C–C Coupling

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Do Carbyne Radicals Really Exist in Aqueous Solution?**

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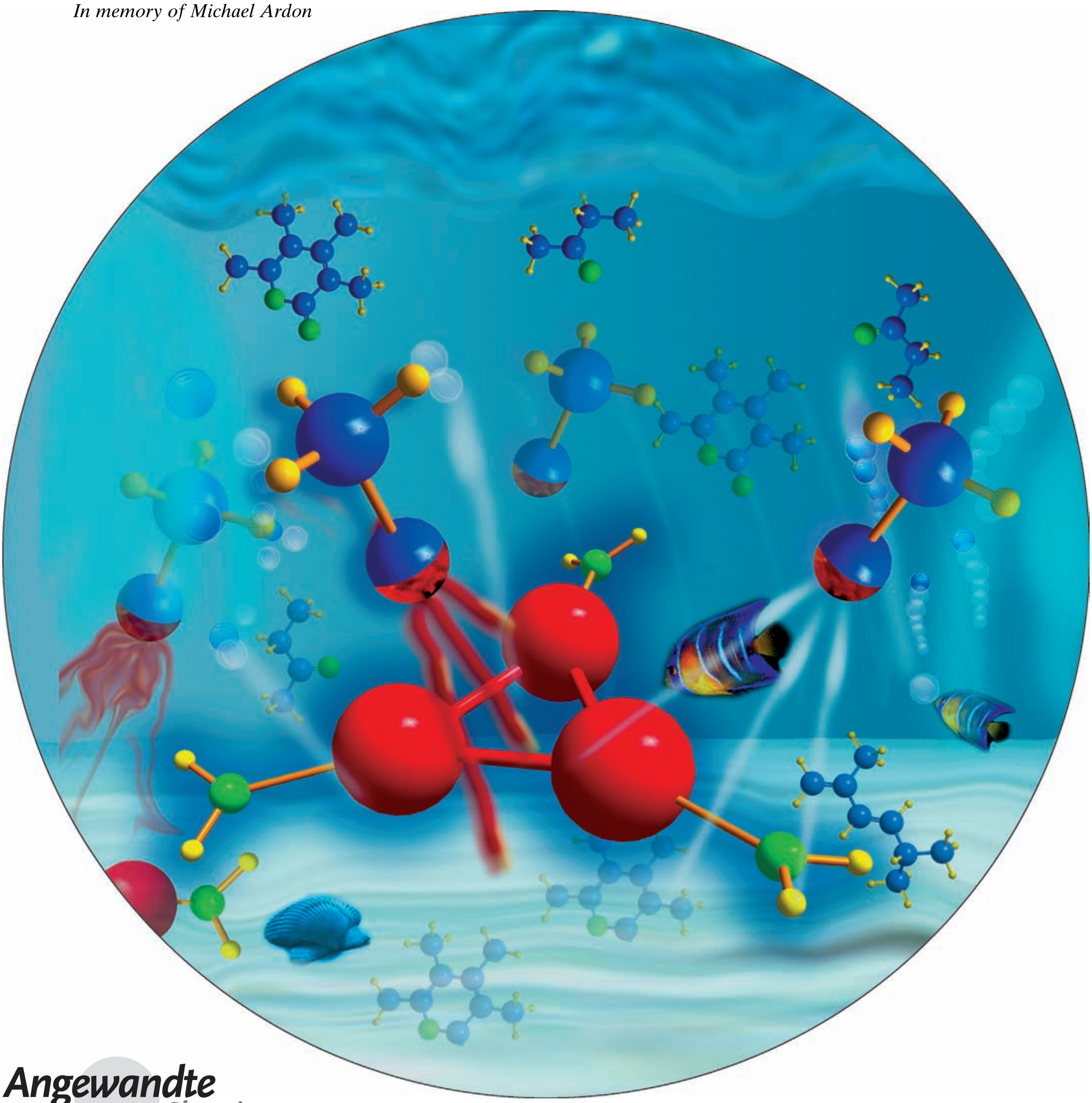
In memory of Michael Ardon



