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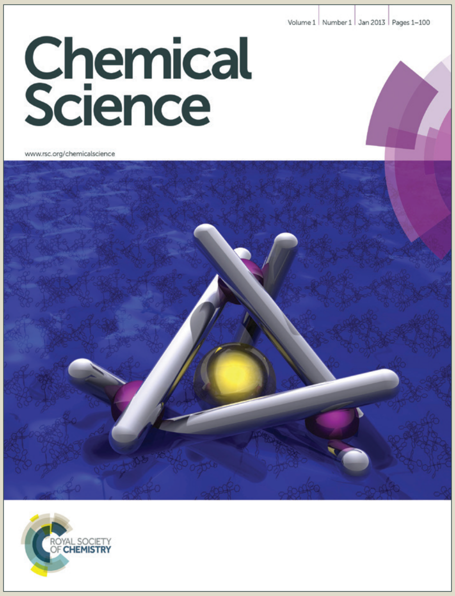

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Mixed-ligand Complexes of Paddlewheel Dinuclear Molybdenum as Hydrodehalogenation Catalysts for Polyhaloalkanes

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We developed a hydrodehalogenation reaction of polyhaloalkanes catalyzed by paddlewheel dimolybdenum complexes in combination with 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD) as a non-toxic H-atom source as well as a salt-free reductant. A mixed-ligated dimolybdenum complex $Mo_2(OAc)_2[CH(NAr)_2]_2$ (**3a**, Ar = 4-$MeOC_6H_4$) having two acetates and two amidinates exhibited high catalytic activity in the presence of $^nBu_4NCl$, in which $[^nBu_4N]_2[Mo_2\{CH(NAr)_2\}_2Cl_4]$ (**9a**), derived by treating **3a** with $ClSiMe_3$ and $^nBu_4NCl$, was generated as a catalytically-active species in the hydrodehalogenation. All reaction processes, oxidation and reduction of the dimolybdenum complex, were clarified by the controlled experiments, and the oxidized product, $[^nBu_4N][Mo_2\{CH(NAr)_2\}_2Cl_4]$ (**10a**), was characterized by the EPR and X-ray diffraction study. Kinetic analysis of the hydrodehalogenation reaction as well as a deuterium-labelling experiment using MBTCD-d_8 suggested that the H-abstraction was the rate-determining step for the catalytic reaction.

Introduction

The M_2L_4-type paddlewheel dinuclear complexes having monoanionic bridging ligands comprise the simplest metal cluster motif, and intensive investigation has been focused on their structures, redox behaviors, and spectroscopic properties, as well as their catalytic applications.[1-3] Dinuclear paddlewheel complexes of late transition metals such as rhodium and ruthenium act as useful and versatile catalysts for cyclopropanation of olefins and for functionalizing C-H, O-H, N-H, and Si-H bonds *via* the generation of metal-carbene, $[M_2L_4(=CR^1R^2)]$, metal-alkoxide, and -nitride species, $[M_2L_4(Z)]$ (Z = OR, N).[3c-3e,4-6] In all cases, because four supporting ligands tightly coordinate to the adjacent two metal centers while maintaining the dinuclear paddlewheel skeleton and the metal-metal bond, the architecture of the four supporting ligands was tunable to control redox behavior and catalytic performance of the paddlewheel complexes. In sharp contrast, few studies have examined the catalytic application of paddlewheel complexes of early transition metals. As an example, $Mo_2(OAc)_4$ was used for an aza-Diels-Alder reaction of acyl hydrazones and dienes;[7] however, the original paddlewheel structure was not maintained during the reaction. We and others have continued to investigate the stoichiometric and catalytic application of quadruply bonded M_2 complexes of group 6 metals for organic radical generation by designing bridging ligands,[8-10] and have achieved catalytic radical addition and polymerization reactions.[9] During these transformations, the metal-metal bond responses to the one-electron redox processes without decomposition of the dinuclear structure. The structural stability of the dinuclear motif owes to both the surrounding four ligands and the metal-metal multiple bonds. As further catalytic applications of the M_2 complexes, we used a cyclohexadiene derivative instead of α-olefins as a substrate for organic radicals generated from polyhaloalkanes, leading to the formation of hydrodehalogenated products. Although hydrodehalogenation is one of the key reactions for decomposing environmentally unfriendly polyhaloalkanes, precious metal catalysts are often used.[11] Herein, we report that paddlewheel Mo_2 complexes, as shown in Figure 1, act as catalysts for hydrodehalogenation reactions of polyhaloalkanes upon combination with 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD)[12] as an H-atom donor, and reveal the mechanism and actual active species in this catalytic process.

