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1,1-Insertion of substituted alkynes into the Ir–O bond of η^2-carboxylato iridium complexes

Chong Shik Chin *, Hyungeui Lee *, Myung Ki Lee, Soyoung Noh, Min-Sik Eum, Seunggweon Hong

Chemistry Department, Sogang University, 1 Shinsoo-dong, Mapo-gu, Seoul 121-742, Republic of Korea

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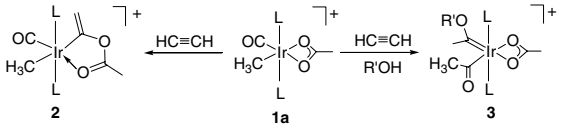
Abstract

Alkyl-carbonyl-iridium $[Ir(CH_3)(CO)(\eta^2\text{-}O_2CR')(PPh_3)_2]^+$ (**1**, R′ = CH_3, Ph, *p*-$C_6H_4CH_3$) react with alkynes (RC≡CH; R = Ph, *p*-$C_6H_4CH_3$) in the presence of NEt_3 to give acyl-alkynyl-iridium $Ir(C(=O)CH_3)(-C\equiv CR)(\eta^2\text{-}O_2CR')(PPh_3)_2$ (**4**) which further react with RC≡CH to give alkyl-carbonyl-*cis*-bis(alkynyl) iridium $Ir(CH_3)(CO)(C\equiv CR)_2(PPh_3)_2$ (**5**). *cis*-Bis(alkenyl)iridium complexes, $Ir(-CH=CH_2)_2(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (**6**) and $Ir(\text{-}CH=CHCH=CH)(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (**7**) react with substituted alkynes RC≡CH (R = Ph, *p*-$C_6H_4CH_3$, cyclohex-1-enyl) to give *cis*-bis(alkynyl) $Ir(C\equiv CR)_2(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (**9**) that further react with RC≡CH to undergo the alkyne insertion reaction into the Ir–O bond to produce iridacycles containing vinyl acetate ligands, $Ir(C(=CHR)OC(CH_3)=O)(-C\equiv CR)_2(PPh_3)_2$ (**8**).

Keywords: 1,1-Insertion; Iridium; Alkynes; Vinylidenes; M–C–O bond formation

1. Introduction

Reactions of transition metals with alkynes have been extensively investigated as they produce not only a variety of interesting organic compounds [1] but also metal-hydrocarbyls [2], such as metal-alkenyls, -alkynyls, -carbenes, and -vinylidenes which are reactive precursors as well as intermediates of various reactions. During our studies on reactions of iridium compounds with alkynes, we have isolated a variety of iridium hydrocarbyls that undergo various types of C–C bond forming reactions to produce interesting conjugated organic compounds [3]. We also found some interesting types of reactions such as 1,1-insertion of HC≡CH into the Ir–O bond of an acetato-iridium complex (**1a**) to form new Ir–C(=CH_2)-O– moiety (**2**) and alkyl migration to carbonyl ligand followed by formation of Ir=C(OR)CH_3 groups from reactions with HC≡CH and alcohols to produce acyl-alkoxycarbene complexes (**3**) (Eq. (1)) [4]. Reactions of **1** with substituted alkynes (RC≡CH), however, give somewhat different types of metal complexes with different types of hydrocarbyl ligands (see below).



(1)

We now wish to report new acyl-alkynyl-iridium from reactions of alkyl-carbonyl-iridium (**1**) with RC≡CH and *cis*-bis(alkynyl)-iridacycles containing vinyl acetate (–C(=CHR)-OC(CH_3)O–) ligand via 1,1-insertion of RC≡CH into Ir–O bond of η^2-carboxylato iridium complexes.

* Corresponding authors. Tel.: +82 2 705 8448; fax: +82 2 701 0967 (C.S. Chin), Tel.: +82 2 714 5915 (H. Lee).
E-mail addresses: cschin@sogang.ac.kr (C.S. Chin), hleegood@sogang.ac.kr (H. Lee).

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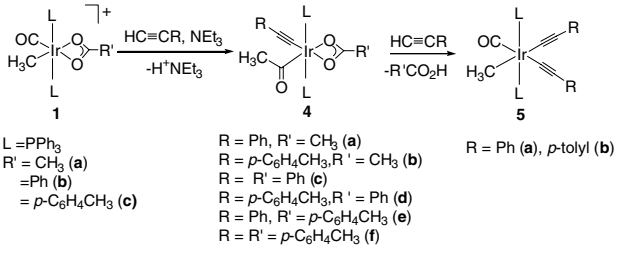
2. Results and discussion

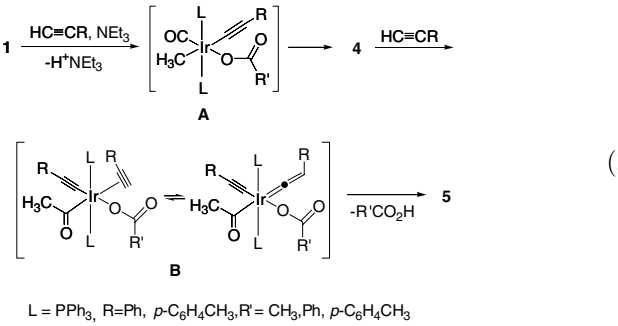
Unlike those reactions of HC≡CH in Eq. (1), reactions of **1** with substituted alkynes (RC≡CH: R = Ph, *p*-$C_6H_4CH_3$) give neither the insertion products (analogue of **2**) nor the carbene complexes (analogue of **3**) but a mixture of uncharacterized complexes. In the presence of NEt_3, however, acyl-alkynyl-iridium complexes (**4**) are obtained in high yields from reactions of **1** with RC≡CH (Eq. (2)). Formation of acyl-alkynyl iridium complexes **4** may be understood by the similar reaction pathway suggested for the formation of acyl-alkoxycarbene iridium complexes **3** [4] obtained from the reactions of **1a** with HC≡CH in the presence of ROH (R = CH_3, CH_2CH_3) (Eq. (1)).



