coated by PNBE, the oxidation of the neat surface is immediate as evidenced by the very fast formation of metallic Cu. In contrast, the coated surface remains unchanged at least for 12 h (Figure 5).

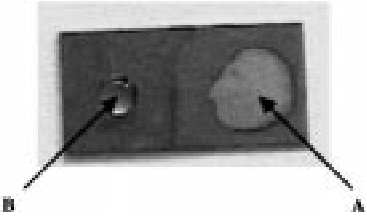

Figure 5. Steel plate after application of two drops of a $CuSO_4$ solution: A) neat steel: copper from the reaction with $CuSO_4$; B) PNBE grafted steel: the drop of $CuSO_4$ solution does not react.

Modification of carbon fibers by well-adhering polymer chains that contain reactive double bonds is also of importance in the field of composite materials. Finally the general concept illustrated in this paper can be extended to the ROMP of functionalized NBE, so paving the way to functionalized surfaces with tunable properties.

Experimental Section

NBE-A was prepared by reaction of 5-norbornene-2-methanol (41 mmol) with excess acryloyl chloride (123 mmol) in the presence of triethylamine (123 mmol), and dried before use.

Monomers, solvents, and conducting-salt were dried before use. Electrochemical experiments were carried out in a one-compartment cell with a platinum pseudoreference counter-electrodes with a PAR EG&G potentiostat (Model 273A). All the experiments were carried out in a glovebox under a dried inert atmosphere.

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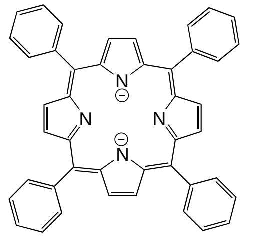
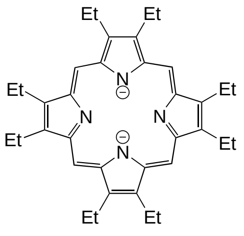
The First Quadruple Bond Between Elements of Different Groups**

James P. Collman,* Roman Boulatov, and Geoffrey B. Jameson

Whereas many homonuclear quadruply bonded compounds are known,[1] heteronuclear analogs remain rare. Discovery of the first bridged heteronuclear quadruple bond in 1974[2] was followed by the synthetically more challenging preparation of the unbridged $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ unit in 1984.[3] Yet to date, fewer than twenty such heterometallic systems have been characterized, all containing either the $\mathrm{Cr}\overset{4}{-}\mathrm{Mo}$ or the $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ core. We report here the preparation of the first compound with a quadruple bond between elements from different triads: the heterometallic "dimer" $[(\mathrm{tpp})\mathrm{Mo}\overset{4}{-}\mathrm{Re}(\mathrm{oep})]\mathrm{PF}_6$ (**1**) (TPP = *meso*-tetraphenylporphyrin dianion, OEP = octaethylporphyrin dianion).


TPP



OEP

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

The formation of a quadruple bond requires at least four valence orbitals and exactly eight valence electrons (Figure 1) to occupy all of the bonding and none of the antibonding orbitals of the [M$\overset{4}{-}$M′]$^{x+}$ core. The unique preference of unbridged L$_4$M$\overset{4}{-}$M′L′$_4$ complexes for an eclipsed conformation, in which nonbonding repulsions are strongest, is the direct result of the drive to maximize the d$_{xy}$ – d$_{xy}$ overlap. The effect of the polarity of the quadruple bond on its properties remains one of the unsettled issues of chemical bonding. Bridged Mo$\overset{4}{-}$W bonds are often shorter, or have higher force constants, than their homonuclear counterparts,[4] while the properties of the unbridged Mo$\overset{4}{-}$W bonds are approximately the average of those of their homonuclear congeners.[5] Quadruply bonded metalloporphyrin dimers are excellent systems to study this issue. Porphyrins (por) such as TPP and OEP combine the high binding affinity of a chelating ligand with almost no bridging capacity. They provide a symmetrical, relatively rigid, square-planar coordination environment. Their steric bulk can be modified by peripheral substitution, while preserving the general structural motif of the core.[6] Moreover, our synthetic strategy for metalloporphyrin dimers is applicable to many transition metals, permitting systematic studies of M$\overset{4}{-}$M′ entities. In contrast, a lack of general preparative methods has limited the variety of accessible quadruple bonds in non-porphyrin environments.

