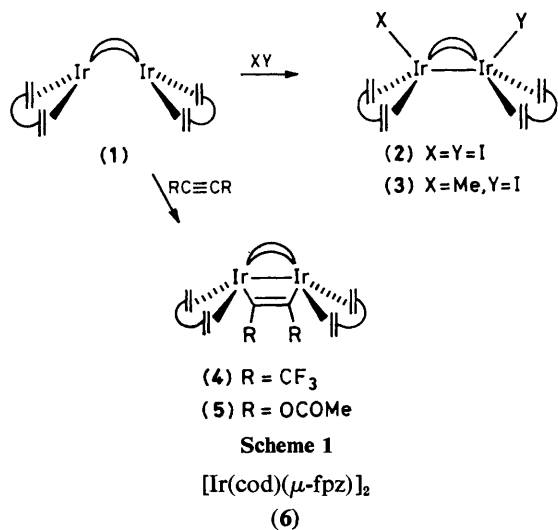


Two-centre Oxidative Addition of Hexafluorobut-2-yne to a Bis(μ -pyrazolyl)di-iridium(I) Complex leading to Bridge-elimination *via* H-Transfer from Co-ordinated Cyclo-octa-1,5-diene: X-Ray Crystal Structure of a Mixed-bridge, Mixed-valence Iridium Dimer incorporating a 1—3,5,6- η -C₈H₁₁ Ligand

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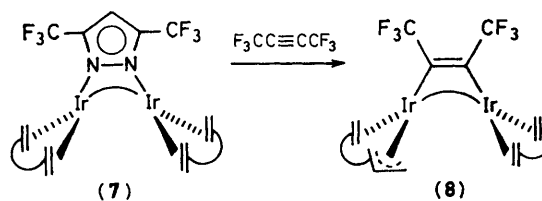
Reaction of the unsymmetrically-bridged di-iridium(I) complex $[(\text{cod})\text{Ir}(\mu\text{-pz})(\mu\text{-fpz})\text{Ir}(\text{cod})]$, [cod = cyclo-octa-1,5-diene; pzH = pyrazole; fpzH = 3,5-bis(trifluoromethyl)pyrazole] with hexafluorobut-2-yne (C₄F₆) leads to bridge-replacement of μ -fpz by C₄F₆; the latter is incorporated in a parallel-type bonding mode to give a di-iridium product having Ir–Ir 2.85 Å and one Ir centre terminally co-ordinated by a 1—3,5,6- η -C₈H₁₁ (*i.e.* -dienyl) unit.

The brick-red pyrazolyl-bridged di-iridium(I) complex $[(\text{cod})(\mu\text{-pz})_2]_2$ (1) (pzH = pyrazole, cod = cyclo-octa-1,5-diene) reacts with I₂ or MeI to afford purple 1 : 1 adducts (2) or (3), respectively, which we have shown^{1,2} by X-ray crystal structure methods to be products of two-centre, two-fragment oxidative addition (see Scheme 1).[†] Surprisingly, however, the Ir–Ir distances in these compounds [(2) 3.085;² (3) 3.112 Å] are only a little shorter than that of unoxidized (1) (3.216 Å), despite the requirement for spin-pairing between the d⁷ metal-centres¹ in a (formally) iridium(II) dimeric configuration. In the colourless products (4) and (5) of reactions between complex (1) and the acetylenes hexafluorobut-2-yne (C₄F₆) or dimethyl acetylenedicarboxylate (DMAD), the adjacent Ir centres are within bonding distance (C₄F₆; Ir–Ir 2.623 and DMAD; 2.633 Å,² respectively), but to what extent this is attributable to the introduction of a third bridge by 'parallel-type'³ acetylene addition is difficult to assess. A definitive example of the anticipated response to this kind of two-centre addition is provided⁴ by the behaviour of the blood-red, carbonyl(phosphine) analogue $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pz})_2]$ (Ir₂ separation 3.162 Å) with Cl₂ to give the pale yellow complex $[\text{Ir}(\text{CO})(\text{PPh}_3)(\text{Cl})(\mu\text{-4-Cl-pz})_2]$ in which Ir–Ir 2.737 Å is consistent with spin-pairing *via* bond-formation. Here we summarize some related observations which show that further dramatic changes in the reactivity of the binuclear unit may be induced by modification of the bridging pyrazolyl ligand.



The purple-pink complex $[\text{Ir}(\text{cod})(\mu\text{-fpz})_2]$ (6), prepared by the reaction of $[\text{Ir}(\text{cod})(\mu\text{-Cl})_2]$ with 3,5-bis(trifluoromethyl)pyrazole (fpzH), was unaffected by stirring in tetrahydrofuran (THF) (48 h, 20 °C) under C₄F₆ (2 atm), and neither could any reaction be detected with DMAD, I₂, or MeI at ambient temperature. It seems possible that steric interference by the pyrazolyl CF₃ substituents with the axial Ir sites is sufficient to inhibit the initial step of the oxidative addition reaction. Mixing $[\text{Ir}(\text{cod})\text{Cl}]_2$ with both pzH and fpzH (1 : 1 mol. equiv., NEt₃-THF solution) results in the formation, in *ca.* statistical ratio, of the symmetrical dimers (1) and (6) together with a third, purple, mixed-bridge analogue $[\text{Ir}(\text{cod})(\mu\text{-pz})(\mu\text{-fpz})\text{Ir}(\text{cod})]$ (7) which can be isolated in a pure state[‡] by fractional crystallization. The addition of C₄F₆ to this compound occurred slowly; over 18 h at 20 °C in THF (2 atm C₄F₆) the solution gradually lightened to yellow, whence addition of hexane followed by reduction in volume precipitated a material which was deep brown. Extraction with Et₂O followed by recrystallization from CH₂Cl₂ provided well-formed, clear, purple crystals of a product (8), *ca.* 60% yield, the ¹H n.m.r. spectrum (250 MHz) of which contained signals characteristic of μ -pz;[§] however a 4-H resonance attributable to μ -fpz could not be found, and the high-frequency (*i.e.*, low-field) portion of the cod multiplet differed from that observed for (1), (6), or (7). Since suitable crystals were available the identification of this compound was pursued using X-ray diffraction.

