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Substitution chemistry of MM quadruply bonded complexes (M = Mo or W) supported by the anion of 2-hydroxy-6-methylpyridine†‡

Douglas J. Brown, Malcolm H. Chisholm* and Christopher W. Gribble

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The compounds $M_2(mhp)_4$, where M = Mo or W and mhp is the anion formed from deprotonation of 2-hydroxy-6-methylpyridine, are shown to react with carboxylic acids RCOOH to give an equilibrium mixture of products $M_2(O_2CR)_n(mhp)_{4-n}$ where R = 2-thienyl and phenyl. The equilibrium can be moved in favor of $M_2(O_2CR)_4$ by the addition of excess acid or by the favorable crystallization of these products. The latter provides a facile synthesis of the $W_2(O_2CR)_4$ compound where R = 9-anthracene. Reactions involving 2,4,6-triisopropyl benzoic acid, TiPBH, yield $M_2(TiPB)_2(mhp)_2$ compounds as thermodynamic products. Reactions involving Me_3OBF_4 (1 and 2 equiv.) yield the complexes $Mo_2(mhp)_3(CH_3CN)_2BF_4$ and $Mo_2(mhp)_2(CH_3CN)_4(BF_4)_2$, respectively. The latter compound has been structurally characterized and shown to have mirror symmetry with two *cis* mhp ligands: MoMo = 2.1242(5) Å, Mo–O = 2.035(2) Å, Mo–N(mhp) = 2.161(2) Å, and Mo–N(CH_3CN) = 2.160(3) and 2.170(3) Å. Reactions involving $Mo_2(mhp)_3(CH_3CN)_2^{2+}$ and $Mo_2(mhp)_2(CH_3CN)_4^{2+}$ with $^nBu_4NO_2CMe$ (1 and 2 equiv.) yield the complexes $Mo_2(mhp)_3(O_2CMe)$ and $Mo_2(mhp)_2(O_2CMe)_2$ which are shown to be kinetically labile to ligand scrambling. Reactions between $Mo_2(mhp)_3(CH_3CN)_2^+BF_4^-$ (2 equiv.) and $[^nBu_4N^+]_2[O_2C–X–CO_2]^{2-}$ yielded dimers of dimers $[Mo_2(mhp)_3]_2(\mu\text{-}O_2C–X–CO_2]$ where X = nothing, 2,5- or 3,4-thienyl and 1,4-C_6H_4. Reactions between $Mo_2(mhp)_2(CH_3CN)_4^{2+}(BF_4^-)_2$ and tetra-*n*-butylammonium oxalate and terephthalate yield compounds $[Mo(mhp)_2bridge]_n$ which by MALDI-TOF MS are proposed to be a mixture of molecular squares (*n* = 4) and triangles (*n* = 3) along with minor products of $[Mo_2(mhp)_3]_2$(bridge) and $Mo_2(mhp)_4$ that arise from ligand scrambling.

Introduction

One of the simplest and easiest routes into the chemistry of MoMo quadruply bonded compounds is *via* the $Mo_2(O_2CR)_4$ compounds which are readily prepared from $Mo(CO)_6$ according to the reaction shown in eqn (1).[1]

$$2Mo(CO)_6 + 4RCOOH \xrightarrow[C_6H_4Cl_2]{\Delta} Mo_2(O_2CR)_4 + 12CO + 2H_2 \quad (1)$$

Regrettably the analogous reaction involving $W(CO)_6$ does not yield $W_2(O_2CR)_4$ but rather products of further oxidation and degradation of carboxylate ligand.[2–4] Because of this, the chemistry of the WW quadruple bond still remains relatively undeveloped when compared to that of molybdenum.[5] In fact, the synthesis of $W_2(O_2CR)_4$ compounds is considerably more tedious and typically involves a reduction of WCl_4 by Na/Hg or a similar reducing agent in THF followed by a salt metathesis reaction with NaO_2CR.[6,7] Even then the yields of the highly reactive $W_2(O_2CR)_4$ compounds are relatively low.

There is, however, one reaction involving the $M(CO)_6$ compounds (M = Mo or W) that does lead to MM quadruply bonded compounds in high yields and that is the reaction shown in eqn (2) where mhpH is the neutral ligand 2-hydroxy-6-methylpyridine and mhp represents the deprotonated anion.[8]

$$2M(CO)_6 + 4mhpH \xrightarrow[\text{diglyme}]{\Delta} M_2(mhp)_4 + 12CO + 2H_2 \quad (2)$$

This prompted us to investigate the substitution chemistry of the $M_2(mhp)_4$ complexes and to attempt an alternate route to $W_2(O_2CR)_4$ compounds from that described above.

Results and discussion

Reactions involving carboxylic acids

The reactions between $W_2(mhp)_4$ and RCOOH, where R = Ph and 2-thienyl yield a mixture of $W_2(mhp)_{4-x}(O_2CR)_x$ according to the reaction shown in eqn (3), where *x* = 1–4.

$$W_2(mph)_4 + 4RCOOH \xrightarrow[\text{toluene}]{60–70\,^\circ C} \quad (3)$$
$$W_2(mhp)_{4-x}(O_2CR)_x + x\text{mhpH} + (4-x)RCOOH$$

This reaction can be followed by both NMR spectroscopy and mass spectrometry though NMR is somewhat ambiguous due to the possibility of the existence of various isomers. As shown in Fig. 1 with increasing equivalents of added RCOOH the equilibrium can be driven in favor of the $W_2(O_2CR)_4$ compound although this is not a very satisfactory new general synthesis for $W_2(O_2CR)_4$ compounds. However, in the case of R = 9-anthracene the compound $W_2(O_2CR)_4$ is significantly less soluble than the $W_2(mhp)_{4-x}(O_2CR)_x$ compounds and so can be readily separated from the equilibrium mixture. Indeed, in reaction (3) employing ≥4 equiv. of 9-anthracenecarboxylic acid, the synthesis of this

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Department of Chemistry, The Ohio State University, 100 W. 18th Ave, Columbus, Ohio, 43210, USA

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‡ Based in part on the B.S. Honor Thesis of C. W. G.

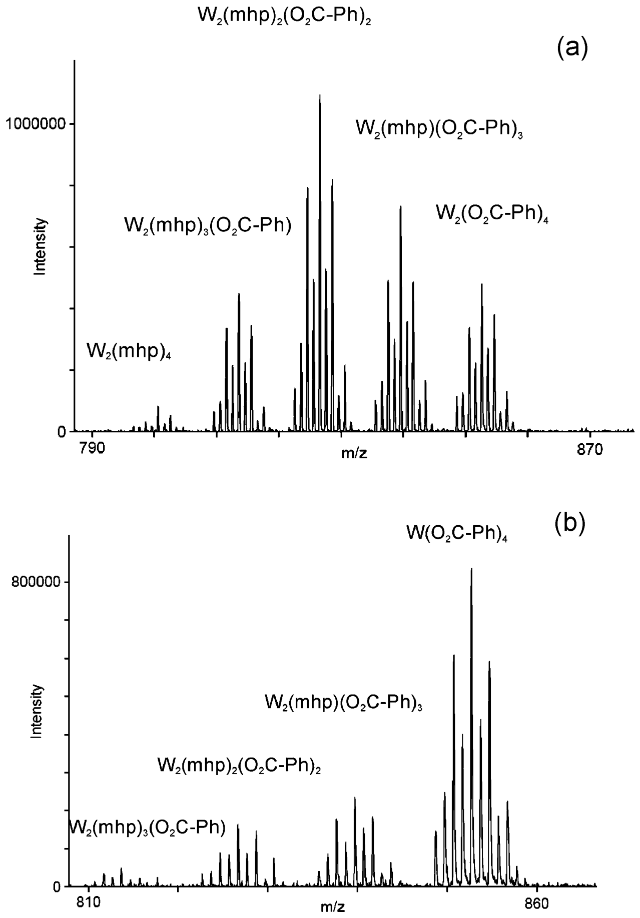


Fig. 1 MALDI-TOF MS of the products obtained from the reaction between $W_2(mhp)_4$ and 4 equiv. PhCOOH (a) and $W_2(mhp)_4$ and 16 equiv. PhCOOH (b).

