Phosphine-substituted Derivatives of Dodecacarbonyltetrairidium. Synthesis and *X*-Ray Characterization of $[Ir_4(CO)_8(Ph_2PCH=CHPPh_2)_2]$ and of the Hydrido *ortho*-Metallated Derivative $[HIr_4(CO)_7(Ph_2PCH=CHPPh_2)(PhC_6H_4PCH=CHPPh_2)]$

Vincenzo G. Albano,[*a] **Dario Braga,**[a] **Renzo Ros,**[b] **and Alberto Scrivanti**[b]

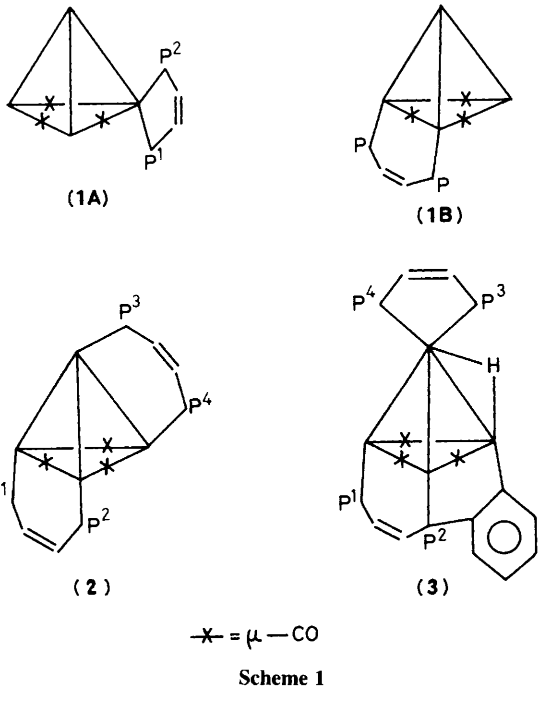
[a] *Istituto Chimico 'G. Ciamician' dell'Università, Via F. Selmi 2, Bologna, Italy*

[b] *Istituto di Chimica Industriale dell'Università e Centro di Chimica Metallorganica del C.N.R., Via Marzolo 9, Padova, Italy*

Reaction of $[Ir_4(CO)_{12}]$ with *cis*-1,2-bis(diphenylphosphino)ethene (dpp) in refluxing tetrahydrofuran (THF) gives first $[Ir_4(CO)_{10}(dpp)]$ and then $[Ir_4(CO)_8(dpp)_2]$ which is converted into the hydrido *ortho*-metallate $[HIr_4(CO)_7(dpp)(PhC_6H_4PCH=CHPPh_2)]$ on standing; *X*-ray crystallography has shown that, in the latter species, dpp forms a new tridentate ligand upon *ortho*-metallation of a phenyl ring.

While carrying out substitution reactions of $[Ir_4(CO)_{12}]$ with mono- and bi-dentate phosphines,[1,2] we have isolated the new hydrido *ortho*-metallated species $[HIr_4(CO)_7(dpp)(PhC_6H_4PCH=CHPPh_2)]$ [dpp = *cis*-1,2-bis(diphenylphosphino)ethene]. Although *ortho*-metallation reactions are often observed when an *ortho* C–H bond is activated in systems containing the X–C–C–H unit (where X is co-ordinated to a metal) no other examples involving a tetrahedral Ir_4 unit are known.

$[Ir_4(CO)_{12}]$ was treated with 1 mol. equiv. of dpp in tetrahydrofuran (THF) affording an orange mixture from which the complexes $[Ir_4(CO)_{10}(dpp)]$ (**1**), $[Ir_4(CO)_8(dpp)_2]$ (**2**), and $[HIr_4(CO)_7(dpp)(PhC_6H_4PCH=CHPPh_2)]$ (**3**) were separated by preparative t.l.c. (silica gel, dichloromethane–hexane). Complex (**1**) was formulated on the basis of elemental analysis and i.r. spectroscopy.† Two isomers (**1A**) and (**1B**) (molar ratio 2 : 1) were detected by analytical h.p.l.c. (silica gel) and ^{31}P n.m.r. spectroscopy,† but their separation on a preparative scale proved impossible. The n.m.r. data suggest that the structures of (**1A**) and (**1B**) can be derived from the C_{3v} geometry of $[Co_4(CO)_{12}]$ as shown in Scheme 1.[3]



