

# Multiple Metal-Metal Bonds in 4d and 5d Metal-Porphyrin Dimers

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**Introduction and Historical Overview.** Studies of multiple bonding between transition metals within discrete complexes offer fundamental insight into the nature of bonding between metal atoms. This understanding facilitates prediction of the physical properties and the reactivities of metal complexes containing metal-metal multiple bonds. We have used porphyrin ligands and a general synthetic scheme to prepare an unprecedented, comprehensive series of homologous homometallic and heterometallic metal-metal bonded compounds. In this Account, we describe these compounds and our current understanding of metal-metal bonding within porphyrin dimers.

Before this century, models of bonding did not include direct interactions between metals in discrete complexes. In 1935, Brosset<sup>1</sup> showed that the W-W separation in  $K_3[W_2Cl_9]$  (2.41 Å) is shorter than that in elemental tungsten (2.74 Å). He suggested that a bonding interaction existed between the tungsten atoms, but did not recognize that there was a triple bond. In 1947, Pauling<sup>2</sup> applied the concept of covalency to bonds between metal atoms in early transition metal complexes and proposed that they can have "bond numbers" greater than 1. In 1956, Figgis and Martin<sup>3</sup> invoked d-orbital bonding concepts developed by Craig *et al.*<sup>4</sup> to suggest that  $[Cr(\text{acetate})_2]_2$  contains a Cr-Cr quadruple bond. Wider acceptance of multiple metal-metal bonds followed from two contemporaneous structure determinations<sup>5,6</sup> of the anion  $[Re_3Cl_{12}]^{3-}$  and Cotton's<sup>6</sup> proposal that the short Re-Re distances (2.48 Å, versus 2.74 Å in elemental rhenium) result from a Re-Re double bond. Cotton established the currently accepted model for multiple metal-metal bonding in 1964,<sup>7-10</sup> by demonstrating the presence of a quadruple bond in  $[Re_2Cl_8]^{2-}$ . This dianion has  $D_{4h}$  symmetry (the two  $ReCl_4$  fragments are eclipsed), no bridging

ligands are present, and the Re-Re bond (2.24 Å) is extremely short. Since 1964, voluminous studies of multiple metal-metal bonds have appeared; the subject has been extensively reviewed.<sup>11-15</sup>

Our laboratory entered this field in 1981 with the preparation of  $[Ru(\text{OEP})]_2$ ,<sup>16</sup> which has a Ru-Ru double bond.<sup>17,18</sup> At that time, we recognized that transition metal porphyrin dimers could be used to study systematically the properties of metal-metal bonds<sup>17-20</sup> because they satisfy all of the following criteria: (1) The dimer syntheses are general; metals from several triads can be used to prepare both homometallic and heterometallic dimers. (2) Dimers containing metals from different triads can be prepared with the same ligands and charge. (3) The dimers are discrete molecular systems. (4) The dimers contain no labile or bridging ligands. (5) The dimers have high symmetry.

Thus we have been able to study a wide range of homometallic and heterometallic dimers to determine how the properties of the metal-metal bonds are affected when we change one variable *without* changing any other variables. Since there are no bridging ligands, the major interaction between the monomers is the bonding interaction between the two metal centers. In addition, because these dimers have high symmetry, a simple molecular orbital diagram can be used to make experimentally verifiable predictions about their physical properties.

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Hilary J. Arnold is a fifth-year graduate student in the research group of James P. Collman at Stanford University. She is currently conducting research on the topic presented in this Account, homometallic and heterometallic multiple metal-metal bonds in porphyrin dimers. While performing this research, Hilary Arnold has been supported by a National Science Foundation Predoctoral Fellowship. Before starting graduate school, she worked as a summer student research assistant at ICI Europa in Everberg, Belgium. She received a B.S. in chemistry with honors from the University of Chicago in 1989 and conducted undergraduate research in the laboratories of Gerhard L. Closs, Jack Halpern, and Larry E. Overman.

