Opening of an Ir_4 Cluster: The Reactions of $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ with $PPh_2C{\equiv}CPh$

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Reaction of $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **1** with $PPh_2C{\equiv}CPh$ yields the CO replacement compound $[HIr_4(CO)_9(PPh_2C{\equiv}CPh)(\mu\text{-}PPh_2)]$ **3**, that is readily converted to the species $[Ir_4(CO)_7(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}HC_2Ph)]$ **4**; reaction of **1** with $PPh_2C{\equiv}CPh$ in the presence of base, followed by protonation, affords the novel compound $[HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}PPh_2C_2Ph)(\mu\text{-}PPh_2)]$ **5**.

The reactions of di- and poly-nuclear carbonyl compounds of the iron subgroup with phosphinoacetylenes $PR_2C{\equiv}CR'$ have been widely investigated over the last 15 years.[1,2] It has been established that P–C bond cleavage can generally be induced by thermolysis,[3] photolysis[1] and chemical activation using Me_3NO,[4] to generate phosphido $-PR_2$ and $-C_2R'$ bridging fragments. The mechanism of the P–C bond cleavage is unknown, but the formation of a π-interacting acetylene intermediate, followed by oxidative insertion into the P–C bond, has been proposed.[1,5]

Considering that both $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **1** and the monoanion $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ **2**[6] are extremely reactive towards phosphines but inert towards acetylenes,[7] we thought it was worth investigating their reactions with $PPh_2C{\equiv}CPh$, as an alternative route for obtaining acetylide and acetylene coordinated species. Indeed, the presence of a hydride ligand in **1** could extend the type of reactivity generally observed by the possible insertion of the C–C triple bond into the Ir–H bond. The literature gives only two precedents for this type of reaction with the clusters $[HRu_3(CO)_9(\mu\text{-}PPh_2)]$[2] and $[PPh_4][HFe_3(CO)_{11}]$.[8]

$$[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$$

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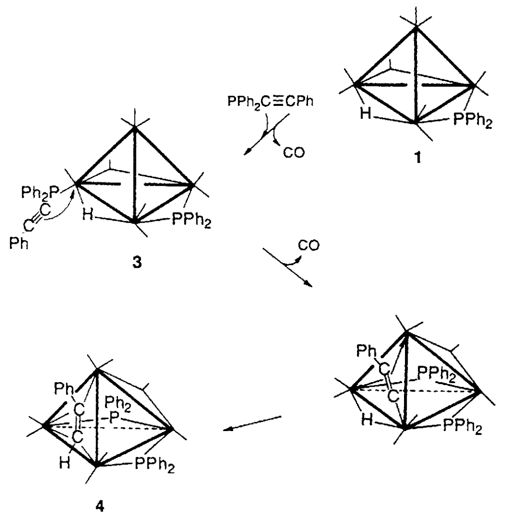
The reaction of **1** with L ($PPh_2C{\equiv}CPh$; 1 equiv.) in CH_2Cl_2 gives the CO replacement compound $[HIr_4(CO)_9L(\mu\text{-}PPh_2)]$ **3** (70% yield after TLC (CH_2Cl_2–hexane, 3 : 7, as eluent). This compound was characterized by analysis and spectroscopic



data,† that confirm that its structure is similar to that of the L = PPh_3 derivative **3a**, which has been established by X-ray diffraction.[7]

When a solution of **3** in CH_2Cl_2 was kept at room temperature for 24 h, quantitative conversion to $[Ir_4(CO)_7(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^3\text{-}HC_2Ph)]$ **4** took place, complex **4** being isolated in 90% yield after crystallization from hexane and fully characterized by analysis and spectroscopic data.† The molecular structure of **4** was established by an X-ray diffraction study‡ and is shown in Fig. 1. The species exhibits a tetrahedral metal framework, with two elongated edges [Ir(1)–Ir(3) 3.180(3) and Ir(1)–Ir(2) 2.976(3) Å], which are spanned by the two three-electron donor phosphido bridges. The phenylacetylene is σ-bonded to Ir(2) and Ir(4) and π-bonded to Ir(3) and as such it bonds to the cluster in the common $\mu_3\text{-}\eta^2\text{-}\|$ fashion contributing four electrons to the cluster orbitals. The C–C (alkyne) bond distance [1.512(6) Å] is much longer than the values associated with clusters of this kind capped on a triangular face with an acetylene unit (1.33–1.43 Å).[9] The eight terminal CO groups are distributed one on Ir(1) and two on each remaining Ir atom, and a semi-bridging carbonyl spans the Ir(1)–Ir(4) edge [Ir(1)–C(2) 1.92(4) and Ir(4)–C(2) 2.15(5) Å].

