Diastereocontrolled synthesis of *cis*-olefins by selective C–C bond formation between alkyl and alkynyl groups coordinated to "Ir(CH=CHPPh₃)(CO)(PPh₃)₂"†

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cis,cis-1,4-Dipropenylbenzene (*cis,cis*-*p*-C₆H₄(CH=CHCH₃)₂, *cis*-**DPB**) and *cis,cis,cis*-1,3,5-tripropenylbenzene (*cis,cis,cis*-*m,m*-C₆H₃(CH=CHCH₃)₃, *cis*-**TPB**) are obtained in high yields by reactions of di- and tri-nuclear alkyl–alkenyl–alkynyl iridium(III) compounds, [*p*-C₆H₄(C≡C–Ir(CH₃)(CH=CHPPh₃)(CO)(PPh₃)₂)₂]²⁺ **1** and [*m,m*-C₆H₃(C≡C–Ir(CH₃)(CH=CHPPh₃)(CO)(PPh₃)₂)₃]³⁺ **3** with HCl. The reaction of the mono-nuclear alkyl–alkenyl–alkynyl iridium(III) complex, [Ir(CH₃)(CH=CHPPh₃)(C≡C-*p*-C₆H₄CH₃)(CO)(PPh₃)₂]⁺ **7a** with DCl selectively gives *cis*-CD₃CD=CD(*p*-C₆H₄CH₃) **8a**-*d₅* while two isomers, *cis*-C₆H₅CD₂CD=CD(*p*-C₆H₄CH₃) **8b**-*d₄* and *cis*-C₆H₅CD=CDCD₂(*p*-C₆H₄CH₃) **8b′**-*d₄* are obtained from the reaction of [Ir(CH₂Ph)(CH=CHPPh₃)-(C≡C-*p*-C₆H₄CH₃)(CO)(PPh₃)₂]⁺ **7b** with DCl. Plausible reaction pathways containing the initial attack of H⁺ on the β-carbon of the alkynyl ligands to produce *cis*-alkenyl complexes that give η²-allene complexes are suggested for the selective and diastereocontrolled C–C bond forming reactions between alkyl and alkynyl groups to give *cis*-olefins, **8**, *cis*-**DPB**, and *cis*-**TPB**.

Introduction

In the design of chemical reaction schemes to obtain selective and regiospecific products, transition metal-mediated carbon–carbon bond forming reactions have been widely studied.[1] Metal–hydrocarbyls such as metal–alkyls, metal–alkenyls and metal–alkynyls are useful precursors and key intermediates in these C–C bond forming reactions between neighboring hydrocarbyl ligands.[2] We have studied C–C bond forming reactions mediated by alkynyl iridium complexes and recently reported synthesis of cross conjugated olefins and linear dienynes by the regio- and stereo-selective C–C bond formation between alkenyl and alkynyl ligands.[3]

In this paper, we report a diastereocontrolled synthesis of *cis,cis*-1,4-dipropenylbenzene ***cis*-DPB** and *cis,cis,cis*-1,3,5-tripropenylbenzene ***cis*-TPB** in high yields from the selective C–C bond formation between alkyl and alkynyl groups of alkyl–alkenyl–alkynyl iridium(III) compounds and suggest plausible reaction pathways.

Results and discussion

Reactions of di- and tri-nuclear alkyl–alkenyl–alkynyl iridium(III) complexes, [*p*-C₆H₄(C≡C–Ir(CH₃)(CH=CHPPh₃)(CO)-(PPh₃)₂)₂]²⁺ **1** and [*m,m*-C₆H₃(C≡C–Ir(CH₃)(CH=CHPPh₃)-(CO)(PPh₃)₂)₃]³⁺ **3** with HCl give *cis,cis*-1,4-dipropenylbenzene ***cis*-DPB**[4] and *cis,cis,cis*-1,3,5-tripropenylbenzene ***cis*-TPB** in high yields (eqns. (1) and (2)).

***cis*-DPB** and ***cis*-TPB** have been unequivocally identified by detailed data (¹H, ¹³C NMR, ¹H NOE and ¹H,¹³C-2D COSY spectral data and GC/MS measurements) (see Experimental section).
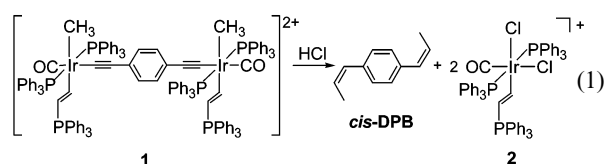

(1)
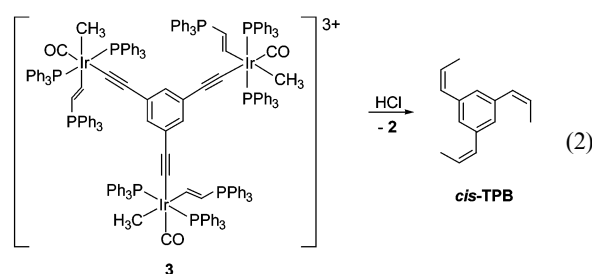
Those di- and tri-nuclear alkyl–alkenyl–alkynyl iridium(III) complexes **1** and **3** have been prepared from the reactions of alkyl–alkynyl iridium(III) complexes **5** and **6** with HC≡CH and PPh₃ in the presence of AgOTf as shown in Scheme 1.