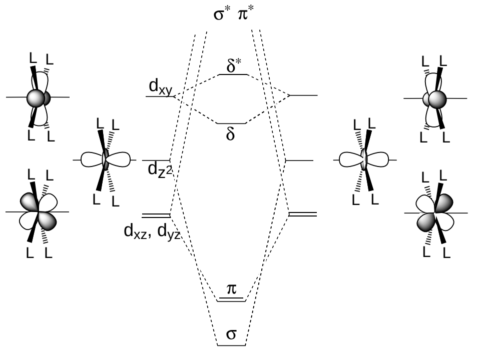
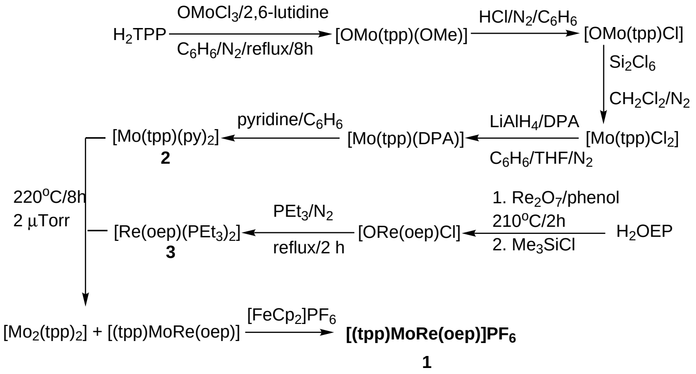


Figure 1. Qualitative MO diagram of metal – metal bonding between two square-planar ML$_4$ units.

The OEP – TPP combination in **1** was chosen on the basis of its complementary substitution pattern, which eliminates unfavorable steric interactions between the peripheral groups in both the eclipsed and staggered conformations of the dimer, thereby minimizing steric perturbation of the metal – metal bond. In addition, a heteroleptic dimer should be free of the solid-state disorder common for heterodimetallic systems, wherein the two crystallographic sites for metal ions are randomly occupied.

The synthesis of **1** starts with metalation of the corresponding porphyrins (Scheme 1). Although such reactions are usually carried out at high temperatures and proceed in only moderate yields,[7] we were able to achieve high-yielding Mo insertion under mild conditions.[8] This finding makes accessible Mo complexes of highly functionalized, temperature-sensitive porphyrins. The heterodimer is obtained by high-vacuum solid-state pyrolysis of mixtures of the monometallic precursors **2** and **3**. Loss of thermally labile axial ligands generates four-coordinate (tpp)Mo and (oep)Re fragments, which randomly dimerize to a mixture of hetero- and homodimers. Precursors of comparable thermal stability should produce such fragments in nearly equimolar amounts during the pyrolysis, thus maximizing the yield of the heterodimer. This criterion dictates the combination of axial ligands used to maintain the mononuclearity of **2** and **3**. Isolation and purification of **1** is achieved with cycles of selective oxidation and reduction.[9]



Scheme 1. Synthesis of [(tpp)MoRe(oep)]PF$_6$ (**1**). DPA = diphenylacetylene. See the Experimental Section and Supporting Information for experimental details.

In the solid state, **1** adopts the fully eclipsed conformation, unequivocally proving the presence of the quadruply bonded Mo$\overset{4}{-}$Re moiety (Figure 2). In contrast, bis-porphyrin "sandwich" compounds, (por)$_2$M, wherein the relative orientation of the macrocycles is determined by purely steric interactions, invariably adopt a staggered geometry.[10] Among all [d – d]$^{8-9}$ metalloporphyrin dimers studied to date, various degrees of deviation from an eclipsed conformation have been observed, which in some cases leads to annihilation of the δ bond (Table 1).[11–13] For example, as a result of severe steric repulsions between the phenyl substituents, the d^4 – d^4 [Mo$_2$(tpp)$_2$] dimer adopts an N-Mo-Mo-N dihedral angle of

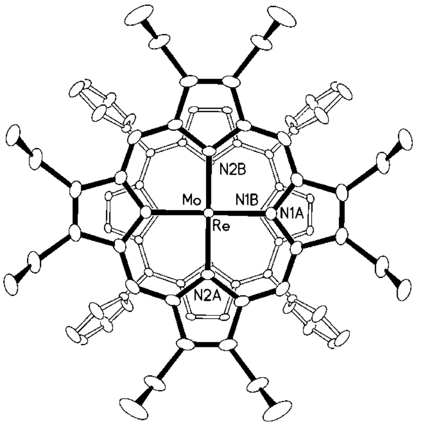


Figure 2. ORTEP view of the cation in **1** along the Re – Mo vector (thermal ellipsoids for 20 % probability). The perspective is exaggerated to better show the perfectly eclipsed alignment of the porphyrin ligands. Hydrogen atoms are omitted.

