Synthesis, Characterizations, and Catalytic Activity of a Cubic [Mo_3S_4Pd] Cluster Bearing Bulky Cyclopentadienyl Ligands

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Dedication to Prof. Masanobu Hidai

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Abstract: A cubic metal-sulfur cluster containing three Mo ions and a Pd ion, [$Cp^{SiEt3}{}_3Mo_3S_4Pd$]Cl (**Mo_3Pd**, Cp^{SiEt3} = $C_5Me_4SiEt_3$), was synthesized by the incorporation of the Pd ion into a Mo_3S_4 cluster [$Cp^{SiEt3}{}_3Mo_3S_4$] (**Mo_3**). **Mo_3Pd** was characterized by ^{1}H NMR, UV-vis, X-ray crystallography, and cyclic voltammetry measurements. The electrochemical measurements demonstrated reversible one- and two-electron reduction processes for **Mo_3Pd**, which suggested potential catalytic activity for two-electron substrate reductions such as hydrogen evolution reaction. Controlled potential electrolysis in the presence of **Mo_3Pd** and trifluoroethanol in THF solvent displayed H_2 formation with a constant current over 60 min. The amount of generated H_2 by **Mo_3Pd** was two times higher than **Mo_3**, indicating the catalytic activity facilitated by the Pd center. The mechanism of the catalytic cycle was determined by density functional theory.

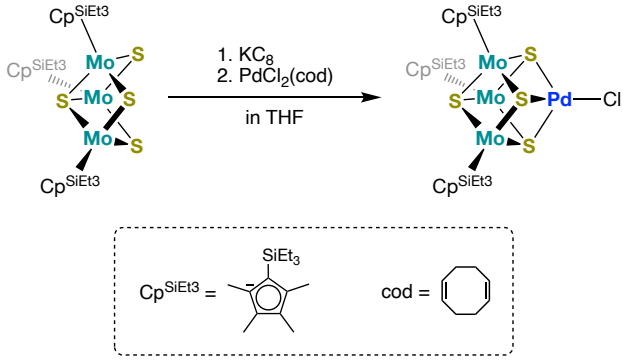

Figure 1. Synthesis of [$Cp^{SiEt3}{}_3Mo_3S_4Pd$]Cl (**Mo_3Pd**, Cp^{SiEt3} = $C_5Me_4SiEt_3$) from $Cp^{SiEt3}{}_3Mo_3S_4$ (**Mo_3**).

Introduction

Transition metal-sulfur clusters, which consist of multiple metal centers and sulfur atoms, are known to show variable redox behaviors attributed to their core structures, supporting ligands, and metal compositions.[1-5] Various metalloproteins thus employ the clusters as cofactors to realize a wide range of physiological roles such as electron transfer, molecular sensing, and catalytic material conversions.[6-10] In one example, mammalian aconitase (also known as iron regulatory protein 1) employs redox-and cellular Fe supply-dependent interconversion between cubic [Fe_4S_4] cluster and triangular [Fe_3S_4] cluster toward maintaining iron homeostasis.[6]

The metal incorporation into [M_3S_4] clusters to generate [M_4S_4] cubic clusters has been demonstrated using synthetic compounds.[11-22] For instance, homo- and hetero-metallic [Mo_3S_4-M] cubes were prepared by reactions of [Mo_3S_4] clusters with transition metals.[23,24] Some of the synthesized cubic clusters are known to catalyze conversions of organic substrates such as

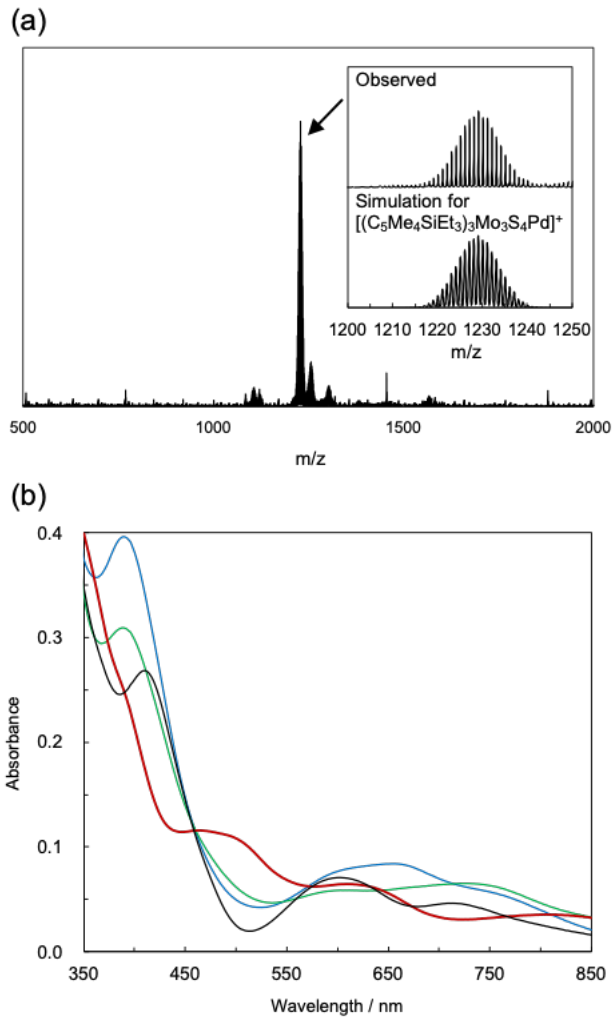

Figure 2. (a) An electro-spray ionization mass spectrum of **Mo_3Pd** in THF. (b) UV-vis absorption spectra of **Mo_3Pd** (50 μM, red line), **Mo_3^+** (50 μM, black line), **Mo_3** (50 μM, blue line), and **Mo_3^-** (50 μM, green line) in THF.

alkynoic acids,[23-29] aminoalkynes,[23-29] alkenes,[30,31] allylic alcohols,[32,33] and N_2H_4.[34]

We have also reported the synthesis of [Mo_3S_4M] cubes and their reactivity in a relevant manner.[35-37] The precursor of our [Mo_3S_4M] cubes is cyclopentadienyl ($C_5Me_4SiEt_3$, Cp^{SiEt3})-supported [Mo_3S_4] platform, of which three μ_2-sulfides can uptake and hold one M atom. Steric protection around M imposed by the substituents of Cp^{SiEt3} ligands is a unique feature of our platform and prevents undesirable decomposition or aggregation of the resultant [Mo_3S_4M] cubes. The [$Cp^{SiEt3}{}_3Mo_3S_4M$] was thus shown to be stable under reducing conditions, to capture small molecules at the M site, and to catalytically reduce the captured molecule.[38,39] In this sense, expanding the variety of introduced M atoms could enhance catalytic applications of our clusters as bio-inspired and homogeneous catalysts.

Herein, we report the synthesis, characterization, and catalytic activity of a Pd-incorporated [Mo_3S_4] cluster ([$Cp^{SiEt3}{}_3Mo_3S_4Pd$]Cl, **Mo_3Pd**). Electrochemical measurements of **Mo_3Pd** under a N_2 atmosphere displayed two reversible redox

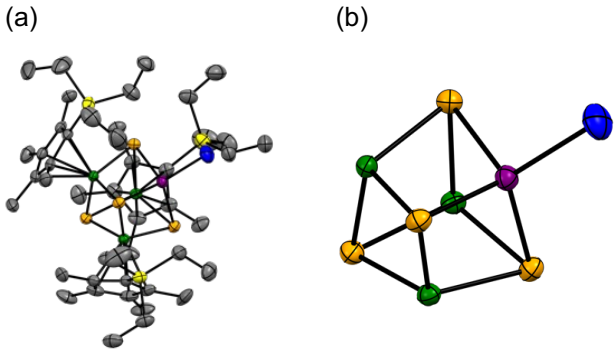

Figure 3. (a) Molecular and (b) core structures of **Mo_3Pd** with thermal ellipsoids set at 50% probability. Note that one of two independent molecules is shown, and that hydrogen atoms and solvent molecules are omitted for clarity. C = gray, Si = yellow, S = orange, Cl = blue, Mo = green, and Pd = purple.

events at potentials more negative than the rest potential, which implies the utility of the cluster for two-electron reduction of substrates. Cyclic voltammogram (CV) measured in the presence of **Mo_3Pd** and a proton source (trifluoroethanol, TFE) exhibited current enhancement from the absence of TFE, which is attributable to the catalytic hydrogen evolution reaction (HER). A controlled potential electrolysis experiment of a THF solution of **Mo_3Pd** in the presence of TFE resulted in the formation of H_2 as suggested by the cyclic voltammetry analysis. Computational analyses on the HER mechanism proposed that a Pd-hydride species generated via the reduction and protonation of **Mo_3Pd** is a key intermediate for HER.

