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Journal of Organometallic Chemistry 602 (2000) 144–150

Journal of Organometallic Chemistry

π-Allyliridium(I) complexes, $Ir(\eta^3\text{-}CH_2CHCHAr)(CO)(PPh_3)_2$ (Ar = Ph, C_6H_4Me-*p*, C_6H_4Br-*p*). Comparison of their structures and chemical properties with analogous Rh complexes

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Received 13 December 1999; received in revised form 7 February 2000; accepted 15 February 2000

Abstract

Arylallenes such as (4-methylphenyl)allene, phenylallene, and (4-bromophenyl)allene react with $IrH(CO)(PPh_3)_3$ to give the π-allyliridium(I) complexes, $Ir(\eta^3\text{-}CH_2CHCHAr)(CO)(PPh_3)_2$ (Ar = C_6H_4Me-*p*, Ph, and C_6H_4Br-*p*). Crystallographic studies of the complexes showed a similar coordination geometry to that of $Rh(\eta^3\text{-}CH_2CHCHX)(CO)(PPh_3)_2$. An equimolar reaction of phenylacetylene with $Ir(\eta^3\text{-}CH_2CHCHC_6H_4Me\text{-}p)(CO)(PPh_3)_2$ gives a mixture of *trans*-$Ir(C{\equiv}CPh)(CO)(PPh_3)_2$ and *trans*,*trans*-$IrH(C{\equiv}CPh)_2(CO)(PPh_3)_2$ accompanied by the liberation of 1-(4-methylphenyl)-1-propene. The Ir(III) acetylide complex is obtained separately from the reaction of excess phenylacetylene with the π-allyliridium(I) complex. The respective square-planar and octahedral structures of these complexes are determined by X-ray and NMR analyses. The NMR spectra of the reaction mixture indicate concurrent formation of the Ir(I) and Ir(III) complexes having the phenylethynyl ligands.

Keywords: Iridium; Allene; π-Allyl complex; Insertion; Alkynyl complex

1. Introduction

π-Allyl iridium complexes [1–6] were regarded as stable and less reactive than the π-allyl complexes of 1st and 2nd row late transition metals such as Ni, Pd, Fe, Ru, and Co which play important roles in various C–C bond forming reactions, as well as polymerization and oligomerization of alkenes and dienes via π-allyl intermediates. Recent reports on unique reactivity of the π-allyliridium complexes toward nucleophiles [7,8] as well as an efficient allyl alkylation using an Ir catalyst [9] have reinforced attention to the properties of π-allyliridium complexes.

One of the convenient methods to prepare π-allyliridium complexes is the reaction of diene with hydridoiridium complexes leading to the insertion of a double bond into the Ir–H bond [10]. In the course of study of Rh complex promoted oligomerization and polymerization of arylallenes [11], we found insertion of allene to hydridorhodium complexes to afford several π-allyl rhodium complexes which served as initiators of the polymerization of arylallenes and their copolymerization with CO. As depicted in Scheme 1(i), the reaction of excess phenylallene with $RhH(PPh_3)_4$ gives the complex containing a tetramer of arylallene as the π-allyl ligand (**A**) [11d]. Complex **A** is the sole product even in the equimolar reaction. The complex $Rh(\eta^3\text{-}CH_2CHCHPh)(PPh_3)_2$ seems to be formed in the reaction but is not observed in the reaction mixture probably because it undergoes rapid further insertion of phenylallene into the Rh–π-allyl bond. On the other hand, an equimolar reaction of phenylallene with $RhH(CO)(PPh_3)_3$ affords the product of insertion of a single molecule of phenylallene into the Rh–H bond, $Rh(\eta^3\text{-}CH_2CHCHPh)(CO)(PPh_3)_2$ (**B**), in a high yield (ii) [12]. Complex **B** with an 18 electron configuration is stable enough to be isolated, but it reacts with an excess amount of phenylallene to cause elimination of the carbonyl ligand and insertion of three phenylallene molecules into the Rh–π-allyl bond to give **A** together with **B** (Scheme 1(iii)). Chemistry of the

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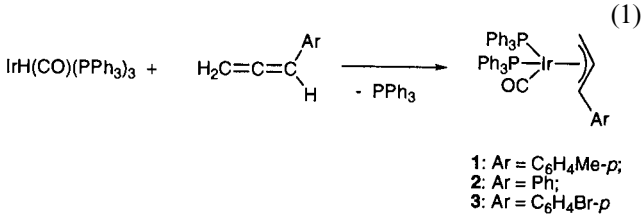
0022-328X/00/$ - see front matter
PII: S0022-328X(00)00142-X

above insertion of allene into the M–H and M–C bond and of the resulting π-allyl complexes of other transition metals is of a significant interest from the viewpoint of its relevance to the mechanism of late transition metal complex catalyzed polymerization and oligomerization of allenes, dienes and other unsaturated molecules. In this paper we report structure and reactions of π-allyliridum complexes and the comparison of their properties with those of analogous Rh complexes.

