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Heterometallic and Homometallic Ruthenium and Osmium Double Bonds in Metalloporphyrin and Metallotetraazaporphyrin Dimers

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Studies of multiple bonds in discrete complexes provide fundamental insight into the nature of metal–metal bonds. However, few compounds containing *heterometallic* multiple bonds have been reported,[1,2] and no general synthetic method has been developed for the synthesis and isolation of heterometallic multiply bonded compounds. Here, we report a simple, general procedure for the synthesis and isolation of unprecedented heterometallic and heteroporphyrin multiply bonded dimers.

Transition-metal porphyrin dimers constitute a unique series for the systematic study of metal–metal bonds. A comprehensive set of homometallic metal–metal multiply bonded OEP and TTP[3] dimers has been prepared and characterized for 4d and 5d transition metals.[4] Herein, the OETAP ligand[5] was employed because it is a good structural analogue of OEP but also because it confers significantly different redox properties upon the metal center. Experimentally verifiable predictions of the bond order and spin states for these dimers can be made on the basis of a simple molecular orbital diagram.[6] This model assumes that only d electrons are involved in bonding. In the case of Ru and Os in the II+ oxidation state, 12 d electrons are involved in the metal–metal bond; the molecular orbital diagram predicts a ground-state configuration of $\sigma^2\pi^4\delta^{nb4}\pi^{*2}$, with a spin quantum number 1 and a bond order 2.[2,6] Ru and Os have the same Pauling electronegativity (2.2)[7] and hence are expected to form primarily covalent bonds. Thus the heteroporphyrin and heterometallic dimers should exhibit properties qualitatively similar to those of the homodimers.

The new dimer precursors, Ru(OETAP)(py)$_2$ and Os(OETAP)(py)$_2$, were prepared in a manner similar to that reported for the OEP analogues.[4,8,9] The dimers, [Ru(OETAP)]$_2$ and [Os(OETAP)]$_2$, were prepared by vacuum pyrolyses of axially ligated monomers.[4,10] These dimers exhibit ^{1}H NMR spectra similar to those of the corresponding OEP dimers,[4] in that they display narrow-line, paramagnetically shifted resonances (Table I).[11] This is consistent with the prediction that these dimers should have a spin quantum number of 1 in their ground states. For the Ru and Os dimers, interconversion of the monocation and the neutral species changes the number of d electrons in the metal–metal bond. The E^0 for this process is affected not only by the metal (e.g., [Os(OEP)]$_2$ is easier to oxidize than [Ru(OEP)]$_2$ by 0.4 V), but also by the nature of the ligand (e.g., [Ru(OEP)]$_2$ is easier to oxidize than [Ru(OETAP)]$_2$ by 0.4 V).[10,12,13]

The difference in metal-centered redox potentials between OETAP and OEP dimers can be exploited to prepare a ruthenium *heteroporphyrin* dimer. The heteroporphyrin dimer [(OEP)RuRu(OETAP)] is synthesized by pyrolyzing a mixture of the two ruthenium monomers, Ru(OEP)(py)$_2$ and Ru(OETAP)(py)$_2$, resulting in a nonstatistical distribution of [Ru(OEP)]$_2$ (16%), [Ru(OETAP)]$_2$ (16%), and [(OEP)RuRu(OETAP)] (68%).[10,14] The heterodimer cation [(OEP)RuRu(OETAP)][BF$_4$] is then isolated by a series of redox titrations,[15] made possible by the different redox potentials which the two ligands confer upon the metal centers (Figure 1).[10,16] The isolated heterodimer cation is reduced to yield the neutral heteroporphyrin dimer [(OEP)RuRu(OETAP)].[10,17] The reduction potential of [(OEP)RuRu(OETAP)]$^{+/0}$ (−0.50 V) is the average of those of the constituent homodimers [Ru(OEP)]$_2^{+/0}$ (−0.73 V) and [Ru(OETAP)]$_2^{+/0}$ (−0.30 V).[10,12,13] In addition, [(OEP)RuRu(OETAP)] exhibits a ^{1}H NMR spectrum which, like those of the corresponding homoporphyrin dimers, contains narrow-line, paramagnetically shifted resonances (Table I).[4,11,17]

Furthermore, this general synthetic scheme of copyrolysis followed by redox titrations has been used to prepare *heterometallic* heteroporphyrin dimers, such as [(OEP)OsRu(OET-

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(3) We use the following abbreviations for porphyrins: OEP = octaethylporphyrin; TTP = tetratolylporphyrin; OETAP = octaethyltetraazaporphyrin.