Results and Discussion

A [Mo_3S_4Pd] cluster **Mo_3Pd** was synthesized by the Pd^{II} ion insertion reaction into an *in-situ* generated anionic [Mo_3S_4] cluster ([$Cp^{SiEt3}{}_3Mo_3S_4$]$^-$, **Mo_3^-**) (Figure 1). A neutral [Mo_3S_4] cluster ([$Cp^{SiEt3}{}_3Mo_3S_4$], **Mo_3**) prepared using the literature procedure[35,36] was reduced by potassium graphite (KC_8, 1.2 equiv. to **Mo_3**) in THF to give **Mo_3^-**. The suspension was then mixed with $PdCl_2$(cod) (cod = 1,5-cyclooctadiene), followed by heating to 70˚C and stirring for 17 h. After the removal of graphite by filtration, the filtrate was evaporated to dryness under vacuum. The obtained brown residue was extracted with a mixed solvent (THF/hexane = 1/2), and the extract was kept at −40˚C to give crystals of **Mo_3Pd** in 60% yield.

A ^{1}H NMR spectrum of **Mo_3Pd** was measured in C_6D_6 and displayed diamagnetic signals assigned to the protons of Cp^{SiEt3} ligands of **Mo_3Pd** (Figure S3). An electro-spray ionization mass spectrometry (ESI-MS) analysis of **Mo_3Pd** exhibited cationic signals at around *m/z* = 1229.1, of which isotope pattern fits well with signals calculated for [$Cp^{SiEt3}{}_3Mo_3S_4Pd$]$^+$, corresponding to [**Mo_3Pd** − Cl]$^+$ (Figure 2a).

A UV-vis spectrum of **Mo_3Pd** in THF showed peaks at 494, 463, and 622 nm. The Pd incorporation changed the absorption behaviors of [Mo_3S_4] clusters significantly, as shown in spectral comparisons of **Mo_3Pd** with **Mo_3**, **Mo_3^-**, and **Mo_3^+** (Figure 2b). This

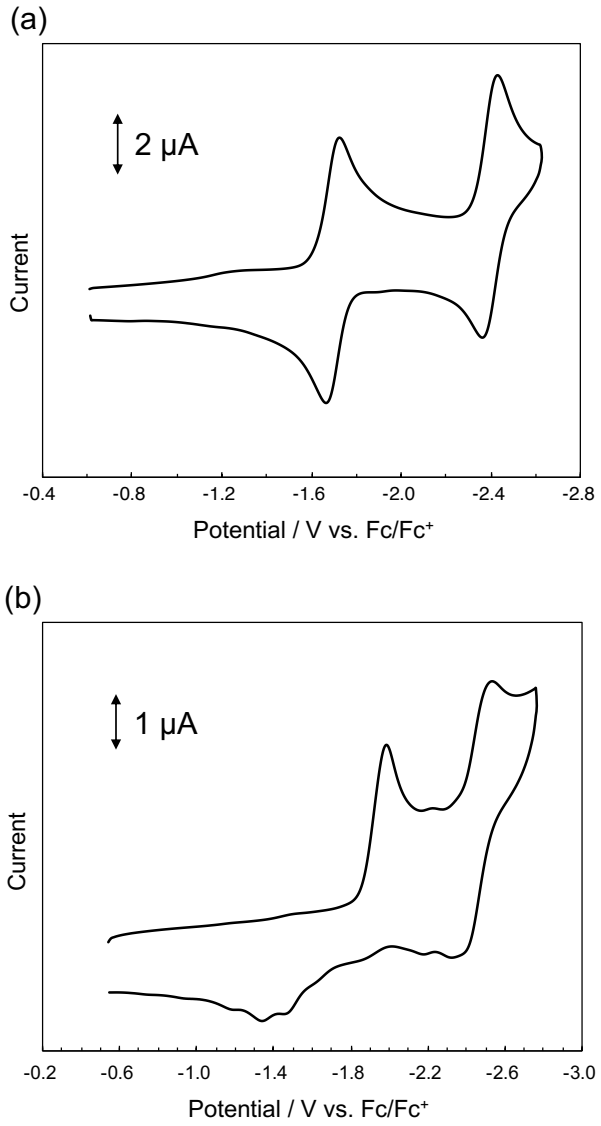

Figure 4. Cyclic voltammograms of Mo_3Pd (0.2 mM) in (a) MeCN and (b) THF with $TBAPF_6$ (0.1 M) under N_2 (scan rate: 100 mV/s). Working electrode: glassy carbon, auxiliary electrode: Pt wire, and reference electrode: Ag/AgCl.

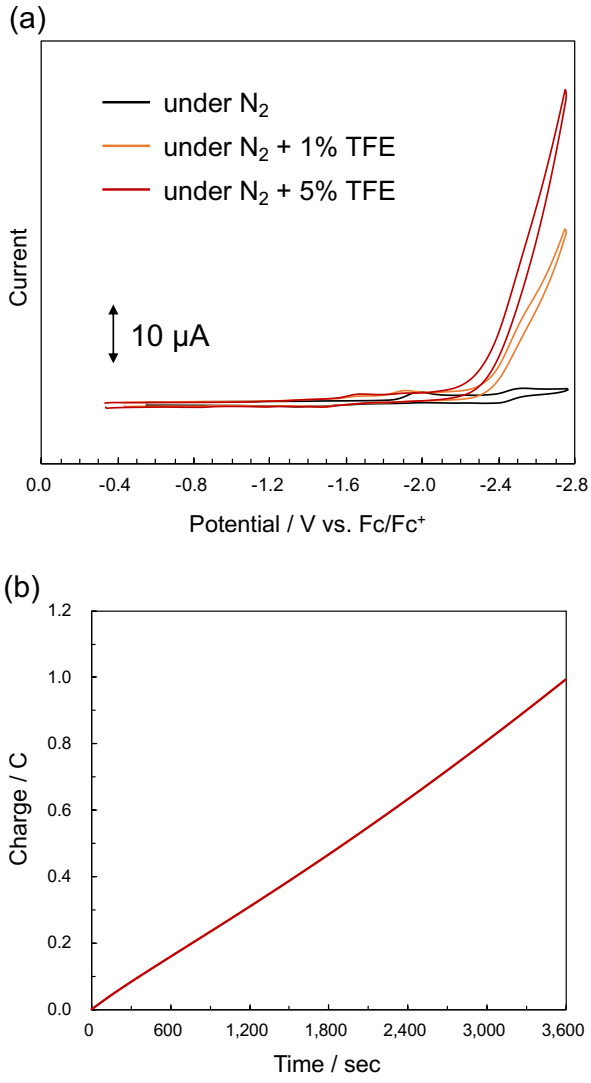

Figure 5. (a) Cyclic voltammograms of Mo_3Pd (0.2 mM) in THF with $TBAPF_6$ (0.1 M) in the absence of TFE (black line) and in the presence of 10% TFE (red line) under N_2 (scan rate: 10 mV/s). (b) Electrolysis data of Mo_3Pd (0.2 mM) in THF with $TBAPF_6$ (0.1 M) in the presence of 10% TFE under N_2 at a potential of −1.9 V vs. Ag/AgCl. Working electrode: glassy carbon, counter electrode: Pt wire, and reference electrode: Ag/AgCl.

feature prompted us to monitor the stability of **Mo_3Pd** to the air and moisture by using UV-vis spectroscopy, where the most plausible decomposition process, a Pd elimination from the $[Mo_3S_4Pd]$ core, is detectable by the diagnostic spectral differences between **Mo_3Pd** and **$Mo_3^{-/0/+}$**. However, the UV-vis spectrum of **Mo_3Pd** remained intact even after exposure to the air for up to 2 days (Figure S4). These results demonstrated that **Mo_3Pd** is unreactive to the air and moisture at least within a timescale of several days.