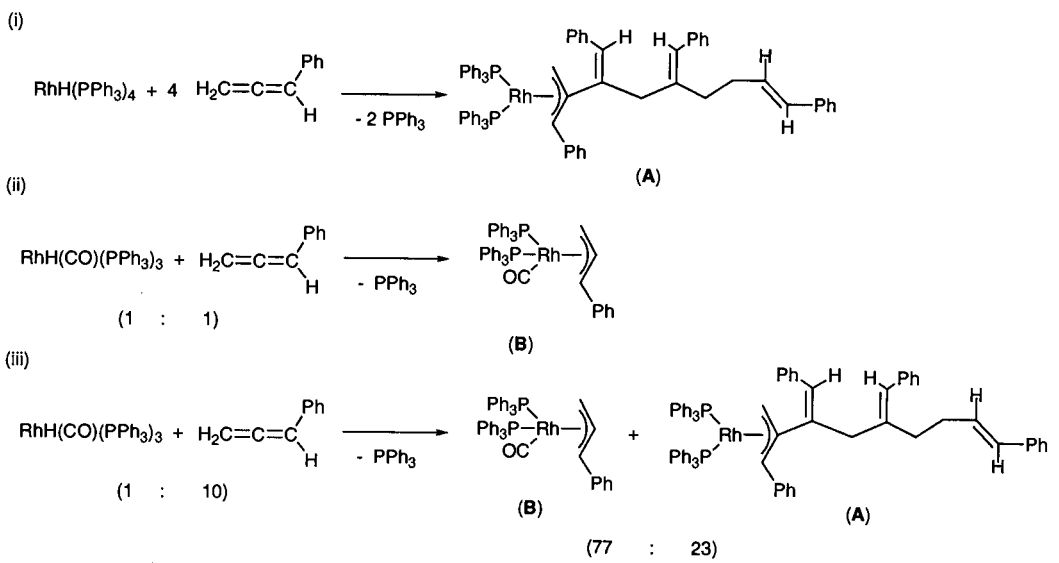
2. Results and discussion

The reaction of arylallenes such as (4-methylphenyl)allene, phenylallene, and (4-bromophenylallene) with $IrH(CO)(PPh_3)_3$ leads to the insertion of a double bond of the substrate into the Ir–H bond to give π-allylirdium(I) complexes $Ir(\eta^3\text{-}CH_2CHCHAr)(CO)(PPh_3)_2$ (**1**: Ar = C_6H_4Me-*p*, **2**: Ar = Ph, **3**: Ar = C_6H_4Br-*p*) as shown in Eq. (1). The insertion proceeds smoothly at room temperature (r.t.) similarly to the already reported reaction of the unsubstituted allene [10] and shows no significant difference in the reaction rate from the reaction with $RhH(CO)(PPh_3)_3$. Fig. 1 depicts ORTEP drawings of **1** and **3** whose crystals are isomorphous to each other and also to $Rh(\eta^3\text{-}CH_2CHCHC_6H_4Me\text{-}p)(CO)(PPh_3)_2$ [12]. The angles of coordination bonds (Table 1) resemble among these three Rh and Ir complexes. Since the angles, made up of the bonds, Ir–P1, Ir–P2, Ir–C1, and Ir–C3 fall in the range, 96–119°, the structure of the complexes is represented as a somewhat distorted tetrahedral composed of the four ligands around the Ir center or a piano-stool type coordination having the π-allyl ligand at the top.

(1)



The NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra of **1**–**3** in solutions provided information about the structures in solution. The $^{13}C\{^1H\}$-NMR spectrum of **1** contains three signals δ 67.8, 55.5, and 29.8 which are assigned to CH(–Ar), CH, and CH_2 carbons of the π-allyl ligand, respectively, based on its comparison with the gated decoupled spectrum ($^1J(CH) = 150–173$ Hz) and



Scheme 1.