compound is efficient and provides a notable improvement over the more traditional route.

The reaction involving 2,4,6-triisopropyl benzoic acid proceeds to give the compound $W_2(mhp)_2(TiPB)_2$, where TiPB = 2,4,6-triisopropyl benzoate. This intensely bright red colored complex appears to be the thermodynamically favored product. No further mhp substitution is observed, possibly due to the steric demands of this bulky carboxylate ligand. The ^1H NMR spectrum reveals the presence of one isomer and even at 500 MHz there is no evidence for diastereotopic isopropyl groups. Thus, we propose that the complex adopts the *trans* geometry as we have found for a number of other complexes of formula $M_2(TiPB)_2(O_2CR)_2$, where R = thienyl, bithienyl and terthienyl.[9,10]

Reactions involving $Mo_2(mhp)_4$ proceed qualitatively similarly and both the $Mo_2(mhp)_2(TiPB)_2$ and $Mo_2(mhp)_3(TiPB)$ complexes have been isolated in pure form. The $Mo_2(mhp)_3(TiPB)$ complex has been prepared by the salt metathesis reaction between $[Mo_2(mhp)_3(CH_3CN)_2]^+BF_4^-$ and $[^nBu_4N][TiPB]$.

Electronic absorption spectra of $Mo_2(mhp)_{4-x}(TiPB)_x$ (x = 0, 1, 2, 4) and $W_2(mhp)_2(TiPB)_2$

A comparison of the electronic absorption spectra of the Mo_2-containing complexes is shown in Fig. 2. A notable difference between the spectra of $Mo_2(mhp)_4$ and $Mo_2(TiPB)_4$ is the presence of the intense absorption at 280 nm in the spectrum of the mhp complex and indeed all mhp containing complexes. We assign this to a ligand π to π* transition. At lower energy there are intense absorptions due to $M_2\delta$ to ligand charge transfer. In the mixed $M_2(mhp)_{4-x}(TiPB)_x$ compounds where $x = 2$ and 3, the $M_2\delta$ to mhp and $M_2\delta$ to TiPBπ* transitions overlap.

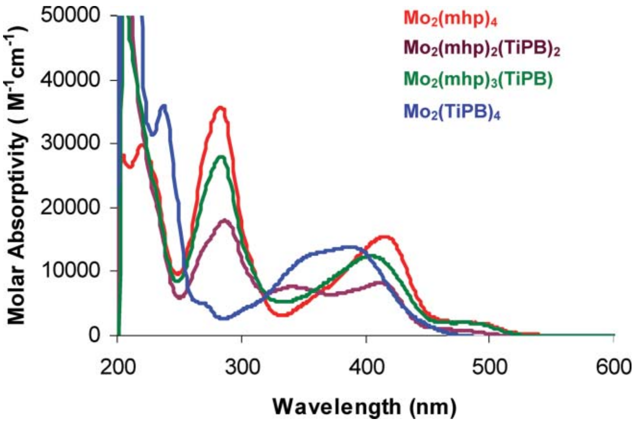


Fig. 2 UV-vis spectra recorded in THF solution.

A comparison of the spectra of the complexes $M_2(mhp)_2(TiPB)_2$ where M = Mo and W is shown in Fig. 3. In both metal complexes the absorption at 280 nm is present which is consistent with our suggestion that this is a ligand based transition involving mhp. The lower energy bands are, however, quite different and the essential difference is that the $M_2\delta$ to ligand π* transitions are red shifted where M = W by *ca.* 0.5 eV, consistent with the higher energy of the $W_2\delta$ orbitals.[11]

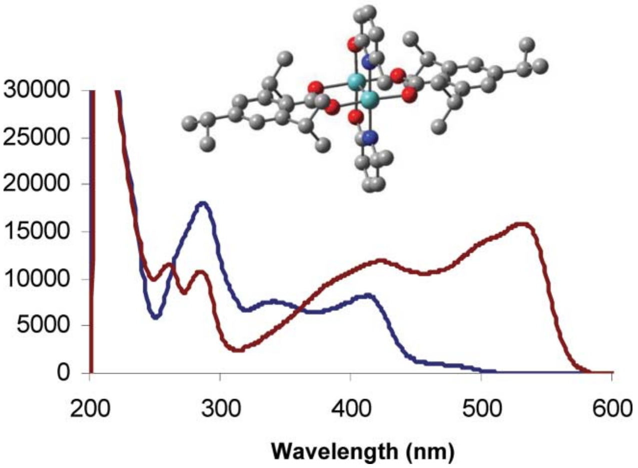


Fig. 3 UV-vis spectra of $M_2(TiPB)_2(mhp)_2$ in THF M = Mo (blue) and M = W (brown).

In comparing the spectra of the $Mo_2(mhp)_2(TiPB)_2$ with that of $Mo(mhp)_4$ and $Mo_2(TiPB)_4$ we note that the $Mo_2\delta$ to mhp absorption occurs at longer wavelength, 420 nm. Also for the sterically demanding TiPB ligand the aromatic group commonly twists significantly out of the CO_2 plane with a dihedral angle >50°.[9,10] This leads us to suggest that for $Mo_2(mhp)_2(TiPB)_2$ the absorption at 340 nm arises from $Mo_2\delta$ to TiPB MLCT.

$[M_2(mhp)_{4-x}(CH_3N)_{2x}]^{x+}[BF_4^-]_x$, where $x = 1, 2$

The reaction between $Mo_2(mhp)_4$ and Meerwein's reagent, $Et_3O^+BF_4^-$ in acetonitrile has previously been shown to give the monocation ($x = 1$) and this was structurally characterized as a weakly associated dimer *via* intermolecular $Mo_2 \cdots O(mhp)$ bonds.[12] In this work we have extended these studies to prepare the dication, $x = 2$, by the use of ≥ 4 equiv. of $Et_3O^+BF_4^-$. However, these reactions only proved successful for M = Mo. All attempts to prepare related tungsten complexes failed to give the desired complexes. The only isolable compound from these reactions was $W_2(mhp)_4$. Also a reaction involving $W_2(mhp)_3Cl_2$ (2 equiv.)[13] and Zn (1 equiv.) in acetonitrile was undertaken in an attempt to prepare the salt $[W_2(mhp)_3(CH_3CN)_2]_2^+[ZnCl_4]^{2-}$ but again the only isolable product was $W_2(mhp)_4$. Furthermore, in an attempt to introduce a substitutionally labile halide ligand reactions involving $W_2(mhp)_4$ and each of BI_3 and Me_3SiI (1 equiv.) were carried out. However, a product of the form $[W_2(mhp)_3(\mu\text{-}I)]_2$ was not isolated and, although there was a reaction, only the compound $W_2(mhp)_4$ was obtained as a crystalline product. These reactions testify to the high formation tendency of $W_2(mhp)_4$ and the kinetic lability of the mhp ligand toward ligand scrambling.

