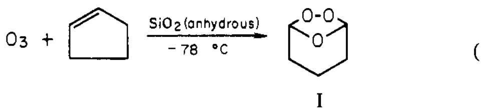
The low-temperature ozonation of alkenes adsorbed on silica gel has not, to our knowledge, been investigated.[13] We report here our results, which indicate that the product distribution and mechanism of ozonation of silica gel supported alkenes differ markedly from the course of ozonation in aprotic and nonparticipating solvents.[14]

In general, the ozonation of 1,2-disubstituted alkenes in nonparticipating aprotic solvents under anhydrous conditions results in formation of monomeric ozonides, polymeric peroxides, and/or polymeric ozonides.[14] By contrast, we find that ozonation of 1,2-disubstituted alkenes adsorbed on dried silica gel results in formation of virtually pure ozonides, and ozonation with water-containing silica gel results in double-bond scission with formation of equimolar amounts of carboxylic acid and aldehyde. Ozonation of simple unsubstituted cyclic alkenes with water-containing silica gel gives the expected aldehydic acid.

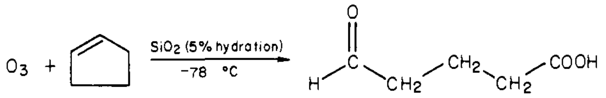
Ozonation[15] of cyclopentene with silica gel vacuum dried at 300 °C results in formation of the normal monomeric ozonide (I)[16,17] in high yield as the only product (eq 1). Some cyclopentene is swept away in the gas stream, even at -78 °C, thereby lowering the yield. Nevertheless, the monomeric ozonide is isolated in excess of 80% yield. In contrast, normal ozonation of cyclopentene results in formation of mostly polymeric ozonide together with a low and highly concentration-dependent yield of monomeric ozonide.



(1)

I

We have also performed ozonation of cyclopentene adsorbed on silica gel loaded to a 5% water content (eq 2). Under these conditions, we find that ozonation of cyclopentene results in oxidative cleavage of the double bond to give 5-oxopentanoic acid as the only major product; cyclopentene is completely consumed, and 5-oxopentanoic acid is formed in a yield exceeding 80%. Ozonation of cyclohexene on water-containing silica gel gave corresponding results, with 6-oxohexanoic acid formed as the major product. Ozonation of 1-methylcyclohexene under similar conditions gave 6-oxoheptanoic acid as the major product.



(2)

The ozonation to completion of 2-pentene supported on dried silica gel resulted in formation of the normal ozonide in a yield exceeding 90%.[15] Ozonation of 2-pentene at -70 °C, either neat or in pentane solution, results in formation of cross ozonides, i.e., the ozonides of 2-butene and 3-hexene, as well as the ozonide of 2-pentene, in addition to acetaldehyde, propionaldehyde, and polymeric peroxidic material.[18]

Ozonation of *trans*-stilbene adsorbed on silica gel heated in air at 200 °C results in the formation of equimolar amounts of benzaldehyde and benzoic acid in high yield. Approximately 1% stilbene ozonide was detected under these conditions. Ozonation of *trans*-stilbene with silica gel hydrated to approximately 5% water content gave benzaldehyde and benzoic acid as major products without detection of ozonide.[19] Ozonation on silica gel vacuum dried at 300 °C gave *cis*- and *trans*-stilbene ozonides[20] as the only products.

Ozonation of alkenes in participating and generally protic solvents usually results in formation of α-oxyalkyl hydroperoxides.[14] Ozonation in water results in formation of aldehydes or ketones and carboxylic acids, presumably because the intermediate hydroxyalkyl hydroperoxides are too unstable to permit isolation.[21] It has long been recognized that acid-catalyzed decomposition of ozonides results in formation of aldehydes or ketones and carboxylic acids.[22] Ozonides are also subject to rapid decomposition into aldehydes and carboxylic acids in dimethyl sulfoxide and dimethylformamide.[23]