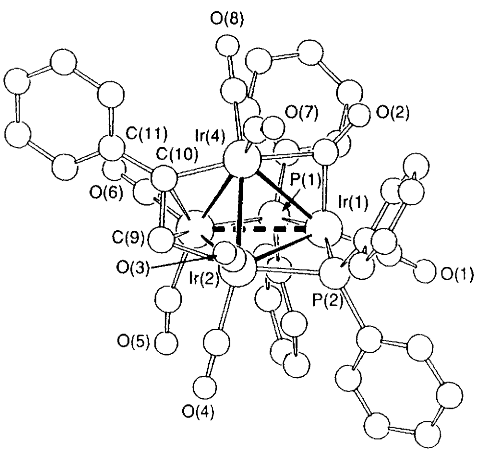


Fig. 1 The molecular structure of $[Ir_4(CO)_7(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}HC_2Ph)]$ **4**. Relevant bond distances (Å) and angles (°); Ir(1)–Ir(2) 2.976(3), Ir(1)–Ir(3) 3.180(3), Ir(1)–Ir(4) 2.861(3), Ir(2)–Ir(3) 2.847(3), Ir(2)–Ir(4) 2.730(3), Ir(3)–Ir(4) 2.696(3), Ir(1)–P(1) 2.28(1), Ir(3)–P(1) 2.34(1), Ir(1)–P(2) 2.26(1), Ir(2)–P(2) 2.37(1), Ir(2)–C(9) 2.00(5), Ir(3)–C(9) 2.27(4), Ir(3)–C(10) 2.40(5), Ir(4)–C(10) 1.95(5), C(9)–C(10) 1.512(6), Ir(1)–C(2)–Ir(4) 89(2), Ir(1)–P(1)–Ir(3) 87.1(4), Ir(1)–P(2)–Ir(2) 79.9(5), C(9)–C(10)–C(11) 118(4).

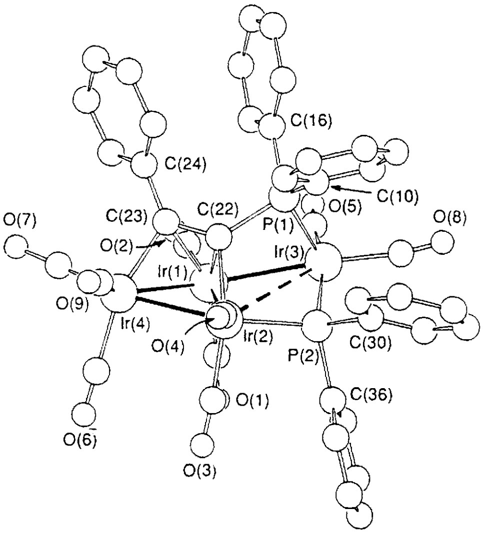


Fig. 2 The molecular structure of $[HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}PPh_2C_2Ph)(\mu\text{-}PPh_2)]$ **5**. Relevant bond distances (Å) and angles (°): Ir(1)–Ir(2) 2.627(2), Ir(1)–Ir(3) 2.828(2), Ir(1)–Ir(4) 2.713(2), Ir(2)–Ir(3) 3.686(2), Ir(2)–Ir(4) 2.723(2), Ir(1)–C(23) 2.29(4), Ir(1)–C(22) 2.11(2), Ir(2)–C(22) 2.11(2), Ir(4)–C(23) 2.07(4), C(22)–C(23) 1.33(4), Ir(3)–P(1) 2.37(1), P(1)–C(22) 1.85(2), Ir(2)–P(2) 2.36(1), Ir(3)–P(2) 2.34(1), C(24)–C(23)–C(22) 128(3), C(23)–C(22)–P(1) 130(2), C(22)–P(1)–Ir(3) 96(1), Ir(2)–P(2)–Ir(3) 103.3(3).