(2)

Insertion of RC≡CH into the Ir–O bond of **1** has never been detected while the methyl group migration to the CO ligand (**1** → **4**) seems to readily occur as seen from reactions of **1** with HC≡CH in the presence of alcohol (**1a** → **3** in Eq. (1)). The crystal structure of complex **4f** (Fig. 1) shows Ir–O2 (2.526 Å) being much longer than Ir–O1 (2.142 Å) distance implying the lability of the Ir–O2 (*trans* to the acyl ligand) bond in **4**. Complexes **4** further react with another RC≡CH to give up the η^2-carboxylato ligands and take two alkynyl groups instead to give *cis*-bis(alkynyl) complexes **5** [5] (Eq. (2)).

Both the CH_3 ligand migration to the CO ligand (**1** → **4**) and the retro-migration of the CH_3 group of the acyl ligand to the metal (**4** → **5**) are possible probably due to the facile rearrangement of the carboxylato ligands from η^2- to η^1-bonding mode to provide an extra coordination site for incoming alkyne. Accordingly, η^1-carboxylato complexes **A** and **B** are suggested as the intermediates for the formation of **4** and **5**, respectively (Eq. (3)).



(3)

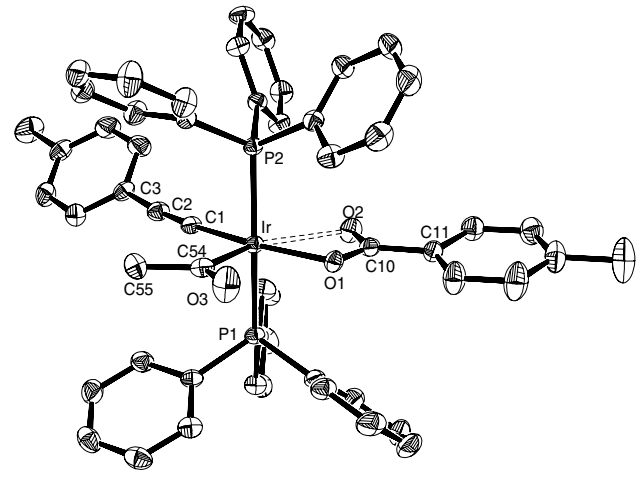
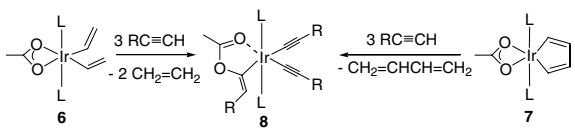


Fig. 1. ORTEP drawing of Ir(η^2-$O_2CC_6H_4CH_3$)(C≡$CC_6H_4CH_3$)-(C(=O)CH_3)(PPh_3)$_2$ (**4f**) with 50% thermal ellipsoids probability. Selected bond distances (Å): Ir–P_1 = 2.3410(8); Ir–P_2 = 2.3428(8); Ir–C_1 = 1.977(3), Ir–C_{54} = 1.996(3), Ir–O_1 = 2.124(2); Ir–O_2 = 2.526, O_1–C_{10} = 1.273(4), O_2–C_{10} = 1.266(4), O_3–C_{54} = 1.204(4), C_1–C_2 = 1.213(5), C_2–C_3 = 1.441(5), C_{10}–C_{11} = 1.488(5). Selected bond angles (°): C_1–Ir–C_{54} = 94.77(14); C_{54}–Ir–O_1 = 94.32(12), C_1–Ir–P_1 = 89.47(9), C_{54}–Ir–P_1 = 93.13(10), O_1–Ir–P_1 = 90.64(6), O_2–Ir–P_1 = 88.20(6), C_1–Ir–P_1 = 86.18(9), C_{54}–Ir–P_2 = 92.04(10), O_1–Ir–P_2 = 92.89(6), O_2–Ir–P_2 = 89.31(6), C_{10}–O_1–Ir = 101.65(19), C_{10}–O_2–Ir = 115.38(19), O_2–C_{10}–O_1 = 119.6(3).

It may be mentioned that the CH_3 ligand migration to the CO ligand has never been observed for related complexes, $[(OH_2)(OA)Ir(CH_3)(CO)(PPh_3)_2]^+$ containing the two labile O-ligands (OH_2 and OA ($OClO_3^-$, OTf^-)) that are *cis* to each other and *trans* to CH_3 and CO, respectively [6].

In order to see the insertion of substituted alkynes into the Ir–O bond, another types of η^2-acetato iridium complexes **6** and **7** have been investigated. Both complexes **6** and **7** have two Ir–C σ-bonds *cis* to each other and *trans* to the η^2-O_2CCH_3 ligand as do the complexes **1** that readily undergo the insertion reaction of the unsubstituted alkyne (HC≡CH) into the Ir–O bond (Eq. (1)). Complexes **6** and **7** readily undergo the 1,1-insertion reaction of substituted alkynes (RC≡CH) into the Ir–O bond to produce iridacycles (**8**) containing η^2-vinyl acetate (–C(=CHR)–OC–(CH_3)O–) ligands (Eq. (4)). Such 1,1-insertion of substituted terminal alkynes (HC≡CPh, HC≡CCO_2Me) into the M–O bond between the metal and η^2-carboxylato ligands has been previously reported for ruthenium [7] and osmium [7b] complexes to produce new M–C(=CHR)–O– units.

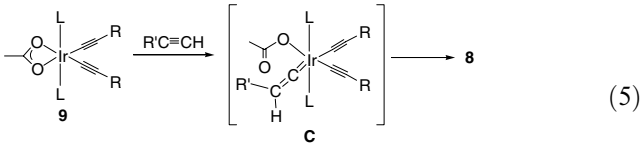


(4)

Reactions of **6** and **7** with two equivalent alkynes (RC≡CH), respectively give the same *cis*-bis(alkynyl)-η^2-acetato complexes ($Ir(-C{\equiv}CR)_2(\eta^2\text{-}O_2CR)(PPh_3)_2$, **9** in Eq. (5)) in high yields while no compound containing η^2-vinyl acetate ligands (–C(=CHR)OC(CH_3)O–) has been observed from reactions of complexes **6** and **7** with one equivalent RC≡CH.

