An Easy Route to Monofunctionalized Organoimido Derivatives of the Lindqvist Hexamolybdate

Pingfan Wu,[a,c] Qiang Li,[b] Ning Ge,[a] Yongge Wei,*[a] Yuan Wang,[a] Ping Wang,[b] and Hongyou Guo*[b]

Keywords: Organoimido Derivatives / Polyoxometalates / Acid Catalysis / Dehydration / Organic−inorganic hybrid

In the presence of a carbodiimide (DCC) a proton can dramatically speed up the reaction of α-$[Mo_8O_{26}]^{4-}$ with aromatic amines under mild conditions and convenient bench manipulations, which results in the easy synthesis of monofunctionalized organoimido derivatives of $[Mo_6O_{19}]^{2-}$ even bearing an electron-withdrawing group such as bromo or chloro groups.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

The surface modification of polyoxometalates, that is, the substitution of a terminal oxo or M=O group with organic species,[1,2] has received increasing interest in recent years because it can afford a way to conveniently and effectively construct novel organic−inorganic hybrid materials[3−9] with the so-called "value-adding properties"[10] and possible synergistic effects.[11] Organoimido derivatives,[8,9,11−24] which were first reported by E. A. Maatta et al.,[15] are amongst the most important organic derivatives of polyoxometalates obtained by surface modification, since the π electrons in the organic component may extend their conjugation to the inorganic framework and thus dramatically modify the electronic structure and redox properties of the corresponding parent polyoxometalates.[10−12] In addition, organoimido derivatives of polyoxometalates with a remote, active functional group may be exploited to prepare covalently-linked nano-dumbbells,[13,14] polymeric chains[9] and even networks of polyoxometalates in more controllable manners.

So far, the synthesis of organoimido derivatives of polyoxometalates has focused mainly on Lindqvist polyoxometalates such as the hexamolybdate ion, $[Mo_6O_{19}]^{2-}$, the hexatungstate ion, $[W_6O_{19}]^{2-}$, and the pentatungstenmolybdate ion, $[MoW_5O_{19}]^{2-}$, obtained by reactions with phosphinimines,[15,16] isocyanates[17−19] or aromatic amines.[20,21] As we know, it is very difficult to prepare organoimido derivatives of polyoxometalates bearing an electron-withdrawing group in reasonable yield and high purity using the three approaches mentioned above. However, one of us, together with his co-workers[22,23] at UMKC, has recently developed an efficient and convenient reaction protocol to give monofunctionalized arylimido derivatives of polyoxometalates with a carbodiimide, that is, DCC (*N*,*N*′-dicyclohexylcarbodiimide), as the dehydrating agent. Furthermore, a first attempt to modify the α-octamolybdate ion, α-$[Mo_8O_{26}]^{4-}$, with this approach resulted in the selective synthesis of bifunctionalized arylimido derivatives of hexamolybdate, in a degradation and re-assembly process, with reasonable yield and high purity.[9] However, under such active reaction conditions, it was still not possible to functionalize polyoxometalates with aromatic amines bearing electron-withdrawing groups, for example, bromo and chloro groups, because of the weak nucleophilicity and easy oxidization of these kinds of amines. In this communication, we report our recent discovery that a proton can dramatically speed up the reaction of α-$[Mo_8O_{26}]^{4-}$ with aromatic amines under much milder conditions and, in the meanwhile, monofunctionalized organoimido derivatives of $[Mo_6O_{19}]^{2-}$, bearing even electron-withdrawing groups such as *para*-chloroaniline, *meta*-chloroaniline, *ortho*-chloroaniline and *para*-bromoaniline, are selectively synthesized in high purity and moderate yield with easy bench manipulations. As examples, the synthesis and structural characterization of five arylimido derivatives, $(Bu_4N)_2[Mo_6O_{18}(=NAR)]$, (where AR = *o*-$CH_3C_6H_4$ **1**, AR = *p*-ClC_6H_4 **2**, AR = *o*-ClC_6H_4 **3**, AR = *m*-ClC_6H_4 **4**, AR = *p*-BrC_6H_4 **5**) will be introduced here.[25]

[a] State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China
Fax: + 86-10-62751708
E-mail: ygwei@pku.edu.cn
[b] Department of Chemistry, Beijing University of Chemical and Technology, Beijing 100029, China
E-mail:guohy@public.fhnet.cn.net
[c] Department of Bioengineering, Hubei Polytechnic University, Wuhan 430068, China

