Investigation of the Monomer−Dimer Equilibria of Molybdocenes in Water

Christoph Balzarek,† Timothy J. R. Weakley,† Louis Y. Kuo,*,‡ and David R. Tyler*,†

Departments of Chemistry, University of Oregon, Eugene, Oregon 97403, and Lewis & Clark College, Portland, Oregon 97219

Received February 28, 2000

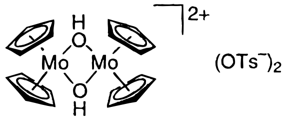
Molybdocenes form monomeric and dimeric complexes upon dissolution in water. The solution structures of the molybdocenes at neutral pH are inferred as the monomeric $[(CpR)_2Mo(OH_2)(OH)]^+$ and the dimeric $[(CpR)_2Mo(\mu\text{-}OH)_2Mo(CpR)_2]^{2+}$. The equilibrium constants for the monomer−dimer equilibria were obtained from ^{1}H NMR dilution studies as $K'_{eq} = (7.9 \times 10^{-2}) \pm (1.0 \times 10^{-3})$ M for R = CH_3 at pD 7 and as $K_{eq} = (3.5 \times 10^{-2}) \pm (1.3 \times 10^{-3})$ M for R = H at pD 3.5. Qualitatively, the monomer of the CpMe molybdocene is more favored than the Cp analogue, compared to their respective dimers.

Introduction

The metallocene dihalide bis(η^5-cyclopentadienyl)molybdenum(IV) dichloride (Cp_2MoCl_2, **1**; Cp = η^5-C_5H_5) has received recent attention with regard to its rich variety of water-based chemistry. The coordination of aquated Cp_2MoCl_2 to DNA constituents[1−3] serves to model the fundamental bioinorganic chemistry of metallocene antitumor drugs[4,5] with its putative biomolecular target. The studies in this area subsequently led to the finding that Cp_2MoCl_2 effectively promotes the hydrolysis of activated[6] and unactivated phosphate esters[7] with rate accelerations similar to those of coordination compounds that effect the same chemistry.[8,9] Cp_2MoCl_2 has also been studied for its potential as a catalyst in systems for photochemical water splitting.[10] More recently, aqueous solutions containing hydrolyzed $[Cp'_2Mo]^{2+}$ complexes (Cp′ = η^5-$C_5H_4CH_3$) were shown to catalyze C−H bond activation.[11]

Crucial to the understanding of this metallocene's rich chemistry in water is the fundamental knowledge of its speciation in aqueous solution. To date, the most complete report of Cp_2MoCl_2 aqueous chemistry[1] shows that the metallocene rapidly loses both of its chloride ligands ($\tau_{1/2} \approx 20$ min in unbuffered water) while the Cp ligands remain bound even at neutral pH. Potentiometric measurements yielded two titratable protons with pK_a's of 5.5 and 8.5. In a later potentiometric study, a third reproducible equivalence point (pK_a = 2.8) was found.[12] No evidence was presented, however, from which the existence of a monomeric, dimeric, or higher oligomeric species could be deduced.

Recent work on molybdocene-promoted phosphate hydrolysis[7] raised the question of a possible monomer−dimer equilibrium for this group VI metallocene. The rate of phosphate hydrolysis was found to be half-order in Cp_2MoCl_2,[7] which was interpreted in terms of an active molybdocene monomer that is in equilibrium with a dimeric species. The possibility for dimer formation is reasonable in light of the reports by Ito,[13−15] who described a molybdocene complex in which two molybdocene fragments are bridged by two hydroxide ligands (**2**).



2

The first investigation of a dimeric molybdocene complex in water was reported in the context of C−H bond activation chemistry promoted by water-soluble molybdocenes.[11] The reaction solution, prepared from $[Cp'_2Mo(\mu\text{-}OH)_2MoCp'_2](OTs)_2$ (**2′**), was found to contain two molybdocene species. These two complexes were proposed to be the dication $[Cp'_2Mo(\mu\text{-}OH)_2MoCp'_2]^{2+}$ and its hydrolysis product, the catalytically active $[Cp'Mo(OH)(OH_2)]^+$ monomer.