It is interesting to notice that the η^2-carboxylato ligands of **1** are replaced by the two alkynyl groups leaving the two Ir–C bonds (***Ir–C***H_3 and ***Ir–C***O) intact (Eq. (2)) while the η^2-carboxylato ligands of **6** and **7** remain intact in the reactions with RC≡CH with the Ir–C bonds (two ***Ir–C***H=CH_2 or ***Ir-C***H=CHCH=***C***H) being replaced by two other Ir–C bonds (***Ir–C***≡CR) (Eq. (3)).

It has been also confirmed that complexes **9** further react with RC≡CH to give complexes **8**. It is most likely that the 1,1-insertion of RC≡CH into the Ir–O bond (Eq. (4)) occurs *via* the intramolecular C–O bond forming reaction between the oxygen atom of the acetato ligand and the α-carbon of the vinylidene ligand of the intermediate **C** as shown in Eq. (5). The two alkynyl ligands *cis* to each other in complexes **9** may allow the insertion of substituted alkynes (RC≡CH) into the Ir–O bond as they occupy smaller space in the immediate surroundings of the metal than do the two *cis* ligands, CH_3 and CO, of **1**. It may also be said that the two ethenyl groups of **6** and 1,3-butadien-1,4-diyl ligand of **7** are less favorable than the *cis*-bis(alkynyl) ligands in **9** for the insertion of substituted alkynes into the Ir–O bond due to steric reasons.



(5)

L = PPh_3
R = R' = C_6H_5 (**a**); R = R' = *p*-$C_6H_4CH_3$ (**b**); R = *p*-$C_6H_4CH_3$, R' = H (**c**)

New iridium complexes (**4**, **6**–**9**) are unambiguously identified by detailed spectral and elemental analysis data and crystal structure determination by X-ray diffraction data analysis for **4f** (see Section 3 and Supporting Information). Most assignments of spectral signals measured for **4** and **6**–**9** are unambiguously straightforward by comparing numerous data for related compounds previously reported [3,4,7–9].

In summary, we have observed (i) alkyl group migration to CO ligand to give *cis*-alkynyl-acyl-iridium complexes (**4**) from the reactions of *cis*-alkyl-carbonyl-iridium complexes with substituted alkynes, (ii) retro-migration of CH_3 group of the acyl ligands from further reactions of **4** with alkynes to produce alkyl-carbonyl-*cis*-bis(alkynyl) complexes (**5**) and (iii) 1,1-insertion of substituted alkynes into the Ir–O bond in η^2-acetato-bis(alkynyl) iridium complexes (**9**) to produce *cis*-bis(alkynyl)iridacycles (**8**) containing vinyl acetate ligands.

3. Experimental

3.1. General information

A standard vacuum system and Schlenk type glassware were used in most of the experiments in handling metal complexes although most of the compounds are stable enough to be handled in air.

NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer for ^{1}H, 75.4 or 126 MHz for ^{13}C and 81 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205. Elemental analyses were carried out with a Carlo Erba EA1108 at the Organic Chemistry Research Center, Sogang University.

3.2. Synthesis and reactions

$[Ir(CH_3)(CO)(\eta^2\text{-}O_2CR')(PPh_3)_2]OTf$ (**1**) were prepared by the literature method [4].

3.2.1. Synthesis of $Ir(C{\equiv}CR)(COCH_3)(\eta^2\text{-}O_2CR')(PPh_3)_2$ (**4**, R = Ph, R' = CH_3 (**a**), R = *p*-$C_6H_4CH_3$, R' = CH_3 (**b**), R = R' = Ph (**c**), R = *p*-$C_6H_4CH_3$, R' = Ph (**d**), R = Ph, R' = *p*-$C_6H_4CH_3$ (**e**), R = R' = *p*-$C_6H_4CH_3$ (**f**))

These complexes were prepared in the same manner as described below for **4a**. The reaction mixture of **1a** (0.11 g, 0.14 mmol) and PhC≡CH (0.017 mL, 0.14 mmol) in the presence of NEt_3 (0.020 mL, 0.14 mmol) was stirred at room temperature for 10 min. Addition of methanol (20 mL) to the $CHCl_3$ solution resulted in yellow microcrystals of **4a** which were collected by filtration, washed with methanol (3 × 20 mL), and dried under vacuum. The yield was 0.088 g and 98% based on of $Ir(C(=O)CH_3)(-C{\equiv}CC_6H_5)(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (**4a**).

$Ir(C(=O)CH_3)(-C{\equiv}CC_6H_5)(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (**4a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (t, *metha*-protons of Ir–C≡CC_6H_5, *J*(H–H) = 7 Hz, 2H), 6.94 (t, *para*-proton of Ir–C≡CC_6H_5, *J*(H–H) = 7 Hz, 1H) and 6.54 (d, Ir–C≡CC_6H_5, *ortho*-protons, *J*(HH) = 7.5 Hz, 2H), 1.50 (s, Ir–C(=O)CH_3, 3H), 0.56 (s, Ir–η^2–O_2CCH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.6 (t, Ir–*C*=O)CH_3, *J*(CP) = 4 Hz), 182.9 (s, Ir–η^2-O_2CCH_3), 131.0, 127.5 and 124.3 (both s, CH carbons of Ir–C≡CC_6H_5), 106.6 (s, Ir–C≡*C*C_6H_5), 76.0 (t, Ir–*C*≡CC_6H_5, *J*(CP) = 13 Hz), 36.7 (s, Ir–C(=O)*C*H_3), 22.4 (s, Ir–η^2-O_2CCH_3). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 1.50 → 36.7; 0.56 → 22.4. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 8.3 (s, Ir–*P*Ph_3). IR (KBr, cm^{-1}): 2113 (s, $\nu_{C\equiv C}$), 1634 (s, $\nu_{C=O}$). Anal. Calc. for $Ir_1P_2O_3C_{48}H_{41}$: C, 62.66; H, 4.49. Found: C, 62.63; H, 4.48.