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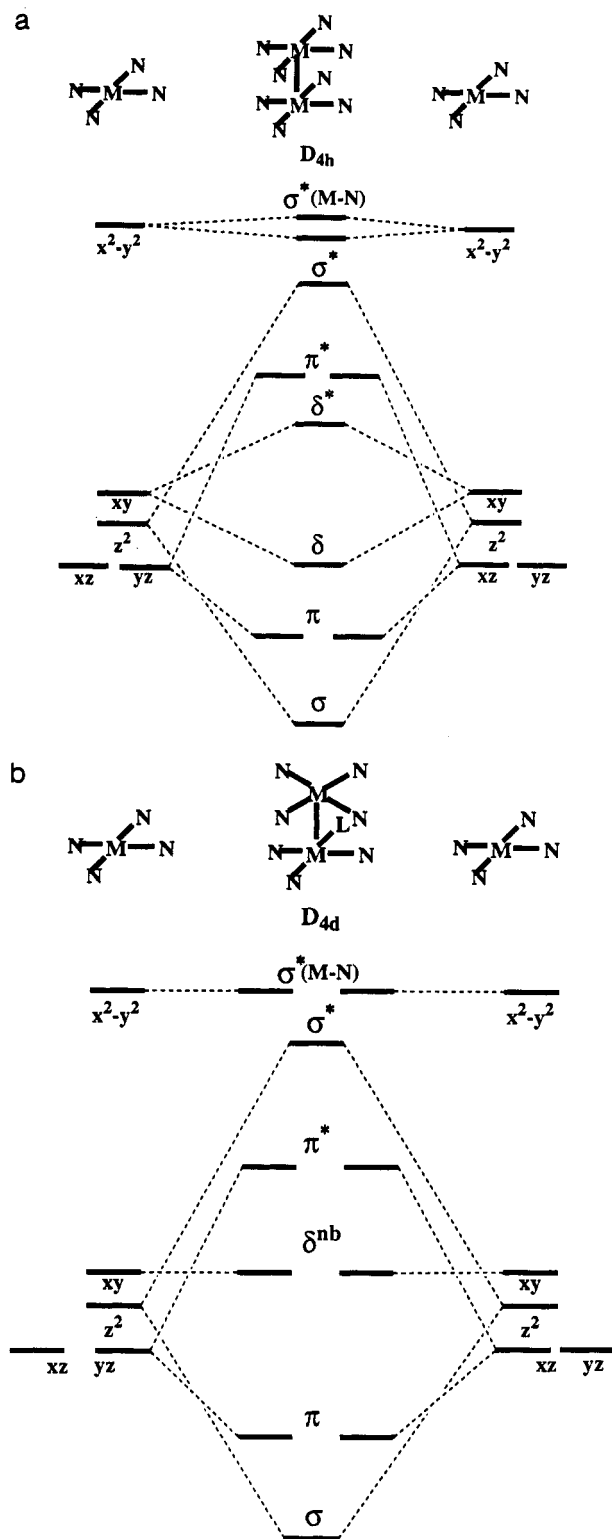


Figure 1. Molecular orbital diagram for (a) eclipsed and (b) staggered homodimers.

**Bonding.** A MO diagram appropriate for homometallic metalloporphyrin dimers was developed by Cotton<sup>7,10</sup> and is similar to that developed independently by Figgis and Martin.<sup>3</sup> This scheme assumes that only d-electrons participate in M-M bonding. In addition, one makes the reasonable assumption that the dimers have  $D_{4h}$  (eclipsed, Figure 1a) or  $D_{4d}$  (staggered, Figure 1b) symmetry. By convention, the  $z$  axis is coincident with the M-M bond. The  $\sigma$  bonds to porphyrinic nitrogen atoms involve the metal  $d_{x^2-y^2}$  levels, and these

Table I. Bond Orders and Spin States of Neutral Homometallic Porphyrin Dimers

metal	bond order	spin state
Mo, W	4	0
Re	3	0
Ru, Os	2	1
Rh, Ir	1	0

high-energy  $\sigma^*$  orbitals may be ignored for M-M bonding. The remaining d-orbitals are available for metal-metal bonding. The ordering of MOs stems from considerations of orbital overlap:  $\sigma > \pi > \delta$ .<sup>10</sup>

These qualitative, first-order MO diagrams predict bond orders and spin states for homometallic dimers which are consistent with the experimental data. The predictions are based on the total number of d-electrons provided by the two metals. For example, the Ru(II) dimer,  $[\text{Ru}(\text{OEP})_2]$ ,<sup>17,18</sup> has 12 ( $2 \times 6$ ) d-electrons. The resulting electronic configurations,  $\sigma^2\pi^4\delta^{nb}4\pi^{*2}$ , produces a formal Ru-Ru double bond with two unpaired electrons. The number of unpaired electrons and bond orders predicted for a series of homometallic dimers are shown in Table I. Neutral homodimers have bond orders of 1, 2, 3, and 4 corresponding to 14, 12, 10 and 8 d-electrons, respectively. For compounds with 8 d-electrons, unfavorable steric interactions are outweighed by the energetic advantage of forming a  $\delta$  bond between the M  $d_{xy}$  orbitals. The  $\delta$  bond is strongest when the ligands are eclipsed: this forces compounds with quadruple bonds to assume  $D_{4h}$  symmetry (*vide infra*). Thus the degeneracy of the  $\delta^{nb}$  orbitals is lifted, resulting in  $\delta$  and  $\delta^*$  orbitals (Figure 1). We have been particularly interested in whether this simple molecular orbital diagram can also be used to predict the properties of heterometallic dimers. Even though the symmetry of heterometallic dimers is lowered to  $C_{4v}$  (eclipsed or staggered), the degeneracies of the d-based  $\pi$  and  $\pi^*$  orbitals should not change. However, in a heterometallic bond the relative ordering of the  $\delta^{nb}$  (or  $\delta$  and  $\delta^*$ ) and  $\pi^*$  orbitals could be altered by the different electronegativities of the two metals. (See Figure 2 for one possible example.)

