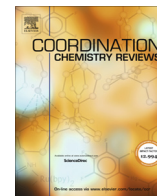




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## Review

## Multiply-bonded dinuclear complexes of early-transition metals as minimum entities of metal cluster catalysts

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## ABSTRACT

Dinuclear complexes of early-transition metals of group 5 (Nb and Ta), 6 (Cr, Mo, and W), and 7 (Re) tend to form multiple bonds between two metal centers, *i.e.*, double, triple, quadruple, and quintuple bonds. These complexes have intrinsic features such as (1) redox properties caused by the multiple metal–metal bond responses for mediating the oxidation and reduction of an organic substrate, and (2) unoccupied  $d\sigma^*$ -orbitals at each axial position of metal–metal multiple bonds for accepting donor molecules as inimitable Lewis acid catalysts. In addition, the metal–metal multiple bonds in the dinuclear complexes participate in metallacycle formation in combination with alkynes. In this review, we summarize the unique reactivity of multiply-bonded dinuclear complexes as reagents and catalysts for some organic transformations such as radical transformation of haloalkanes including radical addition, hydrodehalogenation, and radical polymerization; alkyne cyclotrimerization; ring-opening metathesis polymerization (ROMP) of cyclic alkenes or alkynes; metathesis reaction; hydrogenation of alkenes; Lewis-acid site mediated transformation namely regiospecific ring-opening of  $\alpha,\beta$ -epoxysilanes, Aza-Diels–Alder, Mukaiyama–Aldol, Strecker, and cyclopropanation reaction.

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## Contents

|   |    |
|---|----|
| 1. Introduction   | 00 |
| 2. Quadruply-bonded dinuclear complexes                       | 00 |
| 2.1. Radical reactions of haloalkanes                         | 00 |
| 2.2. Lewis acid-catalyzed C–C bond-forming reaction           | 00 |
| 2.3. Cyclopropanation reaction                                | 00 |
| 2.4. Metathesis reaction                                      | 00 |
| 2.5. Alkyne cyclotrimerization                                | 00 |
| 3. Triply-bonded dinuclear complexes                          | 00 |
| 3.1. Alkyne metathesis  | 00 |
| 3.2. Nitrile metathesis                                       | 00 |
| 3.3. Alkyne cyclotrimerization                                | 00 |
| 3.4. Polymerization of terminal alkynes and norbornene        | 00 |
| 3.5. Hydrogenation of conjugated dienes and cyclic alkenes    | 00 |
| 4. Doubly-bonded dinuclear complexes                          | 00 |
| 4.1. Ring-opening metathesis polymerization of cyclic alkenes | 00 |
| 4.2. Alkyne cyclotrimerization and polymerization             | 00 |
| 5. Quintuply-bonded dinuclear complexes                       | 00 |

Abbreviations: Acac, acetylacetonate; Ar, aryl; Bn, benzyl; Br, bromo; Bu, butyl; Cl, chloro; Cu, copper; DCM, dichloromethane; DMF, dimethylformamide; Et, ethyl; H, hour; Hpp, 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidin-2-ylidene; <sup>i</sup>Pr, *iso*-propyl; K, potassium; Me, methyl; Mo, molybdenum; Na, sodium; Nb, niobium; Ph, phenyl; PMMA, polymethylmethacrylate; Py, pyridine; Re, rhenium; Rh, rhodium; ROMP, ring-opening metathesis polymerization; Ta, tantalum; <sup>t</sup>Bu, *tert*-butyl; THF, tetrahydrofuran; THT, tetrahydrothiophene; TMSCN, trimethylsilyl cyanide; W, tungsten.

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|                                       |    |
|---------------------------------------|----|
| 5.1. Alkyne cyclotrimerizations ..... | 00 |
| 6. Conclusion .....                   | 00 |
| Acknowledgements .....                | 00 |
| Appendix A. Supplementary data .....  | 00 |
| References .....                      | 00 |

## 1. Introduction

Metal-assisted organic transformations have attracted the interest of organic chemists due to the outcomes of transformative reaction processes, which continuously produce chemicals used in daily life. Traditionally, metal catalysts are categorized as homogeneous or heterogeneous catalysts. Homogeneous mononuclear complexes of most useful noble late-transition metals, such as ruthenium, rhodium, iridium, palladium, and platinum undergo two-electron processes involving oxidative addition, reductive elimination, and metallacycle formation, whose fundamental reactivity has been elucidated by comprehensive studies using well-defined mononuclear organometallic complexes [1–6]. Heterogeneous systems have been intensively investigated due to their versatility and reusability for economic production of a vast array of chemicals, whereas the understanding of their mechanisms is limited except for surface model systems [7–13]. Recent studies, therefore, have been focused on downsizing heterogeneous catalysts [14–16], and/or increasing aggregation of metal nuclearity from homogenous metal complexes to multi-metal species such as metal clusters [17–19] and metal nanoparticles [20–22]. In this context, we are interested in the reactivity of metal cluster catalysts, among which dinuclear complexes of transition metals are considered as minimum models.