The reactions leading from **1** to **4** are given in Scheme 1. Although P–C bond cleavage is now an established phenomenon, this process is not usually observed to occur under such mild conditions.[1,2] A similar process has been observed in the reaction of $[HRu_3(CO)_9(\mu\text{-}PPh_2)]$ with $PPh_2C{\equiv}CR$ (R = Ph, Bu^t or Pr^i),[3] while migration of a hydride ligand onto the β-carbon generating a vinylidene ligand has been shown to occur in the reaction of the anionic cluster $[HFe_3(CO)_{11}]^-$ with $PPh_2C{\equiv}CCMe_3$.[8]

The reaction of the anionic species **2** with $PPh_2C{\equiv}CPh$ has also been investigated. Deprotonation *in situ* of **1**[5] with 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of $PPh_2C{\equiv}CPh$ in CH_2Cl_2, followed by protonation with tri-

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† *Spectroscopic data*: **3**: IR (hexane), ν/cm^{-1}, ν(C≡C) 2172w; ν(CO) 2068s, 2032vs, 2004s, 1994m, 1982m, sh and 1830w, br; ^{1}H NMR (CD_2Cl_2) δ −11.78 (dd, hydride) [$J_{H\text{-}P}$/Hz 55.8 (PPh_2) and 6.0 ($PPh_2C{\equiv}CPh$)] and 6.7–7.9 (m, Ph); $^{31}P\{^1H\}$ NMR, δ 283.0 (s, PPh_2) and −41.0 ppm (s, $PPh_2C{\equiv}CPh$), ref. H_3PO_4.

4: IR (hexane) ν(CO)/cm^{-1}, 2062w, 2042s, 2034vs, 2004vw, 1990w and 1853w, br; FAB MS (nitrobenzyl alcohol matrix) (calc. for ^{193}Ir) 1466 $(M)^{\cdot+}$ and 1466 − 28x, x = 1–8 $[M - (CO)_x]^{\cdot+}$; ^{1}H NMR (CD_2Cl_2) δ 9.1 (s, HCCPh) and 7.2–7.8 (m, Ph).

5: IR (hexane) ν(CO)/cm^{-1}, 2074m, 2044vs, 2030vs, 2014vs, 1972w and 1957vw; FAB MS (nitrobenzyl alcohol matrix) (calc. for ^{193}Ir) 1496 $(M)^{\cdot+}$ and 1496 − 28_x, x = 1–9 $[M - CO_x]^{\cdot+}$ $(M - 2CO)^{\cdot+}$; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ − 58.50 (d) and −63.53 (d) ($J_{P\text{-}P}$ 20.3 Hz); Satisfactory elemental analyses.

$[HIr_4(CO)_8\,(PPh_2C{\equiv}CPh)_2(\mu\text{-}PPh_2)]$: IR (hexane) ν/cm^{-1}, ν(C≡C) 2172w; ν(CO) 2068m. 2052m, 2022s, 1987m, br and 1805w, br.

$[HIr_4(CO)_8(PPh_3)(\mu_4\text{-}\eta^3\text{-}PPh_2C_2Ph)(\mu\text{-}PPh_2)]$: IR (hexane), ν(CO)/cm^{-1} 2036vs, 2010s, 1957m, br and 1740w, br; FAB MS (nitrobenzyl alcohol matrix) (calc. for ^{193}Ir) 1727 $(M)^{\cdot+}$ and 1727 − 28x, x = 1–8 $[M - (CO)_x]^{\cdot+}$.

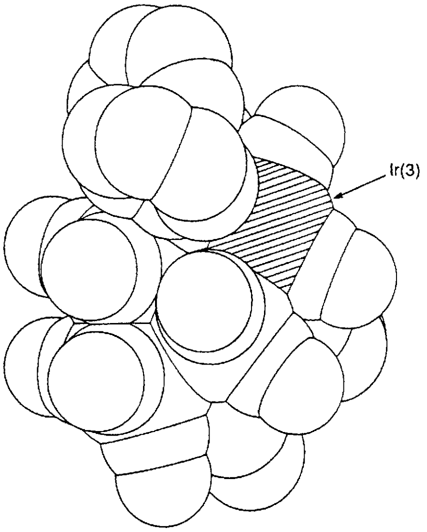

Fig. 3 Space filling diagram of **5** showing the free coordination site on Ir(3)

fluoroacetic acid affords, after TLC (CH_2Cl_2–hexane, 3 : 7, as eluent; up to 50% yield after crystallization from CH_2Cl_2–hexane), the bright yellow compound $[HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}PPh_2C_2Ph)(\mu\text{-}PPh_2)]$ **5**, fully characterized by analysis and spectroscopic data.† As expected on the basis of the analogous reaction with L = PPh_3,[7] the CO substituted tetrahedral species $[HIr_4(CO)_{10\text{-}n}L_n(\mu\text{-}PPh_2)]$ (L = $PPh_2C{\equiv}CPh$, n = 1, **3**, 15%; n = 2,† 10%) are also isolated from the reaction mixture.

