

Synthesis of Cubic [Mo₃S₄M] (M = Rh, Ir) Clusters for Borylation of C–H Bonds in Aromatic Compounds

Hitoshi Izu, Sayaka Shimoyama, Kazuki Tanifuji, and Yasuhiro Ohki*

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

ABSTRACT: The incorporation of Rh or Ir into the [Mo₃S₄] platforms of [Cp^{XL}₃Mo₃S₄] or [Cp^{*}₃Mo₃S₄] (Cp^{XL} = C₅Me₄SiEt₃, Cp^{*} = C₅Me₅) led to the formation of cubic [Mo₃S₄M] clusters, [Cp^{XL}₃Mo₃S₄Rh(cod)] (**1**), [Cp^{XL}₃Mo₃S₄Ir(coe)] (**2**), [Cp^{*}₃Mo₃S₄Rh(coe)] (**3**), and [Cp^{*}₃Mo₃S₄Ir(coe)] (**4**) (cod = 1,5-cyclooctadiene, coe = cyclooctene). These clusters were characterized spectroscopically and crystallographically. They catalyzed the C–H borylation of aromatic compounds (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene) in the presence of HBpin (4,4,5,5-Tetramethyl-1,3,2-dioxaborolane), yielding the corresponding borylated products. Among these, cluster **3** exhibited the highest catalytic activity, while treatment of cluster **2** with excess HBpin generated an MS-detectable potential intermediate, [Cp^{XL}₃Mo₃S₄Ir(Bpin)]⁺. Despite the high affinity of Lewis acidic boron toward sulfur, the robust [Mo₃S₄M] (M = Rh, Ir) cubes protected adequately by Cp ligands have proven effective in borylation chemistry.

INTRODUCTION

Transition-metal–sulfur clusters are ubiquitous enzymatic cofactors that play diverse roles in organisms, ranging from simple electron transfers to complex organic transformations. With unique metal compositions and core structures, several enzymatic clusters are known to convert even inert molecules: a Mo–Fe–S–C cluster of nitrogenase ([*(R*-homocitrate)-MoFe₇S₉C], FeMoco) transforms N₂ into NH₃,^{1–3} and a Ni–Fe–S cluster of CO-dehydrogenase ([NiFe₄S₄], C-cluster) reduces CO₂ to CO.⁴

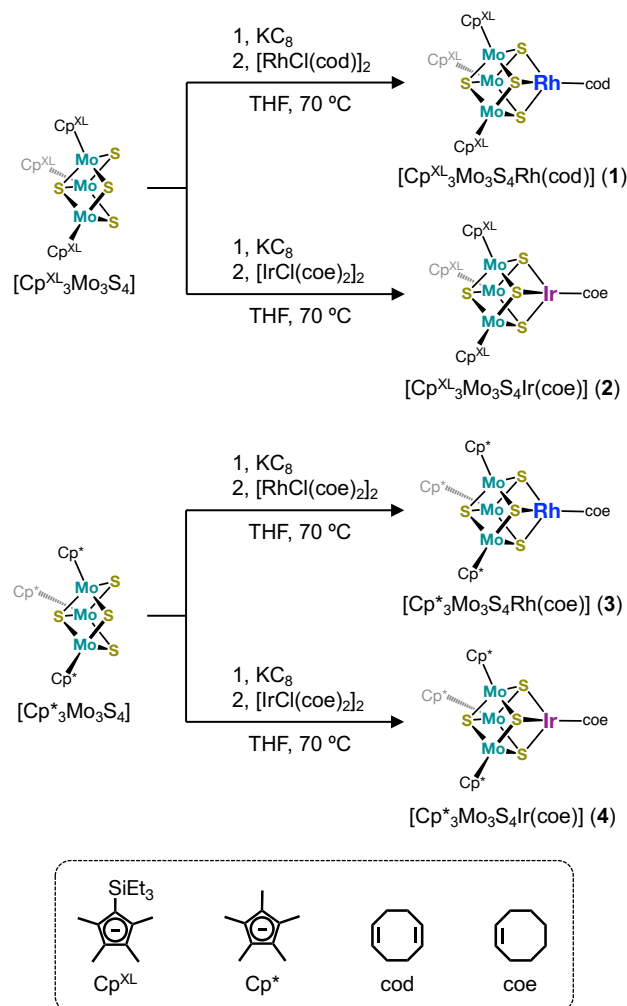
Synthetic metal–sulfur clusters have gained much attention as counterparts of enzymatic cofactors for molecular transformations. Cubic [Mo₃S₄M] clusters (M = transition metals) have been developed as a class of robust and modifiable synthetic clusters^{5–7} due to their stable inorganic core and reactivity at the M site typically limited and controlled by spectator ligands on the Mo atoms.^{8–16} Target substrates of these catalysts include alkynoic acids,^{17–23} aminoalkynes,^{17–23} alkenes,^{24,25} allylic alcohols,^{26,27} and N₂H₄.²⁸ More recently, we have discovered that the [Mo₃S₄M] clusters with bulky cyclopentadienyl ligands on the Mo atoms capture small molecules at the M site,^{29,30} promote H₂ evolution,³¹ and even catalytically reduce N₂ to N(SiMe₃)₃.^{32,33} As these reactivities highly correlate with the reaction site metals and the ligands on the Mo atoms, it is possible for us to develop novel reactivities of the synthetic clusters by expanding this approach. In this context, we are particularly intrigued by the C–H borylation of hydrocarbons as the target reaction, as it is a promising methodology to access various organic compounds from simple hydrocarbon feedstocks.^{34–36} Previous studies proved the effectiveness of Rh and Ir centers for the borylation reactions.^{37–42} For example, the groups of Mindiola and Sanford reported successful Ir or Rh catalysts active for the C–H borylation of methane.^{43,44}

Hartwig and co-workers reported Ir catalysts to activate alkyl C–H bonds.⁴⁵ In addition, Kuninobu, Kanai, and co-workers reported a regioselective C–H borylation of aromatic compounds by using an Ir catalyst,⁴⁶ while Asako, Ilies, and co-workers demonstrated akin regioselective borylation reactions of aromatic compounds induced by remote steric control⁴⁷ and C–H... π interactions between substrates and a ligand.⁴⁸ These precedents indicate substantial reactivity of Rh and Ir centers toward C–H borylation. We report herein the syntheses, characterizations, and catalytic evaluations of Rh- or Ir-incorporated [Mo₃S₄M] clusters [Cp^{XL}₃Mo₃S₄Rh(cod)] (**1**), [Cp^{XL}₃Mo₃S₄Ir(coe)] (**2**), [Cp^{*}₃Mo₃S₄Rh(coe)] (**3**), and [Cp^{*}₃Mo₃S₄Ir(coe)] (**4**) (Cp^{XL} = C₅Me₄SiEt₃, Cp^{*} = C₅Me₅SiEt₃, cod = 1,5-cyclooctadiene, coe = cyclooctene). The cubic [Mo₃S₄M] framework provides a highly stable inorganic core as mentioned, and the strong Mo–Cp^R interactions (Cp^R = Cp^{XL} and Cp^{*}) enhance the stability.^{31–33} Moreover, the different substituents of the Cp^R ligands would switch their reactivity to substrates.^{32,33} Our investigations into C–H borylation of aromatic compounds (benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene) in the presence of **1–4** and HBpin (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) revealed the catalytic activity and the dependency on the M centers. We also successfully observed a potential intermediate, [Cp^{XL}₃Mo₃S₄Ir(Bpin)]⁺, by treating cluster **2** with excess HBpin, suggesting the maintained [Mo₃S₄M] core during catalytic turnover. To our knowledge, this study represents the first example of catalytic C–H borylation by metal–sulfur clusters.

RESULTS AND DISCUSSION

The cubic [Mo₃S₄Rh] clusters with bulky Cp^{XL} ligands (**1**) or Cp^{*} ligands (**3**) on Mo atoms were synthesized by the reaction of in situ-generated anionic [Mo₃S₄] clusters

Scheme 1. Synthesis of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (1**), $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**), $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Rh}(\text{coe})]$ (**3**), and $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**4**).**



$[\text{Cp}^{\text{R}}_3\text{Mo}_3\text{S}_4]^-$; $\text{Cp}^{\text{R}} = \text{Cp}^{\text{XL}}, \text{Cp}^*$)^{15,16} with $[\text{RhCl}(\text{cod})]_2$ or $[\text{RhCl}(\text{coe})_2]_2$ at 70 °C (Scheme 1; see Experimental Section for synthetic details). Clusters **1** and **3** were obtained as crystals in 39 and 31% yields, respectively. The corresponding metal incorporation using $[\text{IrCl}(\text{coe})_2]_2$ led to the formation of cubic $[\text{Mo}_3\text{S}_4\text{Ir}]$ clusters with Cp^{XL} (**2**) or Cp^* ligands (**4**) on Mo atoms in 40 and 39% yields.

Clusters **1–4** were characterized by ^1H NMR and UV–vis spectroscopy and elemental analysis as described in the Experimental Section. The ^1H NMR spectra of **1–4** in C_6D_6 displayed sharp signals attributed to the protons of methyl and triethylsilyl groups of Cp^{R} ligands in the range from 1.0 to 2.2 ppm (Figures S1–S4), indicating a diamagnetic ground state of the clusters. In the ^1H NMR spectrum of **1**, a few sets of signals attributed to the methyl groups in Cp^{XL} ligands were observed, whereas an electrospray ionization (ESI) mass spectrum of **1** displayed signals assignable to $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}-(\text{cod})]^+$ (an in situ-oxidized form of **1**, $m/z = 1334.2$) and its fragments (Figure S9). These results suggest the isomerization of the cod ligand in solution, generating several cluster species with cod isomers.

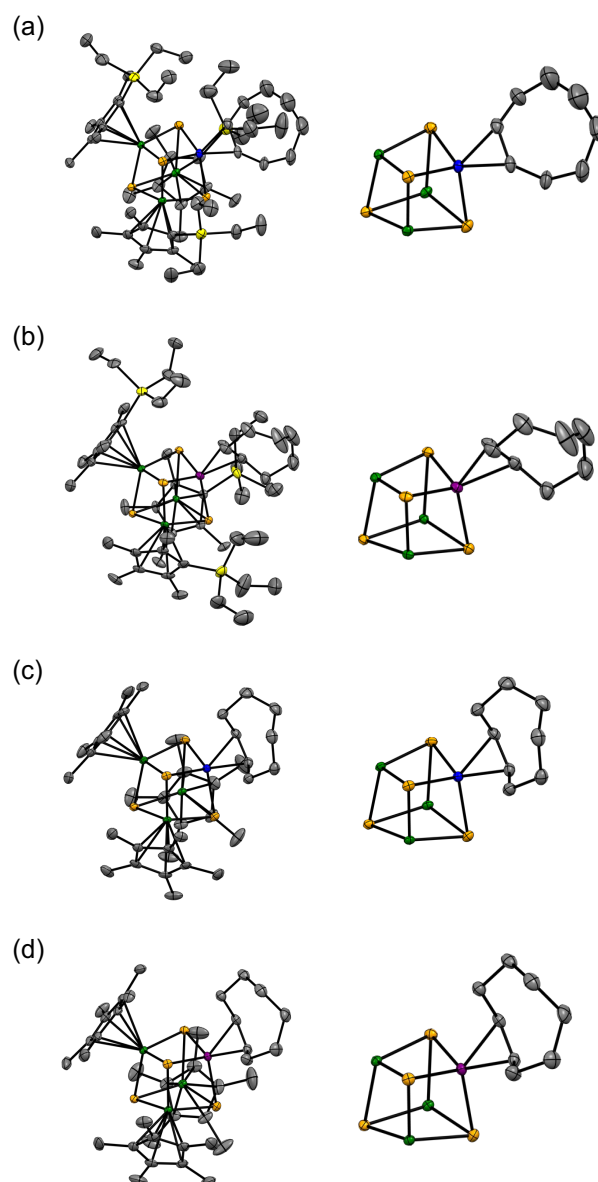


Figure 1. Molecular (left) and core (right) structures of **1** (a), **2** (b), **3** (c), and **4** (d) with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. C = gray, Si = yellow, S = orange, Mo = green, Rh = blue, and Ir = purple.