$Ir(C(=O)CH_3)(-C{\equiv}C\text{-}p\text{-}C_6H_4CH_3)(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (**4b**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.45–6.85 (AB quartet with Δν/*J* = 23.2, Ir–C≡C-*p*-$C_6H_4CH_3$, 4H), 2.24

(s, Ir–C≡C-*p*-$C_6H_4CH_3$, 3H), 1.49 (s, Ir–C(=O)CH_3, 3H), 0.56 (s, Ir–η^2-O_2CCH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.0 (t, Ir–*C*(=O)CH_3), 182.6 (s, Ir–η^2-O_2CCH_3), 130.6 and 128.1 (both s, CH carbons of Ir–C≡C$C_6H_4CH_3$), 106.2 (s, Ir–C≡*C*-*p*-$C_6H_4CH_3$), 73.9 (t, Ir–*C*≡C-*p*-$C_6H_4CH_3$, *J*(CP) = 14 Hz), 36.5 (s, Ir–COCH_3), 22.2 (s, Ir–η^2-O_2CCH_3), 21.1 (s, Ir–C≡C-*p*-$C_6H_4CH_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 2.24 → 21.1; 1.49 → 36.5; 0.56 → 22.2. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 8.3 (s, Ir–*P*Ph_3). IR (KBr, cm^{-1}): 2114 (s, $\nu_{C\equiv C}$), 1634 (s, $\nu_{C=O}$). Anal. Calc. for $Ir_1P_2O_3C_{49}H_{43}$: C, 63.01; H, 4.64. Found: C, 63.00; H, 4.62.

Ir(C(=O)CH_3)(-C≡CC_6H_5)(η^2-$O_2CC_6H_5$)(PPh_3)$_2$ (**4c**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.08–6.61 (m, Ir–η^2-$O_2CC_6H_5$ and Ir–C≡CC_6H_5, 10H), 1.42 (s, Ir–C(=O)CH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 193.4 (t, Ir–*C*(=O)CH_3, *J*(CP) = 5 Hz), 177.8 (s, Ir–η^2-O_2CCH_3), 106.2 (s, Ir–C≡*C*C_6H_5), 75.6 (t, Ir–*C*≡CC_6H_5, *J*(CP) = 14 Hz), 36.9 (s, Ir–C(=O)*C*H_3). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 1.42 → 36.9. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 7.4 (s, Ir–*P*Ph_3). IR (KBr, cm^{-1}): 2113 (s, $\nu_{C\equiv C}$), 1636 (s, $\nu_{C=O}$). Anal. Calc. for $Ir_1P_2O_3C_{53}H_{43}$: C, 64.82; H, 4.41. Found: C, 64.79; H, 4.40.

Ir(C(=O)CH_3)(–C≡C-*p*-$C_6H_4CH_3$)(η^2-$O_2CC_6H_5$)-(PPh_3)$_2$ (**4d**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (t, *para*-proton of Ir–η^2-$O_2CC_6H_5$, *para*, *J*(HH) = 7 Hz, 1H), 7.06 (d, *ortho*-protons of Ir–η^2-$O_2CC_6H_5$, *J*(HH) = 7.5 Hz, 2H) and 6.93 (t, *metha*-protons of Ir-η^2-$O_2CC_6H_5$, *J*(HH) = 7.5 Hz, 2H), 6.56–6.86 (AB quartet with ν/J = 19.6, Ir–C≡C-*p*-$C_6H_4CH_3$, 4H), 2.27 (s, Ir–C≡C-*p*-$C_6H_4CH_3$, 3H), 1.43 (s, Ir–C(=O)CH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3 (t, Ir–*C*(=O)CH_3), 177.6 (s, Ir–η^2-$O_2CC_6H_5$), 130.7 and 128.1 (s, CH carbons of Ir–C≡C-*p*-$C_6H_4CH_3$), 130.3, 128.1 and 126.2 (s, CH carbons of Ir–C≡CC_6H_5), 105.7 (s, Ir–C≡*C*-*p*-$C_6H_4CH_3$), 73.4 (t, Ir–*C*≡C-*p*-$C_6H_4CH_3$), 36.7 (s, Ir–CO*C*H_3), 21.1 (s, Ir–C≡C-*p*-$C_6H_4CH_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 2.27 → 21.1; 1.43 → 36.7. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 7.5 (s, Ir–*P*Ph_3). IR (KBr, cm^{-1}): 2112 (s, $\nu_{C\equiv C}$), 1637 (s, $\nu_{C=O}$). Anal. Calc. for $Ir_1P_2O_3C_{54}H_{45}$: C, 65.11; H, 4.55. Found: C, 65.20; H, 4.49.

Ir(C(=O)CH_3)(–C≡CC_6H_5)(η^2-O_2C-*p*-$C_6H_4CH_3$)-(PPh_3)$_2$ (**4e**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (t, *metha*-protons of Ir–C≡CC_6H_5, *J*(HH) = 7 Hz, 2H) and 6.98 (d, *ortho*-proton of Ir–CCC_6H_5, *J*(HH) = 7.5 Hz, 2H), 6.64–6.74 (AB quartet with $\Delta\nu/J$ = 4.3, Ir–η^2-O_2C-*p*-$C_6H_4CH_3$, 4H), 2.20 (η^2-O_2C-*p*-$C_6H_4CH_3$), 1.45 (s, Ir–C(=O)CH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.4 (t, Ir–*C*(=O)CH_3, *J*(CP) = 5 Hz), 177.8 (s, Ir–η^2-O_2C-*p*-$C_6H_4CH_3$), 106.2 (s, Ir–C≡*C*C_6H_5), 75.6 (t, Ir–*C*≡CC_6H_5, *J*(CP) = 14 Hz), 36.9 (s, Ir–C(=O)*C*H_3), 21.5 (s, η^2-O_2C-*p*-$C_6H_4CH_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 2.20 → 21.5; 1.45 → 36.9. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 7.4 (s, Ir–*P*Ph_3). IR (KBr, cm^{-1}): 2111 (s, $\nu_{C\equiv C}$), 1637 (s, $\nu_{C=O}$). Anal. Calc. for $Ir_1P_2O_3C_{54}H_{45}$: C, 65.11; H, 4.55. Found: C, 65.11; H, 4.46.

