J. Am. Chem. Soc. **2001,** *123,* 4083−4084 4083

An Efficient and Convenient Reaction Protocol to Organoimido Derivatives of Polyoxometalates

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Received November 21, 2000

In this communication, we wish to report a convenient and highly efficient reaction protocol for the direct functionalization of polyoxometalates (POMs). POMs, clusters of early transition metal cations bridged by oxide anions, are a unique class of inorganic compound with fascinating structural, electrochemical, and photophysical properties.[1−4] Developing appropriate approaches to modify the surface of these clusters through covalently bonded organic species may provide a rational way to not only fine-tune the materials properties but also bring about novel synergistic effects between inorganic clusters and organic segments.[5] Indeed, great effort has been made in recent years on the functionalization of POM clusters, particularly the hexamolybdate ion, $[Mo_6O_{19}]^{2-}$.[6−13] Thanks largely to the work of Maatta,[6−10] Proust,[11] and Errington,[12,13] three types of reactions have been discovered, namely reactions with phophinimines, isocyanates, and aromatic amines. They all result in organoimido derivatives of hexamolybdates.

While a number of imido derivatives of $[Mo_6O_{19}]^{2-}$ have been prepared using these three approaches,[6−13] there are some limitations preventing the broad application of these reactions. For example, phosphinimines and isocyanates are not easily accessible. Furthermore, their reaction with $[Mo_6O_{19}]^{2-}$ needs to be carried out under strictly anhydrous conditions for a prolonged time (several days).[6−10] The reaction conditions of $[Mo_6O_{19}]^{2-}$ with aromatic amines are even harsher (benzonitrile as the solvent and a reaction temperature of 150 °C), and only moderate yields can be obtained.[12,13] In this paper, we report our recent discovery that dicyclohexylcarbodiimide (DCC) or other diimides can dramatically facilitate the reaction of $[Mo_6O_{19}]^{2-}$ with aromatic amines. In the presence of 1 equiv of DCC, $[Mo_6O_{19}]^{2-}$ reacts smoothly with a variety of aromatic amines under refluxing acetonitrile. The reaction is usually completed in less than 12 h, and yields greater than 90% (based on *pure crystalline products*) can be readily obtained.

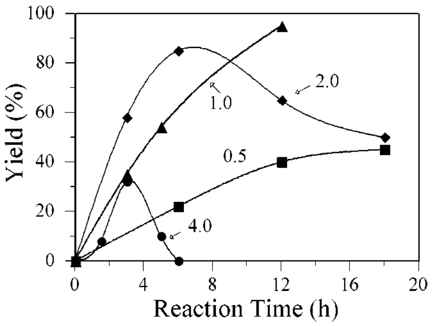

Figure 1. Effect of DCC on the reaction rates and yields of $[Mo_6O_{19}]^{2-}$ with 2,6-dimethylaniline. The reactions were carried out in refluxing acetonitrile under nitrogen. The number next to each curve indicates the number of equiv of DCC added.

The effect of DCC on the reaction of $[Mo_6O_{19}]^{2-}$ with aromatic amines is shown in Figure 1. Without the addition of DCC, no reaction is observed, even after refluxing for a prolonged time (>2 days) and with the addition of triethylamine, a reported catalyst for this reaction.[13] With the addition of 0.5 equiv of DCC, a yield close to 50% can be obtained after 18 h of reaction. If 1 equiv of DCC is added, a yield of 95% can be obtained in only 12 h. Clearly, the addition of DCC dramatically facilitates the reaction of $[Mo_6O_{19}]^{2-}$ with aromatic amines. Replacing DCC with drying agents such as magnesium sulfate or even calcium hydride does not show similar activation effect. This suggests that DCC does not simply serve as a dehydration agent. While more work needs to be done to shed light on the detailed reaction mechanism, the likely role of DCC is to activate the terminal Mo−O bond, similar to its activating effect on the carboxyl group in peptide synthesis.

When more than 1 equiv of DCC is added, the reaction is even faster. However, the reaction yield decreases. As shown in Figure 1, as the reaction time increases, the reaction yield increases initially, reaches the maximum, and then decreases. For example, with the addition of 4 equiv of DCC, the highest yield is only 33% which is reached in merely 3 h. No product is isolated after reacting for 6 h. Presumably, the excess amount of DCC reacts with the initially formed products. We have actually isolated the major side product which is found to be β-$[Mo_8O_{26}]$.[4−14]

It is worth pointing out that, while the above results are based on reactions carried out under nitrogen protection, the reaction of $[Mo_6O_{19}]^{2-}$ with aromatic amines can be carried out in the open air. Yields greater than 90% can still be obtained if slightly over 1 equiv of DCC (1.1−1.2 equiv) is added. This feature makes this new reaction system particularly attractive for the functionalization of other larger polyoxometalates, which usually contain water of crystallization. Work in this area has been undertaken in our laboratory.

Compared to the literature reaction systems, the new reaction protocol has the advantage in that it is faster, more efficient, and the reaction conditions are much milder. With aromatic amines easily accessible, a great number of organoimido derivatives of hexamolybdate can now be synthesized in high yields and with ease. Best of all, the new reaction protocol tolerates functional groups such as halides and ethynyl groups as shown in Table 1. Compounds **Id** and **Ie**, to our knowledge, represent the first

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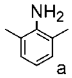
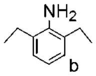
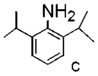
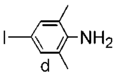
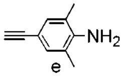
(14) See Supporting Information for detailed structural data.

