Cyclopentadienylmolybdenum(VI) and Molybdenum(V) Oxo Chemistry: New Synthetic and Structural Features

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Keywords: Cyclopentadienyl ligands / Molybdenum / Oxo ligands / X-ray crystallography

Convenient syntheses for Cp, Cp^*, and related cyclopentadienyl derivatives ($^4Cp = C_5HiPr_4$; $Cp''' = C_5H_2tBu_3$-1,2,4) of formula $[(Ring)_2Mo_2O_5]$ are described. Compound $[Cp_2Mo_2O_5]$ was produced in good yields by the rapid oxidation of red $[CpMoO_2]_4$ with PhIO in CH_2Cl_2. $[Cp^*{}_2Mo_2O_5]$ was obtained by CH_3COOH acidification of aqueous solutions of $[Cp^*MoO_3]^-Na^+$, the latter being generated in a single step from $[Cp^*MoCl_4]$ and more than 5 equiv. of aqueous NaOH in air. Minor quantities of $[Cp^*MoO_2]_2$ were also isolated from this reaction, although the formation of this by-product may be reduced by using a two-step basic hydrolysis procedure. Extension of the latter strategy also allowed the preparation of $[^4Cp_2Mo_2O_5]$, $[Cp'''{}_2Mo_2O_5]$, and $[^4CpMoO_2Cl]$ in good yields, in addition to the by-product $[Cp'''MoO_2]_2$. X-ray structures are reported for compounds $[^4Cp_2Mo_2O_5]$, $[Cp'''{}_2Mo_2O_5]$, $[Cp^*MoO_2]_2$, $[Cp'''MoO_2]_2$, and $[^4CpMoO_2Cl]$.

Introduction

High oxidation state organometallic chemistry has experienced rapid development in the last 20 years, mostly justified by the search for efficient oxidation catalysts. Half-sandwich oxo derivatives of rhenium,[1−3] displaying a very rich chemical reactivity and catalytic activity, are an example of a well investigated class of compounds. Some of the earliest high oxidation state organometallics however, are the cyclopentadienyl oxo derivatives of molybdenum, first developed in the laboratory of M. L. H. Green.[4,5]

The stability of high oxidation state complexes requires the presence of electronegative and π-donating ligands such as halides or negatively charged oxygen- (oxo, alkoxo) or nitrogen-based (nitrido, imido, amido) ligands. The organic fragments most compatible with this ligand environment are odd-electron ones, such as alkyls (1-electron), allyls (3-electron), dienyls (5-electron), etc., while neutral organic fragments (olefins, arenes, etc.) need more electron-rich, low-valent metal centers to optimize bonding. These conditions confer a high degree of covalency on the resulting metal−carbon bonds, which consequently become quite resistant to hydrolytic conditions. It is therefore somewhat surprising that the physical behavior and chemical reactivity of high oxidation state organometallics has not been investigated systematically in water, although aqueous reagents are sometimes used for their syntheses. This contrasts with the well-developed aqueous chemistry of high oxidation state oxomolybdenum complexes.[6,7] On the other hand, the rich electrochemical behavior displayed by the metals involved, notably molybdenum, makes these molecules quite interesting for potential electrocatalytic applications. For these reasons, we initiated a research effort aimed at increasing our basic knowledge of the physical properties and chemical reactivity of organomolybdenum compounds in a variety of high oxidation states in water.

Although several investigations of cyclopentadienyl oxo complexes of molybdenum in high oxidation states have been reported,[8,9] routes to these materials cannot be considered to be completely satisfactory. In this first contribution, we focus on improvements in the synthetic procedures to produce compounds $[Cp_2Mo_2O_5]$ and $[Cp^*{}_2Mo_2O_5]$, which we plan to use as starting materials for our studies. We also report an extension of the synthesis of analogues containing differently substituted cyclopentadienyl rings. We are interested in cyclopentadienyl rings with a high degree of substitution, as these are known to afford more inert metal-cyclopentadienyl bonds by restricting access to the

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metal center, while at the same time rendering the other ligands more labile. Interesting reactivity may thus be expected. Some basic aqueous chemistry related to the optimization of the syntheses reported in this paper is also discussed. Detailed studies of the behavior of these compounds in water as functions of pH[10] and of electrode potential[11] have also been completed, and are being reported separately.

Results

The Cyclopentadienyl Oxo Molybdenum(VI) System

Discussion of Previously Reported Routes

As mentioned in the introduction, [$Cp_2Mo_2O_5$] has been known since 1964, but no reliably high-yielding and practical synthesis seems to be available yet. It was first obtained in 20% yield, together with several other products, from the photolytic degradation of [$CpMo(CO)_3]_2$ in chloroform.[4] It has also been formed in low yields by adventitious oxygenation of solutions of various CpMo derivatives.[4,5] A synthesis in higher yield (79%) by oxidation of the dinuclear Mo^V compound [$CpMoO_2]_2$ has been reported. This, however, required use of Ag_2O as the oxygen-transfer agent and warming in CH_2Cl_2 at 55 °C for 1.5 days.[12] The precursor complex could in turn be obtained by hydrolysis of [$CpMoX_4$] (X = Cl, Br) with excess water. A red isomer, formulated as a tetranuclear compound, was obtained immediately, while longer exposure to water or dissolution of the red isomer in acetone or chloroform slowly afforded a dinuclear orange isomer.[5,12] A similar behavior has been described for analogous compounds with monosubstituted cyclopentadienyl ligands.[12] Since the reported behavior of the red tetrameric form suggested that it was a chemically more labile form, we wondered whether the oxidation of this red isomer by sufficiently rapid oxygen-transfer agents might provide an easier route to the desired Mo^{VI} product in high yield before its conversion into the less reactive orange isomer.

New Synthetic Strategy

Several effective reagents are commonly used for oxygen-transfer chemistry, the most easily accessible one being H_2O_2. We were hesitant to use this reagent, because the formation of peroxo compounds of Mo^{VI} or W^{VI}, such as [$Cp^*W(O_2)(O)R$][13−15] or [$Cp^*M(O_2)(O)Cl$] (M = Mo, W),[16,17] by treatment of suitable precursors with either H_2O_2 or hydroperoxides has been described previously. Indeed, oxidation tests with H_2O_2 gave unsatisfactory results. The use of PhIO,[18] on the other hand, provided a rapid and convenient synthesis in two steps (>50% overall yield) from [$CpMoCl_4$], itself easily available from commercially available [$Mo(CO)_6$] [Equations (1) and (2)].[19] The second step was complete within 15 min at room temperature, and the best results were obtained when the solution was worked up immediately. If the product was allowed to stand in the dichloromethane solution, darker, insoluble by-products began to form. The intermediate red Mo^V oxo complex had to be isolated and removed from water; an attempt to carry out the synthetic procedure without this isolation step gave unsatisfactory results. This procedure, however, constitutes a significant improvement over those previously available, especially in terms of time efficiency, as both steps can be carried out at room temperature and the overall procedure may be accomplished in half a day.

$$4\,[CpMoCl_4] + 8\,H_2O \rightarrow [CpMoO_2]_4 + 16\,HCl \qquad (1)$$

$$[CpMoO_2]_4 + 2\,PhIO \rightarrow 2\,[Cp_2Mo_2O_5] + 2\,PhI \qquad (2)$$

The procedure described below for the Cp* and related analogues, via the hitherto unknown [$CpMoO_3]^-$ anion,[20] does not give satisfactory results for the Cp system.

