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

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Convenient syntheses are described for Cp, Cp*, and related cyclopentadienyl derivatives (^{4}Cp = $C_5HPr^i_4$; Cp''' = $C_5H_2Bu^t_3$-1,2,4) of formula $(Ring)_2Mo_2O_5$. Compound $Cp_2Mo_2O_5$ forms in good yields by the rapid oxidation of red $[CpMoO_2]_4$ with PhIO in CH_2Cl_2. $Cp*_2Mo_2O_5$ is 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 > 5 equiv of aqueous NaOH in air. Minor amounts of compound $[Cp*MoO_2]_2$ are also isolated from this reaction but the formation of this by-product may be reduced

by using a two-step basic hydrolysis procedure. Extension of the latter strategy has also allowed the good yield preparation of $^4Cp_2Mo_2O_5$, $Cp'''_2Mo_2O_5$, and $^4CpMoO_2Cl$, 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 a rapid development in the last 20 years, mostly justified by the search for efficient oxidation catalysts. The 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 relies on the presence of electronegative and π-donating ligands such as the halides or negatively charged oxygen (oxo, alkoxo) or nitrogen (nitrido, imido, amido) based ligands. The organic fragments that are 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.) necessitate electron-richer, low-valent metal centers to optimize bonding. These conditions confer a high degree of covalency to the resulting metal–carbon bonds, which consequently become quite resistance to hydrolytic conditions. It is therefore somewhat surprising that the physical behavior and chemical reactivity of high oxidation state organometallics is not systematically investigated 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 concerned metals, notably molybdenum, makes these molecules quite interesting for potential electrocatalytic applications. For these reasons, we have 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] the access routes to these material cannot be considered as completely satisfactory. In this first contribution, we shall focus on the improvements of synthetic procedures to access compounds $Cp_2Mo_2O_5$ and $Cp^*_2Mo_2O_5$, which we plan to use as starting materials for our studies. In addition, we shall report an extension of the synthetic procedure to analogues containing differently substituted cyclopentadienyl rings. We are interested in cyclopentadienyl rings with a high degree of substitution as they are known to afford more inert metal-cyclopentadienyl bonds by way of disfavoring access to the metal center, while at the same time rendering the other ligands more labile. Interesting reactivity may then be expected. Some basic aqueous chemistry which is related to the optimization of the syntheses reported in this paper will also be discussed. Detailed studies of the behavior of these compounds in water as a function of the pH[10] and of the electrode potential[11] have also been completed and are being reported separately.

Results

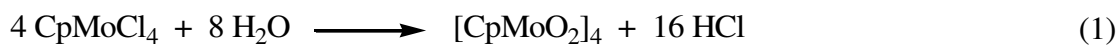### 1. The cyclopentadienyl oxo molybdenum(VI) system.

(a) Discussion of previously reported access routes.

As mentioned in the Introduction, compound $Cp_2Mo_2O_5$ has been known since 1964, but a reliable high yield and practical synthesis does not seem to be yet available. It was first obtained in 20% yield by the photolytic degradation of $[CpMo(CO)_3]_2$ in chloroform, together with several other products.[4] It also forms in small yields by adventitious oxygenation of solutions of various CpMo derivatives.[4, 5] A higher yield synthesis (79%) was reported by oxidation of the dinuclear Mo(V) compound $[CpMoO_2]_2$. This, however, requires use of Ag_2O as the oxygen transfer agent and warming in CH_2Cl_2 at 55° for 1.5 days.[12] The precursor complex, in turn, can be obtained by hydrolysis of $CpMoX_4$ (X = Cl, Br) with excess water. A red isomer, formulated as a tetranuclear compound, is obtained immediately while a longer exposure to water or dissolution of the red isomer in acetone or chloroform slowly afford a dinuclear orange isomer.[5, 12] A similar evolution was described for analogous compounds with monosubstituted cyclopentadienyl ligands.[12] Since the reported behavior of the red tetrameric form suggests that it is a chemically more labile form, we wondered whether the oxidation of this red isomer by sufficiently rapid oxygen transfer agents might provide an easier and high yield access to the desired Mo(VI) product before its conversion to the less reactive orange isomer.

