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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.8b02254 • Publication Date (Web): 09 Jul 2018 Downloaded from http://pubs.acs.org on July 10, 2018

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Cuboidal Mo₃S₄ clusters as a platform for exploring catalysis: A three-center sulfur mechanism for alkyne semihydrogenation

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ABSTRACT: We report a trinuclear Mo_3S_4 diamino cluster that promotes the semihydrogenation of alkynes. Based on experimental and computational results, we propose an unprecedented mechanism in which only the three bridging sulfurs of the cluster act as the active site for this transformation. In the first step, two of these μ -S ligands react with the alkyne to form a dithiolene adduct, this process being formally analogous to the olefin adsorption on MoS₂ surfaces. Then, H₂ activation takes place in an unprecedented way that involves the third μ -S center in cooperation with one of the dithiolene carbon atoms. Notably, this step does not imply any direct interaction between H₂ and the metal centers, and directly results in the formation of an intermediate featuring one (μ -S)–H and one C–H bond. Finally, such half-hydrogenated intermediate can either undergo a reductive elimination step that results in the Z-alkene product, or evolve into an isomerized analogue whose subsequent reductive elimination generates the *E*-alkene product. Interestingly, the substituents on the alkynes have a major impact on the relative barriers of these two processes, with the semihydrogenation of dimethyl acetylenedicarboxylate (dmad) resulting in the stereoselective formation of dimethyl maleate, whereas that of diphenylacetylene (dpa) leads to mixtures of *Z*- and *E*-stilbene. The results herein could have significant implications in the understanding of the catalytic properties of MoS₂-based materials.

KEYWORDS: catalysis, molybdenum disulfide, alkyne semihydrogenation, hydrogen activation, density functional theory.

Catalytic semihydrogenation of alkynes is of great practical significance in chemistry today, and palladium heterogeneous catalysts have proved to be the most effective in achieving this transformation.¹⁻² According to the proposed mechanism,³ H₂ is adsorbed dissociatively over the surface of the metal, whereas the alkyne is adsorbed through its interaction with the π -bonds. Then hydrogenation proceeds via two stepwise C–H bond formations. Due to its well-defined stereochemistry, *Z*-selectivity is intrinsic to this transformation, but the half-hydrogenated intermediate allows for alternative *cis-trans* isomerization and H–D exchange processes.⁴ The use of homogeneous conditions in the palladium catalyzed semihydrogenation of alkynes is, in contrast, much less frequent.^{2,5}

Molybdenum sulphides, traditionally employed in industry for the hydrodesulphurisation (HDS) of fossil fuels, have recently emerged as low-cost alternatives to platinum group metals as hydrogenation and hydrogen evolution reaction (HER) catalysts.⁶ Similarly to the semihydrogenation mechanism, HDS processes start with the adsorption of the Scontaining substrate and dissociation of H₂ at the surface of the catalyst. While substrate adsorption is postulated to occur at coordinatively unsaturated sites, there is no consensus on the H₂ activation mechanism. As a result, two possibilities have been envisioned: the heterolytic dissociation of H₂ to generate Mo–H and S–H bonds, and the homolytic dissociation on disulphides resulting in two S–H groups.⁷ Notably, while the formation of S–H species has been observed spectroscopically, there is no experimental evidence



Figure 1. Topological relationship between the molecular cluster $[1]^+$ and the basal planes of a MoS₂ monolayer.

about the generation of Mo–H hydrides. Nevertheless, this option cannot be ruled out due to the facile migration of adsorbed H atoms from Mo to S in this material.⁸