Figure 3 shows an ORTEP diagram of **Mo_3Pd** determined by single-crystal X-ray structural analysis (see also Figure S1 and Table S1, S2). **Mo_3Pd** crystallizes in the $P2_1/n$ space group, and the asymmetric unit of the cell contains two **Mo_3Pd** and four THF molecules. The Pd ion in **Mo_3Pd** is coordinated by Cl^- ion and three S ligands and in a slightly distorted tetrahedral geometry, while each Mo center has a three-legged piano stool geometry consisting of a Cp^{SiEt3} ligand and three S ligands.

About 20 examples of $[Mo_3S_4Pd]$ clusters have been synthesized and structurally characterized. Various ligands have been used for each metal center in $[Mo_3S_4Pd]$ clusters: for instance, PPh_3[40,41], Cl[42,43], and allyl[32] ligands on the Pd center and 1,4,7-triazacyclononane[25,42], cyclopentadienide derivatives[32,41], and Cl with coordinating solvents[43,45] on the Mo centers. To see the structural features of **Mo_3Pd**, we compared bond distances in **Mo_3Pd** with the reported clusters with a focus on the $[Mo_3S_4Pd]$ core. The averaged distances of Pd-Mo and Mo-Mo in **Mo_3Pd** (2.827(9) and 2.841(10) Å, respectively) are comparable to the known $[Mo_3S_4Pd]$ clusters (2.767(8)-3.04(8) Å for Pd-Mo and 2.744(10)-2.88(5) Å for Mo-Mo), suggesting that the core

Table 1. Summary of the results of the controlled potential electrolysis experiments.[a]

entry	catalyst	Charge / C	Amount of H_2 / μmol	FE[b][c] for H_2 / %
1	**Mo_3Pd**	0.99	1.24	24.2
2	**Mo_3**	0.65	0.58	17.3
3	-	0.61	0.13	4.2

[a] Electrolysis condition: catalyst (0.2 mM) in THF with $TBAPF_6$ (0.1 M) in the presence of TFE (5%, v/v) under N_2 at −1.9 V (vs. Ag/AgCl) for 1 hour. [b] FE = Faradaic efficiency. [c] The fate of the rest of the charge is not clear at this stage.

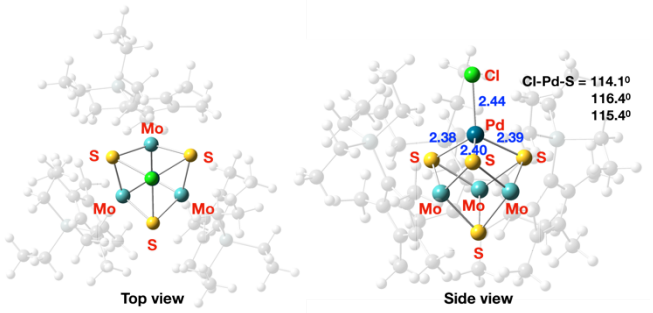

Figure 6. Molecular structure and selected bond distances (Å) and angles (˚) of the optimized *S* = 0 state of **Mo_3Pd**.

structure of **Mo_3Pd** has no obvious deviation from the known. It is also supported by the averaged bond distances of Pd-S and Mo-S in **Mo_3Pd** (2.372(8) and 2.321(7) Å, respectively), which displayed no significant difference to the reported structures. (2.356(2)-2.47(7) Å for Pd-S and 2.315(10)-2.36(2) Å for Mo-S). The core structures of $[Mo_3S_4Pd]$ clusters are not affected by the ligands on the metal centers or the oxidation states of metals (Table S2, S3).

We next performed electrochemical measurements of **Mo_3Pd** to examine redox properties. Cyclic voltammograms (CVs) were recorded under the following conditions: sample concentration, 0.2 mM; solvent, MeCN or THF; supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M). In the CVs of **Mo_3Pd** under a N_2 atmosphere in MeCN (Figure 4a, Table S4), the complex displayed two reversible reduction waves at −1.69 V and −2.39 V (vs. ferrocene/ferrocenium (Fc/Fc^+)). The peak currents corresponding to these redox potentials of **Mo_3Pd** have a linear relationship with the square root of the scan rates (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1 V/s) and follow the Randles-Sevcik equation, indicating that **Mo_3Pd** facilitates rapid electron transfer with the working electrode (Figure S7). These observations point to relatively stable one-and two-electron reduced states of **Mo_3Pd** (**Mo_3Pd^-** and **Mo_3Pd^{2-}**). In contrast, a CV of the cluster measured in THF showed two reduction waves, but the first redox wave, which occurs at the potential close to the resting potential of **Mo_3Pd**, became irreversible (Figure 4b). This irreversible process may arise from the ligand exchange of Cl^- to a solvent molecule triggered by the reduction of the $[Mo_3S_4Pd]$ core but not from the decomposition of the inorganic core, given the stability of **$Mo_3Pd^{-/2-}$** in MeCN solvent.

Based upon the observed and suggested stability of the $[Mo_3S_4Pd]$ core of **Mo_3Pd** against the reduction, the catalytic activity of **Mo_3Pd** in the hydrogen evolution reaction (HER: $2H^+ + 2e^- \rightarrow H_2$) was evaluated in relation to the reported HER catalysis by some $[Mo_3S_4]$ and $[Mo_3S_4Pd]$ clusters.[46-48] The electrochemical measurements of **Mo_3Pd** were performed in the presence of TFE as a proton source under a N_2 atmosphere. The CV measured in the presence of 1.0% (v/v) TFE exhibited an irreversible current enhancement, assignable as a catalytic current, at approximately E_{pc} = −2.2 V (Figure 5a, orange line). The intensity of the irreversible current further increased in the presence of 5.0% TFE (Figure 5a, red line). Notably, such current enhancement was not observed in the absence of **Mo_3Pd**, suggesting that **Mo_3Pd** works as a HER catalyst (Figure S8).

To gain insights into the catalytic activity, we carried out controlled potential electrolysis (CPE) under a N_2 atmosphere and using the following conditions: a 0.1 M $TBAPF_6$/THF solution containing 0.2 mM of **Mo_3Pd** in the presence of 5% (v/v) TFE. In CPE conducted at −1.9 V (vs. Ag/AgCl), the total amount of charge passed over a period of 60 min reached 0.99 C. The produced hydrogen gas was quantified by the headspace-gas analysis using gas chromatography, where 1.23 μmol of the H_2 formation was detected with a faradaic efficiency (FE) of 24.0% (Table 1, entry 1). On the other hand, in the absence of **Mo_3Pd**, only 0.13 μmol of H_2 was generated after the 60-min CPE experiment, indicating HER catalyzed by **Mo_3Pd** (Table 1, entry 2). It is noteworthy that the amount of charge input increased almost linearly during the electrolysis and no obvious catalyst degradation was observable (Figure 4b). UV-vis spectrum of **Mo_3Pd** in the presence of TFE remained intact over 1 hour, suggesting that **Mo_3Pd** has high durability for TFE (Figure S5). In addition, UV-vis absorption spectra of the reaction mixture measured before and after the CPE experiment were almost identical and differ from that of **Mo_3** (Figure S6), supporting the cluster's stability and nonparticipation of decomposed products of **Mo_3Pd** in the catalysis.

We also compared the catalytic activity of **Mo_3Pd** with **Mo_3** that has no Pd site. In the CPE experiment of the latter under similar conditions with **Mo_3Pd**, the total amount of transferred charge was 0.65 C with 0.58 μmol of the H_2 formation (17.1% FE) (Table 1, entry 3 and Figure S9). The comparison confirmed that the Pd incorporation into **Mo_3** enhances the catalytic activity for HER by approximately two times. It is proposed that μ_2-bridging S atoms of Mo_3S_4 cores can be protonated under reducing conditions and that the resultant S-H moiety reacts with a proton to generate hydrogen[49, 50]. While a similar reactivity is expected for **Mo_3**, the Pd incorporation to this cluster should suppress such HER pathway due to the low electron donating ability of μ_3-bridging S atoms. As Mo_3Pd should catalyze HER via the formation of Pd-H species as discussed below, the observed higher HER activity of **Mo_3Pd** than **Mo_3** is attributable to more hydride-like reactivity of the Pd-H species generated from **Mo_3Pd** than the S-H species derived from **Mo_3**.