(b) 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 had previously been described. In fact, 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 $CpMoCl_4$, which is itself easily prepared from commercially available $Mo(CO)_6$ (Equations 1 and 2).[19] The second step is complete within 15 min at room temperature and the best results are obtained when the solution is immediately worked up. If the product is allowed to sit in the dichloromethane solution, darker insoluble by-products start to form. The intermediate red Mo(V) oxo complex must be isolated and removed from water. An attempt to carry through the synthetic procedure without

this isolation step gave unsatisfactory results. This procedure, however, constitutes a significant improvement over the previously available ones, especially in terms of time efficiency as both steps can be carried out at room temperature and the overall procedure may be accomplished in a half day.

$$4 \, CpMoCl_4 \; + \; 8 \, H_2O \longrightarrow [CpMoO_2]_4 \; + \; 16 \, HCl \qquad\qquad (1)$$
$$[CpMoO_2]_4 \; + \; 2 \, PhIO \longrightarrow Cp_2Mo_2O_5 \; + \; 2 \, PhI \qquad\qquad (2)$$

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

2.   The pentamethylcyclopentadienyl oxo molybdenum(VI) system.

(a) Discussion of previously reported access 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 as a small yield by-product from a variety of other reactions.[22-25] A high yield synthesis was reported by Faller and Ma by aerial oxidation of $[Cp*Mo(CO)_2]_2$ in chloroform, but the product is said to be contaminated by ca. 15% of the chloride complex $Cp*MoO_2Cl$ and needs further exposure to acetone/water for purification,[26] while the synthesis of the starting compound from commercially available $Mo(CO)_6$ is not itself 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 in 70-75% yield from $Cp*MoCl_4$ 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 yield syntesis is by protonolysis of the unusual starting compound $Cp*Mo(NBu^t)_2Cl$ with aqueous HCl.[32]

Finally, work carried out in Geoffroy's laboratory has shown that the hydrolysis of $Cp*MCl_4$ (M = Mo, W) in the presence of an amine (Bu^tNH_2) yields $Bu^tNH_3^+[Cp*MO_3]^-$ in good yields,[33] while Sundermeyer has shown that the same anions are also formed upon treatment of the oxo-bridged dimers $Cp*_2M_2O_5$ with tetrabutylammonium hydroxide.[32] The acidification of the anion solution, studied in the Geoffroy study for the tungsten compound, gives back the dinuclear complex via 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.* have reported that the reaction of $Cp*MoCl_4$ with 2 equiv of NaOH in acetone-water in an open flask for more than 30 min gives $Cp*MoO_2Cl$, while use of an unspecified excess of NaOH affords the dinuclear $Cp*_2Mo_2O_5$.[34] The reaction between $Cp*MoO_2Cl$ and excess (3 equivalents)

of NaOH was also reported to yield the dinuclear compound. These observations seem odd to us in view of the above mentioned Sundermeyer result, 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 Bu^tNH_2 (a weaker base than NaOH) yields $Bu^tNH_3^+[Cp*MoO_3]^-$ in good yields under analogous conditions.[34] Furthermore, it was shown that the acidification of dichloromethane solutions of the $Bu^tNH_3^+[Cp*MoO_3]^-$ salt with acetic acid affords $Cp*_2Mo_2O_5$, which was recovered in 58% yields. 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 show that, indeed, yellow $Cp*_2Mo_2O_5$ solutions in $MeOH-H_2O$ become nearly colorless upon treatment with NaOH, and the resulting basic solutions turn back yellow upon lowering the pH by addition of strong acids.

$$Cp*_2Mo_2O_5 + 2\,OH^- \rightleftharpoons 2\,[Cp*MoO_3]^- + H_2O \qquad (3)$$

(b) New synthetic strategy

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

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

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 $Cp*MoO_3^-$ Na^+ precipitate but also minor quantities of a soluble colored by-product (identified as $[Cp*MoO_2]_2$, *vide infra*). Separation of this by-product is accomplished by complete evaporation of the solvent mixture and redissolution in pure water, which dissolves the sodium salt but not the by-product. Since the sodium organomolybdate salt may be difficult to separate by fractional crystallization from NaCl and excess NaOH, we have proceeded directly to its conversion to the neutral dimer, which is insoluble in pure water. Dropwise addition of acetic acid from a burette leads, after neutralization of the excess base, to the instantaneous precipitation of the yellow product. The acid addition is stopped when the administration of one further drop of the acid solution does not cause any further

precipitation. The synthetic procedure can therefore be handled as a simple titration reaction allowing the use of close to the stoichiometric amount of acid. This is important because the 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 gives a pure product with yields in excess of 60 % on a 2 g scale. The synthesis can also be accomplished stepwise by reaction of Cp*MoCl4 with 3 equivalents of NaOH for 1 day, followed by the addition of 3 more equivalents of NaOH. In this fashion, the formation of the Mo(V) by-product is avoided (see discussion). The isolated yield of the desired product, however, is not increased by this modified procedure.

