Notes

Molybdenum Carbonyl Complexes with Citrate and Its Relevant Carboxylates

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Summary: Reactions of ammonium salts of citrate and its relevant carboxylates with a molybdenum(0) carbonyl complex $(C_7H_8)Mo(CO)_3$ *resulted in the formation of* $(Et_4N)_3[(Hcit)Mo(CO)_3]$ (**1**), $(Et_4N)_2[(Hcmal)Mo(CO)_3]$ (**2**), $(Et_4N)_2[(Hmal)Mo(CO)_3]$ (**3**), *and* $(Me_4N)_2[(Meida)Mo(CO)_3]$ (**4**), *which are the first examples of organomolybdenum complexes having a tri- or dicarboxylate. Complexes* **1**−**4** *were characterized by means of IR and UV−vis spectra and elemental analyses. Molecular structures of all complexes were determined by an X-ray diffraction study. The molybdenum center adopts an octahedral coordination geometry with three carbonyl ligands and a tridentate ligand which displays a unique coordination to molybdenum with its carboxylates and hydroxyl group or nitrogen atom.*

Introduction

Tricarboxylic acids serve as important substrates in biochemical processes,[1] some of which are mediated by metalloenzymes. One of the well-characterized enzymes in this class is aconitase, which catalyzes the stereospecific interconversion of citrate and isocitrate via the intermediary *cis*-aconitate.[2] The active site consists of an Fe_4S_4 cluster having a citrate-binding site at one corner. Another enzyme in which the function of tricarboxylic acid is critical, but is insufficiently understood, is nitrogenase.[3] Its active site is unique among the metalloenzymes and exhibits an *R*-homocitrate-$MoFe_7S_9X$ (X = light element such as N or O) cluster, FeMo-co.[4] Within the cluster, the octahedral coordination sphere of molybdenum is occupied by three sulfides, a nitrogen atom from the imidazolyl group of a histidine residue, and two oxygen atoms from the alkoxy group and one carboxylate moiety of *R*-homocitrate. *R*-Homocitrate has been found to be necessary for the construction of a fully active cofactor capable of reducing dinitrogen.[5] Although the recent advances in X-ray structural analysis successfully led to the precise structure of FeMo-co,[4] the role of the organic moiety in dinitrogen reduction remains to be elucidated.[5] The reactivity of molybdenum citrate complex is an important part relating to the function of FeMoco. The synthetic procedure for molybdenum citrate complexes has been limited to the reaction of molybdate with citric acids in aqueous solution.[6] These complexes are insoluble in organic solvents and their oxo ligands are strongly bound to molybdenum, limiting further reactions. With the aim of embarking on the reaction chemistry of molybdenum citrate complexes, we focused on organo-molybdenum compounds with citrate or related polycarboxylate ligands, which have not appeared to date. As such, the synthesis of molybdenum carbonyl complexes was examined in expectation of several important properties, such as solubility in organic solvents, generation of a reaction site under certain conditions, and a strong interaction between molybdenum and polycarboxylates. Herein we describe the first preparation, characterization, and molecular structures of molybdenum carbonyl complexes having citrate and its relevant carboxylates.

Results and Discussion

Synthesis. The cycloheptatriene ligand in $(C_7H_8)Mo(CO)_3$ is readily liberated in solution to be replaced by carboxylates.[7] In the preparation of citrate^{3-} (Hcit^{3-}), 3 equiv of $(Et_4N)(OH)$ was added to a methanol solution of citric acid, giving rise to the ammnonium salt of citrate, $(Et_4N)_3(Hcit)$,[8] in situ. Addition of this solution to a methanol solution of $(C_7H_8)Mo(CO)_3$ at ambient temperature resulted in the color change from orange to yellow over 2 h to afford the organomolybdenum citrate complex $(Et_4N)_3[(Hcit)Mo(CO)_3]$ (**1**). After re-

