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SYNTHESIS AND MOLECULAR STRUCTURE OF THE FIRST INORGANIC QUADRUPLY-BRIDGED Ir(II) DIMER (Ir–Ir)

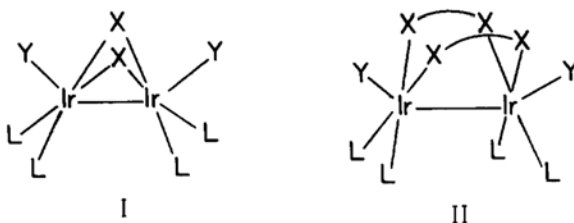
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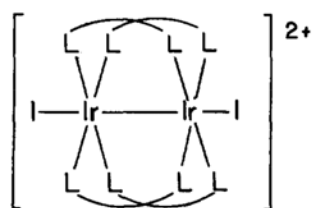
Abstract—Interaction of (COD)Ir(μ -form)₂Ir(OCOCF₃)₂(H₂O) (COD = 1,5-cyclooctadiene; form = *N,N'*-di-*p*-tolylformamidinate ion) with two equivalents of Hform in toluene affords Ir₂(form)₄, the first inorganic Ir(II) dimer to be crystallographically characterized. The reaction involves a formal electron redistribution from a dative Ir(I) → Ir(III) to a covalent Ir(II)–Ir(II) bond. The compound crystallizes in the cubic space group Pn $\bar{3}$ n with $a = 21.300(9)$ Å. The metal–metal separation, 2.524(3) Å, is the shortest ever reported for a bonding interaction between iridium atoms.

Rh(II) dinuclear compounds containing four monoanionic bridging ligands and a single metal–metal bond of $\sigma^2\pi^4\delta^2\delta^*\pi^4$ electronic configuration are well known.¹ The first one, Rh₂(O₂CH)₄(H₂O)₂, was reported in 1960,^{2a} although not initially recognized as such.^{2b} Other dirhodium(II,II) tetracarboxylato compounds have been obtained, mainly by interaction of hydrated RhCl₃ with alkali metal carboxylates in alcoholic media.³ Known compounds with other bridging ligands include Rh₂(xhp)₄ (xhp = 6-X-substituted hydroxypyridinato ion, X = CH₃,^{4,5} Cl⁵), Rh₂(OC(R)NR')₄ (R = CF₃, R' = H;⁶ R = Me, R' = Ph;⁷ R = Ph, R' = H⁸), Rh₂(3,5-Me₂pz)₄ (pz = pyrazolate ion),⁹ Rh₂(PhNpy)₄,¹⁰ Rh₂(N₂PhCPh)₄¹¹ and Rh₂(form)₄ (form = *N,N'*-di-*p*-tolylformamidinate ion),¹² some of which contain axially coordinated neutral ligands. A number of Rh₂⁴⁺ complexes with mixed bridging ligands also exist.¹³ On the other hand, Ir(II) complexes having a similar structure have never been reported, in spite of the existence of a large number of structurally different Ir(II) dinuclear complexes, these being generally of the type represented in I¹⁴ or II.¹⁵

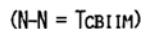
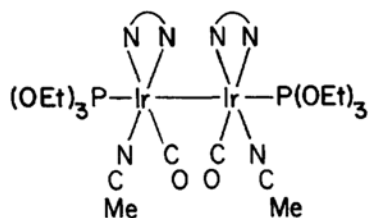


Only five diiridium(II,II) compounds that have the two metals in a square planar configuration with the two square planes parallel to each other (with or without additional axial ligands) seem to have been reported in the literature. These are [Ir₂(TMB)₄I₂]²⁺ (TMB = 2,5-dimethyl-2,5-diisocyanohexane)¹⁶ of structure III, Ir₂(Tcbim)₂(CO)₂(MeCN)₂(P(OEt)₃)₂ (Tcbim = dianion of tetracyanobiimidazole)^{17a} of structure IV, [IrClX(CO)(dppm)]₂ [dppm = bis(diphenylphosphino) methane, X = Cl, CH₃O₂CC=CHCO₂CH₃]^{17b} of structure V, and Ir₂(OEP)₂ (OEP = dianion of octaethylporphyrine)¹⁸ of structure VI. The first four have been structurally characterized and exhibit Ir–Ir distances of 2.803¹⁶ and 2.826(2),^{17a} 2.786(1) and 3.016(1) (average) Å.^{17b} Unfortunately Ir₂(OEP)₂, which is to be regarded as the only known truly inorganic Ir(II) dimer (this