---

† University of Oregon.

‡ Lewis & Clark College.

[1] Kuo, L. Y.; Kanatzidis, M. G.; Sabat, M.; Tipton, A. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 9027−9045.

[2] Kuo, L. Y.; Liu, A. H.; Marks, T. J. *Met. Ions Biol. Sys.* **1996**, *33*, 53−85.

[3] Harding, M. M.; Mokdsi, G.; Mackay, J. P.; Prodigalidad, M.; Lucas, S. W. *Inorg. Chem.* **1998**, *37*, 2432−2437.

[4] Keppler, B. K.; Friesen, C.; Vongerichten, H.; Vogel, E. In *Metal Complexes in Cancer Chemotherapy*; VCH: Weinheim, Germany, 1993; pp 287−323.

[5] Köpf-Maier, P.; Köpf, H. In *Metal Compounds in Cancer Therapy*; Chapman & Hall: London, 1994; pp 109−146.

[6] Kuo, L. Y.; Kuhn, S.; Ly, D. *Inorg. Chem.* **1995**, *34*, 5341−5345.

[7] Kuo, L. Y.; Barnes, L. A. *Inorg. Chem.* **1999**, *38*, 814−817.

[8] Connolly, J. A.; Kim, J. H.; Banaszczyk, M.; Drouin, M.; Chin, J. *Inorg. Chem.* **1995**, *34*, 1094−1099.

[9] Williams, N. H.; Takasaki, B.; Wall, M.; Chin, J. *Acc. Chem. Res.* **1999**, *32*, 485−493.

[10] Baxley, G. T.; Avey, A. A.; Aukett, T. M.; Tyler, D. R. *Inorg. Chim. Acta*, in press.

[11] Balzarek, C.; Tyler, D. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 2406−2408.

[12] Baxley, G. T. Ph.D. Thesis, University of Oregon, Eugene, Oregon, 1997.

[13] Minato, M.; Tomita, H.; Ren, J.-G.; Ito, T. *Chem. Lett.* **1993**, 1191−1194.

[14] Ren, J.-G.; Tomita, H.; Minato, M.; Oksada, K.; Ito, T. *Chem. Lett.* **1994**, 637−640.

[15] Ren, J.-G.; Tomita, H.; Minato, M.; Ito, T. *Organometallics* **1996**, *15*, 852−859.

10.1021/om000180l CCC: $19.00

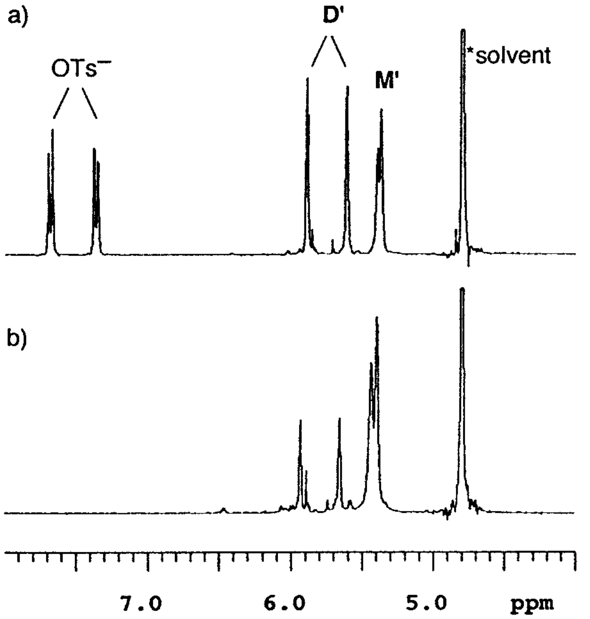


Figure 1. ^{1}H NMR spectra of (a) [Cp′$_2$Mo(μ-OH)MoCp′$_2$](OTs)$_2$ (**2′**; 15 mM, D_2O) and (b) Cp′$_2$MoCl$_2$ after adjusting the pD to 6.9 (**1′**; 10 mM, D_2O).