Scheme 1

---

† *Selected spectroscopic data:* (**1**): ν(CO) (THF) 2067s, 2036vs, 2000vs, 1993s, 1840m, and 1801m cm^{-1}; ^{31}P-{H} n.m.r. (32.2 MHz, CD_3COCD_3): (**1A**) at 30 °C, single resonance, δ 31.2 p.p.m., which broadens below −30 °C and splits at −100 °C into two signals δ (P^2) 47.5 and δ (P^1) 21.7 p.p.m., in the ratio 1 : 1; (**1B**) shows only a single resonance, δ −30.9 p.p.m., over a similar temperature range. (**2**): ν (CO) (THF) 2112vs, 1986vs, 1973s, 1954m, 1845w, 1795s, and 1774s cm^{-1}; ^{31}P-{H} n.m.r. (32.2 MHz, CD_2Cl_2): at 30 °C, single broad resonance, δ −36.1 p.p.m.; at −60 °C four resonances, δ (P^4) 17.3(dd), δ (P^2) −34.5(dd), δ (P^3) −37.4(dd), and δ (P^1) −42.8(dd) p.p.m., $J(P^2P^3)$ 91, $J(P^2P^4)$ 16, $J(P^1P^3)$ 12, and $J(P^1P^4)$ 4 Hz. (**3**): ν (CO) (THF) 2027(sh), 2004s, 1985vs, 1969vs, 1857w, 1809s, and 1785s cm^{-1}; ^1H n.m.r. (80 MHz, CD_2Cl_2, −50 °C) δ −22.15 (tdd), $^2J(HP^3)$ = $^2J(HP^4)$ = 10.5, $^3J(HP^1)$ or $^3J(HP^2)$ 4.5 or 1.5 Hz; ^{31}P-{H} n.m.r. (32.2 MHz, CD_2Cl_2, 30 °C) four unresolved multiplets at δ 22.4, 19.5, −43.0, and −83.7 p.p.m.

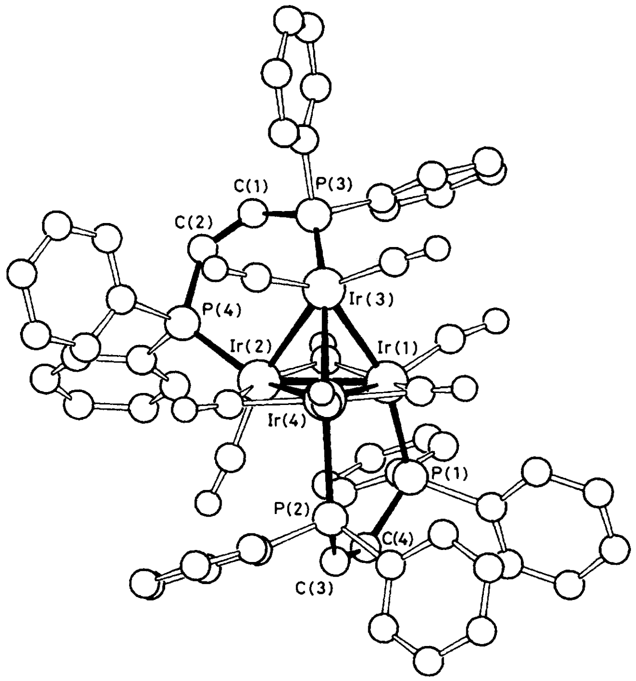


Figure 1. Molecular structure of $[Ir_4(CO)_8(dpp)_2]$ (**2**). Bond lengths Ir(1)–Ir(2) 2.727(1), Ir(1)–Ir(3) 2.697(2), Ir(1)–Ir(4) 2.712(2), Ir(2)–Ir(3) 2.691(2), Ir(2)–Ir(4) 2.736(2), Ir(3)–Ir(4) 2.670(1), Ir(1)–P(1) 2.29(1), Ir(2)–P(4) 2.20(1), Ir(3)–P(3) 2.03(1), Ir(4)–P(2) 2.59(1), C(1)–C(2) 1.30(3), C(3)–C(4) 1.32(3); average P–C(phenyl) 1.83(3), P–C(ethene) 1.80(3), Ir–C(terminal) 1.89(4), Ir–C(bridge) 2.05(4), C–O (terminal) 1.18(1), C–O (bridge) 1.20(4) Å.