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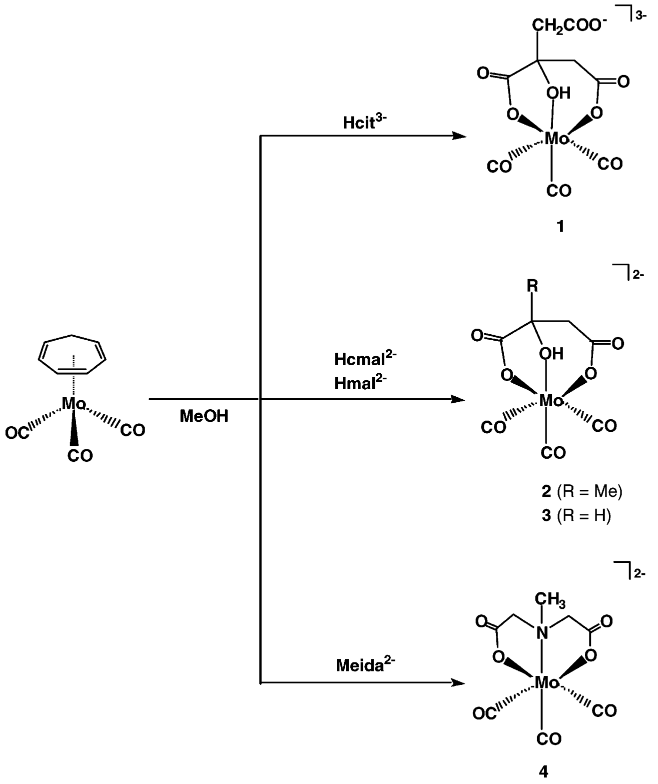
10.1021/om049072f CCC: $30.25

Scheme 1



moval of the solvent under reduced pressure, the product was crystallized as yellow needles from acetonitrile and diethyl ether. Complex **1** is moderately sensitive to oxygen and highly hygrophilic. Exposure of the solid to air leads to immediate deliquescence. This ought to be due to ready formation of hydrogen bonds between the uncoordinated carboxylate group of the Hcit^{3-} ligand and moisture. In contrast to the reported oxo-molybdenum citrate complexes,[6] complex **1** is well-soluble in organic solvents such as acetonitrile and methanol.

The ligand exchange reactions between cycloheptatriene and carboxylate anions were also successful with *R*-citramalate (Hcmal^{2-}), D-malate (Hmal^{2-}), and methyliminodiacetate (Meida^{2-}). These carboxylates were prepared from the reactions of the corresponding carboxylic acids with $(Et_4N)(OH)$ or $(Me_4N)(OH)$ in methanol. Treatment of $(C_7H_8)Mo(CO)_3$ with $(Et_4N)_2(L)$ (L = Hcmal, Hmal) or $(Me_4N)_2$(Meida) in methanol afforded a yellowish-orange solution, from which $(Et_4N)_2[(L)Mo(CO)_3]$ (L = Hcmal, (**2**), L = Hmal, (**3**)) or $(Me_4N)_2[(Meida)Mo(CO)_3]$ (**4**) were isolated as yellow crystals in high yields. Solubility of the products strongly depends on the cation part; as such, the Me_4N salt **4** is insoluble in acetonitrile, whereas the Et_4N salt **1** readily dissolves in acetonitrile.

Structures. The molecular structures of four complexes **1**−**4** were determined by X-ray diffraction studies. Crystallographic data are listed in Table 1.

Single crystals were grown from acetonitrile/ether (**1**), acetonitrile and methanol/ether (**2**, **3**), or methanol/ether (**4**), respectively. Representative drawings are depicted in Figure 1 (for **1**) and Figure 2 (for **4**), with selected bond lengths and angles summarized in Table 2.

The octahedral geometry resembles those of the other known tricarbonyl complexes of general formula $L_3Mo(CO)_3$, such as $Tp^*Mo(CO)_3^-$ (Tp* = hydrotris(3,5-dimethylpyrazolyl)borato),[9] (tiPrTACN)$Mo(CO)_3$ (tiPrTACN = 1,4,7-triisopropyl-1,4,7-triazacyclononane),[10] (TTCN)$Mo(CO)_3$ (TTCN = 1,4,7-trithiacyclononane),[11] and $[B(CH_2SCH_3)_4]Mo(CO)_3^-$.[7] The citrate ligand is bound in a tridentate fashion with its hydroxyl, α-carboxyl, and one of its β-carboxyl groups, while another β-carboxyl group remains intact. Tridentate coordination of citrate through its alkoxy or hydroxyl, α-carboxyl, and β-carboxyl groups is a common feature of the previously reported mono- or dimeric citrate complexes. For instance, this coordination mode has been found in the mononuclear complexes $K_4[MoO_3(cit)]\cdot H_2O$,[6a] $(NH_4)_5Fe(C_6H_4O_7)_2\cdot 4H_2O$,[12] and $(NH_4)_5Al(C_6H_4O_7)_2\cdot 2H_2O$.[13] Citramalate (Hcmal) and malate (Hmal) ligands in **2** and **3** also coordinate to molybdenum in a similar manner. Methyliminodiacetate (Meida) in **4** interacts with molybdenum via two β-carboxyl groups and a nitrogen atom.

