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Journal
Journal of the American Chemical Society, 140(42)

ISSN
0002-7863

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Publication Date
2018-10-24

DOI
10.1021/jacs.8b09616

Peer reviewed

Published in final edited form as:
J Am Chem Soc. 2018 October 24; 140(42): 13609–13613. doi:10.1021/jacs.8b09616.

Syntheses of Molybdenum Oxo Benzylidene Complexes

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Abstract

The reaction between $Mo(O)(CHAr_o)(OR_{F6})_2(PMe_3)$ (Ar_o = *ortho*-methoxyphenyl, OR_{F6} = $OCMe(CF_3)_2$) and two equivalents of LiOHMT (OHMT = O-2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) leads to $Mo(O)(CHAr_o)(OHMT)_2$, an X-ray structure of which shows it to be a trigonal bipyramidal *anti* benzylidene complex in which the *o*-methoxy oxygen is coordinated to the metal *trans* to the apical oxo ligand. Addition of one equivalent of water (in THF) to the benzylidyne complex, $Mo(CAr_p)(OR)_3(THF)_2$ (Ar_p = *para*-methoxyphenyl, OR = OR_{F6} or $OC(CF_3)_3$ (OR_{F9})) leads to formation of $\{Mo(CAr_p)(OR)_2(\mu\text{-}OH)(THF)\}_2(\mu\text{-}THF)$ complexes. Addition of one equivalent of a phosphine (L) to $Mo(CAr_p)(OR_{F9})_3(THF)_2$ in THF, followed by addition of one equivalent of water, all at room temperature, yields $Mo(O)(CHAr_p)(OR_{F9})_2(L)$ complexes in good yields for several phosphines (*e.g.*, PMe_2Ph (69% by NMR), $PMePh_2$ (59%), PEt_3 (69%), or $P(i\text{-}Pr)_3$ (65%)). The reaction between $Mo(O)(CHAr_p)(OR_{F9})_2(PEt_3)$ and two equivalents of LiOHMT proceeds smoothly at 90 °C in toluene to give $Mo(O)(CHAr_p)(OHMT)_2$, a four-coordinate *syn* alkylidene complex. $Mo(O)(CHAr_p)(OHMT)_2$ reacts with ethylene (1 atm in C_6D_6) to give (in solution) a mixture of $Mo(O)(CHAr_p)(OHMT)_2$, $Mo(O)(CH_2)(OHMT)_2$, and an unsubstituted square pyramidal metallacyclobutane complex, $Mo(O)(CH_2CH_2CH_2)(OHMT)_2$, along with ethylene and $Ar_pCH{=}CH_2$. $Mo(O)(CHAr_p)(OHMT)_2$ also reacts with 2,3-dicarbomethoxynorbornadiene to yield *syn* and *anti* isomers of the "first-insertion" products that contain a *cis* C=C bond.

The neopentylidyne ligand in $(t\text{-}BuCH_2)_3M{\equiv}C\text{-}t\text{-}Bu$ (M = W^1 or Mo^2) complexes is formed through what amounts to an intramolecular deprotonation of an α carbon atom in one alkyl ligand by another in some multialkyl intermediate to give an alkylidene first,[3] followed by a

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Supporting Information
Experimental details of the syntheses of all compounds, NMR and spectral data, details of the metathesis experiments, and X-ray crystallographic files. This material is available free of charge via the Internet at http://pubs.acs.org.

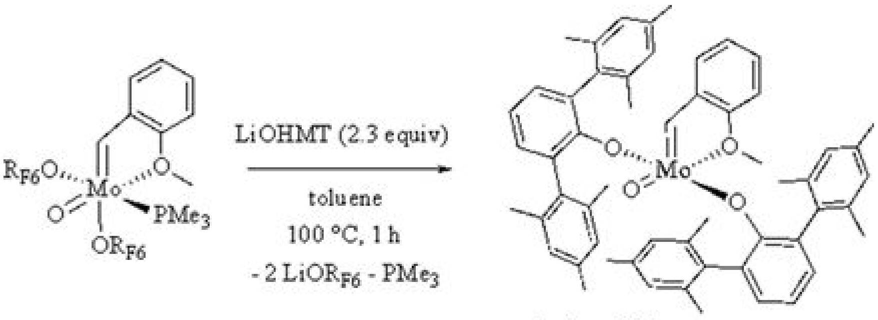
Accession Codes
CCDC 1865865−1865868 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The authors declare no competing financial interests.