*(c) Isolation and structure of the [Cp*MoO2]2 by-product.*

The water-insoluble crop generated during the synthetic procedure described above contains orange-red crystalline [Cp*MoO2]2, which can be recovered in yields up to 20% depending on the operating conditions. It seems that not only the time of exposure to air but also the relative amount of water and acetone is important to determine the ratio between the Mo(V) and Mo(VI) products (see Discussion). Smaller amounts of water seem to favor a greater extent of oxidation. Compound [Cp*MoO2]2 has previously been reported and shown to adopt two possible structures which differ by the relative arrangement of the Cp* and terminal oxo ligands across the central Mo(μ-O)2Mo 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 significantly differ 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 in the *anti* polymorph [2.647(3) Å],[40] certainly because of the butterfly arrangement which allows the metals to approach each other relative to the planar arrangement of the *anti* isomer. The same situation is found for the [(L)2Mo2O4]2+ (L = 1,5,9-triazacyclononane).[41, 42]

I   **II**
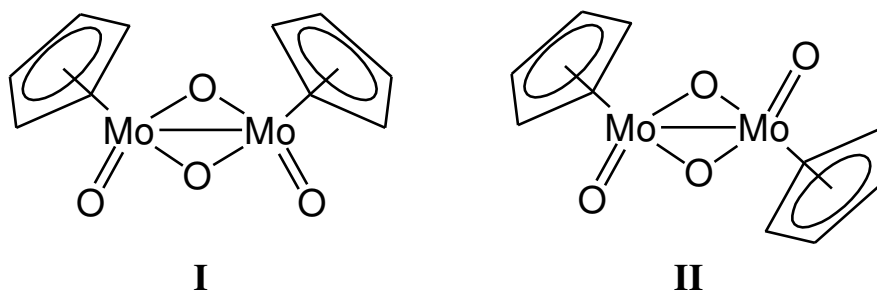
3. Oxo molybdenum(VI) and molybdenum(V) systems with sterically more encumbering cyclopentadienyl rings.

(a) Syntheses.

The procedure described above for the Cp* system was applied in a straightforward manner to the hydrolysis of ^{4}CpMoCl$_4$ and Cp'''MoCl$_4$. Again, the aerial hydrolysis affords in both cases solutions containing the water soluble Na$^+$[(Ring)MoO$_3$]$^-$ salt. This was not isolated, but its presence is indicated by the identical behavior to the corresponding Cp* system described above upon acidification. Compounds ^{4}Cp$_2$Mo$_2$O$_5$ and Cp'''$_2$Mo$_2$O$_5$ were obtained as yellow or yellow-orange crystalline solids that are insoluble in water but soluble in ether. Both were crystallized and their structure was confirmed by X-ray diffraction methods (see next section). They display two IR vibrations that are 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}), like their Cp and Cp* analogues.[4, 22]

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 gave also a water insoluble fraction, from which the dinuclear Mo(V) complex [Cp'''MoO$_2$]$_2$ was recovered. This compound was also characterized by X-ray diffraction methods (see below).

(b) X-ray structures of the (Ring)$_2$Mo$_2$O$_5$ compounds.