UV–vis spectra were measured for **1–4** in THF. All spectra showed broad absorption in the visible region and peaks at the following wavelengths: 482 and 638 nm for **1** (Figure S6a); 460, 588, and 785 nm for **2** (Figure S6b); 435, 484, and 628 nm for **3** (Figure S6c); and 449, 607, and 785 nm for **4** (Figure S6d). The Rh or Ir incorporation changed the absorption properties of $[\text{Cp}^{\text{R}}_3\text{Mo}_3\text{S}_4]$ clusters significantly, as shown in spectral comparisons of the clusters with $[\text{Cp}^{\text{R}}_3\text{Mo}_3\text{S}_4]$, $[\text{Cp}^{\text{R}}_3\text{Mo}_3\text{S}_4]^-$, and $[\text{Cp}^{\text{R}}_3\text{Mo}_3\text{S}_4]^+$ (Figures S7 and S8, Table S6).

Figure 1 shows the ORTEP diagrams of **1–4** determined by single-crystal X-ray structural analysis (see also Tables S1–S3). Each structure contains a single cluster in an asymmetric unit. The clusters having Cp^{XL} ligands (**1**, **2**)

Table 1. Selected and averaged distances (Å) of 1-4.

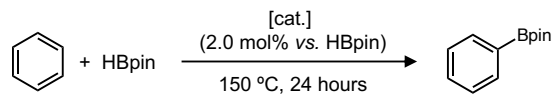
Cluster	Mo-M ^{a,b}	Mo-Mo ^a	M-S ^{a,b}	Mo-S ^a
1	2.84(2)	2.872(10)	2.319(11)	2.338(7)
2	2.84(3)	2.885(13)	2.310(13)	2.344(8)
3	2.83(2)	2.861(8)	2.31(2)	2.337(6)
4	2.84(3)	2.873(6)	2.31(2)	2.345(11)

(a) Averaged when multiple values were available. (b) M = Rh or Ir.

crystallize in the $P2_1/n$ space group, and the clusters having Cp* ligands (**3**, **4**) crystallize in the $P2_1/c$ space group. In **1** and **3**, the Rh atom is coordinated by an η^2 -cod or -coe ligand and three S ligands in a slightly distorted tetrahedral geometry, while each Mo center has a three-legged piano stool geometry consisting of a Cp^{XL} or Cp* ligand and three S ligands. The [Mo₃S₄Rh] cores of clusters **1** and **3** are apparently similar in their bond distances. Average distances of Rh–Mo, Mo–Mo, Rh–S, and Mo–S in **1** (2.84(2), 2.872(10), 2.319(11), and 2.338(7) Å, respectively) and **3** (2.83(2), 2.861(8), 2.31(2), and 2.337(6) Å, respectively) are statistically identical (Table 1). Although the ligands on the composed metals in **1** and **3** are different, their core structure is maintained.

Similarly, in **2** and **4**, the Ir atom is coordinated by an η^2 -coe ligand and three S ligands and is in a slightly distorted tetrahedral geometry, while each Mo center has a three-legged piano stool geometry consisting of a Cp-type ligand and three S ligands. The [Mo₃S₄Ir] core of **2** and **4** also has nearly the same structure, as found in the average distances of Ir–Mo, Mo–Mo, Ir–S, and Mo–S in **2** (2.84(3), 2.885(13), 2.310(13), and 2.344(8) Å, respectively) and **4** (2.84(3), 2.873(6), 2.31(2), and 2.345(11) Å, respectively) (Table 1). It is also clear that the core structure of Ir-incorporated clusters (**2**, **4**) is similar to that of Rh-incorporated clusters (**1**, **3**) probably due to the close ionic radii of Ir and Rh. It is interesting to note that **2** and **4** are the first examples of structurally identified cubic [Mo₃S₄Ir] clusters, while various [Mo₃S₄M] clusters have been reported.

In this study, two [Mo₃S₄Rh] clusters were synthesized and structurally characterized. Thus, we compared the bond distances of the Rh-incorporated clusters (**1**, **3**) with two relevant instances, [(C₅MeH₄)₃Mo₃S₄RhCl(PPh₃)] and [(H₂O)₇Mo₃S₄RhCp*]₂(μ₂-O)₂ (Table S4).^{9,49} The average distances of Rh–Mo and Mo–Mo in **1** (2.84(2) and 2.872(10) Å, respectively) and **3** (2.83(2) and 2.861(8) Å, respectively) are comparable to those of the known [Mo₃S₄Rh] clusters (2.92(3)–3.04(8) Å for Rh–Mo and 2.80(3)–2.833(16) Å for Mo–Mo), suggesting that the core structures of the Rh-incorporated clusters are rigid and have no obvious deviation from the known. It is also supported by the averaged bond distances of Rh–S and Mo–S in **1** (2.319(11) and 2.338(7) Å, respectively) and **3** (2.31(2) and 2.337(6) Å, respectively), which displayed no significant difference from the reported structures (2.36(4)–2.39(2) Å for Rh–S and 2.320(12)–2.35(3) Å for Mo–S).

Table 2. C-H borylation of benzene catalyzed by the [Mo₃S₄M] (M = Rh, Ir) clusters.^(a)

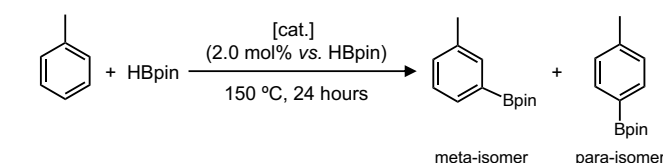
entry	[cat.]	active center	ligands on Mo	Yield ^b / %
1	1	Rh	Cp ^{XL}	55%
2	2	Ir	Cp ^{XL}	12%
3	3	Rh	Cp*	59%
4	4	Ir	Cp*	6%
5	[Cp ^{XL} ₃ Mo ₃ S ₄]	–	Cp ^{XL}	n.d.
6	[Cp* ₃ Mo ₃ S ₄]	–	Cp*	n.d.
7	[RhCl(cod)] ₂	Rh	–	2%
8	[IrCl(coe)] ₂	Ir	–	11%

(a) Reaction condition: HBpin (200 μmol) and [cat.] (2.0 mol% vs. HBpin) in 10 mL of benzene at 150 °C under Ar for 24 hours. (b) Yield was calculated by the following equation: yield = [amount of product (μmol) / HBpin (200 μmol)] × 100. *n.d. means “not detected”.

We also compared the structural features of **1–4** with Co-incorporated congeners, [Cp^{XL}₃Mo₃S₄CoCl] and [Cp*₃Mo₃S₄CoCl], which we have previously reported (Table S5).^{15,16} The average distances of Mo–Mo and Mo–S are almost constant with a narrow variation range among the Rh-, Ir-, and Co-incorporated clusters (2.848(8)–2.885(13) and 2.337(5)–2.345(11) Å, respectively). In contrast, the M–Mo and M–S distances (M = Co, Rh, Ir) tend to be longer in **1–4** than in Co-incorporated clusters (2.83(2)–2.84(3) vs 2.769(9)–2.7778(3) Å in M–Mo distances and 2.310(13)–2.319(11) vs 2.216(5)–2.217(2) Å in M–S distances, respectively). These differences are due to the variation in ionic radii of the incorporated metal; the average distances involving Rh or Ir in **1–4**, which have larger ionic radii, are longer than those in Co-incorporated clusters.

With cubic [Mo₃S₄M] (M = Rh, Ir) clusters in hand, we examined the C–H borylation of benzene to illustrate its reactivity, and the evaluation was performed using the following reaction conditions: HBpin (200 μmol) as the boron source and 2.0 mol % of **1–4** as the catalyst in benzene (10 mL) at 150 °C (oil bath temperature) in an autoclave for 24 h. All clusters gave C₆H₅(Bpin) as the product, along with no side product such as C₆H₄(Bpin)₂ (Table 2, entries 1–4). The clusters with a Rh active site (**1** and **3**) exhibited higher yields (55% for **1** and 59% for **3**) than the Ir variants (12% for **2** and 6% for **4**), indicating that Rh is more suitable as the catalytic center in our system. The steric influence of the Cp ligands was negligible in the borylation of benzene, as evidenced by the comparable yields of C₆H₅(Bpin) by the

Table 3. C-H borylation of toluene catalyzed by the [Mo₃S₄M] (M = Rh, Ir) clusters.^(a)



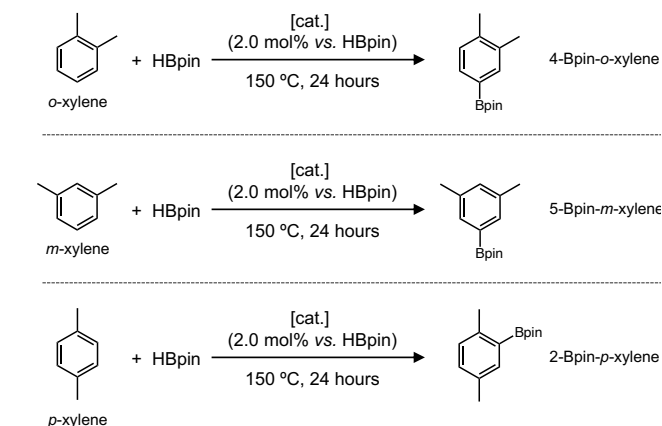
entry	[cat.]	active center	ligands on Mo	Yield ^b / %	
				meta-isomer	para-isomer
1	1	Rh	Cp ^{XL}	9%	5%
2	2	Ir	Cp ^{XL}	2%	1%
3	3	Rh	Cp*	60%	32%
4	4	Ir	Cp*	1%	<1%

(a) Reaction condition: HBpin (200 μmol) and [cat.] (2.0 mol% vs. HBpin) in 10 mL of toluene at 150 °C under Ar for 24 hours. (b) Yield was calculated by the following equation: yield = [amount of product (μmol) / HBpin (200 μmol)] × 100.

clusters with the bulky Cp^{XL} ligands (**1**, **2**) and the less bulky Cp* ligands (**3**, **4**). Further support for catalysis by the Rh or Ir centers in these borylation reactions was provided by the lack of catalytic activity in the [Cp^R₃Mo₃S₄] clusters under the same reaction conditions (Table 2, entries 5 and 6). Interestingly, the catalytic activities of clusters **1** and **3** were superior to those of [RhCl(cod)]₂ and [IrCl(coe)]₂ (Table 2, entries 7 and 8), possibly due to the robust nature of the [Mo₃S₄M] (M = Rh, Ir) framework, which leads to their longer lifetime at elevated temperatures. The robustness of each cluster was monitored by ¹H NMR under the catalytic conditions. The results showed that 95% of **1**, 99% of **2**, 81% of **3**, and 99% of **4** remained intact after the reaction (Figure S5). To our knowledge, this study represents the first example of C–H borylation catalyzed by metal–sulfur clusters, while the B–H bond heterolysis of HBpin at the Ru–S sites of mononuclear Ru(II) thiolate complexes enabled the catalytic electrophilic borylation of nitrogen heterocycles.⁵⁰ In general, Ir is the superior catalyst for arene borylation to Rh, while Rh frequently catalyzes the borylation of alkanes.^{34,38–42} In this sense, our [Cp^R₃Mo₃S₄M] framework shifted the reactivity of Rh to be more suitable for arene borylation.

We next investigated the borylation of toluene catalyzed by **1–4** under the same reaction conditions as in Table 2. For [Mo₃S₄Rh] clusters (**1**, **3**), borylation occurred at the meta- and para-positions of toluene (Table 3, entries 1, 3), while negligible catalytic activity was observed for the [Mo₃S₄Ir] clusters (**2**, **4**) (Table 3, entries 2, 4). Ortho-borylation did not occur, likely due to steric hindrance. In these reactions, the steric influence of the Cp ligands was significant (Table 3, entries 1, 3). In the Cp^{XL} variant (**1**), the space around the Rh site is restricted, limiting the approach of the substrate. The interaction between the Rh or Ir sites and π-electrons of the aromatic ring is essential for this catalytic reaction, as

Table 4. C-H borylation of *o*-, *m*-, and *p*-xylenes catalyzed by the [Mo₃S₄M] (M = Rh, Ir) clusters.^(a)



entry	[cat.]	active center	ligands on Mo	Yield ^b / %		
				<i>o</i> -xy	<i>m</i> -xy	<i>p</i> -xy
1	1	Rh	Cp ^{XL}	10%	2%	2%
2	2	Ir	Cp ^{XL}	6%	4%	n.d.
3	3	Rh	Cp*	87%	97%	55%
4	4	Ir	Cp*	4%	3%	1%

(a) Reaction condition: HBpin (200 μmol) and [cat.] (2.0 mol% vs. HBpin) in 10 mL of *o*-xylene, *m*-xylene, or *p*-xylene at 150 °C under Ar for 24 hours. (b) Yield was calculated by the following equation: yield = [amount of product (μmol) / HBpin (200 μmol)] × 100. **o*-xy = *o*-xylene, *m*-xy = *m*-xylene, *p*-xy = *p*-xylene. *n.d. means “not detected”.

evidenced by the borylation occurring exclusively at the aromatic C–H bonds, leaving the benzylic C–H bonds intact.