Previous hydrolysis studies of metallocenes include the investigation of titanocenes[16−18] as well as Co[19] and Rh[20,21] pentamethylcyclopentadienyl complexes in water. These complexes were reported to form dimeric or oligomeric compounds in solution. Examples of crystallographically characterized hydroxy-bridged metallocenes with two Cp rings on each metal center include [Cp$_2$ZrL(μ-OH)]$_2$ (with L = OCOCF$_3$,[22] NCPr,[23] imidazole[24]) and [Cp$_2$Y(μ-OH)]$_2$·PhCCPh.[25] Their water-based chemistry, however, has not been explored further.

In this report we present evidence for the existence of monomer−dimer equilibria in aqueous solutions of the molybdocene complexes [(CpR)$_2$Mo(μ-OH)$_2$Mo(CpR)$_2$](OTs)$_2$ (CpR = η^5-C$_5$H$_4$R; R = H, CH$_3$). The chemistry of these molybdocenes in water is shown to be independent of the precursor, whether it is the dihalide or the μ-OH dimer, and the speciation depends solely on the pH of the solution. These results contribute to a better understanding of aqueous molybdocene chemistry.

Table 1. Summary of ^{1}H NMR Data[a]

complex	pD	^{1}H NMR (ppm)[b]
Cp′$_2$Mo(OH)(OH$_2$) (**M′**)	6.9	5.46 (m), 5.42 (m), Cp 1.95 (s), Me
[Cp′$_2$Mo(μ-OH)$_2$MoCp′$_2$]$^+$ (**D′**)	6.9	5.89 (m), 5.61 (m), Cp 1.80 (s), Me
[Cp$_2$Mo(μ-OH)$_2$MoCp$_2$]$^+$ (**D**)	7.0	5.97 (s), Cp
Cp$_2$MoCl$_2$(aq), monomer	3.5	6.05 (s), Cp
Cp$_2$MoCl$_2$(aq), dimer	3.5	5.85 (s), Cp

[a] In D_2O. [b] Relative to residual HOD.

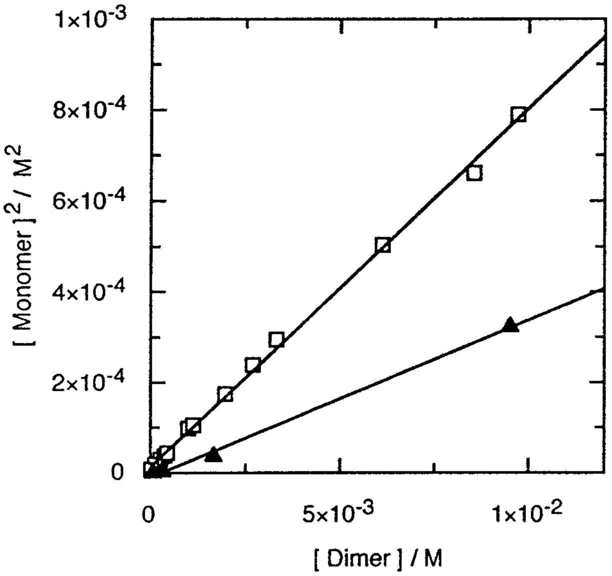


Figure 2. Evaluation of the equilibrium constants. Plots of [monomer]^2 vs [dimer]: (□) **2′** in D_2O at pD 7, K'_{eq} = (7.9 × 10^{-2}) ± (1.0 × 10^{-3}) M; (▲) **1** in D_2O at pD 3.5, K_{eq} = (3.5 × 10^{-3}) ± (1.3 × 10^{-3}) M.

