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COMMUNICATION

Dinuclear molybdenum cluster-catalyzed radical addition and polymerization reactions by tuning the redox potential of a quadruple bonded Mo_2 core†

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We developed dinuclear molybdenum cluster-catalyzed radical addition and polymerization reactions by tuning the redox potential of the Mo_2 core. A 2,4,6-triisopropylbenzoate-supported Mo_2 complex acts as a catalyst for radical addition reactions of polyhaloalkanes to 1-alkenes and cyclopentene, while amidinate- and guanidinate-supported Mo_2 clusters are effective catalysts for the radical polymerization reaction of methyl methacrylate.

Radical addition of halogenated compounds to alkenes and alkynes is one of the most fundamental and useful reactions in organic chemistry.[1] Single electron transfer, activation of halogenated substrates to generate radicals, and bond recombination are considered important reaction processes for realizing various transition metal-catalyzed radical coupling reactions.[2] Among these steps, activation of alkyl halides proceeds by oxidation of the transition metal center to generate carbon-centered radicals, while bond recombination leading to the coupling products is accompanied by reduction of the metal center for Kharash reactions. Thus, tuning the redox potential of the metal center is essential for generating active radical species. Since the discovery of transition metal-catalyzed radical addition[3] and radical polymerization[4] reactions, there has been extensive development of a wide variety of transition metal complexes, such as Cu, Fe, Ru, and Ni.

Although there are numerous studies of mononuclear catalysts of low-valent metal complexes, multinuclear metal clusters with metal–metal multiple bonds have the advantage of activating a wide variety of alkyl and aryl halides *via* precise control of the redox potential.[5–9] Notable previous examples are stoichiometric activation of carbon–halogen bonds of alkyl and aryl halides by dinuclear Mo_2 and W_2 clusters supported by four cyclic guanidinate ligands[6] and dinuclear Rh_2 clusters that have four amidinate or guanidinate ligands.[7] Thus, taking into account the advantageous compatibility of the reversible redox behavior of the M–M bonded cores between $[M_2]^{4+}$ and $[M_2]^{5+}$, whose redox potential can be controlled by changing the supporting ligands (Fig. 1),[5] we hypothesized that dinuclear metal clusters can serve as versatile catalysts for activating various alkyl halides to produce carbon-centered radicals, which initiate both radical addition and radical polymerization reactions. We herein report an application of dinuclear group 6 metal clusters as catalysts for radical addition or radical polymerization reactions that are highly dependent on the electron-donating characteristics of the ligand; the combination of the benzoate-based ligand and Mo_2 core results in the formation of active catalysts for radical addition of CCl_4 to various alkenes, while radical polymerization of methyl methacrylate is accomplished by Mo_2 clusters bearing more electron-donating amidinate and guanidinate-based ligands.

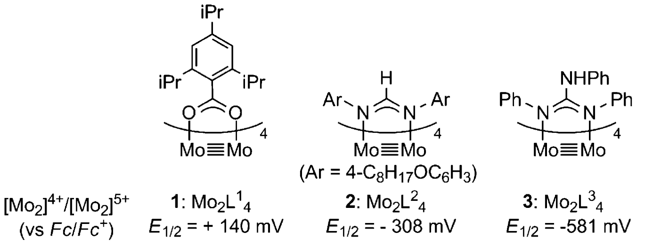

Fig. 1 Dinuclear molybdenum complexes **1–3** and their redox potential of dinuclear molybdenum core, $[Mo_2]^{4+}/[Mo_2]^{5+}$.