The Mo−O(α-carboxyl) and Mo−O(β-carboxyl) distances are similar among **1**−**4**, and they are in the range 2.216(4)−2.254(5) Å. The Mo−O (hydroxyl) bonds are slightly longer (2.230(2) Å (**1**), 2.308(8) Å (**2**), and 2.281(5) Å (**3**)), indicating that the hydroxyl group is not deprotonated. A similar Fe−alcohol interaction in an iron-citrate complex was proposed by Holm et al.[8] The Mo−alcohol interaction makes a contrast with the Mo−alkoxy bonding in the molybdenum site in FeMo-co and the previous citrate complexes, indicating that the coordination of citrate, citramalate, or malate molybdenum is relatively weak in **1**−**3**. The C−Mo−C angles among the carbonyl ligands are essentially 90° to complete the octahedral coordination geometry. The Mo−CO bond distances in **1**−**4** (1.90−1.94 Å) are slightly shorter than those in $Tp^*Mo(CO)_3^-$ (1.94−1.95 Å),[9] (tiPrTACN)$Mo(CO)_3$ (1.91−1.92 Å),[10] and (TTCN)$Mo(CO)_3$ (1.93−1.97 Å).[11]

Spectroscopy. The IR spectra of **1**−**4** exhibited two ν(CO) bands centered around 1900 and 1740 cm^{-1}. Similar vibration patterns have been observed for the molybdenum(0) carbonyl complexes with a tridentate ligand, $Tp^*Mo(CO)_3^-$ (ν(CO) = 1882, 1728 cm^{-1}),[9] (TTCN)$Mo(CO)_3$ (ν(CO) = 1915, 1783 cm^{-1}),[11] and $[B(CH_2SCH_3)_4]Mo(CO)_3^-$ (ν(CO) = 1899, 1784 cm^{-1}).[7] The bands of the coordinated carboxylate group are observed at 1583, 1493, 1441, and 1398 cm^{-1} (**1**), 1608, 1552, 1448, and 1396 cm^{-1} (**2**), 1614, 1549, and 1400 cm^{-1} (**3**), and 1597, 1487, 1452, and 1396 cm^{-1} (**4**). The bands in the ranges 1620−1540 cm^{-1} and 1500−1390 cm^{-1} correspond to the ν_{as} and ν_s for the coordinated carboxylate groups, respectively. The electronic spectra of **1**−**4** show metal-to-ligand charge transfer (MLCT) absorption bands in the range 310−323 nm. Their bright yellow color derives from the absorption maximum just below 400 nm that tails into the visible region of the spectrum.

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Table 1. Crystal Data for $(Et_4N)_3[(Hcit)Mo(CO)_3]$ (1), $(Et_4N)_2[(Hcmal)Mo(CO)_3]$ (2), $(Et_4N)_2[(Hmal)Mo(CO)_3]$ (3), and $(Me_4N)_2[(Meida)Mo(CO)_3]$ (4)

	1	**2**	**3**	**4**
formula	$C_{33}H_{65}N_3O_{10}Mo$	$C_{24}H_{46}N_2O_8Mo$	$C_{23}H_{44}N_2O_8Mo$	$C_{16}H_{31}N_3O_7Mo$
mol wt (g mol^{-1})	759.83	586.58	572.55	473.38
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$(No. 19)	$P2_12_12_1$(No. 19)	$P2_12_12_1$(No. 19)	$P2_12_12_1$(No. 19)
cryst color	yellow	yellow	yellow	yellow
a (Å)	9.994(4)	12.034(4)	12.00(1)	6.773(3)
b (Å)	17.599(7)	13.340(4)	13.27(1)	15.479(7)
c (Å)	22.225(9)	17.719(6)	17.83(2)	20.470(10)
V (Å^3)	3909(2)	2844(1)	2840(4)	2146(1)
Z	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.271	1.264	1.265	1.378
$2\theta_{max}$ (deg)	55	55	55	55
no. of unique rflns	4936	3630	3525	3601
no. of obsd rflns^a	6480	4793	3390	2247
no. of params	424	236	307	245
R^b	0.035	0.082	0.062	0.036
$R_w{}^c$	0.036	0.127	0.067	0.040
GOF^d	1.27	2.90	2.02	1.52

[a] Observation criterion $I > 3\sigma(I)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\{\sum w(|F_o| - |F_c|)^2\}/\sum wF_o{}^2]^{1/2}$. [d] $\mathrm{GOF} = [\{\sum w(|F_o| - |F_c|)^2\}/(N_o - N_p)]^{1/2}$, where N_o and N_p denote the number of data and parameters.