Complexes (**1A**) and (**1B**) reacted with a second molar equivalent of dpp in boiling THF to afford a mixture of the species (**2**) and (**3**) in molar ratios depending on reaction time. Pure compound (**2**) could also be obtained in good yield (*ca.* 85%) by treating (**1**) with dpp at 0 °C in THF in the presence of 2 mol. equiv. of Me_3NO as an oxidative decarbonylating agent.

Complex (**2**) was formulated as $[Ir_4(CO)_8(dpp)_2]$ on the basis of elemental analysis, and i.r. and ^{31}P n.m.r. data.† A single-crystal *X*-ray diffraction‡ study showed the complex to possess the structure depicted in Figure 1. The overall ligand distribution is that of most substituted derivatives of $[Ir_4(CO)_{12}]$ with three CO ligands in edge-bridging geometry around a triangular face.[4,5] Each Ir atom is bonded to a terminal P atom of the dpp ligands, which form two six-membered rings with different conformations. The unusually long Ir(4)–P(2) interaction [2.59(1) Å] indicates a rather strained bonding arrangement which may account for the reactivity of (**2**). Quantitative conversion of (**2**) into (**3**) takes place upon boiling in THF for 25 h.†

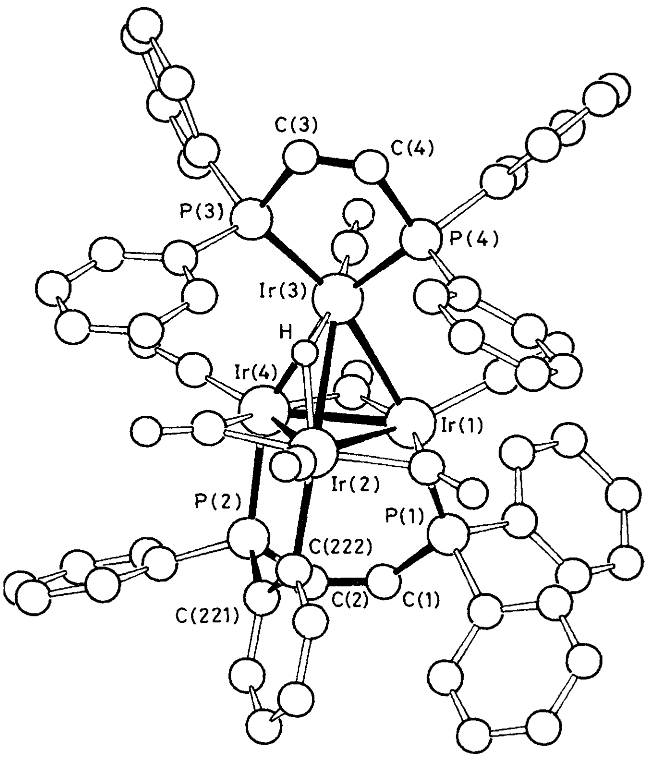


Figure 2. Molecular structure of $[HIr_4(CO)_7(dpp)(PhC_6H_4\text{-}PCH{=}CHPPh_2)]$ (**3**). Bond lengths: Ir(1)–Ir(2) 2.772(1), Ir(1)–Ir(3) 2.752(1), Ir(1)–Ir(4) 2.709(1), Ir(2)–Ir(3) 2.901(1), Ir(2)–Ir(4) 2.677(1), Ir(3)–Ir(4) 2.763(1), Ir(1)–P(1) 2.30(1), Ir(4)–P(2) 2.29(1), Ir(3)–P(3) 2.303(4), Ir(3)–P(4) 2.308(4), Ir(2)–C(222) 2.11(1), C(1)–C(2) 1.33(3), C(3)–C(4) 1.31(2), Ir(2)–H 1.76, Ir(3)–H 1.71; average P–C(phenyl) 1.83(2), P–C(ethene) 1.81(2), Ir–C(terminal) 1.83(3), Ir–C(bridge) 2.07(3), C–O(terminal) 1.17(1), C–O(bridge) 1.19(2) Å.