Results and Discussion

When a mixture of $(Bu_4N)_4$·[α-Mo_8O_{26}], an aromatic amine and its hydrochloride salt, and DCC or other carbodiimides is refluxed in anhydrous acetonitrile under nitrogen, the corresponding monofunctionalized organoimido derivative of $[Mo_6O_{19}]^{2-}$ is formed and this reaction is usually complete in about six hours. However, under the same conditions, no anticipatory dehydrating reaction was observed for $(Bu_4N)_2$·$[Mo_6O_{19}]$. Instead, it was reduced, while the aromatic amine was oxidized. The key role of DCC here is to act as a special dehydrating agent with an activating effect on the terminal Mo−O bond, which is similar to its activating effect on the carboxyl group in the synthesis of amide or peptides.[22] In our tests, the amount of DCC is equivalent to, or slightly higher than that of the water needed to be removed from the reaction system because excess DCC usually results in unexpected side reactions and reduces the yield of the products.[22]

It was observed that no hydrochloride salt is present, *o*-toluidine or other active aromatic amines with an electron-donating group, react with α-$[Mo_8O_{26}]^{4-}$ to produce only the bifunctionalized arylimido derivatives of hexamolybdate.[9] On the other hand, under the same conditions, no reaction occurs between α-$[Mo_8O_{26}]^{4-}$ and *para*-chloroaniline or other inert aromatic amines with an electron-withdrawing group, except for the oxidation of the corresponding amines. However, for both types of aromatic amines, the addition of hydrochloride salts to the reaction mixture results in the formation of monofunctionalized organoimido derivatives of hexamolybdate, for instance, **1** and **2**. Moreover, the reaction can be speeded up by increasing the amount of hydrochloride salts. It is also worth pointing out that this novel routine can be carried out even at room temperature. The hydrochloride salt is, in fact, a proton carrier that introduces the proton into the reaction mixture. While more work needs to be done to shed light on the detailed reaction mechanism, the likely role of the proton is to complex with DCC and hence to increase the electrophilic ability of DCC to attack the oxo group of Mo−O. Additionally, it also promotes the conversion of the octamolybdate into the hexamolybdate through a degradation and re-assembly process since in an acidic organic solvent, hexamolybdates and its derivatives are much more stable than octamolybdates.[9]

The optimum reaction conditions, including the amount of each raw material and the reaction time, can be obtained by monitoring the reaction system by TLC, UV or ^{1}H NMR technology and a favorable routine is given in the Exp. Sect. Compared to previous methods presented in the literature,[15−23] this novel reaction route has many advantages: it is faster and is usually complete in less than 6 h, it is more efficient with easy bench manipulations, and the reaction conditions are much milder. Best of all, this approach tolerates electron-withdrawing functional groups such as chloro and bromo. With aromatic amine chlorides or bromides easily accessible, a great number of organoimido derivatives of hexamolybdate bearing halogen groups can now be easily synthesized in reasonable yield. Thus, this reaction opens alternative ways to make organic−inorganic hybrids based on polyoxometalates in a much more controlled fashion.[24] Related work is underway in our laboratory and will be published in subsequent papers.

The composition and structures of compounds **1**, **2**, **3**, **4**, and **5** were initially obtained according to elemental analysis, and IR, ^{1}H NMR, and UV/Vis spectroscopy studies. The IR spectra of the compounds are similar to those of previously reported mono organoimido derivatives, and the strong shoulder peak near 974 cm^{-1} proves them to be the mono-organoimido substitution derivatives.[15,16,21,26] Compared to the ^{1}H NMR spectra of corresponding free amine ligands, the protons of **1**, **2**, **3**, **4**, and **5**, except for those in the tetrabutylammonium cation, all exhibit significantly downfield chemical shifts, indicating that the shielding nature of $[Mo_5O_{18}(Mo{\equiv}N-)]^{2-}$ is much weaker than that of the amino group NH_2-. The fact that the chemical shifts of the aromatic protons in **2**, **3**, **4**, and **5** are higher than in **1** implies that the Mo≡N bond in **2**, **3**, **4**, and **5** is more electron withdrawing than in **1**, which is in good agreement with the electronic character of their imido ligands: **1** has an electron-donating methyl group (CH_3) whereas **2**, **3**, **4**, and **5** have an electron-withdrawing halogen group (Cl or Br). The lowest energy L→M electronic transition at 325 nm in $[Mo_6O_{19}]^{2-}$ is bathochromically shifted by more than 20 nm and becomes considerably more intense in **1** (350 nm), **2** (346 nm), **3** (345 nm), **4** (344 nm), and **5** (345 nm), which indicates that the Mo−N π-bond is formed in these organoimido derivatives. The bathochromic shift on going from **2**, **3**, **4**, and **5** to **1** is consistent with the trend in the π-donor ability of imido ligands.