second (more facile) α deprotonation of that alkylidene by an alkyl to give the alkylidyne.[4] Synthesis of $M(C\text{-}t\text{-}Bu)(1,2\text{-dimethoxyethane})Cl_3$ and $M(C\text{-}t\text{-}Bu)(OR)_3$ complexes (OR is a sterically demanding alkoxide or aryloxide) and the demonstration that the latter are initiators for catalytic *alkyne* metathesis[5] led to the development of four-coordinate *alkene* metathesis initiators of the type $M(NR')(CHR'')(OR)_2$ (M = Mo or W).[6,7] Synthetic routes to imido alkylidene complexes of Mo and W are based on a single α hydrogen abstraction/deprotonation reaction in a dineopentyl or dineophyl complex.[8] Syntheses of oxo alkylidenes, which have been proposed to be the type of alkene metathesis catalysts present in “classical” heterogeneous catalyst systems,[9] by analogous methods have been more challenging. Tungsten oxo alkylidene complexes were prepared through α hydrogen abstraction in tungsten dialkyls in 2012,[10] but syntheses of molybdenum oxo alkylidene complexes that are active for metathesis of olefins have remained elusive.[11.] Recently we began to explore the synthesis of Mo oxo alkylidene complexes through addition of water to alkylidyne complexes.[7,12]

Addition of one equiv of water to $Mo(CAr_o)(OR_{F6})_3(dme)$ (Ar_o = *ortho*-methoxyphenyl) gives the dimeric benzylidyne hydroxo complex, $\{Mo(CAr_o)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-dme})$ in which each bridging hydroxo proton is hydrogen-bonded to the *ortho* methoxy oxygen in the *o*-methoxybenzylidyne ligand. (This is a rare example of a controlled hydrolysis of a high oxidation state alkylidene or alkylidyne.[13,14]) Addition of PMe_3 to $\{Mo(CAr_o)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-dme})$ led to formation of $Mo(O)(CHAr_o)(OR_{F6})_2(PMe_3)$, from which $Mo(O)(CHAr_o)Cl_2(PMe_3)$ and $Mo(O)(CHAr_o)(OHIPT)Cl(PMe_3)$ (OHIPT = O-2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3$[15]) were prepared. In the presence of $B(C_6F_5)_3$ $Mo(O)(CHAr_o)(OHIPT)Cl(PMe_3)$ was shown to be active for the stereoselective ring-opening metathesis polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNBD) and *rac*-2,3-dicarbomethoxy-5-norbornene (DCMNBE), and the homocoupling of 1-decene to 9-octadecene, consistent with analogous reactions that use tungsten-based initiators[16] and with removal of PMe_3 to form active metathesis initiators. Important questions are whether an *ortho*-methoxy group in the benzylidyne and benzylidene ligands is required for a controlled reaction involving water and an alkylidyne complex and whether phosphine-free complexes that are active for olefin metathesis can be prepared and isolated. Some answers to these questions are provided in this communication.

The synthesis and stability of $W(O)(CH\text{-}t\text{-}Bu)(OHMT)_2$ (OHMT = O-2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$ or hexamethylterphenoxide[17])[10a] suggested that the phosphine-free target should be $Mo(O)(CHAr_o)(OHMT)_2$ (**1-Ar$_o$**); it was prepared from $Mo(O)(CHAr_o)(OR_{F6})_2(PMe_3)$ as shown in eq 1. Trimethylphosphine is lost in the process as a consequence of sterichindrance overall in combination with binding of the methoxide oxygen in the Ar_o group in the *anti* alkylidene to the metal *trans* to the oxo ligand, as shown through an X-ray study (Fig 1; see SI). The τ value[18] (0.78) suggests that the configuration at the metal is closest to a trigonal bipyramid (O2-Mo1-O1 = 166.27(7)°). Alkylidene proton resonances were observed in the initial proton NMR spectrum of **1-Ar$_o$** at 11.92 ppm for the *anti* isomer (97%, J_{CH} = 156 Hz), the isomer found in the solid state (Fig 1), and at 12.02 ppm for the *syn* isomer (J_{CH} = 134 Hz), in which the alkylidene has rotated[19] by 180° and the methoxide is not bound to the metal. After 1 h at 50 °C an 85:15 equilibrium ratio of *anti* to *syn* isomers was observed.

