Facile Insertion of Alkynes into Ir–P (Phosphine) and Ir–As (Arsine) Bonds: Second and Third Alkyne Addition to Mononuclear Iridium Complexes

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Alkynes (HC≡CH, PhC≡CH) insert into Ir–P (phosphine) and Ir–As (arsine) bonds of $[Ir(H)(C{\equiv}CPh)(L_3)(MPh_3)]^+$ and $[Ir{-}CH{=}CH{-}CH{=}CH)(MeCN)(L_3)]^+$ in the presence of MPh_3, to produce $[Ir(H)(C{\equiv}CPh)(L_3)(CH{=}CHR{-}M^+Ph_3)]^+$ and $[Ir(CH{=}CH{-}CH{=}CH)(L_3)(CH{=}CHR{-}M^+Ph_3)]^+$ [R = H, Ph; $L_3 = (CO)(PPh_3)_2$; M = P, As].

Metal-mediated oligomerization and polymerization of alkynes are of interest since they are carbon–carbon bond-forming reactions[1] and produce a variety of new organic materials.[2] In the course of our study on the metal catalysed oligomerization of alkynes,[3] we have found that alkynes (RC≡CH; R = H, Ph) insert into Ir–PPh_3 and Ir–$AsPh_3$ bonds to give Ir–CH=CR–$^+MPh_3$ (M = P, As) species.

While the insertion of an alkyne into metal–phosphorus bonds has been reported,[4] the insertion of an alkyne into a metal–arsenic bond, to our knowledge, has not been observed. The fact that one mole of $[Ir(CO)(PPh_3)_3]ClO_4$ **1a**[5] reacts with three moles of HC≡CH and two moles of PhC≡CH, respectively prompted us to investigate the alkyne adducts **2a**, **2b** and **3** (Scheme 1).

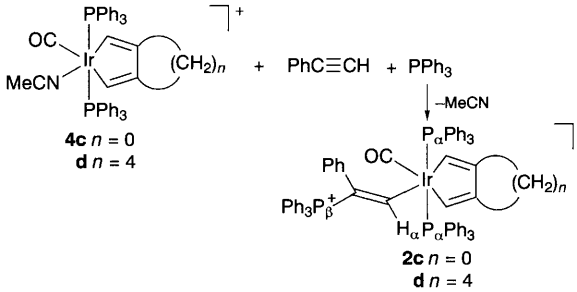
Stirring the yellow solution of **1a** (0.11 g, 0.1 mmol) (or **1b**) in CH_2Cl_2 (10 ml) under HC≡CH (1 atm) at 25 °C resulted in precipitation of beige microcrystals of **2a** (0.09 mmol) (or **2b**) within 1 h. Beige microcrystals of **3** (0.09 mmol) were isolated from a CH_2Cl_2 (20 ml) solution of **1a** (0.1 mmol) and PhC≡CH (0.4 mmol) that was refluxed for three days then cooled down to 25 °C.

These alkenylcarbonyliridacyclopentadienes, **2a** and **2b** and alkenylalkynylhydridocarbonyliridium(III) **3** are stable in solution even under oxygen at room temperature and unambiguously characterized by spectral (^1H, ^{31}P and ^{13}C NMR; IR) data† and satisfactory elemental analysis.