**Synthesis.** The most powerful aspect of the synthesis of metalloporphyrin dimers described below is its generality: one method can produce homologous dimers containing Mo, W, Re, Ru, or Os. The singly bonded Rh<sup>21,22</sup> and Ir<sup>23</sup> dimers, although synthesized by another method, have also been prepared. In addition, this simple method can be used to prepare an unprecedented series of isostructural heterometallic dimers.<sup>24</sup> These heterodimers and their properties are the focus of current research in our laboratory.<sup>25</sup>

The multiply bonded homometallic metalloporphyrin dimers are prepared by vacuum pyrolysis of powdered amorphous samples of a neutral M(II) porphyrin coordinated by one or two volatile axial ligands. In some cases several steps are required to obtain the appropriate ligated M(II) porphyrin complex. Rep-

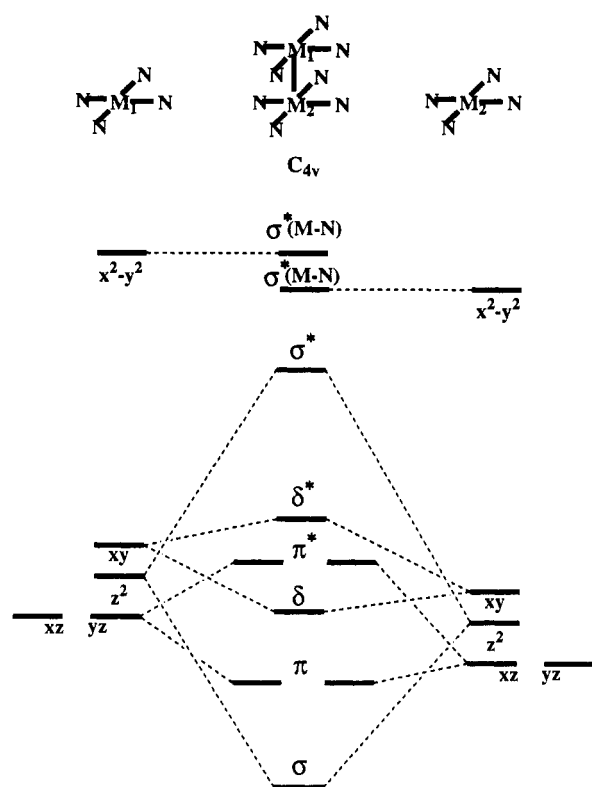
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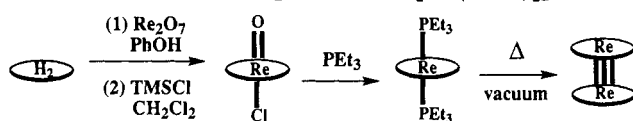
**Figure 2.** Molecular orbital diagram for eclipsed heterodimers: possible orbital ordering.

**Table II. Representative Examples of Metalloporphyrin Dimer Precursors**

metal	ligand 1	ligand 2	porphyrins <sup>a</sup>
Mo	PhC≡CPh		OEP, TTP
W	PhC≡CPh		OEP
Re	PEt <sub>3</sub>	PEt <sub>3</sub>	OEP
	PEt <sub>3</sub>	PEt <sub>3</sub>	OEP, TTP
Ru	PMe <sub>3</sub>	PMe <sub>3</sub>	OEP, TTP
	pyridine	pyridine	OEP, OETAP, TTP
Os	pyridine	pyridine	OEP, OETAP, TTP

<sup>a</sup> OEP = octaethylporphyrin; OETAP = octaethyltetraazaporphyrin; TTP = tetratolylporphyrin.

**Scheme I. Preparation of [Re(OEP)]<sub>2</sub>**

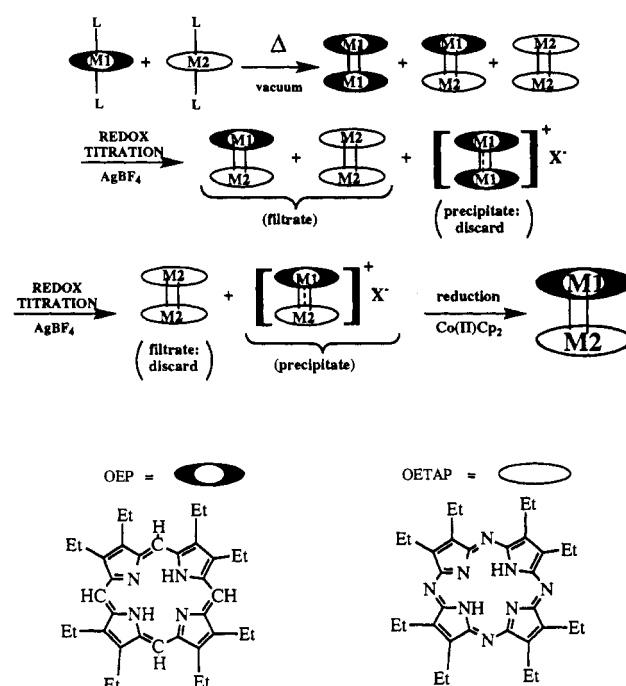


representative examples are listed in Table II.<sup>17-20</sup> Yields of the pyrolyses to the homodimers are nearly quantitative. This method is illustrated by the preparation of a Re(II) dimer (Scheme I). To prepare [Re(OEP)]<sub>2</sub>, we first synthesized Re(OEP)(PEt<sub>3</sub>)<sub>2</sub>, the first reported Re(II) porphyrin complex.<sup>26</sup>