(2)
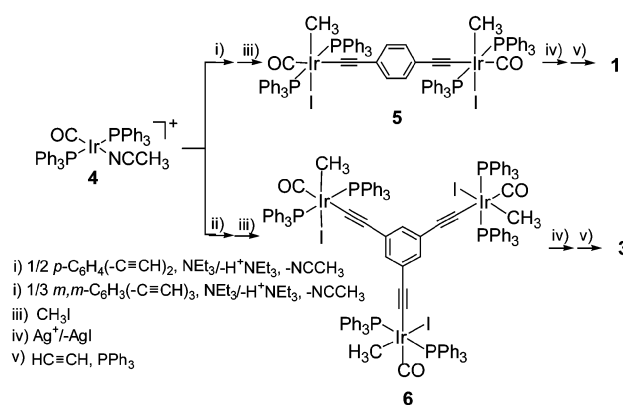
Scheme 1

Complexes **1**, **3**, **5** and **6** have been unambiguously characterized by spectral (¹H, ¹³C, ³¹P NMR, ¹H,¹³C-2D COSY and IR), elemental analysis and FAB-mass data (see Experimental section). Assignments of ¹H NMR signals due to Ir–C*H*=C*H*PPh₃ of **1** and **3** are rather straightforward by comparing the data with those for the related and well-characterized complexes.[3b,5]

Di- and tri-nuclear complexes of transition metals linked by rigid alkynyl–aryl backbones (–C≡C-*p*-C₆H₄–C≡C– and –C≡C-*m,m*-C₆H₃–(C≡C)₂–) have been extensively studied with

† Electronic supplementary information (ESI) available: NMR and mass spectra. See http://www.rsc.org/suppdata/dt/b3/b302153j/

respect to their chemical and physical properties while reactions of those metal complexes have been rarely reported.[6]

In order to investigate the reaction pathways for the formation of *cis*-**DPB** and *cis*-**TPB** in eqns. (1) and (2), mononuclear alkyl–alkenyl–alkynyl iridium(III) complexes, [Ir(R)-(CH=CHPPh$_3$)(C≡C-*p*-C$_6$H$_4$CH$_3$)(CO)(PPh$_3$)$_2$]$^+$ (R = CH$_3$ **7a**, CH$_2$Ph **7b**) have been prepared in the similar manner to that of **1** and **3** (see Experimental section) and their reactions with H$^+$ (D$^+$) have been investigated. Reactions of **7** with HCl give *cis*-olefins, *cis*-CH$_3$CH=CH(*p*-C$_6$H$_4$CH$_3$) **8a**, *cis*-PhCH$_2$CH=CH(*p*-C$_6$H$_4$CH$_3$) **8b** and *cis*-PhCH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$) **8b′** while those with DCl produce *cis*-CD$_3$CD=CD(*p*-C$_6$H$_4$CH$_3$) **8a-*d*$_5$**, *cis*-PhCD$_2$–CD=CD(*p*-C$_6$H$_4$CH$_3$) **8b-*d*$_4$** and *cis*-PhCD=CDCD$_2$(*p*-C$_6$H$_4$CH$_3$) **8b′-*d*$_4$** (eqns. (3) and (4)).

(3)

65%   35%   (4)
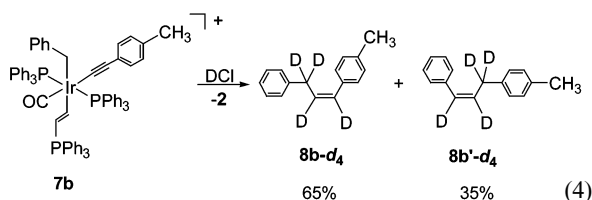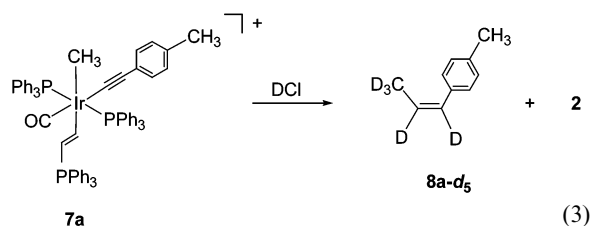
Formation of **8** may be understood by the reaction pathways as shown in Scheme 2. The very similar mechanism was suggested for the formation of **8a** from the reaction of the ammonium ylide, [Ir(CH$_3$)(C≡CR)(CH=CHNEt$_3$)(CO)-(PPh$_3$)$_2$]$^+$ **7′** with H$^+$ (see below).[3c] Accordingly, formation of *cis*-**DPB** and *cis*-**TPB** may also be explained by the same reaction pathways that involve the initial attack of H$^+$ on the β-carbon of the alkynyl group and the C–C bond formation between the α-carbons of the alkyl and alkynyl ligands to give *cis*-alkenyl ligands. This C–C bond formation by an alkyl migration is quite similar to the alkynyl migration to the α-carbon of vinylidene proposed for the dimerization[7] of terminal alkynes to give enynes. The H/D exchange to give the isotopomers (**8a-*d*$_5$**, **8b-*d*$_4$**, **8b′-*d*$_4$**) is also readily explained by the same mechanism previously suggested for the formation of **8a-*d*$_5$** from the reaction of **7′** with D$^+$.[3c]

