

Cofacial Porphyrin Dimers containing Intramolecular Metal–Metal Bonds

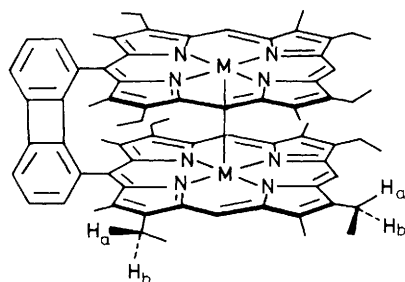
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Diruthenium and dimolybdenum derivatives of a biphenylene-bridged cofacial porphyrin dimer containing intramolecular metal–metal bonds have been synthesized and characterized.

Two classes of dimeric metalloporphyrins have received considerable attention: (1) dimers linked by a metal–metal bond, and (2) dimers covalently linked in a cofacial configuration. The metal–metal bonded dimers have been explored in terms of structure,¹ bonding,² and chemical reactivity.³ Cofacial porphyrin dimers have been successfully employed in the electrocatalytic four electron reduction of oxygen.⁴ Herein we report the first examples of cofacial porphyrin dimer containing an *intramolecular* metal–metal bond: diruthenium and dimolybdenum derivatives of the biphenylene-bridged cofacial porphyrin dimer (DPB).[†]

[†] Abbreviations: DPB = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene tetra-anion; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; DPA = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]anthracene tetra-anion.



(3) M—M = Ru≡Ru

(5) M—M = Mo≡Mo

Ruthenium was inserted into the free base H₄DPB⁵ by a modification of the literature method.⁶ The resulting diruthenium(II) complex was isolated as

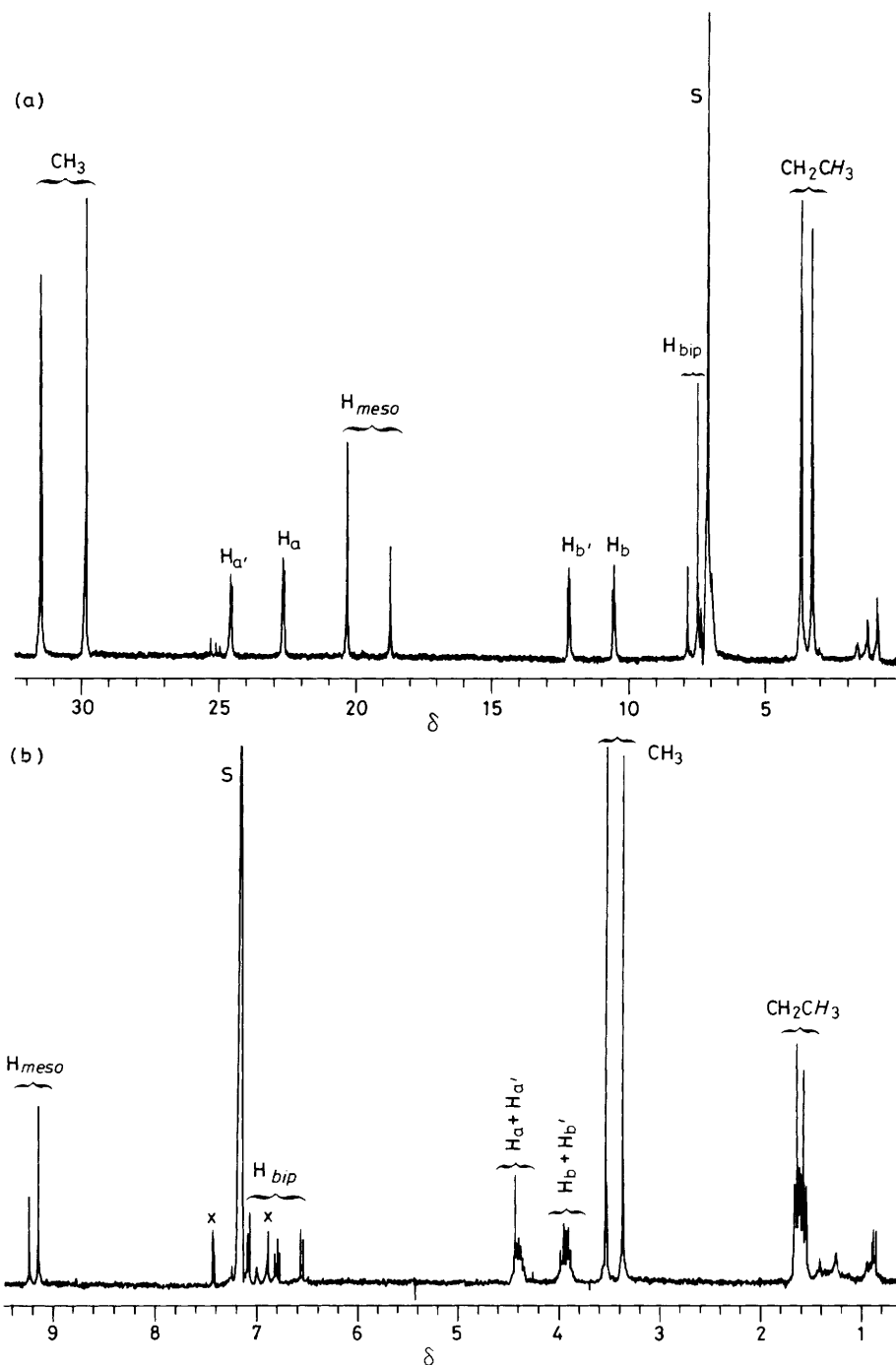
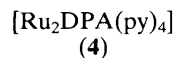
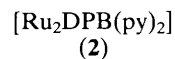
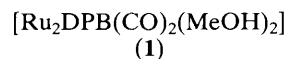