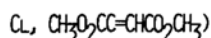
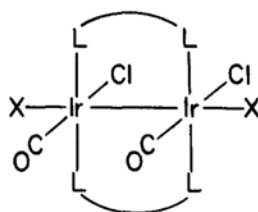
* Author to whom correspondence should be addressed.



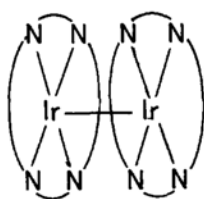
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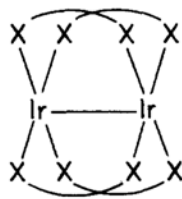
IV



V



VI



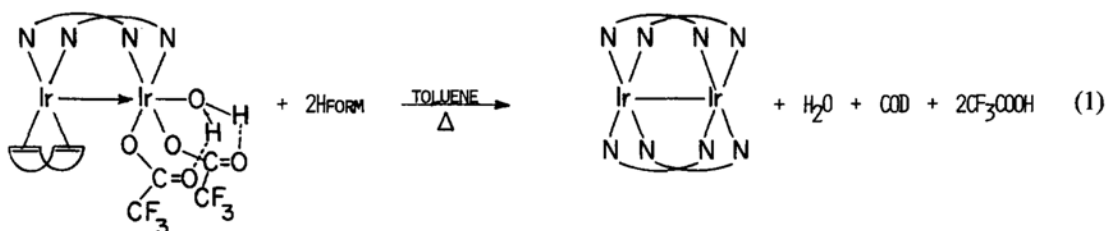
VII

meaning that the coordination sphere around the metal is filled with non-carbon atoms), has not been structurally characterized.

We wish to report here for the first time the synthesis and X-ray crystal structure of an inorganic iridium(II) dimer having a structure of the type VII, i.e. of the same type as the Rh_2^{4+} compounds mentioned above. The mixed-valence Ir(I)–Ir(III) compound, $(\text{COD})\text{Ir}(\mu\text{-form})_2\text{Ir}(\text{OCOCF}_3)_2(\text{H}_2\text{O})$ (COD = 1,5-cyclo-octadiene),¹⁹ reacts smoothly in warm toluene with two equivalents of Hform to

produce an emerald-green solution from which dark-green crystals of $\text{Ir}_2(\text{form})_4$ were obtained in small yields by evaporation to dryness and recrystallization from MeCN.

Such a reaction involves a proton transfer from the weaker acid, Hform, to the stronger one, CF_3COOH . The formation of two new formamidinato bridges between the two iridium centers is presumably the driving force of the reaction. A formal electron redistribution also takes place, from the compound with a dative Ir(I) → Ir(III) bond to



Inorganic quadruply-bridged Ir(II) dimer (Ir–Ir)