We performed a radical addition reaction, *i.e.*, Kharash addition, of CCl_4 to 1-hexene catalyzed by dimolybdenum complexes **1–3** and the results are listed in Table 1. The solvent, *i.e.*, chloroform or THF, influenced the reaction. The chemical yields in $CDCl_3$ were rather low. Reactions catalyzed by complexes **1** and **2** afforded a coupling product, 1,1,1-trichloro-3-chloroheptane, in 19% and 22% yields (runs 1 and 2), respectively, whereas a triphenylguanidinate-ligated complex **3**, which was easily oxidized compared with **1** and **2**, resulted in 4% yield (run 3), probably due to difficulties in the regeneration of $[Mo_2]^{4+}$ species (*vide infra*). In THF-d_8, the radical addition reaction catalyzed by **1** was significantly accelerated, and the coupling product was obtained in 84% yield (run 4), though complexes **2** and **3** did not show

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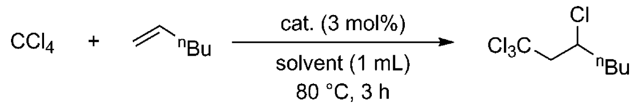
† Electronic supplementary information (ESI) available: General procedures of radical addition and radical polymerization reactions, characterization of the coupling products, terminal group analysis of PMMA, molecular structure of **6**, and UV-vis spectrum of the reaction sequence for the formation of **6**. CCDC reference number 809907. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11129a

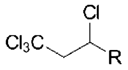
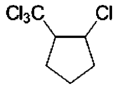
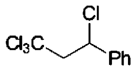
Table 1 Radical addition of CCl_4 to 1-hexene catalyzed by dinuclear group 6 metal complexes[a]



Run	Cat.	Solvent	Yield (%)[b]
1	**1**	$CDCl_3$	19
2	**2**	$CDCl_3$	22
3	**3**	$CDCl_3$	4
4	**1**	THF-d_8	84
5	**2**	THF-d_8	29
6	**3**	THF-d_8	2
7[c]	**1**	$CDCl_3$: THF = 9 : 1	92
8[c]	**1**	$CDCl_3$: 1,4-dioxane = 9 : 1	23
9	**4**[d,e]	THF-d_8	46
10	**5**[e,f]	THF-d_8	35

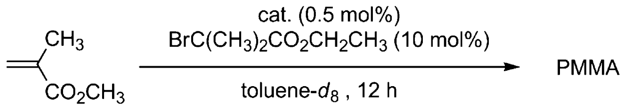
[a] [cat.] : [alkene] : [CCl_4] = 0.03 : 1.0 : 1.3 (in mmol) in solvent (total volume, 1 mL) for 3 h at 80 °C under Ar. [b] Determined by ^1H NMR. [c] Reaction for 2 h. [d] **4**: $Cr_2L^1_4$. [e] Reaction for 24 h. [f] **5**: $W_2L^1_4$

Table 2 Radical addition of CCl_4 to various alkenes[a]

Run	Substrate		Product	Yield (%)
1[b]		R = Cy		77
2		R = CH_2Ph		59
3		R = CH_2OEt		55
4				61
5[c]				50[d]

[a] [**1**] : [alkene] : [CCl_4] = 0.03 : 1.0 : 1.3 (in mmol) in $CDCl_3$ (0.50 mL) for 24 h at 80 °C under Ar. [b] $CDCl_3$–THF (v/v = 9 : 1) was used as the solvent. [c] [alkene] : [CCl_4] = 1.2 : 1.0 (in mmol). [d] Styrene oligomer is formed.

Table 3 Radical polymerization of MMA catalyzed by Mo_2 complexes[a]

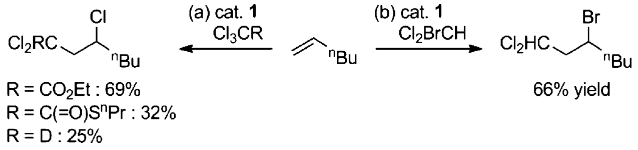


Run	Cat.	Temp. (°C)	Conv. (%)[b]	Mn (× 10^4)[c]	PDI[c]
1	**1**	100	76	1.9	1.7
2	**2**	100	89	0.5	1.7
3	**3**	100	82	2.1	2.2
4	**1**	50	7	6.5	3.2
5	**2**	50	43	1.2	1.4
6	**3**	50	40	5.4	2.0