The inherent difficulties to obtain mechanistic information from heterogeneous catalytic systems have led, over the years, to the design of molecular models capable of emulating the reactivity of the MoS₂ edge sites. Specifically, in the context of HER catalysis, the active edge sites have been successfully mimicked by the mono-, di-, and trinuclear species $[(PY5Me_2)MoS_2]^{2^+,9}$ $[Mo_2(S_2)_6]^{2^-,10}$ and $[Mo_3(\mu_3-S)(\mu-S_2)_3(S_2)_3]^{2^-,11}$ respectively. The latter compound shows evident similarities to the incomplete cubane-type $Mo_3(\mu_3-S)(\mu-S)_3$ clusters. However, whereas $[Mo_3S_{13}]^{2^-}$ represents a model for the edges, $Mo_3(\mu_3-S)(\mu-S)_3$ clusters can be considered as models of the basal planes of MoS_2 , as illustrated in Figure 1 for $[Mo_3(\mu_3-S)(\mu-S)_3Cl_3(dmen)_3]^+$ ([1]⁺). In addition to the structural similarity, MoS_2 and Mo_3S_4 clusters also share behavioural patterns. Thus, the reaction of Mo_3S_4 clusters with alkynes leads to the formation of dithiolene products by means of a [3+2] cycloaddition reaction,¹² with the process being formally analogous to the alkyne adsorption at the MoS_2 surface. Similarly, both Mo_3S_4 clusters¹³ and MoS_2 structures¹⁴ catalyze relevant organic transformations such as the hydrogenation of nitroarenes.

In this Letter, we report that the cluster $[1]^+$ catalyzes the semihydrogenation of alkynes via a mechanism that is significantly different to that assumed for the hydrogenation of unsaturated hydrocarbons at the surface of MoS₂. In the present mechanism: a) only the three bridging sulfur ligands within the cluster take part in all the bond breaking and formation events; b) H₂ activation takes place without prior interaction with the cluster through a step that directly results in the half-hydrogenated intermediate; c) the Mo centers are not directly involved in the process. As the whole set of transformations occurs at the triangle defined by the three μ -S ligands, the possibility of a similar mechanism operating for reactions with MoS₂ must be considered.

This study was prompted not only by previous work on the reactivity of cuboidal Mo_3S_4 clusters towards alkynes,¹² but also by the high activity of $[Mo_3S_4Cl_3(dmen)_3]^+$ ([1]⁺) as a catalyst for the selective hydrogenation of nitroarenes into anilines.¹³ It is well known that the [3+2] cycloaddition reaction between these clusters and alkynes is affected by the nature of the ancillary ligands at the cluster as well as the alkyne substituents.¹² In the case of $[1]^+$, the reaction with dmad results in formation of the corresponding dithiolene adduct, as evidenced by the appearance of a band at 887 nm characteristic of these addition products. The process takes place in a single step with a second-order rate constant of 0.72 \pm 0.02 M⁻¹s⁻¹, a value close to those obtained for $[Mo_3S_4(acac)_3(py)_3]^+$ and $[Mo_3S_4Cl_3(^tBu-bipy)_3)]^{+,12}$ In contrast, alkynes with electron donating substituents, such as dpa, do not react with $[1]^+$. The free energy profiles, obtained at DFT level (see SI for computational details), point out that both processes take place in a concerted fashion, via transition states in which both C-S bonds are formed simultaneously (see Figure S4). However, while the reaction between $[1]^+$ and dmad is slightly exergonic (-2.6 kcal mol⁻¹) and occurs with an activation barrier of 9.5 kcal mol^{-1} , the reaction with dpa is endergonic by 4.2 kcal mol⁻¹ and therefore not thermodynamically favoured. These results thus show the agreement between experimental and computational results.

