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

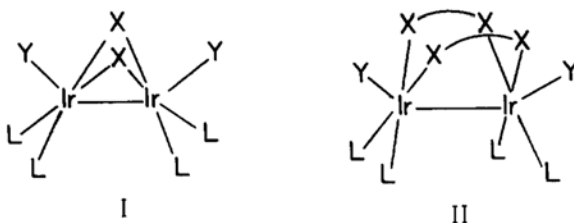
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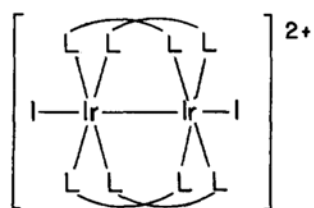
**Abstract**—Interaction of  $(\text{COD})\text{Ir}(\mu\text{-form})_2\text{Ir}(\text{OCOCF}_3)_2(\text{H}_2\text{O})$  (COD = 1,5-cyclooctadiene; form = *N,N'*-di-*p*-tolylformamidinate ion) with two equivalents of Hform in toluene affords  $\text{Ir}_2(\text{form})_4$ , the first inorganic Ir(II) dimer 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  $\text{Pn}\bar{3}\text{n}$  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.<sup>1</sup> The first one,  $\text{Rh}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$ , was reported in 1960,<sup>2a</sup> although not initially recognized as such.<sup>2b</sup> Other dirhodium(II,II) tetracarboxylato compounds have been obtained, mainly by interaction of hydrated  $\text{RhCl}_3$  with alkali metal carboxylates in alcoholic media.<sup>3</sup> Known compounds with other bridging ligands include  $\text{Rh}_2(\text{xhp})_4$  (xhp = 6-X-substituted hydroxypyridinato ion, X =  $\text{CH}_3$ ,<sup>4,5</sup>  $\text{Cl}^5$ ),  $\text{Rh}_2(\text{OC}(\text{R})\text{NR}')_4$  (R =  $\text{CF}_3$ , R' = H;<sup>6</sup> R = Me, R' = Ph;<sup>7</sup> R = Ph, R' = H<sup>8</sup>),  $\text{Rh}_2(3,5\text{-Me}_2\text{pz})_4$  (pz = pyrazolate ion),<sup>9</sup>  $\text{Rh}_2(\text{PhNpy})_4$ ,<sup>10</sup>  $\text{Rh}_2(\text{N}_2\text{PhCPh})_4$ <sup>11</sup> and  $\text{Rh}_2(\text{form})_4$  (form = *N,N'*-di-*p*-tolylformamidinate ion),<sup>12</sup> some of which contain axially coordinated neutral ligands. A number of  $\text{Rh}_2^{4+}$  complexes with mixed bridging ligands also exist.<sup>13</sup> 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 I<sup>14</sup> or II.<sup>15</sup>

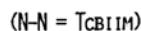
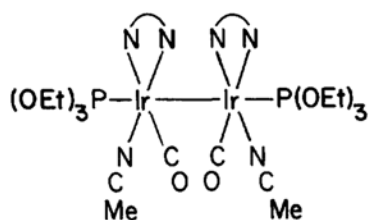


Only five diiridium(II,II) compounds that have the two metals in a square planar configuration with the two square planes parallel to each other (with or without additional axial ligands) seem to have been reported in the literature. These are  $[\text{Ir}_2(\text{TMB})_4\text{I}_2]^{2+}$  (TMB = 2,5-dimethyl-2,5-diisocyanohexane)<sup>16</sup> of structure III,  $\text{Ir}_2(\text{Tcbim})_2(\text{CO})_2(\text{MeCN})_2(\text{P}(\text{OEt})_3)_2$  (Tcbim = dianion of tetracyanobiimidazole)<sup>17a</sup> of structure IV,  $[\text{IrClX}(\text{CO})(\text{dppm})]_2$  [dppm = bis(diphenylphosphino) methane, X = Cl,  $\text{CH}_3\text{O}_2\text{CC}=\text{CHCO}_2\text{CH}_3$ ]<sup>17b</sup> of structure V, and  $\text{Ir}_2(\text{OEP})_2$  (OEP = dianion of octaethylporphyrine)<sup>18</sup> of structure VI. The first four have been structurally characterized and exhibit Ir–Ir distances of 2.803<sup>16</sup> and 2.826(2),<sup>17a</sup> 2.786(1) and 3.016(1) (average) Å.<sup>17b</sup> Unfortunately  $\text{Ir}_2(\text{OEP})_2$ , which is to be regarded as the only known truly inorganic Ir(II) dimer (this

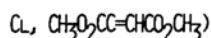
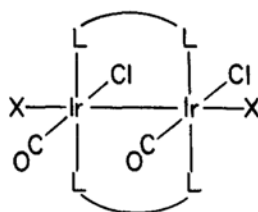
\* Author to whom correspondence should be addressed.