Ir(C(=O)CH_3)(–C≡C-*p*-$C_6H_4CH_3$)(η^2-O_2C-*p*-C_6H_4-CH_3)(PPh_3)$_2$ (**4f**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97–6.55 (m, Ir–η^2-O_2C-*p*-$C_6H_4CH_3$ and Ir–C≡$CC_6H_4CH_3$, 8H), 2.29 (s, Ir–C≡$CC_6H_4CH_3$, 3H), 2.22 (η^2-O_2C-*p*-$C_6H_4CH_3$), 1.43 (s, Ir–C(=O)CH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.0 (t, Ir–C(=O)*C*H_3, *J*(CP) = 5 Hz), 178.0 (s, Ir–η^2-O_2C-*p*-$C_6H_4CH_3$), 130.7, 130.3, 128.1, 126.2 (s, CH carbons of Ir–C≡C-*p*-$C_6H_4CH_3$ and Ir–η^2-O_2C-*p*-$C_6H_4CH_3$), 105.8 (s, Ir–C≡*C*-*p*-$C_6H_4CH_3$), 73.9 (t, Ir–*C*≡C-*p*-$C_6H_4CH_3$, *J*(CP) = 13 Hz), 37.0 (s, Ir–C(=O)*C*H_3), 21.5 (η^2-O_2C-*p*-$C_6H_4CH_3$), 21.3 (s, Ir–C≡C-*p*-$C_6H_4CH_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 2.29 → 21.3; 2.22 → 21.5; 1.43 → 37.0. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 7.4 (s, Ir–*P*Ph_3). IR (KBr, cm^{-1}): 2112 (s, $\nu_{C\equiv C}$), 1637 (s, $\nu_{C=O}$). Anal. Calc. for $Ir_1P_2O_3C_{55}H_{47}$: C, 65.40; H, 4.69. Found: C, 65.36; H, 4.66.

3.2.2. Synthesis of *Ir(CH$_3$)(CO)(–C≡CR)$_2$(PPh$_3$)$_2$* (**5**, *R = Ph* (**a**), *p-C$_6$H$_4$CH$_3$* (**b**))

These complexes were prepared in the same manner as described below for **5b**. The reaction mixture of **4b** (0.11 g, 0.14 mmol) and *p*-tolyl-C≡CH (0.015 g, 0.15 mmol) was stirred at room temperature for 30 min. Acetic acid was removed with water by extraction (2 × 10 mL) and addition of methanol (20 mL) to the $CHCl_3$ solution resulted in yellow microcrystals of **5b** which were collected by filtration, washed with methanol (3 × 20 mL), and dried under vacuum. The yield was 0.11 g and 98% based on of Ir(CH_3)(CO)(C≡C-*p*-$C_6H_4CH_3$)$_2$(PPh_3)$_2$ (**5b**) [3c] which was identified by ^{1}H NMR and IR spectral measurement.

3.2.3. Preparation of *Ir(CH=CH$_2$)$_2$(η^2-O$_2$CCH$_3$)-(PPh$_3$)$_2$* (**6**)

A 0.1 g (0.1 mmol) of [Ir(CH=CH_2)$_2$($NCCH_3$)$_2$-(PPh_3)$_2$]OTf [3d] in $CHCl_3$ (10 mL) was stirred in the presence of CH_3CO_2Na (0.15 mmol) at 25 °C for 3 h before MeOH (30 mL) was added to precipitate beige micro-crystals which were collected by filtration, washed with *n*-pentane (3 × 10 mL) and dried under vacuum. The yield was 0.08 g and 98% based on Ir(CH=CH_2)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$ (**6**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36–7.50 (m, P(C_6H_5)$_3$, 30H), 7.22 (m, Ir–C*H*=CH_2, 2H), 4.94 (d, Ir–CH=$CH_{trans}H_{cis}$, *J*(HH) = 9.3 Hz, 2H), 4.88 (d, Ir–CH=CH_{trans}H$_{cis}$, *J*(HH) = 16.8 Hz, 2H), 0.91 (s, Ir–η^2-O_2CCH_3, 3H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 183.2 (s, Ir–η^2-O_2CCH_3), 124.7 (t, *J*(CP) = 9.5 Hz, Ir–*C*H=CH_2), 116.0 (br s, Ir–CH=*C*H_2), 24.0 (s, Ir–η^2-O_2CCH_3), 135.0, 130.2, 130.0 and 127.9 (P(C_6H_5)$_3$). ^{31}P{^{1}H}

NMR ($CDCl_3$, 81 MHz): δ 8.37 (s, *P*Ph_3). IR (KBr, cm^{-1}): 1553 (m, $\nu_{C=O}$), 1529 (m, $\nu_{C=C}$). Anal. Cald for $Ir_1P_2O_2C_{42}H_{39}$: C, 60.78; H, 4.74. Found: C, 60.76; H, 4.71.

