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Supramolecular Assemblies of Multi-nuclear Transition Metal Complexes: Synthesis and Redox Properties

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Abstract

The synthetic features of supramolecular assemblies comprised of multi-nuclear transition metal complexes were reviewed by classification of the reaction patterns: (1) substitution reaction by bridging ligands, (2) substitution reaction by monodentate ligands, and (3) coupling reaction of functional groups attached to peripheral ligands. Architectural control for assembling multi-nuclear units is difficult because of the complicated ligand substitution reactions of metal clusters; but controlled ligand substitution of multi-metallic complexes recently became a targeted subject of coordination chemistry by introducing suitable bridging and monodentate ligands to keep multi-metallic entities intact, leading to the formation of 1D, 2D, and 3D supramolecules of multi-metallic units. Another synthetic protocol is aimed at transition metal-catalyzed coupling reactions of peripheral ligands that provide selective oligomerization of multi-metallic complexes. These supramolecules are of particular interest because of their unique redox properties centered at multi-metallic units, and their redox behaviors are described.

Abbreviations

DAniF = *N,N'*-bis(*p*-anisyl)formamidinate; DArF = *N,N'*-bis(aryl)formamidinate; DPhF = *N,N'*-diphenylformamidinate; dppm = bis(diphenylphosphino)methane; dppa = 1,2-

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bis(diphenylphosphino)acetylene; py = pyridine

Keywords

Supramolecular metal complexes, Cluster complexes, Redox property, Substitution reactions of linker ligands, coupling reaction of peripheral ligands

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1. Introduction

Molecularly assembled transition metal complexes have attracted considerable attention from chemists in the field of inorganic chemistry as well as material- and nano-chemistry because finely designed molecular architectures can potentially be applied to gas storage [1], separation [2], catalysis [3], and others [4-9]. Because each metal center has an intriguing redox process, the most attractive chemical properties of such assembled molecules are their unique multi-redox nature in association with nanoelectronics [10-13]: e.g., grid-type multi-metallic assemblies of mononuclear metal ions using nitrogen-based polydentate ligands show more than 10 electron redox processes in a stepwise manner [14]. Although any suitable organic linker can be used to connect each mononuclear metal ion, the total redox nature of the resulting architecture is, in principle, dependent on the nature of metal ions incorporated.

Multi-nuclear metal complexes, particularly those with a metal-metal bond, are the most suitable candidates for a multi-redox system [15], though molecular assemblies of multi-nuclear units have rarely been explored, presumably due to their complicated substitution pattern. Nonetheless, assembled supramolecules comprising multi-metallic units are anticipated to have unique redox properties compared with those composed of mononuclear units. Here, we review the supramolecular assemblies of multi-metallic entities classified by reaction patterns of the multi-metal precursors and provide a concise summary of the redox chemistry of supramolecules of multi-metallic entities.

2. Synthetic Methods

The synthetic methodologies developed to date are classified according to the reaction pattern : (1) substitution reaction by bridging ligands (Fig 1a), (2) substitution reaction by monodentate

ligands (Fig 1b), and (3) coupling reaction of functional group attached to peripheral ligands (Fig 1c).

Fig 1. Synthetic methods of supramolecular complexes based on metal cluster complexes. Monodentate linker ligands and bidentate linker ligands were defined as ligands having two or more mono/bidentate moieties, typically, at terminal positions in this review.

3. Substitution Reaction by Bidentate Linker Ligands

3.1. Paddle-wheel Complexes

A dinuclear paddle-wheel complex, in which two metals are proximately supported by four bridging monoanionic ligands and have a metal-metal bond or metal-metal interaction as typically depicted in Fig 2, is the simplest motif of multi-metallic complexes, and, hence, its structural features and chemical properties have continued to attract the interest of inorganic chemists and

have been the focus of intensive studies [16-19]. Such dinuclear paddle-wheel complexes are known for a wide variety of transition metals such as V, Nb, Cr, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, and Cu [16]. Among them, dinuclear complexes of Mo, Rh, and Ru are used mainly for constructing molecular assemblies.

