

Addition of Diphenylphosphine to a Bis(μ -pyrazolyl)di-iridium(I) Complex resulting in H-Transfer to Co-ordinated Cyclo-octa-1,5-diene: X-Ray Crystal Structure of an Iridium Dimer incorporating Unsymmetrical Pyrazolyl and Phosphido Bridging Groups and a 1- σ ,4-5- η -C₈H₁₃ Ligand

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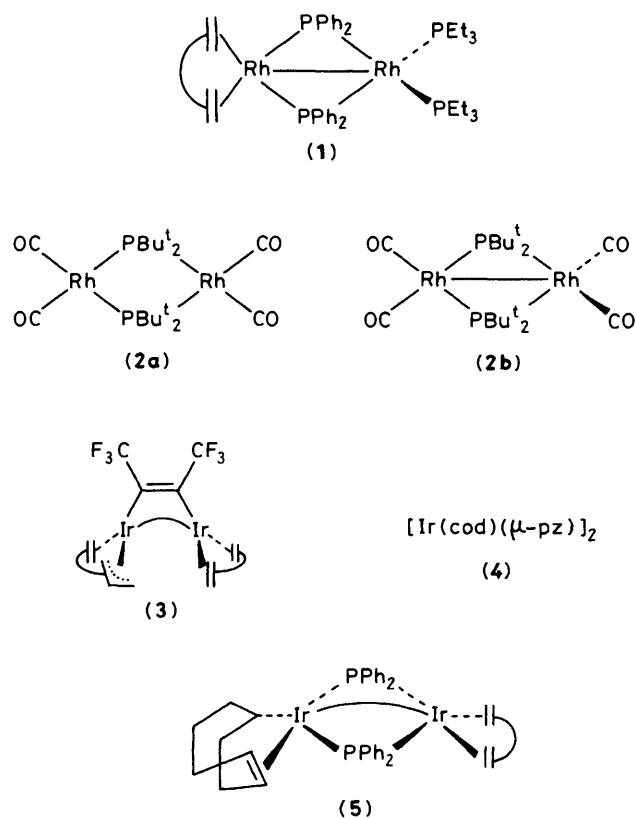
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Reaction of $[\text{Ir}(\text{cod})(\mu\text{-pz})]_2$ (cod = cyclo-octa-1,5-diene; pzH = pyrazole) with Ph₂PH results in hydrogenation of cod at one Ir centre to give a 1- σ ,4-5- η -C₈H₁₃ (*i.e.* -enyl) unit, affording the complex $[\text{Ir}(\text{cod})(\mu\text{-pz})(\mu\text{-PPh}_2)_2\text{Ir}(\text{C}_8\text{H}_{13})]$ in which Ir–Ir = 2.780 Å and both pz and PPh₂ ligands occupy unsymmetrical bridging positions.

The recent rapid development of polynuclear transition-metal chemistry has highlighted the capacity of a variety of ligands to bridge between adjacent metal centres. In this context the diorganophosphido, R₂P-group has achieved prominence^{1–3} within a very short period of time, inchoating an area to which a further dimension has now been added by the structural characterization^{4,5} of two homobimetallic complexes $[(\text{cod})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{PEt}_3)_2]$ (**1**) (cod = cyclo-octa-1,5-diene) and $[\text{Rh}(\mu\text{-Bu}^i_2\text{P})(\text{CO})_2]_2$ (**2**). In the first of these examples, the two independent metal centres display⁴ grossly different co-ordination geometries (square *vs.* tetrahedral), while the second exists⁵ as two isomers of which one (**2a**) is centrosymmetric but the other (**2b**) contains distinguishable Rh environments which closely resemble those in compound (**1**). This relationship between (**1**) and (**2b**) is reinforced by the fact that in each structure the bridging ligands occupy unsymmetrical positions. It is possible to regard compound (**1**) as an amalgamation of $[(\text{cod})\text{Rh}]^+$ and $[\text{Rh}(\text{Ph}_2\text{P-})_2(\text{PEt}_3)_2]^-$ fragments *via* donor-bond formation,^{3,4} a view which implies a mixed-valence character which would be common⁵ to (**1**) and (**2b**). We have suggested⁶ that the geometry of a mixed-bridge

di-iridium complex $[(\text{cod})\text{Ir}(\mu\text{-pz})(\mu\text{-C}_4\text{F}_6)\text{Ir}(1\text{---}3:5\text{-}6\text{-}\eta\text{-C}_8\text{H}_{11})]$ (**3**) (pzH = pyrazole) in which Ir–Ir = 2.850 Å would be consistent with an Ir^I → Ir^{III} formalism (as an alternative to Ir^{II}–Ir^{II}). We have subsequently synthesized a related di-iridium complex in which pyrazolyl and diphenylphosphido bridging ligands exist together; this product is noteworthy for a number of reasons.

