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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-MeOC<sub>6</sub>H<sub>4</sub>) having two acetates and two amidinates exhibited high catalytic activity in the presence of <sup>187</sup>Bu<sub>4</sub>NCl, in which [<sup>187</sup>Bu<sub>4</sub>N]<sub>2</sub>[Mo<sub>2</sub>{CH(NAr)<sub>2</sub>Cl<sub>4</sub>] (**9a**), derived by treating **3a** with ClSiMe<sub>3</sub> and <sup>187</sup>Bu<sub>4</sub>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, [<sup>187</sup>Bu<sub>4</sub>N][Mo<sub>2</sub>{CH(NAr)<sub>2</sub>Cl<sub>4</sub>] (**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*<sub>8</sub> suggested that the H-abstraction was the rate-determining step for the catalytic reaction.

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## Introduction

The M<sub>2</sub>L<sub>4</sub>-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.<sup>1–3</sup> 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, [M<sub>2</sub>L<sub>4</sub>(=CR<sup>1</sup>R<sup>2</sup>)], metal-alkoxide, and -nitrile species, [M<sub>2</sub>L<sub>4</sub>(Z)] (Z = OR, N).<sup>3c–3e,4–6</sup> 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, Mo<sub>2</sub>(OAc)<sub>4</sub> was used for

an aza-Diels–Alder reaction of acyl hydrazones and dienes;<sup>7</sup> 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<sub>2</sub> complexes of group 6 metals for organic radical generation by designing bridging ligands,<sup>8–10</sup> and have achieved catalytic radical addition and polymerization reactions.<sup>9</sup> 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<sub>2</sub> complexes, we used a cyclohexadiene derivative instead of  $\alpha$ -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.<sup>11</sup> Herein, we report that paddlewheel Mo<sub>2</sub> 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)<sup>12</sup> 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<sub>2</sub> 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<sub>2</sub> complexes, kinetic analysis of the reactions, <sup>1</sup>H NMR spectra of the catalytic reactions, identification of the products, CV of selected Mo<sub>2</sub> 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



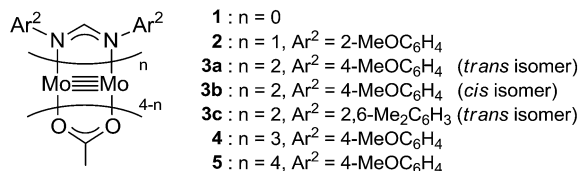


Fig. 1 Paddlewheel dimolybdenum complexes 1–5.

tetrachloropropane, as a model substrate, in  $\text{CD}_3\text{CN}$  in the presence of 1.2 equiv. of MBTCD to give 1,1,3-trichloropropane (Table 1).<sup>13</sup> 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  $\text{C}_6\text{D}_6$ , 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

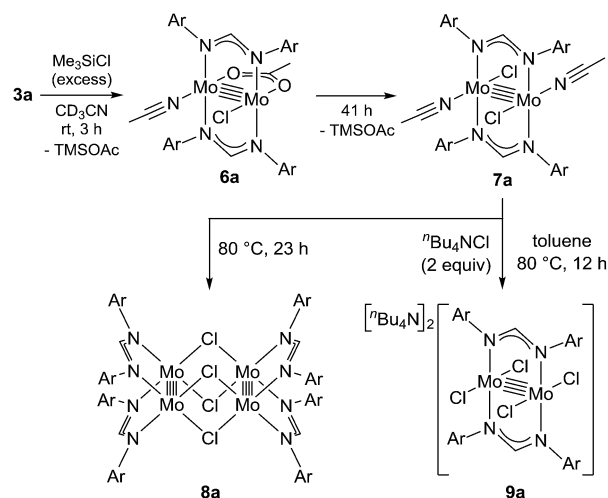
Table 1 Hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane catalyzed by  $\text{Mo}_2$  paddlewheel complexes