The molecular structures of **1** and **2** have also been confirmed by single-crystal X-ray diffraction analysis[27] and their cluster anions are shown in Figure 1. In both struc-

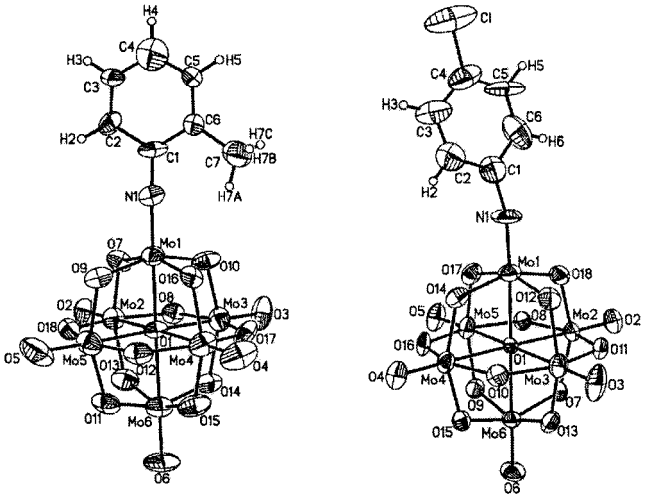
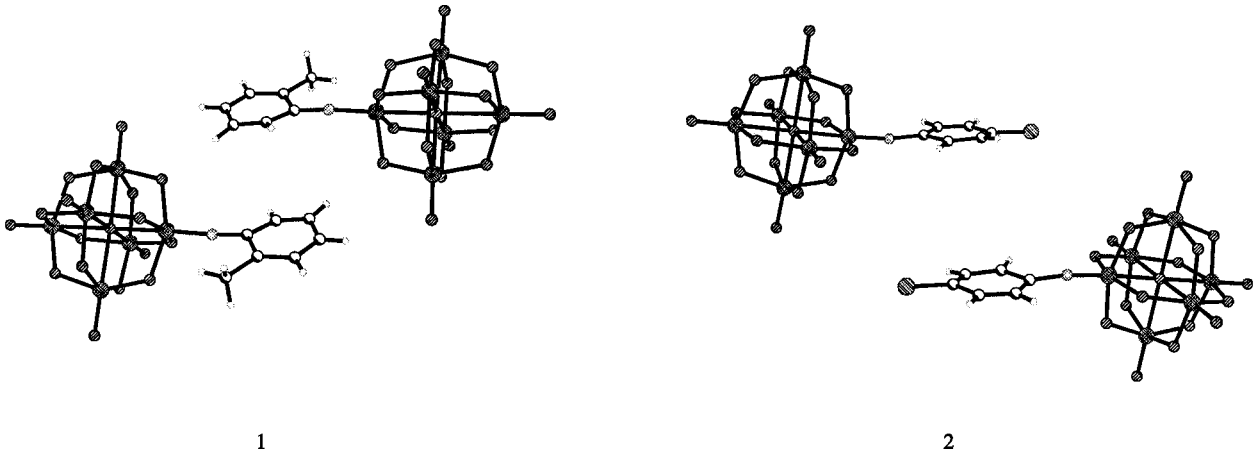