Table 1. Electronic configurations (e.c.) of the frontier orbitals, metal–metal bond orders (b.o.) and metric parameters (in [°] or [Å]) of selected d^{8-9} metalloporphyrin dimers.

Dimer	e.c.	b.o.	N-Mo-M-N	Mo-M	N_4-N_4'[a]	Mo-N_4[b]	M-N_4'[b]
[(tpp)MoRe(oep)]$^+$	**$\sigma^2\pi^4\delta^2$**	**4**	**0**	**2.236**	**3.120**	**0.492**	**0.392**
[(tpp)$_2$Mo$_2$][11]	$\sigma^2\pi^4\delta^2$	4	18	2.239	3.208	0.458	
[(oep)MoRu(tpp)]$^+$[12]	$\sigma^2\pi^4\delta^2(\pi^*)^1$	3.5	4.5	2.211	3.11	0.562	0.334
	$\sigma^2\pi^4(d_{xy})^2(\pi^*)^1$[c]	2.5	43	2.181	3.05	0.578	0.295
[(oep)MoOs(tpp)]$^+$[13][d]	$\sigma^2\pi^4(d_{xy})^2(\pi^*)^1$[c]	2.5	42	2.24	3.14	0.58	0.31

[a] Distance between the least-squares planes of the chelating nitrogen atoms. [b] Displacement of the metal ion from the least-squares plane of the chelating nitrogen atoms. [c] Although the HOMO of the *neutral* dimers was unequivocally determined to be π^*, there is at present no experimental evidence that would favor either a $\sigma^2\pi^4(d_{xy})^2(\pi^*)^1$ (b.o. = 2.5) or a $\sigma^2\pi^4(d_{xy})^2(d'_{xy})^1$ (b.o. = 3) description of the metal–metal bonding in the corresponding *cations*. However, irrespective of the precise description of the Mo–M bonding (M = Ru, Os), the important point in the context of the present discussion is that the d^9 configuration of [(oep)MoM(tpp)]$^+$ does not necessarily yield a δ bond. [d] The bonding in the [MoOs]$^{5+}$ core was originally described as $\sigma^2\pi^4\delta^2(\pi^*)^1$ giving an overall bond order of 3.5; however, at the observed N-Mo-Os-N′ dihedral angle of 42° no more than 10% of the maximum δ–δ overlap remains (ref. [1], p. 20). Therefore, [(oep)MoOs(tpp)]$^+$ should more precisely be consider as having a metal–metal bond order of 2.5 with a pair of nearly nonbonding d_{xy} atomic orbitals.

18°. In contrast, the complementary substitution pattern of the OEP–TPP pair and the d^8 electronic configuration of the [Mo$\overset{4}{-}$Re]$^{5+}$ core engender to **1** a perfectly eclipsed conformation. Common for all metalloporphyrin dimers, the resulting steric crowding is partially relieved by distortions of the macrocycles (see Table 1). Both metal ions in **1** are significantly displaced from the mean plane of the coordinating nitrogen atoms, while the porphyrin cores experience substantial "doming" distortions (Figure 3). Consequently, the closest OEP–TPP contact occurs between the corresponding nitrogen atoms, $N_{OEP}\cdots N_{TPP}$ (3.11(1) Å).

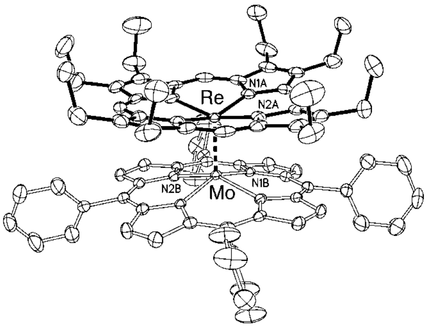


Figure 3. Side view of the cation in **1** showing the doming of the porphyrin ligands (thermal ellipsoids for 40% probability). Hydrogen atoms are omitted.

As a result of the high bond order, the Mo–Re distance in **1** is by far the shortest ever reported for a Mo–Re unit (Table 2). It falls within the range of Re$\overset{4}{-}$Re bond lengths but is slightly longer than the bonds in the Mo$\overset{4}{-}$Mo cores. Notably, metalloporphyrin dimers possess comparable metal–metal separations, irrespective of the formal bond orders (see Table 1).

Table 2. Metal–metal distances in **1** and related dimers.

