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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 $\text{Mo}_2(\text{OAc})_2[\text{CH}(\text{NAr})_2]_2$ (**3a**, Ar = 4-MeOC₆H₄) having two acetates and two amidinates exhibited high catalytic activity in the presence of $^n\text{Bu}_4\text{NCl}$, in which $[^n\text{Bu}_4\text{N}][\text{Mo}_2\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4]$ (**9a**), derived by treating **3a** with ClSiMe_3 and $^n\text{Bu}_4\text{NCl}$, was generated as a catalytically-active species in the hydrodehalogenation. All reaction processes, oxidation and reduction of the dimolybdenum complex, were clarified by control experiments, and the oxidized product, $[^n\text{Bu}_4\text{N}][\text{Mo}_2\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4]$ (**10a**), was characterized by EPR and X-ray diffraction studies. 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.

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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 the 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, $[\text{M}_2\text{L}_4(=\text{CR}^1\text{R}^2)]$, metal-alkoxide, and -nitrile species, $[\text{M}_2\text{L}_4(\text{Z})]$ (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 the early transition metals. As an example, $\text{Mo}_2(\text{OAc})_4$ 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 responds 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. In a further catalytic application of the M_2 complexes, we used a cyclohexadiene derivative instead of α -olefins as a substrate for the 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 Fig. 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.

Results and discussion

We began by searching for the best paddlewheel Mo_2 catalyst among the homoleptic and mixed-ligand complexes listed in Fig. 1 for the hydrodehalogenation reaction of 1,1,1,3-

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† Electronic supplementary information (ESI) available: Experimental details for the synthesis and characterization of Mo_2 complexes, kinetic analysis of the reactions, ¹H NMR spectra of the catalytic reactions, 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). CCDC 1046579–1046582. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc00721f

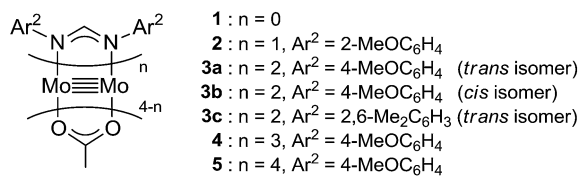


Fig. 1 Paddlewheel dimolybdenum complexes 1–5.

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*- $\text{Mo}_2(\text{OAc})_2[\text{CH}(\text{NAr})_2]_2$ ($\text{Ar} = 4\text{-MeOC}_6\text{H}_4$) (3a) afforded the hydrodehalogenated product in 64% yield, whereas *cis*- $\text{Mo}_2(\text{OAc})_2[\text{CH}(\text{NAr})_2]_2$ (3b) afforded only a very low yield of the dehalogenated product (run 4). In addition, a *trans*-arranged mixed-ligand 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 $\text{THF}-d_8$ and C_6D_6 , the yield of 1,1,3-trichloropropane decreased (runs 8 and 9). Positive additive effects of $^n\text{Bu}_4\text{NCl}$ were observed: addition of $^n\text{Bu}_4\text{NCl}$ (10 mol%) to the reaction mixture in acetonitrile led to the formation of 1,1,3-trichloropropane in

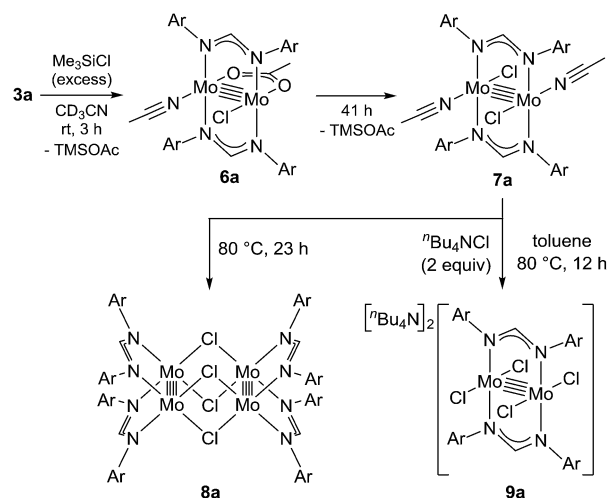
84% yield (run 10). In the blank reaction without MBTCD, no reaction proceeded since MBTCD acts as the H-donor and reductant for the catalytic reaction. When we used HSiEt_3 as a commercially available H-donor instead of MBTCD, the yield decreased (11%), probably due to the inefficient reducing ability of the *in situ* generated intermediate $[\text{Mo}_2]^{5+}$ species (*vide infra*).