Figure 1. ORTEP drawings of the cluster anions of **1** and **2**

 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



1 **2**

Figure 2. Showing of the dimer structure of cluster anions of **1** and **2**

tures, the arylimido ligands are indeed bound to a terminal position of the hexamolybdate in a monodentate fashion. The short Mo−N bond lengths [1.772(18) Å in **1** and 1.686(5) Å in **2**] and the C−N−Mo bond angles close to 180° (173.9° for **1** and 163.6° for **2**) are typical of organoimido groups bound to an octahedral d^0 metal center and are consistent with a substantial degree of Mo≡N triple bond character.[28] The C(1)−N(1)−Mo(1) bond angle of **2** is in agreement with angles of other derivatives bearing *para*-only-replaced phenylimido ligands and substantially smaller than the angles of **1** and other derivatives bearing *ortho*-replaced phenylimido ligands. Since the shortening of the Mo≡N bond is not observed for *ortho*-replaced phenylimido ligands derivatives, and **2** and other derivatives with *para*-only replaced phenylimido groups all crystallize in the same monoclinic space group of No. 14, this difference is probably due to the force of the crystal packing. Compared to the hexamolybdate and other derivatives, the bond lengths of the five terminal oxo ligands of **1** and **2** do not vary appreciably. The Mo(1)−O(1) distances between the Mo-bearing imido group and the central oxygen atom within the cluster anion cage are both significantly shorter than the other Mo−O(1) distances. An analogous contraction was noticed in the structures of other monofunctionalized imido derivatives of Lindqvist polyoxometalates reported in the literature,[11−24] which implies that there are no appreciable differences in their molecular structures. However, an important feature that should be pointed out here is the dimerization of cluster anions of **1** and **2** in the solid state through the π-π stacking of parallel phenyl rings of two neighboring cluster anions (see Figure 2). The existence of supramolecular π-π interactions between the pairs of cluster anions is clearly indicated by the short vertical phenyl ring separation of 3.136 and 3.796 Å in **1** and **2**, respectively. Such a structural feature has not been mentioned before in the reported mono phenylimido derivatives of hexamolybdate.[11−24]

Conclusion

In summary, we have developed a novel reaction route to give organonimido derivatives of Lindqvist polyoxometalates by introducing a proton. Compared to literature methods, even in the case of aromatic amines with an electron-withdrawing halogen group, this new method allows the reaction to be carried out under much milder conditions, even at room temperature, with much faster reaction rates and reasonable yield. With aromatic amine chlorides or bromides widely accessible and much cheaper than the corresponding iodides, this new approach provides an alternative way to efficiently construct novel, hybrid molecular materials containing covalently-bonded metal−oxygen clusters and organic conjugated segments. Extension of this approach to other polyoxometalates is still under study in our laboratory.

Experimental Section

A typical synthesis is as follows: a mixture of $(Bu_4N)_4$·[α-Mo_8O_{26}] (1.0 mmol), DCC (3.4 mmol), aromatic amine (1.34 mmol) and its salt (1.34 mmol) was refluxed under nitrogen in anhydrous acetonitrile (10 mL) for about 6 h. During the course of the reaction the color of the solution changed into red-brown, and some white precipitates (*N*,*N*′-dicyclohexylurea) were formed. The resulting dark-red solution was cooled down to room temperature and the white precipitates were removed by filtration. While most of the acetonitrile evaporated slowly in the open air, the product precipitated from the filtrate as a red colloid-like solid. The product was collected by filtration, washed successively with EtOH or benzene and Et_2O for several times, and then recrystallized twice from the mixture of acetone and EtOH (1:1), the product deposited as orange crystals usually in moderate yield of ca. 40 to 50 %.

1 (yield, 52 %): $C_{39}H_{79}Mo_6N_3O_{18}$ (1453.7): calcd. C 32.22, H 5.48, N 2.89; found C 32.51, H 5.46, N 2.85. ^{1}H NMR (600 MHz, CD_3CN, 300 K): δ = 0.98 (t, 24 H, CH_3-, $[Bu_4N]^+$), 1.38 (m, 16

 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

H, -CH_2-, $[Bu_4N]^+$), 1.62 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 2.61 (s, 3 H, CH_3-, CH_3-Ar), 3.12 (t, 16 H, NCH_2-, $[Bu_4N]^+$), 7.26 (m, 1 H, *o*-ArH), 7.21 (m, 2 H, *m*-ArH), 7.04(m, 1 H, *p*-ArH) ppm. IR (KBr pellet, major absorbances): 2961, 2873, 1638, 1619, 1478, 1378, 1323, 1194, 1173, 1118, 1107, 1064, 1027, 997, 952 with shoulder at 973, 883, 794 with shoulder at 710, 661, 599 cm^{-1}. UV/Vis (MeCN): λ_{max}/nm = 235 (3.2×10^4), 245 (3.3×10^4), 350 (2.0×10^4) $\varepsilon/M^{-1}cm^{-1}$. Crystals suitable for single-crystal X-ray diffraction were grown from a mixed solution of acetone and EtOH (1:1).