Results and Discussion

Monomer−Dimer Equilibria at Neutral pH. In our studies on water-soluble molybdocenes,[11] we found that solutions of [Cp′$_2$Mo(μ-OH)$_2$MoCp′$_2$](OTs)$_2$ (**2′**) in D_2O contain two metallocene species, on the basis of ^{1}H NMR spectra (Figure 1a). After **2′** was dissolved in D_2O at 23 °C, the initial resonances in the Cp′ region of the spectrum at δ 5.9 and 5.65 ppm (**D′**)[26] decreased over a period of 3 h, while new resonances appeared at δ 5.4 ppm (**M′**) (Table 1).[26] No free methylcyclopentadiene could be detected, indicating that the Cp′ ligands remained metal-bound. The pH of a 10.6 mM solution of **2′** in H_2O changed only slightly from pH 6.2, measured immediately after preparation, to pH 6.9, once the monomer−dimer equilibrium was established. No change in the chemical shifts of **M′** and **D′** were observed during the hydrolysis process. The molybdocene solutions then remained stable for weeks with regard to pH, monomer−dimer equilibrium, and Cp ligand hydrolysis.

To investigate the formation of the second species further, the concentrations of **D′** and **M′** were determined for a series of solutions, prepared from varying amounts of **2′** in D_2O. The concentrations of **D′** and **M′** were obtained by integrating the CpCH_3 resonances in the ^{1}H NMR spectrum at δ 1.81 and 1.93 ppm, respectively, versus the integral of the O$_3$SC$_6$H$_4$$CH_3$ resonance at δ 2.40 ppm. The concentration of [**D′**] relative to [**M′**] decreased with decreasing total molybdocene concentration, and the plot of [**M′**]^2 against [**D′**] is linear (Figure 2, □). These data are consistent with the existence of a monomer−dimer equilibrium, with **D′** being the dimeric complex and **M′** being the monomer. From a linear

---

(16) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472−5478.

(17) Thewalt, U.; Honold, J. *J. Organomet. Chem.* **1988**, *348*, 291−303.

(18) Döppert, K. *Naturwissenschaften* **1990**, *77*, 19−24.

(19) Koelle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 753−762.

(20) Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. M.; Smith, P.; Maestre, M.; Fish, R. H. *Organometallics* **1995**, *14*, 2806−2812.

(21) Fish, R. H. *Coord. Chem. Rev.* **1999**, *185*, 569−585.

(22) Klima, S.; Thewalt, U. *J. Organomet. Chem.* **1988**, *354*, 77−81.

(23) Aslan, H.; Eggers, S. H.; Fischer, R. D. *Inorg. Chim. Acta* **1989**, *159*, 55−57.

(24) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. *J. Organomet. Chem.* **1996**, *518*, 17−19.

(25) Evans, W. J.; Hozbor, M. A.; Bott, S. G.; Robinson, G. H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 1990−1993.

(26) The solution species are labeled using capital letters, while the compounds isolated as solids are labeled using numerals.

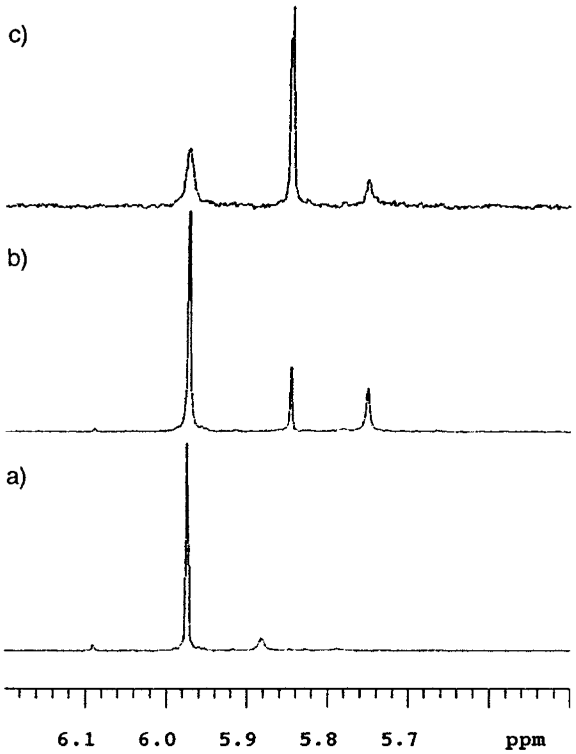
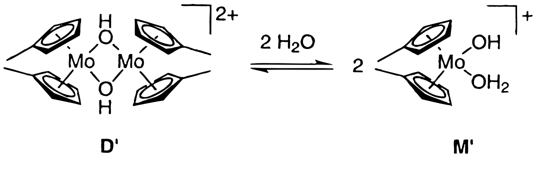