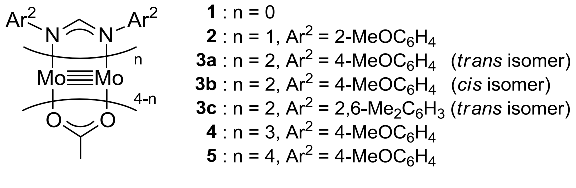


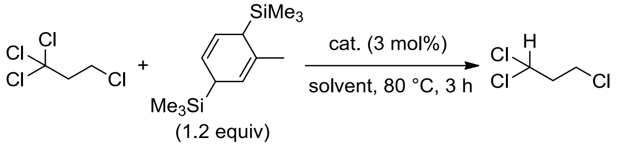
Fig. 1 Paddlewheel dimolybdenum complexes **1-5**.

Results and Discussion

We began by searching for the best paddlewheel Mo_2 catalyst among the homoleptic and mixed-ligand complexes listed in Figure 1 for the hydrodehalogenation reaction of

1,1,1,3-tetrachloropropane, as a model substrate, in CD_3CN in the presence of 1.2 equiv of MBTCD to give 1,1,3-trichloropropane (Table 1).[13] Simple homoleptic complexes **1** and **5** exhibited very low activities (runs 1 and 7), while mixed-ligand complexes of dimolybdenum bearing both acetate and amidinate ligands exhibited moderate catalytic activities (runs 2, 3, and 6). The stereochemistry of the mixed-ligand complexes was a key factor: *trans*-$Mo_2(OAc)_2[CH(NAr)_2]_2$ (Ar = 4-$MeOC_6H_4$) (**3a**) afforded the hydrodehalogenated product in 64% yield, whereas *cis*-$Mo_2(OAc)_2[CH(NAr)_2]_2$ (**3b**) afforded only a very low yield of the dehalogenated product (run 4). In addition, a *trans*-arranged mixed-ligated complex **3c** having bulky 2,6-dimethylphenyl groups at the nitrogen atoms of the amidinate ligand exhibited almost no activity, probably because the substrate approach was sterically prevented (run 5). Accordingly, we examined the solvent and additive effects using **3a** as the catalyst. In THF-d_8 and C_6D_6, the yield of 1,1,3-trichloropropane was decreased (runs 8 and 9). Positive additive effects of $^n Bu_4NCl$ were observed: addition of $^n Bu_4NCl$ (10 mol%) to the reaction mixture in acetonitrile led to the formation of 1,1,3-trichloropropane in 84% yield (run 10). In the blank reaction without MBTCD, no reaction proceeded since MBTCD acts as the H-donor and reductant for the catalytic reaction. When we used $HSiEt_3$ as a commercially available H-donor instead of MBTCD, the yield decreased (11%), probably due to the inefficient reducing ability of the *in situ* generated intermediate $[Mo_2]^{5+}$ species (*vide infra*).

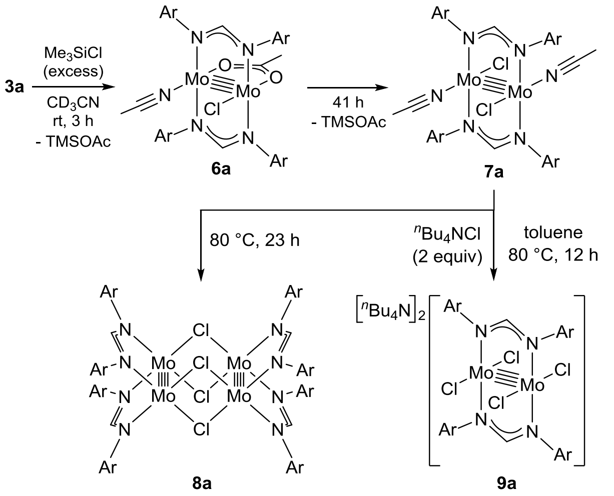
Table 1 Hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane catalyzed by Mo_2 paddlewheel complexes.



run	cat.	solvent	additive	yield (%)[a]
1	**1**	CD_3CN	-	4
2	**2**	CD_3CN	-	47
3	**3a**	CD_3CN	-	64
4	**3b**	CD_3CN	-	9
5	**3c**	CD_3CN	-	1
6	**4**	CD_3CN	-	31
7	**5**	CD_3CN	-	< 1
8	**3a**	THF-d_8	-	59
9	**3a**	C_6D_6	-	42
10[b]	**3a**	CD_3CN	$^n Bu_4NCl$	84 (73)
11	**7a**	CD_3CN	-	71
12[b]	**7a**	CD_3CN	$^n Bu_4NCl$	85
13[b]	**8a**	CD_3CN	$^n Bu_4NCl$	32
14	**9a**	CD_3CN	-	85

[a] Determined by ^1H NMR measurement. Yield in parenthesis was the isolated yield. [b] $^n Bu_4NCl$ (10 mol%) was added to the reaction mixture.