3.2.4. Preparation of Ir(CH=CHCH=CH)(η^2-O_2CCH_3)-(PPh_3)$_2$ (7)

To a solution of [Ir(CH=CHCH=CH)($NCCH_3$)-(CO)(PPh_3)$_2$]OTF [9] (0.1 g, 0.1 mmol) in $CHCl_3$ (10 mL) were Me_3NO (0.019 g, 0.25 mmol) and CH_3CN (0.012 g, 0.3 mmol) added and the reaction mixture was stirred at 25 °C under N_2 for 30 min before the pale yellow solution turned light brown. Excess Me_3NO and NMe_3 were removed by extraction with H_2O (2×10 mL). A light brown solution of $CHCl_3$ was stirred in the presence of CH_3CO_2Na (0.15 mmol) at 25 °C for 3 h before MeOH (30 mL) was added to precipitate beige micro-crystals which were collected by filtration, washed with *n*-pentane (3×10 mL) and dried under vacuum. The yield was 0.097 g and 98% based on Ir(CH=CHCH=CH)(η^2-O_2CCH_3)(PPh_3)$_2$ (**7**). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.3–7.5 (m, P(C_6H_5)$_3$, 30H), 6.86 (m, Ir-C*H*=CHCH=C*H*, 2H), 5.63 (m, Ir-CH=C*H*CH=CH, 2H), 0.48 (s, Ir–η^2-O_2- CCH_3, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 183.5 (s, Ir–η^2-O_2CCH$_3$), 143.6 (s, Ir-CH=*C*HCH=CH), 132.9 (t, *J*(C-P) = 8.0 Hz, Ir-*C*H=CHCH=*C*H), 24.1 (s, Ir–η^2-O_2C*C*H$_3$), 135.05, 129.81, 129.79 and 127.48 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 0.48 → 24.1; 5.63 → 143.6; 6.86 → 132.9. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ 13.36 (s, *P*Ph_3). Anal. Calc. for $Ir_1P_2O_2C_{42}H_{37}$: C, 60.93; H, 4.50. Found: C, 60.90; H, 4.49.

3.2.5. Reactions of complexes 6 and 7 with excess RC≡CH: formation of Ir(-C(=CHR)OC(CH_3)=O)-(–C≡CR)$_2$(PPh_3)$_2$ (8)

Compounds **8** were prepared by the same method as described below for **8a**. A $CHCl_3$ (10 mL) solution of **6** (or **7**) (0.10 g, 0.1 mmol) and $C_6H_5C{\equiv}CH$ (0.033 g, 0.33 mmol) was stirred at 25 °C for 10 min before *n*-pentane (20 mL) was added to precipitate light yellow micro-crystals which were collected by filtration, washed with *n*-pentane (3×10 mL) and dried under vacuum. The yield was 0.11 g and 98% based on Ir(-C(=CHPh)OC(CH_3)=O)(–C ≡ CPh)$_2$(PPh_3)$_2$ (**8a**).

Ir(-C(=CHPh)OC(CH_3)=O)(–C ≡ C–C_6H_5)$_2$(PPh_3)$_2$ (**8a**). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.26–7.94 (m, P(C_6H_5)$_3$, 30H), 6.40–7.20 (m, Ir–C≡C–C_6H_5, 15H), 4.98 (br s, Ir-C(=*C*HPh)OC(CH_3)=O), 1.44 (s, Ir-C(=C*H*Ph)OC(CH_3)=O), 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.1 (s, Ir-C(=*C*HPh)OC(CH_3)=O), 172.3 (t, *J*(CP) = 10.4 Hz, Ir-C(=*C*HPh)OC(CH_3)=O), 137.7 and 130.0 (C_{ipso} carbons of C_6H_5), 131.2, 131.1, 129.9, 129.8, 128.5, 127.4, 126.3, 124.6, 124.2, and 124.0 (CH carbons of C_6H_5), 121.4 (t, *J*(CP) = 3.1 Hz, Ir-C(=*C*HPh)OC(CH_3)=O), 114.8 (t, *J*(CP) = 1.9 Hz) and 100.8 (t, *J*(CP) = 2.5 Hz) (Ir–C≡*C*Ph), 98.5 (t, *J*(CP) = 14.6 Hz) and 68.8 (t, *J*(CP) = 14.2 Hz) (Ir–*C*≡CPh), 16.9 (s, Ir-C(=CHPh)OC(*C*H_3)=O), 135.3, 130.5, 130.2 and 127.6 (P(C_6H_5)). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 1.44 → 16.9; 4.98 → 121.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ −0.79 (s, *P*Ph_3). IR (KBr, cm^{-1}): 2127 and 2111 (s, $\nu_{C{\equiv}C}$), 1631 (s, $\nu_{C=O}$), 1604 (s, $\nu_{C=C}$). Anal. Calc. for $Ir_1P_2O_2C_{62}H_{49}$: C, 68.94; H, 4.57. Found: C, 68.91; H, 4.54.

Ir(–C(=CH-*p*-$C_6H_4CH_3$)OC(CH_3)=O)(–C≡C-*p*-$C_6H_4CH_3$)$_2$(PPh_3)$_2$ (**8b**). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.26–7.95 (m, P(C_6H_5)$_3$, 30H), 6.29–7.01 (m, Ir–C≡C-*p*-$C_6H_4CH_3$, 12H), 4.97 (br s, Ir-C(=C*H*-*p*-$C_6H_4CH_3$)OC(CH_3)=O), 2.35, 2.31 and 2.26 (s, Ir-C(=CH-*p*-$C_6H_4CH_3$)OC(CH_3)=O and Ir–C≡C-*p*-$C_6H_4CH_3$, 9H), 1.40 (s, Ir-C(=CH-*p*-$C_6H_4CH_3$)OC(C*H*$_3$)=O, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.9 (s, Ir-C(=CH-*p*-$C_6H_4CH_3$)O*C*(CH_3)=O), 171.1 (t, *J*(CP) = 10.7 Hz, Ir-*C*(=CH-*p*-$C_6H_4CH_3$)OC(CH_3)=O), 131.0, 130.9, 128.5, 128.4, 128.3, and 128.1 (CH carbons of *p*-$C_6H_4CH_3$), 135.2, 135.1, 133.9, 133.6, 133.5 and 127.2 (C_{ipso} of $C_6H_4CH_3$), 121.4 (t, *J*(CP) = 2.5 Hz, Ir-C(=*C*H-*p*-$C_6H_4CH_3$)OC(CH_3)=O), 114.5 (s) and 100.4 (t, *J*(CP) = 2.3 Hz) (Ir–C≡*C*-*p*-$C_6H_4CH_3$), 97.2 (t, *J*(CP) = 14.6 Hz) and 67.0 (t, *J*(CP) = 14.1 Hz) (Ir–*C*≡C-*p*-$C_6H_4CH_3$), 21.44 and 21.40 (both s, Ir–C≡C-*p*-C_6H_4CH$_3$ and Ir-C(=CH-*p*-C_6H_4CH$_3$)OC(CH_3)=O, 16.8 Ir-C(=CH-*p*-$C_6H_4CH_3$)OC(*C*H_3)=O, 135.4, 130.2, 129.8, and 127.6 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 1.40 → 16.8; 2.35 and 2.31 → 21.44; 2.26 → 21.40; 4.97 → 121.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ −1.00 (s, *P*Ph_3). IR (KBr, cm^{-1}): 2123 and 2109 (s, $\nu_{C{\equiv}C}$), 1636 (s, $\nu_{C=O}$), 1593 (s, $\nu_{C=C}$). Anal. Calc. for $Ir_1P_2O_2C_{65}H_{55}$: C, 69.56; H, 4.94. Found: C, 69.51; H, 4.90.