To reveal the additive effects of $^n\text{Bu}_4\text{NCl}$ 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 a purple powder.¹⁵ Subsequent heating of a solution of 7a at 80 °C resulted in the formation of a dimeric molybdenum cluster, $[\text{Mo}_2\text{-}\{\text{CH}(\text{NAr})_2\}_2(\mu\text{-Cl})_2]$ (8a),¹⁶ which was previously isolated and structurally characterized. The dimeric complex 8a exhibited low catalytic activity even in the presence of $^n\text{Bu}_4\text{NCl}$, 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 $^n\text{Bu}_4\text{NCl}$ in toluene at 80 °C afforded a dianionic Mo_2 species, $[\text{Bu}_4\text{N}]_2[\text{Mo}_2\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4]$ (9a), in which two amidinates and four chloride ligands coordinated to the Mo_2 core, based on single crystal X-ray diffraction analysis (Fig. 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/ $^n\text{Bu}_4\text{NCl}$ (runs 10 and 14). By monitoring the reaction progress using ^1H NMR spectroscopy, we found the induction period for the 3a/ $^n\text{Bu}_4\text{NCl}$ catalyst. Complexes 3a or 7a were slowly catalyzing the hydrodehalogenation reaction. Interestingly, complex 9a initiated the catalytic hydrodehalogenation reaction without any induction

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	$\text{THF}-d_8$	—	59
9	3a	C_6D_6	—	42
10 ^b	3a	CD_3CN	$^n\text{Bu}_4\text{NCl}$	84 (73)
11	7a	CD_3CN	—	71
12 ^b	7a	CD_3CN	$^n\text{Bu}_4\text{NCl}$	85
13 ^b	8a	CD_3CN	$^n\text{Bu}_4\text{NCl}$	32
14	9a	CD_3CN	—	85

^a Determined using ^1H NMR measurements. Yield in parentheses was the isolated yield. ^b $^n\text{Bu}_4\text{NCl}$ (10 mol%) was added to the reaction mixture.

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

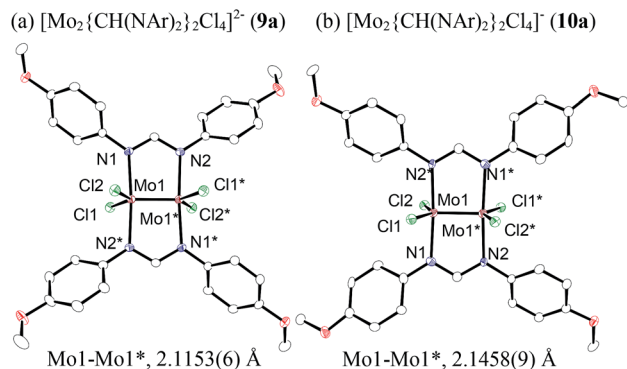
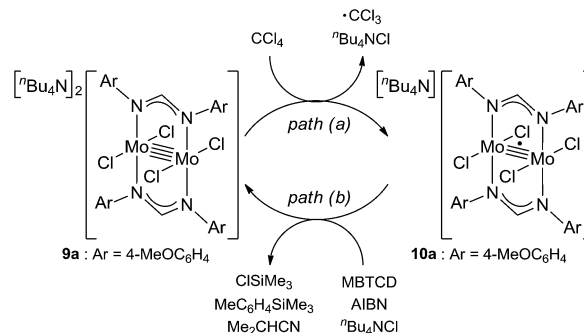


Fig. 2 ORTEP drawing of the molecular structure for dimolybdenum complexes (a) **9a** and (b) **10a**. Hydrogen atoms and the cationic part are omitted for clarity.

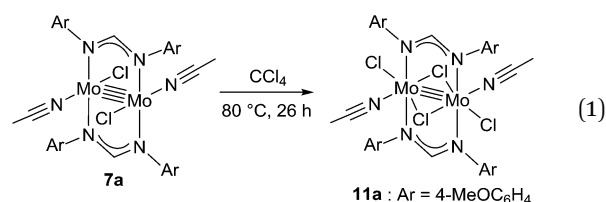
period (Fig. 3), indicating that the dianionic complex **9a** was the identity of the catalytically active species.