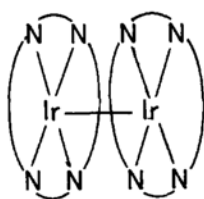
III



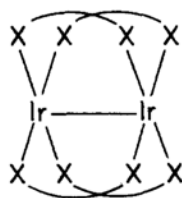
IV



V



VI



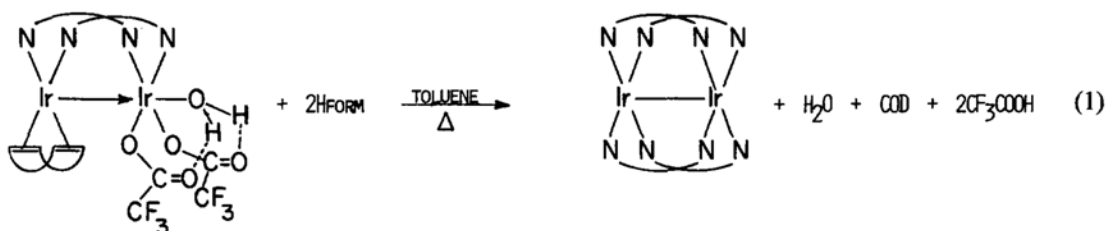
VII

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  $\text{Rh}_2^{4+}$  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),<sup>19</sup> 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,  $\text{CF}_3\text{COOH}$ . 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)

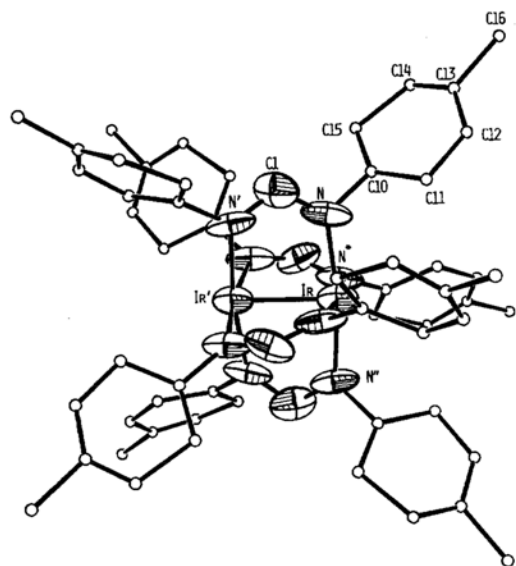


Fig. 1. An ORTEP view of the Ir<sub>2</sub>(form)<sub>4</sub> molecule. The *p*-tolyl carbon atoms are drawn with arbitrary radii for clarity. Distances: Ir–Ir', 2.524(3); Ir–N, 2.04(2); N–Cl, 1.34(2); N–ClO, 1.45(4) Å. Angles: Ir'–Ir–N, 85.4(6); N–Ir–N'', 170.9(9), N–Ir–N\*, 89.6(7); Ir–N–Cl, 124(1); 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<sub>3</sub>COOH and COD that are obtained along with the iridium product were identified by their <sup>1</sup>H-NMR peaks at 13.0 (broad) and 5.55 δ, respectively.

Quite surprisingly, attempts to obtain the same product directly by oxidising [Ir(form)(COD)]<sub>2</sub> with Ag(form) failed. No reaction took place under thermal or photochemical conditions or a combination thereof.

The structure of the Ir<sub>2</sub>(form)<sub>4</sub> molecule is shown in Fig. 1.\* The molecule has D<sub>4h</sub> 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 Rh<sub>2</sub>(form)<sub>4</sub>.<sup>12</sup> 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<sub>4</sub> 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

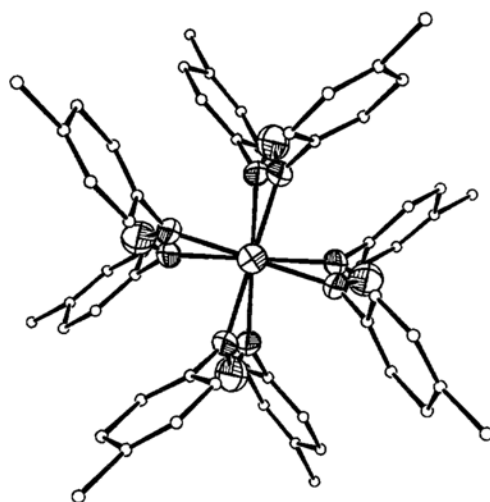


Fig. 2. View of the Ir<sub>2</sub>(form)<sub>4</sub> molecule along the Ir–Ir' direction.

even shorter than the separation in [Ir(CO)(PPh<sub>3</sub>)(η-PPh<sub>2</sub>)]<sub>2</sub>, 2.554 Å, for which a bond order of two has been proposed<sup>20</sup> and it is, expectedly, longer than the Rh–Rh separation (2.4336(4) Å) in the analogous compound Rh<sub>2</sub>(form)<sub>4</sub>.<sup>12</sup> The nearest neighbour separation in metallic iridium is 2.714 Å.<sup>21</sup>

Electrochemical, spectroscopic and theoretical studies on Ir<sub>2</sub>(form)<sub>4</sub> are in progress. The assignment of an electron rich single bond of σ<sup>2</sup>π<sup>4</sup>δ<sup>2</sup>δ\*<sup>2</sup>π\*<sup>4</sup> configuration to the metal–metal interaction, however, is strongly suggested by previous work done on similar rhodium compounds.<sup>22</sup>

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\* Crystal data: cubic, space group Pn $\bar{3}$ n, *a* = 21.300(9) Å, *V* = 966.4(12) Å<sup>3</sup>, *Z* = 6, *d*<sub>calc</sub> = 1.317 g cm<sup>-3</sup>, *R* = 0.0595 (*R*<sub>w</sub> = 0.0770) for 402 reflections having *F*<sub>o</sub><sup>2</sup> > 3σ(*F*<sub>o</sub><sup>2</sup>).

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