Figure 1. ¹H N.m.r. spectra of (a) (3) and (b) (5) in C₆D₆. bip = biphenylene.

[Ru₂DPB(CO)₂(MeOH)₂] (1). ‡ Photolysis of (1) in pyridine yielded [Ru₂DPB(py)₄] (2) in which two co-ordinated pyridine (py) molecules are inside and the other two are outside the diporphyrin cavity. Vacuum pyrolysis (230 °C, 5 × 10⁻⁶ Torr, 12 h) of (2) provided a dark green air-sensitive solid (3) that shows a mass spectrum consistent with the molecular formula Ru₂DPB (*m/z* = 1303, *M* - H⁺). The u.v.-visible spectrum of



(3) [λ_{max} (log ϵ) 375 (4.90), 508 (3.99), 630 (3.59), 734 nm (3.56)] is very similar to that of [{Ru(OEP)}₂]; † addition of an excess of pyridine under N₂, slowly (ca. 24 h) converts the

‡ All compounds described herein gave satisfactory spectroscopic, analytical, and/or mass spectral data.

spectrum of (3) into that of its precursor (2).§ The ^1H n.m.r. spectrum (Figure 1a) of (3) shows paramagnetic shifted signals analogous to those of $[\{\text{Ru}_2(\text{OEP})\}_2]$.¹ The magnetic moment ($2.6 \mu_{\text{B}}$) determined by Evans' method⁷ is close to the theoretical value ($2.84 \mu_{\text{B}}$) corresponding to two unpaired spins. The resemblance in spectroscopic, magnetic, and chemical properties between (3) and $[\{\text{Ru}(\text{OEP})\}_2]$ strongly supports the presence of a metal-metal bond between the two ruthenium atoms in (3). According to the qualitative molecular orbital diagram for metal-metal bonding shown in Fig. 1a of reference 2a, the ground state electronic configuration of (3) is $\sigma^2\pi^4\delta^2\delta^*\pi^*1\pi^*1$; thus the net Ru-Ru bond order is 2. A spin triplet ground state arising from two singly occupied, degenerate π^* orbitals accounts for the observed paramagnetism.

When $[\text{Ru}_2\text{DPA}(\text{py})_4]$ (4),† an anthracene-bridged cofacial diporphyrin⁸ analogous to (2), was subjected to the same pyrolysis conditions used for preparing (3), only starting material and an insoluble black residue were recovered. Treatment of this residue with pyridine led to partial conversion back into (4). Presumably the distance between two metal centres in DPA is too long (*ca.* 1 Å longer than in DPB)⁹ to accommodate an intramolecular Ru-Ru bond, resulting in the formation of an insoluble polymer with intermolecular Ru-Ru bonds.

We previously reported the direct formation of $[\{\text{Mo}(\text{OEP})\}_2]$ from the reaction of H_2OEP and $[\text{MoCl}_2(\text{CO})_4]$.^{2b} Treatment of H_4DPB under similar conditions, followed by a chromatography (silica : benzene) yielded a brown diamagnetic compound (5) (15%). Mass spectral data

are consistent with the molecular formula Mo_2DPB (m/z 1294, M^-). The similarity between the u.v.-visible $[\lambda_{\text{max}} (\log \epsilon)]$ 364 (sh), 385 (4.88), 440 (4.55), 538 (3.94), 572 nm (3.70) and ^1H n.m.r. (Figure 1b) spectra of (5) and those of $[\{\text{Mo}(\text{OEP})\}_2]$ suggests the presence of a metal-metal bond in (5). Since the rigid biphenylene bridge forces the two porphyrin rings to be eclipsed, the molecular orbital diagram (Fig. 1a in reference 2a) predicts a quadruple bond between two Mo^{II} atoms.

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§ Upon addition of pyridine rapid formation of an intermediate is observed. We propose this intermediate to be $[\text{Ru}_2\text{DPB}(\text{py})_2]$ with both pyridines bound outside. Triphenylphosphine reacts with (3) to form $[\text{Ru}_2\text{DPB}(\text{PPh}_3)_2]$ which has been independently synthesized and characterized (manuscript in preparation).