Fig 2. Dinuclear paddle wheel complexes with schematic abbreviations of carboxylate and amidinate moiety in drawings.

Substitution reactions of equatorial bridging bidentate ligands together with equatorial monodentate ligands of dinuclear complexes are among the most advantageous synthetic protocols for building supramolecules of dinuclear entities [15,17-21]. Because the lability of monodentate and bidentate ligands is reliably in accordance with the following order, solvent (typically CH₃CN) > carboxylate > amidinate, it is consistent that replacement of the CH₃CN by suitable polycarboxylate linkers smoothly occurs to produce a number of supramolecules of Mo₂, Ru₂, and Rh₂. In the first demonstration of this reported by Chisholm and coworkers, a dimer complex **3** was prepared by the reaction of partially solvated Mo₂ complex [Mo₂(μ-OCO'Bu)₃(CH₃CN)₂](BF₄) (**2**), which was generated *in situ* from [Mo₂(μ-OCO'Bu)₄] (**1**), with 0.5 equiv of the lithiated dihydroxynaphthilidine (Fig 3) [22]. Dimer complexes of Mo₂ and W₂

bridged by diamidate and dicarboxylate linkers were similarly prepared [23]. A notable property of these dimer complexes is the electronic coupling between the two dimetal units, as evident by electrochemistry and electronic spectra of one-electron oxidized mixed-valent species [17].

Fig 3. Synthesis of a dimer of Mo₂ complex **3**.²⁴

Cotton *et al.* successfully prepared several supramolecules of dimetal entities using three different coordinating ligands on a Mo₂ core, namely amidinate, acetate, and CH₃CN ligands. Controlled substitution reactions of equatorial acetate ligands on [Mo₂(μ-OCOCH₃)₄] afforded a mixed-ligand Mo₂ complex, [Mo₂(μ-DAniF)₃(CH₃CN)₂](BF₄) [DAniF = *N,N'*-bis(*p*-anisyl)formamidinate], bearing three amidinate ligands and two acetonitrile ligands [24], the latter of which were easily replaced by dicarboxylate ligands to give dimer complexes of Mo₂ (**4a—c**) (Fig 4) [25]. Similarly, substitution reaction of the acetate ligand in a triamidinate Ru₂ complex [Ru₂Cl(μ-DArF)₃(μ-OCOCH₃)] with (tBu₄N)₂(O₂CC₆H₄CO₂), oxalic acid, and ferrocenedicarboxylic acid resulted in the formation of the corresponding linear dimers of Ru₂

(**5a—c**) (Fig 4) [26]. Dimers of Mo₂ complexes bridged by diamidate (**6a,b** and **7a—c**) [27], hydroxyquinone (**8a—c**) [28], aminoquinone (**9a,b**) [29], squarate (**10**) [30], sulfate (**11a**) [31], metal oxide (**11b,c**) [31], and metal alkoxide (**12a,b**) [32] were prepared in a similar manner (Fig 5). Electrochemical studies of dimers of Mo₂ showed stepwise one-electron oxidation due to Mo₂⁵⁺/Mo₂⁴⁺. Planar conjugated linker units efficiently promoted the interaction between Mo₂ units, and, thus, large $\Delta E_{1/2}$ values (>500 mV) were observed in complexes **7a—c**, **8a—c**, **9a**, and **9b**.

Fig 4. Structure of dimers of Mo₂ (**4a-c**) and Ru₂ (**5a-c**).

Fig 5. Structure of dimers of Mo₂ (**6-12**) connected by various bidentate linker ligands.