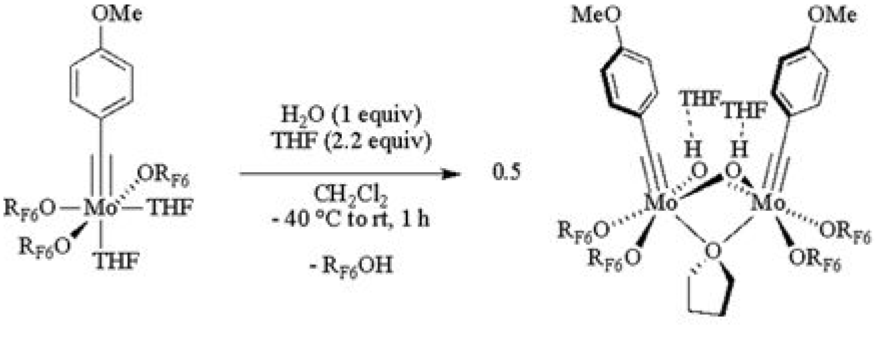


1-Ar$_o$; 37%

(1)

Preliminary studies showed that the rate of reaction of **1-Ar$_o$** with ethylene is slow, perhaps because the lower energy "methoxy-bound" *anti* form only slowly converts to the more reactive *syn* form. We therefore turned to a synthesis of the *p*-methoxybenzylidene analog where intramolecular binding of the methoxy oxygen is not possible.

The *para*-methoxybenzylidyne complex, Mo(CAr$_p$)(dme)Br$_3$ was prepared by the "low oxidation state" procedure.[20] From it Mo(CAr$_p$)(OR$_{F6}$)$_3$(dme)[21] and Mo(CAr$_p$)(OR$_{F6}$)$_3$(THF)$_2$[22] were prepared without complications. Addition of one equivalent of water (in THF, diethyl ether, or dichloromethane) to Mo(CAr$_p$)(OR$_{F6}$)$_3$(THF)$_2$ led to the formation of {Mo(CAr$_p$)(OR$_{F6}$)$_2$(μ-OH)}$_2$(THF)$_3$ (**2-Ar$_p$F$_6$**) in good yield (eq 2). It was crystallized from a mixture of pentane and CH$_2$Cl$_2$ at – 40 °C in the presence of several equivalents of THF and isolated in 70% yield as pale red crystals. Similar reactions starting with Mo(CAr$_p$)(OR$_{F6}$)$_3$(dme) and one equivalent of water (in THF) also led to **2-Ar$_p$F$_6$**, but in poor yield (~10%), while addition of water in dme to Mo(CAr$_p$)(OR$_{F6}$)$_3$(dme) did not lead to an isolable benzylidyne hydroxo complex. Dme appears to be detrimental and THF beneficial for formation of benzylidyne hydroxo complexes in these circumstances.



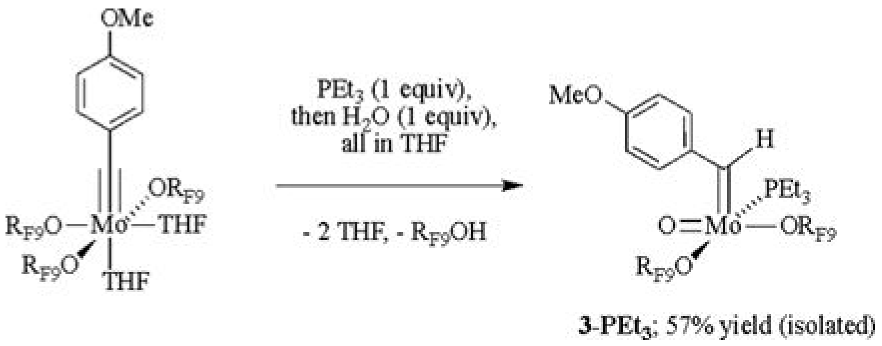
2-Ar$_p$F$_6$; 70% yield (isolated)

(2)

