J. Am. Chem. Soc. **1994,** *116,* 9761-9762

Heterometallic Mixed Triad Multiple Bonds in Metal-Porphyrin Dimers

James P. Collman,* Hilary J. Arnold, Kira J. Weissman, and Jonathan M. Burton

Department of Chemistry, Stanford University
Stanford, California 94305-5080

Received June 27, 1994

Although a large number of compounds have been reported which contain single bonds between two different metal atoms,[1] compounds that contain *heterometallic multiple bonds* are extremely rare. Furthermore, the few definitive examples of heterometallic multiple bonds have contained two metals from the same triad, or contain bridging ligands, or are of such low symmetry that it is difficult to assess the bond order between the metal atoms.[2-4] We recently reported a simple and general scheme for the synthesis and isolation of heterometallic metal-metal bonded porphyrin dimers.[5] Here, we report the application of this procedure to the preparation of two unprecedented *mixed triad* heterometallic multiply bonded dimers, [(OEP)MoOs(OEP)] and [(OEP)MoRu(TOEP)].[6]

Metalloporphyrins are ideal complexes for systematically studying multiple bonds between metal atoms. Porphyrins will bind a wide variety of transition metals in the +2 oxidation state, and several of these metalloporphyrin derivatives (Mo, W, Re, Ru, Os) will form metal-metal multiply bonded dimers.[7] As these dimers contain no axial or bridging ligands, they have high symmetry and can be described using a simple molecular orbital diagram. This bonding model assumes that the metal-metal bond results from overlap of valence d orbitals and has proved to be remarkably useful for accurately predicting not only the properties of homodimers but also those of group 8 heteroporphyrin and heterometallic dimers.[5,7]

The [(OEP)MoOs(OEP)] and [(OEP)MoRu(TOEP)] heterodimers (both d^{10}) are of particular interest because their properties can be compared not only to those of their constituent homodimers, $[Mo(OEP)]_2$ (d^8)[8] and $[Os(OEP)]_2$ (d^{12})[8] or $[Ru(TOEP)]_2$ (d^{12}),[9] but also to those of the *isoelectronic* homometallic dimer, $[Re(OEP)]_2$ (d^{10}, $\sigma^2\pi^4\delta^{nb4}\pi^{*0}\sigma^{*0}$).[10] Because the bond order and spin state of metalloporphyrin dimers depend on the number of valence d electrons, the two heterodimers will have electronic and magnetic properties different from those of their constituent homodimers. In addition, because Mo has a different electronegativity (1.8) than either Os (2.2) or Ru (2.2),[11] we expect that the MoOs and MoRu bonds will have some ionic character and will differ fundamentally from the nonpolar ReRe bond in $[Re(OEP)]_2$.

The heterometallic dimer [(OEP)MoOs(OEP)] is synthesized[12] by co-pyrolysis of molybdenum and osmium monomers, Mo(OEP)(PhC≡CPh)[8,13] and $Os(OEP)(py)_2$.[8,14,15] [(OEP)MoOs(OEP)] is then isolated from the constituent homometallic dimers, $[Mo(OEP)]_2$ and $[Os(OEP)]_2$, using a redox titration (Figure 1). The heterometallic dimer is more readily oxidized than either of the constituent homodimers; thus, addition of $Cp_2Fe^+PF_6^-$ to the mixture of dimers yields $[(OEP)MoOs(OEP)]^+PF_6$, which is separated from the neutral homodimers by filtration. The isolated mixed dimer monocation is then reduced using $Cp_2Co(II)$ to yield the neutral heterometallic dimer, [(OEP)MoOs(OEP)].[16]

Unlike $[Re(OEP)]_2$, which manifests a diamagnetic ^1H NMR spectrum,[10] [(OEP)MoOs(OEP)] exhibits protons resonances which are paramagnetically shifted at room temperature. Whereas the meso proton signal of $[Re(OEP)]_2$ occurs at 6.45 ppm, those of [(OEP)MoOs(OEP)] occur at -50.93 and -67.92 ppm at room temperature; the methylene proton signals of $[Re(OEP)]_2$ occur at 3.97 and 3.70 ppm, and the corresponding resonances of [(OEP)MoOs(OEP)] occur at 20.36, 16.72, 10.31, and 9.20 ppm at room temperature. The NMR spectrum also differs greatly from those of $[Mo(OEP)]_2$,[8,17] which is diamagnetic, and $[Os(OEP)]_2$,[8,18] which exhibits much smaller paramagnetic shifts.