Ozonides have been routinely separated and purified by column chromatography on silica gel, and they are quite stable toward thermal decomposition.[24] It is therefore unlikely that surface silanol groups could effect the catalytic decomposition, at -78 °C, of ozonides. According to the well-established Criegee mechanism of ozonation, a primary ozonide dissociates into a carbonyl moiety and a carbonyl oxide zwitterionic species. Perhaps ozonation on a silica-gel surface containing adsorbed water results in immediate addition of a carbonyl oxide to surface water followed by rapid decomposition of the intermediate hydroxyalkyl hydroperoxide to a carboxylic acid and water, and, in effect, adsorbed water on a silica-gel surface acts in the same manner as a participating water solvent. In the absence of appreciable absorbed water, recombination of absorbed aldehyde and carbonyl oxide gives the normal ozonide, and for ozonation of unsymmetrical olefins, crossed ozonides do not occur because of restricted migration of adsorbed species on the silica surface. Vacuum drying of silica gel above 200 °C substantially removes physically adsorbed and hydrogen-bonded water,[25] and our results are consistent with this fact.

Potential synthetic advantages of silica gel supported ozonation of alkenes are (1) ozonation on dehydrated silica gel should permit high-yield formation of ozonides; (2) ozonation of unsymmetrical alkenes may be carried out without formation of cross ozonides; and (3) ozonation on hydrated silica gel permits high-yield double-bond scission, forming aldehyde or ketone and carboxylic acid functionality.

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(14) Bailey, P. S. "Ozonation in Organic Chemistry, I", Academic Press: New York, 1978; Chapter VII. Bailey, P. S. *Chem. Rev.* **1958**, *58*, 925–1010.

(15) The experimental procedure has been described elsewhere.[9] Either Baker 60–200 mesh or Mallinckrodt SilicAR CC-7 100–200 mesh silica gel was used with identical results. Reactants were directly added to stirred silica gel at room temperature, the mixture was cooled to -78 °C, and a 3% ozone-in-oxygen stream was passed through the silica gel until the mixture displayed a pale blue color (3–4 hours, flow rate approximately 10 mL/min). After the reaction mixture was warmed, the products adsorbed on the silica gel were removed with methylene chloride by Soxhlet extraction or by elution. Silica gel was dried under vacuum at 300 °C.

(16) (a) Criegee, R.; Blust, G.; Lohaus, G. *Justus Liebigs Ann. Chem.* **1953**, *583*, 2–6. (b) Story, P. R.; Morrison, W. H.; Hall, T. K.; Farine, J-C.; Bishop, C. E. *Tetrahedron Lett.* **1968**, 3291–3294; see also ref 14, Chapter VII.

(17) NMR [($CDCl_3$, Me_4Si) 5.73 (t), 1.72 (br s), 1.84 ppm (br s)] data were obtained on a Varian EM-360L spectrometer.

(18) Loan, L. D.; Murray, R. W.; Story, P. R. *J. Am. Chem. Soc.* **1965**, *87*, 737–741.

(19) Products were identified by comparison of VPC retention times and IR and NMR spectra with authentic samples. Benzoic acid was further identified by conversion to its methyl ester with diazomethane.

(20) (a) Criegee, R.; Kerckow, A.; Zinke, H. *Chem. Ber.* **1955**, *88*, 1878–1888. (b) Fliszar, S.; Carles, J. *J. Am. Chem. Soc.* **1968**, *91*, 2637–2643.

(21) Fremery, M. I.; Fields, E. K. *J. Org. Chem.* **1963**, *28*, 2537–2541.

(22) (a) Harries, C. D. *Justus Liebigs Ann. Chem.* **1905**, *343*, 311. (b) Long, L.; Jr. *Chem. Rev.* **1940**, *27*, 427–493. (c) Yur'ev, Y. N.; Razumovskii, S. D.; Berezova, L. V.; Zelikman, E. S. *Zh. Org. Khim.* **1975**, *11*, 7–11; *J. Org. Chem. USSR* (*Engl. Transl.*) **1975**, *11*, 5–12.

(23) Ellam, R. M.; Padbury, J. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1094–1095.

(24) Criegee, R.; Korber, H. *Adv. Chem. Ser.* **1972**, *No. 112*, 22–34.

(25) Iler, R. K. "The Chemistry of Silica", Wiley: New York, 1978.