Several X-ray structural determinations have been reported over the years for various polymorphs of Cp*$_2$Mo$_2$O$_5$[23-26] 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}Cp$_2$Mo$_2$O$_5$ and Cp'''$_2$Mo$_2$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, but 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 around the long end of this range in both cases.
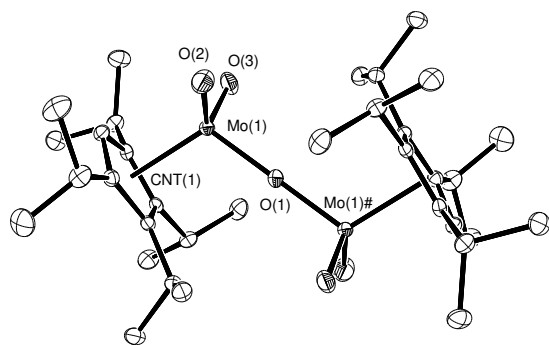
Figure 1. An ORTEP view for one of the two independent molecules of compound $^4\text{Cp}_2\text{Mo}_2\text{O}_5$. Ellipsoids are drawn at the 50% probability level. The atom numbering correspondence for the other molecule is as follows: Mo(2) for Mo(1), O(4) for O(1), O(5) for O(2), O(6) for O(3), and CNT(2) for CNT(1).
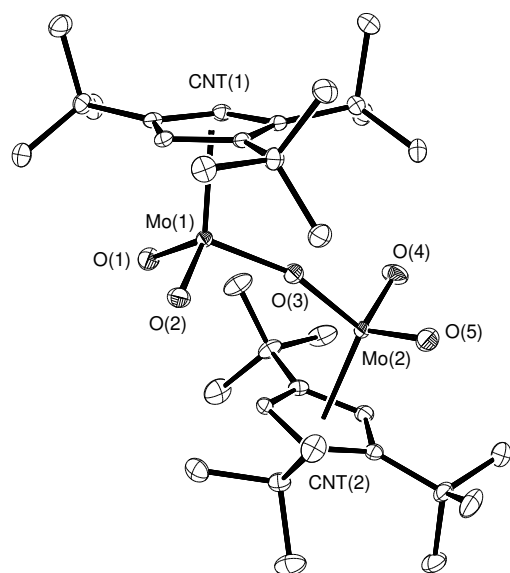
Figure 2. An ORTEP view of compound $\text{Cp'''}_2\text{Mo}_2\text{O}_5$. Ellipsoids are drawn at the 50% probability level.

Table 1. Selected bond distances (Å) and angles (°) for compounds $(\text{Ring})_2\text{Mo}_2\text{O}_5$ (Ring = ^4Cp, Cp''').

	$^4\text{Cp}_2\text{Mo}_2\text{O}_5{}^a$		$\text{Cp'''}_2\text{Mo}_2\text{O}_5$	
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.

(c) X-ray structure of compound [Cp'''MoO$_2$]$_2$.

The geometry of compound [Cp'''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, while they are *syn* for the Cp analogue and both arrangements are possible for the Cp* molecule. Although an unambiguous conclusion cannot 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 reason. Therefore, the *syn* arrangement will be observed in the less crowded cases (*e.g.* 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.
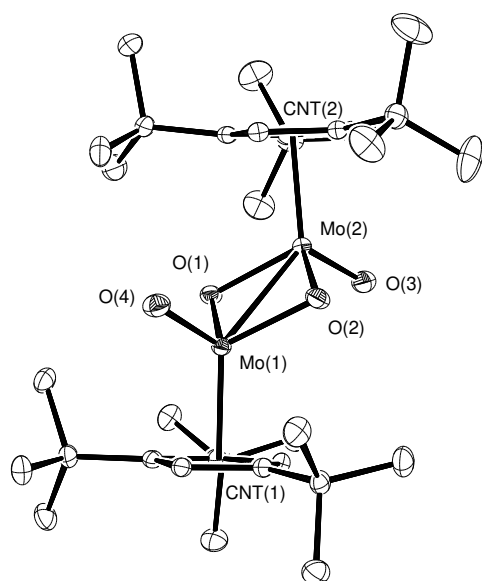
Figure 3. An ORTEP view of compound [Cp'''MoO₂]₂. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond distances (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)		

The Mo-Mo distance in compound [Cp'''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$_2$O$_2$ 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 sensitive to either effect, being essentially identical with those of all other previously described molecules with this stoichiometry, whether of *syn* or *anti* type.

4. The ^{4}CpMoO$_2$Cl system.

According to the previous Cp* literature,[34] the aerobic hydrolysis of the tetrachloro compound with 2 equivalents of aqueous NaOH leads directly to the corresponding dioxochloro derivative. For the less electron-rich Cp system, on the other hand, excess water yields quite rapidly the dioxo system as seen above even in the absence of base.[5] The ^{4}Cp system behaves similarly to the Cp* with 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 3 or 2 equivalents of NaOH. The compound shows essentially identical Mo=O stretching vibrations in the IR spectrum as the related oxo-bridged dinuclear complex and no band in the Mo-O-Mo stretching region, as expected. The structure of this product has also been confirmed by X-ray crystallography (see Figure 4). The relevant bond distances and angles are reported in Table 3. While no structure for a (Ring)MoO$_2$X (X = Cl or other halogen) seem to be reported, 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-Pr$^i_2$C$_6$H$_3$)N(SiMe$_3$)]$_2$Si$_2$O$_2$(OH)$_3$.[44] The Mo=O distances are quite comparable in all these compounds. The Mo-Cl distance compares with related Mo(V)-Cl distances and appears to be affected mostly by the cyclopentadienyl ring steric pressure, as suggested by the comparison of 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]