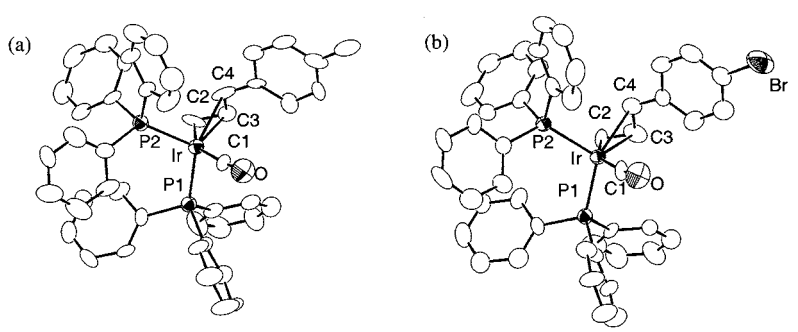


Fig. 1. ORTEP drawings of (a) **1** and (b) **3** at 30% ellipsoidal levels.

Table 1
Selected bond distances (Å) and angles (°) of **1** and **3**

	1	**3**	Rh complex [a]
Bond distances			
Ir–P1	2.299(4)	2.295(6)	2.318(2)
Ir–P2	2.365(5)	2.367(6)	2.443(2)
Ir–C1	1.86(2)	1.82(2)	1.839(8)
C1–O1	1.15(2)	1.19(3)	1.163(8)
Ir–C2	2.18(2)	2.24(2)	2.199(8)
Ir–C3	2.14(2)	2.11(3)	2.145(8)
Ir–C4	2.19(2)	2.24(2)	2.238(8)
C2–C3	1.37(3)	1.40(4)	1.42(1)
C3–C4	1.41(2)	1.43(4)	1.41(1)
Bond angles			
P1–Ir–P2	112.5(2)	112.5(2)	112.61(8)
P1–Ir–C1	95.7(5)	95.6(7)	97.1(2)
P2–Ir–C1	106.2(6)	107.4(7)	106.0(3)
P1–Ir–C2	91.6(5)	90.6(5)	91.2(2)
P1–Ir–C3	108.8(5)	108.4(8)	109.8(2)
P1–Ir–C4	146.1(5)	146.1(6)	146.4(2)
P2–Ir–C2	97.9(6)	98.6(6)	97.0(2)
P2–Ir–C3	118.1(5)	118.4(7)	116.8(2)
P2–Ir–C4	95.2(5)	95.0(7)	94.9(2)
C1–Ir–C3	112.8(4)	112(1)	112.8(4)
Ir–C1–O	174(2)	175(2)	174.1(8)
C2–C3–C4	114(2)	117(2)	116.7(8)

[a] Rh(η^3-$CH_2CHCHC_6H_4Me$-*p*)(CO)(PPh_3)$_2$. Taken from Ref. [5]. Distances and angles of bond including Rh are shown.

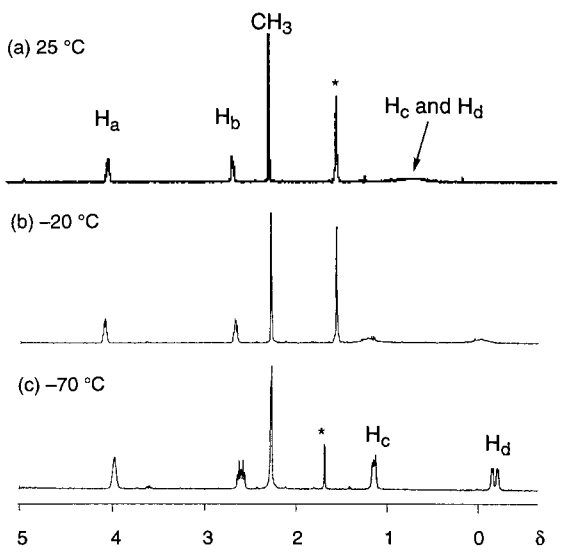
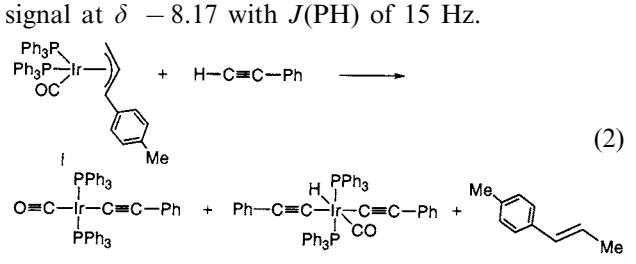