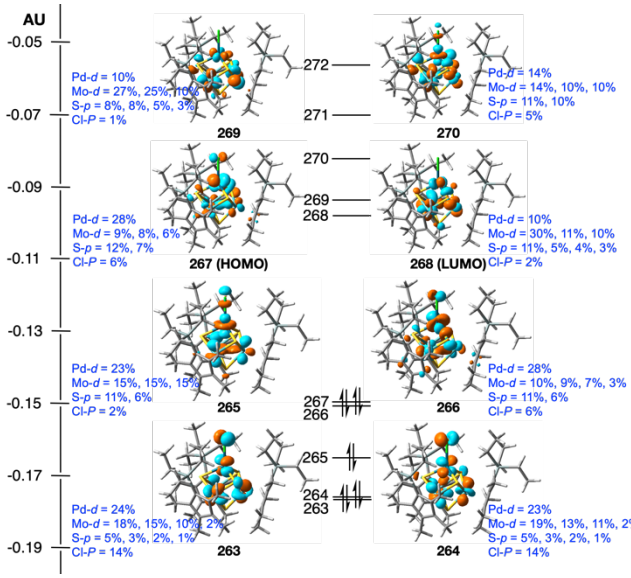

Figure 7. Kohn-Sharm frontier orbitals of the optimized ^{1}R structure and the Mulliken population analysis.

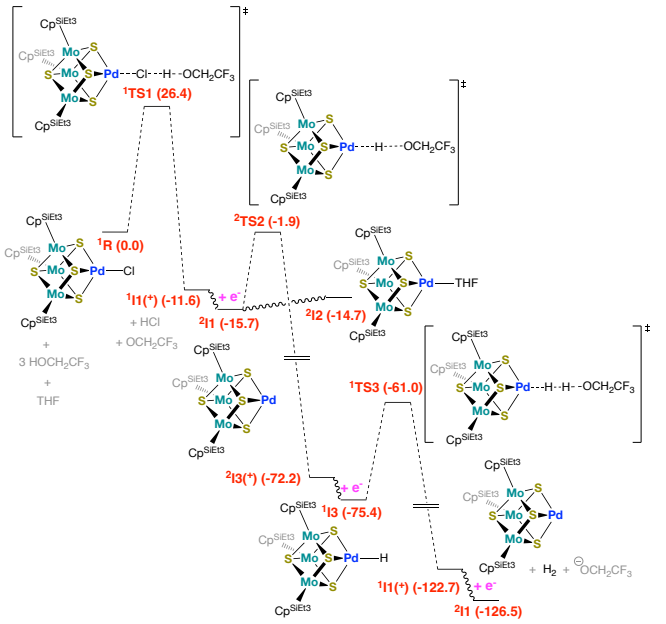

Figure 8. Computed free energy profile (kcal mol^{-1}) for the catalytic H_2 formation.

Computational studies

Starting from the X-ray structure, the *S* = 0, 1, and 2 states of **Mo$_3$Pd** complex (**R**) were optimized. The *S* = 0 state is the ground state (*i.e.*, ^{1}**R**), and *S* = 1 and *S* = 2 states are 18.4 and 38.4 kcal mol^{-1} above the ground state, respectively. The *S* = 0 ground state is in agreement with the diamagnetic nature of **Mo$_3$Pd** observed in the ^{1}H NMR measurement (Figure 6). The averaged Pd-Mo and Mo-Mo distances of the ground state optimized structure are 2.83 and 2.84 Å, which are consistent with the X-ray structure. Also, averaged bond distances of Pd-S and Mo-S are 2.39 and 2.34 Å show an excellent agreement with the X-ray structure. The computed Pd-Cl bond distance of 2.44 Å is slightly longer than the X-ray structure (2.42 Å). The Pd coordination sphere is symmetric and shows the T_d symmetry.

Selected Kohn-Sharm orbitals of the optimized **Mo$_3$Pd** (^{1}**R**) structure are shown in Figure 7. The computed HOMO-LUMO gap is 1.39 eV. In the frontier region, the Kohn-Sharm orbitals show a mixing of Pd-*d*, Mo-*d*, S-*p*, and Cl-*p* orbitals. The HOMO (**267**) is localized mainly on Pd with some partial delocalization on Mo an S (*i.e.* cube). Similarly, HOMO-1 (**266**), HOMO-2 (**265**), HOMO-3 (**264**), and HOMO-4 (**263**) localized mainly on Pd. On the other hand, the LUMO is delocalized mainly on Mo and S.

Starting from the *S* = 0 ground state of **Mo$_3$Pd** (^{1}**R**), mechanism for the H_2 formation was determined (Figure 8). In the presence of $HOCH_2CF_3$ (2,2,2,-trifluoroethanol, TFE), the removal of chloride on palladium gives rise to ^{1}**I1(+)** through a free energy barrier of 26.4 kcal mol^{-1}. ^{1}**I1(+)** is -11.6 kcal mol^{-1} stable compared to ^{1}**R**. During this step, HCl and $^{-}OCH_2CH_3$ are formed as the side products. Then, ^{1}**I1(+)** is reduced to form ^{2}**I1,** enabling $^{-}OCH_2CH_3$ to leave from the metal coordination sphere. ^{2}**I1** is stable than ^{1}**I1(+)** by 4.1 kcal mol^{-1}. The open-shell ^{2}**I1** state is the ground state of **I1**, where the computed spin densities, ρ(Pd) = 0.13 and ρ(Mo_3S_4) = 0.82, indicate that the unpaired electron is mainly stored in the Mo_3S_4 moiety with partial spin delocalization on Pd. The computed <S^2> value of ^{2}**I1**, 0.76, which is similar to the ideal value of 0.75, suggesting no spin contamination. As the next step, the vacant Pd coordination site of ^{2}**I1** can be filled by a solvent molecule or ^{2}**I1** can be reacted with TFE. In the former case, the resulting THF adduct (^{2}**I2**) is only 1.0 kcal mol^{-1} above ^{2}**I1**. In the latter case, the reaction between ^{2}**I2** and TFE has a barrier of 13.8 kcal mol^{-1}, giving rise to ^{2}**I3(+)**, which is 56.5 kcal mol^{-1} stable compared to ^{2}**I1**. Then, ^{2}**I3(+)** is reduced to ^{1}**I3**, allowing $^{-}OCH_2CH_3$ to leave from the metal coordination sphere. After that, the Pd-H intermediate ^{1}**I3** reacts with TFE, where the computed free energy barrier for the reaction is 14.4 kcal mol^{-1}, leading to H_2 and ^{1}**I1(+)**, and this process is exothermic by 47.3 kcal mol^{-1} Finally, the one-electron reduction of ^{1}**I1(+)** regenerates the catalytically active ^{2}**I1**.

According to the computed free energy profile, the generation of the active intermediate, ^{2}**I1**, has a significant free energy barrier. The subsequent reaction steps go through relatively small reaction barriers and two electron reduction processes, leading to the regeneration of the active intermediate, ^{2}**I1**, to continue the catalytic cycle.

Conclusion

In conclusion, we have developed a novel metal-sulfur cluster that consists of a Pd ion and Mo ions bridged by S ligands. (**Mo$_3$Pd**). **Mo$_3$Pd** was synthesized by the incorporation of a Pd ion into the Mo_3 cluster and was structurally characterized. The electrochemical measurements of **Mo$_3$Pd** suggested the presence of a relatively stable two-electron reduced state of the [Mo_3S_4Pd] core. The supposed catalytic current for HER was observed in the CV of **Mo$_3$Pd** measured in the presence of TFE as a proton source, which was further confirmed by the CPE experiment in the presence of TFE in 0.1 M $TBAPF_6$ / THF and following produced gas analyses. Whereas the HER activity was

observed for non-Pd-containing **Mo$_3$**, the Pd incorporation increased the activity by about two times, which suggests the hydrogen evolution at the Pd center. The theoretical simulations proposed the involvement of the Pd-hydride species as a key intermediate during the HER turnover. DFT calculations determined the mechanism of the H_2 formation. Moreover, the reduction of **Mo$_3$Pd** in the presence of $HOCH_2CF_3$ generates an open-shell intermediate (**^{2}I1**) that initiates the catalytic cycle. Then, the reaction with $HOCH_2CF_3$ and one-electron reduction yields a closed-shell Pd-H species **^{1}I3**. The hydride ligand of **^{1}I3** couples with $HOCH_2CF_3$ to produce H_2, and the one-electron reduction of the $[Mo_3S_4Pd]$ core regenerates the catalytically active **^{2}I1**.