Figure 3. Dilution of Cp_2MoCl_2 (pD 7) with D_2O adjusted to pD 7.0. Concentrations for Cp_2MoCl_2 are (a) 40 mM, (b) 0.65 mM, and (c) 0.15 mM. The pD remained at 7.0 over the course of the dilution experiment.

regression, the equilibrium constant $K'_{eq} = [\mathbf{M}']^2/[\mathbf{D}'] = (7.9 \times 10^{-2}) \pm (1.0 \times 10^{-3})$ M was obtained.

The structure of the monomer is inferred as containing one hydroxo and one aquo ligand. This assumption is based on the observation that, upon dissolution of **2′** in H_2O, the pH does not change significantly.[27] This is consistent with a hydrolysis process in which no H^+ or OH^- is generated; i.e., an aquo ligand simply joins the coordination sphere of the metallocene.[28] The monomer−dimer equilibrium is therefore described by eq 1.



(1)

Aqueous solutions containing **D′** and **M′** can also be prepared from the dihalide complex Cp'_2MoCl_2 (**1′**; 16 mM) through pD adjustment by addition of NaOH in D_2O to pD 6.9. As shown in Figure 1b, this results in a solution containing **D′** and **M′**. This result shows that the speciation of molybdocenes in water does not depend on the precursor, but only on the pH of the aqueous solution.

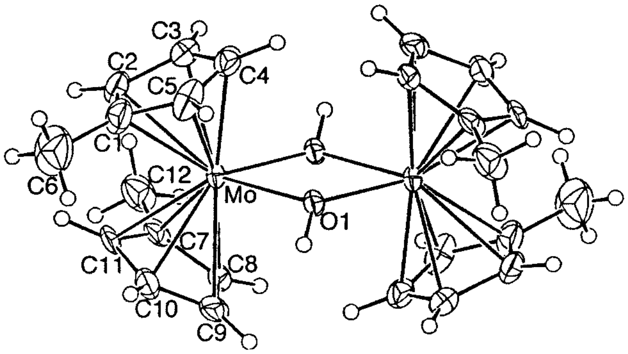


Figure 4. Molecular structure of **1′**. Only the dication is shown.

Table 2. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 2 and 2′

	$[(CpR)_2Mo(\mu\text{-}OH)_2Mo(CpR)_2](OTs)_2$	
	2 (R = H)	**2′** (R = Me)
Mo−O(1)	2.092(2)	2.106(3)
Mo−O(1^i)	2.100(2)	2.095(3)
Mo−Cp(1)^a	2.001(5)	2.001(3)
Mo−Cp(2)^a	1.996(5)	1.997(3)
O(1)−Mo−O(1^i)	66.21(10)	67.0(1)
Mo−O(1)−Mo^I	113.79(10)	113.0(1)
Cp(1)-Mo−Cp(2)^a	128.3	130.0(1)

[a] Cp(1) and Cp(2) are the centroids of rings C(1−5) and C(7−11), respectively.