Run	Cat.	Solvent	Additive	Yield <sup>a</sup> (%)
1	<b>1</b>	$\text{CD}_3\text{CN}$	—	4
2	<b>2</b>	$\text{CD}_3\text{CN}$	—	47
3	<b>3a</b>	$\text{CD}_3\text{CN}$	—	64
4	<b>3b</b>	$\text{CD}_3\text{CN}$	—	9
5	<b>3c</b>	$\text{CD}_3\text{CN}$	—	1
6	<b>4</b>	$\text{CD}_3\text{CN}$	—	31
7	<b>5</b>	$\text{CD}_3\text{CN}$	—	<1
8	<b>3a</b>	$\text{THF-}d_8$	—	59
9	<b>3a</b>	$\text{C}_6\text{D}_6$	—	42
10 <sup>b</sup>	<b>3a</b>	$\text{CD}_3\text{CN}$	${}^n\text{Bu}_4\text{NCl}$	84 (73)
11	<b>7a</b>	$\text{CD}_3\text{CN}$	—	71
12 <sup>b</sup>	<b>7a</b>	$\text{CD}_3\text{CN}$	${}^n\text{Bu}_4\text{NCl}$	85
13 <sup>b</sup>	<b>8a</b>	$\text{CD}_3\text{CN}$	${}^n\text{Bu}_4\text{NCl}$	32
14	<b>9a</b>	$\text{CD}_3\text{CN}$	—	85

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

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  $\text{HSiEt}_3$  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  $\text{ClSiMe}_3$  as the reaction byproducts derived from MBTCD, along with  $\text{Me}_3\text{SiOAc}$ , which was the reaction product of the acetate ligand and  $\text{ClSiMe}_3$ . Because the ligand replacement reaction of an acetate ligand by  $\text{ClSiMe}_3$  was reported by Cotton *et al.*,<sup>14</sup> we examined the reaction of **3a** with excess  $\text{ClSiMe}_3$  in  $\text{CD}_3\text{CN}$  (Scheme 1). In the  ${}^1\text{H}$  NMR spectrum, new resonances assignable to the  $\text{Mo}_2$  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.<sup>15</sup> 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**),<sup>16</sup> 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  $\text{ClSiMe}_3$  in the presence of  ${}^n\text{Bu}_4\text{NCl}$  in toluene at 80 °C afforded a dianionic  $\text{Mo}_2$  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  $\text{Mo}_2$  core, based on single crystal X-ray diffraction analysis (Fig. 2(a)).<sup>15,17</sup> Notably, no conversion of **9a** to the Cl-bridged dimer **8a** was observed, even upon prolonged heating of **9a** in  $\text{CH}_3\text{CN}$ . 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  ${}^1\text{H}$  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

Scheme 1 Ligand substitution and dimerization reactions of **3a** by the addition of  $\text{Me}_3\text{SiCl}$ .

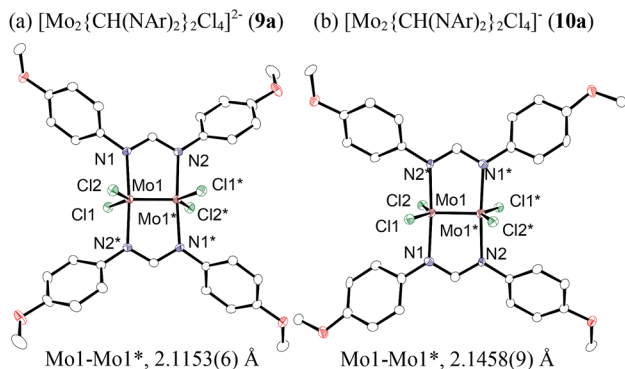
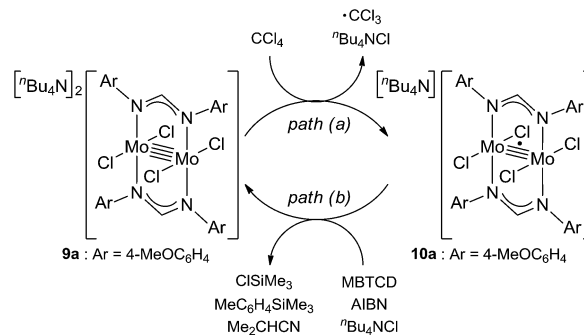


Fig. 2 ORTEP drawing of the molecular structure for dimolybdenum complexes (a) **9a** and (b) **10a**. Hydrogen atoms and the cationic part are omitted for clarity.