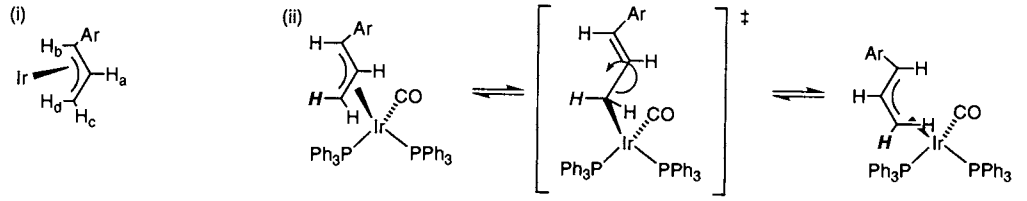
Fig. 2. Temperature dependent ^{1}H-NMR spectra of **1** (in CD_2Cl_2; π-allyl ligand hydrogen region). Peaks with asterisks are due to impurities (probably water) contaminated during the sample preparation.

on the peak positions. Fig. 2 summarizes temperature dependent ^{1}H- and ^{31}P-NMR spectra of **1** (CD_2Cl_2). The spectrum at 25°C contains two CH hydrogen signals of the allyl ligand, H_a and H_b, at δ 4.15 and 2.72, while a broad peak due to CH_2 hydrogens is observed at δ 0.8–0.7. On cooling the solution to −70°C, the broad peak is separated to two signals at δ 1.15 and −0.18. The signals H_a–H_d are assigned as shown in Scheme 2(i) based on homodecoupled ^{1}H-NMR spectra and on the comparison with data of the Rh complexes. The ^{31}P{^{1}H}-NMR spectra of **1** exhibit a temperature dependent change; two doublets (J(PP) = 50 Hz) observed at −70°C coalesce on raising the temperature and is turned to a broad single peak at 20°C (Fig. 3). This fluxional behavior of the complex is attributed to a π–σ–π rearrangement of the allyl ligand on the NMR time scale shown in Scheme 2(ii). The rearrangement of the π-allyl ligand renders the two PPh_3 ligands equivalent in the tetrahedral type coordination of the complex. Difference in the coalescence temperature between the ^{31}P{^{1}H}- and the ^{1}H-NMR signals (ca. 5°C) is smaller than that expected from the peak separation of the ^{31}P{^{1}H} and signals (ca. 1760 Hz) and the ^{1}H-NMR signals (ca. 520 Hz). The small degree of disagreement of the kinetic parameters obtained from the independent NMR measurements can be attributed to the unsatisfactory control of temperature of the solution during the ^{31}P-NMR measurement with ^{1}H irradiation rather than to the presence of another fluxional process of the molecule.

The equimolar reaction of phenylacetylene with π-allyliridium complex **1** at 50°C gives a mixture of *trans*-Ir(C≡CPh)(CO)(PPh_3)$_2$ (**4**) and *trans*,*trans*-IrH(CO)(C≡CPh)$_2$(PPh_3)$_2$ (**5**) accompanied by liberation of 1-(4-methylphenyl)-1-propene as shown in Eq. (2). Complex **4** was separated from the reaction mixture and characterized by comparison of the positions of ^{31}P{^{1}H}- and the ^{13}C{^{1}H}-NMR (acetylide carbons) signals with those of authentic sample [13]. Complex **5** was prepared separately from the reaction of excess phenylacetylene with **1**. Both complexes were isolated as crystals suited for X-ray analyses. Fig. 4 depicts ORTEP drawings of the molecules. Molecule of **4** is composed of phenylethynyl, CO, and PPh_3 ligands forming a square-planar geometry around the metal center with two phosphine ligands at *trans* positions. Complex **5** has an octahedral coordination although position of the hydrido was not determined in the crystallographic results. Table 2 summarizes selected bond distances and angles. A much longer bond between the carbonyl carbon and Ir (Ir–C1, 2.23 Å) of **5** than the corresponding bond distances of **4** (1.78–1.82 Å) is partly due to a large *trans* influence of the hydrido ligand situated at the *trans* position of the alkynyl ligand of **5**. The presence of the hydrido ligand was confirmed unambiguously by the ^{1}H-NMR spectrum of **5** showing a triplet signal at δ −8.17 with J(PH) of 15 Hz.



(2)



Scheme 2.

The reaction of phenylacetylene with **1** was monitored by ^{1}H- and ^{31}P{^{1}H}-NMR spectra of the reaction mixture. Fig. 5 plots amounts of the two complexes during the 5:1 molar reaction at 50°C. The signals of **4** and **5** are observed from the beginning of the reaction and grow in parallel during the initial 10 h. After 21 h, **1** is consumed to leave a mixture of **4** and **5**. Further reaction of phenylacetylene with **4** leads to the conversion of all the complexes to **5**. Similar reaction of phenylacetylene with Rh(η^3-$CH_2CHCHAr$)(CO)(PPh_3)$_2$ gives the monoalkynylrhodium(I) complex as the sole product even when excess amounts of phenylacetylene was allowed to react [11d]. Oxidative addition of C–H bond of ethylene to Ir(I) complexes with tripodal amine ligands giving Ir(III) complex occurs more easily than the reaction with the corresponding Rh(I) complexes [14,15].