Because of the inactivity of MBTCD toward $[\text{Mo}_2]^{4+}$ complexes, the catalytic reaction of **9a** (**3a**/ $^n\text{Bu}_4\text{NCl}$) was assumed to be initiated by the first reductive cleavage of a carbon-halogen bond, which produced a carbon radical and an $[\text{Mo}_2]^{5+}$ species. Thus, we next performed an oxidation reaction of **9a** with CCl_4 at room temperature, and the oxidized $[\text{Mo}_2]^{5+}$ species, $[\text{Mo}_2\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4]^-$ (**10a**), was isolated in 88% yield (Scheme 2, path a). During the reaction, $^n\text{Bu}_4\text{NCl}$ was eliminated, and the ligand system of the Mo_2 core remained intact. A single crystal 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 $[\text{Mo}_2]^{5+}$ species (Fig. 2(b)).^{8a,15,18} The formation of $[\text{Mo}_2]^{5+}$ was further confirmed using EPR spectroscopic analysis, in which resonances typical of $[\text{Mo}_2]^{5+}$ species were detected ($g = 1.955$). The high catalytic activity of **9a** was ascribed to the relatively negative $E_{\text{ox}}([\text{Mo}_2]^{4+/5+})$ value: the $E_{\text{ox}}([\text{Mo}_2]^{4+/5+})$ value of **9a** was -0.29 V, which shifted to a more negative value compared to that of **7a** (-0.14 V) and **8a** (-0.08 V). The other aspect of the high catalytic activity of **9a** is the stability of the $\text{Mo}_2(\text{L})_2\text{Cl}_4$ structure and solubility during the redox processes. In fact, complex **7a** reacted with CCl_4 to form a $[\text{Mo}_2]^{6+}$ species, $[\text{Mo}_2\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4(\text{CH}_3\text{CN})_2]$ (**11a**), as poorly



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

soluble dark-red microcrystals that precipitated from the reaction mixture (eqn (1)).¹⁵



When the oxidized species **10a** was treated with MBTCD in the absence of $^n\text{Bu}_4\text{NCl}$ or without MBTCD in the presence of $^n\text{Bu}_4\text{NCl}$ to reduce **10a**, no reaction was observed, even after heating. On the other hand, in the presence of MBTCD, $^n\text{Bu}_4\text{NCl}$, and AIBN as a carbon radical source, we observed the formation of **9a** together with ClSiMe₃, trimethylsilyltoluene, and isobutyronitrile, after heating at 80°C for 1.5 h (Scheme 2, path b). This indicated that the AIBN-derived carbon radical abstracted one hydrogen atom from MBTCD to generate isobutyronitrile and a radical derivative of MBTCD, which subsequently reduced **10a** to give **9a**, along with ClSiMe₃ 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 dependent on the concentration of 1,1,1,3-tetrachloropropane (Fig. 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 the 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 ^1H NMR

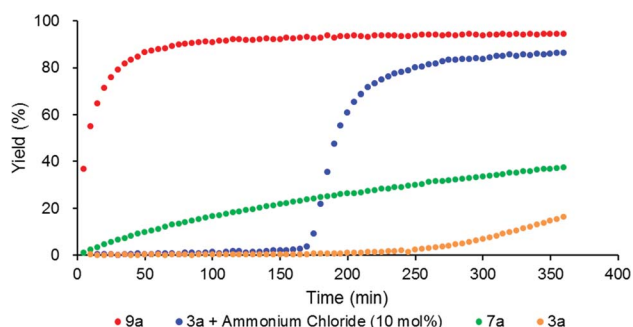


Fig. 3 Reaction profile for the hydrodehalogenation catalyzed by Mo_2 complexes (3 mol%) with MBTCD (1.2 equiv.) at 60°C .