Accordingly, the reaction between $[1]^+$ and a ten molar excess of dmad in acetonitrile at room temperature quantitatively affords a stable 1:1 adduct of formula $[Mo_3(\mu_3-S)(\mu-S)(\mu_3-S)$ $SC(CO_2CH_3)=C(CO_2CH_3)S)Cl_3(dmen)_3]BF_4$ [2]BF₄, see SI for full experimental details). $[2]^+$ was crystallized as the $[2]_2[Mo_6Cl_{18}]$ •3CH₃OH salt and its structure determined by single crystal X-ray diffraction. An ORTEP representation of $[2]^+$ is given in Figure 2. The structure of $[2]^+$ confirms the formation of two C-S bonds, with the addition of the unsaturated molecule resulting in the loss of the C₃ symmetry of the incomplete cuboidal Mo(IV)₃ cluster precursor. While the two Mo- $(\mu$ -S) bonds involved in the dithiolene formation are slightly elongated by *ca.* 0.06-0.13 Å on going from $[1]^+$ to $[2]^{+,15}$ there are no significant changes in the other Mo-ligand bond lengths. The geometry of the resulting dithiolate corresponds to the maleate adduct (Z-isomer), with a C=C bond distance (1.329 Å) far from that of



Figure 2. ORTEP representation of $[2]^+$ (ellipsoids at 50% probability) with the atom-numbering scheme. Hydrogen atoms have been omitted for clarity. Intermetallic distances: Mo(1)–Mo(2) = 2.653 Å, Mo(1)–Mo(3) = 2.772 Å and Mo(2)–Mo(3) = 2.778 Å, C(15)–C(16)=1.329 Å.

the dmad precursor (1.183 Å).¹⁶ The sp^2 character of these carbon atoms is also supported by the values of bond angles close to 120°, similarly to those found in other dinuclear and trinuclear dithiolate derivatives, and also in agreement with a -2 charge for this ligand.¹⁷ This implies an internal electron transfer process induced by the interaction with dmad, which is also reflected in the shortening of the Mo-Mo bond between the Mo centers not involved in the [3+2] cycloaddition reaction from 2.759 Å in $[1]^+$, characteristic of a Mo–Mo single bond, to 2.653 Å in $[2]^+$, typical of a Mo–Mo double bond. Thus, insertion of the alkyne results in a reduction of the metal atoms from $Mo(IV)_3$ to $Mo(III)_2Mo(IV)$, as the dithiolene cluster contains eight cluster skeletal electrons for the formation of two single and one double Mo-Mo bonds.¹⁸ The structure of $[2]^+$ is well reproduced by DFT calculations (see below) and supports the existence of an internal electron transfer also reflected in their redox properties. Thus, whereas the cyclic voltammogram of $[1]^+$ shows a sole reversible reduction at -0.45 V (vs. Ag/AgCl), [2]⁺ undergoes one reversible reduction at -0.34 V and two quasi-reversible oxidations at 0.84 and 1.16 V, respectively (see Figure S1).

After isolation and characterization of $[2]^+$, we investigated its reactivity towards H₂. Hydrogenation of $[2]^+$ at 20 bar and 70 °C for 18 h in CH₃CN resulted in the stereoselective formation of dimethyl maleate, with no evidence of formation of dimethyl fumarate. No conversion was observed when the reaction temperature was lowered to 30 °C. DFT calculations were then performed to unveil the reaction mechanism. A [2+2] addition of H₂ across one of the C–S bonds at $[2]^+$ was computed initially but, as expected, the calculations resulted in a prohibitive free energy barrier of 59.2 kcal mol⁻¹ together with a thermodynamically uphill process ($\Delta G_r = 34.0$ kcal mol⁻¹, see Figure S5). Instead, a more feasible mechanism was found to involve the interaction of H₂ with the remaining μ -S ligand and one of the sp^2 C atoms of the dithiolate ligands (see Figure 3). The process described by **TS2** features a free energy

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Figure 3. Computed pathways for the activation hydrogenation of dmad ($R=CO_2CH_3$) at $[2]^+$. Free energy values are given in kcal mol⁻¹ quoted relative to $[1]^+$ + dmad + H₂. For simplicity, dmen and Cl ligands are not drawn.