Molecular structure of *cis*-$[Mo_2(mhp)_2(CH_3CN)_4][BF_4]_2$

The molecular structure of the Mo_2-containing dication is shown in Fig. 4. The *cis*-arrangement of $[Mo_2(mhp)_2(CH_3CN)_2]^{2+}$ was expected based on the weak *trans*-influence of CH_3CN ligands and the MoMo distance is typical of that for MoMo quadruple bonds.[11] However, that one Mo atom was coordinated to two oxygen atoms and the other to two nitrogen atoms of the mhp ligands was unexpected. Given the known geometry of the O–N bridging ligands in $Mo_2(mhp)_4$ and $Mo_2(mhp)_3(CH_3CN)_2^+$ this again testifies to the kinetic lability of the ligands at the dinuclear center. The observed structure could therefore result from its preferential crystallization from solution but by ^1H NMR spectroscopy we only find evidence for one isomer in solution.

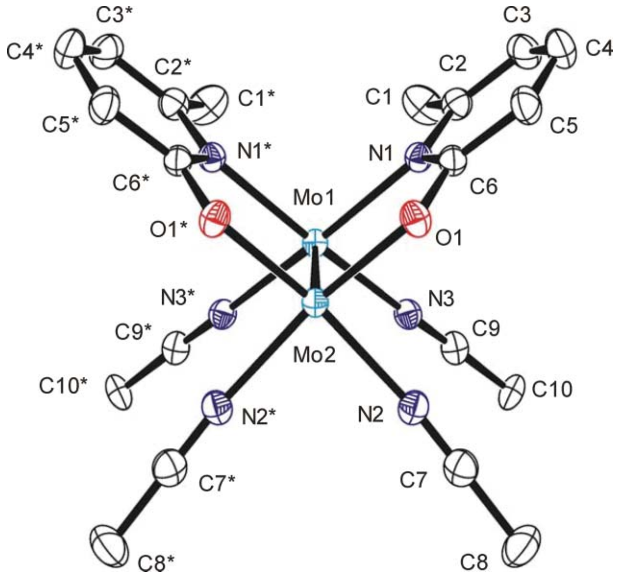


Fig. 4 An ORTEP drawing of the $Mo_2(mhp)_2(CH_3CN)_4^{2+}$ cation showing *cis* arrangement of mhp ligands and the atom number scheme. The molecule has a crystallographically imposed mirror plane of symmetry. Selected bond distances (Å): Mo–Mo = 2.1242(5), Mo–O = 2.035(2), Mo–N(mhp) = 2.161(2), Mo–N(CH_3CN) = 2.160(3) and 2.170(3).

Electronic structure calculations employing density functional theory on *cis*-$Mo_2(mhp)_2(CH_3CN)_4^{2+}$ with C_s and C_2 symmetry were carried out (see Experimental) and these indicated that both isomers in the gas phase had a very similar ground state energy with that of the C_2 isomer being slightly lower in the gas phase. It may well be that the C_s structure, having a polar MoMo bond, is favored in the polar solvent CH_3CN.

Dimers of dimers: $[Mo_2(mhp)_3]_2(O_2C\text{–}X\text{–}CO_2)$

The metathetic reaction involving $[Mo_2(mhp)_3(CH_3CN)_2][BF_4]$ and the tetra-*n*-butyl salt of a dicarboxylic acid in acetonitrile leads to the formation of linked Mo_2 units as shown in eqn (4) where X = nothing, 1,4-C_6F_4, 2,5- and 3,4-thienyl.

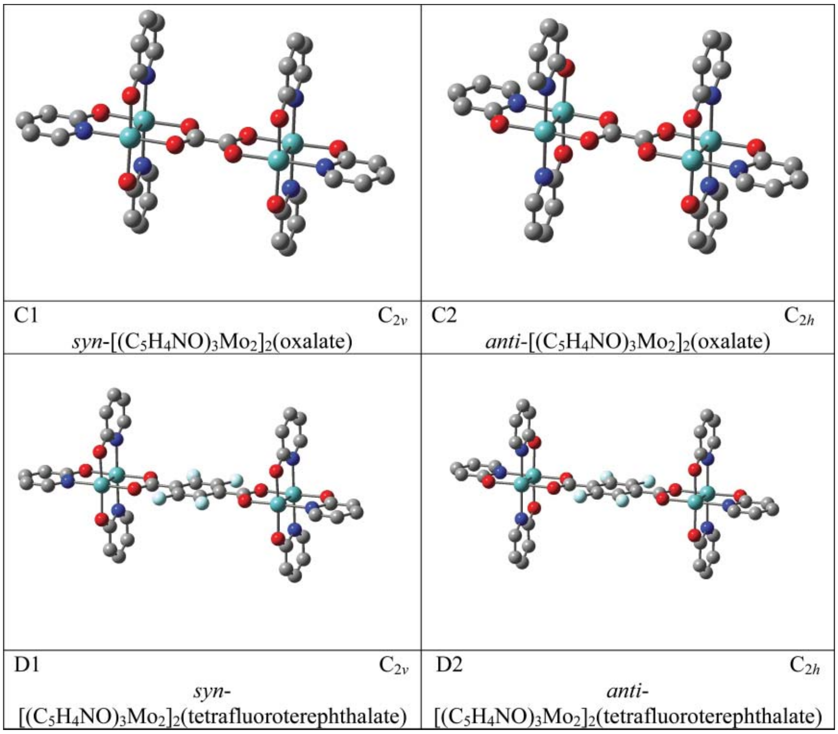
$$2Mo_2(mhp)_3(CH_3CN)_2^+BF_4 + [^nBu_4N]_2O_2C\text{-}X\text{-}CO_2 \xrightarrow[CH_3CN]{25\,^\circ C} [Mo_2(mhp)_3]_2(O_2C\text{-}X\text{-}CO_2) + 2^nBu_4NBF_4 \qquad (4)$$

The dimers of dimers formed in reaction (4) were precipitated from the solution as microcrystalline powders. These were collected and washed with acetonitrile and hexanes. These compounds were very sparingly soluble even in O-donor solvents and DMSO was required to obtain electrochemical data. Even this proved insufficient to obtain measurements on the 2,5-thienyldicarboxylate bridged compound which is essentially insoluble. The oxalate, perfluoroterephthalate and 3,4-thienyldicarboxylate all showed two reversible oxidation waves by cyclic voltammetry and differential pulse voltammetry separated by 282, 240, and 200 mV, respectively. These values for the perfluoroterephthalate are notably larger than those previously reported with pivalate attendant ligands (65 mV).[14] However, all previous electrochemical data were recorded in THF and so a direct comparison is not appropriate.