The solution chemistry of the nonmethylated analogues of **1′** and **2′** under neutral conditions is more complex in that three species are formed. The ^1H NMR spectrum of Cp_2MoCl_2 (**1**; 40 mM) in D_2O, buffered at pD 7 using MOPS,[29] shows the predominant species at δ 5.97 ppm (Figure 3a). Dilution of this solution to 0.65 and 0.15 mM in molybdocene results in the appearance of two new species at 5.85 and 5.75 ppm. Upon addition of $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2](OTs)_2$ (**2**) to a solution of **1**, adjusted to pD 7, only the resonance at 5.97 ppm increased in the ^1H NMR spectrum taken immediately after mixing, identifying this species as $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}$ (**D**) (see Supporting Information). This assignment can be made because hydrolysis of **2** is slow, as shown by a control experiment in which ^1H NMR spectra of **2** in D_2O were recorded over a period of 1 h, with collection of spectra started immediately after mixing. The spectra do not change during this time period, showing that hydrolysis of **2** is slow. The remaining two species at 5.85 and 5.75 ppm could not be identified. The spectrum shown in Figure 3a shows that the dimer **D** is favored over any other hydrolysis product of **2**. Using K'_{eq} the ratio of the resonances of **M′** and **D′** at $[\mathbf{2}'] = 20$ mM is calculated as 3:2; i.e., the monomer is favored in this case. One possible factor influencing this difference in the hydrolysis behavior is the different steric sizes of the Cp and the Cp′ ligands, respectively.

The molecular structure of $[Cp'_2Mo(\mu\text{-}OH)_2MoCp'_2](OTs)_2$ (Figure 4) shows only slight differences in the geometric parameters from that of the unsubstituted Cp analog[15] (Table 2). In fact, the two dimers **2** and **2′** are isostructural. The central Mo−O(1)−Mo^i−O(1^i) tetragons have very similar geometric parameters, and no significant expansion of the metallocene core results from the methyl substituent.

---

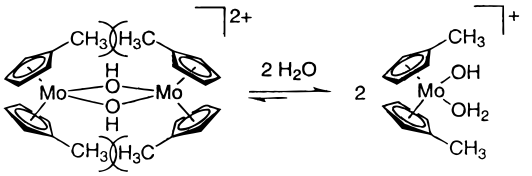
[27] At a concentration of $[\mathbf{1}'] = 10.6$ mM, the concentration of OH^- changes by less than 10^{-3} mM (pH 6.2 → pH 6.7), less than 0.01% of the concentration of solute.

[28] A complex precipitated from an aqueous solution of Cp_2MoCl_2 by addition of $NaBPh_4$ gave an elemental analysis consistent with the formulation $[Cp_2Mo(OH)(OH_2)][BPh_4]\cdot 0.5H_2O$.[1]

[29] Similar experiments were carried out in the absence of MOPS by adjusting the pD using NaOD in D_2O, resulting in identical ^1H NMR spectra. This indicates that the buffer does not coordinate to the metal center.

In solution, however, rotation of the cyclopentadienyl rings in **D′** can bring the methyl substituent into a position above the bridging OH groups, where it can interfere with a Cp methyl group on the second molybdenum center (eq 2). These solution effects may arise despite the fact that in the solid state the two dimers **2** and **2′** show little or no differences in structure.

In addition to steric factors, electronic effects may influence the monomer–dimer equilibria. Ito and Yoden have shown that the methyl substituent on the Cp ring increases the electron density on the metal center in the molybdocene dihydride complex Cp'_2MoH_2.[30]



(2)

Monomer–Dimer Equilibrium at Low pH. A 37 mM aqueous solution of Cp_2MoCl_2 (**1**) has a pD of 3.5, with two singlets of equal intensity at 5.85 and 6.05 ppm in its ^1H NMR spectrum. Upon dilution of this acidic solution with D_2O (pD 3.5, adjusted by addition of HCl), the relative intensities of the two Cp singlets changed (the pD remained at 3.5; Figure 5).[31]