This synthetic methodology has not only yielded a comprehensive set of homologous metal-metal bonded compounds but also allowed us to prepare heterometallic dimers. This process can be used to make not only dimers in which the metals are from the same triad (*intratriad* dimers)<sup>24,27</sup> but also dimers in which the metals are from different triads (*mixed triad* or *intertriad* dimers).<sup>25</sup> In the past, no other *mixed triad*

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**Figure 3.** Synthesis and isolation of heterometallic porphyrin dimers.

heterometallic *multiple* bonds had been reported; all compounds with heterometallic multiple bonds contained only group 6 metals (Cr, Mo, W).<sup>11,28</sup> We synthesize the porphyrin heterodimers by pyrolyzing a mixture of two different axially ligated monomers to yield a mixture of two homodimers and one heterodimer. A series of redox titrations permit the heterodimer to be isolated from the corresponding homodimers.<sup>29</sup> (See Figure 3.) The Nernst equation predicts the distribution of oxidized species from the differences in the oxidation potentials of the compounds.<sup>30</sup> If the two metals of interest do not have sufficiently different oxidation potentials, then the separation can be improved by placing the two metals of the heterodimer in porphyrins which convey significantly different redox properties. In this study, we have employed octaethylporphyrin, OEP, and octaethyltetraazaporphyrin, OETAP,<sup>31</sup> these two porphyrins are structurally similar, but their metal-centered redox potentials differ by 0.4-0.6 V.<sup>24,32</sup> The mixed pyrolysis and subsequent redox titration can be used to prepare a wide variety of intratriad and intertriad heterometallic dimers.

**Correlation of Predictions with Experimental Results.** The formal bond orders<sup>33</sup> and spin states derived from the simple molecular orbital scheme can explain the <sup>1</sup>H NMR spectra, the electrochemical behavior, the magnetic properties, the M-M separation, the M-M vibrational frequencies (and force constants), and the electronic rotational barriers about the metal-metal bonds of porphyrin dimers.

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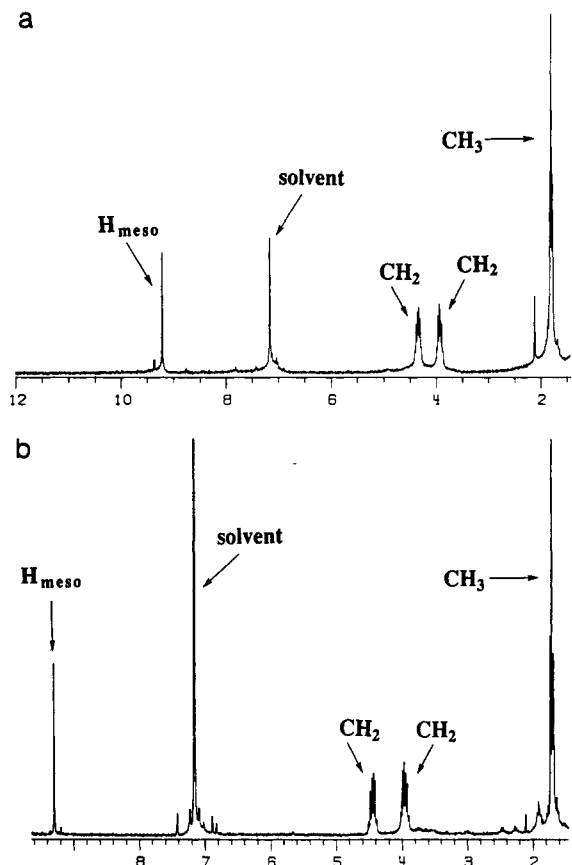


Figure 4.  $^1\text{H}$  NMR spectra of (a)  $[\text{Mo}(\text{OEP})]_2$  and (b)  $[\text{Rh}(\text{OEP})]_2$ .

**$^1\text{H}$  NMR.** All metalloporphyrin dimers exhibit two salient features in their  $^1\text{H}$  NMR spectra: (1) there are no axial ligand resonances, and (2) due to the inequivalence of the two faces of the porphyrin, the methylene protons of OEP and OETAP are diastereotopic and appear as two multiplets.  $^1\text{H}$  NMR reveals whether a given dimer is diamagnetic or paramagnetic. For instance, the simple molecular orbital diagram predicts that both  $[\text{Mo}(\text{OEP})]_2$  ( $\sigma^2\pi^4\delta^2$ )<sup>19</sup> and  $[\text{Rh}(\text{OEP})]_2$  ( $\sigma^2\pi^4\delta^{\text{nb}4}\pi^4$ )<sup>21,22,34</sup> should be diamagnetic, and that they should possess quadruple and single M–M bonds, respectively. All of the proton resonances for both of these dimers (Figure 4) occur between 0 and 10 ppm, consistent with the predictions of diamagnetism. These spectra are surprisingly similar, even though the M–M separations and magnetic anisotropies should be quite distinct.

