

# Functionalization of $[\text{MoW}_5\text{O}_{19}]^{2-}$ with Aromatic Amines: Synthesis of the First Arylimido Derivatives of Mixed-Metal Polyoxometalates

Yongge Wei,<sup>†</sup> Meng Lu,<sup>†</sup> Calida Fung-chi Cheung,<sup>†</sup> Charles L. Barnes,<sup>‡</sup> and Zhonghua Peng<sup>\*,†</sup>

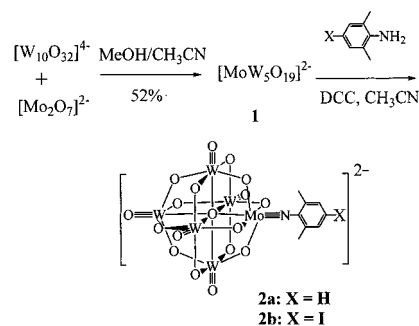
Departments of Chemistry, University of Missouri—Kansas City, Kansas City, Missouri 64110, and University of Missouri—Columbia, Columbia, Missouri 65211

Received August 1, 2001; Revised Manuscript Received September 14, 2001

Surface functionalization of polyoxometalates (POMs) with organic species to generate new hybrid materials with fascinating catalytic, medicinal, electrochemical, and photophysical properties has drawn increasing attention in recent years.<sup>1</sup> The preparation of such hybrid materials, which usually rely on cluster assembly reactions,<sup>1,2</sup> has become more convenient and straightforward with the discovery that they may be synthesized directly from their mother cluster anions.<sup>3–9</sup> For example, the hexamolybdate anion has been found to react with phosphinimines,<sup>4</sup> isocyanates,<sup>5</sup> or aromatic amines<sup>6</sup> to form its imido derivatives. The aryl imido derivatives of POMs, in particular, have drawn significant interest in that the organic  $\pi$ -electrons may extend their conjugation to the inorganic framework, resulting in possible synergistic effects.<sup>7,8</sup> A fairly large number of imido derivatives of  $[\text{Mo}_6\text{O}_{19}]^{2-}$  have now been synthesized and their properties explored.<sup>9</sup>

So far, however, the organo–imido functionalization of POMs has focused only on the hexamolybdate anion. Attempts to functionalize other POMs such as hexatungstates using the parent cluster as the reactant directly have not been successful.<sup>10</sup> We have recently reported a reaction protocol which allows the functionalization of hexamolybdates with aromatic amines under mild conditions and in high yields.<sup>11</sup> In this communication, we

**Scheme 1.** Synthesis of Imido Derivatives of the  $[\text{MoW}_5\text{O}_{19}]^{2-}$  Cluster Anion<sup>a</sup>



<sup>a</sup> The counterion is tetrabutylammonium.

report that this reaction can be extended to the  $[\text{MoW}_5\text{O}_{19}]^{2-}$  cluster, allowing the synthesis, for the first time, of two arylimido derivatives of the mixed-metal  $[\text{MoW}_5\text{O}_{19}]^{2-}$  cluster, one of which carries an additional iodo functional group. With iodo- or ethynyl-functionalized hexamolybdate clusters readily available,<sup>11</sup> it is now possible to construct, rationally, hybrid molecular dumbbells with two different cluster balls linked by a  $\pi$ -conjugated organic rod.