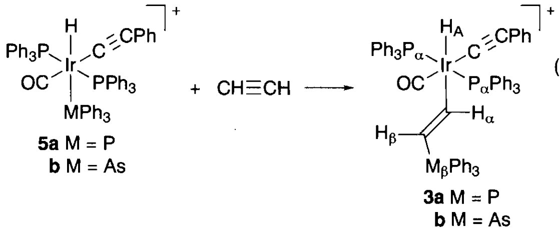
Distinctive signals in the ^1H NMR spectra at δ 9.0–10.5 were assigned to Hα (Scheme 1). α-Protons of metal-bound alkenyl groups have been observed at low field, *e.g.* Re–*CH*=CHP$^+$Me$_3$ δ 12.3.[4a] Those signals at low field (δ 9.74, ddt **2a**; 9.25, dt **2b**; 10.1, dt **3**) are unequivocally assigned to Hα of **2a** ($J_{H\alpha-P\beta}$ 35.8 $J_{H\alpha-H\beta}$ 18.8, $J_{H\alpha-P\alpha}$ 1.7 Hz), **2b** ($J_{H\alpha-H\beta}$ 18.3, $J_{H\alpha-P\alpha}$ 1.8 Hz) and **3** ($J_{H\alpha-P\beta}$ 37.8, $J_{H\alpha-P\alpha}$ 1.9 Hz). The observed coupling constants, $J_{H\alpha-H\beta}$ (18.8 for **2a** and 18.3 Hz for **2b**) suggest that H_α is *trans* to H_β in **2**, and accordingly H_α is suggested to be *trans* to the Ph group in **3**. The triplets of doublet at δ −10.7 ($J_{HA-P\alpha}$ 14.5, $J_{HA-P\beta}$ 16.5 Hz) is certainly due to H_A in **3**. It is not so surprising not to see the coupling between H_A and H_α in **3** while a relatively large coupling constant ($^4J_{P-H}$ 16.5 Hz) was observed between H_A and P_β, which has been confirmed by 2D NMR (COSY) and decoupling measurements, since relatively large $^4J_{P(trans)-H}$ (6.2 Hz,[6b]) have been reported for $(PMe_3)Ir(CR{=}CHR)$[6a] and $(PR_3)Ru(CR{=}CHR)$[6b] species.

Signals (4 × m, δ 5.8–7.5) due to protons of iridacyclopentadiene groups[7] of **2** are all seen at somewhat downfield from those (4 × m, δ 5.5–7.3)‡ of the iridacyclopentadiene complex **4c** [see eqn. (1)] prepared from the reaction of $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ with HC≡CH and characterized by spectroscopy and X-ray crystal structure analysis.‡ The ^{13}C NMR spectrum also confirms $(Ph_3P_\alpha)_2Ir{-}C_\alpha H{=}C_\beta H{-}^+P_\beta Ph_3$ moiety for **2a** by showing a multiplet at δ 181.3 for C_β and a doublet at δ 110.5 ($J_{C\alpha-P\beta}$ 66.1 Hz) for C_α. The ^{31}P NMR ($CDCl_3$) spectrum of **2a** shows $P_\alpha Ph_3$ at δ 1.13 (d, 2 P, $J_{P\alpha-P\beta}$ 4.3 Hz) and $P_\beta{}^+Ph_3$ δ 14.4 (t, 1 P) and are in good agreement with the suggested structure of **2a**.

Insertion of alkynes into Ir–P and Ir–As bonds can also be achieved by the reactions of adducts of an alkyne with other alkynes. Both adducts of HC≡CH and $HC{\equiv}C(CH_2)_4C{\equiv}CH$ (**4c** and **4d**)‡ react with PhC≡CH in the presence of PPh_3 to give adducts (**2c** and **2d**)† of two different alkynes [eqn. (1)] while the PhC≡CH adducts, **5a** and **5b** react with HC≡CH to produce adducts of two different alkynes, **3a** and **3b**† [eqn. (2)].



(1)

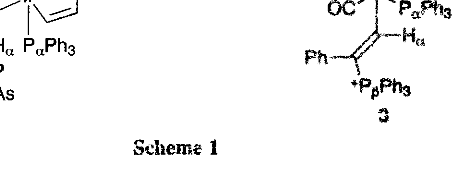


(2)

A mixture of **4c** (0.10 g, 0.1 mmol) (or **4d**), PhC≡CH (12 μl, 0.11 mmol) and PPh_3 (0.03 g, 0.11 mmol) in $CHCl_3$ (10 ml) was stirred for 3 h under N_2 to yield beige microcrystals of **2c** (0.09 mmol) (or **2d**). Beige microcrystals of **3a** (0.09 mmol) (or **3b**) were obtained from the solution of **5a** (0.12 g, 0.1 mmol) kept under HC≡CH (3 atm) for 24 h at 50 °C. Complexes **5a** and **5b** are readily obtained by replacement of RCN in the PhC≡CH adduct, $[IrH(C{\equiv}CPh)(RCN)(CO)(PPh_3)_2]ClO_4$[8] with PPh_3 and $AsPh_3$, respectively.