The Pentamethylcyclopentadienyl Oxo Molybdenum(VI) System

Discussion of Previously Reported Routes

The Cp* compound was first reported in 1985 by Herberhold et al. as the product of the aerial oxidation of [$Cp^*Mo(CO)_2(NO)$],[21] and was subsequently shown to form in low yield as a by-product in a variety of other reactions.[22−25] A high-yielding synthesis by aerial oxidation of [$Cp^*Mo(CO)_2]_2$ in chloroform was reported by Faller and Ma, although the product was said to be contaminated by ca. 15% of the chloride complex [Cp^*MoO_2Cl] and needed further exposure to acetone/water for purification,[26] while the synthesis of the starting compound from commercially available [$Mo(CO)_6$] is itself not free from pitfalls.[27,28] This reaction was re-examined later by Bottomley and shown to yield a host of other incompletely oxidized products under a variety of conditions.[29,30] The preparation from [Cp^*MoCl_4] in 70−75% yield reported by Umakoshi and Isobe[31] is related to the synthetic procedure reported by us here, but was not optimized for large-scale syntheses and uses the exotic sodium oxometallate salts Na_2MoO_4, Na_2WO_4, or $NaVO_3$ as oxidants. Another reported high-yielding synthesis was by protonolysis of the unusual starting compound [$Cp^*Mo(N\mathit{t}Bu)_2Cl$] with aqueous HCl.[32]

Finally, work carried out in Geoffroy's laboratory showed that the hydrolysis of [Cp^*MCl_4] (M = Mo, W) in the presence of an amine ($\mathit{t}BuNH_2$) yields $\mathit{t}BuNH_3{}^+[Cp^*MO_3]^-$ in good yields,[33] while Sundermeyer showed that the same anions also form on treatment of the oxo-bridged dimers [$Cp^*{}_2M_2O_5$] with tetrabutylammonium hydroxide.[32] Acidification of the anion solution, examined in the Geoffroy study for the tungsten compound, gave back the dinuclear complex through the presumed condensation of initially formed [$Cp^*WO_2(OH)$].[33]

A detailed discussion of this reversible anion/dimer transformation and the aqueous chemistry of the tetrachloride compounds is essential, as it forms the basis of our improved synthetic strategy. Geoffroy et al. reported that treatment of [Cp^*MoCl_4] with 2 equiv. of NaOH in acetone/water in an open flask for more than 30 min gave [Cp^*MoO_2Cl], while use of an unspecified excess of NaOH afforded the dinuclear [$Cp^*_2Mo_2O_5$].[34] The reaction between [Cp^*MoO_2Cl] and excess (3 equivalents) NaOH was also reported to yield the dinuclear compound. These observations seemed odd to us in view of Sundermeyer's result mentioned above, which we have confirmed (see next section).[35] In contrast with the apparent lack of reactivity between [$Cp^*_2Mo_2O_5$] and excess aqueous NaOH, excess aqueous tBuNH$_2$ (a weaker base than NaOH) under analogous conditions yielded $t\mathrm{BuNH_3}^+[\mathrm{Cp^*MoO_3}]^-$ in good yields.[34] Furthermore, it was shown that acidification of dichloromethane solutions of the $t\mathrm{BuNH_3}^+[\mathrm{Cp^*MoO_3}]^-$ salt with acetic acid afforded [$Cp^*_2Mo_2O_5$], which was recovered in 58% yield. From these observations, it would seem logical to imagine a pH-dependent equilibrium between the anionic mononuclear and the neutral dinuclear forms [Equation (3)] in water.[36] The anion should therefore be the ultimate product when excess strong base (e.g. NaOH) is present, in contrast to Geoffroy's report. On the basis of this hypothesis, we have developed the new synthetic procedure reported in the following section. Preliminary investigations indeed showed that yellow [$Cp^*_2Mo_2O_5$] solutions in MeOH/H_2O became nearly colorless upon treatment with NaOH, and the resulting basic solutions turned yellow once more when the pH was lowered by addition of strong acids.

$$[\mathrm{Cp^*_2Mo_2O_5}] + 2\,\mathrm{OH^-} \rightleftarrows 2\,[\mathrm{Cp^*MoO_3}]^- + \mathrm{H_2O} \qquad (3)$$

New Synthetic Strategy

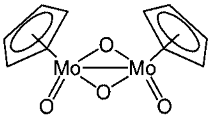
[Cp^*MoCl_4] is conveniently prepared in high yields and purity[37] from commercially available [$Mo(CO)_6$] and was therefore the starting compound of choice for our synthetic work. As mentioned in the previous section, it seemed to us that excess NaOH under aerobic conditions should afford the cyclopentadienyltrioxomolybdate anion directly, according to the stoichiometry of Equation (4).

$$2\,[\mathrm{Cp^*MoCl_4}] + 10\,\mathrm{OH^-} + 1/2\,\mathrm{O_2} \rightarrow 2\,[\mathrm{Cp^*MoO_3}]^- + 8\,\mathrm{Cl^-} + 5\,\mathrm{H_2O} \qquad (4)$$

Treatment of acetone solutions of [Cp^*MoCl_4] with a slight excess (ca. 6 equivalents) of aqueous NaOH in air for over a day at room temperature yielded a suspension of the pale yellow precipitate $[\mathrm{Cp^*MoO_3}]^-\mathrm{Na}^+$, but also minor quantities of a soluble, colored by-product (identified as [Cp^*MoO_2]$_2$, vide infra). Separation of this by-product was accomplished by complete evaporation of the solvent mixture and redissolution in pure water, which dissolved the sodium salt but not the by-product. Since the sodium organomolybdate salt might have been difficult to separate from NaCl and excess NaOH by fractional crystallization, we proceeded directly to its conversion into the neutral dimer, which is insoluble in pure water. Dropwise addition of acetic acid from a burette resulted, after neutralization of the excess base, in the instantaneous precipitation of the yellow product. Addition of acid was stopped when administration of one further drop of the acid solution did not cause any further precipitation. The synthetic procedure could therefore be handled as a simple titration reaction, allowing the use of close to the stoichiometric amount of acid. This was important because excess acetic acid is also partially extracted into the ether layer and large quantities of this compound may interfere with the crystallization procedure or even contaminate the organomolybdenum product. This procedure consistently gave a pure product with yields in excess of 60% on a 2 g scale. The synthesis could also be accomplished stepwise, by treatment of [Cp^*MoCl_4] with three equivalents of NaOH for one day, followed by addition of three more equivalents of NaOH. In this fashion, the formation of the Mo^V by-product was avoided (see discussion). The isolated yield of the desired product, however, was not increased by this modified procedure.