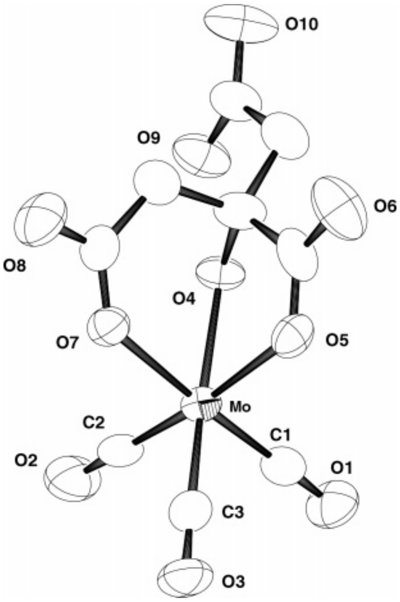

Figure 1. ORTEP drawing of the complex anion of $(Et_4N)_3[(Hcit)Mo(CO)_3]$ (**1**).

Conclusions

We have prepared the first molybdenum carbonyl complexes having citrate and its relevant carboxylates. In the new organo-molybdenum complexes **1**−**4** having a di- or tricarboxylate ligand, citrate and relevant carboxylates serve as facial tridentate ligands which are capable of forming 1:1 adducts with a $Mo(CO)_3$ unit. In the case of citrate complex **1**, the tridentate ligand coordinates with its α- and β-carboxylates and a hydroxyl groups, leaving another β-carboxylate intact. In the protein-bound FeMo-co, homocitrate is coordinated to molybdenum with its alkoxy and α-carboxyl units, indicating that a chelate ring consisting of molybdenum, alkoxy, and α-carboxyl groups is stable, and the coordinated β-carboxylate in our complex may serve as a leaving group. The reactivity study of **1** can provide valuable insights for nitrogenase chemistry, though deprotonation of the hydroxyl group in the citrate ligand is likely required to complete the chelate ring and to prevent the elimination of citrate.

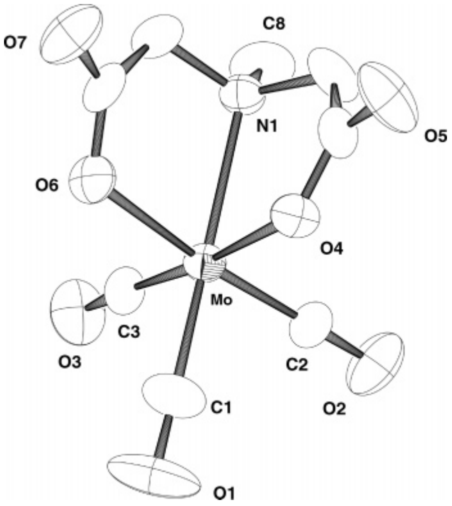

Figure 2. ORTEP drawing of the complex anion of $(Me_4N)_2[(Meida)Mo(CO)_3]$ (**4**).

Experimental Section

General Procedures. All reactions were carried out using a standard Schlenk technique under N_2 atmosphere. Solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under nitrogen. Infrared spectra were recorded on a JASCO FT/IR-410 spectrometer. UV−vis spectra were measured using a JASCO V560 spectrometer. TOF-ESI-MS spectra were obtained from a Micromass LCT TOF-MS spectrometer. Elemental analyses were performed on a LECO-CHN microanalyzer where the crystalline samples were sealed in thin tin tubes in a glovebox. The cyclic voltammogram of **1** was recorded in acetonitrile on a Pt electrode with Bu_4NPF_6 as supporting electrolyte. The potential was reported with a saturated calomel electrode (SCE) as the reference. $(Et_4N)_3(Hcit)$[8] and $(C_7H_8)Mo(CO)_3$[14] were prepared as reported previously. A 25 wt % methanol solution of $(Et_4N)(OH)$ was purchased from Kanto Co., and a 10 wt % methanol solution of $(Me_4N)(OH)$ was purchased from Tokyo Kasei Kogyo Co.