10.1021/ja004033q CCC: $20.00

Table 1. Reaction Yields of $[Mo_6O_{19}]^{2-}$ with Various Aromatic Amines

ArNH2	 a	 b	 c	 d	 e
Product	Ia	Ib	Ic	Id	Ie
Yield (%)[a]	95	95	91	72	91

[a] The reaction yields are calculated on the basis of pure crystalline products, 1 equiv of amine and 1 equiv of DCC were employed. The reaction time is 12 h.

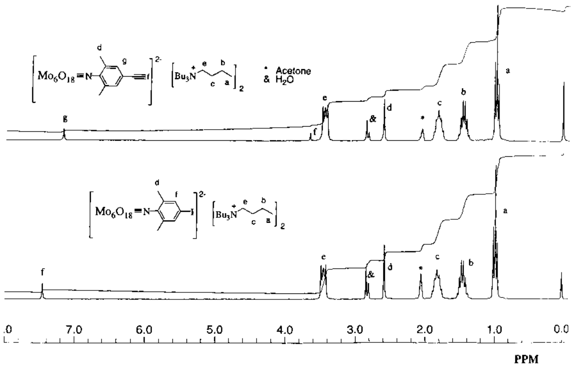


Figure 2. ^1H NMR spectra of compounds **Id** and **Ie** in acetone-d_6.

examples of iodo- and ethynyl-functionalized hexamolybdates, respectively.[15] These compounds are valuable building blocks to construct organic/inorganic hybrid materials. As a matter of fact, we have demonstrated for the first time that these compounds can undergo Pd-catalyzed coupling reactions, and novel hybrid materials containing covalently bonded metal−oxygen clusters and organic conjugated segments can be synthesized. The full details regarding the synthesis of these hybrid materials will be published in a separate paper shortly.

The ^1H NMR spectra of Compounds **Id** and **Ie** are shown in Figure 2. Both spectra show clearly resolved signals which can all be unambiguously assigned. The integration matches well with the proposed structure. Compared to the ^1H NMR spectra of the corresponding free amines (Compounds **d** and **e**), all protons exhibit higher chemical shifts after imido bond formation. For example, the chemical shift for the ethynyl proton has changed from 2.94 ppm in **e** to 3.66 pm in **Ie**. Such a shift is consistent with the electron-withdrawing nature of the Mo−N triple bond.

The electronic properties of functionalized hexamolybdates were studied by UV/vis absorption measurements. The lowest-energy electronic transition is continuously bathochromically shifted from parent $[Mo_6O_{19}]^{2-}$ (325 nm) to **Ia** (350 nm), **Id** (365 nm), and **Ie** (370 nm), indicating that the Mo−N π-bond is delocalized with the organic conjugated π-electrons. In other words, there is a strong electronic interaction between the metal−oxygen cluster and the organic conjugated segment.

The molecular structures of **Ia**, **Id**, and **Ie** have been determined by single-crystal X-ray diffraction. All of these compounds crystallize in the triclinic space group $P\bar{1}$. In the case of **Id** and **Ie**, the asymmetric units contain two crystallographically independent anions, which are conformational isomers differing by a rotation of the aromatic ring relative to the hexamolybdate skeleton. For the sake of simplicity, only one anion for each of the asymmetric units for **Id** and **Ie** is shown in Figure 3. In both structures, the Mo−N−C bond angles are close to 180° (172.3° for **Id** and 172.6° for **Ie**), indicating a substantial degree of Mo≡N triple bond character.[16] The central oxygen atom inside the hexamolybdate cage is drawn closer to the imido-bearing Mo atom, while the four bridge oxygen atoms are pushed away from the imido-bearing Mo atom. Such structural features have been observed in other arylimido derivatives of hexamolybdates.[6−13]

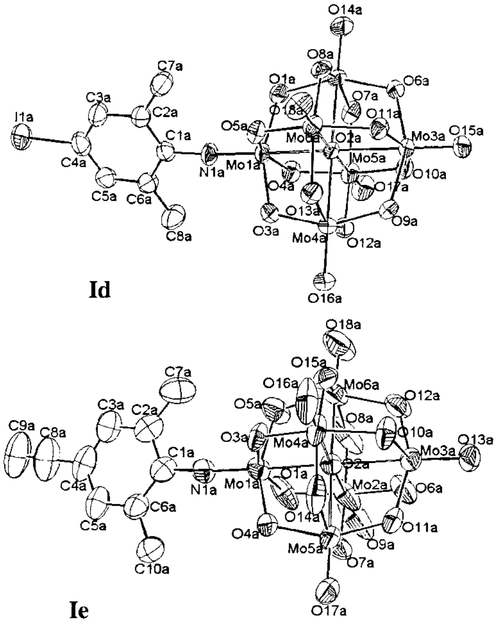


Figure 3. ORTEP representation and labeling scheme for the functionalized hexamolybdate anions within **Id** and **Ie**.

In conclusion, we have discovered a novel reaction protocol for the efficient functionalization of polyoxometalates. Compared to previous reported methods, this new method allows the reaction to be carried out under much milder conditions, with much faster rates and with much higher yields. It can also tolerate a variety of organic functional groups. With aromatic amines widely accessible, a great number of organoimido derivatives of hexamolybdates can now be synthesized in high yields and with ease. The iodo- and ethynyl-functionalized hexamolybdates are valuable building blocks to construct hybrid molecular materials containing covalently bonded metal−oxygen clusters and organic conjugated segments.

Acknowledgment. We thank Research Corporation for the support of this work.

Supporting Information Available: Synthetic procedures, structural data (PDF). X-ray crystallographic files for **Ia**, **Id**, **Ie**, and $[Mo_8O_{26}]^{4-}$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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