Discrete cyclic assemblies of the paddle-wheel entities were obtained by capping nonlabile ligands at *cis*-positions of the dimetal unit. Reaction of *cis*-[Mo₂(μ-DAniF)₂(CH₃CN)₄](BF₄)₂ with rigid dicarboxylic acids gave triangle oligomers **14a—c** and square ones **15a—g** [33], while flexible dicarboxylic acids such as malonic acid resulted in the formation of cyclic dimers **13a—i** (Fig 6) [34]. For tetrafluoroterephthalate- and oxalate-bridged complexes, triangle and square assemblies in solution were in equilibrium [35]. Electrochemical measurements of the Mo₂ tetramer in **15a**, **15c**, and **15d** showed stepwise oxidation processes due to Mo₂⁵⁺/Mo₂⁴⁺, while that of **15b** and **15e—g** showed only one wave. Similarly, cyclic complexes of Rh₂ (**16**, **17**, and **18a—**

g) and Ru₂ (**19a,b**) were synthesized by treating *cis*-capped precursors such as *cis*-[Rh₂(μ-DAniF)₂(CH₃CN)₄](BF₄)₂ and *cis*-[Ru₂Cl(μ-DAniF)₂(μ-OCOCH₃)₂] with the corresponding dicarboxylic acids (Fig 7) [33a,36,37].

Fig 6. Structure of cyclic oligomers of Mo₂ (**13-15**).

Fig 7. Structure of cyclic oligomers of Rh₂ (**16-19**).

Cage molecules **20a** and **20b**, comprising Mo₂ and Rh₂ units and a tridentate ligand, 1,3,5-C₆H₃(CO₂)₃, were reported by Cotton *et al.*: reactions of the *cis*-protected paddle-wheel Mo₂ and Rh₂ precursors, *cis*-[Mo₂(μ-DAniF)₂(CH₃CN)₄](BF₄)₂ and *cis*-[Rh₂(μ-DAniF)₂(CH₃CN)₆](BF₄)₂, with (*n*Bu₄N)₃(1,3,5-C₆H₃(CO₂)₃) afforded cage-like hexamers **20a** and **20b** (Fig 8) [39]. A similar procedure was conducted for the reaction of a Rh₂ complex, *cis*-[Rh₂(μ-

DAniF)₂(CH₃CN)₆](BF₄)₂, with (Et₄N)₄(calix[4]arene(CO₂)₄) to give **21**, in which a NEt₄⁺ cation was encapsulated in the cavity and, hence, the size of cation was crucial for the formation of the cage structure (Fig 8) [39]. Cage compounds comprising a dinuclear unit and bent dicarboxylate ligands were reported by Chisholm *et al.* [40], Zhou *et al.* [41], and Yaghi *et al.* [42]. Cyclic and differential pulse voltammetries of a cage-like hexamer of Rh₂ **20a** showed one wave due to the oxidation of the Rh₂ units (Rh₂⁵⁺/Rh₂⁴⁺), indicating almost no electrochemical communication among Rh₂ units. In contrast, those of **20b** exhibited three stepwise one-electron oxidation processes based on Mo₂⁵⁺/Mo₂⁴⁺, although the Δ*E*_{1/2} values (62 mV and 40 mV) of those processes were relatively small.

Fig 8. Structure of cage complexes of Rh₂ (**20a**, **21**) and Mo₂ (**20b**).

Some monodentate and bidentate phosphine ligands were used as nonlabile ligands for maintaining the dinuclear units [43,44]. Triphenylphosphine acted as a supporting P-C ligand for the Rh₂ unit of *cis*-[Rh₂(μ-OCOCH₃)₂(μ-(C₆H₄)PPh₂)₂(CH₃CO₂H)₂] (**21**) [45]. Molecular triangles **23a—c** were synthesized by the reaction of *cis*-[Rh₂((C₆H₄)PPh₂)₂(CH₃CN)₄](BF₄)₂,