Interestingly, Cp*-supported [Mo₃S₄Rh] cluster **3** proved effective in the borylation of *o*-, *m*-, and *p*-xylenes, giving the borylated xylenes as single regio-isomers in 87, 97, and 55% yields, respectively (Table 4, entry 3). In contrast, clusters **1**, **2**, and **4** yielded only modest amounts of the borylated products (Table 4, entries 1, 2, and 4). Notably, the catalytic activity of cluster **3** increased for the bulkier arenes (entries 3 in Table 2, Table 3, and Table 4), despite the increasing steric hindrance between the Cp* ligands and the substrates, as benzene is replaced by toluene and then by xylene. A possible explanation for this trend is the formation of a transient and catalytically inactive “resting” state, where the Rh site is capped by an aromatic ring (either in η²- or η⁴-coordination modes), preventing HBpin from approaching for further reactions. Such a putative resting state becomes unstable for bulky toluene and xylene compared to benzene due to steric hindrance between the substrates and Cp* ligands. The inhibited formation of the putative resting state could help maintain the cluster in an active state.

To test this hypothesis, we attempted to detect potential intermediates by electrospray ionization mass spectrometry (ESI-MS). Although the speculated arene-capped cluster

was not observed in the catalytic reaction mixtures, further attempts were made to detect cluster species in the presence and absence of arenes. A mixture of cluster **2** and excess HBpin in hexane exhibited an intense signal at $m/z = 1441.2$, which is assignable as $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{Bpin})]^+$ (Figure S10). A similar treatment using **1**, instead of **2**, exhibited signals at $m/z = 1506.5$ and 1632.6 . Isotope patterns of these signals correspond to $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh} + 2\text{HBpin} + \text{H} + \text{Na}]^+$ and $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh} + 3\text{HBpin} + \text{Na}]^+$, respectively (Figure S11). These results implicate that the cluster precatalysts can be activated via treatment with HBpin. The Bpin adduct observed for the Ir cluster is ascribable to one of the intermediates, as proposed in previous Rh- and Ir-catalyzed C–H borylation reactions.^{51–53} We thus propose a similar catalytic cycle, shown in Scheme S1. In this cycle, the oxidative addition of HBpin to Rh or Ir occurs to generate a boryl/hydride intermediate (A), followed by the π -coordination of arenes, a σ -bond metathesis-type reaction for borylation, and subsequent reductive H_2 elimination.

CONCLUSIONS

We have successfully synthesized cubic $[\text{Mo}_3\text{S}_4\text{M}]$ (M = Rh, Ir) clusters featuring rhodium or iridium reaction sites, namely, $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (**1**), $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**), $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Rh}(\text{coe})]$ (**3**), and $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**4**). The Rh or Ir atoms in these clusters served as catalytic sites for the C–H borylation of arenes (benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene), demonstrating the first examples of C–H borylation mediated by metal–sulfur clusters. This is significant given that the interactions between Lewis acidic boron centers and sulfur atoms are typically strong and can retard or quench the anticipated borylation reactions. Although uncertainty remains regarding the pathway of the catalytic reactions, the HBpin adduct of cluster **2** indicates generation of the boryl/hydride intermediate. The choice of the Mo-bound Cp ligands and element M of the reaction site allowed us to modulate the reactivity of the $[\text{Mo}_3\text{S}_4\text{M}]$ (M = Rh, Ir) clusters, supporting the potential of $[\text{Mo}_3\text{S}_4\text{M}]$ cubes for a wide range of applications.

EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of N_2 or Ar using either a Schlenk line or glovebox techniques. Tetrahydrofuran (THF) and hexane were purified by passing over columns of activated alumina and a supported copper catalyst supplied by Hansen & Co. Ltd. $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]$, $(\text{Cp}^{\text{XL}} = \text{C}_5\text{Me}_4\text{SiEt}_3)^{16}$ $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]$, $(\text{Cp}^* = \text{C}_5\text{Me}_5)^{16}$ $[\text{RhCl}(\text{cod})]_2$ (cod = 1,5-cyclooctadiene),⁵⁴ $[\text{IrCl}(\text{coe})]_2$ (coe = cyclooctene),⁵⁵ $[\text{RhCl}(\text{coe})]_2$,⁵⁵ and KC_8 ⁵⁶ were synthesized according to the reported procedure. All other chemicals were purchased from standard commercial sources and used without further purification. Deuterated solvents were dried and vacuum-transferred before use. ^1H NMR spectra were recorded on a Bruker AV400 M. Electrospray ionization mass spectrometry (ESI-MS) was carried out using a Bruker micrOTOFII time-of-flight mass spectrometer. UV–vis spectra were recorded on a JASCO V770 spectrometer. Elemental analysis was carried out on powder crystalline samples sealed in tin capsules under Ar, using a J-Science Micro Corder JM11.

Synthesis of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (**1**).

$[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]$ (450 mg, 0.40 mmol) was dissolved in 20 mL of THF. KC_8 (66 mg, 0.49 mmol) was added to the solution, followed by stirring at room temperature for 5 min. $[\text{RhCl}(\text{cod})]_2$ (201 mg, 0.41 mmol) was added to the mixture, and the reaction mixture was

heated and stirred at 70 °C overnight, affording a brown suspension. The reaction mixture was evaporated to dryness under a vacuum, and the resultant residue was extracted with hexane. The hexane solution was evaporated to dryness under a vacuum. The residue was extracted with a mixed solvent (THF/hexane = 1/2), and the extract was kept at –40 °C to give crystals of **1** (207.9 mg, 0.15 mmol, 39%). ^1H NMR (C_6D_6 , 400 MHz, ppm): δ 2.2–2.0 (m, 18H, C_5Me_4), 1.9–1.7 (m, 18H, C_5Me_4), 1.2–1.0 (m, 45H, SiCH_2CH_3). Anal. Calcd for $\text{C}_{53}\text{H}_{93}\text{Mo}_3\text{S}_4\text{RhSi}_3$: C, 47.73; H, 7.03. Found: C, 47.31; H, 7.04.

Synthesis of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**).

$[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]$ (449 mg, 0.40 mmol) was dissolved in 20 mL of THF. KC_8 (70 mg, 0.52 mmol) was added to the solution, followed by stirring at room temperature for 5 min. $[\text{IrCl}(\text{coe})]_2$ (359 mg, 0.40 mmol) was added to the mixture, and the reaction mixture was heated and stirred at 70 °C overnight, affording a brown suspension. The reaction mixture was evaporated to dryness under vacuum, and the resultant residue was extracted with hexane. The hexane solution was evaporated to dryness under vacuum. The residue was extracted with a mixed solvent (THF/hexane = 1/2), and the extract was kept at –40 °C to give crystals of **2** (227 mg, 0.16 mmol, 40%). ^1H NMR (C_6D_6 , 400 MHz, ppm): δ 2.19 (s, 18H, C_5Me_4), 1.83 (s, 18H, C_5Me_4), 1.2–1.0 (m, 45H, SiCH_2CH_3). Anal. Calcd for $\text{C}_{57}\text{H}_{103}\text{Mo}_3\text{OS}_4\text{IrSi}_3$ (2·THF): C, 45.73; H, 6.94. Found: C, 45.71; H, 6.93.

Synthesis of $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Rh}(\text{coe})]$ (**3**).

$[\text{Cp}^*_3\text{Mo}_3\text{S}_4]$ (331 mg, 0.40 mmol) was dissolved in 20 mL of THF. KC_8 (72 mg, 0.54 mmol) was added to the solution, followed by stirring at room temperature for 5 min. $[\text{RhCl}(\text{coe})]_2$ (288 mg, 0.40 mmol) was added to the mixture, and the reaction mixture was heated and stirred at 70 °C overnight, affording a brown suspension. The reaction mixture was evaporated to dryness under vacuum, and the resultant residue was extracted with hexane. The hexane solution was evaporated to dryness under vacuum. The residue was extracted with a mixed solvent (THF/hexane = 1/2), and the extract was kept at –40 °C to give crystals of **3** (130.1 mg, 0.13 mmol, 31%). ^1H NMR (C_6D_6 , 400 MHz, ppm): δ 1.92 (s, 45H, CMe). Anal. Calcd for $\text{C}_{38}\text{H}_{59}\text{Mo}_3\text{S}_4\text{Rh}$: C, 44.10; H, 5.75. Found: C, 43.72; H, 5.69.

Synthesis of $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**4**).

$[\text{Cp}^*_3\text{Mo}_3\text{S}_4]$ (328 mg, 0.399 mmol) was dissolved in 20 mL of THF. KC_8 (62 mg, 0.46 mmol) was added to the solution, followed by stirring at room temperature for 5 min. $[\text{IrCl}(\text{coe})]_2$ (359 mg, 0.401 mmol) was added to the mixture, and the reaction mixture was heated and stirred at 70 °C overnight, affording a brown suspension. The reaction mixture was evaporated to dryness under vacuum, and the resultant residue was extracted with hexane. The hexane solution was evaporated to dryness under vacuum. The residue was extracted with a mixed solvent (THF/hexane = 1/2), and the extract was kept at –40 °C to give crystals of **4** (173 mg, 0.154 mmol, 39%). ^1H NMR (C_6D_6 , 400 MHz, ppm): δ 1.94 (s, 45H, CMe). Anal. Calcd for $\text{C}_{38}\text{H}_{59}\text{Mo}_3\text{S}_4\text{Ir}$: C, 40.60%; H, 5.29%. Found: C, 40.64; H, 5.29.

X-ray Crystallographic Analysis.

Single-crystal X-ray diffraction data of **1**, **2**, **3**, and **4** were collected on a Rigaku RA-Micro 7 equipped with a PILATUS 200 K detector that uses graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.710690$ 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 18 data frames measured in 0.5° increments of ω . Afterward, the full data sets were also measured in 0.5° intervals of ω . Each frame of data was integrated using the CrystalClear program package, followed by the data correction for absorption using the REQAB program. All structures were solved by direct methods with refinement by full-matrix least squares. OMIT was applied to the data of **1** and **2** because some diffractions were affected by the

beamstop. Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms were placed by using a riding model. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Deposition numbers CCDC 2365446 (for **1**), 2365445 (for **2**), 2365447 (for **3**), and 2365448 (for **4**) contain 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.

General Procedure for Catalytic Borylation of Aromatic Compounds.

In a pressure-resistant reactor, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (200 μ mol) and the catalyst (**1–4**) (4.0 μ mol, 2 mol % vs HBpin) were dissolved in 10 mL of substrates (benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene). The reactor was sealed and held at 150 $^{\circ}$ C for 24 h. After the reaction, the solvent was removed under reduced pressure and the residue was extracted with CDCl₃ containing hexamethylbenzene (0.02 mmol) as an internal standard. The amount of product was evaluated by the ¹H NMR measurement.³⁷

ASSOCIATED CONTENT

Supporting Information

The data that support the findings of this study such as ¹H NMR spectra, UV-vis spectra, and ESI-MS are available in the supporting information of this article.

AUTHOR INFORMATION

Corresponding Author

* (Yasuhiro Ohki) E-mail: ohki@scl.kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

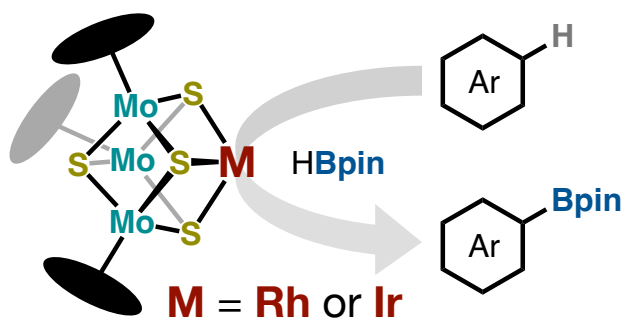
ACKNOWLEDGMENT

This work was financially supported by Grant-in-Aids for Scientific Research (23H01974 for Y.O., 21K20557 and 22 K05143 for K.T., and 23 K13763 for H.I.) from Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT), and CREST grant (JPMJCR21B1 for Y.O.) from JST. We are also grateful for financial support by Mitsubishi Foundation (for Y.O.), the Takeda Science Foundation and Toyota Riken Scholar Program, and “Innovation inspired by Nature” Research Support Program (SEKISUI CHEMICAL CO., LTD.) (for K.T.).