Carbynes, such as HC⁝ (HC) and its derivatives, are monovalent carbon radicals that represent one of the most fundamental hydrocarbon fragments in chemistry. The valence shell of the carbon atom in carbynes contains only five electrons, thus rendering them strong electrophiles. These highly reactive species have been observed spectroscopically in interstellar matter[1] and can be prepared under laboratory conditions by using high-energy techniques such as flash and laser photolysis or pulsed radiolysis. Carbynes such as NCC, HC, XC (X = F, Cl, Br), and $C_2H_5OC(O)C$ have been generated as minor products along with a number of other reactive radicals.[2a–g] Unlike the extensively studied carbene analogues, carbynes are the least elucidated and understood species within the carbon radical family. The lack of simple, clean, and stoichiometric reactions that produce free carbynes under ambient conditions contributes to our poor level of understanding of these species. Carbynes are also known to serve as ligands in metal complexes, wherein a carbon atom and a single metal atom are connected by triple bonds[3a,b] or a carbon atom is connected to three metal atoms by single bonds.[4] In 2005 we reported that the trimolybdenum cluster $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ (**2**; Figure 1), which contains two triply bridging ethylidyne ligands (CH_3C^{3-}), undergoes spontaneous decomposition in aqueous solution to produce 2-butyne ($CH_3C{\equiv}CCH_3$). In this reaction the two CH_3C^{3-} groups are oxidized by the Mo_3 framework to $[CH_3C]^0$ moieties, thus leading to the collapse of all Mo–C bonds. It has been suggested that the coupling of the two C_2 fragments to form a carbon–carbon triple bond is metal-assisted and occurs intramolecularly.[5]

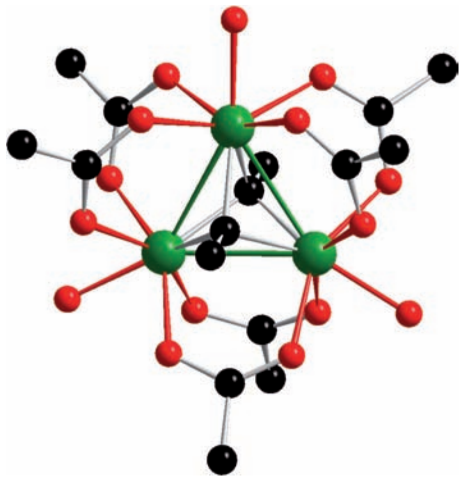


Figure 1. Structure of $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ (**2**). Green Mo; red O; black C; white H (the latter is omitted for clarity).

Herein we report the results of isotope-labeling experiments that prove that the coupling of the two C_2 fragments is not an intramolecular event. We discovered that these fragments are ejected into the aqueous solution as free methyl carbyne radicals. These extremely reactive radicals react with each other in water to generate 2-butyne along with a plethora of other hydrocarbons. The radicals also react with water molecules to form acetic acid and acetaldehyde.

The overall stoichiometry of the reaction of **2** in aqueous solution is given by Equation (1):

$$\begin{aligned}&5\,[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^{2+}{}_{(aq)}\ (\mathbf{2}) + 2\,H_2O_{(l)} \rightarrow \\ &4\,[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^{+}{}_{(aq)}\ (\mathbf{1}) + \\ &[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}{}_{(aq)}\ (\mathbf{3}) + 2\,CH_3C_{(aq)} + 4\,H^{+}{}_{(aq)}\end{aligned} \tag{1}$$

The exact molar ratio between the three trinuclear complexes **1**, **2**, and **3** was previously determined using ion-exchange chromatography and titration techniques.[5] An electron count shows that the products contain six more *d* electrons than the reactants. The origin of these electrons is the two CH_3C^{3-} groups of complex **2** that are oxidized to CH_3C by the Mo_3 system. Four electrons are used to reduce four other complexes of **2** to **1** and two electrons remain in complex **3**, wherein two capping CH_3C groups are replaced by oxide ligands from the solvent. Overall, six Mo–C bonds in one out of five complexes of **2** are replaced by six new Mo–O bonds. 2-Butyne is obtained along with other products by the coupling reaction[5] $2\,CH_3C_{(aq)} \rightarrow CH_3C{\equiv}CCH_3$.