Experimental Section

General Procedures

All reactions were carried out under an atmosphere of N_2 using either Schlenk-line or glovebox techniques. Tetrahydrofuran (THF), hexane, and acetonitrile (MeCN) were purified by passing over columns of activated alumina, and a supported copper catalyst supplied by Hansen & Co. Ltd. $[(C_5Me_4SiEt_3)_3Mo_3S_4]$ (**Mo$_3$**),[35,36] $PdCl_2$(cod) (cod = 1,5-cyclooctadiene),[51] and KC_8[52] were synthesized according to the reported procedure. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized from absolute THF. All other chemicals were purchased from standard commercial sources and used without further purification. Deuterated solvents were dried and vacuum-transferred before use. ^{1}H NMR spectra were recorded on Bruker AV400M. UV-vis spectra were measured on a JASCO V770 spectrometer. Elemental analysis was carried out on powder crystalline samples sealed in tin capsules under N_2, using a J-Science Micro Corder JM11.

Cyclic voltammetry was performed at room temperature on a BAS ALS-660A electrochemical analyzer. Each measurement was carried out using a one-compartment cell with a three-electrode configuration consisting of a glassy carbon disk (diameter 3 mm, BAS Inc.), platinum wire, and Ag/AgCl electrode as the working, auxiliary, and reference electrodes, respectively. The glassy carbon disc working electrode was polished using 0.05 μm alumina paste (BAS Inc.) and washed with purified H_2O. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple at 0 V. Controlled potential electrolysis (CPE) was performed in a gas-tight two-compartment electrochemical cell, where the first compartment held the carbon plate working electrode (2.25 cm^2 surface area) and Ag/AgCl reference electrode in 8.0 ml of 0.1 M $TBAPF_6$/THF with catalyst and proton source, while the second compartment held the Pt auxiliary electrode in 8.0 ml of 0.1 M $TBAPF_6$/THF containing ferrocene (6.7 mM) as a sacrificial electron donor. The two compartments were separated by an anion exchange membrane (Selemion DSV, AGC Engineering Co., Ltd.). The solution was purged vigorously with N_2 for 20 minutes before electrolysis. The electrolysis experiment was performed for 60 min under constant stirring. The amount of H_2 produced was quantified by analyzing the headspace with a Shimadzu GC-2014 with a TCD detector. Hydrogen gas separation was achieved on two Molecular Sieve 13X-S 60/80 columns (3.0 mm ID x 2.0 m length) held at 40˚C under an Ar flow at 25 mL/ min. Calibration curves were made by sampling known amounts of H_2.

Synthesis of $[(C_5Me_4SiEt_3)_3Mo_3S_4PdCl]$ (Mo$_3$Pd)

Mo$_3$ (336 mg, 0.300 mmol) was dissolved in 20 mL of THF. KC_8 (50 mg, 0.37 mmol) was added to the solution, followed by stirring at room temperature for 5 minutes. $PdCl_2$(cod) (87 mg, 0.31 mmol) was added to the mixture, and the reaction mixture was heated and stirred at 70˚C overnight, affording a brown suspension. The insoluble materials were separated by filtration, and THF was removed under reduced pressure to give a brown solid. The brown solid was dissolved in THF/hexane, and the saturated solution was stored at -40 ˚C to give the brown crystals of $[(C_5Me_4SiEt_3)_3Mo_3S_4PdCl]$ (**Mo$_3$Pd**). The crystals were collected by filtration and dried under reduced pressure (243 mg, 0.180 mmol, 60% yield based on **Mo$_3$**). ^{1}H NMR (400 MHz, C_6D_6): δ 2.01 (s, 18H), 1.50 (s, 18H), 1.13 (m, 45H) ppm. Anal. Calcd. for $C_{51}H_{93}ClMo_3O_{1.5}PdS_4Si_3$ (**Mo$_3$Pd**•1.5THF): C, 44.63%; H, 6.83%. Found: C, 44.35%; H, 6.85%.

X-ray Crystallographic Analysis

Single crystal X-ray diffraction data of **Mo$_3$Pd** were collected on a Rigaku RA-Micro 7 equipped with a PILATUS 200K detector that uses graphite-monochromated MoKα radiation (λ = 0.710690 Å) at –150˚C under a cold N_2 stream. Single crystals of the compound were coated with oil (Immersion Oil, Type B: code 1248, Cargille Laboratories, Inc.) and placed on Polyimide crystal mounts. The crystal quality and preliminary cell parameters were determined by eighteen data frames measured at 0.5˚ increments of ω. Afterward, the full data sets were also measured at 0.5˚ intervals of ω. Each frame of data was integrated using the CrystalClear program package, followed by the data correction for absorption using an REQAB program. All structures were solved by the direct methods with refinement by full-matrix least squares. DFIX and SIMU were applied to THF solvent molecules. ISOR and DFIX were applied the disordered structural unit. Anisotropic refinement was applied to all non-hydrogen including crystal solvents. Hydrogen atoms were placed using a riding model. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Deposition number CCDC 2263876 for **Mo$_3$Pd** contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Computational Methods

Structure optimizations were performed using density functional theory (DFT) as implemented in the Gaussian16 program.[53] The TPSSTPSS functional,[54] employing Grimme's dispersion and Becke-Johnson damping,[55] was used. The SDD[56] basis sets and the associated effective core potentials were applied for Pd and Mo, the def2-TZVP basis sets were used for S, Si, and N, and the def2-SVP basis sets were used for C and H.[57] The polarizable continuum model (PCM)[58] was applied as the implicit solvation model, where tetrahydrofuran (ε =7.4257) was used as the

solvent. Vibrational frequency calculations were performed at 298.15 K and 1 atm to confirm the nature of the local minima (i.e., no imaginary frequency), and to calculate zero-point energies. The energy differences of one-electron reduction processes were estimated from calculated redox potentials of those reactions. The corresponding redox potentials were calculated using $\Delta G_{(sol)}/(-nF)$, where $\Delta G_{(sol)}$ is the Gibbs free energy change due to the reaction, n is the number of electrons involved, and F is the Faraday constant.

Supporting Information

Supporting Information is available on …..

Acknowledgements

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Keywords: Metal-sulfur cluster• palladium• molybdenum• hydrogen evolution reaction

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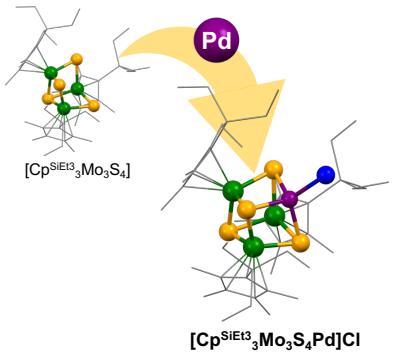

A cubic metal-sulfur cluster, $[Cp^{SiEt3}{}_3Mo_3S_4Pd]Cl$ (**Mo_3Pd**, Cp^{SiEt3} = $C_5Me_4SiEt_3$), was synthesized by the incorporation of the Pd ion into a Mo_3S_4 cluster $[Cp^{SiEt3}{}_3Mo_3S_4]$ (**Mo_3**). **Mo_3Pd** promoted a two-electron reduction process and was utilized for hydrogen evolution reaction (HER). The mechanism of HER was determined by density functional theory (DFT) calculations.