We also found that compound **3** can be obtained from the reaction of **5a** with PhC≡CH at 50 °C; and the reaction of **4c** with HC≡CH in the presence of PPh_3 and $AsPh_3$, respectively produce **2a** and **2b**.

It should be mentioned that attempts to prepare iridacycles containing the $Ir(PPh_3)_2(MPh_3)$ group, $[IrCH{=}CH{-}CH{=}CH)(CO)(PPh_3)_2(MPh_3)]^+$ (M = P, As) by replacing RCN (PhCN, MeCN) of **4** with MPh_3 have been unsuccessful.



Scheme 1

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Footnotes

† *Selected data* for **2a**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 6.70 (dd, 1 H, $J_{\mathrm{H\alpha-H\beta}}$ 18.8 Hz, =C*H*P$^+$Ph$_3$), 5.85, 6.06, 6.72, 7.10 [4 × m, 1 H, (IrC$_4$H$_4$)], 6.9–7.5 (m, 45 H, PC$_6$H$_5$); ^{13}C{^{31}P} NMR (CDCl$_3$, 25 °C) δ 175.8 (t, CO), 129.3 [br, α-C of (IrC$_4$H$_4$)], 153.9 [t, α-carbons of (IrC$_4$H$_4$)] 145.8 [s, β-C of (IrC$_4$H$_4$)] 146.2 [br, β-C (IrC$_4$H$_4$)]; IR (Nujol) ν_{max}/cm^{-1} 1998s (CO), 1100s, br (noncoordinated tetrahedral ClO$_4^-$).

For **2b**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 6.57 (d, 1 H, $J_{\mathrm{H\alpha-H\beta}}$ 18.9 Hz, =C*H*As$^+$Ph$_3$), 5.87, 6.10, 6.63, *ca.* 6.90 [4 × m, 1 H, (IrC$_4$H$_4$)], 6.9–7.5 (m, PC$_6$H$_5$ and AsC$_6$H$_5$); IR (Nujol) ν_{max}/cm^{-1} 1997s (CO), 1100s, br noncoordinated tetrahedral ClO$_4^-$.

For **2c**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 10.45 (dt, 1 H, $J_{\mathrm{H\alpha-P\alpha}}$ 2.94 Hz, $J_{\mathrm{H\alpha-P\beta}}$ 39.5 Hz, Ir–CH$_\alpha$=) 6.70 (d, 2 H, *J* 8.0 Hz, *o*-H C$_6$H$_5$), 6.00 (m, 1 H, Ir–C$_4$H$_4$), 5.45 (m, 1 H, Ir–C$_4$H$_4$); IR (Nujol) ν_{max}/cm^{-1} 1995s (CO), 1100s, br (ClO$_4^-$).

For **2d**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 10.33 (dt, 1 H, $J_{\mathrm{H\alpha-P\beta}}$ 39.3 Hz, $J_{\mathrm{H\alpha-P\alpha}}$ 2.7 Hz, Ir–C*H*=C(Ph)P$^+$Ph$_3$), 6.73 (d, 2 H, *o*-H C$_6$H$_5$), 6.64 (s, 1 H, Ir–C*H*=CCH$_2$), 6.54 (s, 1 H, Ir–C*H*=CCH$_2$), 1.78 (br, 2 H, Ir–CH=CC*H*$_2$), 1.16 (br, 2 H, Ir–CH=CC*H*$_2$), 0.62 (m, 2 H, Ir–CH=CCH$_2$–C*H*$_2$), 0.49 (m, 2 H, Ir–CH=CCH$_2$–C*H*$_2$); IR (Nujol) ν_{max}/cm^{-1} 1992s (CO), *ca.* 1100s, br (noncoordinated tetrahedral ClO$_4^-$).