REFERENCES

- (1) Einsle, O.; Rees, D. C. Structural Enzymology of Nitrogenase Enzymes. *Chem. Rev.* **2020**, *120*, 4969–5004.
- (2) Seefeldt, L. C.; Yang, Z.-Y.; Lukoyanov, D. A.; Harris, D. F.; Dean, D. R.; Raage, S.; Hoffman, B. M. Reduction of Substrates by Nitrogenases. *Chem. Rev.* **2020**, *120*, 5082–5106.
- (3) Jasniowski, A. J.; Lee, C. C.; Ribbe, M. W.; Hu, Y. Reactivity, Mechanism, and Assembly of the Alternative Nitrogenases. *Chem. Rev.* **2020**, *120*, 5107–5157.
- (4) Kung, Y.; Drennan, C. L. A role for nickel-iron cofactors in biological carbon monoxide and carbon dioxide utilization. *Curr. Opin. Chem. Biol.* **2011**, *15*, 276–283.
- (5) Tanifuji, K.; Ohki, Y. Metal-Sulfur Compounds in N₂ Reduction and Nitrogenase-Related Chemistry. *Chem. Rev.* **2020**, *120*, 5194–5251.
- (6) Seino, H.; Hidai, M. Catalytic functions of cubane-type M₄S₄ clusters. *Chem. Sci.* **2011**, *2*, 847–857.
- (7) Coucouvanis, D. Use of Preassembled Fe/S and Fe/Mo/S Clusters in the Stepwise Synthesis of Potential Analogues for the Fe/Mo/S Site in Nitrogenase. *Acc. Chem. Res.* **1991**, *24*, 1–8.
- (8) Herbst, K.; Rink, B.; Dahlenburg, L.; Brorson, M. Heterobimetallic cubane-like cluster compounds prepared as the homologous series [(η^5 -Cp')₃Mo₃S₄M'(PPh₃)₃]⁺ (M' = Ni, Pd, Pt). Crystal Structures Show that Platinum Is Smaller than Palladium. *Organometallics* **2001**, *20*, 3655–3660.
- (9) Herbst, K.; Monari, M.; Brorson, M. Heterobimetallic, Cubane-like Mo₃S₄M' Cluster Cores Containing the Noble Metals M' = Ru, Os, Rh, Ir. Unprecedented Tri(μ -carbonyl) Bridge Between Ruthenium atoms in [(η^5 -Cp')₃Mo₃S₄Ru]₂(μ -CO)₃]²⁺. *Inorg. Chem.* **2001**, *40*, 2979–2985.
- (10) Feliz, M.; Garriga, J. M.; Llusar, R.; Uriel, S.; Humphrey, M. G.; Lucas, N. T.; Samoc, M.; Luther-Davies, B. Synthesis, Structure, and Optical-Limiting Properties of Heterobimetallic [M₃CuS₄] Cuboidal Clusters (M = Mo or W) with Terminal Phosphine Ligands. *Inorg. Chem.* **2001**, *40*, 6132–6138.
- (11) Takei, I.; Suzuki, K.; Enta, Y.; Dohki, K.; Suzuki, T.; Mizobe, Y.; Hidai, M. Synthesis of a New Family of Heterobimetallic Tetranuclear Sulfido Clusters with Mo₂Ni₂S_x (x = 4 or 5) or Mo₃M'S₄ (M' = Ru, Ni, Pd) Cores. *Organometallics* **2003**, *22*, 1790–1792.
- (12) Chen, P.; Chen, Y.; Zhou, Y.; Peng, Y.; Qu, J.; Hidai, M. Heterobimetallic cubane-type clusters [M'Mo₃S₄] (M' = Au, Ag and Cu): synthesis, structures and electrochemical properties, *Dalton Trans.* **2010**, *39*, 5658–5663.
- (13) Pino-Chamorro, J. Á.; Laricheva, Y. A.; Guillaumon, E.; Fernández-Trujillo, M. J.; Algarra, A. G.; Gushchin, A. L.; Abramov, P. A.; Bustelo, E.; Llusar, R.; Sokolov, M. N.; Basallote, M. G. Kinetics Aspects of the Reversible Assembly of Copper in Heterometallic Mo₃CuS₄ Clusters with 4,4'-Di-*tert*-butyl-2,2'-bipyridine. *Inorg. Chem.* **2016**, *55*, 9912–9922.
- (14) Laricheva, Y. A.; Gushchin, A. L.; Abramov, P. A.; Sokolov, M. N. Novel mixed-metal cubane-type {Mo₃NiS₄} and {Mo₃PdS₄} clusters coordinated with 2,2'-bipyridine type ligands. *Polyhedron* **2018**, *154*, 202–208.
- (15) Ohki, Y.; Uchida, K.; Hara, R.; Kachi, M.; Fujisawa, M.; Tada, M.; Sakai, Y.; Sameera, W. M. C. Cubane-type [Mo₃S₄M] clusters with first-row groups 4–10 transition-metal halides supported by C₅Me₅ ligands on molybdenum. *Chem. Eur. J.* **2018**, *24*, 17138–17147.
- (16) Ohki, Y.; Hara, R.; Munakata, K.; Tada, M.; Takayama, T.; Sakai, Y.; Cramer, R. E. Synthesis of [Mo₃S₄] clusters from half-sandwich molybdenum(V) chlorides and their application as platforms for [Mo₃S₄Fe] cubes. *Inorg. Chem.* **2019**, *58*, 5230–5240.
- (17) Shibahara, T. Cubane and Incomplete Cubane-Type Molybdenum and Tungsten Oxo/Sulfido Clusters. *Adv. Inorg. Chem.* **1991**, *37*, 143–173.
- (18) Hidai, M.; Kuwata, S.; Mizobe, Y. Synthesis and Reactivities of Cubane-Type Sulfido Clusters Containing Noble Metals. *Acc. Chem. Res.* **2000**, *33*, 46–52.
- (19) Murata, T.; Mizobe, Y.; Gao, H.; Ishii, Y.; Wakabayashi, T.; Nakano, F.; Tanase, T.; Yano, S.; Hidai, M.; Echizen, I.; Nanikawa, H.; Motomura, S. Syntheses of Mixed-Metal Sulfide Cubane-Type Clusters with the Novel PdMo₃S₄ Core and Reactivities of the Unique Tetrahedral Pd Site Surrounded by Sulfide Ligands toward Alkenes, CO, tBuNC, and Alkynes. *J. Am. Chem. Soc.* **1994**, *116*, 3389–3398.
- (20) Wakabayashi, T.; Ishii, Y.; Murata, T.; Mizobe, Y.; Hidai, M. Stereoselective addition of carboxylic acids to electron deficient acetylenes catalyzed by the PdMo₃S₄ cubane-type cluster. *Tetrahedron Lett.* **1995**, *36*, 5585–5588.
- (21) Wakabayashi, T.; Ishii, Y.; Ishikawa, K.; Hidai, M. A Novel Catalyst with a Cuboidal PdMo₃S₄ Core for the Cyclization of Alkynoic Acids to Enol Lactones. *Angew. Chem. Int. Ed.* **1996**, *35*, 2123–2124.
- (22) Takei, I.; Wakebe, Y.; Suzuki, K.; Enta, Y.; Suzuki, T.; Mizobe, Y.; Hidai, M. Synthesis of Cubane-Type Mo₃NiS₄ Clusters and Their Catalytic Activity for the Cyclization of Alkynoic Acids to Enol Lactones. *Organometallics* **2003**, *22*, 4639–4641.
- (23) Takei, I.; Enta, Y.; Wakebe, Y.; Suzuki, T.; Hidai, M. Intramolecular Cyclization of Aminoalkynes Catalyzed by PdMo₃S₄ Cubane Clusters. *Chem. Lett.* **2006**, *35*, 590–591.