[a] [cat.] : [$BrC(CH_3)_2CO_2CH_2CH_3$] : [MMA] = 0.005 : 0.10 : 1.0 (in mmol) in toluene-d_8 (0.50 mL) for 12 h. [b] Determined by ^1H NMR. [c] Determined by GPC.

adequate solvent effects. Notably, the addition of a small amount of THF was sufficient to accelerate the reaction (run 7), but a non-polar cyclic ether such as 1,4-dioxane was not effective (run 8). Compared with **1**, the corresponding 2,4,6-triisopropylbenzoate-ligated chromium and tungsten complexes, $Cr_2L^1_4$ (**4**) and $W_2L^1_4$ (**5**), were less effective catalysts for the radical addition reaction in THF-d_8, giving the coupling product in 46% and 35% yields after 24 h (runs 9 and 10).

Under optimal conditions using **1**, we checked the applicability of some donor molecules to 1-hexene. The addition of ethyl trichloroacetate and propyl trichlorothioacetate to 1-hexene produced the corresponding coupling products (Scheme 1, a). Coupling of a dichloromethyl radical with 1-hexene proceeded effectively upon treatment with bromodichloromethane as the radical donor compared with chloroform (Scheme 1, b) due to the facile activation of $CHBrCl_2$ compared to chloroform.

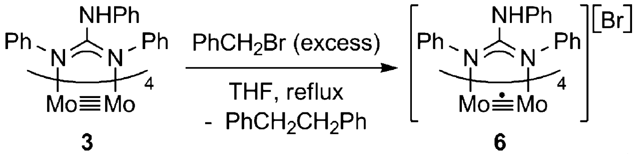


Scheme 1 Radical addition of trihaloalkanes to 1-hexene.

With catalyst **1** for the radical addition reaction in hand, some other alkenes were used, and mono-addition products of Cl–CCl_3 across carbon–carbon double bonds were isolated in moderate yield (Table 2). In contrast to the radical addition to 1-hexene, the reactions in the absence of THF showed better results except for the reaction to vinylcyclohexane. Catalyst **1** was tolerant to the ethereal substrate, resulting in the moderate yields of 1 : 1 adducts in the reactions with 3-ethoxy-1-propene (run 3). When styrene was used as a substrate, 1 : 1 adduct and styrene oligomers were formed (run 5).

Styrene oligomers were obtained in the radical addition reaction of CCl_4 to styrene by **1**; therefore, we examined the catalytic activity of complexes **1–3** for the radical polymerization of methyl methacrylate (MMA) in the presence of excess ethyl 2-bromoisobutyrate, which is a typical initiator for living radical polymerization (Table 3).[10] All the Mo_2 complexes **1–3** afforded PMMA at 100 °C. The catalyst **3** afforded a polymer with a rather broad PDI value (run 3) compared with those observed for complexes **1** and **2** (runs 1 and 2). At 50 °C, among the Mo_2 complexes, the amidinato-supported Mo_2 complex **2** gave the best results in terms of the catalytic activity and polydispersity (run 5).

The oxidation reaction of the Mo_2 core by alkyl halides was investigated under controlled conditions to study the radical reaction mechanism. Treatment of **3** with benzyl bromide in THF under refluxing conditions gave complex **6** as red crystals suitable for X-ray diffraction study (eqn (1)).

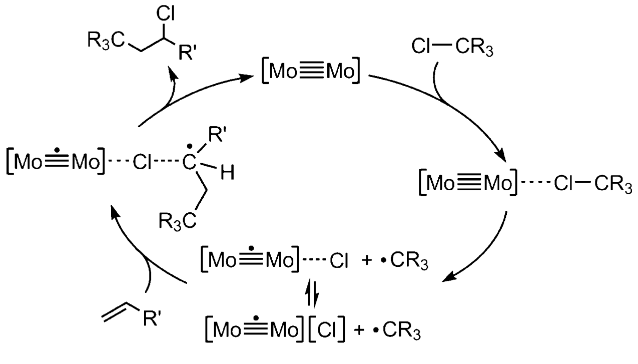


3 **6** (1)

The structure of **6** reveals the formation of the ionic compound, where a bromide anion is found as a well-separated anion[11]