Direct addition to a transition-metal precursor of a diorganophosphine R₂PH has hitherto only rarely been described^{1,7} as a route to μ -phosphido complexes; such compounds are typically synthesized² by nucleophilic reactions of phosphides R₂P[–] or using phosphine halides R₂PX. Nevertheless treatment of a solution of the purple–red di-iridium(I) complex^{6,8} $[\text{Ir}(\text{cod})(\mu\text{-pz})]_2$ (**4**) in tetrahydrofuran (THF) with Ph₂PH (2 mol. equiv., THF solution) was accompanied by an immediate change in colour of the reaction mixture, to orange–yellow; after stirring (30 min, ambient temperature) removal of THF left an orange–red solid, which was redissolved in Et₂O. The resulting solution was filtered (5 cm alumina column) then concentrated to *ca.* 25% volume; slow evaporation afforded bright orange crystals, m.p. 250 °C (decomp.).



This product (5) which was isolated in 60% yield was identified unequivocally using single-crystal *X*-ray diffraction.

Crystal data for (5): $\text{Ir}_2\text{P}_2\text{N}_2\text{C}_{43}\text{H}_{48}\cdot 0.5\text{Et}_2\text{O}$, $M = 1076.3$, monoclinic, space group $P2_1/c$, $a = 16.795(7)$, $b = 11.835(4)$, $c = 20.717(10)$ Å, $\beta = 102.52(4)^\circ$, $D_c = 1.78$ g cm $^{-3}$, Mo- $K_{\alpha 1}$ radiation ($\lambda = 0.71069$ Å), $\mu = 64.7$ cm $^{-1}$, Picker four-circle diffractometer, 3262 independent observable reflections having $I > 3\sigma(I)$ refined to conventional $R = 0.038$.† The molecule is binuclear with Ir(1)–Ir(2) at 2.780(1) Å bridged by a single pyrazolyl and two diphenylphosphido ligands. Simplification of the four phenyl rings in Figure 1 emphasizes the precision of the arrangement whereby the three bridging ligands avoid one another in the limited space between the two metal centres. A Ph group from each P atom sandwiches the heterocyclic $\mu\text{-C}_3\text{N}_2\text{H}_3$ fragment which connects the two Ir atoms, with the planes of all three ring-systems oriented along the Ir $_2$ axis; across the latter the remaining two Ph substituents are rotated into an edge-on relationship. The bridging P atoms occupy very similar unsymmetrical positions with mean Ir(1)–P = 2.315, Ir(2)–P = 2.394 Å; the pyrazolyl coordination is also irregular but in the opposite sense with Ir(1)–N(2) = 2.152, Ir(2)–N(1) = 2.054 Å. As expected^{3,9} for a metal–metal bonded structure the P–Ir–P angle is wide (mean 107.4°) with that at P acute (mean 72.4°). Finally the terminal diolefin at one Ir atom has been structurally modified during the formation of complex (5) from (4), although that attached to the other remains unchanged. Thus Ir(1)–C(4) = 2.159, Ir(1)–C(8) = 2.136, and Ir(1)–C(9) = 2.116 Å but the remaining five carbon atoms lie well outside bonding range to