Isolation and Structure of the [Cp^*MoO_2]$_2$ By-Product

The water-insoluble crop generated during the synthetic procedure described above contained orange-red crystalline [Cp^*MoO_2]$_2$, which could be recovered in yields of up to 20% depending on the operating conditions. It seemed that not only the time of exposure to air but also the relative amount of water and acetone was important in determining the ratio between the Mo^V and Mo^{VI} products (see Discussion), smaller amounts of water seeming to favor a greater degree of oxidation. [Cp^*MoO_2]$_2$ has been reported previously and shown to adopt two possible structures differing in the relative arrangement of the Cp* and terminal oxo ligands across the central Mo(μ-O)$_2$Mo plane: *syn* as in **I**[38] (like the analogous Cp system)[39] or *anti* as in **II**.[40] We have redetermined the structure of the *syn* form at lower temperature with a better precision. The results have been deposited with the CCDC but, since they do not differ significantly from those of the higher temperature structure, they are not explicitly reported here. The metal-metal distance in the *syn* polymorph [2.587(1) Å] is significantly shorter than that in the *anti* polymorph [2.647(3) Å],[40] undoubtedly because of the butterfly arrangement that allows the metals to approach each other, in contrast to the planar arrangement in the *anti* isomer. The same situation has been found for $[(\mathrm{L})_2\mathrm{Mo_2O_4}]^{2+}$ (L = 1,5,9-triazacyclononane).[41,42]



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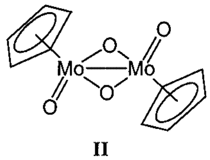


II

Oxo Molybdenum(VI) and Molybdenum(V) Systems with Sterically more Encumbering Cyclopentadienyl Rings

Syntheses

The procedure described above for the Cp* system was applied in a straightforward manner to the hydrolysis of [$^4\text{CpMoCl}_4$] and [$\text{Cp}'''\text{MoCl}_4$]. Again, aerial hydrolysis in both cases afforded solutions containing the water-soluble $\text{Na}^+[(\text{Ring})\text{MoO}_3]^-$ salt. This was not isolated, but its presence was indicated by its behavior upon acidification, identical to that seen in the corresponding Cp* system described above. [$^4\text{Cp}_2\text{Mo}_2\text{O}_5$] and [$\text{Cp}'''_2\text{Mo}_2\text{O}_5$] were obtained as yellow or yellow-orange crystalline solids that were insoluble in water but soluble in ether. Both were crystallized, and their structures were confirmed by X-ray diffraction methods (see next section). Like their Cp and Cp* analogues,[4,22] they displayed two IR vibrations typical of the Mo=O functionalities (symmetric and asymmetric at ca. 885 and 920 cm^{-1}, respectively) and one due to the asymmetric Mo−O−Mo stretch (at ca. 760 cm^{-1}).

While the ^{4}Cp system afforded the expected dinuclear Mo^{VI} product with no indication of incomplete oxidation, the Cp''' system behaved like the Cp* system described above and also gave a water-insoluble fraction, from which the dinuclear Mo^{V} complex [$\text{Cp}'''\text{MoO}_2$]$_2$ was recovered. This compound was also characterized by X-ray diffraction methods (see below).

X-ray Structures of the [(Ring)$_2$Mo$_2$O$_5$] Compounds

Several X-ray structural determinations of various polymorphs of [$\text{Cp*}_2\text{Mo}_2\text{O}_5$][23−26] have been reported over the years and a discussion of the similarities between them is already available.[25] It is interesting to see whether the steric bulk of the cyclopentadienyl ligand plays any role on the other structural parameters. The geometries of compounds [$^4\text{Cp}_2\text{Mo}_2\text{O}_5$] and [$\text{Cp}'''_2\text{Mo}_2\text{O}_5$] are shown in Figures 1 and 2, respectively, and the relevant metric data are compared in Table 1. The ^{4}Cp compound has a symmetry-imposed inversion center on the bridging oxygen atom, and two independent half molecules are contained in the asymmetric unit. The Cp''' compound, on the other hand, has a single entire molecule in the asymmetric unit. While the Mo−O−Mo angle is forced to be linear in the first case, it deviates quite substantially from linearity in the second one. This deviation is larger than the largest one previously observed for the related Cp* polymorphs [172.7(3)°]. The Mo=O and Mo-(μ-O) distances for the Cp* structures were found to be in the 1.67−1.72 Å and 1.85−1.90 Å ranges, respectively. The same parameters are within these ranges for both ^{4}Cp and Cp''' structures, the Mo-(μ-O) distances being towards the long end of this range in both cases.

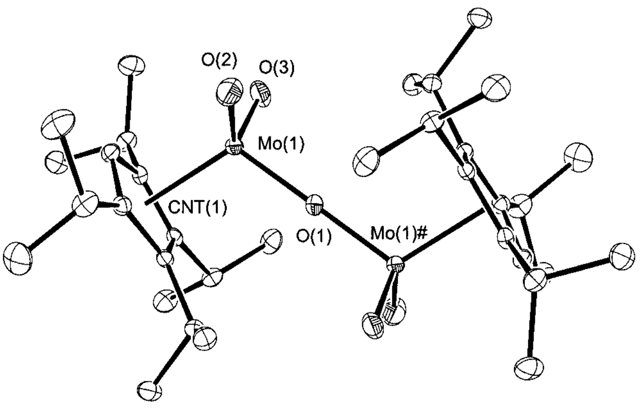


Figure 1. An ORTEP view of one of the two independent molecules of compound [$^4\text{Cp}_2\text{Mo}_2\text{O}_5$]; ellipsoids are drawn at the 50% probability level; the atom numbering scheme for the other molecule is as follows: Mo(2) for Mo(1), O(4) for O(1), O(5) for O(2), O(6) for O(3), and CNT(2) for CNT(1)

X-ray Structure of [$\text{Cp}'''\text{MoO}_2$]$_2$

The geometry of [$\text{Cp}'''\text{MoO}_2$]$_2$ is shown in Figure 3 and selected bonding parameters are reported in Table 2. The immediate striking feature is the relative *anti* arrangement of the two Cp''' groups: these are *syn* in the Cp analogue, while both arrangements are possible for the Cp* molecule. Although no unambiguous conclusion can be drawn, it seems reasonable to imagine that the steric bulk of the Cp''' ligand enforces the *anti* arrangement, while the compound might prefer the *syn* arrangement for electronic reasons. Therefore, the *syn* arrangement should be observed in the less crowded cases (such as Cp). It is easy to imagine how the placement of two Cp''' ligands into the *syn* structure (see drawing **I**) would introduce a severe strain in the molecule.