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Intramolecular Electron-Transfer Induced Carbon–Hydrogen Bond Dissociation in Methyl-Substituted 1,10-Phenanthroline Complexes of Bis(η^5-cyclopentadienyl)titanium

Sir:

Floriani and co-workers have found dicarbonylbis(η^5-cyclopentadienyl)titanium(II) to be a useful reagent in numerous re-

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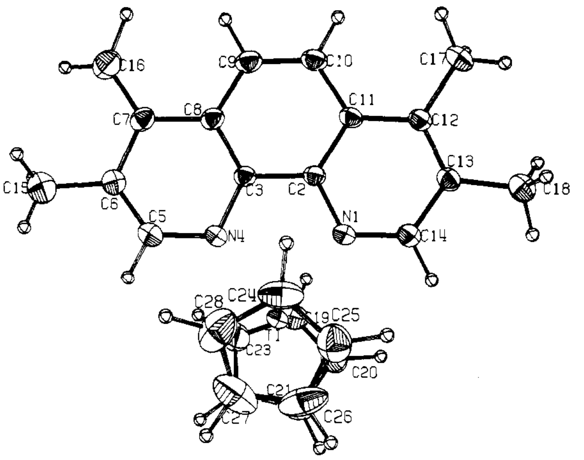

Figure 1. Molecular structure of 4-methylene-3,7,8-trimethyl-1,10-phenanthrolinebis(η^5-cyclopentadienyl)titanium.

actions,[1] including the deoxygenation and disproportionation of CO_2,[2] the disproportionation of phenyl isocyanate,[3] and the reductive coupling of carbonyl or imino functional groups.[4] In this communication, we report that the reaction of $Cp_2Ti(CO)_2$ with 3,4,7,8-tetramethyl-1,10-phenanthroline results in electron transfer upon complexation with (1) subsequent activation and dissociation of a methyl group carbon-hydrogen bond and (2) hydrogenation of the nitrogen-containing aromatic.

In our laboratory, we have been investigating exchange and electron transfer in various bis(η^5-cyclopentadienyl)titanium systems.[5] One study of considerable interest was that of 2,2′-bipyridylbis(η^5-cyclopentadienyl)titanium.[6] Magnetic susceptibility and EPR studies showed the complex to have a triplet excited state which is thermally accessible from the ground-state singlet. The low-lying triplet corresponds to a state in which one unpaired electron formally occupies a molecular orbital which is localized on the Cp_2Ti unit while the other resides in the lowest energy π^* orbital of the bipyridyl group. Thermally accessible triplet–singlet systems of this type are rare in monomeric organometallic complexes which contain one metal atom. This led us to further examine similar systems to increase our understanding of their novel and interesting electronic properties.

In order to investigate the chemical and electronic consequences of changing the ligand properties in 1,4-diimine–titanium complexes, various 1,10-phenanthroline complexes of bis(η^5-cyclopentadienyl)titanium were synthesized by using the ligands 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, 4-methyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline. These compounds are prepared by reaction of the ligand with $Cp_2Ti(CO)_2$ in THF under an inert atmosphere. The resulting products are air-sensitive powders. Because of their air sensitivity, the primary tool of characterization was electron-impact mass spectrometry. Parent molecular ions were observed for all the complexes.

Table I. Important Interatomic Bond Distances (Å) in 4-Methylene-3,7,8-trimethyl-1,10-phenanthroline-bis(η^5-cyclopentadienyl)titanium

C3–N4	1.365 (5)	C7–C16	1.352 (6)
N4–C5	1.367 (5)	C6–C15	1.513 (7)
C5–C6	1.346 (6)	C12–C17	1.511 (6)
C6–C7	1.446 (6)	C13–C18	1.500 (6)
C7–C8	1.469 (5)		
C8–C3	1.396 (5)		