- (24) Feliz, M.; Guillaumón, E.; Llusar, R.; Vincent, C.; Stirba, S.-E.; Pérez-Prieto, J.; Barberis, M. Unprecedented Stereoselective Synthesis of Catalytically Active Chiral Mo_3CuS_4 Clusters. *Chem. Eur. J.* **2006**, *12*, 1486–1492.
- (25) Guillaumón, E.; Llusar, R.; Pérez-Prieto, J.; Stirba, S.-E. Insight into the mechanism of diazocompounds transformation catalyzed by hetero cuboidal clusters $[\text{Mo}_3\text{CuQ}_4(\text{MeBPE})_3\text{X}_4]^+$, ($\text{Q} = \text{S}, \text{Se}$; $\text{X} = \text{Cl}, \text{Br}$): The catalytically active species. *J. Organomet. Chem.* **2008**, *693*, 1723–1727.
- (26) Tao, Y.; Wang, B.; Wang, B.; Qu, L.; Qu, J. Highly Efficient and Regioselective Allylation with Allylic Alcohols Catalyzed by $[\text{Mo}_3\text{S}_4\text{Pd}(\eta^3\text{-allyl})]$ Clusters. *Org. Lett.* **2010**, *12*, 2726–2729.
- (27) Tao, Y.; Wang, B.; Zhao, J.; Song, Y.; Qu, L.; Qu, J. Friedel-Crafts-Type Allylation of Nitrogen-Containing Aromatic Compounds with Allylic Alcohols Catalyzed by a $[\text{Mo}_3\text{S}_4\text{Pd}(\eta^3\text{-allyl})]$ Cluster. *J. Org. Chem.* **2012**, *77*, 2942–2946.
- (28) Takei, I.; Dohki, K.; Kobayashi, K.; Suzuki, T.; Hidai, M. Cleavage of Hydrazine N–N Bonds by RuMo_3S_4 Cubane-Type Clusters. *Inorg. Chem.* **2005**, *44*, 3768–3770.
- (29) Ohki, Y.; Uchida, K.; Tada, M.; Cramer, R. E.; Ogura, T.; Ohta, T. N_2 activation on a molybdenum–titanium–sulfur cluster, *Nat. Commun.* **2018**, *9*, 3200.
- (30) Tanifuji, K.; Sakai, Y.; Matsuoka, Y.; Tada, M.; Sameera, W. M. C.; Ohki, Y. CO Binding onto Heterometals of $[\text{Mo}_3\text{S}_4\text{M}]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$) Cubes. *Bull. Chem. Soc. Jpn.* **2022**, *95*, 1190–1195.
- (31) Izu, H.; Bhave, D. G.; Matsuoka, Y.; Sameera, W. M. C.; Tanifuji, K.; Ohki, Y. Synthesis, Characterization, and Catalytic Activity of a Cubic $[\text{Mo}_3\text{S}_4\text{Pd}]$ Cluster Bearing Bulky Cyclopentadienyl Ligands. *Eur. J. Inorg. Chem.* **2023**, *26*, e202300399.
- (32) Ohki, Y.; Munakata, K.; Matsuoka, Y.; Hara, R.; Kachi, M.; Uchida, K.; Tada, M.; Cramer, R. E.; Sameera, W. M. C.; Takayama, T.; Sakai, Y.; Kuriyama, S.; Nishibayashi, Y.; Tanifuji, K. Nitrogen reduction by the Fe sites of synthetic $[\text{Mo}_3\text{S}_4\text{Fe}]$ cubes. *Nature* **2022**, *607*, 86–90.
- (33) Matsuoka, Y.; Sakai, Y.; Izu, H.; Shimoyama, S.; Fujisawa, M.; Tada, M.; Lakshan, N. M.; Sameera, W. M. C.; Tanifuji, K.; Ohki, Y. Silylation of N_2 catalyzed by cubic $[\text{Mo}_3\text{S}_4\text{Ni}]$ clusters bearing Mo-bound cyclopentadienyl ligands. *Coordination Chemistry Research* **2024**, *1*, 100001.
- (34) Mkhali, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. C–H Activation for the Construction of C–B Bonds. *Chem. Rev.* **2010**, *110*, 890–931.
- (35) Hu, J.; Ferger, M.; Shi, Z.; Marder, T. B. Recent advances in asymmetric borylation by transition metal catalysis. *Chem. Soc. Rev.* **2021**, *50*, 13129–13188.
- (36) Bose, S. K.; Mao, L.; Kuehn, L.; Radius, U.; Nekvinda, J.; Santos, W. L.; Westcott, S. A.; Steel, P. G.; Marder, T. B. First-Row d-Block Element-Catalyzed Carbon–Boron Bond Formation and Related Processes. *Chem. Rev.* **2021**, *121*, 13238–13341.
- (37) Ishiyama, T.; Takagi, J.; Ishida, K.; Miya, N.; Anastasi, N. R.; Hartwig, J. F. Mild Iridium-Catalyzed Borylation of Arenes. High Turnover Numbers, Room Temperature Reactions, and Isolation of a Potential Intermediate. *J. Am. Chem. Soc.* **2002**, *124*, 390–391.
- (38) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E. Jr.; Smith, M. R. III. Remarkably selective iridium catalysts for the elaboration of aromatic C–H bonds. *Science* **2002**, *295*, 305–308.
- (39) Hartwig, J. F. Regioselectivity of the borylation of alkanes and arenes. *Chem. Soc. Rev.* **2011**, *40*, 1992–2002.
- (40) Hartwig, J. F. Borylation and Silylation of C–H Bonds: A Platform for Diverse C–H Bond Functionalizations. *Acc. Chem. Res.* **2012**, *45*, 864–873.
- (41) Ranjana Bisht, Chabush Haldar, Mirja Md Mahamudul Hasan, Md Emdadul Hoque, Jagriti Chaturvedi and Buddhadeb Chattopadhyay. Metal-catalysed C–H bond activation and borylation. *Chem. Soc. Rev.* **2022**, *51*, 5042–5100.
- (42) Ros, A.; Fernández, R.; Lassaletta, J. M. Functional Group Directed C–H Borylation. *Chem. Soc. Rev.* **2014**, *43*, 3229–3243.
- (43) Cook, A. K.; Schimler, S. D.; Matzger, A. J.; Sanford, M. S. Catalyst-controlled selectivity in the C–H borylation of methane and ethane. *Science* **2016**, *351*, 1421–1424.
- (44) Smith, K. T.; Berritt, S.; González-Moreiras, M.; Ahn, S.; Smith III, M. R.; Baik, M.-H.; Mindiola, D. J. Catalytic borylation of methane. *Science* **2016**, *351*, 1424–1427.
- (45) Oeschger, R.; Su, B.; Yu, I.; Ehinger, C.; Romero, E.; He, S.; Hartwig, J. F. Diverse functionalization of strong alkyl C–H bonds by undirected borylation. *Science* **2020**, *368*, 736–741.
- (46) Kuninobu, Y.; Ida, H.; Nishi, M.; Kanai, M. A meta-selective C–H borylation directed by a secondary interaction between ligand and substrate. *Nat. Chem.* **2015**, *7*, 712–717.
- (47) Ramadoss, B.; Jin, Y.; Asako, S.; Ilies, L. Remote steric control for undirected meta-selective C–H activation of arenes. *Science* **2022**, *375*, 658–663.
- (48) Jin, Y.; Ramadoss, B.; Asako, S.; Ilies, L. Noncovalent interaction with a spirobipyridine ligand enables efficient iridium-catalyzed C–H activation. *Nat. Commun.* **2024**, *15*, 2886.
- (49) Akashi, H.; Isobe, K.; Shibahara, T. Synthesis and Characterization of a Twin Cubane-Type Molybdenum–Rhodium–Sulfur Cluster, $[\{\text{Mo}_3\text{RhCp}^*\text{S}_4(\text{H}_2\text{O})_7(\text{O})_2\}_2]^{\text{8+}}$. X-ray Structure of $[\{\text{Mo}_3\text{RhCp}^*\text{S}_4(\text{H}_2\text{O})_7(\text{O})_2\}_2](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_8 \cdot 14\text{H}_2\text{O}$. *Inorg. Chem.* **2005**, *44*, 3494–3498.
- (50) Stahl, T.; Muther, K.; Ohki, Y.; Tatsumi, K.; Oestreich, M. Catalytic Generation of Borene Ions by Cooperative B–H Bond Activation: The Elusive Direct Electrophilic Borylation of Nitrogen Heterocycles with Pinacolborane. *J. Am. Chem. Soc.* **2013**, *135*, 10978–10981.
- (51) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. Iridium-Catalyzed Borylation of Benzene with Diboron. Theoretical Elucidation of Catalytic Cycle Including Unusual Iridium(V) Intermediate. *J. Am. Chem. Soc.* **2003**, *125*, 16114–16126.
- (52) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miya, N.; Hartwig, J. F. Mechanism of the Mild Functionalization of Arenes by Diboron Reagents Catalyzed by Iridium Complexes. Intermediacy and Chemistry of Bipyridine-Ligated Iridium Trisboryl Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 14263–14278.
- (53) Zhong, R.-L.; Sakaki, S. Methane Borylation Catalyzed by Ru, Rh, and Ir Complexes in Comparison with Cyclohexane Borylation: Theoretical Understanding and Prediction. *J. Am. Chem. Soc.* **2020**, *142*, 16732–16747.
- (54) Giordano, G.; Crabtree, R. H. Di- μ -chloro-bis(η^4 -1,5-cyclooctadiene)-dirhodium(I). *Inorg. Synth.* **1990**, *28*, 88–90.
- (55) Van der Ent, A.; Onderdelinden, A. Chlorobis(cyclooctene)rhodium(I) and di- μ -chlorobis[bis(cyclooctene)iridium] (I) complexes. *Inorg. Synth.* **1990**, *28*, 90–92.
- (56) Bergbreiter, D. E.; Killough, J. M. Reactions of potassium-graphite. *J. Am. Chem. Soc.* **1978**, *100*, 2126–2134.



Supporting Information

Synthesis of Cubic [Mo₃S₄M] (M = Rh, Ir) Clusters for Borylation of C-H bonds in Aromatic Compounds

Hitoshi Izu, Sayaka Shimoyama, Kazuki Tanifuji, and Yasuhiro Ohki*

Institute for Chemical Research, Kyoto-University, Gokasho, Uji, Kyoto 611-0011, Japan

E-mail: ohki@scl.kyoto-u.ac.jp

Table of Contents

1. Single crystal X-ray structure determination	3
Table S1. Summary of crystallographic data for 1-4	3
Table S2. Selected bond lengths of Rh-incorporated clusters (1 and 3).	4
Table S3. Selected bond lengths of Ir-incorporated clusters (2 and 4).....	5
Table S4. Selected and averaged atomic distances 1 , 3 and the known [Mo ₃ S ₄ Rh] clusters.....	6
Table S5. Selected and averaged atomic distances of 1-4 and the known [Mo ₃ S ₄ Co] clusters.....	6
2. ¹H NMR measurements	7
Figure S1. ¹ H NMR spectrum of 1	7
Figure S2. ¹ H NMR spectrum of 1	7
Figure S3. ¹ H NMR spectrum of 3	8
Figure S4. ¹ H NMR spectrum of 4	8
Figure S5. ¹ H NMR spectra of 1-4 before and after the borylation reactions	9
3. UV-vis absorption spectra	10
Figure S6. UV-vis absorption spectra of 1-4	10
Table S6. Summary of UV-vis absorption spectra of 1-4	10
Figure S7. UV-vis absorption spectra of 1 , 2 , and the related Mo ₃ clusters	11
Figure S8. UV-vis absorption spectra of 3 , 4 , and the related Mo ₃ clusters	11
4. Electro-spray ionization mass spectrum (ESI-MS).....	12
Figure S9. Positive-mode ESI-MS spectrum of 1	12
Figure S10. ESI-MS spectrum of a reaction mixture of [Cp ^{XL} ₃ Mo ₃ S ₄ Ir(coe)] and HBpin in hexane	13
Figure S11. ESI-MS spectrum of a reaction mixture of [Cp ^{XL} ₃ Mo ₃ S ₄ Rh(cod)] and HBpin in hexane.....	14
5. Possible catalytic cycle in our system	15
Scheme S1. A possible catalytic cycle	15
Table S7. Effect of the boron source (HBpin vs B ₂ pin ₂) in the borylation benzene	15

1. Single crystal X-ray structure determination

Table S1. Summary of crystallographic data for [Cp^{XL}₃Mo₃S₄Rh(cod)] (**1**), [Cp^{XL}₃Mo₃S₄Ir(coe)] (**2**), [Cp^{*}₃Mo₃S₄Rh(coe)] (**3**), and [Cp^{*}₃Mo₃S₄Ir(coe)] (**4**).

	1	2	3	4
Formula	[C ₅₃ H ₉₃ Mo ₃ RhS ₄ Si ₃]	[C ₅₃ H ₉₅ Mo ₃ IrS ₄ Si ₃]	[C ₃₈ H ₅₉ Mo ₃ RhS ₄]	[C ₃₈ H ₅₉ Mo ₃ IrS ₄]
Fw	1333.51	1424.81	1034.82	1124.11
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.82200(10)	11.8413(2)	10.9030(14)	10.9370(14)
<i>b</i> , Å	40.8676(3)	40.8078(6)	17.9583(18)	17.995(2)
<i>c</i> , Å	12.51620(10)	12.5577(2)	21.205(3)	21.163(3)
β , °	106.1130(10)	106.180(2)	104.207(3)	104.393(3)
<i>V</i> , Å ³	5809.48(8)	5827.75(17)	4024.9(9)	4034.4(9)
<i>Z</i>	4	4	4	4
<i>F</i> (000)	2752	2888	2088	2216
<i>d</i> _{calc} , g/cm ³	1.525	1.624	1.708	1.851
<i>T</i> , K	123	123	123	123
<i>R</i> ₁	0.0317	0.0390	0.0283	0.0130
<i>wR</i> ₂	0.0743	0.0798	0.0842	0.0446
GOF	1.084	1.077	0.987	1.182

Table S2. Selected bond lengths of Rh-incorporated clusters (**1** and **3**).

bond		length / Å	
		1	3
Mo-Mo	Mo1-Mo2	2.8589(6)	2.8614(6)
	Mo1-Mo3	2.8838(6)	2.8508(6)
	Mo2-Mo3	2.873(1)	2.8696(6)
	average	2.872(10)	2.861(8)
Rh-Mo	Rh-Mo1	2.8394(6)	2.8504(5)
	Rh-Mo2	2.863(1)	2.8064(6)
	Rh-Mo3	2.8101(4)	2.8329(5)
	average	2.84(3)	2.83(2)
Rh-S	Rh-S1	2.330(1)	2.2996(8)
	Rh-S2	2.3243(7)	2.3043(8)
	Rh-S3	2.3039(9)	2.337(1)
	average	2.319(11)	2.31(2)
Mo-S	Mo1-S1	2.3229(9)	2.3414(9)
	Mo1-S3	2.347(1)	2.3268(9)
	Mo1-S4	2.3361(7)	2.3375(8)
	Mo2-S1	2.3307(7)	2.3293(8)
	Mo2-S2	2.343(1)	2.3379(8)
	Mo2-S4	2.3402(9)	2.3415(9)
	Mo3-S2	2.3479(9)	2.3468(9)
	Mo3-S3	2.3388(7)	2.3340(9)
	Mo3-S4	2.336(1)	2.3362(8)
	average	2.338(7)	2.337(6)

Table S3. Selected bond lengths of Ir-incorporated clusters (**2** and **4**).

bond		length / Å	
		2	4
Mo-Mo	Mo1-Mo2	2.8988(7)	2.8653(6)
	Mo1-Mo3	2.8673(7)	2.8720(6)
	Mo2-Mo3	2.890(1)	2.8806(6)
	average	2.885(13)	2.873(6)
Ir-Mo	Ir-Mo1	2.8451(7)	2.8635(5)
	Ir-Mo2	2.8034(5)	2.8450(5)
	Ir-Mo3	2.869(1)	2.7972(6)
	average	2.84(3)	2.84(3)
Ir-S	Ir-S2	2.299(1)	2.3442(6)
	Ir-S3	2.300(1)	2.2983(6)
	Ir-S4	2.328(1)	2.2942(6)
	average	2.310(13)	2.31(2)
Mo-S	Mo1-S1	2.339(1)	2.3664(5)
	Mo1-S2	2.357(1)	2.3302(6)
	Mo1-S4	2.329(1)	2.3529(6)
	Mo2-S1	2.340(1)	2.3352(5)
	Mo2-S2	2.344(1)	2.3360(6)
	Mo2-S3	2.353(1)	2.3579(6)
	Mo3-S1	2.343(1)	2.3442(6)
	Mo3-S3	2.352(1)	2.3455(5)
	Mo3-S4	2.339(1)	2.3359(5)
	average	2.344(8)	2.345(11)

Table S4. Selected and averaged atomic distances (Å) of Rh-incorporated clusters (**1** and **3**) and the known [Mo₃S₄Rh] clusters. ^(a)

Cluster	Core oxidation state	Average bond length / Å				Ref.
		Mo-Rh	Mo-Mo	Rh-S	Mo-S	
[Cp ^{XL} ₃ Mo ₃ S ₄ Rh(cod)] (1)	[Mo ₃ S ₄ Rh] ³⁺	2.84(2)	2.872(10)	2.319(11)	2.338(7)	(This work)
[Cp [*] ₃ Mo ₃ S ₄ Rh(coe)] (3)	[Mo ₃ S ₄ Rh] ³⁺	2.82(2)	2.861(8)	2.31(2)	2.337(6)	(This work)
[(C ₅ Me ₄) ₃ Mo ₃ S ₄ RhCl(PPh ₃)]	[Mo ₃ S ₄ Rh] ⁵⁺	2.92(3)	2.833(16)	2.36(4)	2.320(12)	Ref. 9
[(H ₂ O) ₇ Mo ₃ S ₄ RhCp [*]] ₂ (μ ₂ -O) ₂	[Mo ₃ S ₄ Rh] ⁵⁺	3.04(8)	2.80(3)	2.39(2)	2.35(3)	Ref. 45

(a) Averaged when multiple values were available.