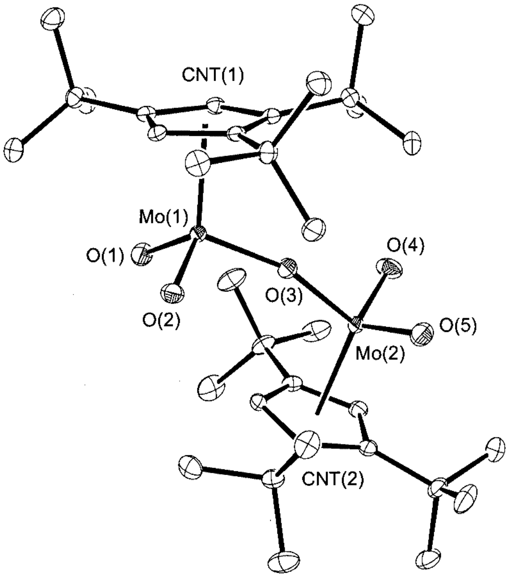


Figure 2. An ORTEP view of compound [$\text{Cp}'''_2\text{Mo}_2\text{O}_5$]; ellipsoids are drawn at the 50% probability level

The Mo−Mo distance in [$\text{Cp}'''\text{MoO}_2$]$_2$ compares quite well with that in the *anti* form of [Cp*MoO_2]$_2$ [2.647(3) Å].[40] This parameter is therefore much more sensitive to the geometry of the central Mo_2O_2 moiety (bent for the *syn* and planar for the *anti*) than to the type of cyclopentadienyl ring. The Mo=O and Mo-(μ-O) distances do not seem

Table 1. Selected bond lengths (Å) and angles (°) for compounds [(Ring)$_2$Mo$_2$O$_5$] (Ring = ^{4}Cp, Cp′′′)

[^{4}Cp$_2$Mo$_2$O$_5$] [a]			[Cp′′′$_2$Mo$_2$O$_5$]	
Mo(1)−O(1)	1.89560(18)	1.89985(17)	Mo(1)−O(3)	1.8950(12)
			Mo(2)−O(3)	1.8978(11)
Mo(1)−O(2)	1.7092(15)	1.7071(15)	Mo(1)−O(1)	1.7088(12)
Mo(1)−O(3)	1.6969(15)	1.7034(14)	Mo(1)−O(2)	1.7125(12)
			Mo(2)−O(4)	1.7101(13)
			Mo(2)−O(5)	1.7050(13)
Mo(1)−CNT(1)	2.125(3)	2.123(3)	Mo(1)−CNT(1)	2.133(3)
			Mo(2)−CNT(2)	2.118(3)
O(1)−Mo(1)−O(2)	103.99(5)	103.46(5)	O(1)−Mo(1)−O(3)	103.43(5)
O(1)−Mo(1)−O(3)	102.93(5)	104.30(5)	O(2)−Mo(1)−O(3)	104.99(6)
			O(3)−Mo(2)−O(4)	103.23(6)
			O(3)−Mo(2)−O(5)	102.52(6)
O(2)−Mo(1)−O(3)	106.03(8)	105.89(8)	O(1)−Mo(1)−O(2)	104.49(6)
			O(4)−Mo(2)−O(5)	104.87(7)
CNT(1)−Mo(1)−O(1)	111.3(2)	112.3(2)	CNT1−Mo(1)−O(3)	111.1(2)
			CNT2−Mo(2)−O(3)	114.0(3)
CNT(1)−Mo(1)−O(2)	114.6(2)	116.1(2)	CNT1−Mo(1)−O(1)	116.9(3)
CNT(1)−Mo(1)−O(3)	116.6(2)	113.6(2)	CNT1−Mo(1)−O(2)	114.5(2)
			CNT2−Mo(2)−O(4)	114.7(3)
			CNT2−Mo(2)−O(5)	115.9(3)
Mo(1)−O(1)−Mo(1)#	180.0	180.0	Mo(1)−O(3)−Mo(2)	162.61(7)

[a] For the numbering scheme of the second independent molecule (second column), see caption of Figure 1.

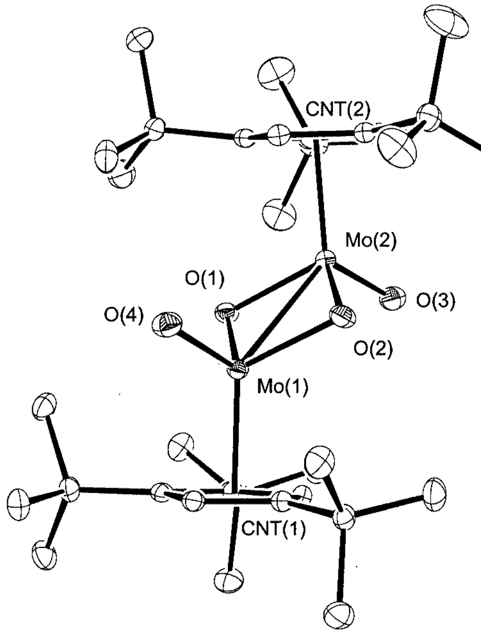


Figure 3. An ORTEP view of [Cp′′′MoO$_2$]$_2$; ellipsoids are drawn at the 50% probability level

sensitive to either effect, and are essentially identical to those of all other previously described molecules with this stoichiometry, whether *syn* or *anti*.

The [^{4}CpMoO$_2$Cl] System

According to previous Cp* literature,[34] the aerobic hydrolysis of the tetrachloro compound with two equivalents of aqueous NaOH directly afforded the corresponding dioxochloro derivative. For the less electron-rich Cp system, on the other hand, excess water quite rapidly yielded the dioxo system, as seen above, even in the absence of base.[5] The ^{4}Cp system behaved similarly to the Cp*, to which it is sterically and electronically more similar. Identical yields of [^{4}CpMoO$_2$Cl] were obtained when [^{4}CpMoCl$_4$] was hydrolyzed in the presence of either three or two equivalents of NaOH. In the IR spectrum, the compound showed, as expected, Mo=O stretching vibrations essentially identical to those in the related oxo-bridged dinuclear complex and no band in the Mo−O−Mo stretching region. The structure of this product has also been confirmed by X-ray crystallography (see Figure 4); the relevant bond lengths and angles are reported in Table 3. While no structure for a [(Ring)MoO$_2$X] (X = Cl or other halogen) seems to have been reported previously, related structures are those of [{C$_5$Ph$_4$[C$_6$H$_3$(OMe)$_2$-2,5]}MoO$_2$(OMe)][43] and [Cp*MoO$_2${(2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$)}$_2$Si$_2$O$_2$(OH)$_3$].[44] The Mo=O distances are quite similar in all these compounds. The Mo−Cl distance compares with related Mo^V−Cl distances and appears to be affected mostly by the steric pressure of the cyclopentadienyl ring, as suggested by the following examples: [Cp*MoOCl]$_2$O: 2.368(2) Å,[31] [CpMoOCl$_2$]: 2.301(4) Å (average),[45] [Cp*MoOCl$_2$]: 2.245(9) and 2.330(5) Å (averages) in two independent reports.[30,46]

Discussion

From the previous literature reports and from our results, the following simplified picture emerges for the aerobic hydrolysis of [(Ring)MoCl$_4$] compounds (see Scheme 1). Hydrolysis of the first two Mo−Cl bonds affords [(Ring)MoOCl$_2$], which can either undergo further hydrolysis to