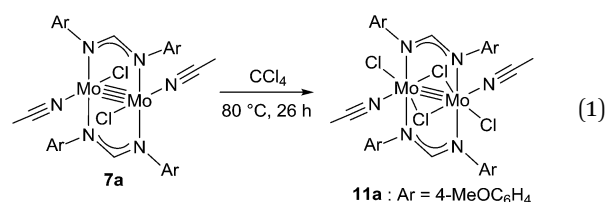
period (Fig. 3), indicating that the dianionic complex **9a** was the identity of the catalytically active species.

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  $\text{CCl}_4$  at room temperature, and the oxidized  $[\text{Mo}_2]^{5+}$  species,  $[{}^n\text{Bu}_4\text{N}][\text{Mo}_2\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4]^{5+}$  (**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  $\text{Mo}_2$  core remained intact. A single crystal X-ray diffraction study of **10a** confirmed the elongation of the Mo–Mo bond by  $\sim 0.04$  Å from **9a**, and the distance of the Mo–Mo bond is typical for  $[\text{Mo}_2]^{5+}$  species (Fig. 2(b)).<sup>8a,15,18</sup> 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  $\text{CCl}_4$  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)).<sup>15</sup>



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  $\text{ClSiMe}_3$ , 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  $\text{ClSiMe}_3$  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 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  ${}^1\text{H}$  NMR

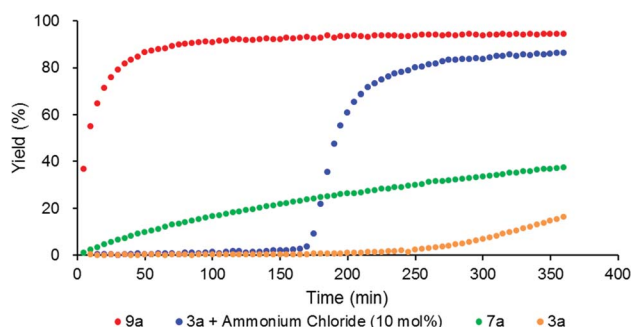


Fig. 3 Reaction profile for the hydrodehalogenation catalyzed by  $\text{Mo}_2$  complexes (3 mol%) with MBTCD (1.2 equiv.) at  $60$  °C.



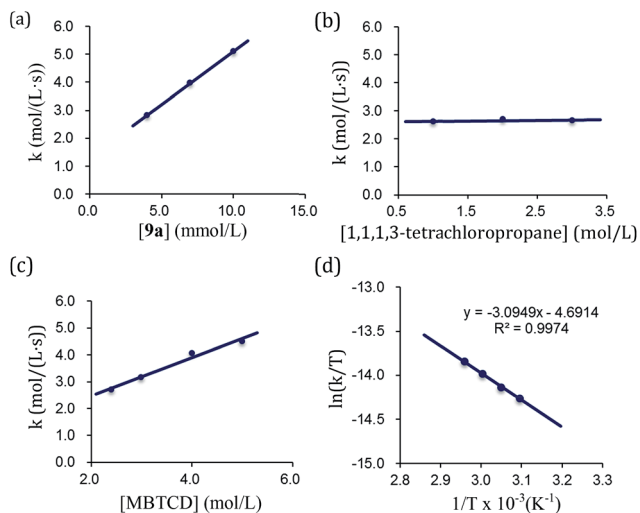
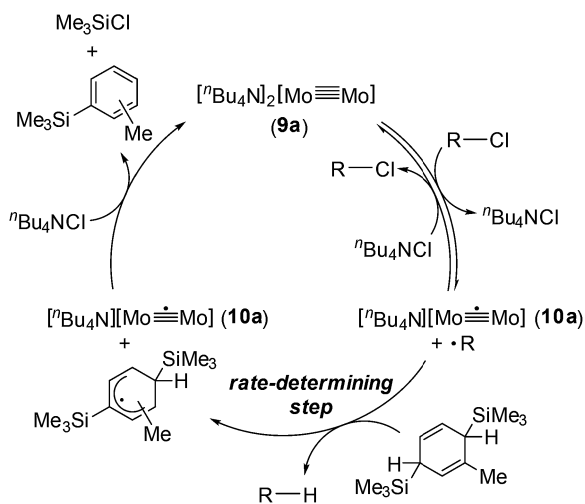