The paramagnetic shifts of [(OEP)MoOs(OEP)] obey the Curie law: they vary linearly with inverse temperature. This temperature dependence would be explained if the ground electronic state of [(OEP)MoOs(OEP)] were paramagnetic ($S = 1$). In Figure 2, a plausible molecular orbital diagram explains how a paramagnetic ground state could arise. Due to the different electronegativities of Mo and Os, the energies of d orbitals in the MoL_4 and in the OsL_4 fragments should not be degenerate. When the metal-metal bond forms, the d_{xy} orbitals may either overlap to form δ and δ^* orbitals or remain localized on the different metals (δ^{nb}). In either case, if the vacant, higher lying orbital (δ^* or δ^{nb}) lies above the degenerate π^* orbitals, then the ground electronic state will be paramagnetic ($\sigma^2\pi^4\delta^{(nb)2}\pi^{*2}\delta^{(*/nb)0}\sigma^{*0}$). The sign and magnitude of the paramagnetic shifts are consistent with unpaired electron density in the d π^* orbitals of the metal-metal bond.[19] If the lowest lying δ orbital is bonding, then the triply bonded [(OEP)MoOs(OEP)] should assume an eclipsed geometry and should exhibit a rotational barrier about the axis of the metal-metal bond. If the δ orbitals are localized on the different metals (δ^{nb}), then [(OEP)MoOs(OEP)] would have a bond order of 2 and should assume a staggered geometry; the dimer would not exhibit a rotational barrier.

In order to differentiate between these bonding possibilities, the heterometallic dimer [(OEP)MoRu(TOEP)] was synthesized and isolated in a manner similar to that described for [(OEP)-

---

[1] Bruce, M. I. *J. Organomet. Chem.* **1985**, *283*, 339-414.

[2] Katovic, V.; Templeton, J. L.; Hoxmeier, R. J.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 5300-5302.

[3] Morris, R. H. *Polyhedron* **1987**, *6*, 793-801.

[4] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993.

[5] Collman, J. P.; Arnold, H. J.; Fitzgerald, J. P.; Weissman, K. J. *J. Am. Chem. Soc.* **1993**, *115*, 9309-9310.

[6] We use the following abbreviations for porphyrins: OEP, octaethylporphyrin; TOEP, 5-(4-methylphenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin; AHEDMP, 5-(4-methoxyphenyl)-2,3,7,8,13,17-hexaethyl-12,18-dimethylporphyrin.

[7] Collman, J. P.; Arnold, H. J. *Acc. Chem. Res.* **1993**, *26*, 586-592.

[8] Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684-7688.

[9] Collman, J. P.; Garner, J. M.; Hembre, R. T.; Ha, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1292-1301.

[10] Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141-8148.

[11] Pauling, L. *The Chemical Bond*; Cornell University Press: Ithaca, NY, 1967.

[12] See supplementary material for experimental procedures.

[13] De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850-1851.

[14] Che, C.-M.; Poon, C.-K.; Chung, W.-C.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 1277-1278.

[15] Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015-3024.