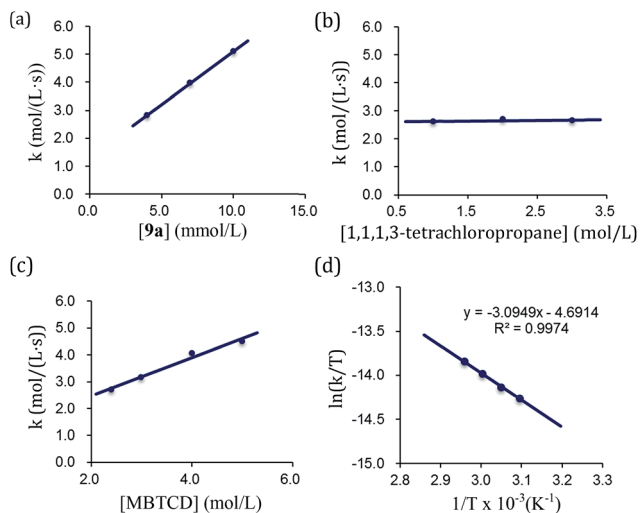
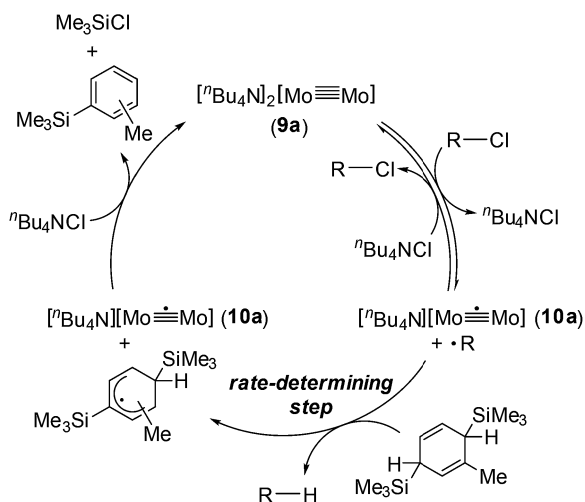


Fig. 4 Kinetic analyses of the catalytic hydrodehalogenation reaction catalyzed by **9a**. (a) Rate-dependence on [9a]. (b) Rate-dependence on [1,1,1,3-tetrachloropropane]. (c) Rate-dependence on [MBTCD]. (d) Eyring plot in the range of 50–65 °C.

spectroscopy. Eyring kinetic analyses of the reaction profile afforded the activation parameters of $\Delta H^\ddagger = 25.7 \pm 0.9$ kJ mol⁻¹, $\Delta S^\ddagger = -56.5 \pm 0.7$ e.u., and $\Delta G^\ddagger(298\text{ K}) = 96.2 \pm 1.8$ kJ mol⁻¹ (Fig. 4(d)). A large negative ΔS^\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.

Based on the above observations for the kinetic study and redox reactions of the Mo₂ 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 [Mo₂]⁵⁺ species **10a** in the presence of alkyl halides, which is often observed for the carbon radical generation by low-valent metal species with



Scheme 3 Plausible mechanism for hydrodehalogenation reactions of alkyl halides catalyzed by the Mo₂ complex **9a**.

Table 2 Substrate scope for hydrodehalogenation reactions catalyzed by **3a**/ⁿBu₄NCl

$\text{R-X} \xrightarrow[\text{CH}_3\text{CN, 80 } ^\circ\text{C, 3 or 24 h}]{\text{cat. (3 mol\% MBTCD (1.2 or 2 equiv))}} \text{R-H}$		
run	R–X	R–H, yield ^a (%)
1 ^b		R ¹ = (CH ₂) ₃ CH ₃ , 76%
2 ^b		= CH ₂ OCH ₂ CH ₃ , 66%
3 ^b		= (CH ₂) ₃ CO ₂ CH ₃ , 82%
4 ^c		62%
5 ^c		R ² = R ³ = CH ₃ , 73%
6 ^c		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.

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 [Mo₂]⁵⁺ cluster is reduced by the MBTCD-derived radical to regenerate the [Mo₂]⁴⁺ species **9a** together with ClSiMe₃ and trimethylsilyltoluene.

Under optimized conditions for the catalytic hydrodehalogenation reaction using **3a**/ⁿBu₄NCl in CH₃CN 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 a 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).

Conclusions

We developed catalytic hydrodehalogenation reactions using paddlewheel Mo₂ complexes in the presence of MBTCD as an H-atom donor as well as a reductant. *Trans*-Mo₂(OAc)₂[CH(NAr)₂]₂ (**3a**, Ar = 4-MeOC₆H₄) exhibited high catalytic activity for the

catalytic reaction in the presence of ${}^n\text{Bu}_4\text{NCl}$. Control experiments revealed that the ligand exchange of two acetate ligands of **3a** by ClSiMe_3 and ${}^n\text{Bu}_4\text{NCl}$ to form an ionic $[{}^n\text{Bu}_4\text{N}]_2[\text{Mo}_2\text{-}\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4]$ (**9a**) were key reaction events to generate the catalytically active species. In addition, kinetic analysis of the catalytic reaction profile, a 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 applications of one electron redox processes by paddlewheel Mo_2 complexes toward various organic transformations are ongoing in our laboratory.

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