Preparation of $(Et_4N)_3[(Hcit)Mo(CO)_3]$ (1). A solution of $(Et_4N)_3(Hcit)$ (0.315 g, 0.54 mmol) in methanol (20 mL) was added to a solution of $(C_7H_8)Mo(CO)_3$ (0.141 g, 0.52 mmol) in

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[14] Cotton, F. A.; Mccleverty, J. A.; White, J. E. *Inorg. Synth.* **1967**, *9*, 121.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $(Et_4N)_3[(Hcit)Mo(CO)_3]$ (1) and $(Me_4N)_2[(Meida)Mo(CO)_3]$ (4)

1		4	
Bond Distances (Å)			
Mo−C1	1.919(4)	Mo−C1	1.920(6)
Mo−C2	1.903(4)	Mo−C2	1.917(7)
Mo−C3	1.908(4)	Mo−C3	1.913(6)
Mo−O4	2.230(2)	Mo−N1	2.344(5)
Mo−O5	2.229(2)	Mo−O4	2.216(4)
Mo−O7	2.246(2)	Mo−O6	2.243(4)
Bond Angles (deg)			
O4−Mo−O5	72.58(9)	O4−Mo−O6	77.7(2)
O4−Mo−O7	78.11(8)	O4−Mo−N1	74.6(2)
O5−Mo−O7	79.89(9)	O6−Mo−N1	75.4(2)
C1−Mo−C2	84.0(2)	C1−Mo−C2	84.5(3)
C1−Mo−C3	83.6(2)	C1−Mo−C3	86.3(3)
C2−Mo−C3	85.6(2)	C2−Mo−C3	85.1(3)
O4−Mo−C1	99.4(1)	O4−Mo−C1	98.4(2)
O4−Mo−C2	101.2(1)	O4−Mo−C2	97.3(2)
O4−Mo−C3	172.8(1)	O4−Mo−C3	174.9(2)
O5−Mo−C1	98.4(1)	O6−Mo−C1	99.2(3)
O5−Mo−C2	173.6(1)	O6−Mo−C2	174.1(2)
O5−Mo−C3	100.5(1)	O6−Mo−C3	99.7(2)
O7−Mo−C1	177.3(1)	N1−Mo−C1	171.8(3)
O7−Mo−C2	97.5(1)	N1−Mo−C2	100.4(2)
O7−Mo−C3	98.8(1)	N1−Mo−C3	100.5(2)

methanol (20 mL). After the mixture was stirred overnight, solvent was evaporated until dryness. The yellow residue was extracted with acetonitrile (5 mL) and was layered with ether (18 mL). Yellow crystals of **1** were isolated in 75% yield (0.297 g, 0.39 mmol). IR (KBr): 2987(w), 1913(w), 1888(m), 1738(s), 1583(vs), 1493(m), 1441(m), 1398(s), 1286(m), 1174(m), 1070(w), 1005(m), 908(w), 854(w), 798(m), 787(m) cm^{-1}. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), acetonitrile): 323 (3680). Anal. Calcd for $C_{33}H_{65}Mo_1N_3O_{10}$: C, 52.16; H, 8.62; N, 5.53. Found: C, 52.05; H, 8.36; N, 5.58. Cyclic voltammmetry (acetonitrile): $E_{1/2}$ −365 mV (rev).

Preparation of $(Et_4N)_2[(Hcmal)Mo(CO)_3]$ (2). A solution of $(Et_4N)(OH)$ (2.97 g, 25 wt % in methanol, 5.0 mmol) was added to a methanol (20 mL) solution of (*R*)-(+)-citramallic acid (0.375 g, 2.5 mmol). The mixture was dried in vacuo, and the residue was dissolved again in methanol (20 mL). This solution was added to a methanol (20 mL) solution of $(C_7H_8)Mo(CO)_3$ (0.683 g, 2.5 mmol) at room temperature, giving rise to a yellow solution. The solution was stirred overnight and was evaporated until dryness. The residue was extracted with acetonitrile (2 mL) and methanol (3 mL), and the solution was layered with ether (18 mL) to afford $(Et_4N)_2[(Hcmal)Mo(CO)_3]$ (**2**) (0.92 g, 1.57 mmol, 63%) as yellow plates. IR (KBr): 2991(w), 1878(s), 1720(s), 1608(s), 1552(s), 1448(m), 1396(m), 1294(w), 1246(w), 1176(m), 1115(w), 1007(w), 922(w), 883(w), 837(w), 793(w), 731(w), 658(w), 538(w), 457(w) cm^{-1}. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), methanol): 311(4400), 406(920). ESI-TOF-MS (MeCN): *m/z* 164 (M^{2-}). Anal. Calcd for $C_{24}H_{46}Mo_1N_2O_8$: C, 49.14; H, 7.90; N, 4.78. Found: C, 49.11; H, 7.55; N, 4.81.