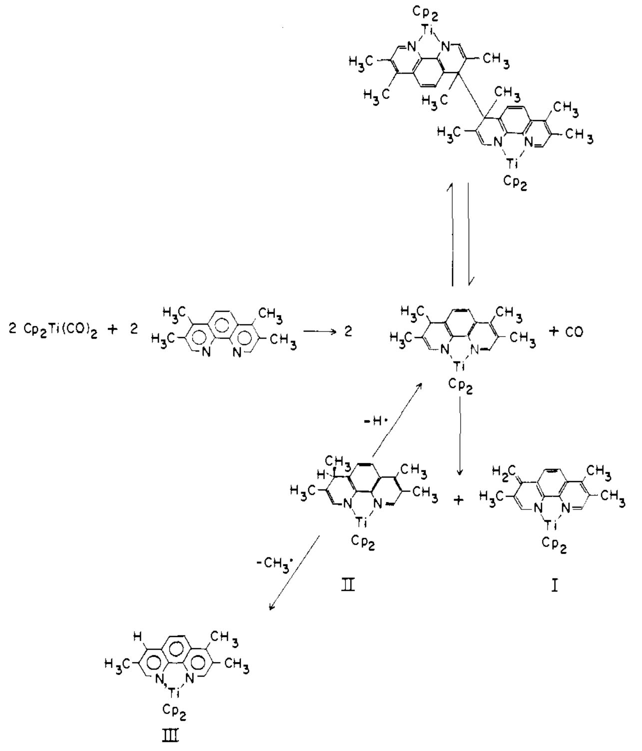

Figure 2. Proposed mechanism.

Our initial investigation of the EPR spectra of toluene/benzene (4:1) glasses of the crystallizing solutions at liquid nitrogen temperatures showed triplet-state spectra. From these results, coupled with Fenske–Hall[7] molecular orbital calculations, it appeared that all these systems were behaving similarly to the 2,2′-bipyridiyl-bis(η^5-cyclopentadienyl)titanium system. However, close examination of the mass spectrum of the bis(η^5-cyclopentadienyl)titanium complex to 3,4,7,8-tetramethyl-1,10-phenanthroline showed the parent ion to be one mass unit less than expected (413 instead of 414). Because of this observation and since crystals were available, a single-crystal X-ray structural determination was undertaken.[8]

The resulting geometry of the molecule 4-methylene-3,7,8-trimethyl-1,10-phenanthrolinebis(η^5-cyclopetadienyl)titanium(I) is shown in Figure 1. Important bond distances are given in Table I. A methyl group configuration was tried at C16; however, only two hydrogen atoms were found in a difference Fourier map, and only a methylene configuration could be refined by least-squares

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(1) Fachinetti, G.; Floriani, C.; Stoechli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297. Floriani, C.; Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1972**, 790. Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1974**, 2433. Floriani, C.; Fachinetti, G. *Ibid.* **1973**, 1954. Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 66.

(2) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

(3) Fachinetti, G.; Biran, C.; Floriani C. *J. Chem. Soc., Dalton Trans.* **1979**, 792.

(4) Pasquali, M.; Floriani C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 4740.

(5) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 1841. Fieselmann, B. F.; Stucky, G. D. *Ibid.* **1978**, *17*, 2074. Corbin, D. R.; Francesconi, L. C.; Hendrickson, D. N.; Stucky, G. D. *J. Chem. Soc., Chem. Commun.* **1979**, 248. *Inorg. Chem.* **1979**, *18*, 3069. Francesconi, L. C.; Corbin, D. R.; Hendrickson, D. N.; Stucky, G. D. *Ibid.* **1979**, *18*, 3074.

(6) McPherson, A. M.; Fieselmann, B. F.; Lichtenberger, D. L.; McPherson, G. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 3425.

(7) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(8) Crystal data for $C_{26}H_{25}N_2Ti$ (I): M_w = 413.4; monoclinic; a = 14.786 (5), b = 9.835 (4), c = 14.902 (4) Å; β = 107.35 (2)°; Z = 4; d_{calcd} = 1.33 g cm^{-3}; space group $P2_1/c$. Cell and intensity data were collected on a Syntex $P2_1$ diffractometer with Mo Kα radiation (λ = 0.71069 Å). Data were collected to 2θ = 55° for a total of 4770 unique reflections of which 2991 were considered observed at the 1.96$\sigma(I)$ significance level. The structure was solved by the heavy-atom technique. Of the hydrogen atoms observed in difference maps, 21 of 45 allowed all of their positions to be calculated by standard techniques. All nonhydrogen atoms were refined on position and anisotropic thermal parameters. The hydrogen atoms on C16 were allowed to refine on position and isotropic thermal parameters. The other hydrogen atoms were fixed at calculated positions but were allowed to refine on isotropic thermal parameters. Final full-matrix least-squares agreement factors for 293 variables were $R_1(\sum||F_o| - |F_c||/\sum|F_o|)$ = 0.061 and $R_2([\sum_w||F_o| - |F_c||^2/\sum_w|F_o|^2]^{1/2})$ = 0.063.