The compounds all show low energy electronic transitions in the visible region of the spectrum associated with $Mo_2\delta$ to bridge π^* transitions in addition to $Mo_2\delta$ to mhp transitions at slightly higher energy (see Experimental).

Because of the nature of the O–N mhp ligand a number of isomers are possible for $[Mo_2(mhp)_3]_2(O_2C\text{–}X\text{–}CO_2)$ compounds. The planar bridged structures are favored by $M_2\delta$ bridge π^* backbonding[15,16] and assuming that the $Mo_2(mhp)_3$ framework adopts the same geometry as that found for the monocation, $Mo_2(mhp)_3(CH_3CN)_2^+$ then C_{2v} and C_{2h} isomers are possible as shown in Fig. 5. Electronic structure calculations on the model compounds, where the mhp methyl group was replaced by a hydrogen atom in order to allow for a reduction in computational time, indicated that the two structures were of very similar energy. Consequently, the geometries were optimized for the C_{2h} structures. A frequency analysis of the optimized geometry of the perfluoroterephthalate model compound revealed a transition state with one imaginary frequency which related to rotation of the C_6-phenyl ring out of the plane of the carboxylate groups.

As in previous calculations performed on oxalate and perfluoroterephthalate bridged Mo_4-containing compounds, the HOMO and HOMO-1 are out-of-phase and in-phase combinations of the two $Mo_2\delta$ combinations, respectively, with the later being stabilized by its interaction with the LUMO of the bridge.[14] The LUMO is the out-of-phase combination of M_4-bridge HOMO-1.[14]



C1 C_{2v} *syn*-$[(C_5H_4NO)_3Mo_2]_2$(oxalate)

C2 C_{2h} *anti*-$[(C_5H_4NO)_3Mo_2]_2$(oxalate)

D1 C_{2v} *syn*-$[(C_5H_4NO)_3Mo_2]_2$(tetrafluoroterephthalate)

D2 C_{2h} *anti*-$[(C_5H_4NO)_3Mo_2]_2$(tetrafluoroterephthalate)

Fig. 5 Model structures employed for $[Mo_2(mhp)_3]_2$(oxalate) (C1 and C2) and $[Mo_2(mhp)_3]_2$(terephthalate) (D1 and D2) employed in the electronic structure calculations.

The HOMO–LUMO electronic transition is fully allowed and represents the MLCT to the bridge.[14] An indication of the magnitude of the electronic coupling is seen in the energy separation between the HOMO and the HOMO-1 and this is calculated to be 0.33 eV and 0.15 eV for the oxalate and perfluoroterephthalate complexes, respectively. These calculations closely resemble those earlier on model compounds $[(HCO_2)_3Mo_2]_2(O_2C–X–CO_2)$.[15,16] Thus while the oxalate bridged complex could be Class III in its mixed valence singly oxidized state the other compounds under study are almost surely Class II. Attempts to obtain epr data for the singly oxidized compounds have been hindered by their sparing solubility and the high dielectric constant of DMSO.

Higher order assemblies: molecular squares and triangles

Cotton and coworkers have made extensive use of the $[Mo_2(DAnif)_2(CH_3CN)_4]^{2+}$ cation in the synthesis of molecular squares and triangles by employing metathetic reactions involving linking groups such as dicarboxylates [DAnif = CH(N-*p*-anisyl)$_2$].[17] Furthermore they have shown that molecular triangles and squares in certain cases co-exist in a dynamic equilibrium.[18] We were consequently interested to undertake related reactions involving the *cis*-templating $Mo_2(mhp)_2(CH_3CN)_4{}^{2+}$ dication.

When the blue solution of $Mo_2(mhp)_2(CH_3CN)_4(BF_4)_2$ in acetonitrile was allowed to react with $(^nBu_4N)_2(O_2CC_6F_4CO_2)$ in the same solvent an immediate reaction occurred yielding a dark red solution and a brick red precipitate. The latter was completely insoluble in acetonitrile and other common organic solvents. An elemental analysis suggested the product of formula $[Mo_2(mhp)_2(O_2CC_6F_4CO_2)]$ and by MALDI-TOF mass spectrometry both triangles and square were seen together with an ion corresponding to $[Mo_2(mhp)_3]_2(O_2CC_6F_4CO_2)^+$. The latter is present as an impurity and probably arises from mhp ligand exchange reactions (see later). It is also quite likely that polymeric species $[Mo_2(mhp)_2(O_2CC_6F_4CO_2)]_n$ are present in the solid and are not detectable by mass spectrometry.

$Mo_2(mhp)_3(O_2CMe)$ and $Mo_2(mhp)_2(O_2CMe)_2$

From the above it was inferred that mhp ligand scrambling is kinetically facile. In order to check for this the reactions between (i) $[Mo_2(mhp)_3(CH_3CN)_2)][BF_4]$ and $^nBu_4NO_2CMe$ (1 equiv.) and (ii) $Mo_2(mhp)_2(CH_3CN)_4(BF_4)_2$ and $^nBu_4NO_2CMe$ (2 equiv.) were carried out in acetonitrile solution. In each reaction the anticipated products, namely $Mo_2(mhp)_3(O_2CMe)$ and $Mo_2(mhp)_2(O_2CMe)_2$ were formed in (i) and (ii), respectively. However, other species co-existed in solution as evidenced from both ^{1}H NMR spectroscopy and mass spectrometry. Most notably were the species $Mo_2(mhp)_4$ and other $Mo_2(mhp)_{4-x}(O_2CMe)_x$ compounds, where $x = 1–3$. This clearly confirms the kinetic lability of the mhp ligands toward ligand exchange.

Concluding remarks

The potential utility of the easily prepared compound $W_2(mhp)_4$ in the synthesis of $W_2(O_2CR)_4$ has been demonstrated for R = 9-anthracene. This is because the product is sparingly soluble in certain solvents and so can readily be removed from dynamic equilibria of $W_2(mhp)_{4-x}(O_2CR)_4$ compounds. This synthetic procedure would seem likely to find only modest general utility although under forcing conditions the equilibria can be driven in favor of the $W_2(O_2CR)_4$ compound. An exception to this is the formation of the $M_2(mhp)_2(TiPB)_2$ compounds which appear to be the thermodynamic products.

The $[Mo_2(mhp)_3]_2(O_2C–X–CO_2)$ compounds are similar to their pivalate analogues but much less soluble in common organic solvents. This too has limited the characterization of potential molecular squares and triangles of formula $[Mo_2(mhp)_2(O_2C–X–CO_2)]_n$, where $n = 3$ or 4. Another problem that is common to mhp and O_2CBu^t ligands is ligand scrambling which complicates the isolation and characterization of well defined discrete complexes. This problem is not encountered when formamidinate ligands are used as is well exemplified by the successful synthetic strategy employed by Cotton and coworkers.[17]

Experimental

All reactions were carried out under an inert atmosphere of UHP-grade argon or nitrogen using standard Schlenk techniques and under a dry oxygen-free nitrogen atmosphere using standard glovebox techniques. All solvents were dried and degassed by standard methods prior to use. THF was dried by refluxing over sodium/benzophenone while toluene and hexanes were dried by refluxing over sodium metal. Acetonitrile and dichloromethane (DCM) was dried by refluxing over calcium hydride.