Scheme 1 shows the synthesis and structure of two arylimido derivatives of  $[\text{MoW}_5\text{O}_{19}]^{2-}$ . The tetrabutylammonium salt of  $[\text{MoW}_5\text{O}_{19}]^{2-}$  (compound **1**) has previously been obtained from an aqueous solution of  $\text{Na}_2\text{MoO}_4$  with an active form of  $\text{WO}_3 \cdot \text{H}_2\text{O}$  at  $\text{pH} > 6$ <sup>12</sup> or by a nonaqueous route involving the hydrolysis of tungsten alkoxide  $[\text{WO}(\text{OMe})_4]$  with  $[\text{Bu}_4\text{N}]_2[\text{MoO}_4]^{2-}$ .<sup>2c</sup> Both approaches rely on the random assembly of two metal oxides, and, as expected, unsatisfactory yields are obtained and pure products are difficult to separate from side products. We recognized that  $[\text{MoW}_5\text{O}_{19}]^{2-}$  may be more efficiently assembled by the combination of a  $[\text{W}_5\text{O}_{18}]^{6-}$  block with a  $[\text{MoO}_4]^{2-}$  block. Such a block assembly approach has previously been applied for the synthesis of  $[\text{VW}_5\text{O}_{19}]^{2-}$ <sup>13</sup> and other POMs.<sup>12,14</sup> Indeed, we found that  $[\text{MoW}_5\text{O}_{19}]^{2-}$  can be prepared in good yields by refluxing a methanol/acetonitrile (1:2) solution of  $[\text{W}_{10}\text{O}_{32}]^{4-}$  with  $[\text{Bu}_4\text{N}]_2[\text{Mo}_2\text{O}_7]$ . The active  $[\text{W}_5\text{O}_{18}]^{6-}$  block and the  $[\text{MoO}_4]^{2-}$  block were generated in situ by the dissociation of  $[\text{W}_{10}\text{O}_{32}]^{4-}$  and  $[\text{Mo}_2\text{O}_7]^{2-}$ , respectively. The reaction is completed in 4–6 h, and analytically pure products can be easily separated by simple recrystallization from acetone in over 50% yield.

The reaction of  $[\text{MoW}_5\text{O}_{19}]^{2-}$  with 2,6-dimethylaniline or 2,6-dimethyl-4-iodoaniline was carried out in acetonitrile. Dicyclohexylcarbodiimide (DCC) (1.5 equiv) was added into the reaction mixture to facilitate the reaction.<sup>11</sup> As expected, the terminal

\* To whom correspondence should be addressed. Telephone: (816) 235-2288. Fax: (816) 235-5502. E-mail: pengz@umkc.edu.

<sup>†</sup> University of Missouri—Kansas City.

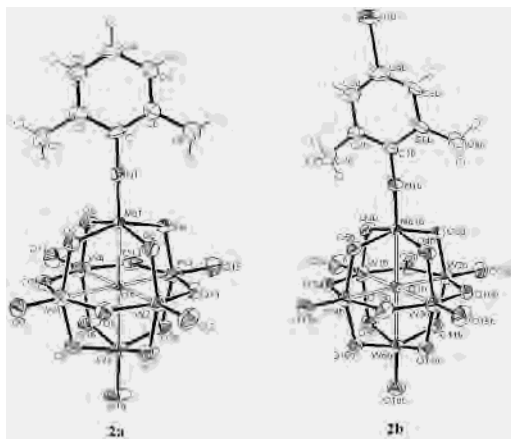
<sup>‡</sup> University of Missouri—Columbia.

- (1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (c) *Polyoxometalates: From Planotic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994. (d) Hill, C. L., Guest Ed. *Chem. Rev.* **1998**, *98*.
- (2) (a) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1985**, *24*, 4055. (b) Kang, H.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1192. (c) Clegg, W.; Elsegood, M. R. J.; Errington, R. J.; Havelock, J. J. *Chem. Soc., Dalton Trans.* **1996**, 681.
- (3) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759. (b) Hsieh, T. C.; Zubieta, J. A. *Polyhedron* **1986**, *5*, 1655. (c) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265. (d) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030.
- (4) Du, Y.; Rheingold, A. L.; Maatta, E. A. *J. Am. Chem. Soc.* **1992**, *114*, 346.
- (5) (a) Clegg, W.; Errington, R. J.; Fraser, K. A.; Lax, C.; Richards, D. G., in ref 1c, p 113. (b) Strong, J. B.; Ostrander, R.; Rheingold, A. L.; Maatta, E. A. *J. Am. Chem. Soc.* **1994**, *116*, 3601.
- (6) Clegg, W.; Errington, R. J.; Fraser, K.; Holmes, S. A.; Schäfer, A. *J. Chem. Soc., Chem. Commun.* **1995**, 455.
- (7) Stark, J. L.; Young, V. G., Jr.; Maatta, E. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2547.
- (8) Xu, B.; Wei, Y. G.; Barnes, C. L.; Peng, Z. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2290.
- (9) (a) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77. (b) Strong, J. B.; Yap, G. P. A.; Ostrander, R.; Liable-Sands, L. M.; Rheingold, A. L.; Thouvenot, R.; Gouzerh, P.; Maatta, E. A. *J. Am. Chem. Soc.* **2000**, *122*, 639.
- (10) (a) Mohs, T. R.; Yap, G. P. A.; EHINGOLD, A. L.; Maatta, E. A. *Inorg. Chem.* **1995**, *34*, 9. (b) Errington, R. J.; Lax, C.; Richards, D. G.; Clegg, W.; Fraser, K. A., in ref 1c, p 105.
- (11) Wei, Y. G.; Xu, B.; Barnes, C. L.; Peng, Z. *J. Am. Chem. Soc.* **2001**, *123*, 4083.