Scheme 2
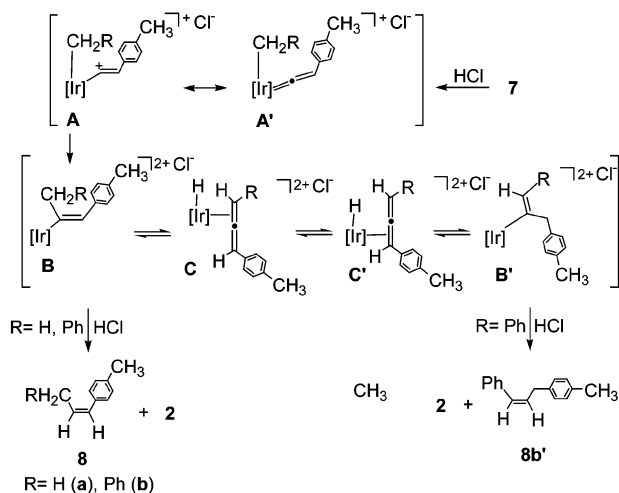
It is somewhat surprising that the alkenyl ligands (Ir–*CH*=CHPPh$_3$) of **1**, **3** and **7** are not involved in the C–C bond forming reactions between adjacent alkynyl ligands while the alkenyl ligand (Ir–*CH*=CHNEt$_3$) in [Ir(CH$_3$)(C≡CR)-(CH=CHNEt$_3$)(CO)(PPh$_3$)$_2$]$^+$ **7′** readily participates in the C–C bond forming reaction.[3c] We recently found that *cis*-CH$_3$CH=CHR could be partly isolated only when the reaction is quenched at the early stage but [Et$_3$NCH=CH–C(CH$_3$)=CH-(*p*-C$_6$H$_4$CH$_3$)]$^+$ is the major product in high yield in the reaction of **7′** with H$^+$.[3c] This inertness of the Ir–C bond of Ir–CH=CHPPh$_3$ may be understood by previous studies that predict the M–C bonds being very much stabilized by various resonance forms such as M^+=CH–CH=PR$_3$ and M–CH=CH–$^+$PR$_3$.[5c,8]

The yield of the *cis*-olefins seems dependent on the *trans* ligand (–CH=CHPPh$_3$) to the alkyl group. A variety of other products (such as CH$_3$CH=CH-*p*-C$_6$H$_4$–CH=CHCH$_2$-Cl, CH$_3$C≡C-*p*-C$_6$H$_4$–CH=CHCH$_2$Cl, CH$_3$C≡C-*p*-C$_6$H$_4$–CH=CHCH$_3$ and CH$_3$C≡C-*p*-C$_6$H$_4$–CH=CHCl) are obtained with the *trans* ligand being I$^-$ (**5**) or CH$_3$CN (**5′**) in dinuclear complexes. It may also be mentioned that di- and tri-nuclear complexes containing the CH=CHNEt$_3$ ligand in place of –CH=CHPPh$_3$ of **1** and **3** have not been prepared yet and the yield of **8a** is quite low (≤40%) from the reaction of **7′** with H$^+$.

In conclusion, the introduction of CH=CHPPh$_3$ ligand *trans* to alkyl group leads to selective and diastereocontrolled C–C bond formation between alkyl and alkynyl groups in the mono, di- and tri-nuclear alkyl–alkenyl–alkynyl iridium(III) complexes to give *cis*-olefins in high yields.

Experimental

General

A standard vacuum system and Schlenk type glassware were used in most of experimental procedures in handling metal compounds, although most of the compounds seem to be stable enough to be handled without much precautions in air.

DCl (37 wt% in D$_2$O) and HCl (32 wt% in H$_2$O) were purchased from Aldrich and Merck, respectively. [Ir(NCCH$_3$)-(CO)(PPh$_3$)$_2$]OTf **4**[9] was prepared by the literature method.

NMR spectra were recorded on either a Varian Gemini 200, 300 or 500 spectrometer (^{1}H, 300 or 500 MHz; ^{13}C, 126 MHz; ^{31}P, 81 MHz). IR spectra were obtained on a Nicolet 205 spectrophotometer. Gas chromatography/mass spectra were determined by Hewlett Packard HP5890A and VG-trio 2000 instruments. Elemental analyses were carried out by a Carlo Erba EA 1108 CHNS–O analyzer at Organic Chemistry Research Center, Sogang University. FAB mass measurements were carried out with a JMS-HX110/110A tandem mass spectrometer at the Korea Basic Science Institute.