Since the discovery of quadruply-bonded complexes such as  $K_2Re_2Cl_8 \cdot 2H_2O$  [23] and  $Mo_2(OCOCH_3)_4$  [24], many dinuclear complexes with multiple metal–metal bonds (double, triple, quadruple, and quintuple) [25–30] have been prepared using mono- or di-anionic bidentate bridging ligands, such as carboxylate (**L1**), sulfonate (**L2**), thioate (**L3**), formamidinate (**L4**), guanidinate (**L5**), triazenido (**L6**), carboxamidate (**L7**), pyridylolate (**L8**), pyridylamidinate (**L9**), enolate (**L10**), and carbonate (**L11**) (Fig. 1) [25]. The close proximity of the two metal centers enables to show oxidative addition of substrates across the metal–metal multiple bonds as well as metallacycle formation in the presence of unsaturated hydrocarbons [31–36]. The presence of energetically high  $\delta$ -bonding electrons in the metal–metal quadruple bond is expected to participate in redox reactions such as radical transformations [37–39]. Another feature of paddlewheel metal–metal multiple bonds is the unoccupied  $d\sigma^*$ -orbitals in axial positions, with which any donor molecules can interact, allowing for their potential actions as unique Lewis acid catalysts. In this review, we focus on early-transition metal dinuclear complexes bearing metal–metal bonds with the bond order of two or more than two to emphasize these attractive properties and demonstrate their stoichiometric and catalytic organic transformations, though citing some review articles and representative references of paddlewheel dinuclear complexes of ruthenium and rhodium used for cyclopropanation [40–46], oxygenation of sulfides [47–50], oxidation of alcohols and amines [51,52], benzylic or allylic oxidation [53–55], ring-opening metathesis polymerization (ROMP) [56], olefin metathesis [57,58], hydrogenation [59,60], C–H functionalization [61–65], aziridination [66–68], and hetero-Diels–Alder reaction [69,70].

## 2. Quadruply-bonded dinuclear complexes

Dinuclear complexes of group 6 metals (Cr, Mo, and W) in an oxidation state of two and rhenium (III) typically possess a quadru-

ple metal–metal bond ( $\sigma^2\pi^4\delta^2$ ) (Fig. 2) supported either by monodentate ligands or by four bridging ligands, such as carboxylates, amides, pyrolidines etc. [25,27]. In the case of four bridging ligands ligated dinuclear complexes, especially in group 6 metals, such complexes referred to as “paddlewheel complexes” based on the paddlewheel appearance of the four bridging ligands exhibit (1) redox properties of the electron rich dinuclear moiety, with which a one- or two-electron process proceeds reversibly to mediate some redox reactions, including radical transformations, and (2) open coordination sites at both of the axial positions of the dinuclear unit, where vacant  $\sigma^*$ -orbitals act as acceptors and are clearly differentiated from other vacant  $\delta^*$ - and  $\pi^*$ -orbitals.

### 2.1. Radical reactions of haloalkanes

Many quadruply-bonded dinuclear complexes with bridging ligands have the lowest energy for metal  $\delta$ -orbital to ligand  $\pi^*$ -orbital charge transfer (MLCT) [71]. The MLCT process also supports the one-electron redox process from the quadruply-bonded dinuclear complexes to the external substrates, which resulted in reductively cleaving a carbon–halogen bond in organic halides to generate organic radicals [37–39,72–76], though various transition metals have been used as catalysts for radical transformations of haloalkanes and haloaryls, including the Kharasch addition [77–83], radical polymerization [84–88], hydrodehalogenation reaction [89–91], and others [92–94], as well as similar phenomena are observed with Ru and Rh metal–metal bonded complexes [95,96]. In fact,  $Mo_2(OPO(OPh)_2)_4$  (**2**) reacted with 1,2-dichloroethane under photoirradiation to form ethylene and the one-electron oxidized complex,  $Mo_2(OPO(OPh)_2)_4Cl$  (**3**) (Scheme 1) [72]. Photoirradiation ( $h\nu > 435$  nm) of  $W_2(dppm)_2Cl_4$  (**4**:  $dppm = \text{bis}(\text{diphenylphosphino})\text{methane}$ ) in the presence of iodomethane proceeded smoothly to give  $W_2(dppm)_2(\mu-Cl)_2Cl_2(CH_3)I$  (**5**) (Scheme 2) [73]. The reaction pathway was assumed to involve the zwitterionic excited state of mixed-valence dinuclear species **4'** containing W(I) and W(III), the former tungsten(I) which reacted with iodomethane to give complex **5** [97–100]. A similar carbon–halogen bond cleavage in a thermal reaction was reported for a tungsten complex of  $W_2(hpp)_4$  (**6**:  $hpp = \text{the anion of 1,3,4,6,7,8-h exahydro-2H-pyrimido}[1,2-a]\text{pyrimidine}$ ), in which the ligation of four  $hpp$  ligands significantly enhanced the reactivity of the  $W_2$  core to readily undergo reductive cleavage of a  $C(sp^2)–Cl$  bond of 1,2-dichlorobenzene, giving  $W_2(hpp)_4Cl_2$  (**7**) along with the formation of 2,2'-dichlorobiphenyl (Scheme 3a) [76]. A molybdenum- $hpp$  analogue,  $Mo_2(hpp)_4$  (**8**), reacted with dichloromethane to give the one-electron oxidized  $Mo_2(II/III)$  complex,  $Mo_2(hpp)_4Cl$  (**9**), with the bond-order of 3.5 (Scheme 3b) [74].

We are interested in the redox properties of such quadruply-bonded dimolybdenum complexes. In fact, we found that one-electron redox property of  $Mo_2(OCOAr)_4$  (**10**:  $Ar = 2,4,6\text{-}iPr_3C_6H_2$ ) was used for a catalytic radical addition reaction of  $CCl_4$  to 1-hexene in THF- $d_8$  at 80 °C to give 1,1,1,3-tetrachloroheptane regioselectively in 84% yield (Scheme 4) [37]. Such catalytic performance of complex **10** led us to search for more active catalysts. Because the redox properties of the  $Mo_2$  complexes are changed by replacing the carboxylate ligands with other chelating ligands, we applied other homoleptic  $Mo_2$  complexes such as a tetraakis(amidinate)dimolybdenum complex,  $Mo_2(ArNCHNAr)_4$  (**11**:

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