(12) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3194.

(13) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93.

(14) Tézé, A.; Cadot, E.; Béreau, V.; Hervé, G. *Inorg. Chem.* **2001**, *40*, 2000.

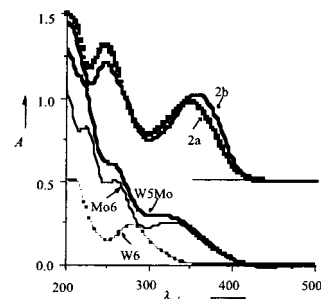


**Figure 1.** ORTEP representation at the 50% probability level of the anions **2a** and **2b**.

oxygen bonded to the molybdenum is more reactive and is selectively replaced by an aryl imido substituent. Compared to the hexamolybdate anion,  $[\text{MoW}_5\text{O}_{19}]^{2-}$  shows slightly less reactivity, and the reaction is further complicated by the competing conversion of  $[\text{MoW}_5\text{O}_{19}]^{2-}$  to  $[\text{W}_6\text{O}_{19}]^{2-}$  under the reaction conditions. This conversion, however, is relatively slow and can be minimized by decreasing the reaction time which can be achieved by adding more than 1 equiv of DCC and the aromatic amine. By limiting the reaction time to about 12 h, analytically pure functionalized mixed-metal POMs **2a** and **2b** can be prepared in over 50% yield. This result opens a general route for the synthesis of organo imido derivatives of less reactive POM clusters, namely, by replacing one of the inert terminal metal–oxygen bonds with a functionalizable Mo–O bond.

Both compounds **2a** and **2b** are soluble in common organic solvents. Their structures are confirmed by elemental analysis, spectroscopic measurements, and X-ray single-crystal structure determination. The  $^1\text{H}$  NMR spectra of compounds **2a** and **2b** in acetone- $d_6$  show clearly resolved signals, all of which can be unambiguously assigned (see Supporting Information). The integration matches well with the desired structure. Compared to the  $^1\text{H}$  NMR spectra of their corresponding imido derivatives of hexamolybdate,<sup>11</sup> the protons of **2a** and **2b**, except for those in the tetrabutylammonium cation, all exhibit higher chemical shifts, indicating stronger electron-withdrawing power of the Mo–N bond in  $[\text{W}_5\text{O}_{18}\text{Mo}(\text{NAr})]^{2-}$  than in  $[\text{Mo}_6\text{O}_{18}(\text{NAr})]^{2-}$ .

The molecular structures of **2a** and **2b** have been determined by single-crystal X-ray diffraction and are shown in Figure 1.<sup>15</sup> The structures of **2a** and **2b** are isomorphous with the corresponding previously reported hexamolybdate analogues  $[\text{Mo}_6\text{O}_{18}(\text{NAr})]$  **1a** and  $[\text{Mo}_6\text{O}_{18}(\text{NArI})]$  **1d**, respectively.<sup>11</sup> Both compounds crystallize in the triclinic space group  $P\bar{1}$ . In the case of **2b**, the asymmetric unit contains two crystallographically independent



**Figure 2.** UV/vis absorption spectra of  $[\text{Mo}_6]$ ,  $[\text{W}_6]$ ,  $[\text{W}_5\text{Mo}]$ , **2a**, and **2b**.