Figure 4. For TS2, schematic representation of the two main symmetry-allowed orbital interactions between $[2]^+$ and H₂. For simplicity, additional orbital contributions from the Mo atoms were not drawn, see Figure S7.

barrier of 35.1 kcal mol⁻¹ and implies the cleavage of the H–H σ bond together with the formation of new (µ-S)–H and C–H bonds. In fact, the concerted nature of the process is highlighted by the frontier molecular orbital (FMO) analysis of such structure in Figure 4. This shows a main interaction between the HOMO of $[2]^+$, which features contributions from a lone pair of the (μ -S) ligand and the π orbital of the dithiolene C=C moiety, and the σ^* orbital of H₂. Furthermore, there is an additional interaction between the LUMO of the cluster, partly located at the π * orbital of the dithiolene C=C moiety, and the σ orbital of H₂. The product of this reaction, the cluster [3]⁺, is 19.2 kcal mol⁻¹ less stable than its precursors (see Figure 3), and a comparison of its structure with that of $[2]^+$ shows that the interaction with H₂ results in a rearrangement of the electron density within the cluster core. Thus, $[3]^+$ can be viewed as featuring a C-C simple bond, in agreement with its longer bond distance (1.50 Å, cf. 1.35 Å in $[2]^+$), whereas the different C^b–S^b and C^a–S^a bond distances (1.92 and 1.77 Å, respectively) are in line with simple and double C-S bonds, respectively. From $[3]^+$, dimethyl maleate can be released in a subsequent reductive elimination step between the H atom at µ-SH and C^a via TS3. Such transition state appears only 0.5 kcal mol^{-1} above $[3]^+$ (see Figure 3) and so, once the latter species is formed, it will readily undergo exergonic elimination of dimethyl maleate. Note that, in relation to heterogeneous catalysis, $[3]^+$ is formally analogous to the half-hydrogenated intermediate involved in processes such as the cis-trans isomerization of alkenes,¹⁹ and indeed the computations show that $[3]^+$ can also rearrange into $[3iso]^+$ through a process that implies the cleavage of the C^b-S^b bond. This allows for the operation of a parallel pathway that results in the thermodynamically more stable E-alkene via TS3iso. Importantly, the free energy difference between TS3 and TS4 determines the extent in which kinetic (dimethyl maleate) and thermodynamic (dimethyl fumarate) products are formed. The computations in Figure 3 show that elimination of dimethyl maleate from $[3]^+$ is 7.8 kcal mol⁻¹ more facile than its isomerization, a $\Delta\Delta G^{\#}$ value that is in agreement with the stereoselective formation of dimethyl maleate.

According to our observations regarding the regeneration of $[1]^+$ upon semihydrogenation of $[2]^+$ and the above calculated mechanism, the process is expected to be catalytic. Unfortunately, the catalytic hydrogenation of dmad requires harsh conditions that are incompatible with the stability of the organic precursor. Then, the catalytic hydrogenation of dpa, which does not react with $[1]^+$ in the absence of H₂ to an appreciable extent, was investigated by varying the hydrogen pressure, temperature, amount of catalyst and reaction time (see Table 1 and Tables SI1 and SI2 in the SI). The best results were obtained after 65 hours at 150 °C in the presence of 12% catalyst, using CH₃CN as the solvent and H₂ at 100 bar (see Table 1, entry 7). These conditions led to 62% conversion, with Z- and E-alkenes in yields of 53% and 9%, respectively. Thus, in this case the reduction of the unsaturated molecule is not stereoselective (see Table 1), and an average Z:E ratio of 6.5:1 is observed.

Table 1. Variation of the catalyst loading and reaction time in the semihydrogenation of dpa.^a



-	Entry	Catalyst loading (mol%)	Time (h)	Conversion (%) ^b	Yield (%) ^b	
_					Ζ	Е
-	1	5	18	21	18	3
	2	7	18	28	25	3
	3	9	18	30	26	4
	4	12	18	35	30	5
	5	5	65	32	28	4
	6	8	65	48	41	7
	7	12	65	62	53	9

^a Reaction conditions: dpa (0.1 mmol), H_2 (100 bar), 150 °C, CH₃CN (2 mL). ^b Determined by GC analysis using n-hexadecane as an internal standard.