To reveal the additive effects of $^n Bu_4NCl$ to **3a**, we conducted control experiments. We observed the formation of trimethylsilyltoluene and $ClSiMe_3$ as the reaction byproducts derived from MBTCD, along with Me_3SiOAc, which was the reaction product of the acetate ligand and $ClSiMe_3$. Because the ligand replacement reaction of an acetate ligand by $ClSiMe_3$ was reported by Cotton *et al*,[14] we examined the reaction of **3a** with excess $ClSiMe_3$ in CD_3CN (Scheme 1). In the ^1H NMR spectrum, new resonances assignable to the Mo_2 complex **6a** appeared within 30 minutes at room temperature, and, after 41 h, all of **3a** was converted to **7a**, which was isolated as purple powders.[15] Subsequent heating of a solution of **7a** at 80 °C resulted in the formation of a dimeric molybdenum cluster, $[Mo_2\{CH(NAr)_2\}_2(\mu\text{-}Cl)_2]_2$ (**8a**),[16] which was previously isolated and structurally characterized. The dimeric complex **8a** exhibited low catalytic activity even in the presence of $^n Bu_4NCl$, probably due to the low solubility of **8a** in the reaction media (run 13). In contrast, treatment of complex **3a** with $ClSiMe_3$ in the presence of $^n Bu_4NCl$ in toluene at 80 ºC afforded a dianionic Mo_2 species, $[^n Bu_4N]_2[Mo_2\{CH(NAr)_2\}_2Cl_4]$ (**9a**), in which two amidinates and four chloride ligands coordinated to the Mo_2 core, based on X-ray analysis (Figure 2(a)).[15,17] Notably, no conversion of **9a** to the Cl-bridged dimer **8a** was observed, even upon prolonged heating of **9a** in CH_3CN. The catalytic activity of **9a** was equal to that of **3a**/$^n Bu_4NCl$ (runs 10 and 14). By monitoring the reaction progress using ^1H NMR, we found the induction period for the **3a**/$^n Bu_4NCl$ catalyst. Complexes **3a** or **7a** were slowly catalyzing the hydrodehalogenation reaction. Interestingly, complex **9a** initiated the catalytic hydrodehalogenation reaction without any induction period (Figure 3), indicating that the dianionic complex **9a** was identified as a catalytically active species.



Scheme 1 Ligand substitution and dimerization reactions of **3a** by the addition of Me_3SiCl.

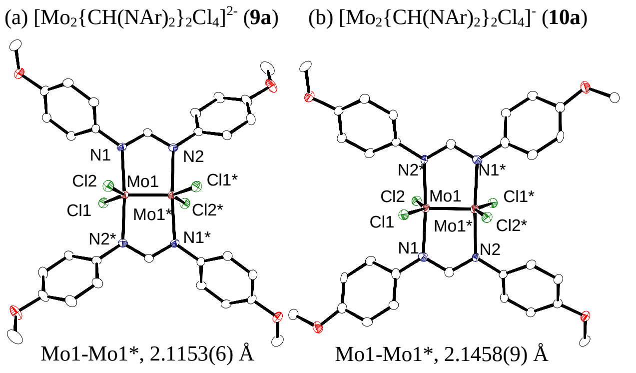


Fig. 2 ORTEP drawing of molecular structure for dimolybdenum complexes (a) **9a** and (b) **10a**. Hydrogen atoms and the cationic part are omitted for clarity.