**Table 1.** Comparison of Bond Lengths (Å) and Bond Angles (deg) of Selected Bonds

	<b>1a</b>	<b>2a</b>	<b>1d</b>	<b>2b</b>
Mo–N–C	178.4	178.7	172.8	172.8
Mo–N	1.723	1.705	1.733	1.717
Mo–O <sup>c</sup>	2.232	2.259	2.222	2.238

cluster anions, which are conformational isomers differing by a rotation of the aromatic ring relative to the cluster skeleton. For simplicity, only one anion in the asymmetric unit of **2b** is shown in Figure 1. As expected, the arylimido ligand bonds to the molybdenum atom on each cluster cage. Compared to their hexamolybdate analogues, **2a** and **2b** have noticeably shorter Mo–N bonds and longer Mo–O<sup>c</sup> (central oxygen atom inside the octahedral cage) bonds (Table 1). These results suggest a stronger Mo–N triple-bond character in **2a** and **2b** than in their corresponding hexamolybdate analogues, which is consistent with the above NMR results.

Figure 2 shows the UV/vis absorption spectra of the tetrabutylammonium salts of  $[\text{Mo}_6\text{O}_{19}]^{2-}$ ,  $[\text{W}_6\text{O}_{19}]^{2-}$ ,  $[\text{MoW}_5\text{O}_{19}]^{2-}$ , **2a**, and **2b**. The ligand-to-metal charge-transfer (LMCT) band for  $[\text{W}_6\text{O}_{19}]^{2-}$  is at 280 nm, and that for  $[\text{Mo}_6\text{O}_{19}]^{2-}$  is at 325 nm. Both bands appear in the absorption of the  $[\text{MoW}_5\text{O}_{19}]^{2-}$  anion. After functionalization, the lowest energy electronic transition is continuously bathochromically shifted from parent  $[\text{MoW}_5\text{O}_{19}]^{2-}$  anion to **2a** (346 nm) and **2b** (356 nm), indicating that the Mo–N  $\pi$ -bond is delocalized with the organic conjugated  $\pi$ -electrons.

In summary, we have successfully synthesized the first two arylimido derivatives of the mixed-metal hexametalates, one of which carries an additional iodo functional group. With our previous demonstration that iodo- or ethynyl-functionalized POMs can undergo Pd-catalyzed coupling reactions,<sup>8</sup> it is now possible to construct, rationally, hybrid molecular dumbbells with two different cluster balls linked by a  $\pi$ -conjugated organic rod. Work in this area is in progress at our laboratory.

**Acknowledgment.** We thank Research Corporation, the Petroleum Research Fund, administered by the American Chemical Society, and the office of Naval Research for supporting this work.

**Supporting Information Available:** Listings of X-ray crystallographic data in CIF format. Synthetic procedures, analytic,  $^1\text{H}$  NMR, and UV/vis data in a PDF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0155683

(15) Summary of crystal structure data for  $[\text{Bu}_4\text{N}]_2\cdot\mathbf{2a}$ : triclinic,  $P\bar{1}$ ,  $a = 12.1263(8)$  Å,  $b = 12.5352(8)$  Å,  $c = 19.6952(13)$  Å,  $\alpha = 107.4000(10)^\circ$ ,  $\beta = 97.4770(10)^\circ$ ,  $\gamma = 100.2830(10)^\circ$ ,  $V = 2756.7(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 2.298$  g cm<sup>-3</sup>, 19872 reflections,  $R1 = 0.0646$ ,  $wR2 = 0.1685$ . Summary of crystal structure data for  $[\text{Bu}_4\text{N}]_2\cdot\mathbf{2b}$ : triclinic,  $P\bar{1}$ ,  $a = 12.4733(7)$  Å,  $b = 18.9703(11)$  Å,  $c = 25.5648(15)$  Å,  $\alpha = 103.6750(10)^\circ$ ,  $\beta = 91.9540(10)^\circ$ ,  $\gamma = 99.4630(10)^\circ$ ,  $V = 5780.9(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 2.336$  g cm<sup>-3</sup>, 41944 reflections,  $R1 = 0.0589$ ,  $wR2 = 0.1418$ .