In contrast, the MO diagram indicates that  $[\text{Ru}(\text{OEP})]_2$  ( $\sigma^2\pi^4\delta^{\text{nb}4}\pi^{*2}$ )<sup>17,18</sup> should be paramagnetic ( $S = 1$ ), and the spectrum of the Ru(II) dimer (Figure 5) differs dramatically from those of the diamagnetic dimers. The resonances of the diastereotopic  $\text{CH}_2$  protons still have narrow line widths, but are shifted downfield and have chemical shift values separated by 15 ppm. These signals change with temperature; plots of chemical shift versus  $1/T$  are linear over the temperature range  $-90$  to  $+95$  °C.<sup>18</sup> This behavior is consistent with a fast electron relaxation time and a ground-state triplet. The  $^1\text{H}$  NMR spectra of other paramagnetic M–M homodimers (e.g.,  $[\text{Ru}(\text{OEP})]_2^+$ ,

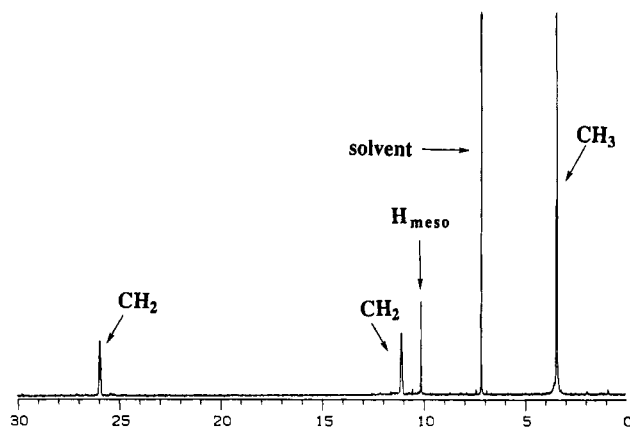


Figure 5.  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\text{OEP})]_2$ .

$[\text{Ru}(\text{OETAP})]_2$ , and  $[\text{Os}(\text{OEP})]_2$ ) also exhibit narrow, temperature-dependent signals.<sup>18,19,24,35</sup>

We have also examined the  $^1\text{H}$  NMR data for group 8 *intratriad* heterodimers and group 8 homodimers.<sup>24</sup> The exact chemical shift values differ dramatically from compound to compound: the  $\text{CH}_2$  protons of  $[(\text{OEP})\text{-RuRu}(\text{OETAP})]$  appear between 34.66 and 10.98 ppm, while those for  $[\text{Os}(\text{OETAP})]_2$  occur at 3.49 and 2.65 ppm. In spite of this disparity, all of the compounds exhibit narrow line, temperature-dependent  $^1\text{H}$  NMR spectra. This was expected, since Ru and Os have the same Pauling electronegativities; hence  $\text{Ru}_2$ ,  $\text{RuOs}$ , and  $\text{Os}_2$  dimers should have the same MO diagram and orbital occupancy (Figure 1b,  $\sigma^2\pi^4\delta^{\text{nb}4}\pi^{*2}$ ), and the same spin state and similar physical properties. The observed chemical shift differences for similar compounds could be attributed to differences in zero-field splitting (*vide infra*) and to changes in the electron density at the metal center which are conferred by the different porphyrins.

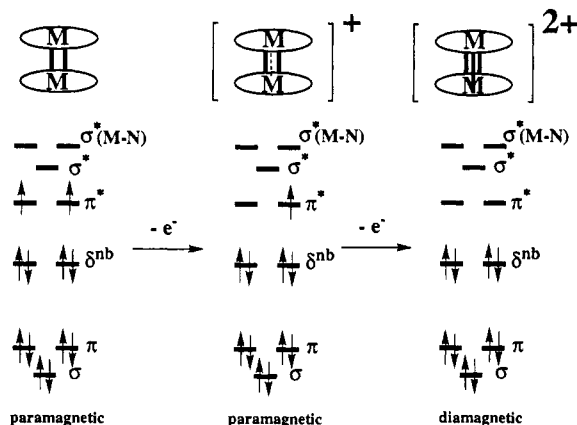
**Redox Chemistry.** The molecular orbital diagram predicts the effect of dimer oxidation on the bond order, BO.<sup>20,35</sup> For dimers having an antibonding HOMO, such as Ru and Os ( $\sigma^2\pi^4\delta^{\text{nb}4}\pi^{*2}$ , BO = 2), oxidation should increase the formal M–M bond order. Removal of an electron from the nonbonding HOMO of the Re dimer ( $\sigma^2\pi^4\delta^{\text{nb}4}$ , BO = 3) should break the degeneracy of the  $\delta^{\text{nb}}$  orbitals (resulting in  $\delta$  and  $\delta^*$  orbitals) and increase the formal M–M bond order ( $\sigma^2\pi^4\delta^2\delta^{*1}$ , BO = 3.5).

The electrochemical reactions of the dimers<sup>35</sup> are reversible on the time scale of cyclic voltammetry (CV), and chemical redox titrations can be used for preparative purposes<sup>20,35</sup> (Scheme II). Chemical oxidation yields the cationic dimers shown in Table III; nonintegral bond orders of 2.5 (e.g.  $[\text{Ru}(\text{OEP})]_2^+$ ) and 3.5 (e.g.,  $[\text{Re}(\text{OEP})]_2^+$ ) have been obtained in this way. The UV–vis spectra reveal that positions and intensities of the Soret bands (porphyrin  $\pi$  to  $\pi^*$  transitions) of monocations and dications do not differ greatly from those observed in the corresponding neutral species. This indicates that the oxidation is metal-based, rather than porphyrin-based.<sup>35</sup> The well-defined redox chemistry of these dimers also enables the isolation of heterodimers by oxidative titrations.