The reaction of arylallene with IrH(CO)(PPh_3)$_3$ shown in this study smoothly gives the π-allyliridium complexes, Ir(η^3-$CH_2CHCHAr$)(CO)(PPh_3)$_2$, similarly to RhH(CO)(PPh_3)$_3$. The Ir complexes do not react with arylallenes on further addition of excess arylallene at r.t., whereas the Rh complexes were reported to undergo multiple insertion of arylallene molecules into the π-allyl–Rh bond. The latter reaction seems to be triggered by initial dissociation of the CO ligand to give coordinatively unsaturated Rh(η^3-$CH_2CHCHAr$)-(PPh_3)$_2$ which undergoes rapid insertion of arylallene molecules into the Rh–C bond until complex **A** in Scheme 1 with a sterically demanding π-allyl ligand is formed.

In summary, chemistry of the π-allyliridium complexes shown here has several characteristics uncommon to the version of π-allylrhodium complexes. Further studies on chemical properties of the π-allyl complexes of Group 9 transition metals would provide new aspects of the stoichiometric and catalytic reactions promoted by these metal complexes.

3. Experimental

Manipulations of the complexes were carried out under nitrogen or argon using standard Schlenk technique. The NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded on a JEOL EX-400 spectrometer at 25°C unless otherwise stated. Elemental analyses were carried out by a Yanaco MT-5 CHN Autocorder. IrH(CO)(PPh_3)$_3$ [16] and arylallenes [17] were prepared according to the literature.

3.1. Reaction of arylallenes with $IrH(CO)(PPh_3)_3$

To a toluene (10 cm^3) solution of IrH(CO)(PPh_3)$_3$ (90 mg, 90 μmol) was added (4-methylphenyl)allene (12 mg, 92 μmol) at r.t. After stirring the reaction mixture for 20 h, the solvent was removed under vacuum. The resulting oily material was washed repeatedly with hexane to give **1** as a yellow solid (78 mg, 98%). Recrystallization of the product from THF–hexane gave yellow single crystals suited for X-ray analysis (60 mg, 75%). Anal. Calc. for $C_{47}H_{41}OP_2Ir$: C, 64.44; H, 4.68. Found C, 64.41; H, 4.90%. ^{1}H-NMR (400 MHz at 25°C in C_6D_6): δ 7.51 (d, 2H, C_6H_4, $J = 8$ Hz), 7.50–7.46 (m, 14H, PPh_3 (*ortho*) and C_6H_4), 6.98–6.96 (m 18H, PPh_3 (*meta* and *para*)), 4.58 (1H, q, H_a, $J = 6$ Hz), 3.17 (1H, q, H_b, $J = 6$ Hz), 2.16 (s, 3H, CH_3), 1.1 (br, 2H, H_c and H_d); (400 MHz at 25°C in CD_2Cl_2): δ 7.33–7.06 (m, 34H, aromatic), 4.15 (q, 1H, H_a, $J = 6$Hz), 2.72 (q, 1H, H_b, $J = 6$ Hz), 2.30 (s, 3H, CH_3), 0.8–0.7 (br, 2H, H_c and H_d); (400 MHz at −70°C in CD_2Cl_2): δ 7.33–7.06 (m, 34H, aromatic), 3.98 (m, 1H, H_a), 2.60 (dt, 1H, H_b, $J = 18$ and 7 Hz), 2.28 (s, 3H, CH_3), 1.15 (m, 1H, H_c), −0.18 (dd, 1H, H_d, $J = 24$ and 6 Hz). ^{13}C-NMR (100 MHz at 25°C in C_6D_6): δ 185.1 (CO), 142.1, 137.7, 137.3, 135.5, 134.7, 133.8, 133.1, 131.7, 129.9, 129.3, 129.1, 128.8, 127.5, 127.2, 126.7, 126.1, 67.8 (CHAr,