An X-ray study of **2-Ar_pF_6** (Fig 2) shows its structure to be analogous to that of previously reported[12] $\{Mo(CAr_o)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-}dme)$ with one of the THFs bridging the two Mo centers and one THF hydrogen-bonded to each of the two bridging hydroxos. The OH···O angles and O···O distances are consistent with a “classical” hydrogen bond between the bridging hydroxo protons and THF oxygens.[23] The hydroxo proton resonance in **2-Ar_pF_6** is found at 6.60 ppm in the proton NMR spectrum in CD_2Cl_2 (*cf.* 9.30 ppm for the hydroxo protons in $\{Mo(CAr_o)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-}dme)$). The Mo-O distance to the bridging THF is 2.485(2) Å. The Mo-C-C_{ipso} angles are 179.4(2)°, in contrast to 168.57(7)° and 167.33(7)° in $\{Mo(CAr_o)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-}dme)$, which result from the hydroxo protons being hydrogen bonded to the *o*-methoxy oxygens in the Ar_o group instead of to THF, as found in **2-Ar_pF_6**. Other distances and angles are not unusual (see SI). In solution, proton NMR resonances for the bridging THF are distinct from those for the hydrogen-bonded THFs or THF in solution. The hydrogen-bonded THFs are readily lost from solid samples, especially *in vacuo*, to give $\{Mo(CAr_p)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-}THF)$, and exchange rapidly on the NMR scale with free THF in solution, as shown through proton NMR studies. Addition of dioxane to an NMR sample of $\{Mo(CAr_p)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-}THF)$ led to formation of a mixture of the μ-THF (δ_{OH} at 6.63 ppm) and μ-dioxane (δ_{OH} at 6.51 ppm) complexes.

Addition of one equivalent of water (in THF) to $Mo(CAr_p)(OR_{F9})_3(THF)_2$ in CH_2Cl_2 led to formation of $\{Mo(CAr_p)(OR_{F9})_2(\mu\text{-}OH)\}_2(\mu\text{-}THF)$, which could be isolated in 43 % yield as lime-green crystals; in the presence of additional THF it crystallizes as $\{Mo(CAr_p)(OR_{F9})_2(\mu\text{-}OH)(THF)\}_2(\mu\text{-}THF)$ (**2-Ar_pF_9**). An X-ray structural study showed its structure to be entirely analogous to that for **2-Ar_pF_6** (see SI for details). The two molecules of hydrogen-bonded THF in **2-Ar_pF_9** again are lost readily from solid samples, especially *in vacuo.* The μ-OH resonance is found at 8.21 ppm in **2-Ar_pF_9** in CD_2Cl_2 (*cf.* 6.60 ppm in **2-Ar_pF_6**).

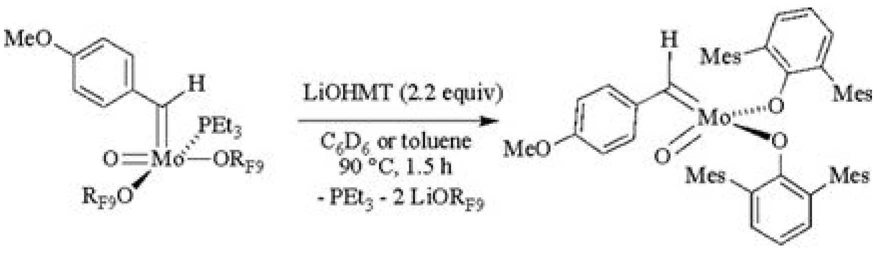
Reactions between **2-Ar_pF_6** or **2-Ar_pF_9** and PMe_3 or PEt_3 (L) do *not* yield $Mo(O)(CHAr_p)(OR)_2(L)$ complexes readily and in high yield. However, addition of one equivalent of L to $Mo(CAr_p)(OR_{F9})_3(THF)_2$, followed by addition of one equivalent of water, *all at room temperature in THF*, yields $Mo(O)(CHAr_p)(OR)_2(L)$ complexes (**3**) in good yields for several phosphines L (*e.g.*, PMe_2Ph (69% by NMR), $PMePh_2$ (59%), PEt_3 (69%), or P(*i*-Pr)$_3$ (65%)). For example, $Mo(O)(CHAr_p)(OR_{F9})_2(PEt_3)$ (**3-PEt_3**) can be prepared in this manner (eq 3). These results suggest that in most cases it is best to *avoid* formation of bis(μ-OH) dimers. We propose that THF discourages formation of a hydroxo benzylidyne dimer from monomeric $Mo(CAr_p)(OR_{F9})_2(OH)(THF)_x$ (x unknown). We also propose that the hydroxo proton migrates to the benzylidyne α carbon intramolecularly in intermediate $Mo(CAr_p)(OR_{F9})_2(OH)(THF)_x$ to give $Mo(O)(CHAr_p)(OR_{F9})_2(THF)_x$, which is then trapped by L to give $Mo(O)(CHAr_p)(OR_{F9})_2(L)$ complexes. Phosphines can also bind to Mo in $Mo(CAr_p)(OR_{F9})_2(OH)(THF)_x$ and help prevent formation of μ-OH products and promote (perhaps along with THF itself) migration of the proton from O to C. Formation of OR_{F6} analogs of **3** at room temperature in THF does not appear to be as successful, most likely because the migrating proton is less acidic in OR_{F6} hydroxo benzylidyne complexes. Studies that address multiple mechanistic issues are ongoing.