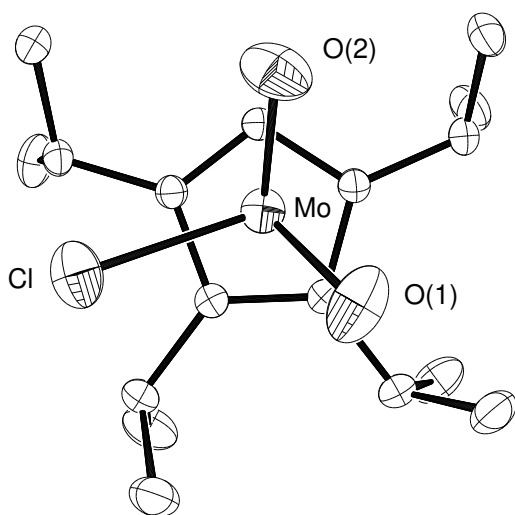**Figure 4.** An ORTEP view of compound ^{4}CpMoO$_2$Cl. Ellipsoids are drawn at the 50% probability level.

Table 3. Selected bond distances (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)

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 leads to (Ring)MoOCl$_2$, which can proceed either to further hydrolysis leading to [(Ring)MoO$_2$]$_2$ or it may be oxidized to (Ring)MoO$_2$Cl. Finally, the dioxo Mo(V) dimer can be oxidized and the chlorodioxo Mo(VI) complex can be hydrolyzed, in both cases leading to (Ring)$_2$Mo$_2$O$_5$. Under basic conditions, however, the final product converts to the [(Ring)MoO$_3$]$^-$ anion. Of course, other intermediates must also form during these transformations, notably hydroxo complexes whose relative stability is supported by some evidence.[12, 31, 34]
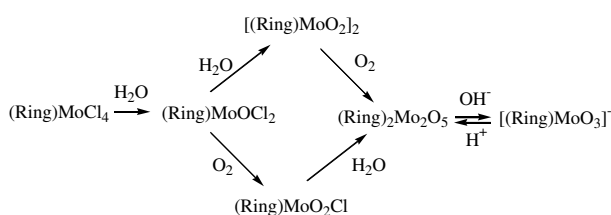
Scheme 1

If hydrolysis prevails over oxidation at the level of the first dichlorooxo intermediate leading to 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$_5$ via this route by using PhIO has been 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. The oxidation of the dichlorooxo Mo(V) species, on the other hand, should be made more favourable by electron-richer ligands. At any rate, the oxidation step may then prevail over hydrolysis leading to the chlorodioxo Mo(VI) species provided there is dioxygen available. This is the situation encountered for the Cp* system, for which the aerobic hydrolysis in the presence of 2 equiv of NaOH was reported to give a good yield of Cp*MoO₂Cl.[34] The same occurs also for the ^{4}Cp system reported here with either 2 or 3 equivalents of NaOH. The use of neutral aqueous conditions should produce 3 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 acification) is ^{4}Cp₂Mo₂O₅.