In addition, comparing the redox potentials of heterometallic and homometallic dimers provides insight into the nature of different heterometallic bonds.

(34) This  $^1\text{H}$  NMR spectrum was kindly provided by Yunkyoung Ha.

(35) Collman, J. P.; Prodollet, J. W.; Leidner, C. R. *J. Am. Chem. Soc.* 1986, 108, 2916–2921.

**Scheme II. Oxidation of Ruthenium(II) and Osmium(II) Metalloporphyrin Dimers**

**Table III. Cationic Homometallic Dimers**

dimer	electron confign	bond order	spin state
[Re(OEP)] <sub>2</sub> <sup>+</sup>	$\sigma^2\pi^4\delta^*1$	3.5	1/2
[Re(OEP)] <sub>2</sub> <sup>2+</sup>	$\sigma^2\pi^4\delta^2$	4	0
[Ru(OEP)] <sub>2</sub> <sup>+</sup>	$\sigma^2\pi^4\delta nb^4\pi^*1$	2.5	1/2
[Ru(OEP)] <sub>2</sub> <sup>2+</sup>	$\sigma^2\pi^4\delta nb^4$	3	0
[Os(OEP)] <sub>2</sub> <sup>+</sup>	$\sigma^2\pi^4\delta nb^4\pi^*1$	2.5	1/2
[Os(OEP)] <sub>2</sub> <sup>2+</sup>	$\sigma^2\pi^4\delta nb^4$	3	0

**Table IV. Ruthenium and Osmium Dimers: Potentials for Interconversion between Monocations and Neutral Species<sup>a</sup>**

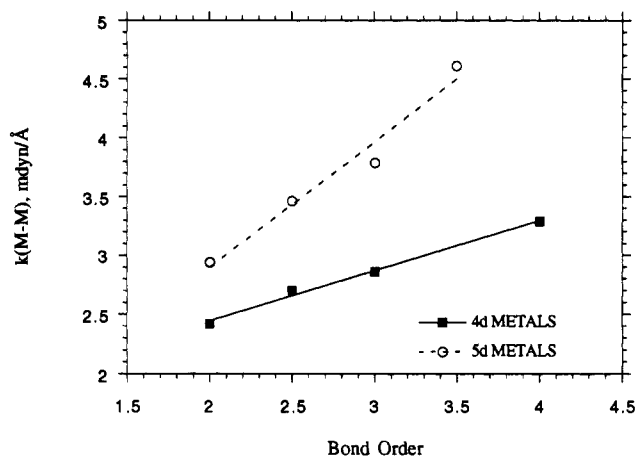
	<i>E</i> (dimer <sup>+</sup> /dimer <sup>0</sup> ), V
[Ru(OETAP)] <sub>2</sub>	-0.30
[Ru(OEP)] <sub>2</sub>	-0.73
[Os(OETAP)] <sub>2</sub>	-0.54
[Os(OEP)] <sub>2</sub>	-1.15
[(OETAP)RuRu(OEP)] <sup>+</sup>	-0.50
[(OETAP)RuOs(OEP)] <sup>+</sup>	-0.73

<sup>a</sup> All potentials were taken from cyclic voltammograms and are given versus the ferrocenium/ferrocene couple. Experiments were performed on 3–5 mM dimer in 0.2 M TBAPF<sub>6</sub> in THF.

It is particularly informative to compare the potentials for the interconversion between the monocation and the neutral species, because these potentials are relevant to the redox titrations and reflect the number of electrons in the metal–metal bond (Table IV). For instance, the potential of [(OEP)OsRu(OETAP)]<sup>+0</sup> (–0.73 V) is the average of the potentials of its constituent homodimers ([Os(OEP)]<sub>2</sub><sup>+0</sup>, –1.15 V, and [Ru(OETAP)]<sub>2</sub><sup>+0</sup>, –0.30 V).<sup>24</sup> This is unsurprising: Ru and Os have the same Pauling electronegativities and should participate in a primarily covalent bond. We are interested in examining the redox properties of intertriad heterometallic dimers: due to electronegativity differences, the bonds in these compounds should also have some ionic character, which should cause them to differ from the covalent homometallic bonds.

**Magnetic Properties.** We have studied the magnetic properties of group 8 dimers: these are the only neutral homometallic dimers which have unpaired electrons. The molecular orbital diagram predicts that [Ru(OEP)]<sub>2</sub> and [Os(OEP)]<sub>2</sub> ( $\sigma^2\pi^4\delta nb^4\pi^*2$ ) should both be ground-state triplets. The solution magnetic moments obtained for [Ru(OEP)]<sub>2</sub> ( $2.3 \pm 0.2 \mu_B$ ) and [Os(OEP)]<sub>2</sub> ( $1.2 \pm 0.3 \mu_B$ )<sup>27</sup> are lower than the free spin value ( $2.83 \mu_B$  for  $S = 1$ ).<sup>36</sup> In addition, the solid-state

(36)  $\mu_s$  (in  $\mu_B$ ) =  $g(S)(S + 1)^{1/2}$ , where  $g = 2.0023$ .