3.2.6. Reactions of Ir(–CH=CH_2)$_2$(η^2-O_2CCH_3)-(PPh_3)$_2$ (6) with two equivalent RC≡CH: Formation of Ir(–C≡CR)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$ (9, R = Ph (a), p-tolyl (b), cyclohex-1-enyl (c)) and ethylene (CH_2=CH_2)

These compounds were prepared by the same method as described below for **9a**. A $CHCl_3$ (10 mL) solution of **6** (0.10 g, 0.1 mmol) and $C_6H_5C{\equiv}CH$ (0.020 g, 0.20 mmol) was stirred at 25 °C for 10 min before *n*-pentane (20 mL) was added to precipitate light yellow micro-crystals which were collected by filtration, washed with *n*-pentane (3×10 mL) and dried under vacuum. The yield was 0.11 g and 98% based on Ir(–C≡C–C_6H_5)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$ (**9a**).

Ir(–C≡CC_6H_5)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$ (**9a**). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.18–7.77 (m, P(C_6H_5)$_3$, 30H), 6.84–6.93 (m, *metha*- and *para*-protons of C≡CC_6H_5, 6H), 6.14 (d, *ortho*-protons of C≡CC_6H_5, 4H), 0.62 (s, Ir–η^2-O_2CCH_3, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 188.1 (s, Ir–η^2-O_2CCH$_3$), 131.3, 126.9 and 124.2 (s,

CH carbons of Ir–C≡CC_6H_5), 128.8 (s, *ipso*-carbons of Ir–C≡CC_6H_5), 103.9 (s, Ir–C≡*C*), 60.8 (t, *J*(C–P) = 13.0 Hz, Ir–*C*≡C), 23.3 (s, Ir–η^2-O_2CCH_3), 135.2, 130.2, 130.0 and 127.9 ($P(C_6H_5)_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 6.91 → 126.9; 6.86 → 124.2; 6.14 → 131.3; 0.62 → 23.3. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 10.43 (s, *P*Ph_3). IR (KBr, cm^{-1}): 2118.4 (s, C≡C). Anal. Calc. for $Ir_1P_2O_2C_{54}H_{43}$: C, 66.31; H, 4.43. Found: C, 66.25; H, 4.38.

Ir(–C≡C-*p*-$C_6H_4CH_3$)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$ (**9b**). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.20–7.77 (m, $P(C_6H_5)_3$, 30H), 6.04–6.74 (AB quartet, Ir–C≡C–$C_6H_4CH_3$, Δ*v*/*J* = 42.7, $J(H_A–H_B)$ = 8.0 Hz, 8H), 2.21 (s, $C_6H_4CH_3$, 6H), 0.62 (s, Ir–η^2-O_2CCH_3, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 188.0 (s, Ir–η^2-O_2CCH_3), 133.7 and 129.5 (both s, C_{ipso} of Ir–C≡C-*p*-$C_6H_4CH_3$), 131.1 and 127.7 (both s, CH carbons of Ir–C≡C-*p*-$C_6H_4CH_3$), 103.6 (s, Ir–C≡*C*-*p*-$C_6H_4CH_3$), 58.9 (t, *J*(C–P) = 10.1 Hz, Ir–*C*≡C-*p*-$C_6H_4CH_3$), 23.3 (s, Ir–η^2-O_2CCH_3), 21.0 (s, Ir–C≡C-*p*-$C_6H_4CH_3$), 135.2, 130.1, 129.1 and 127.8. ($P(C_6H_5)_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 6.73 → 127.7; 6.05 → 131.1; 2.21 → 21.0; 0.62 → 23.3. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 10.43 (s, *P*Ph_3). IR (KBr, cm^{-1}): 2119.8 (s, $\nu_{C\equiv C}$). Anal. Calc. for $Ir_1P_2O_2C_{56}H_{47}$: C, 66.85; H, 4.71. Found: C, 66.88; H, 4.76.

Ir(-C≡C-C=CH$(CH_2)_3$CH$_2$)(η^2-O_2CCH_3)(PPh_3)$_2$ (**9c**). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.11–7.86 (m, $P(C_6H_5)_3$, 30H), 4.56 (s, Ir-C≡C-C=C*H*$(CH_2)_3$CH$_2$, 2H), 0.54 (s, Ir–η^2-O_2CCH_3, 3H) 1.14–1.90 (m, Ir-C≡C-C=CH$(CH_2)_3$C*H*$_2$, 16H). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 9.82 (s, *P*Ph_3). Anal. Calc. for $Ir_1P_2O_2C_{54}H_{51}$: C, 65.77; H, 5.21. Found: C, 65.79; H, 5.28.