The molecular structure of **5** has been established by X-ray diffraction‡ and is shown in Fig. 2. The metal framework of **5** can be described as a spiked triangle, or alternatively as a flat butterfly with an elongated edge. A complex pattern of ligand to cluster bonding interactions are observed: (*i*) the 'long' Ir–Ir edge [3.686(2) Å] is spanned by a three-electron donor phosphinidene ligand: (*ii*) the phosphinoacetylene ligand interacts with the four iridium atoms, formally contributing a total of six electrons to the cluster orbitals *via* a two-electron P–Ir bond and two σ-interactions and one π-interaction from the acetylene system: (*iii*) three of the nine carbonyl groups are on the wing-tip Ir(4) atom which is interacting in a σ-manner with the acetylene, each remaining Ir atom having two carbonyl groups; (*iv*) the hydride ligand is probably bound in a terminal fashion to the Ir(3) atom, which exhibits a 'free' coordination site in the space-filling diagram shown in Fig. 3. The metal core is almost flat [angle between the Ir(1)–Ir(2)–Ir(4) and Ir(1)–Ir(2)–Ir(3) planes 17°]. Both the C–C bond length [C(22)–C(23) 1.33(4) Å] and the C(Ph)–C=C and C=C–P angles [128(3) and 130(2)°, respectively] indicate that the hybridization of the acetylene atoms is essentially sp^2.

To our knowledge **5** represents the only case of a phosphinoacetylene acting as a 6-electron donor to a carbonyl cluster, in which the bridged metal atoms are all linked by M–M bonds.[10] Attempts at cleaving the P–C bond in **5** have so far been unsuccessful. Heating **5** in toluene (50–90 °C), photolysis (hexane; λ_{max} 366 nm) and reaction with Me_3NO only lead to decomposition. Heating **5** in CH_2Cl_2 under reflux in the presence of PPh_3 or the reaction of **5** with Me_3NO–PPh_3 gives quantitative yields of the canary yellow species $[HIr_4(CO)_8(PPh_3)(\mu_4\text{-}\eta^3\text{-}PPh_2C_2Ph)(\mu\text{-}PPh_2)]$† which also does not undergo P–C bond cleavage under the conditions just described. These results suggest that the ease with which such a process occurs does not only depend on the facility of formation of free coordination sites on the clusters *via* CO loss.[10] It seems that an intermediate containing the phosphinoacetylene as tightly bound to a rigid metal frame as in **5** should be ruled out in the formation of $-PPh_2$ and $-C_2Ph$ containing clusters and that the activation of the P–C bond is probably best achieved through a transient two electron π-interaction of the acetylene with a metal centre upon CO loss or M–M bond cleavage.

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‡ *Crystal data* for **4**: $C_{40}H_{26}Ir_4O_8P_2$, M = 1465, space group $P2_1/n$, a = 8.94(2), b = 39.05(2), c = 11.954(6) Å, β = 104.57(8)°, U = 4037.1 Å^3, Z = 4, D_c = 2.41 g cm^{-3}, F(000) = 2672, μ(Mo-Kα) = 127.8 cm^{-1}, θ range 2–20°, final R 0.069, R_w 0.073, for 2108 out of 2872 observed unique reflexions with $F_o > 4\,\sigma(F_o)$.

Crystal data for **5**: $C_{41}H_{25}Ir_4O_9P_2$, M = 1492, space group $P2_1/n$, a = 11.840(3), b = 18.745(9), c = 18.695 (8) Å, β = 100.63(3)°, U = 4077.9 Å^3, Z = 4, D_c = 2.43 g cm^{-3}, F(000) 2724, μ(Mo-Kα) = 126.5 cm^{-1}, θ range 2.5–20°, final R 0.058, R_w 0.060, for 2609 out of 2642 observed unique reflexions with $F_o > 4\sigma(F_o)$. An absorption correction was applied by the Walker and Stuart method[11] (correction range 0.44–1.00). Common to both species: intensity data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer by the ω–2θ scan method. Fast decay under X-ray exposure prevented extension of the data collection beyond θ = 20°. All atoms but the hydrogens and the phenyl carbon atoms in **5** were allowed to vibrate anisotropically. The H atoms of the phenyl groups were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their respective C atoms; a single isotropic thermal parameter was also refined for the H atoms [0.15(6) and 0.14(4) Å for **4** and **5**, respectively]. The structures were solved by direct methods.[12] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre; see Notice to Authors, Issue No. 1.