The reaction in Equation (1) goes to completion in about 3 hours at 25 °C at initial pH values between 5 and 6. The mechanism of these reactions has been studied using isotope-labeling experiments. We reacted a 1:1 mixture of **2** and $[Mo_3(CCD_3)_2(O_2CCD_3)_6(H_2O)_3]^{2+}$ ($[D_{24}]$-**2**)[6a,b] in H_2O, and analyzed the resulting 2-butyne by gas chromatography/mass spectrometry (GC/MS). The 1:2:1 molar ratio between $CH_3C{\equiv}CCH_3$ (MW = 54), $CD_3C{\equiv}CCH_3$ (MW = 57), and $CD_3C{\equiv}CCD_3$ (MW = 60), respectively, rules out an intramolecular mechanism for the formation of 2-butyne in this reaction (see Figure S1 in the Supporting Information). Additional support for this view comes from the following sets of experiments with complexes that contain only one bridging or terminal alkylidyne group rather than two: a) When the pH value of a solution of the mono-ethylidyne complex[7a] $[Mo_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$, or of its mono-propylidyne analogue[7b] $[Mo_3O(CCH_2CH_3)(O_2CCH_2CH_3)_6(H_2O)_3]^+$, is adjusted to about 8, 2-butyne and 3-hexyne are formed respectively. A 1:1 mixture of the two complexes at pH value of 8 produces 2-pentyne along with 2-butyne and 3-hexyne. b) The tri-tungsten mono-ethylidyne complex[7c] $[W_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]^{2+}$ decomposes spontaneously in water, and 2-butyne is produced. c) When the water insoluble compound ethylidyne tricobalt nonacarbonyl, $[Co_3(CCH_3)(CO)_9]$,[4] is introduced to a 0.1 M aqueous solution of NaOH, 2-butyne is formed. d) We also

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examined the chemistry of a known alkyne metathesis catalyst with a W≡CR system, namely, tris(*tert*-butoxy)(2,2-dimethylpropylidyne) tungsten(VI),[8] in aqueous solution under the same reaction conditions as used for the reaction shown in Equation (1). The water insoluble compound decomposed, thus producing the coupling product 2,2,5,5-tetramethyl-3-hexyne along with several other compounds.[9]

Since the experimental data exclude an intramolecular coupling pathway, we have examined other potential mechanistic routes. In complex **2**, each of the CH_3C groups resides inside a deep cavity formed by the bridging acetate ligands (Figure 2). A bimolecular pathway in which two bulky clusters collide and two CH_3C groups from different clusters detach, and are then coupled through a 180° flip in a concerted manner seems complicated and highly improbable. The extreme kinetic stability of the trinuclear clusters with an M_3X_{17} structure[10] (as in complex **2**) and the relatively high coordination number about the metal atoms (nine) rules them out as participants in the formation of the carbon–carbon triple bond. It is believed that such a process requires considerable accessibility to the metal atom and at least two adjacent open coordination sites.[8] We have also considered coupling mechanisms that involve a mononuclear M≡CR system that may be formed by some unobserved degradation of trinuclear clusters. To the best of our knowledge, reactions in which a triply bridging alkylidyne is spontaneously transformed into a mononuclear M≡CR species in aqueous solution in air are unprecedented. Moreover, in the case of cobalt, there are no reports of Co≡CR systems. Furthermore, our results show that a compound containing an M≡CR system is unstable in aqueous media and releases carbyne that in turn couples to yield the corresponding alkyne and other coupling products. Electrospray ionization high-resolution MS experiments on the reaction mixture of **2** and $[D_{24}]$-**2** show that bridging acetate ligands in the final products $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ (**3**) and $[Mo_3O_2(O_2CCD_3)_6(H_2O)_3]^{2+}$ ($[D_{18}]$-**3**) do not scramble (see Figure S2 in the Supporting Information). This result rules out ligand exchange between two colliding clusters or reassembly of mononuclear metal fragments in solution to form Mo_3 species such as **3**. Direct evidence for the existence of free radicals in solutions of complex **2** arises from the following experiment: Complex **2** reacts with 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) in solution and forms an ABTS radical with a typical absorption band at $\lambda = 416$ nm, thus indicating the presence of oxidizing free radicals in solution.[11]