Synthesis

Preparation of [*p*-C$_6$H$_4$(C≡C–Ir(CH$_3$)(CH=CHPPh$_3$)(CO)-(PPh$_3$)$_2$)$_2$](OTf)$_2$ 1. A reaction mixture of **5** (0.19 g, 0.10 mmol) and AgOTf (0.06 g, 0.23 mmol) in CHCl$_3$ (15 mL) was stirred for 30 min before AgI was removed by filtration. The reaction mixture was stirred under HC≡CH (1 atm) in the presence of PPh$_3$ (0.06 g, 0.23 mmol) at 25 °C for 12 h before *n*-pentane (30 mL) was added to precipitate beige microcrystals which were collected by filtration, washed with *n*-pentane (3 × 10 mL) and dried under vacuum (0.27 g, 97%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.79 (ddt, *J* = 33.0, 19.0, 1.5 Hz, Ir–C*H*=CHPPh$_3$, 2H), 6.8–8.0 (m, Ir–PPh$_3$ and Ir–CH=CHP(C$_6$H$_5$)$_3$, 90H), 6.78 (s, Ir–C≡CC$_6$H$_4$–, 4H), 6.36 (ddt, *J* = 36.0, 19.0, 1.5 Hz, Ir–CH=C*H*PPh$_3$, 2H), 0.26 (t, *J* = 5.5 Hz, Ir–CH$_3$, 6H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 181.7 (m, Ir–*C*H=CHPPh$_3$), 172.8 (s, Ir–CO), 129.9 (s, CH of Ir–C≡C*C*$_6$H$_4$–), 125.0 (s, C_{ipso}, Ir–C≡C*C*$_6$H$_4$–), 111.8 (s, Ir–C≡*C*), 110.8 (dm, *J* = 67.9 Hz, Ir–CH=*C*HPPh$_3$), 89.3 (br s, Ir–*C*≡C), −27.6 (dt, *J* = 6.0 Hz, Ir–CH$_3$). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 9.79 → 181.7;

$6.78 \rightarrow 129.9$; $6.36 \rightarrow 110.8$; $0.26 \rightarrow -27.6$. $^{31}P\{^1H\}$ NMR (81 MHz, CDCl$_3$): δ 14.50 (t, $J = 3.8$ Hz, Ir–CH=CHPPh$_3$), -14.36 (d, $J = 3.8$ Hz, Ir–PPh$_3$). IR (KBr, cm^{-1}): 2121 (w, $\nu_{C\equiv C}$), 2032 (s, ν_{CO}), 1272, 1151, 1031 (uncoordinated OTf). MS (FAB): m/z 2369 [M$^+$ – OTf]. Anal. Calc. for Ir$_2$P$_6$O$_8$S$_2$F$_6$C$_{128}$H$_{104}$: C, 61.04; H, 4.16. Found: C, 61.20; H, 4.20%.

Preparation of [m,m-C$_6$H$_3$(C≡C–Ir(CH$_3$)(CH=CHPPh$_3$)(CO)-(PPh$_3$)$_2$)$_3$](OTf)$_3$ 3. This compound was prepared by a similar method as described above for **1** by using **6**. Yield: 0.11 g, 85%. ^{1}H NMR (500 MHz, CD$_3$COCD$_3$): δ 9.77 (dd, $J = 33.0$, 19.0 Hz, Ir–C*H*=CHPPh$_3$, 3H), 7.0–8.0 (m, Ir–PPh$_3$, Ir–CH=CHP-(C$_6$H$_5$)$_3$ and m,m-C$_6$H$_3$–C≡C–Ir, 138H), 6.34 (dd, $J = 35.0$, 19.0 Hz, Ir–CH=C*H*PPh$_3$, 3H), 0.33 (t, $J = 5.5$ Hz, Ir–CH$_3$, 9H). ^{13}C NMR (126 MHz, CD$_3$COCD$_3$): δ 180.8 (m, Ir–*C*H=CHPPh$_3$), 172.7 (s, Ir–CO), 113.2 (s, Ir–C≡*C*), 113.0 (dm, $J = 62.4$ Hz, Ir–CH=*C*HPPh$_3$), 88.8 (br s, Ir–*C*≡C), -26.9 (dt, $J = 6.0$ Hz, Ir–CH$_3$). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) $\rightarrow$ ^{13}C (126 MHz)): δ 9.77 $\rightarrow$ 180.8; 6.34 $\rightarrow$ 113.0; 0.33 $\rightarrow$ -26.9. $^{31}P\{^1H\}$ NMR (81 MHz, CD$_3$COCD$_3$): δ 15.27 (t, $J = 3.5$ Hz, Ir–CH=CHPPh$_3$), -19.26 (d, $J = 3.5$ Hz, Ir–PPh$_3$). IR (KBr, cm^{-1}): 2116 (w, $\nu_{C\equiv C}$), 2035 (s, ν_{CO}), 1266, 1149, 1032 (uncoordinated OTf). MS (FAB): m/z 3589 [M$^+$ – OTf]. Anal. Calc. for Ir$_3$P$_9$O$_{12}$S$_3$F$_9$C$_{189}$H$_{153}$: C, 60.71; H, 4.12. Found: C, 60.54; H, 3.99%.