$$2\ ^4CpMoCl_4\ +\ 3\ H_2O + \tfrac{1}{2}\,O_2\ \longrightarrow\ 2\ ^4CpMoO_2Cl + 6\ Cl^- + 6\ H^+ \qquad (5)$$
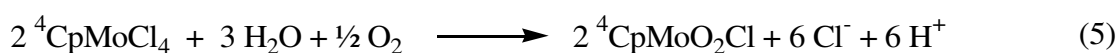
The relative rate of hydrolysis and oxidation for (Ring)MoOCl₂ should depend also on other factors such as the concentration of water, the nature of the organic solvent, and the pH. Although we have not carried out a comprehensive study of these effects, we do have qualitative indications that more Mo(V) dimer complex is obtained when using a larger amount of water 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 leading to the [(Ring)MoO₂]₂ system. Indeed, we do obtain a significant amount of this compound as a by-product when the hydrolysis is carried out in the presence of >5 equivalents of NaOH, whereas a good yield of Cp*MoO₂Cl was obtained by Geoffroy *et al.* by using only 2 equivalents, with no mention of the formation of the Mo(V) product.[34] Indeed, repeating the synthesis of Cp*₂Mo₂O₅ by stepwise addition of 3 equivalents of NaOH, followed by three more equivalents a day later (without isolation of the intermediate Cp*MoO₂Cl complex) completely avoided the formation of the [Cp*MoO₂]₂ by-product. Some subtleties, however, are not yet completely understood. For instance, the Mo(V) dimer was obtained for the Cp''' system like for the Cp* system, but an analogous product was not obtained for the ^{4}Cp system, even when using 5 equiv of NaOH. The use of excess NaOH, however, provided that the oxidation route is followed, allows access to the water soluble sodium salts of (Ring)MoO₃⁻. 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 with that of the Cp* system: acidification of the water solutions yields the yellow water insoluble (Ring)₂Mo₂O₅ 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 by using 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 encumbering 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 the 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). ^1H NMR spectra were recorded using 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. Compounds (Ring)$MoCl_4$ (Ring = Cp, Cp* and ^{4}Cp) were prepared as described in the literature.[19, 37, 47] 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 Cp'''Na (2.66 g , 10.3 mmol) were mixed as solids and suspended in 40 ml THF. The suspension turned to an orange solution during a 10 min period. It was then refluxed for 18 h. An IR monitoring indicated the formation of Cp'''$Mo(CO)_3^-Na^+$ (strong peaks at 1885, 1784 and 1736 cm^{-1}, comparable with literature values for the Cp* analogue). After cooling to room temperature, MeI (700 µl, 11.25 mmol) was added to the deep orange-red solution causing darkening to brown. After an additional reflux for 3 h the solvent was removed *in vacuo* leaving a yellow brown residue which was extracted in 60 ml CH_2Cl_2. After filtration, the deep orange solution was evaporated to dryness yielding 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 4.99 g (18.2 mmol) $PhICl_2$ 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 reflux for 90 min, the mixture was cooled to room temperature and evaporated to dryness. The violet black residue was washed with 2x20 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 %). Elem. Anal.: Calcd for $C_{17}H_{29}Cl_4Mo$: 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), Cp₂Mo₂O₅: Compound CpMoCl₄ (0.555 g, 1.83 mmol) was added to 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 ({CpMoO₂}₄)[12] was separated by decanting off the mother liquor, washed with water (3x10 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 to the resulting solution was added solid PhIO (0.22 g, 1.0 mmol). The mixture was stirred at room temperature for 15 m, 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 CH₂Cl₂/pentane, and dried *in vacuo*. Yield 0.207 g, 71.1% (56.5% from CpMoCl₄). The analytical (IR, NMR) properties of the compound correspond to those reported in the literature[4] and confirm its purity.

Tetraoxo-μ-oxobis(pentamethylcyclopentadienyl)dimolybdenum(VI), Cp*₂Mo₂O₅ and Dioxodi-μ-oxobis(pentamethylcyclopentadienyl)dimolybdenum(V), [Cp*MoO₂]₂. Deep violet Cp*MoCl₄ (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 causing a lightening of the colour to orange and the precipitation of a pale yellow solid. After evaporation to dryness the brownish residue was extracted in 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 4x100 ml portions of ether, the last extract being colourless. The combined organic layers were washed with distilled water and dried over MgSO₄ overnight. Evaporation of the solvent yielded 1.55 g (2.86 mmol; 61.3 %) of [(Cp*MoO₂)₂O] as a yellow solid. The ¹H NMR spectrum of this compound (singlet at 2.01 ppm in CDCl₃) corresponds with that described in the literature.[26]