Starting materials $Mo_2(mhp)_4$,[8] $[Mo_2(mhp)_3(MeCN)_2]^+(BF_4^-)$,[11] $W_2(mhp)_4$,[8] and $W_2(mhp)_3Cl_2$[13] were prepared according to the literature procedures. 2-Hydroxy-6-methylpyridine, triethyloxonium tetrafluoroborate (1.0 M in DCM), *n*-butylammonium acetate, *n*-butylammonium hydroxide (1.0 M), oxalic acid, tetrafluoroterephthalic acid, trimethylsilyl iodide, boron triiodide, and zinc metal were purchased from commercial sources and used as received. Other *n*-butylammonium salts were prepared by the 1 : 1 reaction of the appropriate acid with a 1 M solution of *n*-butylammonium hydroxide in methanol. After stirring for 1 h at room temperature, the mixture was stripped to dryness and dried under vacuum at 50 °C for several hours.

Physical measurements

NMR spectra were recorded on a 400 MHz Bruker DPX spectrometer. All ^1H NMR chemical shifts are reported in ppm relative to the protio impurity in MeCN-d_3 at 1.53 ppm, THF-d_8 at 3.58 ppm, or DMSO-d_6 at 2.50 ppm. UV-vis spectra were recorded at room temperature using a Perkin-Elmer Lambda 900 spectrometer. Spectra in THF solution were obtained using an air-tight 1 mm quartz cell. Microanalyses were carried out by Atlantic Microlab, Inc.

Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded at OSU's Campus Chemical Instrument Center (CCIC) using a Bruker Reflex III MALDI-TOF mass spectrometer. Samples were run pure or mixed with dithrinol matrix to aid in the flight of the molecule. All complexes were kept in an inert atmosphere.

Cyclic voltammetric and differential pulse voltammetric data were collected with the aid of a Princeton Applied Research (PAR) 173A potentiostat–galvanostat equipped with a PAR 176 current-to-voltage converter with *iR* compensation capability. A single compartment voltammetric cell was equipped with a platinum working electrode, a platinum wire auxiliary electrode, and a pseudo reference electrode consisting of a silver wire in 0.1 M $[^nBu_4N][PF_6]$–DMSO separated from the bulk solution by a Vycor tip. The standard three electrode cell was utilized in a drybox with an inert atmosphere. Ferrocene was added as an internal reference and typically was found at +0.75 V under these conditions.

Computational details

Density functional theory (DFT) calculations were performed with the hybrid Becke-3 parameter exchange functional and the Lee–Yang–Parr non-local correlation functional (B3LYP)[19] implemented in the Gaussian03 (Revision B.04) program suite[20] in conjunction with the 6–31G* basis set for all non-metal atoms and the SDD basis set with effective core pseudo-potential (ECP) for all metal atoms.[21] The calculations were carried out on simplified models in which each methyl substituent was replaced with a hydrogen atom. All geometries were fully optimized at the above levels using the default optimization criteria of the program. Each stationary point was confirmed to be a minimum on the potential energy surface (PES) by a vibrational frequency analysis unless otherwise noted. Orbital analyses were completed with GaussView.[22] To gain insight into the electronic transitions responsible for the observed UV-vis spectrum of all compounds, time-dependent density functional theory (TD-DFT) calculations were performed using the Gaussian program suite. All calculations were run on an Itanium 2 Cluster running Linux version 2.4.18 located at the Ohio Supercomputer Center.

X-Ray structure determination

All single crystals were coated with Paratone oil and mounted on a quartz fiber or a nylon cryoloop affixed to a goniometer head. Diffraction data were collected using a Nonius Kappa CCD diffractometer. All work was done at 150 K using an Oxford Cryosystem Cryostream Cooler. Data integration was done with Denzo.[23] Scaling and merging of data was done with Scalepack. The structure was solved by the Direct or Patterson method and the refinement were completed in SHELXL-97.[24] A summary of crystal data is given in Table 1.

[$M_2(mhp)_4$ compounds were prepared from $M(CO)_6$ according to published procedures.][8]

CCDC reference number 632258.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618957a

Preparation of $[cis\text{-}Mo_2(mhp)_2(CH_3CN)_4]^{2+}(BF_4^-)_2$

To a stirred solution of $Mo_2(mhp)_4$ (600 mg, 0.96 mmol) in 40 mL of MeCN was added 5 mL of 1.0 M Et_3OBF_4. The solution immediately turned purple and after stirring for 1.5 h at 70 °C all the starting material appeared consumed. After stirring at room temperature overnight, the solvent was reduced to approximately 5 mL. Approximately 10 mL of toluene was then added to force the product to precipitate out of solution. The blue precipitate was collected on a frit, washed three times with approximately 20 mL of toluene and dried under vacuum. Overall yield: 575 mg (80%).

Microanalysis found: C 31.80; H 3.24; N 10.97; F 21.31%. $B_2C_{20}F_8H_{24}N_6O_2Mo_2$ requires: C 32.20; H 3.24; N 11.27; F 20.38%. NMR (MeCN-d_6): ^1H (400 MHz) 1.57 (s, 3H), 6.68 (d, 1H), 7.16 (d, 1H), 7.65 (t, 1H).

Table 1 Crystal data and structure refinement for [*cis*-$Mo_2(mhp)_2(CH_3CN)_4]^{2+}(BF_4^-)_2$ (**1**)

Empirical formula	$C_{22}H_{24}Mo_2N_6O_2 \cdot 2(C_2H_3N) \cdot 2(BF_4)$
Formula weight	828.06
Temperature/K	150(2)
Wavelength/Å	0.71073
Crystal system	Orthorhombic
Space group	$P2_1nm$
a/Å	7.26150(10)
b/Å	12.0539(2)
c/Å	19.1113(3)
V/Å^3	1672.9(4)
α/°	90
β/°	90
γ/°	90
Z	2
Density (calculated)/Mg m^{-3}	1.644
Absorption coefficient/mm^{-1}	0.830
F(000)	824
Crystal size/mm^3	0.04 × 0.08 × 0.38
θ range for data collection/°	3.28 to 27.49
Index ranges	$-9 \le h \le 9, 0 \le k \le 15, 0 \le l \le 24$
Reflections collected	19161
Independent reflections	3950 [R(int) = 0.0336]
Completeness to θ = 27.49° (%)	99.7
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3950/1/221
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0282$, $wR2 = 0.0671$
R indices (all data)	$R1 = 0.0324$, $wR2 = 0.0687$
Absolute structure parameter	0.02(4)
Largest diff. peak and hole/e Å^{-3}	0.544 and −0.381

Preparation of $[Mo_2(mhp)_3]_2(O_2CCO_2)$

To a stirring solution of $[Mo_2(mhp)_3(CH_3CN)_2]^+(BF_4^-)$ (0.300 g, 0.438 mmol) in approximately 10 mL of MeCN was added a solution of $(^nBu_4N)_2(O_2CCO_2)$ (0.125 g, 0.219 mmol) in approximately 10 mL of MeCN. An immediate reaction took place with the formation of a red precipitate. After stirring for 30 min, the red precipitate was collected by filtration, washed several times with CH_3CN, and dried under vacuum. Overall yield: 205 mg (84%).