The structure of (**3**) was ascertained by *X*-ray crystallography.‡ The molecule, shown in Figure 2, possesses unusual features arising from an unpredictable intramolecular reaction. While one of the dpp ligands adopts a chelating mode of bonding to the apical Ir(3) atom, the other becomes a tridentate ligand on the tetrahedron base since one *ortho*-phenyl carbon atom undergoes metallation by insertion of Ir(2). Consequently one CO ligand is replaced by the newly formed Ir–C bond and the phenyl H atom migrates on the cluster surface.

The hydridic nature of (**3**) was assumed from electron counting. Structural evidence such as a significant elongation of the Ir(2)–Ir(3) bond [2.901(1) Å; av. Ir–Ir 2.735(3) Å], and the presence of an electron density peak above the long edge indicated an edge-bridging location for the H-atom. Further evidence was obtained from space-filling diagrams that showed a 'niche' in the close-packed ligand coverage, which could accommodate the H atom.[6] The observed values of 1.76 and 1.71 Å for the Ir–H distances agree with other reported Ir–H bond lengths.[7] ^1H N.m.r. data confirmed the hydridic nature of (**3**).†

---

‡ *Crystal data:* (**2**) $C_{60}H_{44}Ir_4O_8P_4$, $M = 1785.1$, monoclinic, space group $P2_1/n$, $a = 12.29(1)$, $b = 15.45(1)$, $c = 32.79(1)$ Å, $\beta = 95.08(2)°$, $Z = 4$, $U = 6197.66$ Å^3, $D_c = 1.91$ g cm^{-3}, θ range 2.5—25°, present R value 0.064 ($R' = 0.061$) for 4065 absorption-corrected independent reflections $[F_o > 6\sigma(F_o)]$, $\mu(\text{Mo-}K_\alpha) = 83.80$ cm^{-1}.

(**3**) $C_{59}H_{44}Ir_4O_7P_4 \cdot 0.44CH_2Cl_2$, $M = 1795.06$, triclinic, space group $P\bar{1}$, $a = 12.334(2)$, $b = 12.316(2)$, $c = 19.384(2)$ Å, $\alpha = 92.03(1)$, $\beta = 94.14(1)$, $\gamma = 85.50(1)°$, $Z = 2$, $U = 2926.49$ Å^3, $D_c = 2.03$ g cm^{-3}, θ range 2—25°, present R value 0.053 ($R' = 0.050$) for 6392 absorption-corrected independent reflections $[F_o > 5\sigma(F_o)]$, $\mu(\text{Mo-}K_\alpha) = 89.59$ cm^{-1}.

For both structures phenyl rings were refined as rigid groups, and hydrogen atoms included in calculated positions and not refined. SHELX[8] was used for all calculations. A final difference-Fourier synthesis computed for (**3**) showed a few residual peaks of *ca.* 1 e Å^{-3}, one of which, placed above the Ir(2)–Ir(3) edge, was attributed to the H(hydride) atom. Its co-ordinates were included in the model though not refined.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

It is noteworthy that in complex (**3**), as well as in (**1A**), the bidentate dpp ligand is chelating, in contrast with observations for less rigid diphosphines found in bis-axial positions as in (**1B**).[2] Morevover the presence of both isomers (**1A**) and (**1B**) suggests that the two different co-ordination modes of dpp have comparable stability. Studies on the kinetics of these reactions and on the fluxional behaviour of complexes (**1**) and (**2**) are in progress.

We acknowledge financial support by the Ministero Pubblica Istruzione and C.N.R. of Italy.

Received, 18th December 1984; Com. 1768

References

1 R. Ros, F. Canziani, and R. Roulet, *J. Organomet. Chem.*, 1984, **267**, C9.
2 V. G. Albano, D. Braga, R. Ros, and A. Scrivanti, unpublished results.
3 F. H. Carrè, F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, 1976, **15**, 380.
4 V. G. Albano, P. Bellon, and V. Scatturin, *Chem. Commun.*, 1967, 730.
5 A. J. Blake and A. G. Osborne, *J. Organomet. Chem.*, 1984, **260**, 227.
6 SCHAKAL84, E. Keller, University of Freiburg, 1984.
7 R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **1**, 44.
8 SHELX76, G. M. Sheldrick, University of Cambridge, 1976.