Laboratory Twitter account: https://twitter.com/omkuicr

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1. Single crystal X-ray structure determination

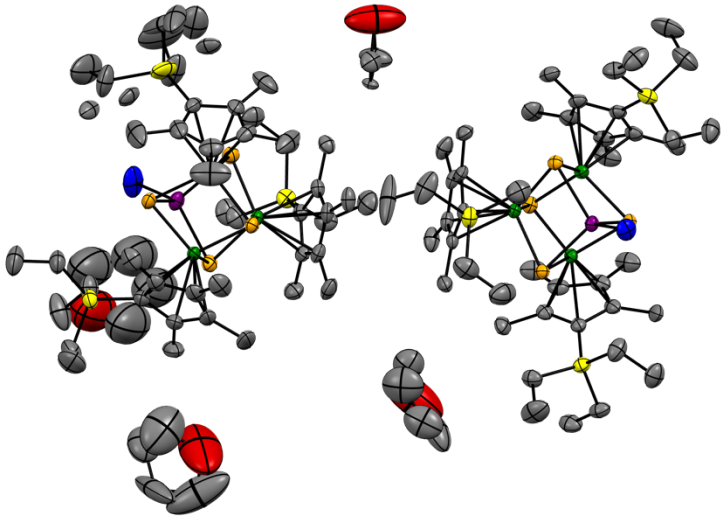

Figure S1. ORTEP drawing of the crystal structure of 2[$(C_5Me_4SiEt_3)_3Mo_3S_4PdCl$]·4THF. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% level. Color legend: C, grey; Si, yellow; Cl, blue; S, orange; O, red; Mo, green; and Pd, purple.

Table S1. Summary of crystallographic data for 2[$(C_5Me_4SiEt_3)_3Mo_3S_4PdCl$]·4THF.

Formula	$2[C_{45}H_{81}ClMo_3Pd_1S_4Si_3]\bullet4(C_4H_8O)$
Fw	12310.6
Crystal system	monoclinic
Space group	*P* 2_1/n
a, Å	22.488(2)
b, Å	22.2370(15)
c, Å	25.084(2)
β, °	101.062(2)
V, Å ^{3}	12310.6(17)
Z	4
F (000)	5808
d_{calc}, g/cm^3	1.520
T, K	123
R_1	0.0383
wR_2	0.1238
GOF	1.092

Table S2. Selected bond lengths of 2[$(C_5Me_4SiEt_3)_3Mo_3S_4PdCl$]·4THF.

	bond	length / Å
Mo-S	Mo1-S2	2.3256(9)
	Mo1-S3	2.3294(9)
	Mo1-S4	2.321(1)
	Mo2-S1	2.3181(9)
	Mo2-S3	2.318(9)
	Mo2-S4	2.3267(9)
	Mo3-S1	2.3184(9)
	Mo3-S2	2.3252(9)
	Mo3-S4	2.32581)
	Mo4-S5	2.304(1)
	Mo4-S7	2.3304(9)
	Mo4-S8	2.326(1)
	Mo5-S5	2.306(1)
	Mo5-S6	2.3183(9)
	Mo5-S8	2.325(1)
	Mo6-S6	2.322(1)
	Mo6-S7	2.327(1)
	Mo6-S8	2.319(9)
average		**2,321(7)**

	bond	length / Å
Pd-S	Pd1-S1	2.3771(9)
	Pd1-S2	2.3768(9)
	Pd1-S3	2.3649(9)
	Pd2-S5	2.384(1)
	Pd2-S6	2.362(1)
	Pd2-S7	2.37(1)
average		**2.372(8)**

	bond	length / Å
Pd-Mo	Pd1-Mo1	2.8264(7)
	Pd1-Mo2	2.8269(7)
	Pd1-Mo3	2.8246(7)
	Pd2-Mo4	2.8255(7)
	Pd2-Mo5	2.8427(7)
	Pd2-Mo6	2.813(7)
average		**2.827(9)**

	bond	length / Å
Mo-Mo	Mo1-Mo2	2.8397(7)
	Mo1-Mo3	2.8515(6)
	Mo2-Mo3	2.8439(6)
	Mo4-Mo5	2.8243(7)
	Mo4-Mo6	2.8542(6)
	Mo5-Mo6	2.8324(6)
average		**2.841(10)**

Table S3. Selected bond lengths of **Mo_3Pd** and the known [Mo_3S_4Pd] clusters.

reference	oxidation state	ligand on Pd	ligand on Mo	average bond length / Å			
				Pd-S	Mo-S	Pd-Mo	Mo-Mo
This work	**$[Mo_3S_4Pd]^{4+}$**	**Cl**	**Cp^{SiEt3}**	**2.372(8)**	**2.321(7)**	**2.827(9)**	**2.841(10)**
59	$[Mo_3S_4Pd]^{6+}$	h_3-allyl	Cp*	2.47(7)	2.323(8)	3.04(8)	2.835(13)
60	$[Mo_3S_4Pd]^{5+}$	$CRuCl_2(Pcy)_3$	methyl-Cp	2.393(10)	2.33(2)	2.89(2)	2.83(3)
61	$[Mo_3S_4Pd]^{5+}$	PPh_3	oxalate, H_2O	2.362(2)	2.332(1)	2.8184(6)	2.755(1)
62	$[Mo_3S_4Pd]^{4+}$	Maleic anhydride	Cp*	2.42(5)	2.315(10)	2.92(2)	2.838(8)
63	$[Mo_3S_4Pd]^{4+}$	alkene	Cp*	2.41(3)	2.320(7)	2.90(3)	2.844(8)
63	$[Mo_3S_4Pd]^{4+}$	PPh_3	Cp*	2.395(4)	2.328(3)	2.899(4)	2.88(5)
59	$[Mo_3S_4Pd]^{4+}$	π-allyl-Ph	Cp*	2.45(8)	2.322(7)	2.98(4)	2.84(2)
64	$[Mo_3S_4Pd]^{4+}$	PPh_3	methyl-Cp	2.385(4)	2.326(9)	2.866(8)	2.837(4)
65	$[Mo_3S_4Pd]^{4+}$	PPh_3	Cl, H_2O	2.47(8)	2.326(8)	2.807(10)	2.745(2)
66	$[Mo_3S_4Pd]^{4+}$	Cl	Cl, H_2O	2.367(6)	2.332(8)	2.767(8)	2.763(2)
67	$[Mo_3S_4Pd]^{4+}$	$P(OH)_3$	Cl, H_2O	2.356(2)	2.333(10)	2.828(1)	2.760(1)
67	$[Mo_3S_4Pd]^{4+}$	$As(OH)_3$	Cl, H_2O	2.360(3)	2.328(6)	2.797(1)	2.762(1)
68	$[Mo_3S_4Pd]^{4+}$	$SbPh_3$	Cl, H_2O	2.363(6)	2.337(14)	2.85(3)	2.800(1)
69	$[Mo_3S_4Pd]^{4+}$	Cl	tacn	2.366(9)	2.352(13)	2.793(4)	2.820(4)
69	$[Mo_3S_4Pd]^{4+}$	*cis*-butene-1,4-diol	tacn	2.361(5)	2.341(12)	2.825(8)	2.799(8)
70	$[Mo_3S_4Pd]^{4+}$	Cl	tris(hydrotris(pyrazolyl)ethanol)	2.3807(5)	2.36(2)	2.7797(5)	2.8193(2)
71	$[Mo_3S_4Pd]^{4+}$	PPh_3	tris(tiourea)borate	2.39(3)	2.34(3)	2.85(2)	2.78(2)
72	$[Mo_3S_4Pd]^{4+}$	thiourea	5,5'-^{t}Bu$_2$bpy, Cl	2.375(5)	2.342(14)	2.797(5)	2.81(2)
69	$[Mo_3S_4Pd]^{4+}$	H_2O	(dimer)	2.39(7)	2.342(7)	2.80(3)	2.744(10)
73	$[Mo_3S_4Pd]^{3+}$	CO	tacn	2.343(12)	2.329(7)	2.788(6)	2.759(2)