3-PEt$_3$; 57% yield (isolated)

(3)

Mo(O)(CHAr$_p$)(OR$_{F9}$)$_2$(PEt$_3$) (**3-PEt$_3$**) was chosen to proceed further toward the goal of preparing a four-coordinate complex. The reaction between **3-PEt$_3$** and two equivalents of LiOHMT proceeds smoothly at 90 °C in toluene over a period of 1.5 h to give Mo(O)(CHAr$_p$)(OHMT)$_2$ (**1-Ar$_p$**) which could be isolated as plum-purple needles (eq 4). The alkylidene proton resonance is found at 11.20 ppm (in C_6D_6) with J_{CH} = 130 Hz, consistent with the alkylidene being in the *syn* conformation. The corresponding *anti* isomer was not found in solution even upon heating a sample of **1-Ar$_p$** at 100 °C, which suggests that coordination of an *ortho* methoxide in **1-Ar$_o$** (Fig 1) stabilizes the *anti* form. The OHMT ligands in the proton NMR spectrum at 22 °C are equivalent on the NMR time scale through mirror symmetry. The purple color of **1-Ar$_p$** (λ_{max} = 532 nm with ε_{532} ~ 400) is unusual for a "d^0" complex of this general type. We propose that the purple color arises from a weak LMCT transition that involves the *p*-methoxybenzylidene ligand. Compound **1-Ar$_p$** also was prepared from **3-PMePh$_2$** in 66% yield on a 500 mg scale at 70 °C in 3.5 h.



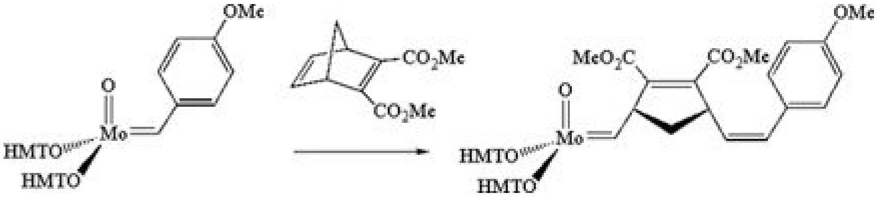
1-Ar$_p$; 71% yield (NMR); 44% isolated

(4)

An X-ray structural study of **1-Ar$_p$** (Fig 3) reveals that the OHMT terphenyl groups are roughly "interlocked," as they are in W(O)(CH$_2$)(OHMT)$_2$,[10b] although they rotate readily around the Mo-O bonds on the NMR time scale in solution at 22 °C. The relevant distances and angles are similar to those in **1-Ar$_o$** (see Fig 1 and SI). Together the two OHMT ligands prevent PEt$_3$ or PMePh$_2$ from remaining bound to the metal in the final product and also provide a significant degree of steric protection against bimolecular decomposition reactions.

Compound **1-Ar$_p$** reacts with ethylene (1 atm in C_6D_6 at 22 °C) to give an orange solution that contains a mixture of **1-Ar$_p$**, $Mo(O)(CH_2)(OHMT)_2$, and an unsubstituted metallacyclobutane complex, $Mo(O)(CH_2CH_2CH_2)(OHMT)_2$, along with $Ar_pCH{=}CH_2$, and ethylene, according to proton NMR studies. At a molybdenum concentration of 17 mM in C_6D_6, the ratio of $Mo{=}CHAr_p$: $Mo{=}CH_2$: $Mo(C_3H_6)$: $Ar_pCH{=}CH_2$ is 57:5:38:43 (43% conversion) after 1.5 h. The 1:1:2:2 pattern of the four metallacycle proton resonances in $Mo(O)(CH_2CH_2CH_2)(OHMT)_2$ at 2.92, 2.39, 1.68, and 0.45 ppm suggest that it has a square pyramidal structure.[24] So far, efforts to isolate $Mo(O)(CH_2CH_2CH_2)(OHMT)_2$, an analog of isolable $W(O)(CH_2CH_2CH_2)(OHMT)_2$,[10b] have not been successful.