which was generated by a solvation reaction of **22**, with $(^n\text{Bu}_4\text{N})_2(\text{O}_2\text{CCO}_2)$, $(^n\text{Bu}_4\text{N})_2(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)$, and $(^n\text{Bu}_4\text{N})_2(\text{O}_2\text{C}(\text{C}_6\text{H}_4)_2\text{CO}_2)$, respectively (Fig 9) [46]. Because of the chirality of **22**, resolved complexes **R-22** and **S-22** afforded the corresponding enantiopure triangles **RRR-23a—c** and **SSS-23a—c**, which were applied as homogeneous and heterogeneous catalysts for cyclopropanation of styrene with diazoethylacetate [47]. Walton *et al.* used a Re_2 complex $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\mu\text{-OCOCH}_3)]$ supported by diphosphine ligands to prepare dimer complexes **24a** and **24b** and a cyclic trimer, **25** (Fig 10) [48]. The electrochemical measurement of **23a** revealed oxidation processes as three separate redox waves attributed to $\text{Rh}_2^{5+}/\text{Rh}_2^{4+}$, indicating electrochemical coupling of the Rh_2 moieties through a short oxalate linker. Stepwise redox processes due to $\text{Re}_2^{6+}/\text{Re}_2^{5+}$ in complexes **24a** and **25** were also reported.

Fig 9. Structure of monomer (**22**) and trimers (**23**) of Rh_2 .

Fig 10. Structure of dimer (**24a,b**) and trimer (**25**) of Re_2 .

Notably, supramolecular compounds containing mononuclear group 10 metal entities were developed by Fujita *et al.* for Pd [50] and Stang *et al.* for Pt [20,50]; however, only a few dinuclear moieties of group 10 metals have been investigated. Yu *et al.* reported cyclic dimers **26a,b**, trimers **27a,b**, and tetramers **28a—f** bearing Pd_2 and Pt_2 units (Fig 11)[51].

Fig 11. Structure of cyclic dimers (**26a,b**), trimers (**27a,b**) and tetramers (**28a-f**) of Pd_2 .

3.2. Square Tetraplatinum Complexes

Mashima and co-workers have focused their efforts on an acetate-bridged tetraplatinum cluster complex $[\text{Pt}_4(\mu\text{-OCOCH}_3)_8]$ (**29**) [52,53] because of its potential to serve as a precursor for supramolecules containing tetraplatinum cluster entities. Ito *et al.* demonstrated that the four *in-plane* acetate ligands of **29** were selectively substituted by carboxylic acids [54], amines [55], amides [56], thiophosphite [57], pyridine [58], and so on [59], whereas the four *out-plane* acetate ligands of **29** remained intact. Simple addition of a half equivalent of dicarboxylic acid, which was thought to be the most straightforward synthetic route of its dimer, resulted in the formation of insoluble precipitates, presumably due to uncontrolled full substitution [60]. Thus, Mashima *et al.* synthesized four amidinate complexes of tetraplatinum that were used for preparing supramolecular assemblies containing a tetraplatinum core [61,62]. Electrochemical study of these tetraplatinum complexes bearing amidinate ligands revealed stepwise one-electron oxidation processes due to $\text{Pt}_4^{10+}/\text{Pt}_4^{9+}$ and $\text{Pt}_4^{9+}/\text{Pt}_4^{8+}$ [62]. Treatment of the *cis*-capped complex **30** with dicarboxylic acids yielded the corresponding cyclic tetramer **31**, and dimers **32a** and **32b**, whose structures were determined by single crystal X-ray analysis (Fig 12). The cyclic dimer **32a** connected by ferrocenedicarboxylic acid exhibited four step oxidation processes due to $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Pt}_4^{9+}/\text{Pt}_4^{8+}$, and $\text{Pt}_4^{10+}/\text{Pt}_4^{9+}$ in the electrochemical measurement. Notably, two ferrocenyl units oxidized in a stepwise manner, indicating that two iron centers electrochemically coupled through a Pt_4 moiety.

Fig 12. Synthesis and oligomerization of a bisamidinate tetraplatinum complex **30**.

Guanidinate ligands are also used for the capping group of tetraplatinum entities. The strongly donative nature of guanidinate ligands enables a unique stepwise substitution sequence in the substitution reaction of **33** with amidinate ligands. Upon treatment of a guanidinate-modified tetraplatinum complex **33** with bisamidine, a linear-shaped dimer **34** was isolated (Fig 13) [63]. Because **34** has a total of six acetate ligands at *in-plane* sites of two tetraplatinum cores, a substitution reaction of **34** with carboxylic acids proceeded. Electrochemical measurement of **33** and **34** exhibited a reversible oxidation process, which was attributed to Pt₄⁹⁺/Pt₄⁸⁺.