Microanalysis found: C 37.16; H 3.31; N 6.57%. $C_{38}H_{36}N_6O_{10}Mo_4$ requires: C 40.73; H 3.24; N 7.50%. NMR (DMSO-d_6): ^{1}H (400 MHz) 1.62 (s, 6H), 1.75 (s, 3H), 6.40 (d, 1H), 6.49 (d, 2H), 6.73 (d, 1H), 6.83 (d, 2H), 7.34 (t, 1H), 7.42 (t, 2H). MALDI-MS: 1120.9 (100%, M$^+$).

Preparation of $[Mo_2(mhp)_3]_2(O_2CC_6F_4CO_2)$

The reaction was carried out under similar conditions outlined for above using 300 mg of $[Mo_2(mhp)_3(CH_3CN)_2]^+(BF_4^-)$ (0.438 mmol) and 158 mg of $(^nBu_4N)_2(O_2CCO_2)$ (0.219 mmol). 171 mg of a purple precipitate was isolated. Overall yield: 171 mg (78%).

Microanalysis found: C 40.77; H 2.77; N 6.44; F 5.91%. $C_{44}F_4H_{36}N_6O_{10}Mo_4$ requires: C 41.66; H 2.86; N 6.62; F 5.99%. NMR (DMSO-d_6): ^{1}H (400 MHz) 1.78 (s, 3H), 1.94 (s, 6H), 2.35 (s, 3H), 6.30 (d, 1H), 6.38 (d, 2H), 6.67 (d, 1H), 6.81 (d, 2H), 7.21 (t, 1H), 7.32 (t, 2H). MALDI-MS: 1266.9 (100%, M$^+$).

Preparation of $Mo_2(mhp)_3(O_2CCH_3)$

To a stirring solution of $Mo_2(mhp)_3(CH_3CN)_2{}^+(BF_4^-)$ (450 mg, 0.657 mmol) in approximately 10 mL of MeCN was added a solution of $(^nBu_4N)(O_2CMe)$ (198 mg, 0.657 mmol) in approximately 10 mL of MeCN. The solution immediately turned from red to orange. After stirring for 30 min, the orange precipitate was washed three times with approximately 20 mL of MeCN and dried under vacuum for 3 h. Overall yield: 320 mg (85%).

Microanalysis found: C 42.35; H 3.84; N 8.81%. $C_{20}H_{21}N_3O_5Mo_2$ requires: C 41.76; H 3.68; N 7.30%. NMR (THF-d_8): ^{1}H (400 MHz) 1.78 (s, 3H), 1.94 (s, 6H), 2.35 (s, 3H), 6.30 (d, 1H), 6.38 (d, 2H), 6.67 (d, 1H), 6.81 (d, 2H), 7.21 (t, 1H), 7.32 (t, 2H). MALDI-MS: 575.0 (100%, M$^+$).

Preparation of *cis*-$Mo_2(mhp)_2(O_2CCH_3)_2$

To a stirred solution of [*cis*-$Mo_2(mhp)_2(CH_3CN)_4]^{2+}(BF_4^-)_2$ (160 mg, 0.21 mmol) in 10 mL of CH_3CN was added $(^nBu_4N)(O_2CCH_3)$ (160 mg, 0.53 mmol) in 10 mL of CH_3CN. An immediate reaction took place as observed by a color change to yellow but no precipitate formed. After stirring for 30 min, the solvent was reduced to a minimum to precipitate a yellow product that was collected by filtration, and dried under vacuum. Overall yield: 67 mg (59.4%).

Microanalysis found: C 36.51; H 3.87; N 5.08%. $C_{16}H_{18}N_2O_6Mo_2$ requires: C 36.52; H 3.45; N 5.32%. NMR (THF-d_8): ^{1}H (400 MHz) 1.71 (s, 3H), 2.49 (s, 3H), 6.34 (d, 1H), 6.79 (d, 1H), 7.27 (t, 1H). MALDI-MS: 525.9 (100%, M$^+$).

Attempted preparation of $[Mo_2(mhp)_2(O_2CCO_2)]_4$

To a stirred solution of [*cis*-$Mo_2(mhp)_2(CH_3CN)_4]^{2+}(BF_4^-)_2$ (426 mg, 0.64 mmol) in 10 mL of CH_3CN was added $(^nBu_4N)_2(O_2CCO_2)$ (367 mg, 0.64 mmol) in 10 mL of CH_3CN. An immediate reaction took place with the formation of an apparent red precipitate. After stirring for 30 min, the crude product could not be collected by filtration and was re-evaluated to be an oil. The oil was collected by separation for analysis. ^{1}H NMR and MALDI-TOF spectroscopy could only identify the product as a mixture of species.

Attempted preparation of $[Mo_2(mhp)_2(O_2CC_6F_4CO_2)]_4$

To a stirred solution of [*cis*-$Mo_2(mhp)_2(CH_3CN)_4]^{2+}(BF_4^-)_2$ (400 mg, 0.60 mmol) in 10 mL of CH_3CN was added $(^nBu_4N)_2(O_2CC_6F_4CO_2)$ (387 mg, 0.60 mmol) in 10 mL of CH_3CN. An immediate reaction took place with the formation of a red precipitate. After stirring for 30 min, the crude product was collected by filtration, washed several times with CH_3CN, and dried under vacuum. The reaction yielded 207 mg of a red solid that was determined to be a mixture of pairs of dimers, molecular triangles, and molecular squares by MALDI-TOF spectroscopy.

Microanalysis found: C 36.35; H 1.98; N 4.81%. $C_{80}H_{48}F_{16}Mo_8N_8O_{24}$ requires: C 37.29; H 1.88; N 4.35%.

Attempted preparation of $[W_2(mhp)_{4-n}]^{n+}$

Method A. To a solution of $W_2(mhp)_4$ (800 mg, 1.000 mmol) in 25 mL of CH_2C1_2 and 1 mL of MeCN was added 5 mL of 1.0 M Et_30BF_4. The solution immediately turned reddish green and within the first hour was green. After 2 h, stirring was stopped and the solution was allowed to sit at room temperature overnight. No green solid was isolated by cannula removal of the mother liquor.

The solution was split into two halves. Diethyl ether (~25 mL) was added to one half. This resulted in the precipitation of a green solid. The solvent was then removed *via* cannula and the green solid was dried under vacuum for 3 h. The yield was 440 mg of an unknown material that could not be identified as the desired complex. The second half was placed in a −20 °C refrigerator over the weekend. No crystals formed.

Method B. To a stirred solution of $W_2(mhp)_4$ (400 mg, 0.500 mmol) in approximately 40 mL of acetonitrile was added iodotrimethylsilane (0.068 mL, 0.500 mmol). After stirring overnight, the volume of the solvent was reduced to a minimum. A red solid was collected by filtration and washed 2 × 10 mL of hexanes. The red solid was characterized by ^{1}H NMR as recovered starting material, $W_2(mhp)_4$.