Compound **1-Ar$_p$** does not react readily with several equivalents of *Z*-5-decene at 22°C. It does react with 2,3-dicarbomethoxynorbornadiene (4 equiv) to yield a 17:1 mixture of *syn* (δ H_α at 11.63 ppm; eq 5) and *anti* isomers (not shown in eq 5) of the first insertion product, each of which contains a *cis* C=C bond.[25] (The yield (by NMR) is ~90%; see SI for details.) Both results are consistent with a relatively sterically demanding coordination sphere that limits access to an alkylidene, in contrast to $Mo(O)(CHAr_o)(OHIPT)Cl$ formed through removal of PMe_3 from $Mo(O)(CHAr_o)(OHIPT)(PMe_3)Cl$, which forms polymers from 2,3-dicarbomethoxynorbornadiene readily.[12]



(5)

We conclude that the *o*-methoxy group is not required, either for forming a benzylidene ligand from a benzylidyne ligand or for stabilizing a bis(OHMT) oxo benzylidene complex. The most successful syntheses of oxo alkylidene complexes involve intramolecular α proton migrations from O to C, where C is the benzylidyne α carbon, and are most successful when OR is OR_{F9}, the solvent is THF, and a phosphine is available to trap the oxo benzylidene product and possibly help form it. Several phosphine adducts of molybdenum oxo benzylidene complexes are accessible via reactions between $Mo(CAr_p)(OR)_3(THF)_2$ complexes and water. We can now predict that other metathesis-active molybdenum oxo alkylidene complexes will be observed or isolated under the right circumstances, and look forward to comparing their metathesis reactions with those catalyzed by tungsten analogs.[10,16]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

We are grateful for financial support from the National Institutes of Health (GM-59426). We also thank the NSF for support of X-ray diffraction instrumentation (CHE-0946721).

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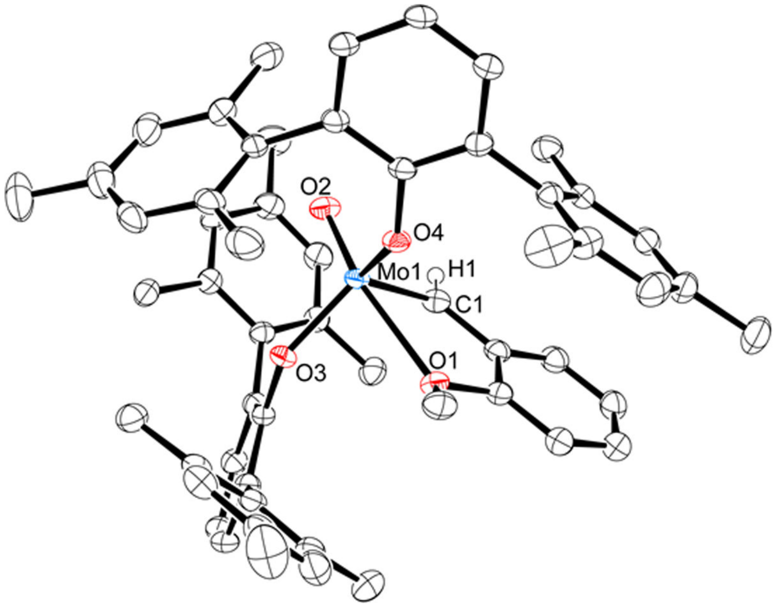

Figure 1.

A drawing of the structure of **1-Ar$_o$**; Mo1-C1 = 1.933(2) Å, Mo1-O2 = 1.6698(14) Å, Mo1-O1 = 2.4865(17) Å, Mo1-O3 = 1.915(2) Å, Mo1-O4 = 1.9295(15) Å.