Fig 13. Synthesis and dimerization of a guanidinate tetraplatinum complex **33**.

3.3. Metal Carbonyl Complexes

Multi-metal carbonyls are typical organometallic clusters. A substitution reaction of CO ligands by donor ligands such as phosphines and nitrogen-based ligands was controllable, and, thus the addition of bidentate as well as polydentate donor ligands led to the oligomerization of multi-metal carbonyl clusters [63-69]. Reaction of a pentanuclear ruthenium carbide cluster, $[\text{Ru}_5\text{C}(\text{CO})_{15}]$, with N^1, N^1, N^4, N^4 -tetrakis((diphenylphosphino)methyl)butane-1,4-diamine afforded a dimer complex **35** (Fig 14) [70]. 3,3'-Bis(diphenylphosphino)-4,4'-bipyridine reacted with $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ and $[\text{Rh}_6(\text{CO})_{15}(\text{CH}_3\text{CN})]$ as well as their mixture to give the corresponding homodimer and heterodimer complexes **36—38** (Fig 15) [71].

Fig 14. Structure of complex **35**.

Fig 15. Structure of complex **36-38**

Cyclic trimers of dinuclear ruthenium carbonyl complex **40** were prepared by treating $[\text{Ru}_3(\text{CO})_{12}]$ (**39**) with tartaric acid, in which the nuclearity was decreased from three to two, accompanied by unique oxidative formation of Ru(I) that was bridged by two carboxylates (eq 1) [72]. The addition of a monodentate phosphine ligand did not induce the replacement of

carbonyl; but the phosphine coordinated to the axial positions of Ru₂ moieties to afford phosphine adducts of cyclic dimer (**41**), trimers (**42a,b**), and a tetramer (**43**) (Fig 16) [73].

Fig 16. Structure of cyclic oligomers of Ru₂ (**41-43**)

Alkyne units of diynes and triynes work as π -coordination ligands to the multi nuclear core to form linked supramolecules [74-77]. Dimers of Ir-Mo and Ir-W mixed-metal cluster complexes (**46a—c**, **47a,b**) were synthesized by substitution reactions of CO ligands in [M₂Ir₂(CO)₁₀(η^5 -C₅H₄Me)₂] (**44**: M = Mo, **45**: M = W) with diyne compounds (eq 8). Trimers of those mixed metal complexes were also prepared by treating **44** or **45** with triyne compounds [77a].

Electrochemical measurements of dimer complexes (**46a—c**, **47a,b**) revealed a one-electron reversible oxidation process, suggesting the presence of stable one-electron oxidized mixed-valence species. The $\Delta E_{1/2}$ values attributed to mixed-valence species, however, were not determined as a second oxidation process was irreversible.

4. Substitution Reaction by Monodentate Linker Ligands

4.1. Paddle-wheel Complexes

Another synthetic protocol for constructing discrete oligomers of paddle wheel dinuclear complexes is an axial coordination of bifunctional donor molecules [15,18,19]. Coordination of pyrazine axial position of two Ru₂ units formed a cationic dimer of Ru₂ complex **48** (Fig 17) [78], as a dimetallic analogue of the Creuz-Taube ion {[(NH₃)₅Ru]₂(C₄H₄N₂)}⁵⁺. Alkynyl linkages were introduced by Ren *et al.* who synthesized alkyne-bridged dimers of Ru₂ (**49a—e**) (Fig 17).

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The electron transfer behavior of **49a—e** revealed that two Ru₂ units electronically communicate with each other [79]. The coupling efficiency between Ru₂ units was highly dependent on the structure of linker units: the $\Delta E_{1/2}$ values due to stepwise redox processes of Ru₂⁵⁺/Ru₂⁴⁺ were 389 mV for **49a**, 180 mV for **49b**, and 190 mV for **49d**, whereas the redox process of **49c** was observed as only one wave ($\Delta E_{1/2} = 0$ mV). Moreover, a linear trimer of Ru₂ complex **50** had one central Ru^{III}Ru^{III} moiety and two terminal Ru^{II}Ru^{III} moieties bridged by two C $\equiv$ C–C $\equiv$ C diyne units [80] (Fig 17).. Recently, the synthesis and redox properties of a Ir₈ complex in which two Ir₄ units were connected by π -conjugated molecule were reported [81].

3,5) with 1 equiv of isonicotinic acid to give a square tetramer **53**, where one of benzoate derivative was replaced by the carboxylate group of an isonicotinate, and one of two axial sites of Rh₂ was occupied by a pyridyl moiety of the isonicotinate ligand (eq 3) [83]. Cyclic voltammetry of **51** and **53** did not show any splitting of the oxidation processes of Rh₂⁵⁺/Rh₂⁴⁺.

Fig 18. Structure of cyclic tetramer of Rh₂ (**51**)

4.2. Metal Carbonyl Complexes

Selective replacement of acetonitrile coordinated to a triosmium cluster, $[\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]$ (**54**), by 1,2-bis(diphenylphosphino)acetylene gave a dimer complex $[\text{Os}_3(\text{CO})_{11}]_2(\text{dppa})$ (**55**) (dppa = 1,2-bis(diphenylphosphino)acetylene) (eq 4) [84]. Similarly, dimers **56a** and **56b** of triruthenium carbonyl analogues were prepared by reactions of $[\text{Ru}_3(\text{CO})_{12}]$ (**43**) with diphosphine ligands such as 1,2-bis(diphenylphosphino)ethane and 1,4-bis(diphenylphosphino)benzene, respectively (eq 4) [85].

Polyacetylide ligands serve as a linker of platinum clusters bearing carbonyl and bulky phosphine ligands. Reaction of $[\text{Pt}_3(\mu\text{-P}^t\text{Bu}_2)_3(\text{CO})_2\text{Cl}]$ (**57**) with half an equivalent of triethynylbenzene in the presence of CuI and diethylamine afforded a dimer **58** of Pt₄ units (eq 5). This dimer **58** was further coupled with $[\text{Pt}_6(\mu\text{-P}^t\text{Bu}_2)_4(\text{CO})_4\text{Cl}_2]$ (**59**) under the same conditions, giving a supramolecule **60** (eq 6) [86].

4-3. Oxo-triruthenium Complexes

A series of oligomers of oxo-centered trinuclear ruthenium complexes $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-OCOCH}_3)_6(\text{L})_3]$ ($\text{L} = \text{pyridine}, \text{H}_2\text{O}, \text{CO}$ and so on) were prepared because those oligomers show a peculiar mixed valent electrochemistry among cluster units [87]. Meyer and co-workers first prepared dimers **61a** and **61b** and trimers **63a** and **63b** of ‘ Ru_3O ’ units bridged by pyridine and 4,4’-bipyridine by methanol substitution reactions of $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-OCOCH}_3)_6(\text{py})_2(\text{MeOH})]$ as

well as $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-OCOCH}_3)_6(\text{py})(\text{MeOH})_2]$ with complexes $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-OCOCH}_3)_6(\text{py})_2(\text{E-E})]$ (E-E = pyradine or 4,4'-bipyridine) (Fig 19) [88]. Ito and Kubiak *et al.* demonstrated that the electron transfer rate between two 'Ru₃O' units is as high as the rate of CO vibration ($\sim 1 \times 10^{12}$) using IR spectra of **62a** and **62b** together with their one or two electron-reduced dimer complexes [89].

Fig 19. Structure of dimers (**61,62**) and trimers (**63**) of Ru₃O.

4.4. Rhenium-selenide Complexes

Hexanuclear chalcogenide clusters $[\text{M}_6(\mu_3\text{-Q})_8]^{2-}$ (M = Mo, W, Re, Q = S, Se, and Te) comprise a discrete class of superconductive Chevrel phases. Among these hexanuclear clusters, the rhenium selenide cluster is the most extensively studied because of its stability under standard

synthetic conditions, including aerobic handling [90]. Upon treating $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PEt}_3)_5(\text{CH}_3\text{CN})](\text{BF}_4)$ (**64**) with polypyridine linkers, dimers **65a—c** were selectively obtained (eq 7) [91]. Similarly, cyclic tetramers **67a—c** were formed by the reaction of *cis*-capped cluster *cis*- $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PEt}_3)_4(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ (**66**) with polypyridine linkers (eq 8) [92]. Star-shaped trimers, tetramers [93], and dendrimers [94] were also prepared by treating a partially solvated precursor **64** with polypyridyl ligands. Oxidation processes due to the ‘ $\text{Re}_6(\mu_3\text{-Se})_8$ ’ core were observed as one wave in cyclic voltammetries of dimers **65a—c** and tetramers **67a—c**, and hence, there was almost no electronic coupling among cluster units.

5. Coupling Reactions on Peripheral Ligands

5.1. Olefin metathesis reaction

The coupling reaction of organic functional groups attached to each metal cluster unit is a powerful tool for preparing supramolecules [95]. An olefin metathesis approach to construct dimer clusters was first reported by Mashima *et al.* [60]. An equatorially-bridged dimer complex of Pt₄ **69** was synthesized as a mixture of *cis/trans* isomers by an olefin metathesis reaction of [Pt₄(μ-OCOCH₃)₇(μ-OCOCH₂CH₂CH=CH₂)] (**68**), which was prepared by a selective substitution reaction of an acetate ligand of **29** with 5-hexanoic acid (Fig 20). Ren *et al.* also reported the synthesis of dimer of paddle-wheel Ru₂ complexes **72** by an olefin metathesis reaction at the terminal olefin of complex **71** (Fig 7) [96].

Fig 20. Olefin metathesis reaction for dimerizing Pt₄ [60].

Fig 21. Olefin metathesis reaction for dimerizing Ru₂ [96].

5.2. Coupling reaction of terminal alkynes (Sonogashira Coupling)

Bis(alkynyl)PtL₂ complexes can be coupled to give rod-like poly(yne) polymers, that have unique liquid crystalline properties [97,98]. The same reaction was applied by Lehn *et al.* for coupling axially alkynyl Ru₂ complexes. Copper-catalyzed homo coupling of butandiyl-Ru₂ complex **73** and hetero coupling between **73** and **75** afforded a dimer **74** and a trimer **76**, respectively (eqs 9 and 10) [99]. Because of their instability in solution, however, electrochemical studies of these complexes were not reported. Diruthenium complexes bearing terminal alkyne moieties at equatorial positions [100] and some carbonyl clusters [77c,101] have also been coupled via transition metal-catalyzed reactions.

6. Concluding Remarks

In this review, we summarized supramolecular metal complexes based on a multi-metallic core from the synthetic point of view. Some supramolecular assemblies of paddle-wheel, tetraplatinum, and carbonyl complexes have been rationally synthesized by a controlled ligand substitution reaction by bridging-type linkers such as dicarboxylic acid, phosphines, and alkynes. Monodentate linker ligands such as diphosphines and oligopyridines also act as spacer groups of supramolecules comprising paddle-wheel complexes, carbonyl complexes, oxo-triruthenium complexes, and rhenium-selenide cluster complexes. Coupling reactions of the designed multi-metallic precursor complexes are another efficient methodology for synthesizing molecular assemblies, although reported examples are still limited. Additionally, some supramolecules show a fascinating redox property due to redox-active multi-metallic units, which is rarely observed in supramolecular complexes comprising monometallic complexes. We anticipate that this new series of redox-active supramolecular metal complexes will allow us to access molecular recognition as well as homogeneous catalysis by controlling the redox state of multi-metallic building blocks.

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GRAPHICAL ABSTRACT