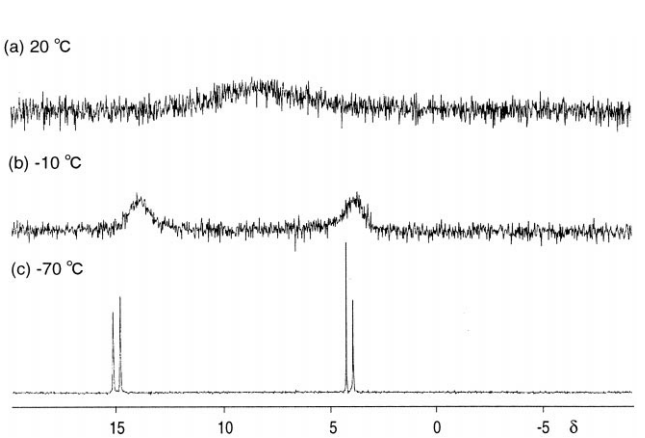


Fig. 3. Temperature dependent ^{31}P{^{1}H}-NMR spectra of **1** (in CD_2Cl_2).

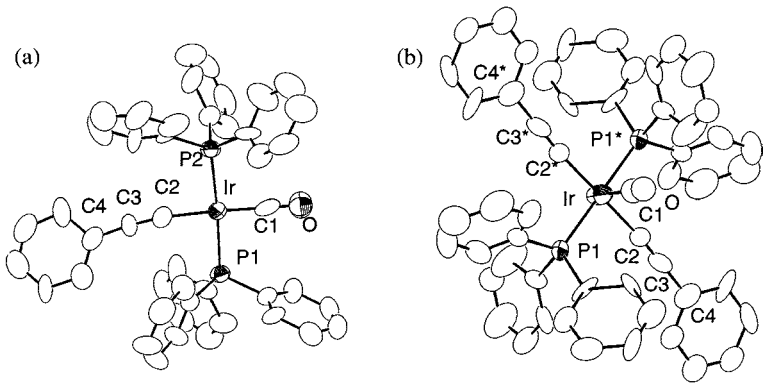


Fig. 4. ORTEP drawings of (a) **4** and (b) **5**. One of the two crystallographically independent molecules of **4** is shown. The molecule of **5** contains a crystallographic *C*2 symmetry around the Ir center. The atoms with asterisks at the numbers are crystallographically equivalent to those with the same number without asterisk. C1 and O atoms are expressed by a simple ball–stick model. One of the crystallographically equivalent carbonyl ligands is omitted for simplicity. The hydrido of **5** was not located.

J(CH) = 173 Hz), 55.5 (CH, J(CH) = 156 Hz), 29.8 (CH_2, J(CH) = 150 Hz), 21.3 (CH_3, J(CH) = 125 Hz). $^{31}P\{^1H\}$-NMR (160 MHz at 25°C in C_6D_6): δ 9.8 (br); (160 MHz at −70°C in CD_2Cl_2) 15.0 and 4.1 (d, J(PP) = 50 Hz).

Complexes **2** and **3** were obtained analogously in 75 and 53%, respectively. Data of **2**. Anal. Calc. for $C_{46}H_{39}OP_2Ir$: C, 64.12; H, 4.53. Found C, 64.04; H, 4.88%. IR (KBr, cm^{-1}): 1939 [ν(C≡O)]. ^{1}H-NMR (400 MHz at 25°C in C_6D_6): δ 7.56 (d, 2H, C_6H_5 (*ortho*), J = 8 Hz), 7.50–7.40 (m, 12H, PPh_3 (*ortho*)), 7.31 (t, C_6H_5 (*para*), J = 8 Hz), 7.05–6.90 (m, 20H, PPh_3 (*ortho* and *para*) and C_6H_5 (*meta*)), 4.57 (1H, q, H_a, J = 6 Hz), 3.13 (1H, q, H_b, J = 6 Hz), 1.1 (br, 2H, H_c and H_d). $^{13}C\{^1H\}$-NMR (100 MHz at 25°C in C_6D_6): δ 185.0 (CO), 145.1, 137.6, 137.2, 133.9, 133.8, 129.2, 128.5, 128.3, 127.9, 126.8, 125.1, 67.6 (CHAr), 55.25 (CH), 29.6 (CH_2). $^{31}P\{^1H\}$-NMR (160 MHz at 25°C in C_6D_6): δ 9.5 (br). Data of **3**. Anal. Calc. for $C_{46}H_{38}BrOP_2Ir$: C, 58.74; H, 4.04. Found C, 58.85; H, 4.14%. IR (KBr, cm^{-1}): 1935 [ν(C≡O)]. ^{1}H-NMR (400 MHz at 25°C in C_6D_6): δ 7.40–7.37 (m, 14H, PPh_3 (*ortho*) and C_6H_4), 7.21 (d, 2H, C_6H_4Br), 6.9 (br, 18H, PPh_3 (*meta* and *para*)), 4.42 (1H, q, H_a, J = 6 Hz), 2.93 (1H, q, H_b, J = 6 Hz), 1.07 (br, 2H, H_c and H_d); $^{13}C\{^1H\}$-NMR (100 MHz at 25°C in C_6D_6): δ 184.4 (CO), 144.1, 136.8, 136.3, 133.4, 133.3, 130.9, 129.0, 127.8, 127.6, 117.4, 66.7 (CHAr), 52.3 (CH), 29.0 (CH_2). $^{31}P\{^1H\}$-NMR (160 MHz at 25°C in C_6D_6): δ 8.8 (br).