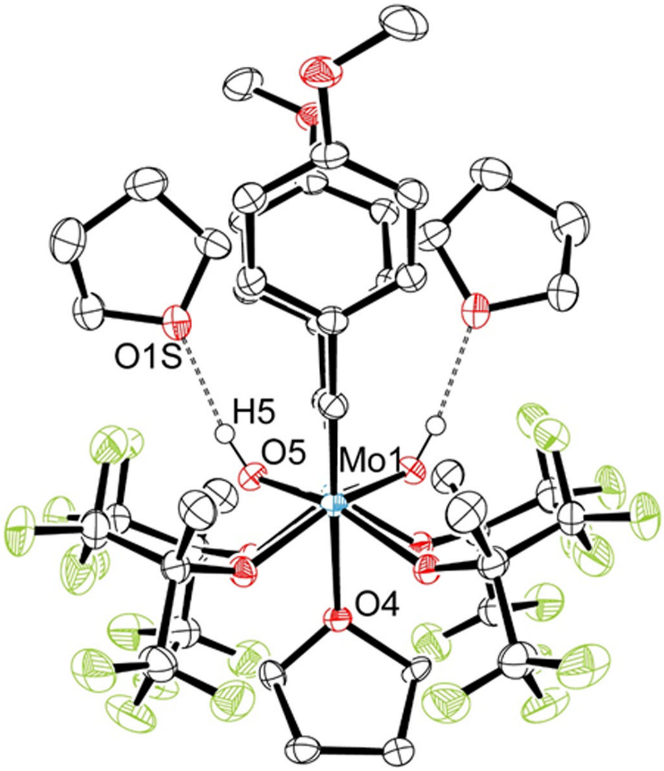

Figure 2.

End view of the structure of **2-Ar$_p$F$_6$**.

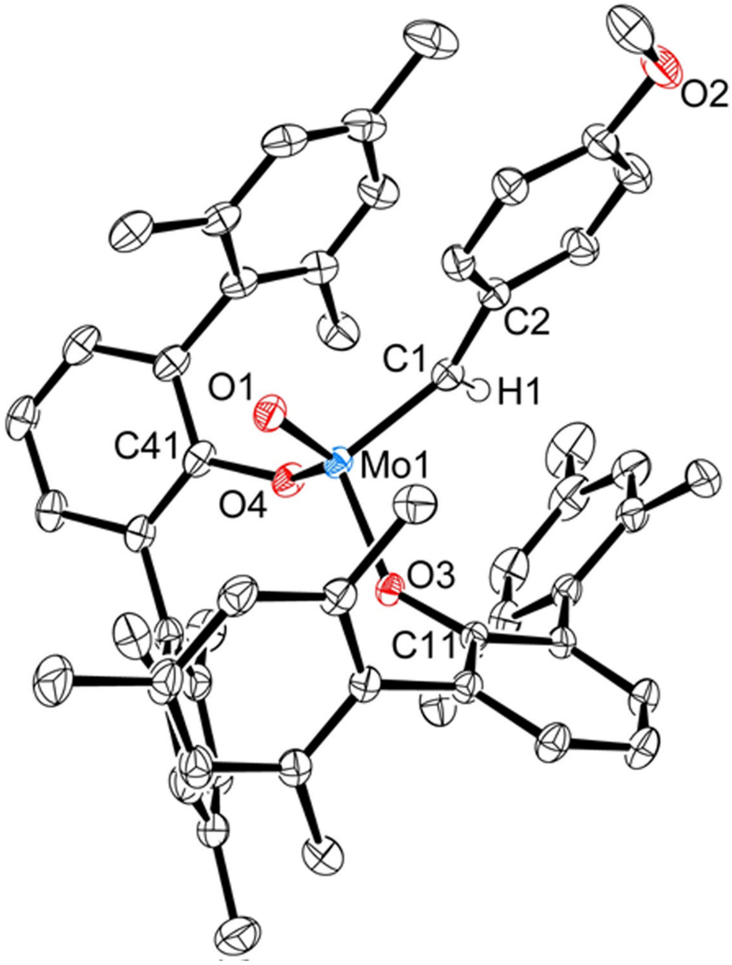

Figure 3.

A drawing of the structure of **1-Ar$_p$**;

Mo1-C1 = 1.9004(13) Å, Mo1-O1 = 1.6803(10) Å, Mo1-O3 = 1.9064(9) Å, Mo1-O4 = 1.9113(9) Å, Mo1-C1-C$_{ipso}$ = 137.42(10)°, Mo1-O3-C$_{ipso}$ = 143.11(8)°, Mo1-O4-C$_{ipso}$ = 127.58(8)°.