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(10) See supplementary materials for experimental details.

(11) The magnetic susceptibility and variable-temperature ^{1}H NMR of these compounds are currently under investigation and will be the subject of forthcoming publications.

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(13) Electrochemical measurements were performed on the neutral species for the homoporphyrin dimers ([Ru(OEP)]$_2$, [Ru(OETAP)]$_2$ and [Os(OEP)]$_2$) and on the monocations for the heteroporphyrin dimers ([(OEP)RuRu(OETAP)][BF$_4$] and [(OEP)OsRu(OETAP)][BF$_4$]). All potentials were taken from cyclic voltammograms and are given versus the ferrocenium/ferrocene couple. Experiments were performed on 3–5 mM of dimer in 0.2 M TBAPF$_6$ in THF. The potentials for the interconversion between monocations and neutral species are as follows: [Ru(OETAP)]$_2$, −0.30 V; [Ru(OEP)]$_2$, −0.73 V; [Os(OEP)]$_2$, −1.15 V; [(OEP)RuRu(OETAP)]$^+$, −0.50 V; [(OEP)OsRu(OETAP)]$^+$, −0.73 V.

(14) Mixed pyrolyses had been performed in previous experiments, but the heterodimers were not isolated. (a) Barnes, C. E. Ph.D. Thesis, Stanford University, Stanford, CA, 1982. (b) Woo, L. K. Ph.D. Thesis, Stanford University, Stanford, CA, 1984.

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(16) The following mixture of dimers was dissolved in toluene (5 mL): [Ru(OEP)]$_2$ (16%, 0.005 mmol), [(OEP)RuRu(OETAP)] (68%, 0.02 mmol), and [Ru(OETAP)]$_2$ (16%, 0.005 mmol) (percentages determined on the basis of integration in ^{1}H NMR; total mass 38 mg). Titration 1: AgBF$_4$ (1.07 mg, 0.0055 mmol, 1.1 equiv relative to [Ru(OEP)]$_2$) in toluene (0.1 mL) was added to the mixture of dimers. The solution was stirred (~24 h) and then filtered through a fritted filter and rinsed with toluene. The filtrate was concentrated under vacuum. On the basis of ^{1}H NMR, the filtrate consisted of 15% [Ru(OETAP)]$_2$ and 85% [(OEP)RuRu(OETAP)]. No [Ru(OEP)]$_2$ or [Ru(OEP)]$_2$[BF$_4$] was observed by ^{1}H NMR. Titration 2: the filtrate was redissolved in toluene (5 mL), and to this was added AgBF$_4$ (2.92 mg, 0.15 mmol, 0.8 equiv relative to [(OEP)RuRu(OETAP)]) in toluene (0.3 mL). This mixture was stirred (12 h) and then filtered through a fritted filter; the precipitate was washed with toluene and *n*-hexane. The solid was eluted off the filter with CH$_2$Cl$_2$ and concentrated under vacuum: [(OEP)RuRu(OETAP)][BF$_4$]. ^{1}H NMR (ppm, CD$_2$Cl$_2$): porphyrinic resonances, $-CH_2$-CH$_3$ 12.24 (br, 8H), 10.81 (m, 8H), 7.30 (m, 8H), 6.08 (m, 8H); $-$CH$_2$CH_3 2.52 (t, 24H), 2.16 (br, 24H); H_{meso} 13.53 (s, 4H). Mass spectrum (Ru^{102}) P (*m*/*e*): 1272, 634.

(17) [(OEP)RuRu(OETAP)][BF$_4$] dissolved in toluene (5 mL) was stirred with excess Co(II)Cp$_2$ (30 min). The toluene, Co(III)Cp$_2$, and excess Co(II)Cp$_2$ were removed by heating under vacuum to give [(OEP)RuRu(OETAP)]. ^{1}H NMR (ppm, C$_6$D$_6$): porphyrinic resonances, $-$CH_2CH$_3$ 34.66 (m, 8H), 24.80 (m, 8H), 18.26 (m, 8H), 10.98 (m, 8H); $-$CH$_2$CH_3 3.75 (t, 24H), 3.39 (t, 24H); H_{meso} 12.73 (s, 4H).

(18) Research in progress.