Table 2. Selected bond lengths (Å) and angles (°) for compound [Cp'''MoO]$_2$

Mo(1)−Mo(2)	2.65115(19)	CNT(2)−Mo(2)−Mo(1)	127.7(1)
Mo(1)−CNT(1)	2.082(2)	CNT(1)−Mo(1)−O(1)	114.5(1)
Mo(2)−CNT(2)	2.082(1)	CNT(2)−Mo(2)−O(1)	113.1(1)
Mo(1)−O(1)	1.9475(11)	CNT(1)−Mo(1)−O(2)	117.8(1)
Mo(2)−O(1)	1.9428(11)	CNT(2)−Mo(2)−O(2)	117.5(1)
Mo(1)−O(2)	1.9464(11)	CNT(1)−Mo(1)−O(4)	116.7(2)
Mo(2)−O(2)	1.9488(11)	CNT(2)−Mo(2)−O(3)	117.3(2)
Mo(1)−O(4)	1.7045(12)	O(2)−Mo(1)−O(1)	94.09(5)
Mo(2)−O(3)	1.7063(12)	O(1)−Mo(2)−O(2)	94.16(5)
Mo(2)−Mo(1)−O(1)	46.97(3)	O(1)−Mo(1)−O(4)	106.20(5)
Mo(1)−Mo(2)−O(1)	47.11(3)	O(1)−Mo(2)−O(3)	106.94(5)
Mo(2)−Mo(1)−O(2)	47.15(3)	O(2)−Mo(1)−O(4)	104.64(5)
Mo(1)−Mo(2)−O(2)	47.07(3)	O(2)−Mo(2)−O(3)	105.06(6)
Mo(2)−Mo(1)−O(4)	111.79(4)	Mo(1)−O(1)−Mo(2)	85.92(4)
Mo(1)−Mo(2)−O(3)	115.06(4)	Mo(1)−O(2)−Mo(2)	85.78(4)
CNT(1)−Mo(1)−Mo(2)	131.5(2)		

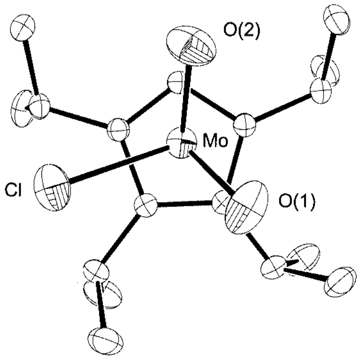
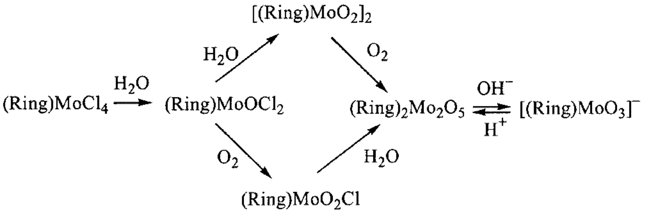


Figure 4. An ORTEP view of compound [^{4}CpMoO$_2$Cl]; ellipsoids are drawn at the 50% probability level

Table 3. Selected bond lengths (Å) and angles (°) for compound [^{4}CpMoO$_2$Cl]

Mo−Cl	2.3251(7)	Cl−Mo−O(2)	101.54(8)
Mo−O(1)	1.720(2)	Cl−Mo−CNT	108.8(2)
Mo−O(2)	1.700(2)	O(1)−Mo−O(2)	106.83(11)
Mo−CNT	2.113(3)	O(1)−Mo−CNT	118.1(2)
Cl−Mo−O(1)	102.15(8)	O(2)−Mo−CNT	117.2(3)

give [(Ring)MoO$_2$]$_2$ or may be oxidized to give [(Ring)MoO$_2$Cl]. Finally, the dioxo Mo^V dimer can be oxidized and the chlorodioxo Mo^{VI} complex can be hydrolyzed, to yield [(Ring)$_2$Mo$_2$O$_5$] in both cases. Under basic conditions, however, the final product converts to the [(Ring)MoO$_3$]$^-$ anion. Of course, other intermediates must also be formed during these transformations, notably hydroxo complexes, the relative stability of which is supported by some evidence.[12,31,34]



Scheme 1

If hydrolysis prevails over oxidation at the level of the first dichlorooxo intermediate, resulting in the dinuclear, metal-metal bonded dioxo compound [(Ring)MoO$_2$]$_2$, further oxidization by dioxygen to the Mo^{VI} dimer is rather difficult. This is what happens for the simple Cp system. In fact, even oxygen-delivering agents such as Ag$_2$O react with it slowly.[12] However, the kinetic red form is more reactive, and a successful strategy for the formation of [Cp$_2$Mo$_2$O$_5$] with PhIO by this route is presented in this paper.

The rate of hydrolysis seems to decrease as the steric bulk of the cyclopentadienyl ring increases. The greater donating power of the bulkier rings may also retard the complete hydrolysis for electronic reasons. Oxidation of the dichlorooxo Mo^V species, on the other hand, should be made more favorable by more electron-rich ligands. At any rate, the oxidation step may then prevail over hydrolysis, resulting in the chlorodioxo Mo^{VI} species provided there is dioxygen available. This is the situation encountered for the Cp* system, for which aerobic hydrolysis in the presence of two equivalents of NaOH was reported to give a good yield of [Cp*MoO$_2$Cl].[34] The same also occurs for the ^{4}Cp system reported here with either two or three equivalents of NaOH. The use of neutral aqueous conditions should produce three acid equivalents, as shown in Equation (5). Evidently, the last chloride ligand is not hydrolyzed under neutral conditions, whereas at high pH (excess NaOH) the only recovered product (after acidification) is [^{4}Cp$_2$Mo$_2$O$_5$].

$$2\,[^4\mathrm{CpMoCl_4}] + 3\,\mathrm{H_2O} + 1/2\,\mathrm{O_2} \rightarrow 2\,[^4\mathrm{CpMoO_2Cl}] + 6\,\mathrm{Cl^-} + 6\,\mathrm{H^+} \tag{5}$$

The relative rates of hydrolysis and oxidation for [(Ring)MoOCl$_2$] should also depend on other factors such as the concentration of water, the nature of the organic solvent, and the pH. Although we have not carried out a comprehensive study of these effects, we do have qualitative indications that more Mo^V dimer complex is obtained when a larger amount of water is used for the Cp* and Cp′′′ systems. If Scheme 1 is valid, one would expect that a greater concentration of OH^- (larger NaOH excess) should favor the hydrolysis pathway, resulting in the $[(Ring)MoO_2]_2$ system. Indeed, we did obtain a significant amount of this compound as a by-product when the hydrolysis was carried out in the presence of more than five equivalents of NaOH, whereas a good yield of $[Cp^*MoO_2Cl]$ was obtained by Geoffroy et al. with only two equivalents, with no mention of formation of the Mo^V product.[34] Indeed, repetition of the synthesis of $[Cp^*_2Mo_2O_5]$ by stepwise addition of three equivalents of NaOH, followed by three more equivalents a day later (without isolation of the intermediate $[Cp^*MoO_2Cl]$ complex) completely avoided the formation of the $[Cp^*MoO_2]_2$ by-product.

Some subtleties, however, are not yet completely understood. For instance, the Mo^V dimer was obtained for the Cp′′′ system, as for the Cp* system, but no analogous product was obtained for the ^{4}Cp system, even when five equivalents of NaOH were used. The use of excess NaOH, however, allows access (provided that the oxidation route is followed) to the water-soluble sodium salts of $[(Ring)MoO_3]^-$. Although we have not isolated and characterized the new anions of this type for the ^{4}Cp and Cp′′′ systems, their formation is indicated by the protonation reactivity, which is identical to that of the Cp* system: acidification of the water solutions yields the yellow, water-insoluble $[(Ring)_2Mo_2O_5]$ products.[36]

Conclusion

High oxidation state monocyclopentadienyl oxo derivatives of molybdenum are often the end products of oxidative decompositions of lower valent derivatives and were previously available only in low yields or through the use of impractical starting materials and/or reagents. The hydrolytic route from the easily accessible cyclopentadienylmolybdenum(V) tetrachlorides has been optimized and extended to the preparation of new compounds with sterically more encumbered rings. The stability of these compounds in air and aqueous media makes the exploration of their aqueous chemistry and electrochemistry possible. Investigations in those directions are ongoing in our laboratory.