**Figure 6.** Plot of  $k(M-M)$  versus bond order.

magnetic moment of [Ru(OEP)]<sub>2</sub><sup>27</sup> decreases with decreasing temperature and approaches 0  $\mu_B$  at liquid helium temperatures. This effect can be attributed to zero-field splitting.<sup>27</sup> More detailed experiments (in collaborations with J. C. Marchon and P. Maldivi) are currently in progress.

**Vibrational Spectra.** The M–M vibrational frequencies for many of the homometallic dimers have been obtained from resonance Raman studies (in collaboration with Tait, Sattleberger, and Woodruff<sup>37,38</sup>). These measurements comprise the most extensive set of vibrational frequencies and force constants for M–M multiple bonds within any structurally congruent series of molecules. The M–M force constants<sup>39</sup> can be derived from the frequencies, and the force constants then can be compared with the formal bond orders. A plot of  $k(M-M)$  versus bond order (Figure 6) illustrates two points: force constants increase linearly with increasing bond order, and bonds between 5d (third row) metals are stronger than those between 4d (second row) metals. For instance, oxidizing [Ru(OEP)]<sub>2</sub> to the monocation and the dication increases the bond order (2 to 2.5 to 3) and the force constants (2.42 to 2.70 to 2.86 mdyin/Å). In addition, the force constant of [Os(OEP)]<sub>2</sub> (5d) (2.94 mdyin/Å) is substantially larger than that for [Ru(OEP)]<sub>2</sub> (4d) (2.42 mdyin/Å), even though the two dimers have the same bond order and charge. The latter property reflects the greater radial extension and better orbital overlap of the 5d element.

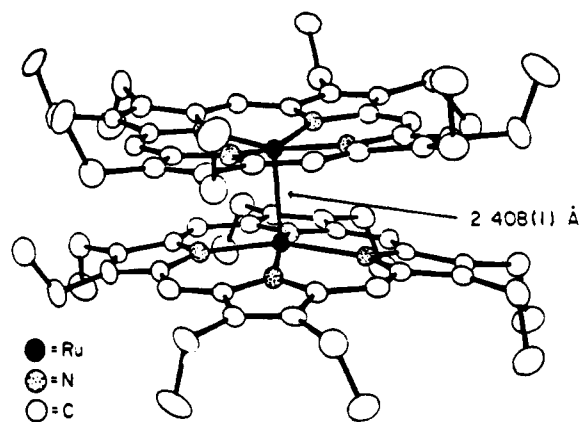
We also compared the infrared and resonance Raman spectra of the dimers to those of Ni(OEP), a square planar monomer.<sup>37</sup> The absence of any additional porphyrin modes or overtones in the dimers suggests that the two porphyrins of a given dimer do not participate in  $\pi$ – $\pi$  interactions, and that the main interaction within a dimer is the metal–metal bond.

**Structural Studies.** Good single crystals have been difficult to obtain; as a result, very few X-ray diffraction studies have been performed on these M–M bonded porphyrin dimers. The structure of [Ru(OEP)]<sub>2</sub> ( $\sigma^2\pi^4\delta nb^4\pi^*2$ )<sup>18</sup> (Figure 7) is an exception. Of particular interest is the short Ru–Ru distance of 2.408 Å (compared to 2.65 Å in elemental Ru), which is

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Figure 7. Crystal structure of [Ru(OEP)]<sub>2</sub>.

consistent with the formulation of a Ru-Ru double bond. In addition, each Ru is 0.3 Å out of the mean porphyrin plane; the two porphyrin planes are separated by 3.26 Å. The relatively large porphyrin-porphyrin distance accounts for the fact that no  $\pi$ - $\pi$  interactions are observed within the dimer (*vide supra*). Due to steric constraints, the two porphyrin planes are expected to be staggered 45° relative to each other. In fact, the dihedral angle along the Ru-Ru axis is 23.8° from the eclipsed conformation; this distortion is attributed to the effect of crystal packing. Except for Goedken's X-ray structure of [Mo(TTP)]<sub>2</sub><sup>40</sup> ( $d(\text{Mo-Mo}) = 2.239$  (1) Å, versus 2.7251 Å in elemental Mo), other M-M bond distances have so far been obtained only from EXAFS spectra and derived from vibrational spectra.<sup>37,38,41</sup> We are currently attempting to crystallize other dimers.

**Rotational Barriers.** The molecular orbital diagram can be used to predict whether or not a given dimer will have a  $\delta$  bond. Unlike the  $\sigma$  and  $\pi$  bonds, this  $\delta$  bond does not have cylindrical symmetry; instead, the  $\delta$  bond strength maximizes when the compound assumes an eclipsed conformation. Thus, dimers with  $\delta$  bonds (e.g., Mo and W homodimers) will exhibit rotational barriers and will assume eclipsed conformations, while dimers without  $\delta$  bonds should exhibit very minimal rotational barriers and should assume a staggered conformation to minimize steric strain.<sup>11,42,43</sup>