2. ^{1}H NMR measurements

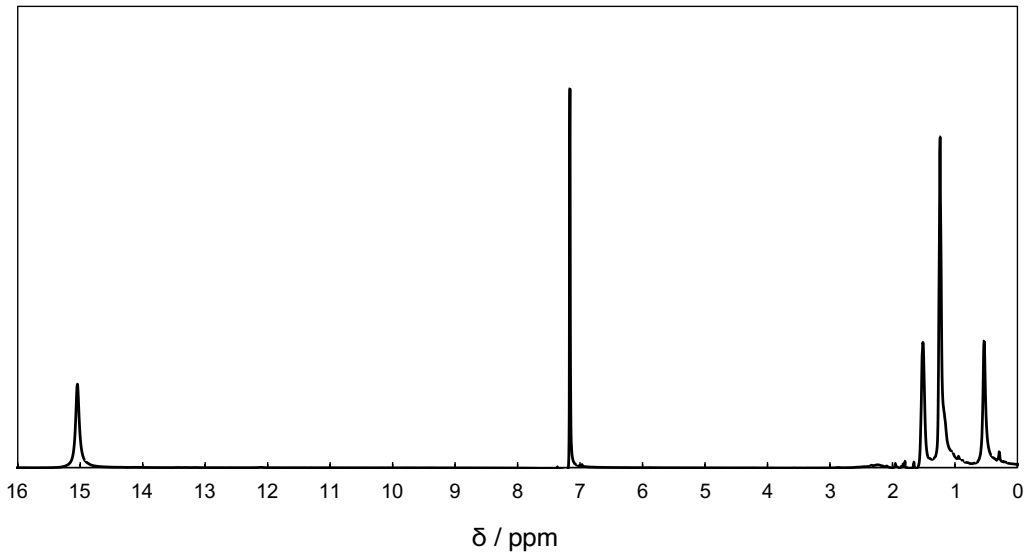

Figure S2. ^{1}H NMR spectrum of **Mo$_3$** (400 MHz, C_6D_6).

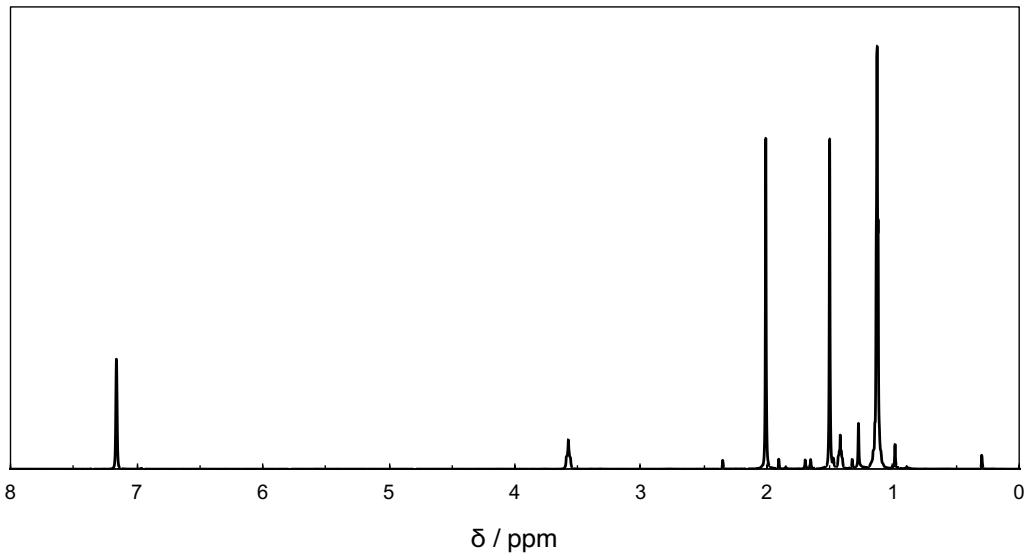

Figure S3. ^{1}H NMR spectrum of **Mo$_3$Pd** (400 MHz, C_6D_6).

3. UV-vis absorption spectra

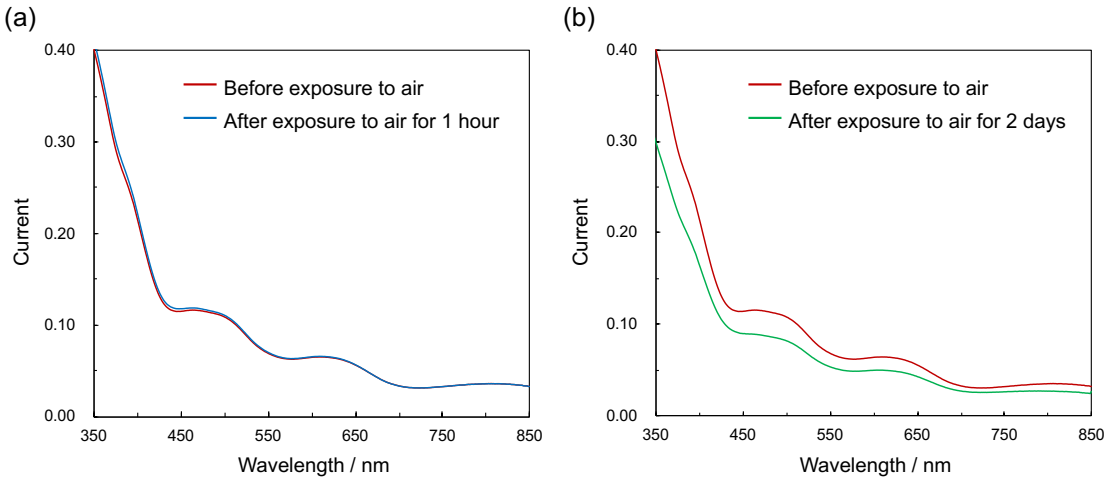

Figure S4. UV-vis absorption spectra of **Mo_3Pd** (50 μM, red line) in THF before and after the exposure to air for (a) 1 hour and (b) 2 days.

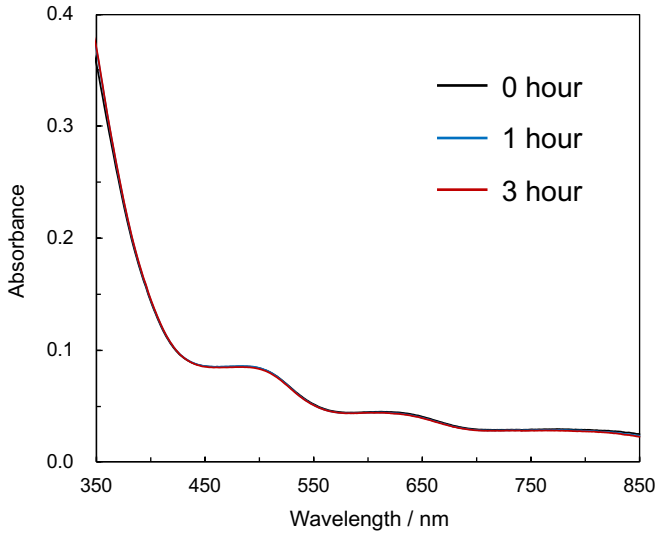

Figure S5. UV-vis absorption spectra of THF solution of **Mo_3Pd** (50 μM) in the presence of TFE (5%, v/v) for 0 hour (black line), 1 hour (blue line), and 3 hours (red line) later under N_2.

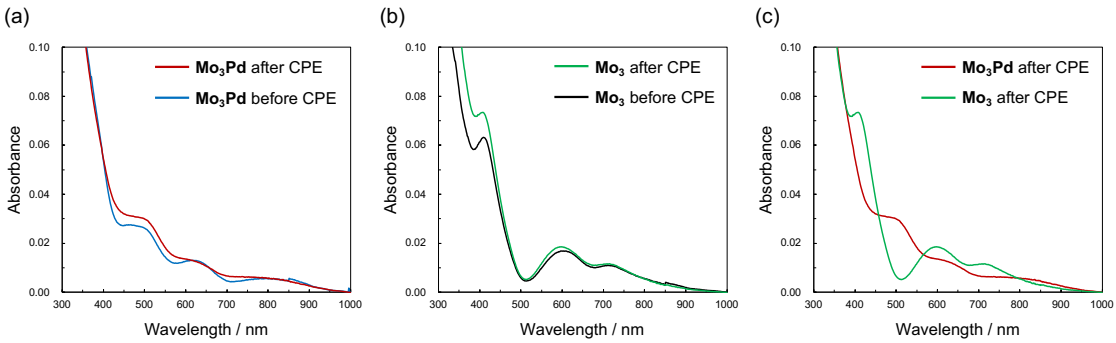

Figure S6. (a) UV-vis absorption spectra of **Mo$_3$Pd** before (blue line) and after (red line) the controlled potential electrolysis (CPE). (b) UV-vis absorption spectra of **Mo$_3$** before (black line) and after (green line) CPE. (c) UV-vis absorption spectra of **Mo$_3$Pd** (red line) and **Mo$_3$** (green line) after CPE. The CPE experiments were performed in THF with 0.1 M $TBAPF_6$ in the presence of TFE (5%, v/v) under N_2 at −1.9 V vs. Ag/AgCl for 1 hour. Noted that the solution was 15 times diluted by 0.1 M $TBAPF_6$/THF before the measurements.