Experimental Section

General Remarks: All reactions were carried out in a Jacomex glove box or by use of standard Schlenk techniques under an argon atmosphere. The solvents were dried by conventional methods (THF, Et_2O, heptane, and pentane from sodium benzophenone ketyl and CH_2Cl_2 from P_4O_{10}) and distilled under argon prior to use. EPR measurements were carried out at the X-band microwave frequency on a Bruker ESP300 spectrometer. The spectrometer frequency was calibrated with DPPH ($g = 2.0037$). ^{1}H NMR spectra were recorded on a Bruker AC 200 and referenced to the residual solvent protons of the deuterated solvent. The elemental analyses were carried out by the analytical service of the Laboratoire de Synthèse et d'Electrosynthèse Organométallique with a Fisons EA 1108 apparatus. The compounds $[(Ring)MoCl_4]$ (Ring = Cp, Cp* and ^{4}Cp) were prepared as described in the literature.[19,37,47] The compound $[Cp'''MoCl_4]$ was prepared by a straightforward adaptation of those procedures as described below.

Tetrachloro(1,2,4-tri-*tert*-butylcyclopentadienyl)molybdenum(V), $[Cp'''MoCl_4]$: $Mo(CO)_6$ (2.64 g, 10.0 mmol) and NaCp′′′ (2.66 g, 10.3 mmol) were mixed as solids and suspended in 40 mL THF. The suspension turned into an orange solution during a 10 min period. It was then heated under reflux for 18 h. IR monitoring indicated the formation of $[Cp'''Mo(CO)_3]^-Na^+$ (strong peaks at 1885, 1784 and 1736 cm^{-1}, similar to literature values for the Cp* analogue). After the mixture had cooled to room temperature, MeI (700 µL, 11.25 mmol) was added to the deep orange-red solution, causing darkening to brown. After additional heating under reflux for 3 h, the solvent was removed in vacuo to leave a yellow brown residue, which was extracted into 60 mL CH_2Cl_2. After filtration, the deep-orange solution was evaporated to dryness to yield 4.13 g (9.64 mmol; 96.4%) of yellow-brown $[Cp'''Mo(CO)_3Me]$.

A portion of this product, (3.11 g, 7.26 mmol) was dissolved in 40 mL CH_2Cl_2. A suspension of $PhICl_2$ (4.99 g, 18.2 mmol) in 50 mL CH_2Cl_2 was added in small portions, causing a darkening of the orange brown solution to brown and then to deep violet with vigorous CO evolution. After having been heated under reflux for 90 min, the mixture was allowed to cool to room temperature and the solvents were evaporated to dryness. The violet black residue was washed with 2 × 20 mL pentane to remove the iodobenzene by-product. The deep violet solid $[Cp'''MoCl_4]$ was dried in vacuo. Yield 3.21 g, (93.7%). $C_{17}H_{29}Cl_4Mo$ (471.2): calcd. C 43.34, H 6.20; found C 43.57, H 6.44. EPR (CH_2Cl_2): $g = 1.99$, $a_{Mo} = 38.2$ G.

Tetraoxo-µ-oxodicyclopentadienyldimolybdenum(VI), $[Cp_2Mo_2O_5]$: $[CpMoCl_4]$ (0.555 g, 1.83 mmol) was placed in a flask containing distilled water (10 mL). Shaking of the resulting suspension for a few minutes gave rise to the formation of fine, deep red microcrystals. The product ($[CpMoO_2]_4$)[12] was separated by decantation of the mother liquor, washed with water (3 × 10 mL) and quickly with acetone (5 mL), and dried in vacuo for 2 h (yield 0.28 g, 79.5%). This material (1.45 mmol of Mo) was then dissolved in dichloromethane (ca. 100 mL), and solid PhIO (0.22 g, 1.0 mmol) was added to the resulting solution. The mixture was stirred at room temperature for 15 min, resulting in a color change from red to yellow. A longer reaction time should be avoided as it affords larger amounts of insoluble by-products. The solution was filtered and the filtrate was evaporated to give yellow microcrystals. The product was purified by recrystallization from CH_2Cl_2/pentane, and dried in vacuo. Yield 0.207 g, 71.1% (56.5% from $[CpMoCl_4]$). The analytical (IR, NMR) properties of the compound corresponded to those reported in the literature[4] and confirmed its purity.

Tetraoxo-µ-oxobis(pentamethylcyclopentadienyl)dimolybdenum(VI), $[Cp^*_2Mo_2O_5]$ and Dioxodi-µ-oxobis(pentamethylcyclopentadienyl)dimolybdenum(V), $[Cp^*MoO_2]_2$: Deep violet $[Cp^*MoCl_4]$ (3.48 g; 9.33 mmol) was added to a stirred solution of aqueous NaOH (19 mL; 3 M; 57 mmol) in acetone (200 mL) in an open beaker. The resulting dark brown suspension was stirred for 18 h, resulting in a lightening of the color to orange and the precipitation of a pale yellow solid. After evaporation to dryness the brownish residue was extracted into 75 mL of distilled water and filtered. The pale yellow filtrate was acidified with diluted glacial acetic acid, causing precipitation of a yellow solid at pH 3.8−4.0. The acetic acid addition was stopped when the addition of one further drop did not cause any additional precipitation. The precipitate was extracted with 4 × 100 mL portions of ether, the last extract being colorless. The combined organic layers were washed with distilled water and dried over $MgSO_4$ overnight. Evaporation of the solvent yielded 1.55 g (2.86 mmol; 61.3%) of $[(Cp^*MoO_2)_2O]$ as a yellow solid. The ^1H NMR spectrum of this compound (singlet at $\delta = 2.01$ in $CDCl_3$) corresponded to that described in the literature.[26]

In another experiment, starting from 2.03 g of $[Cp^*MoCl_4]$, the water-insoluble orange-red solid remaining from the water extraction was also worked up. It was washed with 20 mL ether and then with 20 mL pentane, and was dried in vacuo to afford the dinuclear Mo^V compound $[(Cp^*MoO_2)_2]$ as an orange, crystalline solid (192 mg, 0.37 mmol; 13.6%). $C_{10}H_{15}MoO_2$ (263.2): calcd. C 45.64, H 5.74; found C 45.36, H 5.71. The ^1H NMR spectrum ($\delta = 1.98$ in $CDCl_3$) corresponded to that reported in the literature.[38] Suitable single crystals for X-ray diffraction could be grown by layering a saturated THF solution with heptane at room temperature. Normally up to ca. 20% of this by-product was recovered, depending on the reaction conditions.