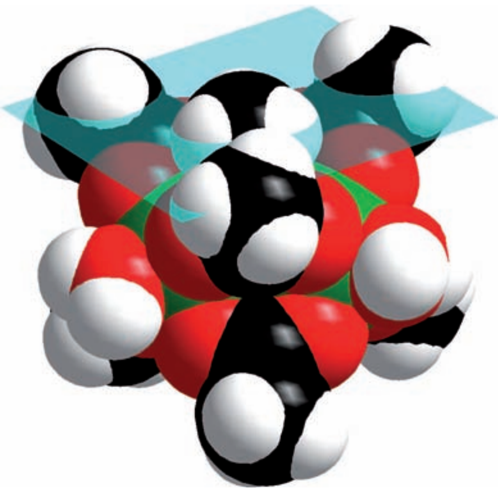


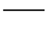
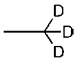
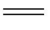
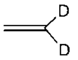
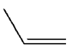
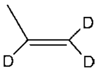
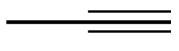
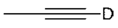
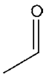
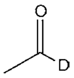
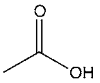
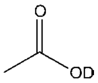
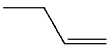
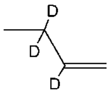
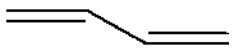
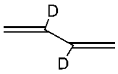
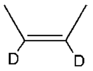
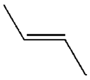
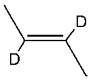
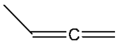
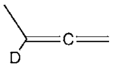
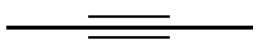
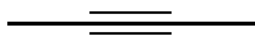
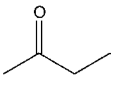
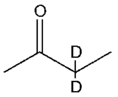
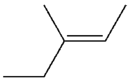
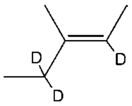
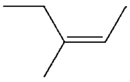
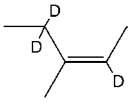
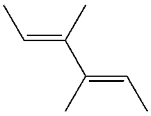
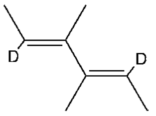
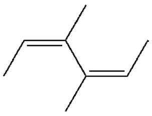
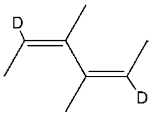
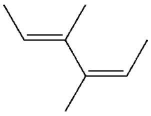
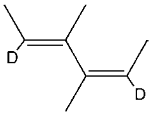
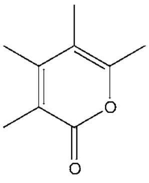
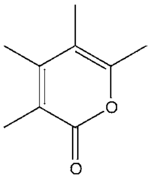
Figure 2. Space-filling model of **2**. The light-blue plane bisects the three methyl groups of the upper bridging acetate ligands. The methyl group of the ethylidyne ligand is seen in the center of the plane. The color scheme for the atoms is the same as that used in Figure 1.

In view of these results, we conclude that in all of the above reactions, free carbyne radicals are formed and ejected from metal complexes into solution and that all subsequent reactions occur in solution and without assistance from the metal complexes.

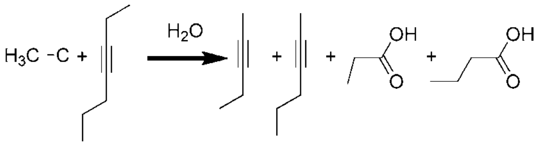
Unfortunately, the presence of the paramagnetic metal clusters **1** and **2**[6a] in solution [Eq. (1)] precludes the use of electron paramagnetic resonance (EPR) techniques as a tool for the detection of radicals. However, we have obtained some additional results for the reaction of complex **2** [Eq. (1)] that support the proposal mentioned above: a) About 50–60 % of the methyl carbyne radicals react with water and form acetic acid presumably according to $RC + 2H_2O \rightarrow RCOOH + 3/2H_2$. Small amounts of dihydrogen have been detected in the headspace of the reaction vessel (see Figure S3 in the Supporting Information). Experiments in $H_2{}^{18}O$ clearly indicate that the two oxygen atoms of the acid are derived from the bulk water molecules (see Figure S4). Small amounts of acetaldehyde with ^{18}O ($< 0.2\,\%$ based on CH_3C) were also detected. In a similar experiment we reacted a modified complex **2** containing two capping CH_3C groups, but six deuterated bridging acetate ligands, $[Mo_3(CCH_3)_2(O_2CCD_3)_6(H_2O)_3]^{2+}$ (see Figures S5 and S6).[12] The resulting CH_3COOH product indicates that the origin of the acetic acid is the methyl carbyne radical and not the bridging acetate ligands. b) 2-Butyne accounts for about 7 % of the final products. Several other products are also detected and are shown in Table 1, along with products of the reaction of **2** in D_2O. We assume that these products account for most of the remaining carbon mass (ca. 30 %).

Previous reports show that carbyne radicals which are generated by high-energy processes and are assumed to possess a doublet ground state,[2f] react with alkenes, and presumably form a "vibrationally-excited cyclopropyl radical which may undergo further unimolecular reactions".[2e] Here we report that carbyne radicals generated from trinuclear metal complexes as described above do not react with alkenes.[13] However, these radicals do react with alkynes and produce new alkynes and carbyne radicals according to $R^1C + R^2C{\equiv}CR^3 \rightarrow R^1C{\equiv}CR^3 + R^2C$ or $R^1C{\equiv}CR^2 + R^3C$. When an asymmetric alkyne such as 3-heptyne was reacted with **2** in water, 2-pentyne and 2-hexyne (1:2) and propionic and butyric acids (2:1) were formed (Scheme 1). The carboxylic acids are formed by the reaction of the corresponding carbyne radicals with water molecules, in a similar process in where the acetic acid is formed from methyl carbyne radicals and water. We conclude that asymmetric alkynes serve as