Preparation of p-C$_6$H$_4$(C≡C–Ir(CH$_3$)(I)(CO)(PPh$_3$)$_2$)$_2$ 5. A reaction mixture of **4** (0.20 g, 0.21 mmol) and p-C$_6$H$_4$(C≡CH)$_2$ (0.014 g, 0.11 mmol) in CHCl$_3$ (10 mL) was stirred in the presence of NEt$_3$ (0.03 mL, 0.25 mmol) for 20 min to produce p-C$_6$H$_4$(C≡C–Ir(CO)(PPh$_3$)$_2$)$_2$ before excess CH$_3$I (0.07 mL, 1.12 mmol) was added to the dark brown reaction mixture. The reaction mixture turned pale yellow within 1 h. A 10 mL portion of water was added to the solution, and excess NEt$_3$ and H$^+$NEt$_3$OTf$^-$ in the aqueous layer were separated from the reaction mixture. Addition of n-pentane (30 mL) to the CHCl$_3$ solution resulted in precipitation of beige microcrystals of **5**, which were collected by filtration, washed with n-pentane (3×10 mL) and dried under vacuum (0.16 g, 84%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.0–8.2, 7.3–7.4 (Ir–PPh$_3$, 60H), 6.85 (s, Ir–C≡CC$_6$H$_4$, 4H), 0.77 (t, $J = 5.4$ Hz, Ir–CH$_3$, 6H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 169.8 (t, $J = 6.5$ Hz, Ir–CO), 134.6 (t), 131.8 (t), 130.3 (s), 127.9 (t) (Ir–PPh$_3$), 130.2 (s), 125.2 (s) (Ir–C≡CC$_6$H$_4$), 114.1 (s, Ir–C≡*C*), 88.3 (t, $J = 18.5$ Hz, Ir–*C*≡C), -14.9 (t, $J = 3.4$ Hz, Ir–CH$_3$). $^{31}P\{^1H\}$ NMR (81 MHz, CDCl$_3$): δ -17.17 (s, Ir–PPh$_3$). IR (KBr, cm^{-1}): 2120 (w, $\nu_{C\equiv C}$), 2051 (s, ν_{CO}). MS (FAB): m/z 1897 [M$^+$]. Anal. Calc. for Ir$_2$P$_4$O$_2$I$_2$-C$_{86}$H$_{70}$: C, 54.43; H, 3.72; Found: C, 54.43; H, 3.73%.

Preparation of m,m-C$_6$H$_3$(C≡C–Ir(CH$_3$)(I)(CO)(PPh$_3$)$_2$)$_3$ 6. This compound was prepared by the similar method as described above for **5** by using m,m-C$_6$H$_3$(C≡CH)$_3$ (0.17 g, 86%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.0–8.2, 7.0–7.3 (Ir–PPh$_3$ and m,m-C$_6$H$_3$–C≡C–Ir, 93H), 0.87 (t, Ir–CH$_3$, 9H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 169.7 (m, Ir–CO), 113.6 (s, Ir–C≡*C*), 87.1 (t, $J = 18.0$ Hz, Ir–*C*≡C), -14.9 (t, $J = 3.0$ Hz, Ir–CH$_3$). $^{31}P\{^1H\}$ NMR (81 MHz, CDCl$_3$): δ -18.34 (s, Ir–PPh$_3$). IR (KBr, cm^{-1}): 2122 (w, $\nu_{C\equiv C}$), 2043 (s, ν_{CO}). MS (FAB): m/z 2808 [M$^+$]. Anal. Calc. for Ir$_3$P$_6$O$_3$I$_3$C$_{126}$H$_{102}$: C, 53.91; H, 3.66. Found: C, 54.01; H, 3.70%.

Preparation of [Ir(R)(CH=CHPPh$_3$)(C≡C-p-C$_6$H$_4$CH$_3$)-(CO)(PPh$_3$)$_2$]OTf (R = CH$_3$ 7a, CH$_2$Ph 7b). Compound **7b** was prepared by the same method as described below for **7a** by using PhCH$_2$Br instead of CH$_3$I. The reaction mixture of **4** (0.10 g, 0.11 mmol) and HC≡C(p-C$_6$H$_4$CH$_3$) (0.016 mL, 0.13 mmol) in CHCl$_3$ (10 mL) was stirred in the presence of NEt$_3$ (0.02 mL, 0.15 mmol) for 5 min to produce Ir(C≡C-p-C$_6$H$_4$-CH$_3$)(CO)(PPh$_3$)$_2$ before excess CH$_3$I (0.04 mL, 0.6 mmol) was added to the dark brown reaction mixture. The reaction

mixture turned pale yellow within 1 h. A 10 mL portion of water was added to the solution, and excess NEt$_3$ and H$^+$NEt$_3$-OTf$^-$ in the aqueous layer were separated from the reaction mixture. AgOTf (0.04 g, 0.15 mmol) was added to the reaction mixture, which was stirred for 30 min. After AgI was removed by filtration, the reaction mixture was stirred under HC≡CH (1 atm) in the presence of PPh$_3$ (0.05 g, 0.2 mmol) at 25 °C for 5 h before n-pentane (30 mL) was added to precipitate beige microcrystals which were collected by filtration, washed with n-pentane (3×10 mL) and dried under vacuum (0.138 g, 96%).