Method C. To a stirred solution of $W_2(mhp)_4$ (400 mg, 0.500 mmol) in approximately 40 mL of acetonitrile was added boron triiodide (0.068 mL, 0.500 mmol). After stirring overnight, the solvent was stripped to dryness. The mixture yielded no tractable product.

Method D. Approximately 40 mL of acetonitrile was added to a reaction vessel containing $W_2(mhp)_3Cl_2$ (400 mg, 0.500 mmol) and excess Zn dust (7.2 g, 110 mmol). After stirring for 1 h, the orange solution turned red. The mixture was allowed to continue stirring overnight before workup. The mixture was then filtered over Celite and the solvent of the filtrate stripped to dryness. The red solid was characterized by ^{1}H NMR as $W_2(mhp)_4$.

All experiments were conducted using standard glove box and Schlenk techniques. Solvents were dried and degassed prior to use. All reactions and subsequent workups were carried out under an argon environment. All reagents were used as received.

Reaction of $W_2(mhp)_4$ and benzoic acid ($Ph\text{-}CO_2H$) (4 equiv.)

A Schlenk flask was charged with 0.153 g (1.25 mmol) of benzoic acid, 0.250 g (0.31 mmol) of $W_2(mhp)_4$, and 15 mL of toluene. The flask was placed in a 70 °C oil bath, and the reaction mixture was stirred gently for 24 h. The solution turned from a red to a dark purple color, within minutes. The solution was allowed to stir in the oil bath for 3 days. After which, the reaction mixture was cooled to room temperature and the solid product was collected on a frit. The product was washed once with toluene (10 mL) and three times with hexanes (15 mL), then dried under vacuum. The ^{1}H NMR spectrum was complex with multiple multiplets appearing in the aromatic range (6.0–8.0 ppm), which was indicative of a mixture of products. MALDI-TOF: calculated MW for $W_2C_{24}N_4O_4H_{23}$: 799.37 (M^+), calculated MW for $W_2C_{25}N_3O_5H_{22}$: 812.3 (M^+), calculated MW for $W_2C_{26}N_2O_6H_{21}$: 825.23 (M^+), calculated MW for $W_2C_{27}NO_7H_{20}$: 838.16 (M^+), calculated MW for $W_2C_{28}O_8H_{19}$: 851.09 (M^+), observed: 799.85, 812.84, 825.84, 838.82, and 821.81.

Reaction of $W_2(mhp)_4$ and benzoic acid ($Ph\text{-}CO_2H$) (16 equiv.)

A Schlenk flask was charged with 2.345 g (19.2 mmol) of benzoic acid, 1.000 g (1.25 mmol) of $W_2(mhp)_4$, and 50 mL of toluene. The flask was placed in a 60 °C oil bath, and the reaction mixture was stirred gently for 16 h. The solution turned from a red to a dark purple color, within minutes. The solution was allowed to stir in the oil bath for 3 days. After which, the reaction mixture was cooled to room temperature and the solid product was collected on a frit. The product was washed once with toluene (10 mL) and three times with hexanes (15 mL), then dried under vacuum. The ^{1}H NMR spectrum displayed similar behavior to those above, but the corresponding peaks for coordinated benzoate were much more intense than before. MALDI-TOF: calculated MW for $W_2C_{24}N_4O_4H_{23}$: 799.37 (M^+), calculated MW for $W_2C_{25}N_3O_5H_{22}$: 812.3 (M^+), calculated MW for $W_2C_{26}N_2O_6H_{21}$: 825.23 (M^+), calculated MW for $W_2C_{27}NO_7H_{20}$: 838.16 (M^+), calculated MW for $W_2C_{28}O_8H_{19}$: 851.09 (M^+), observed: 812.67, 825.68, 838.69, and 851.70.

Reaction of $W_2(mhp)_4$ and 9-anthracenylcarboxylic acid ($Anth\text{-}9\text{-}CO_2H$)

A Schlenk flask was charged with 0.278 g (1.25 mmol) of Anth-9-CO_2H, 0.250 g (0.313) of $W_2(mhp)_4$, and 15 mL of toluene. The flask was placed in a 60 °C oil bath, and the reaction mixture was stirred gently for 16 h. The solution turned from a red to a dark purple color, within minutes. The solution was allowed to stir in the oil bath for 3 days. After which, the reaction mixture was cooled to room temperature and the solid product was collected on a frit. The product was washed three times with toluene (15 mL total), once with DMSO (5 mL), and three times with hexanes (15 mL), and then dried under vacuum. 0.220 g of product was recovered (66% yield). ^{1}H NMR (DMSO, δ, ppm): 6.92, 6.95, 6.95 (t), 7.28, 7.29, 7.32 (t), 7.96, 7.99 (d), 8.43 (s), 8.47, 8.50 (d). MALDI-TOF: calculated MW for $W_2C_{60}O_8H_{36}$: 1251.57 (M^+), observed 1252.2.

Preparation of $W_2(mhp)_2(TiPB)_2$

A Schlenk flask was charged with 0.248 g (1.0 mmol) of TiPBH, 0.200 g (0.25 mmol) of $W_2(mhp)_4$, and 10 mL of toluene. The flask was placed in a 45 °C oil bath, and the reaction mixture was stirred gently for 16 h. The solution turned from a red to an intensely bright red color, within minutes. The solution was allowed to stir in the oil bath for 3 days. After which, the reaction mixture was cooled to room temperature and the solid product was collected on a frit. The product was washed three times with hexanes (15 mL), and then dried under vacuum. 0.143 g of product was recovered: $W_2(mhp)_2(TiPB)_2$.

^{1}H NMR (DMSO, δ, ppm): 0.99, 1.02 (d, CH_3 of TiPB), 1.19, 1.22 (d, CH_3 of TiPB), 2.22 (s, CH_3 of mhp), 2.45–2.58 (m, CH of TiPB), 2.77–2.89 (m, CH of TiPB), 6.46, 6.47, 6.49 (t, CH of mhp), 6.95 (s, CH of TiPB), 7.08–7.10 (m, CH of mhp). MALDI-TOF: calculated MW for $W_2C_{44}O_6N_2H_{57}$: 1077.44 (M^+), observed 1077.1.

Reaction of $W_2(mhp)_4$ and 2-thienylcarboxylic acid ($th\text{-}2\text{-}CO_2H$) (4 equiv.)

A Schlenk flask was charged with 0.128 g (1.0 mmol) of 2-thienylcarboxylic acid, 0.200 g (0.25 mmol) of $W_2(mhp)_4$, and 15 mL of toluene. The flask was placed in a 50 °C oil bath, and the reaction mixture was stirred gently. The solution turned from a red to a dark purple color, within minutes. The solution was allowed to stir in the oil bath for 3 days. After which, the reaction mixture was cooled to room temperature and the product was collected on a frit. The product was washed three times with toluene (15 mL total) and once with hexanes (5 mL), then dried under vacuum. The ^{1}H NMR spectrum was complex with multiple multiplets appearing in the aromatic range (6.0–8.0 ppm), which was indicative of a mixture of products. MALDI-TOF: Calculated MW for $W_2C_{24}N_4O_4H_{23}$: 799.37 (M^+), calculated MW for $W_2C_{23}N_3O_5SH_{20}$: 818.32 (M^+), calculated MW for $W_2C_{22}N_2O_6S_2H_{17}$: 837.27 (M^+), calculated MW for $W_2C_{21}NO_6S_3H_{16}$: 842.25 (M^+), calculated MW for $W_2C_{20}O_8S_4H_{11}$: 875.17 (M^+): observed: 799.55, 818.49, 837.45, 856.41, and 875.36.