2 (yield, 45 %): $C_{38}H_{76}ClMo_6N_3O_{18}$ (1474.1): calcd. C 30.96, H 5.20, N 2.85; found C 30.54, H 5.22, N2.49. ^{1}H NMR (600 MHz, CD_3CN, 300 K): δ = 0.98 (t, 24 H, CH_3-, $[Bu_4N]^+$), 1.38 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 1.62 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 3.12 (t, 16 H, NCH_2-, $[Bu_4N]^+$), 7.23, 7.24 (2 H, *o*-H-Ar), 7.40, 7.41 (2 H, *m*-H-Ar) (AA′BB′ "quadruplet', 4 H, Ar) ppm. IR (KBr pellet, major absorbances): 2963, 2874, 1639, 1620, 1473, 1380, 1336, 1171, 1090, 954 with shoulder at 975, 884, 795 with shoulder at 710, 602 with shoulder at 637 cm^{-1}. UV/Vis (MeCN): λ_{max}/nm = 226 (3.5×10^4), 254 (3.5×10^4), 346 (2.2×10^4) $\varepsilon/M^{-1}cm^{-1}$. X-ray quality crystals were obtained from a mixed solution of acetone and EtOH (1:1).

3 (monofunctionalized derivative of *o*-chloroaniline: yield, 50 %): ^{1}H NMR (600 MHz, CD_3CN, 300 K): δ = 0.99 (t, 24 H, CH_3-, $[Bu_4N]^+$), 1.40 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 1.63 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 3.13 (t, 16 H, NCH_2-, $[Bu_4N]^+$), 7.35 (m, 2 H, *p*-H-Ar), 7.47 (m, 2 H, *o*-H-Ar) ppm. UV/Vis (MeCN): λ_{max}/nm = 223, 247, 345.

4 (monofunctionalized derivative of *m*-chloroaniline: yield, 48 %): ^{1}H NMR (600 MHz, CD_3CN, 300 K): δ = 0.99 (t, 24 H, CH_3-, $[Bu_4N]^+$), 1.40 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 1.63 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 3.12 (t, 16 H, NCH_2-, $[Bu_4N]^+$), 7.20(m, 1 H, *m*-*m*-H-Ar), 7.24 (s, 1 H, *o*-*o*-H-Ar), 7.38, 7.39 (d, 2 H, *o*-*p*-H-Ar) ppm. UV/Vis (MeCN): λ_{max}/nm = 225, 248, 344.

5 (monofunctionalized derivative of *p*-bromoaniline: yield, 48 %): ^{1}H NMR (600 MHz, CD_3CN, 300 K): δ = 0.99 (t, 24 H, CH_3-, $[Bu_4N]^+$), 1.40 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 1.63 (m, 16 H, -CH_2-, $[Bu_4N]^+$), 3.12 (t, 16 H, NCH_2-, $[Bu_4N]^+$), 7.14, 7.15 (2 H, *o*-H-Ar), 7.56, 7.57 (2 H, *m*-H-Ar) (AA′BB′ "quadruplet', 4 H, Ar) ppm. UV/Vis (MeCN): λ_{max}/nm = 223, 246, 345.

Acknowledgments

This work is sponsored by NFSC No 20201001, SRF for ROCS of SEM and MOST No TG2000077503. It is also partially supported by the university funding from Hubei Polytechnic University. Y. W. also thanks Prof. Peng for professional support when he was at UMKC.