Tetraoxo-μ-oxobis(tetraisopropylcyclopentadienyl)dimolybdenum(VI), $[^4Cp_2Mo_2O_5]$: Deep purple $[^4CpMoCl_4]$ (609 mg, 1.29 mmol) was quickly added, as a solid, to a stirred mixture of acetone (75 mL), THF (75 mL) and aqueous NaOH (2.6 mL, 3 м, 7.8 mmol) in an open beaker. A brown suspension formed immediately, which lightened to orange yellow over a period of 2 h. After the mixture had been stirred overnight, the solvents were evaporated and the resulting yellow residue was extracted with 100 mL of warm water (50 °C). After filtration, the aqueous phase was acidified with diluted glacial acetic acid as described in the previous section, causing the precipitation of a yellow solid at pH 4. Extraction of this solid with 3 × 100 mL portions of ether, followed by separation of the organic layer, washing with water, and drying over $MgSO_4$, yielded a yellow ether solution, which was allowed to stand overnight and then was evaporated to dryness to yield 222 mg (0.3 mmol; 46.6%) of yellow $[(^4CpMoO_2)_2O]$. $C_{34}H_{58}Mo_2O_5$ (738.7): calcd. C 55.28, H 7.91; found C 54.69, H 8.25. IR (Nujol mull): $\tilde{\nu} = 919$ s, 889 s, 760 s cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.01$ (s, 1 H, ring-H), 3.10 (m, 4 H, $CHMe_2$), 1.39 [d, $J_{H,H} = 7.3$ Hz, 6 H, $CH(CH_3)_2$], 1.30 [d, $J_{H,H} = 7.3$ Hz, 12 H, $CH(CH_3)_2$], 1.19 [d, $J_{H,H} = 6.7$ Hz, 6 H, $CH(CH_3)_2$]. ^1H NMR (C_6D_6): $\delta = 6.14$ (s, 1 H, ring-H), 3.14 (m, 4 H, $CHMe_2$), 1.47 [d, $J_{H,H} = 6.7$ Hz, 6 H, $CH(CH_3)_2$], 1.44 [d, $J_{H,H} = 7.0$ Hz, 6 H, $CH(CH_3)_2$], 1.23 [d, $J_{H,H} = 7.0$ Hz, 6 H, $CH(CH_3)_2$], 1.02 [d, $J_{H,H} = 7.0$ Hz, 6 H, $CH(CH_3)_2$]. The ^1H NMR spectrum did not show any detectable Mo^V by-product. Yellow-orange single crystals suitable for X-ray diffraction were grown by slowly cooling a hot saturated heptane solution to room temperature.

Attempted Synthesis of Dioxodi-μ-oxobis(tetraisopropylcyclopentadienyl)dimolybdenum(V), $[^4CpMoO_2]_2$: $[^4CpMoCl_4]$ (670 mg, 1.42 mmol) was added to 150 mL of a stirred 1:1 mixture of acetone and distilled water, immediately yielding a brown suspension. The mixture was stirred for 40 hours, during which aliquots were withdrawn and the solid was separated, washed with water, and investigated by ^1H NMR spectrosopcy, showing the spectrum of $[^4Cp_2Mo_2O_5]$ as the only NMR-active species. The final mixture was filtered and the solid was washed with water and redissolved in pentane. After evaporation of the solvent, the residue was dried in vacuo to leave 240 mg (0.33 mmol; 46.8%) of $[^4Cp_2Mo_2O_5]$ as a orange powder (confirmed by ^1H NMR spectroscopy). Orange-red crystals could be grown by slowly cooling a hot saturated heptane solution to room temperature or by cooling a pentane solution to −25 °C. A single crystal from this batch showed the same unit cell as that of the yellow-orange crystals obtained from the procedure in the previous section.

Tetraoxo-μ-oxobis(1,2,4-tri-*tert*-butylcyclopentadienyl)dimolybdenum(VI), $[Cp'''_2Mo_2O_5]$ and Dioxodi-μ-oxobis(pentamethylcyclopentadienyl)dimolybdenum(V), $[Cp'''MoO_2]_2$: Purple $[Cp'''MoCl_4]$ (1.36 g, 2.89 mmol) was added to a stirred mixture of THF (75 mL), acetone (75 mL), water (10 mL) and aqueous NaOH (5.7 mL, 3 м, 17.1 mmol) in an open beaker. Some foaming occurred, and a Bordeaux-red solution formed immediately. No precipitate was detected during the following 24 hours of stirring at room temperature. Subsequent gentle heating (40−50 °C) of the mixture for two hours caused the precipitation of a red-violet product, which was collected on a filter, washed with water, and redissolved in THF. The solvents were evaporated to dryness to leave the Mo^V dimer $[(Cp'''MoO_2)_2]$ as the main product. Yield: 380 mg (0.53 mmol, 36.7%). $C_{17}H_{29}MoO_2$ (361.4): calcd. C 56.51, H 8.09; found C 56.72, H 8.12. IR (Nujol mull): $\tilde{\nu} = 922$ s, 885 s, 764 vs cm^{-1}. ^1H NMR (C_6D_6): $\delta = 6.43$ (s, 2 H, ring-H), 1.46 (s, 18 H, CMe_3 1,2-positions), 1.37 (s, 9 H, CMe_3 4-position). Suitable single crystals were grown by slowly cooling a hot saturated heptane solution to room temperature.

The orange-yellow filtrate was collected and the solvents were evaporated to dryness. The resulting yellow residue was extracted with 70 mL of distilled water and the extract was acidified with diluted glacial acetic acid to pH 4, as described above for the Cp* analogue. The yellow solid that precipitated was extracted with several portions of ether, and the combined organic layers (300 mL) were washed with 200 mL of distilled water and dried over $MgSO_4$. The lustrous yellow ether phase was allowed to stand overnight and was then evaporated to dryness, yielding 120 mg (0.16 mmol. 11.2%) of yellow $[(Cp'''MoO_2)_2O]$. $C_{34}H_{58}Mo_2O_5$ (738.7): calcd. C 55.28, H 7.91; found C 55.04, H 7.94. ^1H NMR (C_6D_6): $\delta = 5.63$ (s, 2 H, ring-H), 1.58 (s, 18 H, CMe_3 1,2-position), 1.48 (s, 9 H, CMe_3 4-position). Suitable single crystals were grown by slowly cooling a hot saturated heptane solution to room temperature.

Alternative Route to Pure $[Cp'''_2Mo_2O_5]$: Acetone (120 mL) was mixed with an aqueous NaOH solution (6.6 mL, 3 м, 19.8 mmol). Purple $[Cp'''MoCl_4]$ (1.55 g, 3.29 mmol) was added, producing a deep red solution, followed by the supernatant slowly turning orange with formation of a white yellow precipitate within a 3 h period. After the mixture had been stirred overnight, all solvents were evaporated under reduced pressure and the yellowish residue was extracted with 100 mL of water and layered with 100 mL of ether. The ether layer remained colorless until the aqueous one was acidified with diluted acetic acid, causing the formation of a lustrous yellow precipitate, which was extracted by the ether. After addition of the last traces of acid to give rise to further precipitation, the aqueous phase was clear and colorless. The ether phases was washed three times with distilled water and dried over $MgSO_4$ overnight. Evaporation to dryness gave 890 mg (1.20 mmol, 73.2%) of orange-yellow $[Cp'''_2Mo_2O_5]$ without any detectable Mo^V by-product.

