

Synthesis and X-Ray Crystallographic Characterisation of the Diphosphane bridged Cluster $[\text{Ir}_4(\text{CO})_{11}\text{PhPPPhIr}_4(\text{CO})_9(\text{AuPEt}_3)_2]$

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Deprotonation of $[\text{Ir}_4(\text{CO})_{11}\text{PPhH}_2]$ followed by oxidation with $\text{Ag}[\text{ClO}_4]$ in the presence of $[\text{AuPEt}_3]^+$ affords the cluster $[\text{Ir}_4(\text{CO})_{11}\text{PhPPPhIr}_4(\text{CO})_9(\text{AuPEt}_3)_2]$, which has been shown by an X-ray analysis to contain an Ir_4 and an Ir_4Au_2 unit linked by a diphosphane (PhPPPh) ligand.

The synthesis and reactivity of metal carbonyl clusters stabilised by bridging phosphorus donor ligands is a well explored field.¹ However, it is only recently that a high nuclearity carbonyl cluster has been characterised, in which there is a direct bond between two phosphorus atoms of the ligand. In $[\text{Ni}_5(\text{CO})_6\{(\text{Me}_3\text{Si})_2\text{CHPPCH}(\text{SiMe}_3)_2\}_2\text{Cl}]$ the two P atoms of the diphosphane ligand are linked by a formal P=P double bond.² We now report the synthesis and crystallographic characterisation of a carbonyl cluster which contains a

P–P single bonded diphosphane fragment as part of the cluster framework.

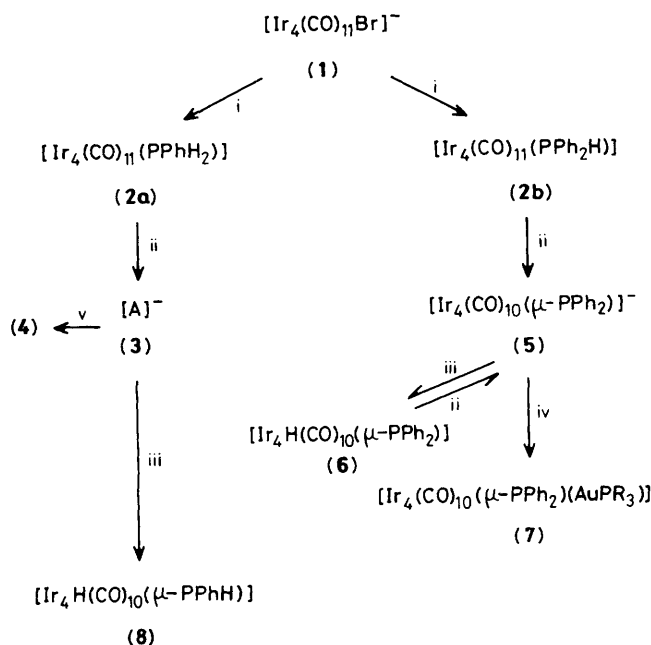
The low temperature oxidation of $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$ (**1**)^{3†} by silver salts in the presence of monoalkenes⁴ or MeCN⁵ has been shown to give $[\text{Ir}_4(\text{CO})_{11}\text{L}]$ (L = $\text{RHC}=\text{CH}_2$, MeCN) in high yield. This approach has now been extended to include

† (**1**) ν_{CO} (thf) incorrect in ref. 3: 2079w, 2047vs, 2038ssh, 2006vs, 1886vw, 1838m, 1831msh cm^{-1} .

the synthesis of phosphine derivatives $[\text{Ir}_4(\text{CO})_{11}\text{PPhHR}]$ [$\text{R} = \text{H}$ (**2a**), Ph (**2b**)] in better than 90% yield, as shown in Scheme 1. The subsequent deprotonation of (**2a**) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CH_2Cl_2 affords the monoanion $[\text{A}]^-$ (**3**). Oxidation of this species *in situ* with $\text{Ag}[\text{ClO}_4]$ in the presence of $[\text{AuPEt}_3][\text{ClO}_4]$, at 0 – 20°C , followed by t.l.c., using $1:4 \text{ CHCl}_3\text{--CCl}_4$ as eluant, affords the cluster $[\text{Ir}_4(\text{CO})_{11}\text{PhPPPhIr}_4(\text{CO})_9(\text{AuPEt}_3)_2]$ (**4**) in 31% yield after recrystallisation from CH_2Cl_2 –hexane.‡