[Ir(CH$_3$)(CH=CHPPh$_3$)(C≡C-p-C$_6$H$_4$CH$_3$)(CO)(PPh$_3$)$_2$]OTf **7a**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.79 (ddt, $J = 33.5$, 19.0, 1.5 Hz, Ir–C*H*=CHPPh$_3$), 6.8–8.0 (Ir–PPh$_3$, Ir–CH=CHP(C$_6$H$_5$)$_3$ and p-C$_6$H$_4$CH$_3$, 49H), 6.41 (ddt, $J = 36.8$, 19.0, 1.5 Hz, Ir–CH=C*H*PPh$_3$), 2.32 (s, Ir–C≡C-p-C$_6$H$_4$C*H*$_3$, 3H), 0.27 (t, $J = 6.0$ Hz, Ir–CH$_3$, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 182.2 (m, Ir–*C*H=CHPPh$_3$), δ 172.8 (t, $J = 7.0$ Hz, Ir–CO), 111.3 (s, Ir–C≡*C*-p-C$_6$H$_4$CH$_3$), 110.4 (m, $J = 65.9$ Hz, Ir–CH=*C*HPPh$_3$), 86.3 (t, $J = 17.6$ Hz, Ir–*C*≡C-p-C$_6$H$_4$CH$_3$), 21.1 (s, Ir–C≡C-p-C$_6$H$_4$*C*H$_3$), -27.9 (q, $J = 6.2$ Hz, Ir–CH$_3$). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) $\rightarrow$ ^{13}C (126 MHz)): δ 9.79 $\rightarrow$ 182.2; 6.41 $\rightarrow$ 110.4; 2.32 $\rightarrow$ 21.1; 0.27 $\rightarrow$ -27.9. $^{31}P\{^1H\}$ NMR (81 MHz, CDCl$_3$): δ 14.14 (t, $J = 3.5$ Hz, Ir–CH=CHPPh$_3$), -14.34 (d, $J = 3.5$ Hz, Ir–PPh$_3$). IR (KBr, cm^{-1}): 2123 (s, $\nu_{C\equiv C}$), 2035 (s, ν_{CO}), 1270, 1150, 1032 (br s, due to uncoordinated triflate). Anal. Calc. for IrP$_3$O$_4$SF$_3$C$_{68}$H$_{57}$: C, 62.23; H, 4.38. Found: C, 62.30; H, 4.25%.

[Ir(CH$_2$Ph)(CH=CHPPh$_3$)(C≡C-p-C$_6$H$_4$CH$_3$)(CO)(PPh$_3$)$_2$]-OTf **7b**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.80 (ddt, $J = 27.3$, 19.0, 1.5 Hz, Ir–C*H*=CHPPh$_3$), 6.8–8.0 (Ir–PPh$_3$, Ir–CH=CHP(C$_6$H$_5$)$_3$ and p-C$_6$H$_4$CH$_3$, 49H), 6.25 (ddt, $J = 35.0$, 19.0, 1.5 Hz, Ir–CH=C*H*PPh$_3$), 6.76 (t), 6.68 (t), 5.78 (d) (Ir–CH$_2$C$_6$H$_5$, 5H), 3.26 (t, $J = 5.5$ Hz, Ir–C*H*$_2$C$_6$H$_5$, 2H), 2.38 (s, Ir–C≡C-p-C$_6$H$_4$C*H*$_3$, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 178.0 (m, Ir–*C*H=CHPPh$_3$), δ 173.6 (t, $J = 5.0$ Hz, Ir–CO), 122.3 (s), 124.2 (s), 127.1 (s), 127.9 (s) (Ir–CH$_2$C$_6$H$_5$), 113.4 (s, Ir–C≡*C*-p-C$_6$H$_4$CH$_3$), 109.9 (d, $J = 66.6$ Hz, Ir–CH=*C*HPPh$_3$), 84.9 (t, $J = 17.7$ Hz, Ir–*C*≡C-p-C$_6$H$_4$CH$_3$), 21.1 (s, Ir–C≡C-p-C$_6$H$_4$*C*H$_3$), 1.45 (m, Ir–*C*H$_2$C$_6$H$_5$). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) $\rightarrow$ ^{13}C (126 MHz)): δ 9.80 $\rightarrow$ 178.0; 6.25 $\rightarrow$ 109.9; 6.76 $\rightarrow$ 122.3; 6.68 $\rightarrow$ 127.1; 5.78 $\rightarrow$ 127.9; 3.26 $\rightarrow$ 1.45; 2.38 $\rightarrow$ 21.1. $^{31}P\{^1H\}$ NMR (81 MHz, CDCl$_3$): δ 13.42 (t, $J = 3.6$ Hz, Ir–CH=CHPPh$_3$), -18.77 (d, $J = 3.6$ Hz, Ir–PPh$_3$). IR (KBr, cm^{-1}): 2123 (s, $\nu_{C\equiv C}$), 2037 (s, ν_{CO}), 1273, 1151, 1031 (br s, due to uncoordinated triflate). Anal. Calc. for IrP$_3$O$_4$SF$_3$C$_{74}$H$_{61}$: C, 64.01; H, 4.43. Found: C, 64.21; H, 4.49%.

Reactions

Reactions of di- and tri-nuclear alkyl–alkenyl–alkynyl iridium(III) complexes with HCl: formation of cis,cis-p-C$_6$H$_4$-(CH=CHCH$_3$)$_2$, cis-DPB and cis,cis,cis-m,m-C$_6$H$_3$(CH=CHCH$_3$)$_3$, cis-TPB. These reactions were carried by the same manner as below for the reaction of **1** with HCl to give cis-DPB. HCl (0.05 mL, 0.52 mmol of H$_2$O containing 32 wt% HCl) was added to a solution of **1** (0.38 g, 0.15 mmol) in CHCl$_3$ (15 mL) at 25 °C, and the reaction mixture was stirred for 12 h. Excess HCl was removed by washing with H$_2$O. Addition of n-pentane (10 mL) to the CHCl$_3$ solution resulted in the beige microcrystals of [IrCl$_2$(CH=CHPPh$_3$)(CO)(PPh$_3$)$_2$]OTf **2** which were collected by filtration. The filtrate was distilled at 25 °C under vacuum to less than 1.0 mL and the residue was eluted with n-pentane on a column packed with silica gel to obtain cis-DPB. The yield of cis-DPB was ca. 92% measured by ^{1}H NMR in CDCl$_3$.