Fig. 4 Kinetic analyses of the catalytic hydrodehalogenation reaction catalyzed by **9a**. (a) Rate-dependence on **[9a]**. (b) Rate-dependence on [1,1,1,3-tetrachloropropane]. (c) Rate-dependence on [MBTCD]. (d) Eyring plot in the range of 50–65 °C.

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

Based on the above observations for the kinetic study and redox reactions of the Mo<sub>2</sub> 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<sub>2</sub>]<sup>5+</sup> 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 Mo<sub>2</sub> complex **9a**.

Table 2 Substrate scope for hydrodehalogenation reactions catalyzed by **3a**/<sup>n</sup>Bu<sub>4</sub>NCl

R-X		cat. (3 mol%) MBTCD (1.2 or 2 equiv) CH <sub>3</sub> CN, 80 °C, 3 or 24 h	R-H, yield <sup>a</sup> (%)
run	R-X		R-H, yield <sup>a</sup> (%)
1 <sup>b</sup>			R <sup>1</sup> = (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> , 76%
2 <sup>b</sup>			= CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> , 66%
3 <sup>b</sup>			= (CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> , 82%
4 <sup>c</sup>			62%
5 <sup>c</sup>			R <sup>2</sup> = R <sup>3</sup> = CH <sub>3</sub> , 73%
6 <sup>c</sup>			R <sup>2</sup> = Ph, R <sup>3</sup> = H, 79%
7 <sup>c</sup>			70%

<sup>a</sup> Isolated yield for runs 1–3, and NMR yield for runs 4–7. <sup>b</sup> In the presence of 1.2 equiv. of MBTCD for 3 h. <sup>c</sup> In the presence of 2.0 equiv. of MBTCD for 24 h.

alkyl halides.<sup>19</sup> 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<sub>2</sub>]<sup>5+</sup> cluster is reduced by the MBTCD-derived radical to regenerate the [Mo<sub>2</sub>]<sup>4+</sup> species **9a** together with ClSiMe<sub>3</sub> and trimethylsilyltoluene.

Under optimized conditions for the catalytic hydrodehalogenation reaction using **3a**/<sup>n</sup>Bu<sub>4</sub>NCl in CH<sub>3</sub>CN 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,  $\alpha$ -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 Mo<sub>2</sub> complexes in the presence of MBTCD as an H-atom donor as well as a reductant. *Trans*-Mo<sub>2</sub>(OAc)<sub>2</sub>[CH(NAr)<sub>2</sub>]<sub>2</sub> (**3a**, Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>) 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  $\text{ClSiMe}_3$  and  ${}^n\text{Bu}_4\text{NCl}$  to form an ionic  $[\text{Bu}_4\text{N}]_2[\text{Mo}_2\text{-}\{\text{CH}(\text{NAr})_2\}_2\text{Cl}_4]$  (**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  $\text{Mo}_2$  complexes toward various organic transformations are ongoing in our laboratory.

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