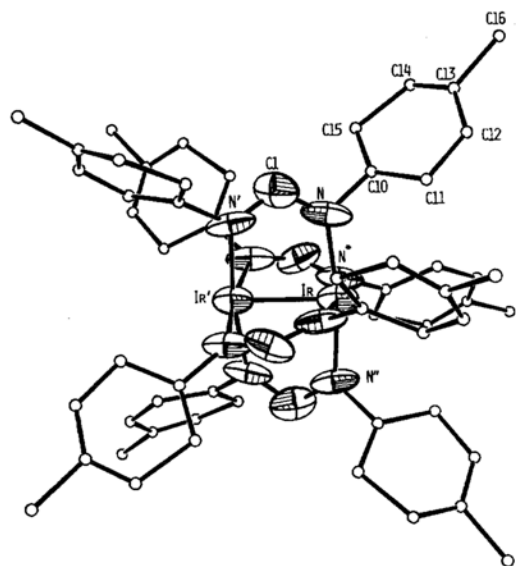


Fig. 1. An ORTEP view of the $\text{Ir}_2(\text{form})_4$ molecule. The *p*-tolyl carbon atoms are drawn with arbitrary radii for clarity. Distances: Ir–Ir', 2.524(3); Ir–N, 2.04(2); N–Cl, 1.34(2); N–ClO, 1.45(4) Å. Angles: Ir'–Ir–N, 85.4(6); N–Ir–N'', 170.9(9), N–Ir–N*, 89.6(7); Ir–N–Cl, 124(1); Ir–N–ClO, 123(2); Cl–N–ClO, 113(2); N–Cl–N', 116(2)°.

the covalently bonded Ir(II)–Ir(II) product. Both CF_3COOH and COD that are obtained along with the iridium product were identified by their $^1\text{H-NMR}$ peaks at 13.0 (broad) and 5.55 δ , respectively.

Quite surprisingly, attempts to obtain the same product directly by oxidising $[\text{Ir}(\text{form})(\text{COD})]_2$ with $\text{Ag}(\text{form})$ failed. No reaction took place under thermal or photochemical conditions or a combination thereof.

The structure of the $\text{Ir}_2(\text{form})_4$ molecule is shown in Fig. 1.* The molecule has D_4 imposed symmetry, the fourfold axis passing through the two iridium atoms and the twofold axes passing through and between pairs of trans-methylidyne groups. The compound is isostructural with $\text{Rh}_2(\text{form})_4$.¹² Each iridium atom is bonded to four nitrogen atoms in a square planar arrangement. The iridium atom is displaced by 0.16(2) Å from the N_4 plane in the outward direction. The two square planes are twisted away from the eclipsed configuration by 15.6(5)° (see Fig. 2). The metal–metal distance is 2.524(3) Å and is the shortest Ir–Ir bond length ever reported. It is

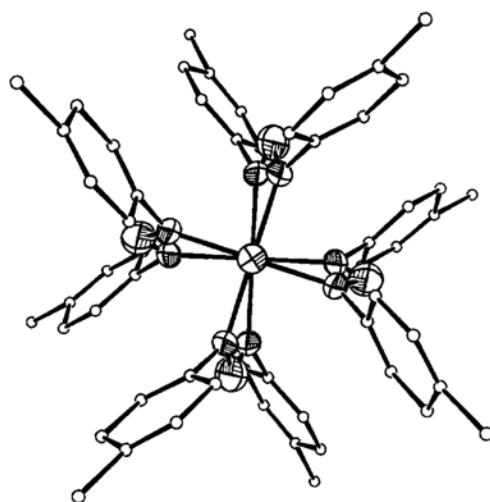


Fig. 2. View of the $\text{Ir}_2(\text{form})_4$ molecule along the Ir–Ir' direction.

even shorter than the separation in $[\text{Ir}(\text{CO})(\text{PPh}_3)(\eta\text{-PPh}_2)]_2$, 2.554 Å, for which a bond order of two has been proposed²⁰ and it is, expectedly, longer than the Rh–Rh separation (2.4336(4) Å) in the analogous compound $\text{Rh}_2(\text{form})_4$.¹² The nearest neighbour separation in metallic iridium is 2.714 Å.²¹

Electrochemical, spectroscopic and theoretical studies on $\text{Ir}_2(\text{form})_4$ are in progress. The assignment of an electron rich single bond of $\sigma^2\pi^4\delta^2\delta^*\pi^4$ configuration to the metal–metal interaction, however, is strongly suggested by previous work done on similar rhodium compounds.²²

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* Crystal data: cubic, space group $\text{Pn}\bar{3}\text{n}$, $a = 21.300(9)$ Å, $V = 966.4(12)$ Å³, $Z = 6$, $d_{\text{calc}} = 1.317$ g cm⁻³, $R = 0.0595$ ($R_w = 0.0770$) for 402 reflections having $F_o^2 > 3\sigma(F_o^2)$.

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