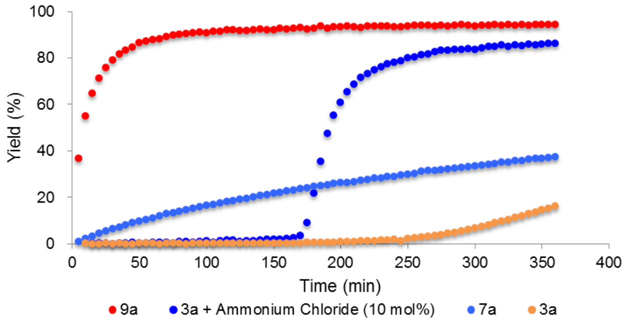
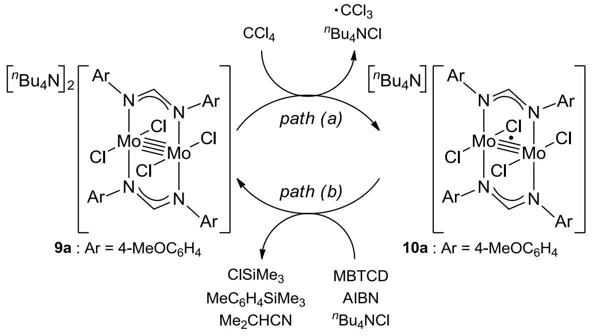
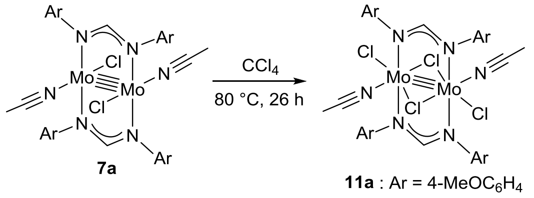


Fig. 3 Reaction profile for the hydrodehalogenation catalyzed by Mo_2 complexes (3 mol%) with MBTCD (1.2 equiv) at 60 °C.

Because of the inactivity of MBTCD toward $[Mo_2]^{4+}$ complexes, the catalytic reaction of **9a** (**3a**/^{n}Bu$_4$NCl) was assumed to be initiated by the first reductive cleavage of a carbon-halogen bond, which produced a carbon radical and an $[Mo_2]^{5+}$ species. Thus, we next performed an oxidation reaction of **9a** with CCl_4 at room temperature, and the oxidized $[Mo_2]^{5+}$ species, $[^nBu_4N][Mo_2\{CH(NAr)_2\}_2Cl_4]$ (**10a**), was isolated in 88% yield (Scheme 2, path a). During the reaction, ^{n}Bu$_4$NCl was eliminated, and the ligand system of the Mo_2 core remained intact. An X-ray diffraction study of **10a** confirmed the elongation of the Mo-Mo bond by ~0.04 Å from **9a**, and the distance of the Mo-Mo bond is typical for $[Mo_2]^{5+}$ species (Figure 2(b)).[8a,15,18] The formation of $[Mo_2]^{5+}$ was further confirmed by EPR spectrum analysis, in which resonances typical of $[Mo_2]^{5+}$ species were detected (g = 1.955). The high catalytic activity of **9a** was ascribed to the relatively negative $E_{ox}([Mo_2]^{4+/5+})$ value: the E_{ox} $([Mo_2]^{4+/5+})$ of **9a** was -0.29 V, which shifted to negative compared to that of **7a** (-0.14 V) and **8a** (-0.08 V). The other aspect of the high catalytic activity of **9a** is its stability of the $Mo_2(L)_2Cl_4$ structure and solubility under the redox processes. In fact, complex **7a** reacted with CCl_4 to form $[Mo_2]^{6+}$ species, $[Mo_2\{CH(NAr)_2\}_2Cl_4(CH_3CN)_2]$ (**11a**), as poorly soluble dark-red microcrystals that precipitated from the reaction mixture (eq. 1).[15]



Scheme 2 Redox reactions of **9a** and **10a**.



(1)

When the oxidized species **10a** was treated with MBTCD in the absence of ^{n}Bu$_4$NCl or without MBTCD in the presence of ^{n}Bu$_4$NCl to reduce **10a**, no reaction was observed, even after heating. On the other hand, in the presence of MBTCD, ^{n}Bu$_4$NCl, and AIBN as a carbon radical source, we observed the formation of **9a** together with $ClSiMe_3$, trimethylsilyltoluene, and isobutylonitrile, after heating at 80 °C for 1.5 h (Scheme 2, path b), indicating that the AIBN-derived carbon radical abstracted one hydrogen atom from MBTCD to generate isobutylonitrile and a radical derivative of MBTCD, which subsequently reduced **10a** to give **9a**, along with $ClSiMe_3$ and trimethylsilyltoluene.