cis,cis-p-C$_6$H$_4$(CH=CHCH$_3$)$_2$, cis-DPB. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.32 (s, C$_6$H$_4$(CH=CHCH$_3$)$_2$, 4H), 6.46 (dd, $J = 11.7$, 1.5 Hz, C$_6$H$_4$(C*H*=CHCH$_3$)$_2$, 2H), 5.82 (dq, $J = 11.7$, 7.4 Hz, C$_6$H$_4$(CH=C*H*CH$_3$)$_2$, 2H), 1.96 (dd, $J = 7.4$, 1.5 Hz, C$_6$H$_4$(CH=CHC*H*$_3$)$_2$, 6H). ^{1}H NOE measurement (500 MHz, CDCl$_3$): irradiation of the signal at 5.82 ppm shows a positive NOE

effect on the signal at 6.46 ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ 133.8 (s, C_{ipso}, C_6H_4(CH=CHCH$_3$)$_2$), 129.6 (s, C_6H_4(CH=CHCH$_3$)$_2$), 128.6 (s, CH carbons of C_6H_4(CH=CHCH$_3$)$_2$), 126.7 (s, C_6H_4(CH=CHCH$_3$)$_2$), 14.7 (s, C_6H_4(CH=CHCH$_3$)$_2$). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) $\rightarrow$ ^{13}C (126 MHz)): δ 7.32 $\rightarrow$ 128.6; 6.46 $\rightarrow$ 129.6; 5.82 $\rightarrow$ 126.7; 1.96 $\rightarrow$ 14.7. MS: m/z 158 (M$^+$).

cis,cis,cis-m,m-C$_6$H$_3$(CH=CHCH$_3$)$_3$, *cis*-TPB. ^{1}H NMR (500 MHz, CDCl): δ 7.04 (s, C$_6$H$_3$(CH=CHCH$_3$)$_3$, 3H), 6.38 (dm, J = 11.6 Hz, C$_6$H$_3$(CH=CHCH$_3$)$_3$, 3H), 5.74 (dq, J = 11.6, 7.5 Hz, C$_6$H$_3$(CH=CHCH$_3$)$_3$, 3H), 1.87 (dd, J = 7.5, 1.5 Hz, C$_6$H$_3$(CH=CHCH$_3$)$_3$, 9H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 137.2 (s, C_{ipso}, C_6H_4(CH=CHCH$_3$)$_2$), 129.9 (s, C_6H_4(CH=CHCH$_3$)$_2$), 127.4 (s, CH carbons of C_6H_4(CH=CHCH$_3$)$_2$), 126.8 (s, C_6H_4(CH=CHCH$_3$)$_2$), 14.7 (s, C_6H_4(CH=CHCH$_3$)$_2$). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) $\rightarrow$ ^{13}C (126 MHz)): δ 7.04 $\rightarrow$ 127.4; 6.38 $\rightarrow$ 129.9; 5.74 $\rightarrow$ 126.8; 1.87 $\rightarrow$ 14.7. MS: m/z 198 (M$^+$).

[IrCl$_2$(CH=CHPPh$_3$)(CO)(PPh$_3$)$_2$]OTf **2**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.48 (ddt, J = 29.7, 17.5, 3.3 Hz, Ir–CH= CHPPh$_3$), 6.8–8.2 (m, Ir–PPh$_3$ and Ir–CH=CHP(C$_6$H$_5$)$_3$, 46H). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 14.14 (t, J = 3.5 Hz, Ir–CH= CHPPh$_3$), $-$14.34 (d, J = 3.5 Hz, Ir–PPh$_3$). IR (KBr, cm^{-1}): 2056 (s, v_{CO}), 1271, 1154, 1031 (br s, due to uncoordinated triflate). Anal. Calc. for IrP$_3$O$_4$SF$_3$C$_{58}$H$_{47}$: C, 58.93; H, 4.01. Found: C, 59.03; H, 4.07%.

Reaction of [Ir(R)(CH=CHPPh$_3$)(C≡C-*p*-C$_6$H$_4$CH$_3$)(CO)-(PPh$_3$)$_2$]OTf (R = CH$_3$ 7a, CH$_2$Ph 7b) with H(D)Cl: formation of *cis*-CH$_3$(D$_3$)CH(D)=CH(D)(*p*-C$_6$H$_4$CH$_3$) 8a, *cis*-C$_6$H$_5$CH$_2$-(D$_2$)CD=CD(*p*-C$_6$H$_4$CH$_3$) 8b and *cis*-C$_6$H$_5$CH(D)=CH(D)CH$_2$-(D$_2$)(*p*-C$_6$H$_4$CH$_3$) 8b′. These reactions were carried by the same manner as above for **1** with HCl. The yield of *cis*-CH$_3$CH= CH(*p*-C$_6$H$_4$CH$_3$) **8a** was *ca.* 95% measured by ^{1}H NMR in CDCl$_3$. The ratio (65 : 35) of *cis*-C$_6$H$_5$CH$_2$C=C(*p*-C$_6$H$_4$CH$_3$) **8b** to *cis*-C$_6$H$_5$CH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$) **8b′** was determined by ^{1}H NMR in CDCl$_3$.