For **3**: ^{1}H NMR (CDCl$_3$, 25 °C) *o*-H δ 6.18 (d, 2 H *o*-H C$_6$H$_5$), 6.43 (m, 2 H), 6.5–7.9 (m); ^{31}C{^{13}P} NMR (CDCl$_3$, 25 °C) δ 122 (d, $J_{\mathrm{C\alpha-P\beta}}$ 58.1 Hz, Ir–*C*$_\alpha$H=C$_\beta$-(Ph)P$_\beta^+$PPh$_3$), 180.1 (br, Ir–CH=*C*(Ph)P$^+$PPh$_3$), 98.1 (t, $J_{\mathrm{C-P\alpha}}$ 19.1 Hz, Ir–*C*≡CPh), 109.5 (s, Ir–C≡*C*Ph), 172.4 (t, $J_{\mathrm{C-P\alpha}}$ 6.8 Hz, Ir–CO), 120–140 (P–*C*$_6$H$_5$); ^{31}P NMR (CDCl$_3$, 25 °C) δ 20.11 (t, $J_{\mathrm{P\alpha-P\beta}}$ 3.6 Hz, CH=C(Ph)–*P*$_\beta^+$Ph$_3$), −1.99 (d, $J_{\mathrm{P\alpha-P\beta}}$ 3.6 Hz, Ir–P$_\alpha$Ph$_3$); IR (Nujol) ν_{max}/cm^{-1} 2025s (CO), 2118w (Ir–H), 1100s, br ClO$_4^-$.

For **3a**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 9.79 (dd, 1 H, Ir–CH$_\alpha$=, $J_{\mathrm{H\alpha P\beta}}$ 33.9, $J_{\mathrm{H\alpha-H\beta}}$ 19.2 Hz), 6.75 (dd, 1 H, Ir–CH$_\alpha$=C*H*$_\beta$, $J_{\mathrm{H\beta-P\beta}}$ 37.7, $J_{\mathrm{H\alpha-H\beta}}$ 19.2 Hz), 6.42 (d, 2 H, *o*-H C$_6$H$_5$) and −10.29 (tdd, $J_{\mathrm{HA-P\alpha}}$ 14.8, $J_{\mathrm{HA-P\beta}}$ 14.7 Hz, $J_{\mathrm{HA-H\alpha}}$ 2.5 Hz); ^{31}P NMR (CDCl$_3$, 25 °C) 14.04 (t, 1 P, $J_{\mathrm{P\alpha-P\beta}}$ 3.8 Hz, P$_\beta$), −1.55 (d, 2 P, $J_{\mathrm{P\alpha-P\beta}}$ 3.8 Hz, P$_\alpha$); IR (Nujol) ν_{max}/cm^{-1} 2016s (CO), 2114w (Ir–H), 1100s, br (ClO$_4^-$).

For **3b**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 9.09 (d, 1 H, $J_{\mathrm{H\alpha-H\beta}}$ 18.5 Hz, Ir–CH$_\alpha$=), 6.58 (d, 1 H, $J_{\mathrm{H\alpha-H\beta}}$ 18.5 Hz, Ir–CH$_\alpha$=C*H*$_\beta$), 6.46 (m, 2 H, *o*-H ≡CC$_6$H$_5$), −10.40 (dt, 1 H, $J_{\mathrm{HA-P\alpha}}$ 14.6, $J_{\mathrm{HA-H\alpha}}$ 2.0 Hz); IR (Nujol) ν_{max}/cm^{-1} 2020s (CO), 2113w (Ir–H) and 1100s, br (ClO$_4^-$).

‡ Preparation and X-ray crystal structure details for **4c** and **4d** will be published elsewhere *Selected spectral data* for **4c**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 5.64 (m, 1 H, Ir–CH=), 5.98 (m, 1 H, Ir–CH=C*H*), 6.70 (m, 1 H, Ir–CH=C*H*) and 7.27 (m, 1 H, Ir–CH=).

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