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Table I. ^{1}H NMR (300 or 400 MHz) Resonances of OEP and OETAP Dimers at 25 °C under Nitrogen Atmosphere

	CH_2CH_3 (CH$_2$ protons)	CH_2CH_3 (CH$_3$ protons)	H_{meso}
$[Ru(OETAP)]_2$ in C_6D_6	30.29 (m, 8H) 15.69 (m, 8H)	3.44 (t, 24H)	
$[Ru(OEP)]_2$[4] in C_6D_6	25.98 (m, 8H) 11.10 (m, 8H)	3.42 (t, 24H)	10.12 (s, 4H)
$[Os(OETAP)]_2$ in C_6D_6	3.49 (m, 8H) 2.65 (m, 8H)	0.95 (t, 24H)	
$[Os(OEP)]_2$[4b] in C_6D_6	11.50 (m, 8H) 7.77 (m, 8H)	1.92 (t, 24H)	−1.02 (s, 4H)
$[(OEP)RuRu(OETAP)][BF_4]$ in CD_2Cl_2	12.24 (br, 8H) 10.81 (m, 8H) 7.30 (m, 8H) 6.08 (m, 8H)	2.52 (t, 24H) 2.16 (br, 24H)	13.53 (s, 4H)
$[(OEP)RuRu(OETAP)]$ in C_6D_6	34.66 (m, 8H) 24.80 (m, 8H) 18.26 (m, 8H) 10.98 (m, 8H)	3.75 (t, 24H) 3.39 (t, 24H)	12.73 (s, 4H)
$[(OEP)OsRu(OETAP)][BF_4]$ in CD_2Cl_2	8.27 (br, 8H) 7.77 (br, 8H) 5.89 (br, 8H) 5.67 (br, 8H)	2.23 (br, 24H) 1.89 (br, 24H)	11.32 (br, 4H)
$[(OEP)OsRu(OETAP)]$ in C_6D_6	14.32 (m, 8H) 13.70 (m, 8H) 9.37 (m, 8H) 8.53 (m, 8H)	2.59 (t, 24H) 2.20 (t, 24H)	6.68 (s, 4H)

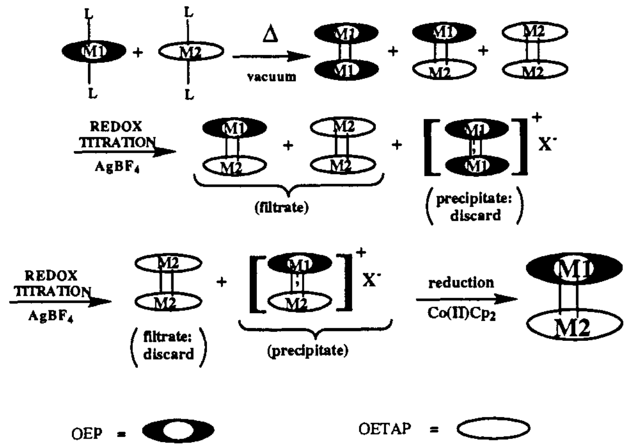

Figure 1. Synthesis and isolation of heteroporphyrin and heterometallic porphyrin and tetraazaporphyrin dimers.

AP)].[10] The reduction potential of $[(OEP)OsRu(OETAP)]^{+/0}$ (−0.73 V) is the average of the potentials of the constituent homodimers $[Os(OEP)]_2^{+/0}$ (−1.15 V) and $[Ru(OETAP)]_2^{+/0}$ (−0.30 V).[12,13] The neutral heterometallic dimer exhibits narrow-line, paramagnetically shifted resonances in the ^{1}H NMR spectrum, similar to those of the homodimers (see Table I).[4,10,11] These data are consistent with the assertion that the two heterodimers, [(OEP)RuRu(OETAP)] and [(OEP)OsRu(OETAP)], have the same ground-state electronic configurations as the homodimers ($\sigma^2\pi^4\delta^{nb4}\pi^{*2}$) and can be included in a systematic study of metal–metal bonding.

In summary, we report not only a new class of metal–metal-bonded compounds, tetraazaporphyrin dimers, but also a general procedure for the preparation of both heteroporphyrin and heterometallic metal–metal-bonded dimers. We have illustrated these syntheses with examples using Ru and Os. According to the molecular orbital diagram, these dimers should all have bond order 2 and spin state 1. The data obtained thus far are consistent with both of these predictions. The Ru and Os heteroporphyrin and heterometallic dimers appear to be qualitatively similar to the corresponding homodimers. We are currently probing the nature of the metal–metal bond in these compounds through their crystallographic, vibrational, and magnetic properties. In addition, the application of this general synthetic methodology to the synthesis of unprecedented *intertriad* heterometallic multiply bonded dimers is the subject of forthcoming publications.[18]

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Supplementary Material Available: Experimental section including synthetic protocols and characterization of the compounds reported herein (7 pages). Ordering information is given on any current masthead page.