By using the complex **9a** as a catalyst for the hydrodehalogenation of 1,1,1,3-tetrachloropropane, we checked the initial reaction rate dependence for the catalyst, 1,1,1,3-tetrachloropropane, and MBTCD. A first-order rate dependence on the catalyst and MBTCD concentration was observed, whereas the reaction was not depending on the concentration of 1,1,1,3-tetrachloropropane (Figure 4(a)-(c)). During the catalytic reaction as described in Table 1, we did not find any byproducts such as radical homo-coupling and disproportionated products, suggesting that the reaction of **9a** and 1,1,1,3-tetrachloropropane is in fast equilibrium with **10a** before reacting with MBTCD. Zero-order in 1,1,1,3-tetrachloropropane might indicate the saturation of the reactive intermediate composed of **10a** and the carbon radical in the coordination sphere, which is consistent with the large negative entropy value (*vide infra*). In addition, MBTCD-d_8 was applied to the catalytic reaction: the KIE value was 1.71, suggesting that the H-abstraction from MBTCD by organic radical was involved in the rate-determining step. Furthermore, the rate of the catalytic reaction over a temperature ranging from 50 to 65 °C was monitored by ^{1}H NMR spectroscopy. Eyring kinetic analyses of the reaction profile afforded the activation parameters of $\Delta H^\ddagger$ = 25.7±0.9 kJ/mol, $\Delta S^\ddagger$ = -56.5±0.7 e.u., and $\Delta G^\ddagger$(298 K) = 96.2±1.8 kJ/mol (Figure 4(d)). Large negative $\Delta S^\ddagger$ value indicated an ordered transition state for the H-abstraction step: we presume that the organic radical derived from 1,1,1,3-tetrachloropropane stays in the coordination sphere of **10a** after C-Cl reductive cleavage, while the radical abstracts the H-atom from MBTCD.

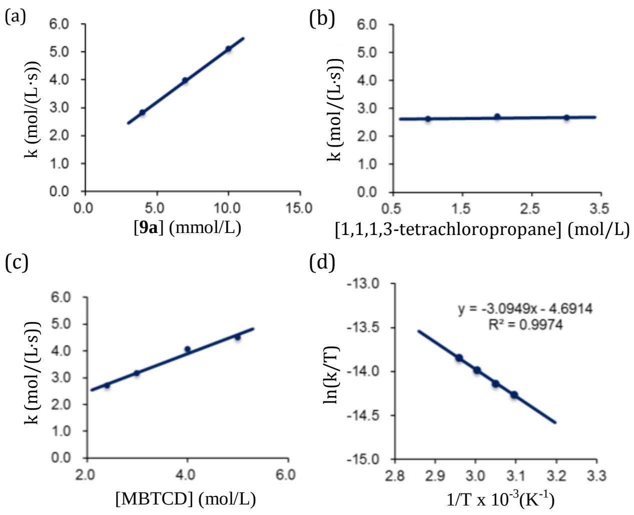
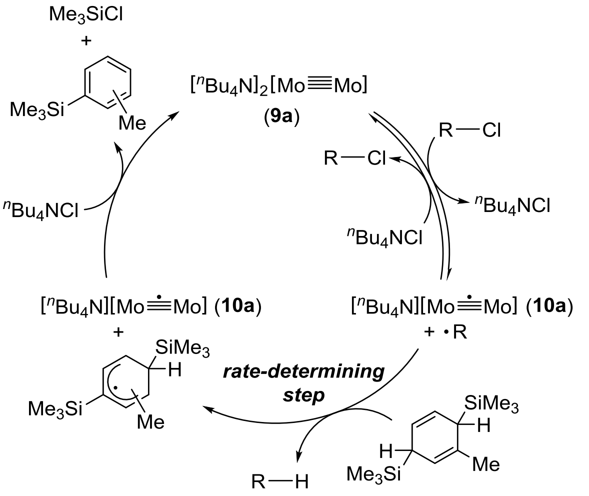


Fig. 4 Kinetic analyses of the catalytic hydrodehalogenation reaction catalyzed by **9a**. (a) rate-dependence on [**9a**]. (b) rate-dependence on [1,1,1,3-tetrachloroethane]. (c) rate-dependence on [MBTCD]. (d) Eyring plot in the range of 50–65 °C.