3.2.7. Reactions of Ir(–C≡Cp-tolyl)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$ (**9b**) with HC≡CH: formation of Ir(O=C(CH_3)-O-C=CH_2)(–C≡C-p-tolyl)$_2$(PPh_3)$_2$ (**8c**)

A 0.1 g (0.1 mmol) of **9b** in $CHCl_3$ (10 mL) was stirred under HC≡CH (1 atm) at 25 °C. Within 30 min, beige micro-crystals were precipitated and were collected by filtration, washed with *n*-pentane (3 × 10 mL) and dried under vacuum. The yield was 0.11 g and 98% based on Ir(C(=CH$_2$)-OC(CH_3)=O)(–C≡C-$C_6H_4CH_3$)$_2$(PPh_3)$_2$ (**8c**). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30–8.10 (m, $P(C_6H_5)_3$, 30H), 6.26–6.92 (m, Ir–C≡C–$C_6H_4CH_3$, 8H), 5.02 (d, *J*(HH) = 1.5 Hz) and 4.18 (d, *J*(HH) = 1.5 Hz) (Ir-C(=C*H*$_2$)-O-C(CH_3)=O, 2H), 2.29 and 2.24 (s, $C_6H_4CH_3$, 6H), 1.15 (s, Ir-C(=CH$_2$)-OC(C*H*$_3$)=O, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 180.1 (s, Ir-C(=CH$_2$)-O*C*(CH_3)=O), 175.0 (t, *J*(CP) = 10.6 Hz, Ir-*C*(=CH$_2$)-OC(CH_3)=O), 113.0 and 101.4 (s, Ir–C≡*C*-*p*-$C_6H_4CH_3$), 107.7 (s, Ir-C(=*C*H$_2$)-OC(CH_3)=O), 96.1 (t, *J*(CP) = 15.0 Hz) and 65.2 (t, *J*(CP) = 14.3 Hz) (Ir–*C*≡C-*p*-$C_6H_4CH_3$), 20.9 (s, Ir–C≡C-*p*-$C_6H_4CH_3$), 15.7 (s, Ir-C(=CH$_2$)-OC(*C*H$_3$)=O), 130.4, 130.3, 127.9 and 127.6 (s, CH carbons of Ir–C≡C-*p*-$C_6H_4CH_3$), 133.0, 132.9.5, 131.9 and 131.8 (s, C_{ipso} of Ir–C≡C-*p*-$C_6H_4CH_3$), 134.8, 130.3, 129.3 and 127.1. ($P(C_6H_5)_3$). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ −3.33 (s, *P*Ph_3). IR (KBr, cm^{-1}): 2122.3 and 2107.8 (s, $\nu_{C\equiv C}$). Anal. Calc. for $Ir_1P_2O_2C_{58}H_{49}$: C, 67.49; H, 4.78. Found: C, 67.47; H, 4.79.

3.3. X-ray structure determination of Ir(C(=O)CH_3)(–CC-p-$C_6H_4CH_3$)(η^2-O_2C-p-$C_6H_4CH_3$)(PPh_3)$_2$ (**4f**)

Crystals of **4f** were grown by slow evaporation from $CHCl_3$ solution. Preliminary examination and data collection were performed using a Bruker SMART CCD Detector single crystal X-Ray diffractometer using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) source equipped with a sealed tube X-ray source at −100 °C for **4f**. Preliminary unit cell

Table 1
Details of crystallographic data collection for **4f**

	4f
Chemical formula	$C_{55}H_{47}IrO_3P_2$
Chemical formula weight	1010.14
Temperature (K)	173(2)
Crystal dimension (mm)	0.30 × 0.28 × 0.10
Crystal system	Triclinic
Space group	$P\bar{1}$
Color of crystal	Yellow
Unit cell dimensions	
a (Å)	9.9059(7)
b (Å)	11.9810(9)
c (Å)	20.9544(16)
α (°)	94.4990(10)
β (°)	90.6670(10)
γ (°)	98.2910(10)
V (Å^3)	2452.7(3)
Z	2
$\rho_{(calc)}$ (g cm^{-1})	1.529
μ (mm^{-1})	2.995
F(000)	1132
Radiation	Mo Kα
Wavelength	0.71069
θ Range (°)	1.72–28.28
hkl Range	$-11 \leqslant h \leqslant 13$
	$-15 \leqslant k \leqslant 7$
	$-26 \leqslant l \leqslant 27$
No. of reflections	15301
No. of unique data	11015
No. of observed ($\|F_o\| > \sigma F_o$) data	9861
No. of parameters	589
Scan type	π and ω scan
R_1	0.0355
wR_2	0.0759
Goodness-of-fit	1.048

$R_1 = [\sum|F_o| - |F_c|/|F_o|]$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.
weighting_scheme
$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 1.8667P]$, where $P = (F_o^2 + 2F_c^2)/3$.

constants were determined with a set of 45 narrow frames (0.3 in ω) scans. A data set collected consists of 1286 frames of intensity data collected with a frame width of 0.3 in ω and counting time of 10 s/frame at a crystal to detector distance of 5.0 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages (Bruker Analytical X-ray, Madison, WI, 1997) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of 5225 reflections ($2.3 < \theta < 28.2$). Collected data were corrected for absorbance using SADABS based upon the Laue symmetry using equivalent reflections. Crystal data and intensity data collection parameters are listed in Table 1. Structure solution and refinement of the structure were carried out using the SHELXTL-PLUS (5.03) software package (Sheldrick, G.M., Siemens Analytical X-Ray Division, Madison, WI, 1997). The structure was solved by direct method and refined successfully in the space group P-1. Full-matrix least-squares refinement was carried out by minimizing $(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were treated using appropriate riding model. 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 the tables of Supplementary material.

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Appendix A. Supplementary material

Crystallopraphic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 237800. 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, ^{13}C NMR and HETCOR (^{1}H–^{13}C) spectra data of complexes **4f**, **6**, **7**, **8a**, **8c** and **9a** have been provided as PDF file. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.11.040.

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[5] *cis*-Bis (alkynyl) iridium complexes $Ir(C{\equiv}CR)_2(CH_3)(CO)(PPh_3)_2$ (**5**) have been also synthesized by other method in our laboratory (see [3c]).

[6] Unpublished results. $[(OH_2)(OClO_3)Ir(CH_3)(CO)(PPh_3)_2]^+$ was previously reported C.S. Chin, M. Lee, M. Oh, G. Won, Y.J. Park, M. Kim. Organometallics 19 (2000) 1572, and $[(OH_2)(OTf)Ir(CH_3)(CO)(PPh_3)_2]^+$ is readily prepared by replacing $OClO_3^-$ with OTf^-.

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