4. Electrochemical measurements

Table S4. Redox potentials ($E_{1/2}$/V vs. Fc/Fc^+) of **Mo_3Pd** (0.2 mM) in an acetonitrile solution containing 0.1 M $TBAPF_6$.

	$E_{1/2}$ / V vs. Fc/Fc^+	
	1st wave	2nd wave
Mo_3Pd	-1.69	-2.39

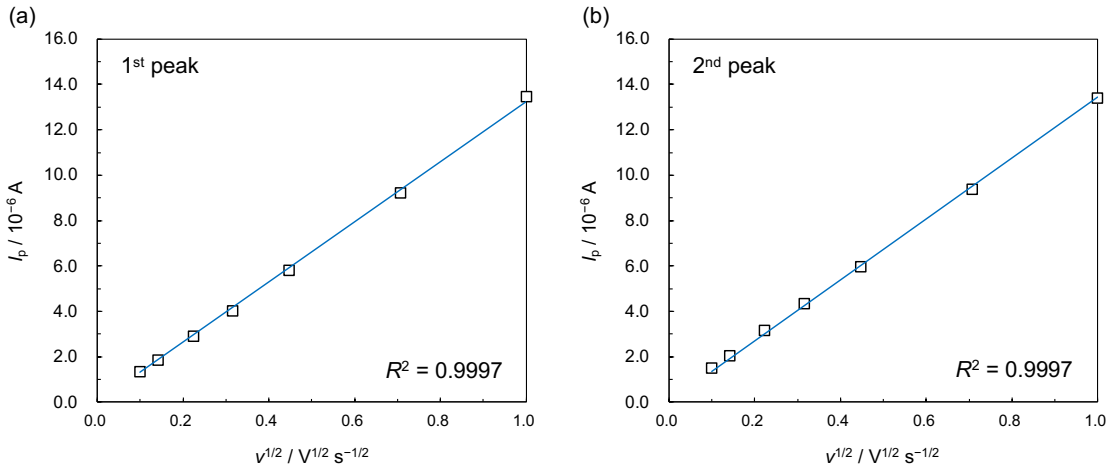

Figure S7. Variation of the peak current of **Mo_3Pd** (0.2 mM) in 0.1 M $TBAPF_6$/MeCN (a) at the first redox wave and (b) at the second redox wave.

*The Randles-Sevcik equation is shown below.

$$I_p = 0.4463nFAC_{cat}\sqrt{\frac{nFv}{RT}}\sqrt{D_{cat}}$$

where n is the number of electrons (n = 1), F is the Faradaic constant (96485 C mol^{-1}), A is the electrode surface area (0.071 cm^2), C_{cat} is the concentration of the catalyst (mol cm^{-3}), R is the gas constant (8.31 J K^{-1} mol^{-1}), v is the scan rate (V s^{-1}), D_{cat} is the diffusion coefficient of the catalyst (cm^2 s^{-1}), and T is the temperature (298.15 K).

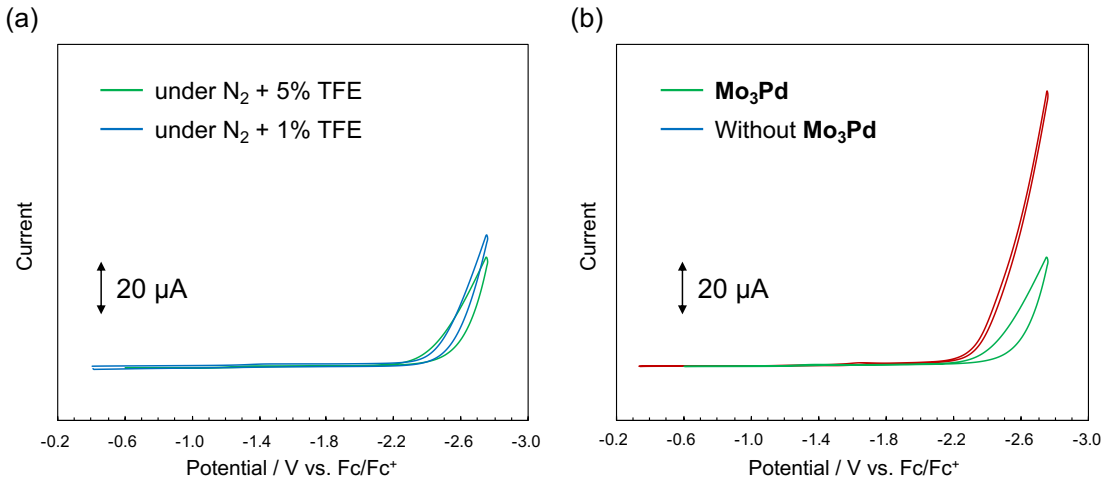

Figure S8. (a) CVs of 0.1 M $TBAPF_6$/THF in the presence of TFE. (b) CVs of **Mo_3Pd** (0.2 mM, red line) and blank (in the absence of **Mo_3Pd**, green line) in THF with $TBAPF_6$ (0.1 M) in the presence of 5% TFE under N_2 (scan rate: 10 mV/s). Electrodes: Working electrode, glassy carbon; counter electrode, Pt wire; and reference electrode, Ag/AgCl.

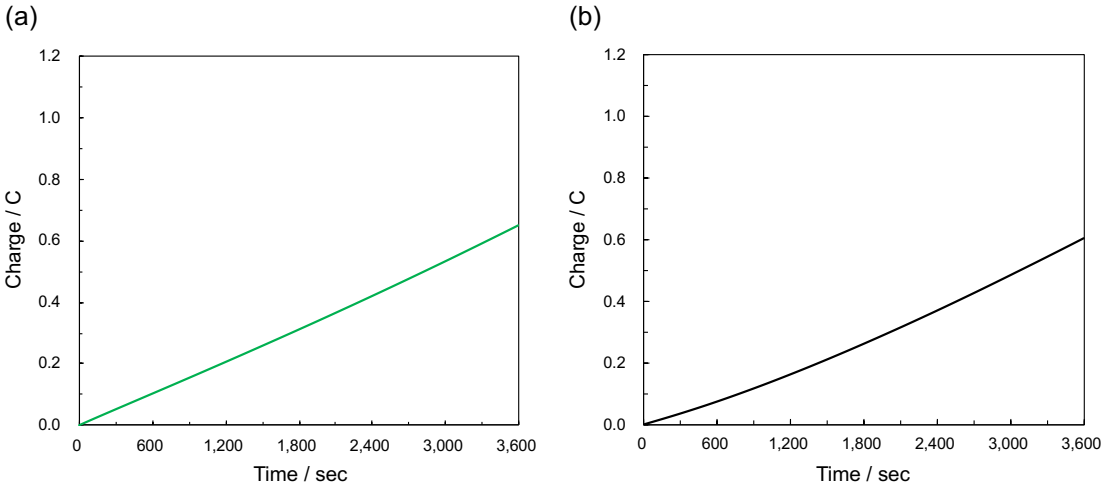

Figure S9. (a) Electrolysis data of Mo_3 (0.2 mM) in THF with $TBAPF_6$ (0.1 M) in the presence of 5% TFE under N_2 at a potential of −1.9 V vs. Ag/AgCl. (b) Electrolysis data of blank experiment in THF with $TBAPF_6$ (0.1 M) in the presence of 5% TFE under N_2 at a potential of −1.9 V vs. Ag/AgCl. Electrodes: Working electrode, glassy carbon; counter electrode, Pt wire; and reference electrode, Ag/AgCl.

5. Cartesian coordinates of the optimized structures (Å) and their energies (Sum of electronic and thermal Free Energies, AU).

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