Based on the above observations for the kinetic study and redox reactions of the Mo_2 complexes, we propose a plausible catalytic cycle as shown in Scheme 3. In the initial stage, the dinuclear metal cluster **9a** is in equilibrium with $[Mo_2]^{5+}$ species **10a** in the presence of alkyl halides, which is often observed for the carbon radical generation by low-valent metal species with alkyl halides.[19] Because of the zero-order dependence on the substrate concentration and no observation of the radical homo-coupling and disproportionated compounds, this equilibrium is very fast, and the reactive intermediate, **10a** and the carbon radical in the coordination sphere, is generated. Next, the carbon radical abstracts a hydrogen atom from MBTCD, which is a rate-determining step in this catalytic cycle, to form hydrodehalogenated products and a radical derivative of MBTCD. Finally, the $[Mo_2]^{5+}$ cluster is reduced by the MBTCD-derived radical to regenerate $[Mo_2]^{4+}$ species **9a** together with $ClSiMe_3$ and trimethylsilyltoluene.

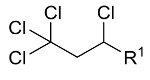
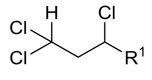
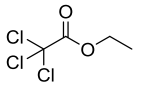
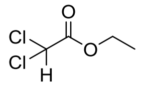
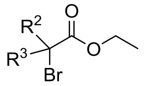
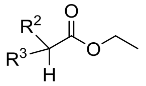
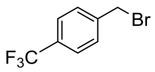
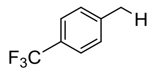


Scheme 3 Plausible mechanism for hydrodehalogenation reaction of alkyl halides catalyzed by Mo_2 complex **9a**.

Under optimized conditions for the catalytic hydrodehalogenation reaction using **3a**/^{n}Bu$_4$NCl in CH_3CN at 80 °C as described in Table 1, the substrate scope was surveyed for haloalkanes having a trichloromethyl or a bromomethyl group, and the results are summarized in Table 2. Tetrachloroalkanes having longer alkyl chain, ether, and ester groups were effectively dehalogenated to give the corresponding trichloroalkanes in 66%—82% yields (runs 1—3). In addition, α-halocarbonyl ester derivatives and benzyl bromide derivatives were applicable for the hydrodehalogenation reaction in the presence of 2 equiv of MBTCD to afford the corresponding products in good yields (runs 4—7).

Table 2 Substrate scope for hydrodehalogenation reaction catalyzed by **3a**/^{n}Bu$_4$NCl.

$$R{-}X \xrightarrow[\text{CH}_3\text{CN, 80 °C, 3 or 24 h}]{\text{cat. (3 mol\%)} \quad \text{MBTCD (1.2 or 2 equiv)}} R{-}H$$

run	R−X	R−H , yield (%)^a	
1^b 2^b 3^b			$R^1 = (CH_2)_3CH_3$, 76% $= CH_2OCH_2CH_3$, 66% $= (CH_2)_3CO_2CH_3$, 82%
4^c			62%
5^c 6^c			$R^2 = R^3 = CH_3$, 73% $R^2 = Ph, R^3 = H$, 79%
7^c			70%

^{a} isolated yield for runs 1-3, and NMR yield for runs 4-7. ^{b} in the presence of 1.2 equiv of MBTCD for 3 h. ^{c} in the presence of 2.0 equiv of MBTCD for 24 h.

Conclusions

We developed catalytic hydrodehalogenation reactions using paddlewheel Mo_2 complexes in the presence of MBTCD as an H-atom donor as well as a reductant. *Trans*-$Mo_2(OAc)_2[CH(NAr)_2]_2$ (**3a**, Ar = 4-MeOC_6H_4) exhibited high catalytic activity for the catalytic reaction in the presence of ^{n}Bu$_4$NCl. Controlled experiments revealed that the ligand exchange of two acetate ligands of **3a** by $ClSiMe_3$ and ^{n}Bu$_4$NCl to form an ionic $[^nBu_4N]_2[Mo_2\{CH(NAr)_2\}_2Cl_4]$ (**9a**) were key reaction events to generate the catalytically active species. In addition, kinetic analysis of the catalytic reaction profile, deuterium-labeling experiment using MBTCD-d_8, and isolation of the oxidized species **10a** clarified the catalytic cycle and the rate-determining step in the catalytic reaction. Further studies of the application of one electron redox processes by paddlewheel Mo_2 complexes toward various organic transformations are ongoing in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details for the synthesis and characterization of Mo_2 complexes, kinetic analysis of the reaction, ^{1}H NMR spectra of the catalytic reaction, identification of the products, CV of selected Mo_2 complexes, and crystal data for **7a** (CCDC 1046579), **9a** (CCDC 1046580), **10a** (CCDC 1046581), and **11a** (CCDC 1046582). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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