cis-CH$_3$CH=CH(*p*-C$_6$H$_4$CH$_3$) **8a**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.12–7.22 (AB quartet with $\delta v/J$ = 2.3, J = 8.0 Hz, *p*-C$_6$H$_4$CH$_3$, 4H), 6.40 (dd, J = 11.4, 1.5 Hz, CH$_3$CH=CH-(*p*-C$_6$H$_4$CH$_3$)), 5.74 (dq, J = 11.4, 7.2 Hz, CH$_3$CH=CH(*p*-C$_6$H$_4$-CH_3)), 2.36 (s, *p*-C$_6$H$_4$CH_3, 3H), 1.89 (dd, J = 7.2, 1.5 Hz, CH_3CH=CH(*p*-C$_6$H$_4$CH$_3$), 3H). ^{1}H NOE measurement (500 MHz, CDCl$_3$): irradiation of the signal at 5.74 ppm shows a positive NOE effect on the signal at 6.40 ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ 136.1, 134.8, 129.7, 128.8, 128.7, 126.0 (olefinic carbons and *p*-C$_6$H$_4$CH$_3$), 21.1 (s, *p*-C$_6$H$_4$CH_3), 14.6 (s, CH_3CH=CH(*p*-C$_6$H$_4$CH$_3$)). MS: m/z 132 (M$^+$).

cis-CD$_3$CD=CD(*p*-C$_6$H$_4$CH$_3$) **8a**-d_5. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.12–7.22 (AB quartet with $\delta v/J$ = 2.3, J = 8.0 Hz, *p*-C$_6$H$_4$CH$_3$, 4H), 2.36 (s, *p*-C$_6$H$_4$CH_3, 3H). MS: m/z 137 (M$^+$).

cis-PhCH$_2$CH=CH(*p*-C$_6$H$_4$CH$_3$) **8b**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.2–7.3 (m, C$_6$H$_5$CH$_2$CH=CH(*p*-C$_6$H$_4$CH$_3$), 9H), 6.59 (d, J = 11.5 Hz, PhCH$_2$CH=CH(*p*-C$_6$H$_4$CH$_3$)), 5.85 (dt, J = 11.5, 7.5 Hz, PhCH$_2$CH=CH(*p*-C$_6$H$_4$CH$_3$)), 3.72 (dd, J = 7.5, 1.0 Hz, PhCH_2CH=CH(*p*-C$_6$H$_4$CH$_3$), 2H), 2.39 (s, *p*-C$_6$H$_4$CH_3, 3H). ^{1}H NOE measurement (500 MHz, CDCl$_3$): irradiation of the signal at 5.85 ppm shows a positive NOE effect on the signal at 6.59 ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ 130.0 (PhCH$_2$CH=CH(*p*-C$_6$H$_4$CH$_3$)), 129.8 (PhCH$_2$CH= CH(*p*-C$_6$H$_4$CH$_3$)), 34.7 (PhCH$_2$CH=CH(*p*-C$_6$H$_4$CH$_3$)), 21.2 (s, *p*-C$_6$H$_4$CH_3). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) $\rightarrow$ ^{13}C (126 MHz)): δ 6.59 $\rightarrow$ 129.8; 5.85 $\rightarrow$ 130.0; 3.72 $\rightarrow$ 34.7; 2.89 $\rightarrow$ 21.2. MS: m/z 208 (M$^+$).

cis-PhCD$_2$CD=CD(*p*-C$_6$H$_4$CH$_3$) **8b**-d_4. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.2–7.3 (m, C$_6$H$_5$CD$_2$CD=CD(*p*-C$_6$H$_4$CH$_3$), 9H), 2.89 (s, *p*-C$_6$H$_4$CH_3, 3H). MS: m/z 212 (M$^+$).

cis-PhCH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$) **8b′**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.2–7.3 (m, C$_6$H$_5$CH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$), 9H),

6.61 (d, J = 11.5 Hz, PhCH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$), 5.88 (dt, J = 11.5, 7.5 Hz, PhCH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$)), 3.67 (dd, J = 7.5, 1.0 Hz, PhCH=CHCH_2(*p*-C$_6$H$_4$CH$_3$), 2H), 2.36 (s, *p*-C$_6$H$_4$CH_3, 3H). ^{1}H NOE measurement (500 MHz, CDCl$_3$): irradiation of the signal at 5.88 ppm shows a positive NOE effect on the signal at 6.61 ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ 131.0 (PhCH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$)), 129.7 (PhCH=CHCH$_2$-(*p*-C$_6$H$_4$CH$_3$)), 34.2 (PhCH=CHCH$_2$(*p*-C$_6$H$_4$CH$_3$)), 21.0 (s, *p*-C$_6$H$_4$CH_3). ^{1}H,^{13}C-2D COSY (^{1}H (500 MHz) $\rightarrow$ ^{13}C (126 MHz)): δ 6.61 $\rightarrow$ 129.7; 5.88 $\rightarrow$ 131.0; 3.67 $\rightarrow$ 34.2; 2.36 $\rightarrow$ 21.0. MS: m/z 208 (M$^+$).

cis-PhCD=CDCD$_2$(*p*-C$_6$H$_4$CH$_3$) **8b′**-d_4. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.2–7.3 (m, C$_6$H$_5$CD=CDCD$_2$(*p*-C$_6$H$_4$CH$_3$), 9H), 2.36 (s, *p*-C$_6$H$_4$CH_3, 3H). MS: m/z 212 (M$^+$).

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