A single crystal X-ray analysis of (**4**)§ (Figure 1) shows that the cluster contains an Ir_4 tetrahedral unit and an Ir_4Au_2 bicapped tetrahedral unit linked in an asymmetric fashion by the PhPPPh ligand. This group is terminally co-ordinated to the ' $\text{Ir}_4(\text{CO})_{11}$ ' species, to which it formally donates two electrons. The carbonyl ligand distribution around this Ir_4 tetrahedron is similar to that proposed for $[\text{Ir}_4(\text{CO})_{11}\text{PPh}_3]$,⁶ with three bridging carbonyls lying close to the Ir_3 basal plane. The average Ir--Ir distance [$2.732(5) \text{ \AA}$] within the tetrahedron is similar to that of $2.73 \text{ \AA}$ found in the substituted clusters $[\text{Ir}_4(\text{CO})_{12-n}(\text{PPh}_3)_n]$ ($n = 2, 3$),⁷ and distortions in the metal frameworks resulting from the influence of the bridging carbonyls are also similar.

Both P atoms of the PhPPPh ligand co-ordinate to the Ir_4Au_2 unit, capping an Ir_3 triangular face, *via* two links from P(3) and one link from P(4). As such, the ligand formally donates four electrons to the metal framework. The P(3)–P(4) distance [$2.186(13) \text{ \AA}$] is as yet the longest reported in a RPPR group co-ordinated to a polynuclear metal carbonyl complex. It is *ca.* $0.11 \text{ \AA}$ longer than the P–P distances found in $[\text{Fe}_2(\text{CO})_6(\text{Bu}^t\text{PPBu}^t)]$ ⁸ [$2.059(3) \text{ \AA}$] and $[\text{Ni}_5(\text{CO})_6\{(\text{Me}_3\text{Si})_2\text{CHPPCH}(\text{SiMe}_3)_2\}\text{Cl}]$ ² ($2.098 \text{ \AA}$) where the P–P interaction has been described as a double bond. It is better, therefore, to consider the PhPPPh group in (**4**) as a diphosphane, with a P–P single bond, since the P–P distance



Scheme 1. Reagents and conditions: i, PPhRH , $\text{R} = \text{H}$ (**2a**), $\text{R} = \text{Ph}$ (**2b**), 1 equiv. AgSbF_6 , thf , $-30 \rightarrow -15^\circ\text{C}$; yield $\text{R} = \text{H}$ 96%, $\text{R} = \text{Ph}$ 90%; ii, 1 equiv. DBU, thf/N_2 , room temp.; iii, $\text{H}[\text{BF}_4]$, $\text{CH}_2\text{Cl}_2/\text{N}_2$, room temp.; iv, $[\text{AuPR}_3][\text{ClO}_4]$, CH_2Cl_2 , room temp.; v, $\text{Ag}[\text{ClO}_4]$, $[\text{AuPEt}_3][\text{ClO}_4]$, 0 – 20°C .

‡ **Spectroscopic data:** (**2a**) ν_{CO} (hexane) 2096m, 2058vs, 2040s, 2017m, 2007m, 2000m, 1980w, 1965vw, 1958vw, 1857vw, 1836vw cm^{-1} ; ^1H n.m.r. (CDCl_3) 6.46 [d, $J(\text{P--H})$ 376.7 Hz], 7.60 (m, PPhH_2); m/z 1190 (calc. on ^{193}Ir 1190).

(**2b**) ν_{CO} (hexane) 2094m, 2057vs, 2038vs, 2015m, 2005m, 1998w, 1855vw, 1830vw cm^{-1} ; ^1H n.m.r. (CD_2Cl_2) 7.4 [d, $J(\text{P--H})$ 386.5 Hz], 7.45–7.49, 7.55–7.63 (m, PPh_2H); m/z 1266 (calc. on ^{193}Ir 1266).

(**3**) ν_{CO} (thf, HDBU⁺ salt) 2052w, 2020vs, 2004s, 1990msh, 1978msh, 1969msh, 1952msh, 1837w, 1808m cm^{-1} .

(**4**) ν_{CO} (hexane) 2083m, 2051vs, 2038msh, 2012s, 1965wsh, 1841mbr; m/z not observed; satisfactory analysis obtained.

(**5**) ν_{CO} (thf, HDBU⁺ salt) 2051m, 2014s, 1990vs, 1927w, 1800vwbr cm^{-1} .