Moiety	M–M distance, range [Å]	
	Nonbridging ligands	Bridging ligands
[(tpp)Mo$\overset{4}{-}$Re(oep)]$^+$	**2.236**	
Mo$\overset{4}{-}$Mo[a]	2.110–2.175[b]	2.010–2.186
Re$\overset{4}{-}$Re[a]	2.188–2.296	2.178–2.260
Re$\cdots$Mo[c]	2.844–3.184	2.656–3.199

[a] Compiled from data in ref. [1]. [b] Excludes [Mo$_2$(tpp)$_2$]. [c] Compiled from Cambridge Structural Database.

The diamagnetic $\sigma^2\pi^4\delta^2$ ground-state configuration of **1** and its 1:1 TPP-to-OEP ratio are confirmed by solution ^{1}H NMR spectroscopy. The chemical shift differences ($\Delta\delta_{endo/exo}$) within the diastereotopic pairs of protons (Figure 4) in **1** point to a significant magnetic anisotropy. This phenomenon is observed whenever two porphyrin macrocycles, at least one of which containing phenyl groups, are positioned in parallel at a relatively close separation. In order to relieve the ensuing steric congestion, the phenyl groups tilt back, which places their *endo* protons into the deshielding region of the combined magnetic field of the porphyrin ring currents. The magnetic anisotropy experienced by the diastereotopic pairs of such protons is dependent on the interporphyrin separation, as this separation affects both the strength of the combined magnetic field and the degree to which the phenyl rings are "tilted back". Nonetheless, the $\Delta\delta_{endo/exo}$ values in **1** are larger than those observed for other bis-porphyrin systems with comparable interporphyrin separations, such as [Th(tpp)$_2$] (Table 3).[14, 15]

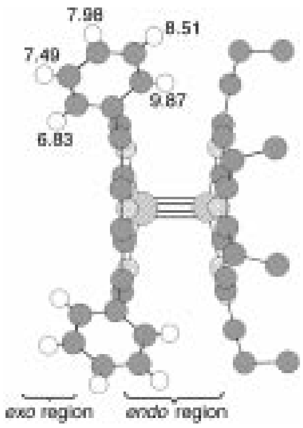


Figure 4. Chemical shifts (δ vs. TMS) of the *endo* and *exo* protons of the phenyl substituents in [(tpp)Mo$\overset{4}{-}$Re(oep)]$^+$. All other hydrogen atoms are omitted.

Table 3. Chemical shifts of the phenyl hydrogen atoms and the interporphyrin distances in selected bis-porphyrin complexes.

Compound	Ct–Ct[a]	*ortho-endo/exo* ($\Delta\delta_{endo/exo}$)[b]	*meta-endo/exo* ($\Delta\delta_{endo/exo}$)[b]
[(tpp)Mo$\overset{4}{-}$Re(oep)]$^+$	**3.514**	**9.87/6.83 (3.04)**	**8.51/7.49 (1.02)**
[Ce(tpp)(oep)][14]	3.38	9.68/6.40 (3.28)	8.25/7.25 (1.00)
[Th(tpp)$_2$][15]	3.47	9.33/6.56 (2.77)	8.00/7.23 (0.77)
[Mo$_2$(tpp)$_2$][11]	$\geq$ 3.7	9.28/6.90 (2.38)	7.92/7.38 (0.54)

[a] Distance between the least-squares planes of 24 atoms of the porphyrin core. [b] Chemical shifts (δ vs. TMS in CDCl$_3$) and the differences for the diastereotopic pairs of the *ortho* and *meta* protons of the phenyl groups.

The additional contribution may be attributable to the $\mathrm{Mo}\overset{4}{-}\mathrm{Re}$ bond, by analogy with the very large diamagnetic anisotropies of $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bonds.[16] However, whereas the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ unit has a *deshielding* effect on the *endo* groups (corresponding to a negative magnetic anisotropy), the $\mathrm{Mo}\overset{4}{-}\mathrm{Re}$ moiety in **1** apparently causes *shielding* of the *endo* protons. This may reflect different electronic properties of heteronuclear and homonuclear quadruple bonds.