Table S5. Selected and averaged atomic distances (Å) of **1-4** and the known [Mo₃S₄Co] clusters. ^(a)

reference	Core oxidation state	Average bond length / Å				Ref.
		Mo-M ^(b)	Mo-Mo	M ^(b) -S	Mo-S	
[Cp ^{XL} ₃ Mo ₃ S ₄ Rh(cod)] (1)	[Mo ₃ S ₄ Rh] ³⁺	2.84(2)	2.872(10)	2.319(11)	2.338(7)	(This work)
[Cp ^{XL} ₃ Mo ₃ S ₄ Ir(coe)] (2)	[Mo ₃ S ₄ Ir] ³⁺	2.84(3)	2.885(13)	2.310(13)	2.344(8)	(This work)
[Cp [*] ₃ Mo ₃ S ₄ Rh(coe)] (3)	[Mo ₃ S ₄ Rh] ³⁺	2.82(2)	2.861(8)	2.31(2)	2.337(6)	(This work)
[Cp [*] ₃ Mo ₃ S ₄ Ir(coe)] (4)	[Mo ₃ S ₄ Ir] ³⁺	2.84(3)	2.873(6)	2.31(2)	2.345(11)	(This work)
[Cp ^{XL} ₃ Mo ₃ S ₄ CoCl]	[Mo ₃ S ₄ Co] ⁴⁺	2.769(9)	2.861(9)	2.216(5)	2.337(5)	Ref. 16
[Cp [*] ₃ Mo ₃ S ₄ CoCl]	[Mo ₃ S ₄ Co] ⁴⁺	2.7778(3)	2.848(8)	2.217(2)	2.339(4)	Ref. 15

(a) M = Co or Rh or Ir. (b) Averaged when multiple values were available.

2. ^1H NMR measurements

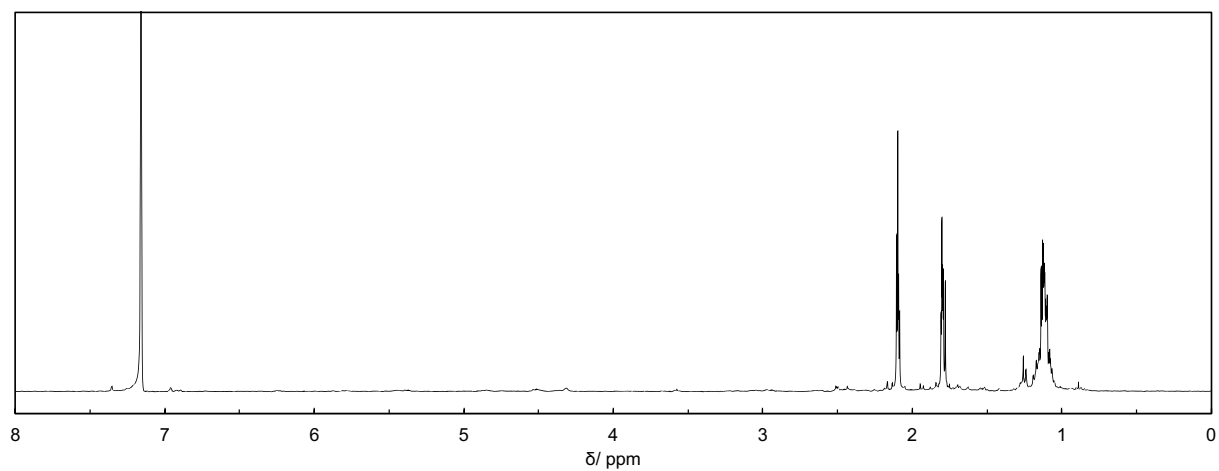


Figure S1. ^1H NMR spectrum of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (**1**) (400 MHz, C_6D_6).

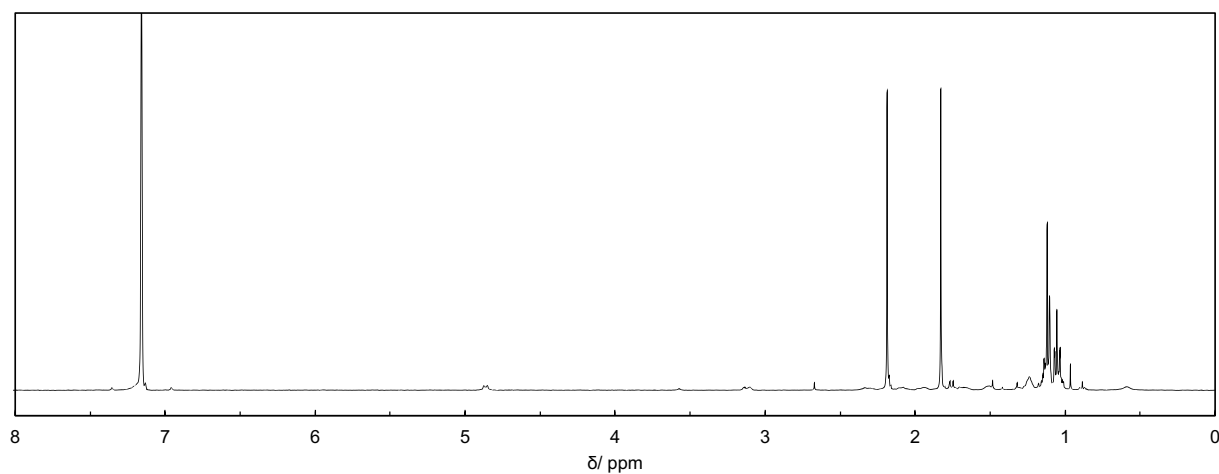


Figure S2. ^1H NMR spectrum of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**) (400 MHz, C_6D_6).

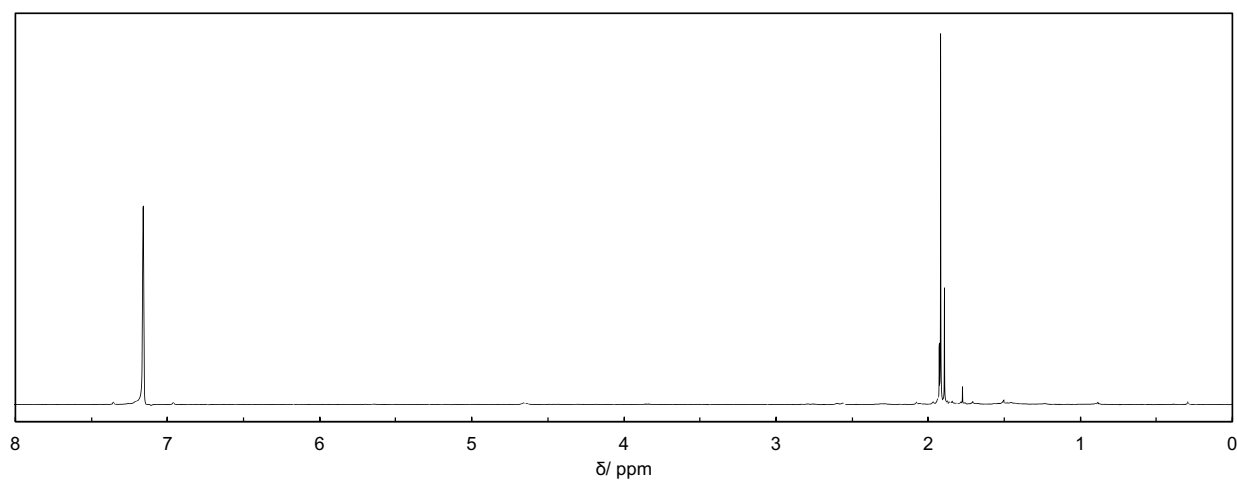


Figure S3. ^1H NMR spectrum of $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Rh}(\text{coe})]$ (**3**) (400 MHz, C_6D_6).

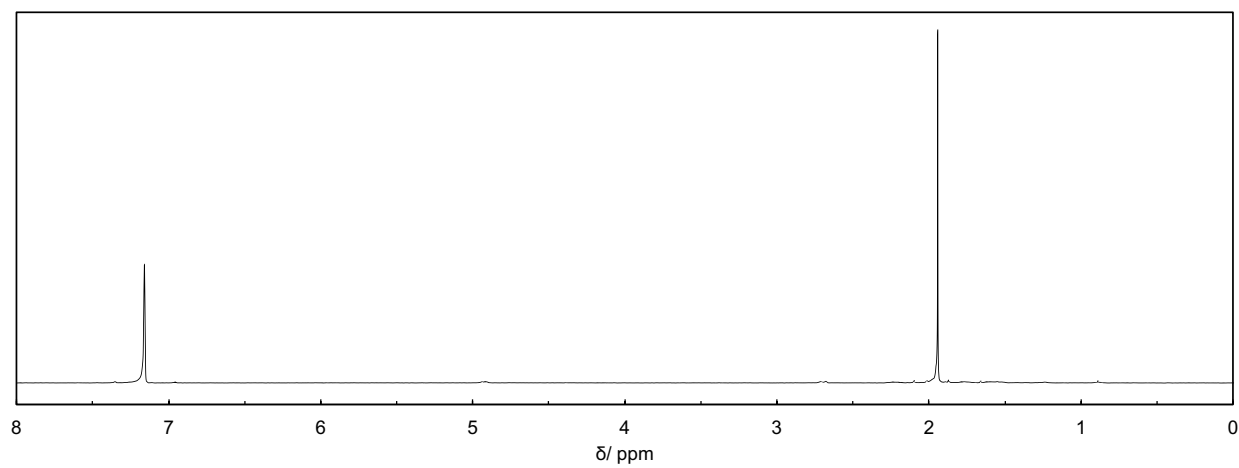


Figure S4. ^1H NMR spectrum of $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**4**) (400 MHz, C_6D_6).

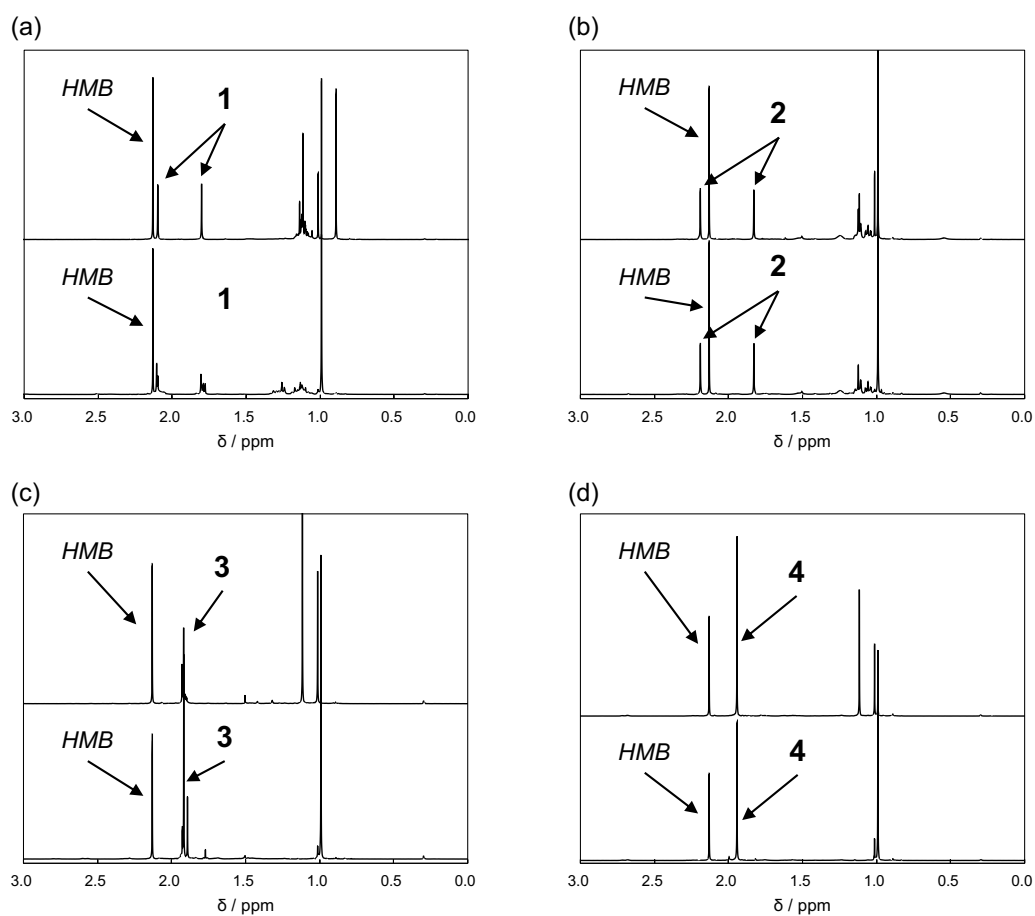


Figure S5. ^1H NMR spectra of (a) **1**, (b) **2**, (c) **3**, and (d) **4** before (bottom) and after (top) the reaction using following condition: HBpin (10.0 μmol) as the boron source and **1-4** (2.0 μmol) as the catalyst in C_6D_6 containing hexamethylbenzene (HMB, 2.0 μmol) as an internal standard at 150 $^\circ\text{C}$ (oil bath temperature) in an NMR tube for 24 hours.