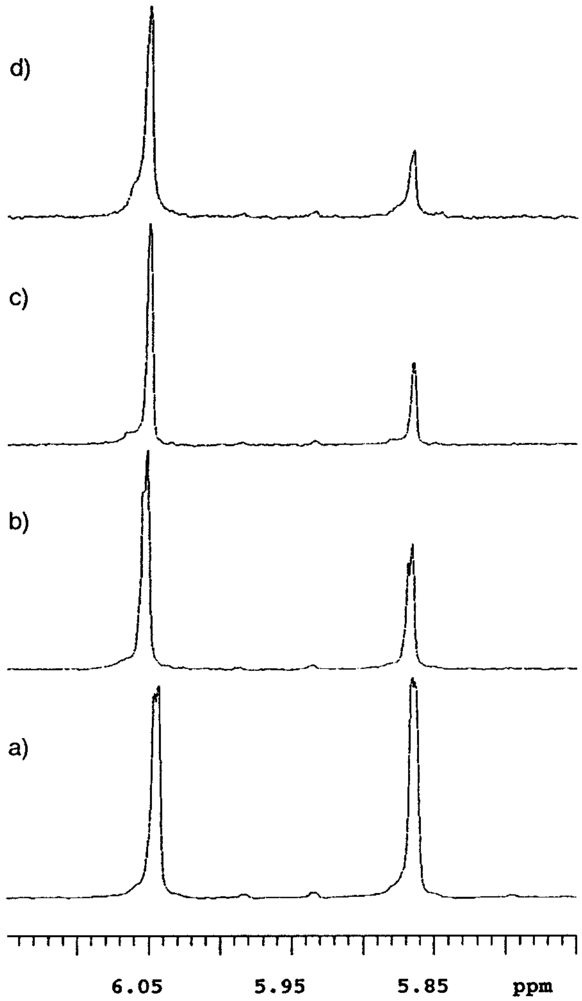


Figure 5. Dilution of Cp_2MoCl_2 (pD 3.5) with D_2O (adjusted to pD 3.5).[31] Concentrations for Cp_2MoCl_2 are (a) 37 mM, (b) 9.3 mM, (c) 2.3 mM, and (d) 0.58 mM. The pD remained at 3.5 over the course of the dilution experiment.

Similar to the cases described above, the concentrations of the two species were obtained from integration of the resonances at 6.05 and 5.85 ppm, assigning the downfield resonance, which decreases upon dilution relative to the upfield resonance, to a dimeric complex. A monomer–dimer equilibrium at low pH is consistent with the half-order rate dependency for phosphate hydrolysis promoted by Cp_2MoCl_2.[7] From the plot of $[\text{monomer}]^2$ vs [dimer] (Figure 2, ▲), the equilibrium constant $K_{eq} = (3.5 \times 10^{-2}) \pm (1.3 \times 10^{-3})$ M is obtained.[32] Attempts to isolate these two forms of Cp_2-Mo(aq) under acidic conditions for more thorough analysis were unsuccessful.

Conclusion. Molybdocenes exist in monomer–dimer equilibria in aqueous solution. The speciation of the molybdocene complexes depends only on the pH. The Cp′ ligand renders formation of the monomer more facile than in complexes containing the Cp ligand. Both steric and electronic factors may influence the monomer–dimer equilibria. The results of this study are of fundamental importance for further investigations in the area of aqueous molybdocene chemistry and its application in C–H bond activation catalysis[11] and phosphate hydrolysis.[6,7]

Experimental Section

All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere, and all aqueous solutions were thoroughly purged with prepurified nitrogen prior to use. Anhydrous manipulations were done in a Vacuum Atmosphere glovebox with less than 1 ppm of O_2. The pH/pD measurements were carried out using a Shindengen pH BOY-P2 pH meter or a Beckman Φ10 pH meter with a 4 mm diameter probe (Beckman) inserted directly into the NMR tube, and the reported pD values are the uncorrected pH meter readings. The pD of Cp_2MoCl_2(aq) was adjusted with concentrated deareated HCl or NaOH. Solutions at pH 7 were buffered using 4-morpholinepropanesulfonic acid, hemisodium salt (MOPS). ^1H NMR (299.95 MHz) spectra were recorded on a Varian Inova 300 spectrometer. Proton chemical shifts were referenced to residual solvent resonances. Molybdocene dichloride was purchased from Strem Chemical Co. (Newburyport, MA) and used as received. Deuterium oxide (99.9% D) was purchased from Cambridge Isotope Laboratories (Andover MA), and all other necessary reagents were purchased from Aldrich Chemcal Co. (Milwaukee, WI) and used as received. Molybdocene dihydride[33] and $[(CpR_2)Mo(\mu\text{-}OH)]_2(OTs)_2$ (R = H, Me)[15,11] were prepared according to literature procedures.