The reaction with dpa was also modelled using DFT calculations and the results for a mechanism analogous to that in Figure 3 are shown in Figure S8. As previously anticipated,¹ alkyne substituents have a large effect not only on the kinetics and thermodynamics of the dithiolene product formation $[2_{Ph}]^+$ (the subindex Ph is used to refer to dpa), but also on its further reactivity with H₂. The formation of $[3_{Ph}]^+$ is computed to be thermodynamically uphill by 30.7 kcal mol⁻¹, with a free energy barrier of 42.0 kcal mol⁻¹. Despite the unfavourable thermodynamics, the process is still feasible under the experimental conditions and release of Z-stilbene from $[\mathbf{3}_{Ph}]^{\dagger}$ via $\mathbf{TS3}_{\mathbf{Ph}}$ ($\Delta G^{\#} = 37.0$ kcal mol⁻¹), or its isomerization into $[\mathbf{3iso_{Ph}}]^+$ via $\mathbf{TS4_{Ph}}$ ($\Delta G^{\#} = 38.9$ kcal mol⁻¹) and subsequent release of E-stilbene, are two significantly exergonic processes that complete the catalytic cycle. Notably, the computed $\Delta\Delta G^{\#}$ value for these two processes is only 1.9 kcal mol⁻¹, which translates into a predicted Z:E ratio of 9.6:1. In spite of the slight overestimation on the formation of the Z-isomer, it is worth noting that the theoretical $\Delta\Delta G^{\#}$ for the obtained average Z: E ratio is 1.5 kcal mol⁻¹, thus leading to an error of only 0.4 kcal mol⁻¹ in this calculation. This is well within the limits of the so-called chemical accuracy, and all in all gives further support to the proposed mechanism.

In summary, herein we show that Mo_3S_4 clusters are able to catalyze the semihydrogenation of alkynes. Based on experimental and computational results, we propose an unprecedented mechanism whereby only the three (μ -S) ligands of the cluster are directly involved in all the bond breaking and formation events. Two of these initially interact with the *sp*hybridized C atoms of the alkyne resulting in the formation of a dithiolene adduct. This species subsequently reacts with H₂ in a process that results in the concerted cleavage of the H–H σ bond together with the formation of one (μ -S)–H and one C–H bond. Finally, a reductive elimination step from the previously generated intermediate or from its isomerized analogue releases the Z- and E-alkenes, respectively. Hence, the stereochemistry of the alkene product depends on the relative barriers for the isomerization and reductive elimination of such intermediate. Remarkably, the present results clearly show that an adequate arrangement of three S atoms allows for the alkyne and H_2 interaction required for the semihydrogenation process to take place, without direct participation of the Mo atoms in any of the reaction steps.

Given the structural similarity between Mo_3S_4 clusters and MoS_2 basal planes, which also display three-sulfur triangles linked through Mo atoms (see Figure 1), the possibility of analogous chemical transformations at MoS_2 -based materials should be considered.

ASSOCIATED CONTENT

Detailed synthetic and experimental procedures, kinetic data, crystal structure determination and computational details. Cartesian coordinates of all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Financial support from the Spanish Ministerio de Economía y Competitividad and FEDER funds of the EU (Grants CTQ2015-65207-P, CTQ2015-65707-C2-2-P, and CTQ2015-71470-REDT), Universitat Jaume I (UJI-A2016-05, UJI-B2017-44) and Generalitat Valenciana (PrometeoII/2014/022) is gratefully acknowledged.

ABBREVIATIONS

PY5Me₂, 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine; dmen, Me₂NCH₂CH₂NMe₂; dmad, dimethyl acetylenedicarboxylate; dpa, diphenylacetylene.

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