[16] In a nitrogen atmosphere drybox, the following mixture of dimers was dissolved in benzene (7 mL): $[Mo(OEP)]_2$ (18%, 4.6 μmol), [(OEP)MoOs(OEP)] (74%, 18.6 μmol), and $[Os(OEP)]_2$ (5%, 1.3 μmol) (percentages determined from the integration of the ^1H NMR spectrum; total mass 33.1 mg). Oxidation: to this mixture was added $Cp_2Fe^+PF_6^-$ (5.4 mg, 16 μmol, 0.88 equiv relative to [(OEP)MoOs(OEP)]). This was stirred overnight and then filtered through Celite. The precipitate was rinsed with benzene and then eluted from the Celite using methylene chloride. The solution was concentrated under vacuum. Reduction: to the residue was added an excess of $Cp_2Co(II)$ in benzene (5 mL), and the mixture was stirred overnight. The solution was concentrated with heating under vacuum to yield [(OEP)MoOs(OEP)]. No homodimers were visible in the ^1H NMR or the mass spectrum. ^1H NMR (ppm, C_6D_6): $-CH_2CH_3$ 20.36 (br, 8H), 16.72 (br, 8H), 10.31 (br, 8H), 9.20 (br, 8H); $-CH_2CH_3$ 0.87 (br, 24H), 0.20 (br, 24H); H_{meso} -50.93 (br, 4H), -67.92 (br, 4H). Mass spectrum ($Mo^{98}Os^{192}$): parent ion calcd, 1354.6; found, $m/e = 1353$ (M^+, cluster).

[17] $[Mo(OEP)]_2$ ^1H NMR in C_6D_6: H_{meso} 9.20 (s, 4H); CH_2CH_3 4.32 (m, 8H), 3.92 (m, 8H); CH_2CH_3 1.78 (t, 24H) ppm.

[18] $[Os(OEP)]_2$ ^1H NMR in C_6D_6: H_{meso} -1.08 (s, 4H); CH_2CH_3 11.56 (m, 8H), 7.83 (m, 8H); CH_2CH_3 1.97 (t, 24H).

[19] La Mar, G. N.; Walker (Jensen), F. A. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61-157.

0002-7863/94/1516-9761$04.50/0

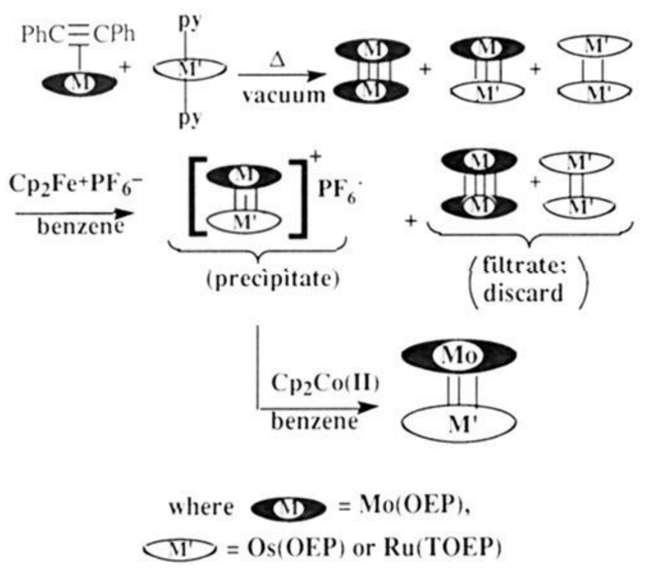

Figure 1. Synthesis and isolation of MoOs and MoRu mixed triad heterometallic dimers.

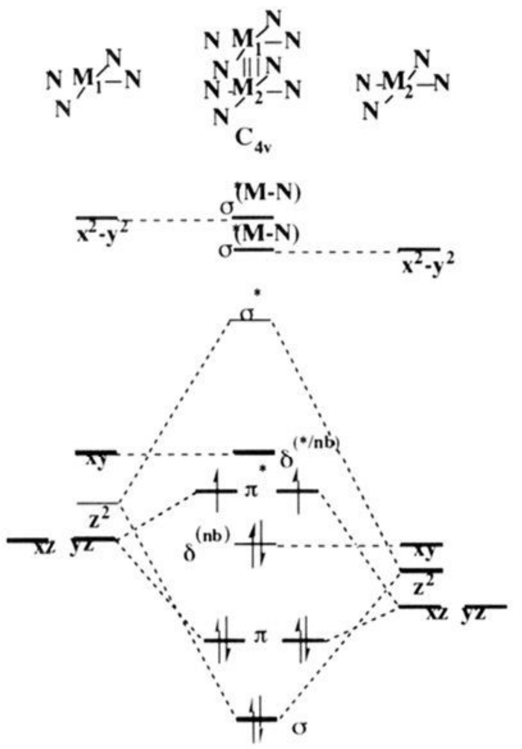

Figure 2. Molecular orbital diagram proposed for mixed triad heterometallic dimers [(OEP)MoOs(OEP)] and [(OEP)MoRu(TOEP)], both d^{10}.