$Mo_2(mhp)_2(TiPB)_2$

A Schlenk flask was charged with 0.395 g of TiPB (1.59 mmol, FW = 248.36 g mol^{-1}), 0.250 g of $Mo_2(mhp)_4$ (0.4 mmol, FW = 624 g mol^{-1}), and 10 mL of toluene. The flask was placed in a 60 °C oil bath, and the reaction mixture was stirred for 24 h. The solution turned from a rusty orange color to a bright yellow color within a half hour at 60 °C. After 24 h at elevated temperature, the reaction mixture was cooled to room temperature and the product was collected on a frit. The product was washed three times with hexane (15 mL total), then dried under vacuum. 0.294 g of a bright yellow powder was recovered (62% yield). ^{1}H NMR (DMSO, δ, ppm): 0.90, 0.92 (d, CH_3 of TiPB), 1.16, 1.18 (d, CH_3 of TiPB), 1.59 (s, CH_3 on mhp), 2.53–2.60 (m, CH of TiPB), 2.76–3.90 (m, CH of mhp), 6.55, 6.57 (d, H of mhp), 6.96 (s, H of TiPB), 7.05, 7.08 (d, H of mhp), 7.55, 7.58, 7.62 (t, H of mhp). MALDI-TOF: calculated MW for $Mo_2C_{44}N_2O_6H_{58}$, 901.83 (M^+); found 902.13.

$[Mo_2(mhp)_3(CH_3CN)_2][BF_4]$

The $[Mo_2(mhp)_3(CH_3CN)_2]^+$ cation was prepared as per the literature.[12]

$[^nBu_4N]$[2,4,6-triisopropylbenzoate]

To a solution of 0.500 g of 2,4,6-triisopropylbenzoic acid (approximately 2 mmol, FW = 248.36 g mol^{-1}) in 5 mL of methanol was added 2.0 mL of a 1 M solution of n-butylammonium hydroxide in methanol. The mixture was stirred at room temperature for 1 h and then stripped to dryness under vacuum at 50 °C.

$Mo_2(mhp)_3(TiPB)$

A solution of 0.200 g of $[Mo_2(mhp)_3(CH_3CN)_2][BF_4]$ (2.9 mmol, FW = 686.65 g mol^{-1}) in 15 mL of acetonitrile was combined with 0.143 g (2.9 mmol, FW = 490.36 g mol^{-1}) of $[^nBu_4N]$[2,4,6-triisopropylbenzoate] in a 10 mL solution of acetonitrile. Upon addition, a precipitate immediately formed and was collected on a frit. The product was washed three times with acetonitrile (15 mL total) and once with hexanes (5 mL), then dried under vacuum. ^{1}H NMR (DMSO, δ, ppm): 0.92, 0.95 (d, CH_3 of TiPB), 1.19, 1.22 (d, CH_3 of TiPB), 2.30 (s, CH_3 of mhp), 2.34 (s, CH_3 of mhp), 2.46–2.57 (m, CH of TiPB), 2.78–2.86 (m, CH of TiPB), 6.34, 6.37 (d, CH of mhp), 6.40, 6.43 (d, CH of mhp), 6.76, 6.79 (d, CH of mhp), 6.88, 6.92 (d, CH of mhp), 6.91 (s, CH of TiPB), 7.07–7.18 (m, CH of mhp), 7.23 (m, CH of mhp), 7.26–7.27 (m, CH of mhp). MALDI-TOF: calculated MW for $Mo_2C_{34}O_5N_3H_{40}$, 762.57 (M^+); found 763.03.

$[^nBu_4N]_2[3,4\text{-th}(CO_2)_2]$

To a solution containing 0.028 g of 3,4-thienyldicarboxylic acid in 10 mL of methanol was added 0.320 mL of a 1 M solution of *n*-butylammonium hydroxide in methanol. The solution was stirred at room temperature for 1 h and then stripped to dryness at 50 °C under vacuum.

$[^nBu_4N]_2[2,5\text{-th}(CO_2)_2]$

To a solution containing 0.037 g of 2,5-thienyldicarboxylic acid in 5 mL of methanol was added 0.430 mL of a 1 M solution of *n*-butylammonium hydroxide in methanol. The solution was stirred at room temperature for 1 h and then stripped to dryness at 50 °C under vacuum.

$[(mhp)_3Mo_2]_2\{\mu\text{-3,4-th-}(CO_2)_2\}$

A solution of 0.32 mmol of $[Mo_2(mhp)_3(CH_3CN)_2][BF_4]$ in 20 mL of acetonitrile was combined with a solution of 0.16 mmol of $[^nBu_4N]_2[3,4\text{-th}(CO_2)_2]$ in 10 mL of acetonitrile. A precipitate formed and was collected on a frit. The product was washed three times with acetonitrile (15 mL total) and once with hexanes (5 mL), then dried under vacuum. ^{1}H NMR (DMSO, δ, ppm): 1.65 (s, CH_3 of mhp), 1.76 (s, CH_3 of mhp), 6.45, 6.48 (d, CH of mhp), 6.56, 6.59 (d, CH of mhp), 6.78–6.83 (m, CH of mhp), 7.348–7.513 (m, CH of mhp), 8.061, 8.067 (d, CH of thiophene). MALDI-TOF: calculated MW for $Mo_4C_{42}N_6O_{10}SH_{37}$, 1201.64 ($M^+$).

$[(mhp)_3Mo_2]_2\{\mu\text{-2,5-th-}(CO_2)_2\}$

A solution of 0.36 mmol of $[Mo_2(mhp)_3(CH_3CN)_2][BF_4]$ in 20 mL of acetonitrile was combined with a solution of 0.18 mmol of $[^nBu_4N]_2[2,5\text{-th}(CO_2)_2]$ in 10 mL acetonitrile. A precipitate formed and was collected on a frit. The product was washed three times with acetonitrile (15 mL total) and once with hexanes (5 mL), then dried under vacuum.

^{1}H NMR (DMSO, δ, ppm): 1.66 (s, CH_3 of mhp), 1.82 (s, CH_3 of mhp), 6.41, 6.42 (d, H of mhp), 6.50, 6.52 (d, H of mhp), 6.74, 6.76 (d, H of mhp), 6.85, 6.87 (d, H of mhp), 7.16, 7.18 (d, H of mhp), 7.23, 7.24 (d, H of mhp), 7.33, 7.35 (d, H of mhp), 7.40, 7.42, 7.44 (t, H of mhp), 7.64 (s, H of thiophene). MALDI-TOF: calculated MW for $Mo_4C_{42}N_6O_{10}SH_{37}$, 1201.64 ($M^+$).

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