(**6**) ν_{CO} (CH_2Cl_2) 2088m, 2058vs, 2047vs br, 2012mbr, 1972vwsh, 1957vwsh, 1831w cm^{-1} ; ^1H n.m.r. (CD_2Cl_2) -12.90 [d, $J(\text{P--H})$ 55.09 Hz, hydride], 7.1–7.8 (m, PPh_2); ^{31}P n.m.r. (CD_2Cl_2) -148.18 [d of m, $J(\text{P--H})$ 55.09 Hz] {ref. $(\text{MeO})_3\text{P}$ 1% $[\text{H}]\text{benzene}$ p.p.m.; m/z 1238 (calc. ^{193}Ir 1238).

(**7a**) ν_{CO} (hexane) 2072s, 2045vs, 2030vs, 2016vs, 2004s, 1995s, 1977w, 1963w, 1832m cm^{-1} ; ^1H n.m.r. (CD_2Cl_2) 1.25 [d of t, $J(\text{H--P})$ 18.6 Hz], 1.97 [d of q, $J(\text{H--P})$ 12.4 Hz] (CH_2CH_3), 7.12–7.85 (m, PPh_2).

(**8**) ν_{CO} (pentane) 2092m, 2065vs, 2053sbr, 2023msh, 2020s, 2003s, 1855m cm^{-1} ; ^1H n.m.r. (CDCl_3) -14.12 [d, $J(\text{P--H})$ 60.5 Hz, hydride].

§ **Crystal data:** $\text{C}_{44}\text{H}_{40}\text{Au}_2\text{Ir}_8\text{O}_{20}\text{P}_4 \cdot 1/2\text{CH}_2\text{Cl}_2$, $M = 2986.64$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.045(3)$, $b = 14.041(3)$, $c = 19.423(6) \text{ \AA}$, $\alpha = 105.27(2)$, $\beta = 99.40(2)$, $\gamma = 101.22(2)^\circ$, $U = 3270 \text{ \AA}^3$, $Z = 2$, $D_c = 3.03 \text{ g cm}^{-3}$, $F(000) = 2638$, $\mu(\text{Mo--K}\alpha) = 201.93 \text{ cm}^{-1}$. Data recorded on a Stoe-Siemens diffractometer using graphite monochromated $\text{Mo--K}\alpha$ radiation; 2θ range 5 – 47.5° , 6765 unique observed [$F > 5\sigma(F)$] absorption corrected reflections, $R = 0.080$, $R_w = 0.078$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