techniques. Moreover, the shortened carbon–carbon (C7–C16) bond length of 1.352 (6) Å indicated a C7–C16 double bond. The ring system N1–C2–C11–C12–C13–C14 is clearly aromatic in nature with an average carbon–carbon bond length of 1.404 (5) Å. The quinoid configuration found for the ring system N4–C5–C6–C7–C8–C3 suggested the possibility of intramolecular electron transfer, inducing carbon–hydrogen bond dissociation in the methyl group at the 4-position in 3,4,7,8-tetramethyl-1,10-phenanthroline.

This led to further investigation of the mechanism involved. A qualitative gas chromatographic examination of the gas above the reaction mixture showed hydrogen and carbon monoxide as well as methane. Subsequently, crystals of another complex (II) were isolated from the same reaction mixture. Mass spectral data for this complex showed a parent molecular ion one mass unit higher than expected for the original 3,4,7,8-tetramethyl-1,10-phenanthroline derivative (415 vs. 414).

These data have led to the proposed mechanism given in Figure 2. Upon reaction, there is an electron transferred from the electron-rich titanium(II) to the aromatic ring, with the greatest electron density of the unpaired electron at C7. This thermally driven electron transfer has been confirmed in bpy(η^5-C_5H_5)$_2$Ti and in phenanthroline complexes which do not contain a methyl group in the 4-position (i.e., C7 or C12 in Figure 1). The electron transfer is also predicted by Fenske–Hall molecular orbital calculations which show a high percent of the carbon p_x character in the highest occupied molecular orbital at this position. The resulting quinoid configuration is also proposed to be an important aspect of flavin electron transfer in biological systems. A bimolecular intermediate through the 4-position, as proposed for the flavin one-electron-transfer process,[9] is probably responsible for subsequent hydrogen radical transfer, leading to the two isolated complexes I and II.

Glass EPR spectra of toluene/benzene (4:1) solutions of I and II at liquid nitrogen temperatures show doublet states for both. These complexes do not account for the triplet-state spectrum observed for the crystallizing solution. Also, the mechanism does not account for the hydrogen and methane gases observed. These gases result from reaction of a methyl or hydrogen radical species upon dissociation of II with the α-hydrogen atoms of the THF or unreacted ligand. The mass spectrum obtained on the gases evolved from the reaction when run in tetrahydrofuran-d_8 shows deuterated methane, suggesting a radical process with the solvent as the primary source of the hydrogen. Compound III, resulting from loss of a methyl radical, could account for the triplet-state spectrum since formally it should be a titanium(II) complex with the possibility of intramolecular electron transfer into a low-lying π^* orbital on the ligand. Loss of a hydrogen radical from II gives the original radical species which can continue through the mechanism. This radical species could also account for the triplet-state spectrum in the crystallizing solution. Ion peaks corresponding to complex III are observed in the mass spectra of I and II.

This intramolecular electron-transfer induced carbon–hydrogen bond dissociation appears to be occurring for all the 4-methyl-substituted 1,10-phenanthrolines but is not observed in the similar 4,4′-dimethyl-2,2′-bipyridyl. Whereas a large contribution for the carbon p_x orbital at the 4-position in the phenanthroline ring was obtained from the molecular orbital calculations, the 4-position in the bipyridyl ring had a smaller electron density. Additional studies are presently being performed to further characterize these systems and other electron-transfer processes leading to alkyl C–H bond dissociation.