3.2. Reaction of phenylacetylene with *1*

To a benzene (10 cm^3) solution of **1** (97 mg, 0.11 mmol) was added phenylacetylene (11 mg, 0.11 mmol) at 50°C. Color of the solution changed from yellow to orange during the heating. After 60 h, the solvent was evaporated to dryness under vacuum. The ^{1}H-NMR analyses of the product showed formation of 1-(4-methylphenyl)-1-propene (100%). The product was washed several times with hexane to give a mixture of orange crystals (19 mg) and a dark orange solid (73 mg). The former crystals, separated from the solid, were characterized by X-ray crystallography and comparison of the NMR data with authentic sample and identified to *trans*-Ir(C≡CPh)(CO)$(PPh_3)_2$ (**4**). IR (KBr, cm^{-1}): 1962 [ν(C≡O)]. ^{1}H-NMR (400 MHz at 25°C in C_6D_6): δ 7.93, 7.00 (m, 35H, C_6H_5). $^{13}C\{^1H\}$-NMR (75 MHz in $CDCl_3$): δ 125.1 (Ir–C), 127.3 (C≡CPh). $^{31}P\{^1H\}$-NMR (160 MHz at 25°C in C_6D_6): δ 4.63 (s). The NMR spectra of the remaining dark orange solid contained the signals of *trans*,*trans*-IrH$(C{\equiv}CPh)_2(CO)(PPh_3)_2$ (**5**) and unreacted **1**.

Complex **5** was prepared separately from the reaction of an excess amounts of phenylacetylene with **1**. To a

Table 2
Selected bond distances (Å) and angles (°) of **4** and **5**

	4 [a]	**5**
Bond distances		
Ir–P1	2.286(7) [2.313(9)]	2.329(5)
Ir–P2	2.291(6) [2.309(9)]	–
Ir–C1	1.82(3) [1.78(3)]	2.23(5)
C1–O1	1.18(3) [1.20(3)]	1.18(5)
Ir–C2	2.04(2) [1.99(3)]	2.04(2)
C2–C3	1.21(3) [1.22(3)]	1.15(2)
Bond angles		
P1–Ir–P2	173.3(2) [174.7(2)]	180.0
P1–Ir–C1	91(1) [91(1)]	89(1)
P1–Ir–C2	87(1) [92(1)]	92.5(5)
P2–Ir–C1	95(1) [93(1)]	–
P2–Ir–C2	87(1) [85(1)]	–
C1–Ir–C2	174.4(2) [177(1)]	92(1)
Ir–C1–O	177(2) [179(3)]	165(4)
Ir–C2–C3	174(2) [173(2)]	174(2)
C2–C3–C4	179(3) [174(3)]	178(2)
C1–Ir–C1	–	180.0

[a] Bond parameters of one of the crystallographically independent molecules are shown in brackets.

Table 3
Crystallographic data and details of structure refinement

Complex	1	3	4	5
Formula	$C_{47}H_{41}OP_2Ir$	$C_{46}H_{38}BrOP_2Ir$	$C_{45}H_{35}OP_2Ir$	$C_{53}H_{41}OP_2Ir$
Formula weight	875.74	940.63	845.94	947.80
Dimensions (mm)	$0.3\times0.3\times0.4$	$0.1\times0.1\times0.9$	$0.1\times0.2\times0.4$	$0.2\times0.2\times0.4$
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a (Å)	9.589(2)	9.613(3)	12.329(6)	13.364(2)
b (Å)	18.400(4)	18.355(4)	35.01(1)	9.280(1)
c (Å)	21.746(2)	21.740(3)	9.424(5)	17.419(1)
α (°)			93.85(4)	
β (°)	91.981(1)	91.92(2)	106.16(5)	97.171(9)
γ (°)			96.60(6)	
V (Å^3)	3834(1)	3834(1)	3861(1)	2143.3(4)
Z	4	4	4	2
$\rho_{calc.}$ (g cm^{-3})	1.517	1.630	1.455	1.469
$F(000)$	1752	1856	1680	948
μ(Mo–K$_\alpha$) (mm^{-1})	3.61	4.656	3.583	3.236
Reflection measured	9617	9614	10061	5432
Unique reflections	9091 ($R_{int}=0.109$)	9090 ($R_{int}=0.101$)	10059 ($R_{int}=0.118$)	5217 ($R_{int}=0.074$)
Used reflections ($I>1.5\sigma(I)$)	3589	3529 [a]	6287	2028
Variables	460	460	883	258
R (R_w)	0.059 (0.062)	0.050 (0.060)	0.065 (0.079)	0.080 (0.092)