From another experiment starting from 2.03 g of Cp*MoCl₄, the water insoluble orange-red solid remaining from the water extraction was also worked up. It was washed with 20 ml ether then with 20 ml pentane and dried in vacuo affording the dinuclear Mo(V) compound [(Cp*MoO₂)₂] as a orange crystalline solid (192 mg, 0.37 mmol; 13.6 %). Elem. Anal.: Calcd for C₁₀H₁₅MoO₂:C, 45.64; H, 5.74 %. Found: C, 45.36; H, 5.71 %. The ¹H NMR spectrum (1.98 ppm in CDCl₃) corresponds with 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), ⁴Cp₂Mo₂O₅. To a stirred mixture of acetone (75 mL), THF (75 mL) and aqueous NaOH (2.6 mL, 3 M, 7.8 mmol) in an open beaker was quickly added deep purple ⁴CpMoCl₄ as a solid (609 mg, 1.29 mmol). A brown suspension immediately formed which lightened to orange yellow over a period of 2 h. After stirring 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 3x100 ml portions of ether, followed by separation of the organic layer, washing with water and drying over MgSO₄ 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 [(⁴CpMoO₂)₂O]. Elem. Anal.: Calcd for C₃₄H₅₈Mo₂O₅: C, 55.28; H, 7.91 %. Found: C, 54.69; H, 8.25 %. IR (Nujol mull): 919s, 889s, 760s cm⁻¹. ¹H NMR (CDCl₃): 6.01 ppm (s, 1H, ring-H), 3.10 ppm (m, 4H, C*H*Me₂), 1.39 ppm (d, 6H, J_{HH} = 7.3 Hz, CH(C*H*₃)₂), 1,30 ppm (d, 12H, J_{HH} = 7.3 Hz, CH(C*H*₃)₂),

1.19 ppm (d, 6H, J_{HH} = 6.7 Hz, CH(CH_3)$_2$). ^{1}H NMR (C$_6$D$_6$): 6.14 ppm (s, 1H, ring-H), 3.14 ppm (m, 4H, CHMe$_2$), 1.47 ppm (d, 6H, J_{HH} = 6.7 Hz, CH(CH_3)$_2$), 1.44 ppm (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)$_2$), 1.23 ppm (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)$_2$), 1.02 ppm (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)$_2$). The ^{1}H 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), [^{4}CpMoO$_2$]$_2$.
Compound ^{4}CpMoCl$_4$ (670 mg, 1.42 mmol) was added to 150 ml of a stirred 1:1 mixture of acetone and distilled water, yielding immediately a brown suspension. The mixture was stirred for 40 hours, during which aliquots were withdrawn, the solid was separated, washed with water, and investigated by ^{1}H NMR, showing the spectrum of ^{4}Cp$_2$Mo$_2$O$_5$ 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* leaving 240 mg (0.33 mmol; 46.8 %) of ^{4}Cp$_2$Mo$_2$O$_5$ as a orange powder (confirmed by ^{1}H NMR). 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'''$_2$Mo$_2$O$_5$ and Dioxodi-μ-oxobis(pentamethylcyclopentadienyl)dimolybdenum(V), [Cp'''MoO$_2$]$_2$. To a stirred mixture of THF (75 mL), acetone (75 mL), water (10 mL) and aqueous NaOH (5.7 mL, 3 M, 17.1 mmol) in an open beaker was added purple Cp'''MoCl$_4$ (1.36 g , 2.89 mmol). 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, redissolved in THF and evaporated to dryness leaving the Mo(V) dimer [(Cp'''MoO$_2$)$_2$] as the main product. Yield: 380 mg (0.53 mmol, 36.7 %). Elem. anal. Calcd for C$_{17}$H$_{29}$MoO$_2$: C, 56.51; H, 8.09 %. Found: C, 56.72; H, 8.12 %. IR (Nujol mull): 922s, 885s, 764vs cm^{-1}. ^{1}H NMR (C$_6$D$_6$): 6.43 ppm (s, 2H, ring-H), 1.46 ppm (s, 18H, CMe$_3$ 1,2-positions), 1.37 ppm (s, 9H, 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 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 which 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 shiny yellow ether phase was allowed to stay overnight and was then evaporated to dryness, yielding 120 mg (0,16 mmol. 11.2 %) of yellow [(Cp'''MoO$_2$)$_2$O]. Elem. anal. Calcd for C$_{34}$H$_{58}$Mo$_2$O$_5$: C, 55.28; H, 7.91 %. Found: C, 55.04; H, 7.94 %. ^{1}H NMR (C$_6$D$_6$): 5.63 ppm (s, 2H, ring-H), 1.58 ppm (18H, CMe$_3$ 1,2-position), 1.48 ppm (9H, 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'''$_2$Mo$_2$O$_5$. Acetone (120 mL) was mixed with an aqueous NaOH solution (6.6 mL, 3 M, 19.8 mmol). Purple Cp'''MoCl$_4$ (1.55 g, 3.29 mmol) was added causing a deep red solution followed by slow turning of the supernatant to orange with formation of a white yellow precipitate within a 3 h period. After stirring 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 shiny yellow precipitate, which was extracted by the ether. After addition of the last traces of acid, which led 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, 3M, 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 forming a white precipitate. Stirring overnight changed the color of the supernatant to a bright yellow-orange. All solvents were removed *in vacuo* leaving a yellow residue which was extracted with 200 ml of pentane. This pentane solution was dried over Na2SO4, filtered and evaporated to dryness leaving 1.0 g of a yellow-orange solid (2.52 mmol, 87 %), which was then recrystallized from a saturated heptane solution at -30 °C. Elem. anal. Calcd for $C_{17}H_{29}ClMoO_2$: C, 51.45; H, 7.36 %. Found: C, 51.04; H, 7.87 %. IR (Nujol mull): 920s, 890s cm^{-1}. ^1H NMR ($CDCl_3$): 6.06 ppm (s, 1H, ring-H), 3.14 ppm (m, 4H, C*H*Me_2), 1.40 ppm (d, 6H, J_{HH} = 7.4 Hz, CH(CH_3)_2), 1.35 ppm (d, 6H, J_{HH} = 7.3 Hz, CH(CH_3)_2), 1.31 ppm (d, 6H, J_{HH} = 6.7 Hz, CH(CH_3)_2), 1.25 ppm (d, 6H, J_{HH} = 7.0 Hz, CH(CH_3)_2). A suitable single crystal for the 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 collected in Table 4. All set of data were collected on an Enraf-Nonius KappaCCD diffractometer at 110 K using Mo Kα radiation. The structures were solved via 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 distances and angles are listed in Table 1 for both independent molecules of $^4Cp_2Mo_2O_5$ and for $Cp'''_2Mo_2O_5$, in Table 2 for for $[Cp'''MoO_2]_2$, and in Table 3 for $^4CpMoO_2Cl$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-173139-173143. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Table 4. Crystal data and structure refinement for all compounds.