Chlorodioxo(tetraisopropylcyclopentadienyl)molybdenum(VI), $[^4CpMoO_2Cl]$: Aqueous NaOH (2.89 mL, 3 м, 8.67 mmol) was added to 250 mL of acetone. After addition of solid $[^4CpMoCl_4]$ (1.362 g, 2.89 mmol) the solution turned red and a white precipitate was formed. Stirring overnight changed the color of the supernatant to a bright yellow-orange. All solvents were removed in vacuo, leaving a yellow residue that was extracted with 200 mL of pentane. This pentane solution was dried over Na_2SO_4 and filtered, and the solvents were evaporated to dryness to leave 1.0 g of a yellow-orange solid (2.52 mmol, 87%), which was then recrystallized from a saturated heptane solution at −30 °C. $C_{17}H_{29}ClMoO_2$ (396.8): calcd. C 51.45, H 7.36; found C 51.04, H 7.87. IR (Nujol mull): $\tilde{\nu}$ = 920 s, 890 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 6.06 (s, 1 H, ring-H), 3.14 (m, 4 H, C*H*Me$_2$), 1.40 [d, $J_{H,H}$ = 7.4 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.35 [d, $J_{H,H}$ = 7.3 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.31 [d, $J_{H,H}$ = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.25 [d, $J_{H,H}$ = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$]. A single crystal suitable for X-ray analysis was grown by slowly cooling a hot saturated heptane solution to room temperature. The same reaction was found to take place with just two equivalents of NaOH used, yielding the same product in an identical overall yield.

X-ray Crystallographic Study: The crystal and refinement parameters for all structures are listed in Table 4. All sets of data were collected on an Enraf−Nonius KappaCCD diffractometer at 110 K, using Mo-K_α radiation. The structures were solved by means of a Patterson search program[48] and refined with full-matrix, least-squares methods[49] based on $|F^2|$ with the aid of the WINGX program.[50] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on final Fourier difference maps and freely refined with isotropic temperature factors fixed to 1.2 or 1.5 (for CH$_3$) times those of the corresponding parent atoms. Selected bond lengths and angles are listed in Table 1 for both independent molecules of [^{4}Cp$_2$Mo$_2$O$_5$] and for [Cp'''$_2$Mo$_2$O$_5$], in Table 2 for [Cp'''MoO$_2$]$_2$, and in Table 3 for [^{4}CpMoO$_2$Cl]. CCDC-173139−173143 contain the supplementary crystallographic data for this paper. 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 CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to the Ministère de la Recherche and the CNRS for support through UMR 5632 and the French and German Ministries of Foreign Affairs for a bilateral Procope grant. DS thanks the Conseil Régional de Bourgogne for a postdoctoral fellowship and FD thanks the Scientific and Technical Research Council of Turkey (TUBITAK) for a NATO Science Fellowship Programme scholarship, and Celal Bayar University for a leave of absence.

Table 4. Crystal data and structure refinement for all compounds

Compound	[^{4}Cp$_2$Mo$_2$O$_5$], **1**	[Cp$_2'''$Mo$_2$O$_5$], **2**	[Cp*$_2$Mo$_2$O$_4$], **3**	[Cp'''MoO$_2$]$_2$, **4**	[^{4}CpMoO$_2$Cl], **5**
Empirical formula	$C_{34}H_{58}Mo_2O_5$	$C_{34}H_{58}Mo_2O_5$	$C_{20}H_{30}Mo_2O_4$	$C_{34}H_{58}Mo_2O_4$	$C_{17}H_{29}ClMoO_2$
Formula mass	738.68	738.68	526.32	722.68	396.79
T; K	110(2)	110(2)	110(2)	110(2)	110(2)
Crystal system	monoclinic	monoclinic	tetragonal	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	*P*4bar2$_1$*c*	$P\bar{1}$	$P2_1/c$
a, Å	11.8993(2)	14.8025(2)	11.5418(9)	10.3976(1)	8.8290(2)
b, Å	20.0429(3)	10.3088(1)	11.5418(9)	11.9801(2)	12.3811(3)
c, Å	14.7150(2)	23.6064(3)	15.3875(3)	14.0109(2)	17.1372(6)
α, °	90	90	90	84.658(1)	90
β, °	95.597(1)	107.226(1)	90	88.904(1)	103.690(1)
γ, °	90	90	90	88.898(1)	90
V, Å^3	3492.74(9)	3440.66(7)	2049.8(2)	1737.09(4)	1820.09(9)
Z	4	4	4	2	4
F(000)	1544	1544	1064	756	824
$D_{calcd.}$, g/cm^3	1.405	1.426	1.705	1.382	1.448
Diffract., scan type	Kappa CCD, mixture of φ rotations and ω scans				
λ, Å	0.71073				
μ, mm^{-1}	0.755	0.766	1.245	0.755	0.870
Crystal size, mm^3	0.30 × 0.25 × 0.13	0.43 × 0.25 × 0.25	0.20 × 0.20 × 0.12	0.32 × 0.25 × 0.20	0.25 × 0.15 × 0.08
sin(θ)/λ max, Å^{-1}	0.65	0.65	0.65	0.65	0.69
Index ranges	*h*: −15; 15 *k*: −25; 26 *l*: −19; 19	*h*: −19; 19 *k*: −13; 12 *l*: −30; 30	*h*: −12; 14 *k*: −14; 13 *l*: −19; 18	*h*: −12; 13 *k*: −15; 15 *l*: −18; 18	*h*: −12; 6 *k*: −16; 15 *l*: −21; 23
RC = Refl. Collected	25939	22209	10012	13541	8953
IRC = unique RC/R(int)	7990/0.0403	7828/0.0243	2317/0.0284	7847/0.0141	4530/0.0190
IRCGT = IRC and [$I > 2\sigma(I)$]	5940	6728	2198	7073	3952
Refinement method	Full-matrix L.S. on F^2				
Data/restr./param.	7990/0/545	7828/0/545	2317/0/164	7847/0/535	4530/0/277
R for IRCGT	*R*1[a] = 0.0291 *wR*2[b] = 0.0594	*R*1[a] = 0.0241 *wR*2[b] = 0.0520	*R*1[a] = 0.0213 *wR*2[b] = 0.0455	*R*1[a] = 0.0215 *wR*2[b] = 0.0519	*R*1[a] = 0.0215 *wR*2[b] = 0.0762
R for IRC	*R*1[a] = 0.0507 *wR*2[b] = 0.0650	*R*1[a] = 0.0324 *wR*2[b] = 0.0548	*R*1[a] = 0.0238 *wR*2[b] = 0.0465	*R*1[a] = 0.0255 *wR*2[b] = 0.0539	*R*1[a] = 0.0403 *wR*2[b] = 0.0793
Flack param.	−	−	0.00(4)	−	−
Goodness-of-fit[c]	1.034	0.975	1.055	1.046	1.039
Δρ, max, min, e.Å^{-3}	0.571, −0.478	0.438, −0.499	0.324, −0.601	0.422, −0.620	1.090, −0.894

[a] $R1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. [b] $wR2=[\Sigma w(F_0^2 - F_c^2)^2/\Sigma[w(F_0^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_0^2 + (aP)^2 + bP]$ and $P = (\max(F_0^2,0) + 2{*}F_c^2)/3$ where (*a*,*b*) = (0.028, 0.0) for **1**, (0.023, 1.69) for **2**, (0.26, 0.0) for **3**, (0.018, 0.79) for **4** and (0.024, 2.22) for **5**.

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Received November 5, 2001
[I01431]