Crystal data: Ir₂F₆N₂C₂₃H₂₆, *M* = 828.86, monoclinic, space group *P*₂₁/*n*, *a* = 13.813(5), *b* = 16.564(6), *c* = 10.212(4) Å, β = 99.60(2)°, *D*_c = 2.25 g cm⁻³, Mo-K α radiation (λ = 0.71069 Å), μ = 122.7 cm⁻¹, Picker four-circle diffractometer, 1204 independent observable reflections with *I* > 3 σ (*I*). Refinement of the structure (currently conventional *R* = 0.074) shows that the fpz bridge has indeed been displaced, as suggested by



Scheme 2

[†] In Schemes 1 and 2, unsubstituted pyrazolyl bridging ligands (*i.e.* η^2 -C₂N₂H₂) have been represented as curved lines connecting Ir centres, for clarity.

[‡] A satisfactory elemental analysis was obtained.

[§] At δ 7.40, 7.18 (3,5-H), and 6.25 (4-H). Eleven multiplets due to cod CH, CH₂ resonances were also resolved, in the δ 5.5–2.0 range.

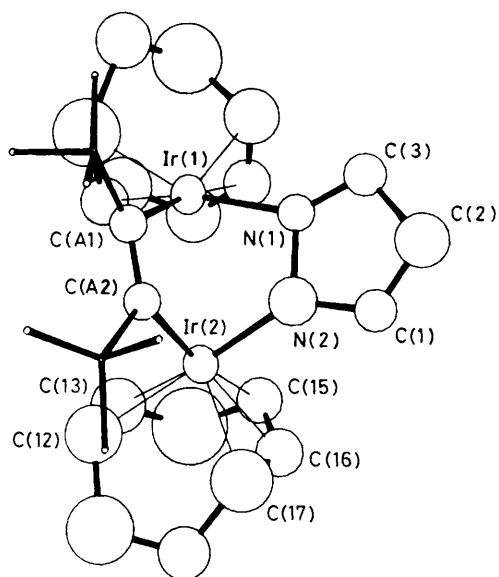


Figure 1. Molecular geometry of compound (8). Ir(1)–Ir(2) 2.850(3), Ir(1)–N(1) 2.09(4), Ir(2)–N(2) 1.96(5), Ir(2)–C(12) 2.15(7), Ir(2)–C(13) 2.41(7), Ir(2)–C(15) 2.35(6), Ir(2)–C(16) 2.26(6), and Ir(2)–C(17) 1.96(7) Å.

the ^1H n.m.r. data.[¶] The molecular arrangement is illustrated in Figure 1. Superficially there is a resemblance to the geometry adopted by the di-iridium(i) complexes (1) and (6), but the C_8 carbocycle at one of the Ir atoms is here bonded as a 1–3,5,6- η - C_8H_{11} entity rather than as η -cod; Ir(2) to C(12), (13), and (15)–(17) are all within bonding range at 1.97–2.42 Å. The two metal atoms which lie 2.85 Å apart are linked by the remaining (unsubstituted) pz and also the C_4F_6 unit which has inserted again^{1,2} as a 'parallel-type' bridge (Scheme 2).

Hydride abstraction by Ph_3C^+ from co-ordinated cod represents the classic entry into (1–3,5,6- η - C_8H_{11})–metal chemistry;⁵ however H-transfer from cod to Ru^{II} , (*i.e.* intramolecular C–H addition), followed by reduction of Ru^{IV} by ejection of H^+ with an unco-ordinated BPh_4^- counter-ion has been suggested as a route to the structurally characterized⁶

[¶] 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.

complex $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)(1\text{--}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$. Protonation of the μ -fpz ligand by H from cod mediated in a similar way by Ir(2) clearly represents a possible route to compound (8). A further close parallel exists with the thermally initiated transformation of $\eta^2\text{-CF}_3\text{C}\equiv\text{CCF}_3$ to $\eta^1\text{-C}(\text{CF}_3)=\text{CHCF}_3$, amounting to net proton transfer from co-ordinated cod at each of two Ir centres to afford a dimeric Ir^{III} product which was also identified⁷ by X-ray crystallography.

This latter comparison emphasizes an ambiguity presented by the structure of compound (8), which could be formulated either as a di-iridium(II) species, or alternatively as an $\text{Ir}^{\text{I}}\text{--Ir}^{\text{III}}$ complex incorporating a donor–acceptor metal–metal interaction of the type recently discussed in relation to di-platinum chemistry by Puddephatt *et al.*⁸ Although we incline towards the latter view on the basis of the arguments advanced previously⁸ and the fact that in complex (8) the Ir–Ir distance (2.85 Å) intrudes abruptly between the two ranges established thus far for a variety of closely-related compounds,^{1,2,4} such a distinction may represent a formalism which is not reflected in spectroscopic or chemical characteristics; this is being investigated further.

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