Compound	$^4Cp_2Mo_2O_5$, **1**	$Cp'''_2Mo_2O_5$, **2**	$Cp^*_2Mo_2O_4$, **3**	$[Cp'''MoO_2]_2$, **4**	$^4CpMoO_2Cl$, **5**
Formula	$C_{34}H_{58}Mo_2O_5$	$C_{34}H_{58}Mo_2O_5$	$C_{20}H_{30}Mo_2O_4$	$C_{34}H_{58}Mo_2O_4$	$C_{17}H_{29}ClMoO_2$
M	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	$P2_1/c$	$P2_1/c$	$P-42_1c$	$P-1$	$P2_1/c$
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; Å³	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_{calc}; g/cm³	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; mm³	0.30x0.25x0.13	0.43x0.25x0.25	0.20x0.20x0.12	0.32x0.25x0.20	0.25x0.15x0.08
sin(θ)/λ max; Å⁻¹	0.65	0.65	0.65	0.65	0.69
Index ranges	h: −15; 15	h: −19; 19	h: −12; 14	h: −12; 13	h: −12; 6
	k: −25; 26	k: −13; 12	k: −14; 13	k: −15; 15	k: −16; 15
	l: −19; 19	l: −30; 30	l: −19; 18	l: −18; 18	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>2σ(I)]	5940	6728	2198	7073	3952
Refinement method		Full-matrix L.S. on F²			
Data / restr. / param.	7990 / 0 / 545	7828 / 0 / 545	2317 / 0 / 164	7847 / 0 / 535	4530 / 0 / 277
R for IRCGT	R1[a] = 0.0291	R1[a] = 0.0241	R1[a] = 0.0213	R1[a] = 0.0215	R1[a] = 0.0215
	wR2[b] = 0.0594	wR2[b] = 0.0520	wR2[b] = 0.0455	wR2[b] = 0.0519	wR2[b] = 0.0762
R for IRC	R1[a] = 0.0507	R1[a] = 0.0324	R1[a] = 0.0238	R1[a] = 0.0255	R1[a] = 0.0403
	wR2[b] = 0.0650	wR2[b] = 0.0548	wR2[b] = 0.0465	wR2[b] = 0.0539	wR2[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] $R1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [b] $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w=1/[\sigma^2(F_o^2+(aP)^2+bP]$ and $P=(Max(F_o^2,0)+2*F_c^2)/3$ 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**.

Acknowledgments

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Graphical Abstract

Improved syntheses are reported for compounds $Cp_2Mo_2O_5$ and $Cp*_2Mo_2O_5$. Extension of these procedures have yielded homologues with sterically more encumbering cyclopentadienyl rings and related compounds, some of which have been structurally characterized.