(Figure S3†), in contrast to the Mo$_2$ complexes with carboxylate- or cyclic guanidinate-based ligands,[6,12] where the halide anion or the halogen atom of BF$_4$ or PF$_6$ coordinates to the axial site of the Mo$_2$ core. The cationic part of **6** is essentially the same as the previously reported [**3**$^+$][BF$_4$],[13] indicating that benzyl bromide acts as an oxidant of **3**. UV-vis spectral monitoring of the oxidation reaction revealed that compound **3** was cleanly converted to compound **6** with an isosbestic point.[14] The activation of the carbon–halogen bond by **3** proceeds through a single electron-transfer mechanism.[15] Recent studies on the mechanism of carbon–halogen bond reductive cleavage of alkyl halides revealed that electron transfer to alkyl halides did not produce anion-radical species *via* an outer-sphere electron transfer mechanism.[15d] In addition, the 2,4,6-triisopropylbenzoate-ligated cluster **1** possesses enough space for coordination of the halogen atom to the axial site.[6,12] We thus presume that the carbon–halogen bond activation proceeds through weak interaction of alkyl halides at the axial position of the Mo$_2$ core in solution. In the case of bulky amidinate or guanidinate ligands, coordination of halide anions to the axial site is unfavorable due to the steric repulsion. Accordingly, the bromide anion was found as a counter anion for the complex **6**.

Based on the oxidation reaction of **3** by alkyl halides *via* a single electron transfer, and the commonly accepted mechanism for the low-valent metal catalyzed radical addition reaction,[3] we propose the catalytic cycle for the radical addition reaction as shown in Scheme 2. At the first stage, the Mo$_2$ complex **3** interacts with alkyl halides to transfer a single electron from the Mo$_2$(II,II) core to yield the carbon radicals, $^{\bullet}CR_3$, the halide anion, and Mo$_2$(II,III) species. The halide anion might weakly interact with the Mo$_2$ core or be positioned as a separated anion, and both species are in equilibrium in solution. In the case of **6**, formation of the ionic species is more favorable due to the steric repulsion between the bromide anion and the guanidinate ligand. Subsequent addition of the carbon radical to alkenes generates Mo$_2$(II,III) and new radical species. Finally, one electron reduction of Mo$_2$(II,III) by the radical species results in the formation of a coupling product and regeneration of the catalytically active species, Mo$_2$(II,II). The low catalytic activity of **3** for the radical addition reaction may be due to the difficulty of the one-electron reduction of Mo$_2$(II,III) species by the radical, leading to deactivation by a recombination of the carbon radicals.



Scheme 2 Plausible reaction mechanism.

In summary, we developed radical addition and polymerization reactions catalyzed by dinuclear group 6 metal complexes bearing a metal–metal multiple bond, where the choice of supporting ligands plays an important role in the catalytic behavior. This is, to the best of our knowledge, the first example of dinuclear group 6 metal complexes having metal–metal multiple bonds for radical addition reactions *via* a single electron transfer process. Further extension of the metal cluster chemistry having metal–metal multiple bonds in the area of various catalytic transformations is ongoing in our laboratory.

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10 Incorporation of alkyl halides to the polymer was confirmed by the ^{1}H NMR spectra. The ^{1}H NMR spectra of the resulting polymers are shown in Supporting Information (Fig. S1 and S2†).

11 X-Ray diffraction data for **6** (CCDC 809907, see Figure S2†). $C_{88}H_{88}BrMo_2N_{12}O_{13}$, orthorhombic, $Pna2_1$, T = 113(2)K, No. of

reflections measured total/unique = 24978/9098, R_{int} = 0.0896, a = 26.340(8) Å, b = 15.955(4) Å, c = 18.695(5) Å, V = 7857(4) Å^3, Z = 4, $R1$ [$I > 2\sigma(I)$] = 0.0809, $wR2$ [$I > 2\sigma(I)$] = 0.1661, $R1$ [all data] = 0.1336, $wR2$ [all data] = 0.2089.

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