3. UV-vis absorption spectra

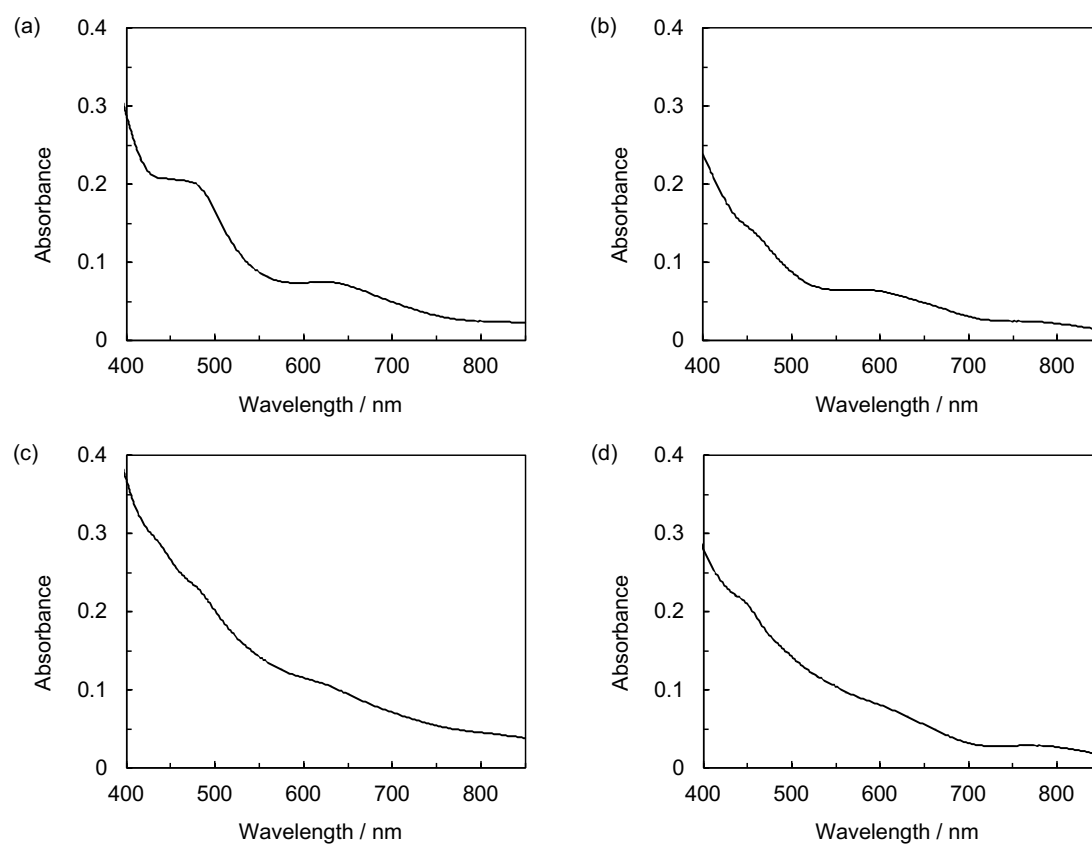


Figure S6. UV-vis absorption spectra of (a) $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (**1**, 50 μM), (b) $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**, 50 μM), (c) $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Rh}(\text{coe})]$ (**3**, 50 μM), and (d) $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**4**, 50 μM) in THF.

Table S6. Summary of UV-vis absorption spectra of **1-4**.

cluster	$\lambda_{\text{max}} / \text{nm}$
1	482 (sh), 638
2	460 (sh), 588, 785
3	435 (sh), 484 (sh), 628 (sh)
4	449 (sh), 607 (sh), 785

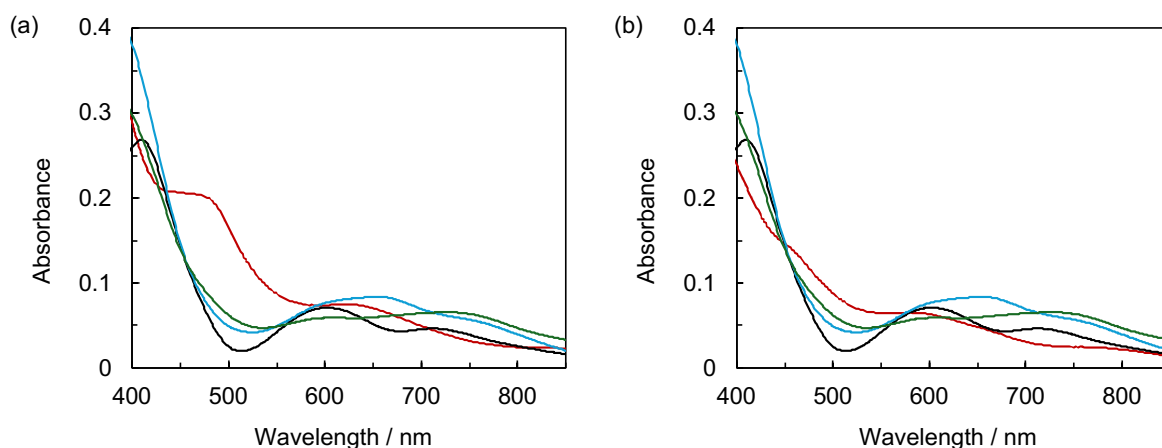


Figure S7. (a) UV-vis absorption spectra of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (**1**, 50 μM , red line), $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]^+$ (50 μM , black line), $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]$ (50 μM , blue line), and $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]^-$ (50 μM , green line) in THF. (b) UV-vis absorption spectra of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**, 50 μM , red line), $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]^+$ (50 μM , black line), $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]$ (50 μM , blue line), and $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4]^-$ (50 μM , green line) in THF.

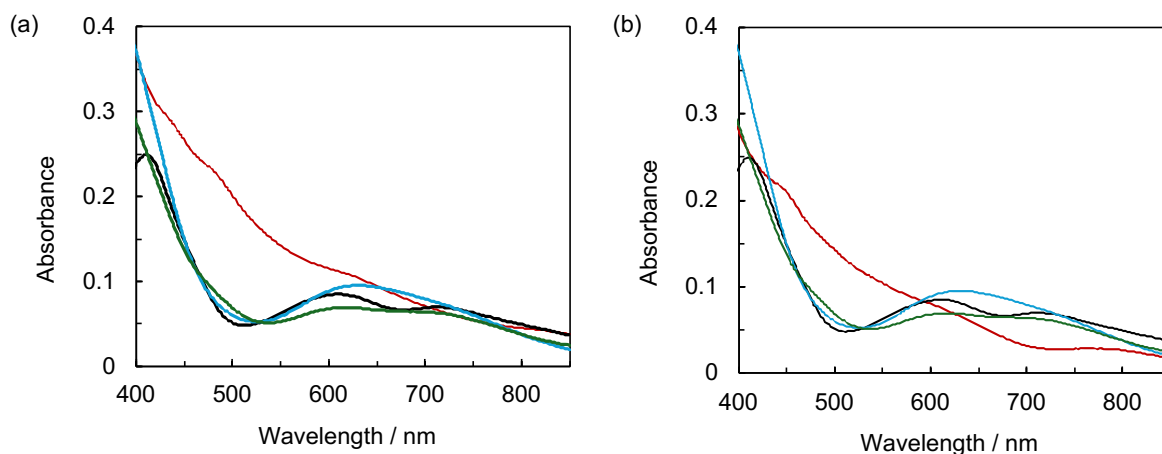


Figure S8. (a) UV-vis absorption spectra of $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Rh}(\text{coe})]$ (**3**, 50 μM , red line), $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]^+$ (50 μM , black line), $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]$ (50 μM , blue line), and $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]^-$ (50 μM , green line) in THF. (b) UV-vis absorption spectra of $[\text{Cp}^*_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**4**, 50 μM , red line), $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]^+$ (50 μM , black line), $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]$ (50 μM , blue line), and $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]^-$ (50 μM , green line) in THF.

4. Electro-spray ionization mass spectrum (ESI-MS)

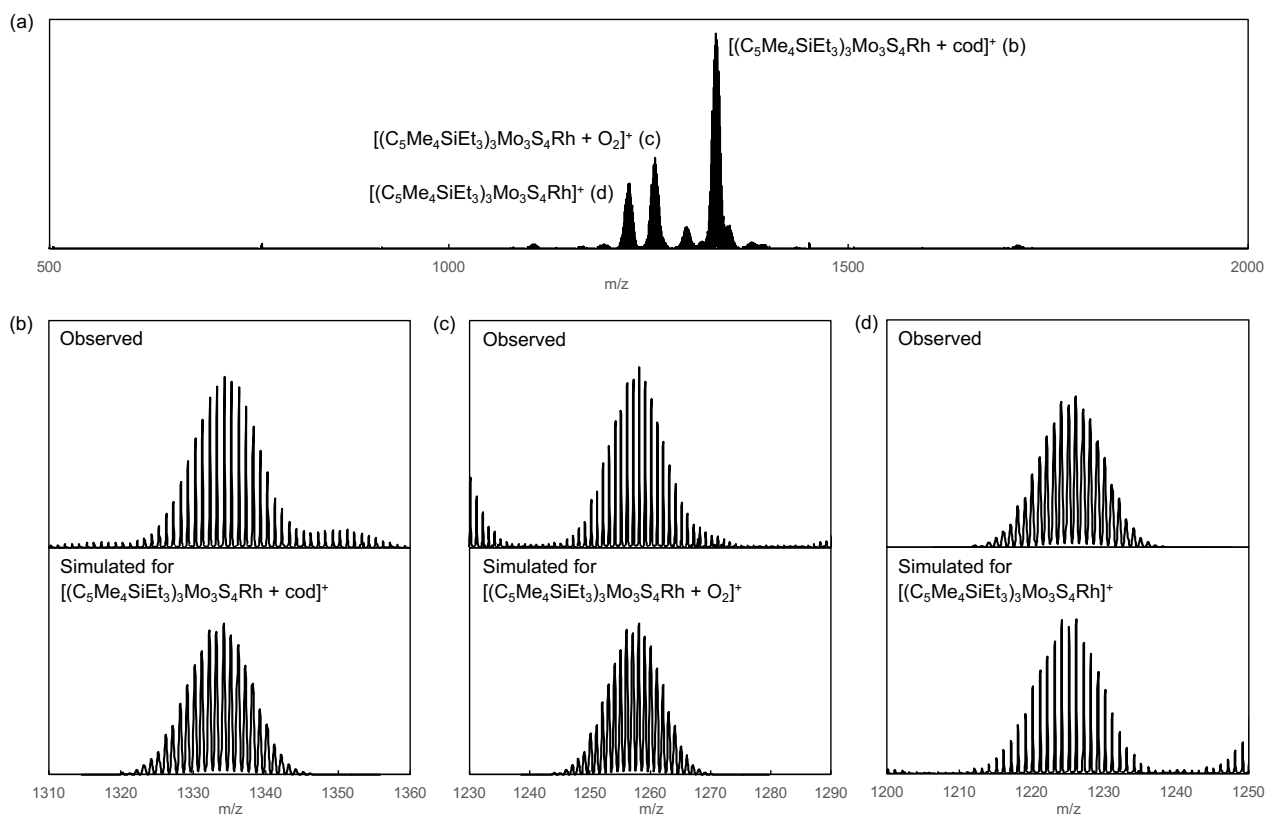


Figure S9. Positive-mode ESI-MS spectrum of $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (1) in THF. (a) overall spectrum, (b) expanded spectrum (1310-1350 m/z) and the simulated isotope pattern for $[(\text{C}_5\text{Me}_4\text{SiEt}_3)_3\text{Mo}_3\text{S}_4\text{Rh} + \text{cod}]^+$, (c) expanded spectrum (1230-1290 m/z) and the simulated isotope pattern for $[(\text{C}_5\text{Me}_4\text{SiEt}_3)_3\text{Mo}_3\text{S}_4\text{Rh} + \text{O}_2]^+$, (d) expanded spectrum (1200-1250 m/z) and the simulated isotope pattern for $[(\text{C}_5\text{Me}_4\text{SiEt}_3)_3\text{Mo}_3\text{S}_4\text{Rh}]^+$. *Note that this cluster is air-sensitive. Therefore, $[(\text{C}_5\text{Me}_4\text{SiEt}_3)_3\text{Mo}_3\text{S}_4\text{Rh} + \text{O}_2]^+$ was detected due to the inevitable air exposure during spraying injection.