Prior to our work, no direct measure of  $\delta$  bond strengths had been obtained. Instead, workers typically estimated the energies of  $\delta$  bonds using the  $\delta \rightarrow \delta^*$  transition energies.<sup>44</sup> Given our set of soluble M-M-bonded dimers, we decided to measure the electronic barrier to rotations about quadruple bonds.<sup>45,46</sup> This was accomplished using variable-temperature <sup>1</sup>H NMR spectroscopy. By placing a substituent which exhibits long-range through-space magnetic deshielding (e.g., CHO, NCO, and aryl groups) at a single meso position, the signals corresponding to the meso-H atoms on the

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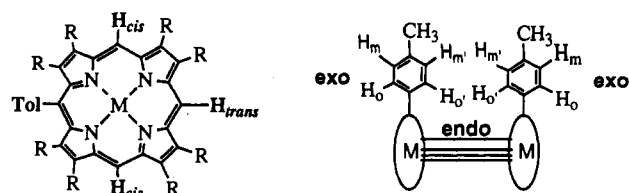
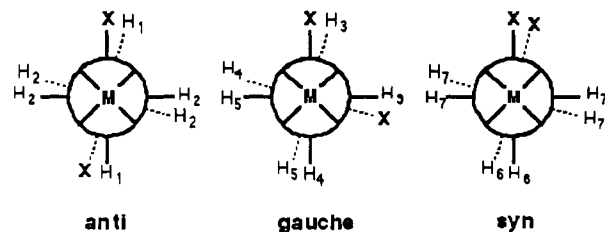
Figure 8. Rotational barrier study: *p*-tolylporphyrin.Figure 9. Rotational barrier study: possible eclipsed conformations of *p*-tolylporphyrin.

Table V. Rotational Activation Energies for Molybdenum and Tungsten Dimers [(OEP-X)MM(OEP-X')]

metal	X	X'	$\Delta G^*_{\text{rot}}$ (kcal/mol)
W	<i>p</i> -tolyl	<i>p</i> -tolyl	12.9 ± 0.1
Mo	<i>p</i> -tolyl	<i>p</i> -tolyl	10.8 ± 0.5
Mo	CHO	CHO	10.7 ● 0.5
Mo	NCO	NCO	9.8 ± 0.5
Mo	CHO	H	9.8 ● 0.5

opposite ring can be split into different sets, provided that the rotation rate about the metal-metal bond is slow on the NMR time scale. This condition can be met by lowering the temperature, and analysis of the appropriate variable-temperature <sup>1</sup>H NMR spectra yields an activation energy for rotation about the M-M bond. This technique had not previously been applied to M-M multiple bonds.

In the metalloporphyrin complexes which we have studied by this method (Figure 8), a functional group (e.g., *p*-tolyl) provides through-space magnetic shielding at a single meso position on each porphyrin ring. At low temperatures the Mo and W dimers are not in free rotation, and the ground-state conformation can be assigned on the basis of the symmetry exhibited in the <sup>1</sup>H NMR spectrum. This analysis suggests an eclipsed, ground-state conformation for the Mo and W dimers. For the W dimer, two conformers, *anti* and *gauche*, are observed; in this example the *syn* conformer is destabilized. (See Figure 9.) Activation energies measured by this technique for several Mo and W porphyrin dimers are displayed in Table V. Note that all of the substituted Mo dimers exhibit the same rotational energy barrier ( $\approx 10$  kcal/mol).<sup>45</sup> In addition, comparison of the barriers of the two *p*-tolyl substituted dimers reveals that the barrier for the 5d W dimer (12.9 ± 0.1 kcal/mol) is about 20% greater than that for the 4d Mo dimer (10.8 ± 0.5 kcal/mol). This result is consistent with data obtained for other inorganic compounds. Due to the greater orbital extension in the 5d metal, the W atoms will have greater overlap than the Mo atoms, which should result in a W-W bond which is stronger. Although the rotational activation barriers include steric contributions, the barriers can be used as a lower limit for the M-M  $\delta$  bond strength. The values obtained for

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the rotational barriers in these dimers are consistent with the spectroscopic studies performed on other quadruply bonded compounds; these studies place an upper limit of 20 kcal/mol on the  $\delta$  bond strength.<sup>47</sup>

The related Ru and Re dimers (having double and triple bonds, respectively) should *not* contain a  $\delta$  bond; thus these dimers should not exhibit a barrier to rotation. In fact, variable-temperature <sup>1</sup>H NMR analysis (400 MHz) of the Ru and Re dimers is consistent with rapid rotation of these M-M bonds, even at -64 °C. These measurements place an upper limit of 7.6 kcal/mol on any rotational barriers for these dimers.<sup>48</sup>

### Conclusion

We have developed a general synthetic method for obtaining a series of isostructural homometallic and heterometallic porphyrin dimers. We are currently investigating unprecedented *mixed triad*<sup>25</sup> heterometallic dimers. The experimental properties of the homometallic dimers correlate with predictions made on the basis of a simple molecular orbital diagram. Although intratriad heterodimers are similar to the corresponding homodimers, mixed triad heterometallic dimers should differ fundamentally from both their constituent homodimers and their isoelectronic ho-

modimers. Through systematic comparison of properties of heterometallic dimers with those of homometallic dimers, we should gain an understanding of the orbital ordering for particular heterometallic dimers. These studies provide fundamental insight into the nature of bonding between metal atoms.

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