[a] ($I>1.0\sigma(I)$).

toluene (10 cm^3) solution of **1** (172 mg, 0.17 mmol) was added phenylacetylene (174 mg, 1.7 mmol) at 50°C. After heating for 47 h, the solvent was evaporated to dryness under vacuum. The product was washed with hexane to give **5** as a solid (70 mg, 43%). Recrystallization from toluene–hexane gave yellow single crystals suited for X-ray analyses (32 mg, 20%). Anal. Calc. for $C_{53}H_{41}OP_2Ir$: C, 67.17; H, 4.33. Found C, 66.83 H, 4.32%. IR (KBr, cm^{-1}): 2010 [ν(C≡O)], 2122 [ν(Ir–H)], 2350 [ν(C≡C)]. ^{1}H-NMR (400 MHz at 25°C in C_6D_6): δ 8.00–7.00 (m, 40H, C_6H_5), −8.17 (t, 1H, Ir–H, J(HP) = 15 Hz). ^{13}C{^{1}H}-NMR (100 MHz at 25°C in C_6D_6): δ 134.6, 132.6, 132.0, 130.8, 130.2, 129.0, 127.8, 127.1, 124.2, 109.2 (C–Ph), 82.0 (t, Ir–C, J(PC) = 13 Hz). ^{31}P{^{1}H}-NMR (160 MHz at 25°C in C_6D_6): δ 1.1.

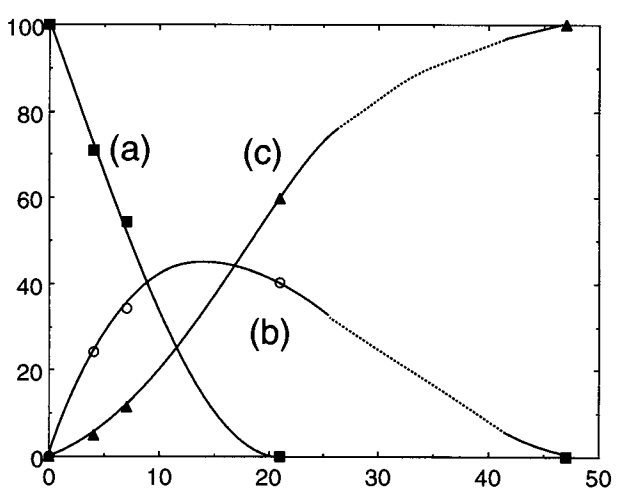


Fig. 5. Profile of the reaction of phenylacetylene with **1** in a 5:1 molar ratio at 50°C in C_6D_6. Relative amounts of (a) **1**, (b) **4**, and (c) **5** determined by the ^{31}P{^{1}H}-NMR peak area ratio of the reaction mixture are shown. The reaction after 25 h was carried out at 100°C.

3.3. X-ray crystallography

Crystals of **1**, **3** **4**, and **5** suitable for X-ray diffraction study were obtained by recrystallization from THF–hexane (**1**) and toluene–hexane (**3**–**5**), and mounted in glass capillaries under argon. Data were collected at 23°C on a Rigaku AFC-5R automated four-circle diffractometer equipped with monochromated Mo–K$_\alpha$ radiation (λ = 0.71073 Å). Calculations were carried out by using a program package TEXSAN for Windows. The structures were solved by a direct method and subsequent Fourier technique. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table 3.

4. Supplementary material

Crystallographic data (excluding structural factors) for the structure in the paper have been deposited with

the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 137738–137741. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported by a Grant-in-aid for Scientific Research from the Ministry of Education, Science, Sport and Culture, Japan. Authors are grateful to Professor Takakazu Yamamoto of our Institute for helpful discussion throughout this study.

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