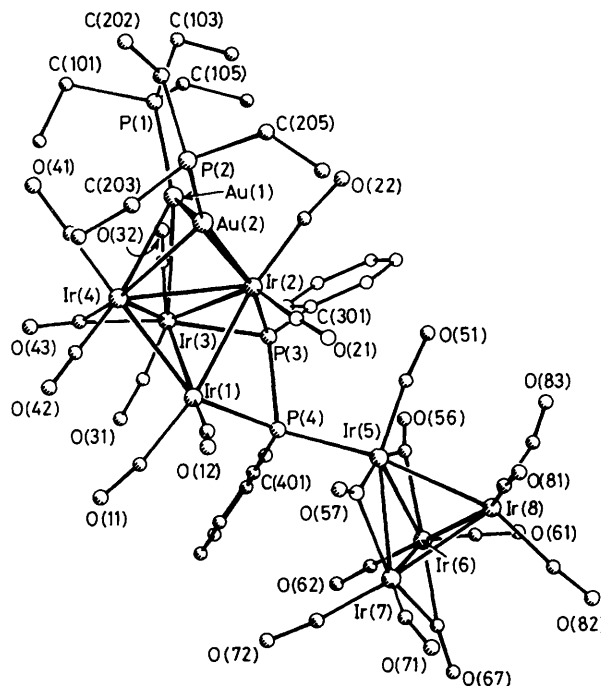


Figure 1. The molecular structure of $[\text{Ir}_4(\text{CO})_{11}\text{PhPPPhIr}_4(\text{CO})_9\text{-(AuPEt}_3)_2]$ (**4**) showing the atom numbering scheme. Bond lengths: $\text{Ir}(1)\text{--Ir}(2)$, $2.708(2)$; $\text{Ir}(1)\text{--Ir}(3)$, $2.724(2)$; $\text{Ir}(1)\text{--Ir}(4)$, $2.707(2)$; $\text{Ir}(2)\text{--Ir}(3)$, $2.879(2)$; $\text{Ir}(2)\text{--Ir}(4)$, $2.943(2)$; $\text{Ir}(2)\text{--Au}(1)$, $2.750(2)$; $\text{Ir}(2)\text{--Au}(2)$, $2.713(3)$; $\text{Ir}(3)\text{--Ir}(4)$, $2.807(3)$; $\text{Ir}(3)\text{--Au}(1)$, $3.007(3)$; $\text{Ir}(4)\text{--Au}(1)$, $2.853(3)$; $\text{Ir}(4)\text{--Au}(2)$, $2.862(2)$; $\text{Au}(1)\text{--P}(1)$, $2.264(12)$; $\text{Au}(1)\text{--Au}(2)$, $3.052(2)$; $\text{Au}(2)\text{--P}(2)$, $2.278(14)$; $\text{Ir}(2)\text{--P}(3)$, $2.302(12)$; $\text{Ir}(3)\text{--P}(3)$, $2.308(9)$; $\text{Ir}(1)\text{--P}(4)$, $2.434(11)$; $\text{P}(3)\text{--P}(4)$, $2.186(13)$; $\text{Ir}(5)\text{--P}(4)$, $2.375(8)$; $\text{Ir}(5)\text{--Ir}(6)$, $2.781(2)$; $\text{Ir}(5)\text{--Ir}(7)$, $2.763(2)$; $\text{Ir}(5)\text{--Ir}(8)$, $2.718(2)$; $\text{Ir}(6)\text{--Ir}(7)$, $2.694(3)$; $\text{Ir}(6)\text{--Ir}(8)$, $2.699(2)$; $\text{Ir}(7)\text{--Ir}(8)$, $2.716(2) \text{ \AA}$.

observed is close to the value of 2.2 Å expected for such a bond.⁹

The geometry of the Ir₄Au₂ framework in the 'Ir₄(CO)₉-(AuPET₃)₂' species is similar to that observed in the clusters [CoRu₃H(CO)₁₂(AuPPh₃)₂]¹⁰ and [Co₂Ru₂(CO)₁₂(AuPPh₃)₂].¹¹ However, the Au(1)–Au(2) distance in (4) is considerably longer than the equivalent distances of 2.787(1) Å in the CoRu₃Au₂ cluster¹⁰ and 2.890(1) Å in the Co₂Ru₂Au₂ cluster.¹¹ The Ir–Ir distances within the Ir(1)–Ir(4) tetrahedron show a greater range than those previously discussed in the Ir(5)–Ir(8) tetrahedron, and the longer Ir(2)–Ir(3) and Ir(2)–Ir(4) edges are bridged by the goldphosphine units.

The structure of (4) shows that the diphosphane ligand has been formed during the course of the reaction through the coupling of two Ir₄ units, by oxidation of the monoanion [A][–], which was obtained by the deprotonation of (2a) in the presence of [AuPET₃]⁺ fragments. This reaction is related to the formation of the diphosphene ligand in [Fe₂(CO)₆Bu⁺P-PBu[–]],⁸ which is obtained by the oxidation of the species which results from the deprotonation of [Fe₂(CO)₆(μ-PHBu[–])₂].

Deprotonation of [Ir₄(CO)₁₁(PPh₂H)] (2b) with DBU in tetrahydrofuran (thf) or CH₂Cl₂ gives the phosphido-bridged anion [Ir₄(CO)₁₀(μ-PPh₂)][–] (5), which exhibits a different i.r. spectrum in the ν(CO) region to that observed for the anion [A][–] (3) (Scheme 1). The monoanion (5) was characterised spectroscopically as the HDBU⁺ salt but was not isolated. Reaction of (5) with H[BF₄] in CH₂Cl₂ gives [Ir₄H(CO)₁₀(μ-PPh₂)] (6) in quantitative yield from (2b). The monoanion (5) is regenerated by the addition of DBU in thf, MeCN or CH₂Cl₂ and reacts with [AuPR₃][ClO₄] (R = Et, Ph) to give [Ir₄(CO)₁₀(μ-PPh₂)(AuPR₃)] [R = Et (7a), Ph (7b)]. In contrast the monoanion (3) is extremely air and moisture

sensitive and could not be isolated. It reacts with H[BF₄] in thf or CH₂Cl₂ to give a mixture of products including [Ir₄H(CO)₁₀(PPhH)] (8) in low yield.

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