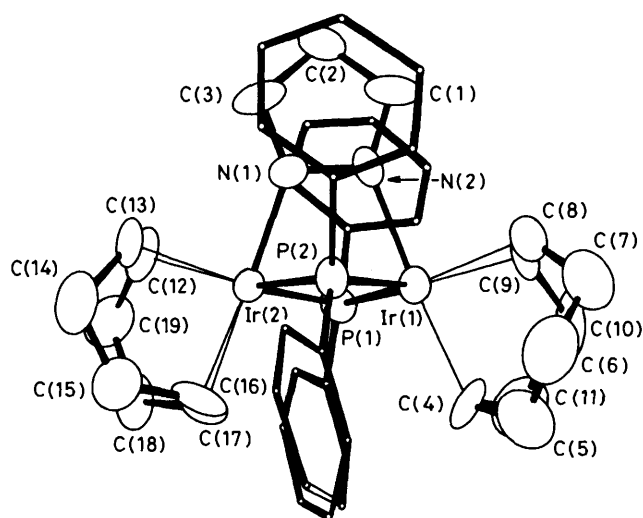


Figure 1. Molecular geometry of compound (5). The phenyl rings of both $\mu\text{-PPh}_2$ groups have been simplified for clarity. Important bond lengths: Ir(1)–Ir(2) 2.780(1), Ir(1)–N(2) 2.152(10), Ir(2)–N(1) 2.054(10), Ir(1)–P(1) 2.322(4), Ir(1)–P(2) 2.308(4), Ir(2)–P(1) 2.396(4), Ir(2)–P(2) 2.392(4), Ir(1)–C(4) 2.159(13), Ir(1)–C(8) 2.136(15), and Ir(1)–C(9) 2.116(14) Å.

Ir(1), signalling hydrogenation of cod to an octenyl coordinating as 1- σ ,4-5- η - C_8H_{13} .

Analytical data for compound (5) are fully consistent with the structure established crystallographically. The ^1H n.m.r. spectrum (250 MHz) showed in addition to broad multiplet envelopes at δ 7.7–7.0 (Ph) and 4.6–1.1 (cod, C_8H_{13}) signals at 6.1, 5.7, and 5.4 resulting from non-equivalence among 3-H, 4-H, and 5-H of the pz bridge. The small degree of asymmetry introduced perpendicular to the Ir $_2$ axis by the disposition of the C_8H_{13} ligand is also reflected in a shift of 0.4 p.p.m. between P(1) and P(2) in the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum (δ –19.5, –19.9 p.p.m. relative to external trimethyl phosphite).

Transformation of $\eta\text{-C}_8\text{H}_{12}$ (*i.e.* cod) to 1- σ ,4-5- η - C_8H_{13} has been shown to result from nucleophilic attack on cod bound¹⁰ to Pd^{II} or electrophilic addition¹¹ of H^+ to $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{cod})]$; the structure of one 2-hydroxycyclo-oct-5-enylpalladium(II) product has been established by *X*-ray diffraction¹² while successive isomerization of $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(1\text{-}\sigma,4\text{-5-}\eta\text{-C}_8\text{H}_{13})]^+$ to $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(1\text{-}\sigma,3\text{-4-}\eta\text{-C}_8\text{H}_{13})]^+$ then $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(1\text{-}3\text{-}\eta\text{-C}_8\text{H}_{13})]^+$ has been inferred from ^1H n.m.r. spectroscopy.¹¹ By contrast protonation of $[\text{Ir}(\eta\text{-C}_5\text{H}_5)(\text{cod})]$ affords a stable $[\text{Ir}(\eta\text{-C}_5\text{H}_5)(\text{cod})\text{H}]^+$ intermediate;¹¹ we consider it likely that the formation of compound (5) proceeds via a similar hydrido-iridium intermediate, because on warming a frozen mixture of complex (4) and Ph_2PH (CD_2Cl_2 solution) a ^{31}P n.m.r. signal appears initially in the terminal P region (*ca.* –120 p.p.m., –80°C). At –70°C a singlet resonance, δ –13.63 could be observed in the ^1H n.m.r. spectrum, attributable to a terminal Ir–H proton; this increased in intensity then collapsed abruptly at about 0°C, at which temperature the ^{31}P n.m.r. spectrum corresponded to that of the product (5).

The disposition of the $\mu\text{-PPh}_2$ groups in compound (5) intuitively suggests a higher oxidation-state for Ir(1) (shorter bonds to P) than for Ir(2), *i.e.* a $[\text{Ir}^{\text{III}}(\text{cod})(\mu\text{-pz})(\mu\text{-PPh}_2)_2\text{Ir}^{\text{III}}(\text{C}_8\text{H}_{13})]$ formulation which may⁶ also be indicated by Ir–Ir = 2.78 Å. To test whether this is a meaningful distinction the relative reactivity of the two metal sites is being investigated.

† 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.

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