Preparation of $(Et_4N)_2[(Hmal)Mo(CO)_3]$ (3). A solution of $(Et_4N)(OH)$ (1.18 g, 25 wt % in methanol, 2.0 mmol) was added dropwise to a solution of D-mallic acid (0.148 g, 1.1 mmol) in 20 mL of methanol with stirring at room temperature. After removal of the solvent in vacuo, the yellow residue was dissolved again into methanol (20 mL). This solution was added to a solution of $(C_7H_8)Mo(CO)_3$ (0.272 g, 1.0 mmol) in methanol (20 mL). After the mixture was stirred for overnight, solvent was removed under reduced pressure. The yellow residue was extracted with acetonitrile (2 mL) and methanol (3 mL), and the solution was layered with ether (18 mL). Yellow crystals of **3** were isolated in 65% yield (0.374 g, 0.65 mmol). IR (KBr): 2987(w), 1880(s), 1720(s), 1614(s), 1549(m), 1495(w), 1400(m), 1315(w), 1178(w), 1072(w), 1007(w), 796(w) cm^{-1}. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), methanol): 310 (sh, 2840), 410 (1680). Anal. Calcd for $C_{23}H_{44}Mo_1N_2O_8$: C, 48.25; H, 7.75; N, 4.89. Found: C, 48.24; H, 7.45; N, 4.93.

Preparation of $(Me_4N)_2[(Meida)Mo(CO)_3]$ (4). A solution of 0.214 g (1.5 mmol) of methyliminodiacetic acid in 20 mL of methanol was treated with 2.65 g (2.9 mmol) of 10 wt % methanol solution of $(Me_4N)(OH)$. Solvent was removed under vacuum, and the residue was dissolved again in methanol (20 mL). This solution was added to a solution of $(C_7H_8)Mo(CO)_3$ (0.411 g, 1.5 mmol) in methanol (20 mL) with stirring at room temperature. The mixture gradually turned yellow and was stirred overnight. After removal of the solvent in vacuo, the yellow residue was extracted with methanol (20 mL). Layering ether onto methanol solution yields $(Me_4N)_2[(Meida)Mo(CO)_3]$ (**4**) as yellow crystals (0.663 g, 1.4 mmol, 90%). IR (KBr): 3018(w), 2939(w), 1900(s), 1749(s), 1597(s), 1487(s), 1452(m), 1396(m), 1346(w), 1290(w), 1250(w), 1147(w), 993(w), 949(m), 912(w), 856(w), 742(w), 648(w), 540(w), 451(w) cm^{-1}. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), methanol): 320 (5200). Anal. Calcd for $C_{16}H_{31}Mo_1N_3O_7$: C, 40.60; H, 6.60; N, 8.88. Found: C, 40.55; H, 6.29; N, 8.91.

X-ray Crystal Structure Determination. Crystallographic data are summarized in Table 1. Single crystals of **1**−**4** suitable for X-ray analysis were coated with oil (Immersion Oil. Type B: Code 1248, Cargille Laboratories, Inc.) and mounted on a loop. Diffraction data were collected on a Rigaku AFC7R equipped with a Mercury CCD area detector. The measurements were made by using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at room temperature. Four preliminary data frames were measured at 0.3° increments of ω, to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.3° intervals of ω. The frame data were integrated using the CrystalClear program package, and the data sets were corrected for absorption using a REQAB program. The calculations were performed with the TEXSAN program package. All structures were solved by a direct method and refined by full-matrix least squares. Anisotropic refinement was applied to all non-hydrogen atoms, and all hydrogen atoms were put at the calculated positions. The absolute configurations were determined on the basis of the Flack parameters, −0.0562(0.0292) (**1**), −0.0041(0.0946) (**2**), and −0.0631(0.0511) (**3**). Inversion of the structure resulted in 1.0503(0.0315) (**1**), 0.9899(0.0937) (**2**), and 1.0386(0.0533) (**3**), respectively.

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Supporting Information Available: Crystallographic data for **1**−**4** (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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