MoOs(OEP)].[12] The MoRu dimer contains a porphyrin, TOEP, which has a tolyl substituent in one of its meso positions. The tolyl substituent exhibits long-range magnetic anisotropy that allows the barrier to rotation about the axis of the metal–metal bond to be measured with use of variable temperature NMR. Similar studies have been performed on homometallic dimers and have revealed that, whereas $[Mo(TOEP)]_2$ and $[W(TOEP)]_2$ do contain δ bonds ($\Delta G_{rot}^{\ddagger} = 10.8 \pm 0.1$ and 12.9 ± 0.1 kcal/mol, respectively), $[Ru(TOEP)]_2$ and $[Re(AHEDMP)]_2$[6] dimers do not exhibit rotational barriers and presumably do not contain δ bonds.[9,20]

[(OEP)MoRu(TOEP)] exhibits large paramagnetic shifts in the ^1H NMR at room temperature.[21] Although these shifts increase and the resonances broaden as the temperature is decreased, only one conformer is observed throughout the entire temperature range (+20 °C to −80 °C). Thus the barrier to rotation about the axis of the metal–metal bond in [(OEP)MoRu(TOEP)] must be too small (≤8 kcal/mol) to be measured by variable temperature NMR.[9] This suggests that a δ bond in a triple bond is weaker than a δ bond in a quadruple bond and/or that the d_{xy} orbitals in the heterometallic dimers are at least partially nonbonding in character.

The mixed triad dimers [(OEP)MoOs(OEP)] and [(OEP)MoRu(TOEP)] are the first definitive examples of compounds containing multiple bonds between metals from different triads. These preliminary results indicate that the mixed triad heterometallic dimers have properties which are different not only from their constituent homodimers but also from the isoelectronic homometallic dimer, $[Re(OEP)]_2$. A complete report of the syntheses and properties of these and other mixed triad multiply bonded dimers is forthcoming. These studies continue to provide unique insights into the differences between heteroatomic and homoatomic multiple bonds between metal atoms.

Acknowledgment. We thank the National Science Foundation for providing funding for the experimental work (Grant CHE9123187) and NMR instruments used in this study (National Science Foundation Grants CHE8109064 and CHE8414329). In addition, we thank the National Science Foundation for supporting H. J. Arnold and J. M. Burton in the form of predoctoral research fellowships. Special thanks to Doris Huang at the Analytical Services Division in the Chemistry Department at Northwestern University for performing the mass spectrometry on the mixed triad dimer and to Pharmacyclics for their generous gift of diethylpyrrole used in the synthesis of H_2OEP and H_2-TOEP.

Supplementary Material Available: Experimental details (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[20] Collman, J. P.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2592–2596.

[21] [(OEP)MoRu(TOEP)] ^1H NMR (ppm, $C_6D_5CD_3$): $-CH_2CH_3$ 10.50 (br, 8H), 8.84 (br, 8H), 6.71 (m, 2H), 6.48 (m, 2H), 6.13 (m, 2H), 5.68 (m, 2H), 4.59 (m, 2H), 4.17 (m, 2H), 3.89 (m, 2H), 2.44 (m, 2H); $-CH_2CH_3$ 1.76 (t, 6H), 1.57 (t, 6H), 1.55 (t, 6H), 1.16 (t, 6H), 0.76 (br, 24H); H_{meso} −12.60 (s, 1H), −26.31 (s, 4H); tolyl-*H* 7.64 (d, 1H), 7.05 (d, 1H), 6.53 (d, 1H), 5.85 (d, 1H); tolyl-CH_3 2.30 (s, 3H). No homodimers were observed in the ^1H NMR.