Molecular Structure of $[(CpMe)_2Mo(\mu\text{-}OH)]_2(OTs)_2$ (2′). The dimeric complex was prepared as described previously.[11] Crystals were grown from methanol. A dark red tabular fragment of approximate dimensions 0.04 × 0.24 × 0.26 mm was attached to a fiber with silicon glue. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range 13° < θ < 14°. Table 3 contains

---

(30) Ito, T.; Yoden, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2365–2370.

(31) Difficulty in shimming the sample occasionally resulted in apparent “splitting” of the resonances. The important information, however, i.e. the change in the relative ratios of the two molybdocene species upon dilution at pH 3.5, could be obtained from these spectra.

(32) This equilibrium constant is in agreement with $K_{eq} = 5.1 \times 10^{-2}$ M obtained from kinetic analysis of dimethyl phosphate hydrolysis promoted by **1**:[6] Kuo, L. Y. Unpublished results.

(33) Luo, L.; Lanza, G.; Fragala, I. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 3111–3122.

Table 3. Crystallographic Data for 2′

composition	$C_{38}H_{44}Mo_2O_8S_2$
fw	884.76
cryst syst	monoclinic
space group	$C2/c$
a	17.751(7) Å
b	8.739(2) Å
c	23.618(5) Å
β	99.32(3)°
V	3616(3) Å^3
Z	4
d_{calcd}	1.625 g cm^{-3}
T	23 °C
radiation, λ	Mo Kα, 0.710 73 Å
μ	8.38 cm^{-1}
rel transmissn coeff	0.834−1.000 (φ)
no. of obsd rflns	2370 ($I \geq \sigma(I)$)
no. of indep rflns	3166
$R(F)$,[a] $R_w(F)$	0.047, 0.052
$R(F^2)$, $R_w(F^2)$[b]	0.083, 0.103

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

a summary of crystal data and the final residuals. A more extensive table including particulars of data collection and structure refinement can be found in the Supporting Information. The systematic absences together with the centric distribution of intensities indicated space-group $C2/c$. Small absorption corrections based on azimuthal (ψ) scans were applied. A SIR92 E-map[34] showed the non-hydrogen atoms of the asymmetric unit. A difference synthesis showed minor alternative sites for the sulfonate oxygen atoms, resulting from a rotation about the S−C bond; these were refined isotropically (refined occupancy factor 0.154(10)). Other hydrogen atoms were refined anisotropically. Hydrogen atoms were included at the calculated positions and updated after each cycle of refinement, except for the H atom of the bridging OH group, which was included at the position indicated by a difference synthesis. The final difference synthesis was featureless. The teXsan program suite,[35] incorporating complex atomic scattering factors, was used in all calculations.

Acknowledgment is made to the NSF for the support of this work.

Supporting Information Available: Detailed crystallographic data for **1′**, including tables of atomic coordinates, anisotropic displacement parameters, bond lengths and angles, least-squares planes and dihedral angles, and torsion angles, and a figure giving ^{1}H NMR spectra showing the addition of **1** to a solution of **2** at pD 7. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000180L

---

(34) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guigliardi, A.; Burla, M. C.; Polidori, G.; Camalli, N. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(35) teXsan Software for Single-Crystal Structure Analysis, version 1.7; Molecular Structure Corp., 3200A Research Forest Drive, The Woodlands, TX 77381, 1997.