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Supplementary Material Available: The final atomic positional and thermal parameters (Table II), bond distances (Table III), bond angles (Table IV), and a complete listing of structure-factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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(9) Hemmerich, P. *Adv Chem. Ser.* **1977**, *No. 162*, 312–329.

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Substitutive Intramolecular Carbonyl Insertion in a Carbomolybdate Cluster: Formation of a Polycentric, Conformationally Flexible Anion Binding Cavity

Sir:

In the course of a continuing investigation of polyoxomolybdate–carbonyl interactions,[1,2] we have examined the reaction chemistry of the α-dialdehyde glyoxal (OHCCHO). As anticipated,[1] the formylated methylenedioxymolybdate $RCHMo_4O_{15}H^{3-}$, R = OHC, is easily prepared as a tetra-*n*-butylammonium salt from $[(n\text{-}C_4H_9)_4N]_2Mo_2O_7$. Remarkably, however, this anion reacts with certain acids, HX, according to eq 1, resulting in replacement of the OH^- group in the reactant

$$OHCCHMo_4O_{15}H^{3-} + HX \rightarrow HCCHMo_4O_{15}X^{3-} + HOH \qquad (1)$$

by an X^- group and insertion of the reactant formylcarbonyl group into a molybdenum–oxygen bond. The product contains a polycentric anion binding site capable of accommodating anions, X^-, having a variety of sizes and shapes. This system offers a rare opportunity for detailed study of (1) the delicate balance between metal–oxygen and carbon–oxygen bond strengths which determines the structure and reactivity of carbomolybdates, (2) mechanistic aspects of polymolybdate–carbonyl interactions, and (3) conformational flexibility in polyoxomolybdate anions.

Reaction of $[(n\text{-}C_4H_9)_4N]_2Mo_2O_7$[3] with an equimolar amount of 70% aqueous $HClO_4$ and excess glyoxal in moist CH_3CN/CH_2Cl_2 followed by addition of ether results in precipitation of a product which analyzes[4] as $[(n\text{-}C_4H_9)_4N]_3OHCCHMo_4O_{15}H$ (**1a**) after crystallization from $CH_2Cl_2/CH_3C_6H_5$. The anion in **1a** is assigned the structure shown in Scheme I[6] on the basis of ^{1}H NMR and IR data.[4] Addition of compound **1a** in CH_2Cl_2 to an equimolar amount of 49% aqueous HF in CH_3CN followed by precipitation with ether and recrystallization from $CH_2Cl_2/CH_3C_6H_5$ yields block-shaped crystals of [(*n*-

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(1) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Liu, R. -S. *J. Am. Chem. Soc.* **1979**, *101*, 491–492.

(2) Adams, R. D.; Klemperer, W. G.; Liu, R. -S. *J. Chem. Soc., Chem. Commun.* **1979**, 256–257.

(3) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 6146–6148.

(4) Anal. Calcd for $C_{50}H_{111}N_3Mo_4O_{16}$: C, 43.08; H, 8.02; N, 3.01; Mo, 27.53. Found: C, 43.18; H, 8.19; N, 3.15; Mo, 27.47. ^{1}H NMR[5] (CD_2Cl_2): δ 10.13 (d, 1, $^3J_{HH}$ = 1.3 Hz, O*H*CCHO$_2$), 5.68 (d, 1, $^3J_{HH}$ = 1.3 Hz, OHCC*H*O$_2$). The IR spectrum of **1a** in a Nujol mull shows the identical pattern of absorptions as the spectrum of $[(n\text{-}C_4H_9)_4N]_3CH_2Mo_4O_{15}H^1$ in the 550–950-cm^{-1} Mo–O stretching region and the 3610–3630-cm^{-1} O–H stretching region.

(5) The ^{1}H NMR spectra of all compounds reported here also display $(n\text{-}C_4H_9)_4N^+$ multiplets centered at ca. δ 3.3, δ 1.5, and δ 1.05.

(6) In Schemes I and II, bonds to molybdenum atoms in the 1.60–1.75-Å range are represented by double lines, bonds to molybdenum atoms whose lengths range between 1.85 and 2.00 Å are represented by single lines, and bonds to molybdenum atoms in the 2.00–2.40-Å range are represented by dotted lines.

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