Table 1: Products of the reactions of the CH_3C radicals produced in the reaction shown in Equation (1) that was run in H_2O and in D_2O.[a]

Entry	Product	**2** in H_2O	**2** in D_2O
1	ethane		
2	ethene		
3	propene		
4	propyne		
5	acetaldehyde		
6	ethanoic acid		
7	1-butene		
8	1,3-butadiene		
9	(*Z*)-2-butene		
10	(*E*)-2-butene		
11	1,2-butadiene		
12	2-butyne		
13	2-butanone		
14	(*Z*)-3-methyl-2-pentene		
15	(*E*)-3-methyl-2-pentene		
16	(*E*,*E*)-3,4-dimethyl-2,4-hexadiene		
17	(*Z*,*Z*)-3,4-dimethyl-2,4-hexadiene		
18	(*E*,*Z*)-3,4-dimethyl-2,4-hexadiene		
19	3,4,5,6-tetramethyl-2*H*-pyran-2-one		

[a] Yields of acetaldehyde (< 0.2%), acetic (ethanoic) acid (50–60%), and 2-butyne (ca. 7%) were determined using calibration curves. Yields of the rest of the products are roughly estimated to be < 3% each.



Scheme 1. Reaction of methyl carbyne and 3-heptyne in aqueous solution.

good reagents for trapping and detecting free carbynes in the aqueous media because four distinct products are formed.

The high reactivity of the methyl carbyne radicals [Eq. (1)] is also demonstrated in the following experiments. The radicals react with acetylene in solution and produce diacetylene, $HC{\equiv}C{-}C{\equiv}CH$, probably as a result of hydrogen abstraction from $HC{\equiv}CH$ rather than $C{\equiv}C$ cleavage. With CN^-, we obtained $CH_3CH_2C{\equiv}N$ (in D_2O the product is $CH_3CD_2C{\equiv}N$), and the reaction with azide (N_3^-) produced $CH_3C{\equiv}N$.

The broad spectrum of products listed in Table 1 includes a carboxylic acid, an aldehyde, a ketone, alkynes, alkenes, and alkanes of various chain lengths. The diversity and large number of products that were created under such benign conditions clearly indicate the high reactivity of the methyl carbyne radical in Equation (1). Most of the products are the result of extensive hydrogen, carbon, or oxygen abstraction reactions from solvent, reactants, and products as expected from such an energetic species. The fact that free carbynes are capable of traveling enough distance in aqueous environment and couple with other carbynes at concentrations that are lower by at least 10^5 times that of the H_2O concentration suggests that the reaction with bulk H_2O is remarkably slow.

In summary, we have shown that free carbyne radicals can be generated in aqueous solution from a variety of metal alkylidyne complexes under mild reaction conditions and in the reaction shown in Equation (1), 0.4 moles of free methyl carbyne radicals, CH_3C, are generated per mole of reactant. Carbon-chain lengthening by the coupling of hydrocarbon moieties, alkyne metathesis, and synthesis of organic compounds in water are some of the most important processes in modern chemistry. The reactions described herein may open new venues to understanding the mechanisms of some of these reactions especially those in which carbon radicals are involved.

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[9] In a typical experiment, 2–3 mg of the title compound were transferred under nitrogen into a vial. 2 mL of H_2O were added by syringe. The dispersion was vigorously stirred for several hours. The water insoluble brown solid decomposed forming white precipitate of presumably oxo/hydroxo W^{VI} compound. Solution and headspace samples were analyzed by GC–MS. The following compounds were detected: 2,2,5,5-tetramethyl-3-hexyne, 2,2-dimethylpropanal, 2,2,5,5-tetramethyl-3-hexene, 2,2,5,5-tetramethyl-3-hexane, 2-methyl-2-propanol, neopentane, and 2,2-dimethylpropan-1-ol.

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[12] $Mo_3(CCH_3)_2(O_2CCD_3)_6(H_2O)_3]^{2+}$ was prepared by reacting **2** with CD_3COOD at 70 °C followed by ion-exchange separation.

[13] List of alkenes that do not react with **2** in aqueous solution: styrene (ethenylbenzene), 1-hexene, (*Z*)- or (*E*)-2-hexene, a mixture of (*Z*)- and (*E*)-3-methyl-2-pentene, cyclohexene, 1,4-cyclohexadiene, 2-buten-1,4-diol, (*Z*)-2-penten-1-ol, acrylonitrile (2-propenenitrile), *p*-benzoquinone (2,5-cylohexadiene-1,4-dione).