Experimental Section[17]

All operations were performed under strictly anaerobic and anhydrous conditions. A mixture of [Mo(tpp)(py)$_2$] **2** (25 mg, 30 μmol) and [Re(oep)(PEt$_3$)$_2$] **3** (8 mg, 8.4 μmol) was lyophilized by rapid removal of the solvent (C_6H_6, 2.5 mL). The resulting amorphous solid was pyrolyzed at 220°C under vacuum (2 μTorr) for 8 h. The pyrolysis was repeated five times, the solids from these five batches were combined (ca. 150 mg),[18] dissolved in C_6H_6 (10 mL), and the solution was filtered through a celite plug on to [Cp$_2$Fe]PF$_6$ (20 μmol, obtained by evaporating 800 μL of a 25 mM stock solution in acetonitrile in the reaction vial) and the mixture was stirred overnight. The precipitate of [Re(oep)(PEt$_3$)$_2$]PF$_6$ (and some **1**) was filtered, and the filtrate was treated with another 20 μmol portion of [Cp$_2$Fe]PF$_6$ to yield after 12 h, crude **1** as a dark-brown solid (the C_6H_6 filtrate contained mostly [Mo$_2$(tpp)$_2$] and a small amount (<10%) of [OMo(tpp)] along with [Cp$_2$Fe] and some [(oep)ReMo(tpp)]). The precipitate was treated with [Cp$_2$Co] (18 μmol, 40 mM stock solution in C_3H_6) in C_6H_6 for 24 h. The remaining solids ([Cp$_2$Co]PF$_6$ and an unidentified Re(oep) species) were separated, and the filtrate (mostly [(tpp)MoRe(oep)]) was subjected to two cycles of oxidation with [Cp$_2$Fe]$^+$ followed by reduction with [Cp$_2$Co] exactly as described above. The main impurity isolated in these subsequent redox cycles was an unidentified Re(oep) species. Recrystallization of the precipitate of the final oxidation from CH_2Cl_2/toluene (1/3) yielded **1** (12 mg, 7.2 μmol, 17% yield based on [Re(oep)(PEt$_3$)$_2$]). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 10.10$ (s, 4H; *meso*-H, Re(oep)), 9.86 (d, ^3J(H,H) = 7 Hz, 4H; *ortho-endo*-H$_{\mathrm{Ph}}$, Mo(tpp)), 8.51 (t, ^3J(H,H) = 8 Hz, 4H; *meta-endo*-H$_{\mathrm{Ph}}$, Mo(tpp)), 8.47 (s, 8H; β-pyrrolic, Mo(tpp)), 7.97 (t, ^3J(H,H) = 8 Hz, 4H; *p*-H$_{\mathrm{Ph}}$, Mo(tpp)), 7.50 (m, 4H; *meta-exo*-H$_{\mathrm{Ph}}$, Mo(tpp)), 6.82 (d, ^3J(H,H) = 7.5 Hz, 4H; *ortho-exo*-H$_{\mathrm{Ph}}$, Mo(tpp)), 4.35 (m, 8H; CH$_2$, Re(oep)), 4.14 (m, 8H; CH$_2$, Re(oep)), 0.86 (t, ^3J(H,H) = 7.5 Hz, 24H; CH$_3$, Re(oep)).

Crystal data for $\mathbf{1}\cdot 3\,C_6H_5CH_3$ ($C_{101}H_{96}F_6MoN_8PRe$): $M_r = 1848.97$, orthorhombic, space group *Pmma*, $a = 26.350(5)$, $b = 15.516(3)$, $c = 9.802(2)$ Å; $V = 4007.6(14)$ Å^3, $Z = 2$ (imposing *mm*2 symmetry on **1**), $\rho_{\mathrm{calcd}} = 1.532$ g cm^{-3}, absorption coefficient 1.757 mm^{-1}, $F(000) = 1888$, reflections collected 18484, independent reflections 3642, GOF = 1.132, $R = 0.05457$, $wR_2 = 0.1344$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149919. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[18] The exact composition of this mixture could not be determined quantitatively due to paramagnetism of [(oep)ReMo(tpp)] and unreacted [Re(oep)(PEt$_3$)$_2$]. A small sample of the mixture was oxidized stepwise by adding small portions of [Cp$_2$Fe]PF$_6$ until mostly diamagnetic NMR spectra were observed. These indicated that the major species in the sample were [(oep)ReMo(tpp)], [Re(oep)(PEt$_3$)$_2$], and [Mo$_2$(tpp)$_2$] in ca. 1:(<1):(<3) ratio.

Synthesis of the Globo H Hexasaccharide Using the Programmable Reactivity-Based One-Pot Strategy**

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Dedicated to Professor Horst Kunz
on the occasion of his 60th birthday

Carbohydrate antigens are the most abundantly expressed antigens on the surface of most cancer cells.[1] Globo H (Scheme 1), a glycosyl ceramide, was isolated and identified as an antigen on prostate and breast cancer cells.[2] Its immunofunction has been characterized by Mènard et al.[3] and Kuryashow et al.[4] The use of this molecule as a vaccine for breast and prostate cancer has been studied by Danishefsky and co-workers.[5]

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