.132
$F(000)$	2181
Radiation	Mo Kα
Wavelength	0.71073
2θ maximum (°)	51.1
hkl range	$-13 \leqslant h \leqslant 13$; $-18 \leqslant k \leqslant 18$; $-28 \leqslant l \leqslant 26$
Number of reflections	30 593
Number of unique data	14 887
Number of observed ($\lvert F_o\rvert > 2\sigma F_o$) data	14 887
Number of parameters	871
Scan type	$\omega/2\theta$ scan
R_1	0.0974
wR_2	0.2072
GOF	1.377

$R_1 = [\sum |F_o| - |F_c|/|F_o|]$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.
Weighting scheme: $w = 1/[\sigma^2 F_o^2 + (0.0573P)^2 + 44.3205P]$ where $P = (F_o^+ 2F_c^2)/3$.

4. Conclusion

Phosporus–carbon bond formation is achieved by the nucleophilic attack of PPh_3 on the carbon of the coordinated HC≡CH to iridium(III)-Cp* to produce Ir–CH=CH–PPh_3 groups and on the ring-methyl carbon of Cp* coordinated to iridium(III) to produce Ir(η^5-$C_5Me_4CH_2$–PPh_3) and Ir(η^5-C_5Me_3(1,3-CH_2–PPh_3)$_2$) groups. Replacement of non-labile ligands such as PPh_3 and Cl^- with labile ligand CH_3CN provides vacant sites for: (i) coordination of HC≡CH to the metal attracting the nucleophilic attack of PPh_3 on the coordinated HC≡CH to form Ir–CH=*C*H–*P*Ph_3 bond and (ii) for the hydrogen transferred from the ring-methyl group of the coordinated Cp* to produce the new Ir(C_5Me_4*C*H_2–*P*Ph_3) bond.

5. Supplementary material

Crystallopraphic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Center, CCDC No. 227514. Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallograhpic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) and ^{1}H NMR (for **4**, **6**, **6-Cl**, **7**, **8**, **10** and **11**), ^{13}C NMR (for **4**, **6**, **6-Cl**, **7** and **8**), ^{1}H, ^{13}C-2D HETCOR (for **4**, **6**, **6-Cl**, **7** and **8**), and ^{31}P NMR (for **4**, **6**, **6-Cl**, **7**, **8**, **10**, and **11**) data have been provided as PDF file.

Acknowledgements

Authors like to thank the Korea Research Foundation (Grant No. KRF-2003-015-C00332) for their financial support of this study.

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