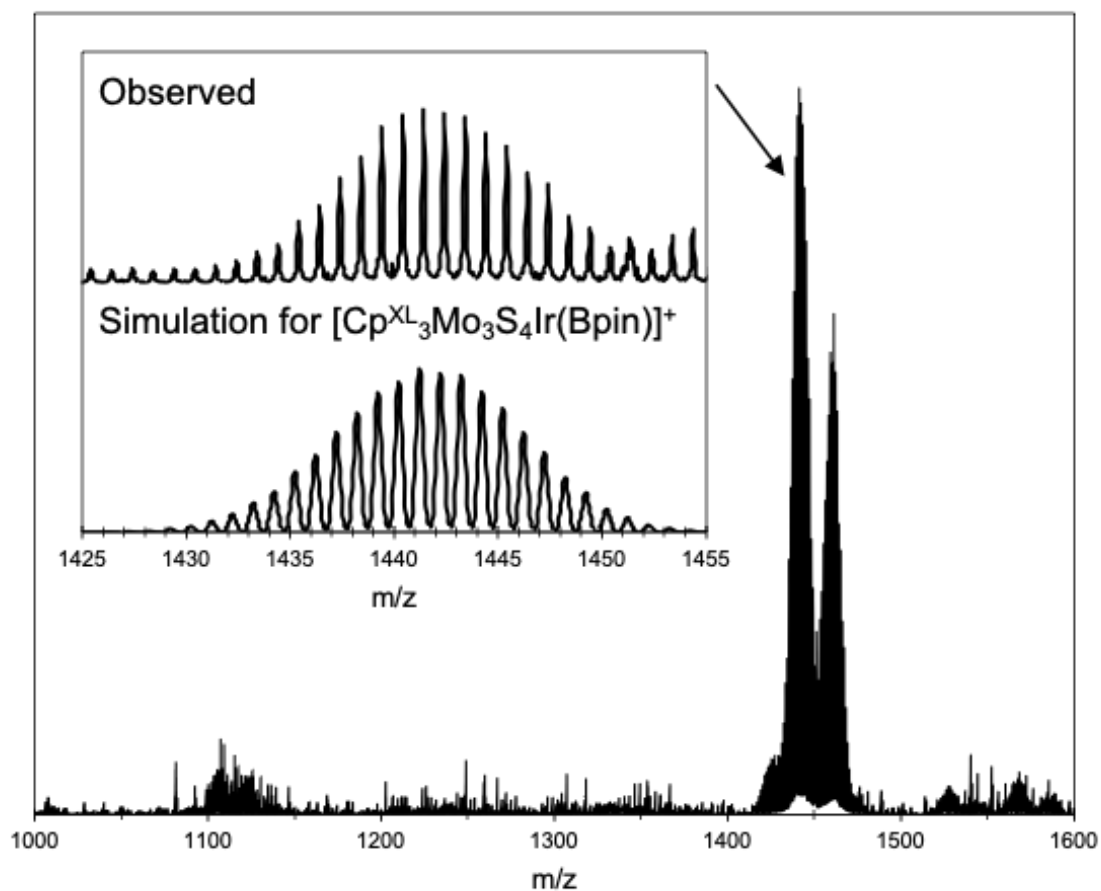


Figure S10. Positive-mode ESI-MS spectrum of a reaction mixture $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**) and HBpin, which was generated by the following condition: $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Ir}(\text{coe})]$ (**2**, 5 μmol) with HBpin (200 μmol) in hexane (10 mL) at 150 $^\circ\text{C}$ under Ar for 24 hours. The reaction was carried out in an autoclave.

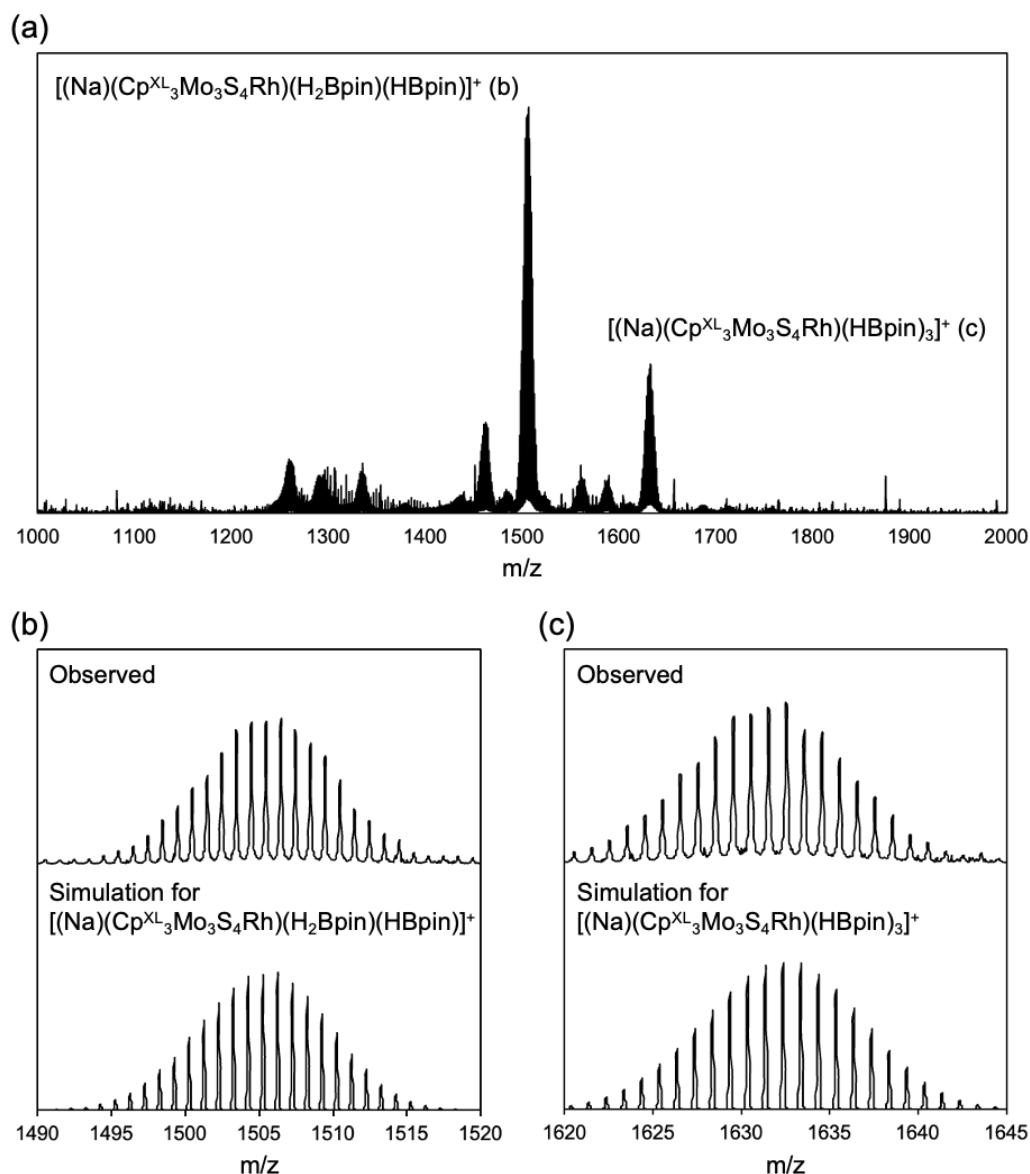


Figure S11. Positive-mode ESI-MS spectrum of a reaction mixture $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (**1**) and HBpin, which was generated by the following condition: $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Rh}(\text{cod})]$ (**1**, 5 μmol) with HBpin (200 μmol) in hexane (10 mL) at 150 $^\circ\text{C}$ under Ar for 24 hours. The reaction was carried out in an autoclave. (a) overall spectrum, (b) expanded spectrum (1490-1520 m/z) and the simulated isotope pattern for $[(\text{Na})(\text{C}_5\text{Me}_4\text{SiEt}_3)_3(\text{Mo}_3\text{S}_4\text{Rh})(\text{H}_2\text{Bpin})(\text{HBpin})]^+$, (c) expanded spectrum (1620-1645 m/z) and the simulated isotope pattern for $[(\text{Na})(\text{C}_5\text{Me}_4\text{SiEt}_3)_3(\text{Mo}_3\text{S}_4\text{Rh})(\text{HBpin})_3]^+$.

The results in Figure S11 suggested that the Rh site has enough space for two or three Bpin moieties. Thus, replacing one of the Bpin moieties with an arene molecule seems possible, as the size of Bpin is comparable to an aromatic ring. The Cp ligands also affect the accessibility of arenes, and the clusters with bulkier Cp^{XL} ligands (cluster **1** and **2**) displayed lower reactivity toward larger substrates such as toluene and xylenes.

5. Possible catalytic cycle in our system

Scheme S1. A possible catalytic cycle

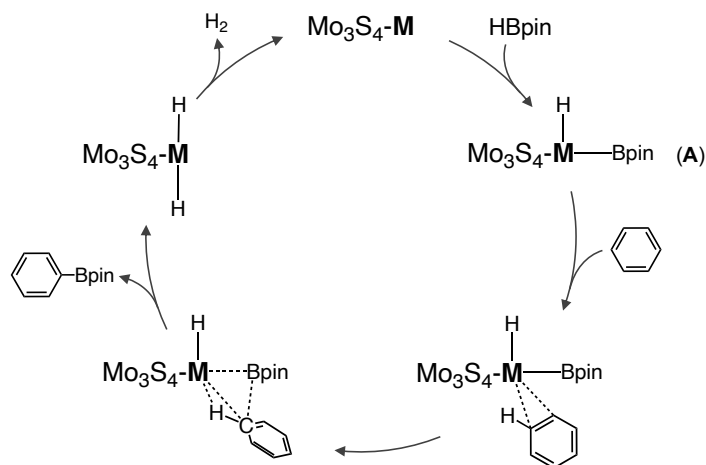


Table S7. Effect of the boron source (HBpin vs B₂pin₂) in the borylation of benzene.

entry	[cat.]	active center	ligands on Mo	boron source	amount of product / μmol
1	1	Rh	Cp ^{XL}	HBpin	107.0
2	1	Rh	Cp ^{XL}	B ₂ (pin) ₂	19.5
3	2	Ir	Cp ^{XL}	HBpin	24.9
4	2	Ir	Cp ^{XL}	B ₂ (pin) ₂	n.d.
5	3	Rh	Cp [*]	HBpin	120.7
6	3	Rh	Cp [*]	B ₂ (pin) ₂	93.8
7	4	Ir	Cp [*]	HBpin	11.3
8	4	Ir	Cp [*]	B ₂ (pin) ₂	n.d.

Conditions: HBpin (200 μmol) or B₂pin₂ (100 μmol) as the boron source and 2.0 mol% (vs. Bpin moiety) of **1-4** as the catalyst in benzene (10 mL) at 150 °C (oil bath temperature) in an autoclave for 24 hours.

The lower reactivity of B₂(pin)₂ might be explicable by the steric hindrance around the B atoms, which prevents B₂(pin)₂ from approaching the M sites, while we cannot draw definitive conclusions from these results only.