[1] *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, 1994.
[2] P. Gouzerh, A. Proust, *Chem. Rev.* **1998**, *98*, 77.
[3] P. Judeinstein, *Chem. Mater.* **1992**, *4*, 4.
[4] C. R. Mayer, V. Cabuil, T. Lalot, R. Thouvenot, *Angew. Chem.* **1999**, *111*, 3878; *Angew. Chem. Int. Ed.* **1999**, *38*, 3672.
[5] R. C. Schroden, C. F. Blanford, B. J. Melde, B. J. S. Johnson, A. Stein, *Chem. Mater.* **2001**, *13*, 1704.
[6] H. Zeng, G. R. Newkome, C. L. Hill, *Angew. Chem.* **2000**, *112*, 1841; *Angew. Chem. Int. Ed.* **2000**, *39*, 1771.
[7] A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot, F. Sécheresse, *Chem. Eur. J.* **2003**, *9*, 2914.
[8] A. R. Moore, H. Kwen, A. B. Beatty, E. A. Maatta, *Chem. Commun.* **2000**, 1793.
[9] L. Xu, M. Lu, B. Xu, Y. Wei, Z. Peng, D. R. Powell, *Angew. Chem.* **2002**, *114*, 4303; *Angew. Chem. Int. Ed.* **2002**, *41*, 4129.
[10] D. E. Katsouli, *Chem. Rev.* **1998**, *98*, 359.
[11] J. L. Stark, V. G. Young Jr., E. A. Maatta, *Angew. Chem.* **1995**, *107*, 2751; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2547.
[12] J. B. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh, E. A. Maatta, *J. Am. Chem. Soc.* **2000**, *122*, 639.
[13] J. L. Stark, A. L. Rheingold, E. A. Maatta, *J. Chem. Soc., Chem. Commun.* **1995**, 1165.
[14] M. Lu, Y. Wei, B. Xu, C. F.-C. Cheung, Z. Peng, D. R. Powell, *Angew. Chem.* **2002**, *114*, 1636; *Angew. Chem. Int. Ed.* **2002**, *41*, 1566.
[15] Y. Du, A. L. Rheingold, E. A. Maatta, *J. Am. Chem. Soc.* **1992**, *114*, 345.
[16] A. Proust, R. Thouvenot, M. Chaussade, F. Robert, P. Gouzerh, *Inorg. Chim. Acta* **1994**, *224*, 81.
[17] W. Clegg, R. J. Errington, K. A. Fraser, C. Lax, D. G. Richards, *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, 1994, p 113.
[18] J. B. Strong, R. Ostrander, A. L. Rheingold, E. A. Maatta, *J. Am. Chem. Soc.* **1994**, *116*, 3601.
[19] T. R. Mohs, G. P. A. Yap, A. L. Rheingold, E. A. Maatta, *Inorg. Chem.* **1995**, *34*, 9.
[20] W. Clegg, R. J. Errington, K. A. Fraser, S. A. Holmes, A. Schäfer, *Chem. Commun.*1995, 455.
[21] R. A. Roesner, S. C. McGrath, J. T. Brockman, J. D. Moll, D. X. West, J. K. Swearingen, A. Castineiras, *Inorg. Chim. Acta* **2003**, *342*, 37.
[22] Y. Wei, B. Xu, C. L. Barnes, Z. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 4083.
[23] Y. Wei, L. Meng, C. F.-C. Cheung, C. L. Barnes, Z. Peng, *Inorg. Chem.* **2001**, *40*, 5489.
[24] B. Xu, Y. Wei, C. L. Barnes, Z. Peng, *Angew. Chem.* **2001**, *113*, 2353; *Angew. Chem. Int. Ed.* **2001**, *40*, 2290.
[25] Coupound **2** has been reported briefly without detailed synthesis and characterization by A Proust et al. (see reference[1], p 34).
[26] W. Nugent, J. E. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, 1988, p 123−125.
[27] Crystal structure data for **1**: C_{39} H_{79} Mo_6 N_3 O_{18}, M_r = 1453.69, triclinic, $P\bar{1}$, a = 12.266(3), b = 12.337(3), c = 19.788(4) Å, α = 105.98(3), β = 97.55(3), γ = 98.44(3)°, V = 2800.6(10) Å^3, Z = 2, $\rho_{calcd.}$ = 1.724 Mg/m^3, T = 293(2) K, $R1$= 0.0661, and $wR2$ = 0.1416 with GOF = 0.718. Crystal structure data for **2**: C_{38} H_{76} Cl Mo_6 N_3 O_{18}, M_r = 1474.11, monoclinic, $P2_1/n$, a = 17.615(4), b = 17.623(4), c = 19.284(4) Å, β = 114.35(3)°, V = 5453.5(19) Å^3, Z = 4, $\rho_{calcd.}$ = 1.795 Mg/m^3, T = 293(2)K, $R1$ = 0.0441, and $wR2$ = 0.0783 with GOF = 0.803. CCDC-217580 and -217581 contain the supplementary crystallographic data for compounds **2** and **1**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB 21EZ,UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam. ac.uk).
[28] D. E. Wigley, *Prog. Inorg. Chem.* **1992**, *42*, 239.

Received February 25, 2004

 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim