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Symmetric and Unsymmetric "Dumbbells" of Ru_2–Alkynyl Units via C–C Bond Formation Reactions

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Oxidative homocoupling (Glaser) reaction of Ru_2 compounds bearing peripheral ethyne resulted in symmetric dimers. Cross-coupling (Sonogashira) reaction between Ru_2 compounds bearing peripheral iodo and ethyne groups yielded an unsymmetric dimer. Voltammetric data indicated that Ru_2 units in the symmetric dimers are noninteracting, and the unsymmetric dimer is best described as a weakly coupled push–pull compound.

Transition-metal ions have played important roles in supramolecular chemistry since its inception as either key structural elements for programmed assembly or donor/acceptor centers for the studies of charge-transfer processes.[1] Metallosupramolecular chemistry has gained tremendous popularity in the recent decade because of the elegant work from the laboratories of Fujita,[2] Stang,[3] Cotton,[4] Kitagawa,[5] and Yaghi,[6] which revealed structural complexity and materials properties surpassing those of organic supramolecules. In the realm of supramolecular assembly of bimetallic units, a number of Mo_2 and Rh_2 paddlewheel species have been organized into dimers, triangular trimers, and square tetramers through equatorial coordination of ditopic linkers.[4] It should be noted that almost all of the aforementioned assemblies were driven by coordination to metal center(s), which may significantly alter the electronic properties of building blocks. An obvious alternative is to assemble supramolecules via reactions at the peripheries of building blocks, where such a modular approach may yield materials of interesting properties.[7] An elegant example of the modular approach is the preparation of hybrid polymers of phenyleneethyne and polyoxometalate monomers through peripheral Sonogashira coupling and the demonstration of promising photoinduced charge separation therein.[8] Aiming at retaining the electronic properties of individual building blocks during the formation of supramolecules, we have developed a series of Ru_2-based compounds bearing reactive functional groups at the ligand periphery and demonstrated the feasibility of the peripheral C−C bond formation via cross-coupling reactions[9] including Suzuki and Sonogashira reactions.[10−12] Reported in this Communication are the first examples of the modular assembly of Ru_2 building blocks containing a single reactive site, namely, a monofunctional module, into both homo- and heterodimers.

The preparation of homodimers **2** is based on the $Ru_2[D(3,5\text{-}Cl_2Ph)F]_3(DMBA\text{-}4\text{-}C_2H)$ type compounds (**1a** and **1b** in Scheme 1), where $D(3,5\text{-}Cl_2Ph)F$ and DMBA-4-C_2H are respectively di(3,5-dichlorophenyl)formamidinate and *N*,*N*′-dimethyl-4-ethynebenzamidinate.[12] The presence of a peripheral ethyne unit enables compounds **1a** and **1b** to undergo the Glaser reaction.[13] Thus, compound **1a**, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)Cl$, was converted under Hay conditions [conditions (i) in Scheme 1] to compound **2a** in an isolated yield of 80%. It was discovered serendipitously that compound **1a** could also be dimerized under aerobic Sonogashira conditions [conditions (ii) in Scheme 1] in a yield (86%) slightly higher than that using Hay conditions. The dimeric nature of compound **2a** was confirmed by the observation of $[\mathbf{2a}]^+$ (2814) in matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The homodimerization was further extended to

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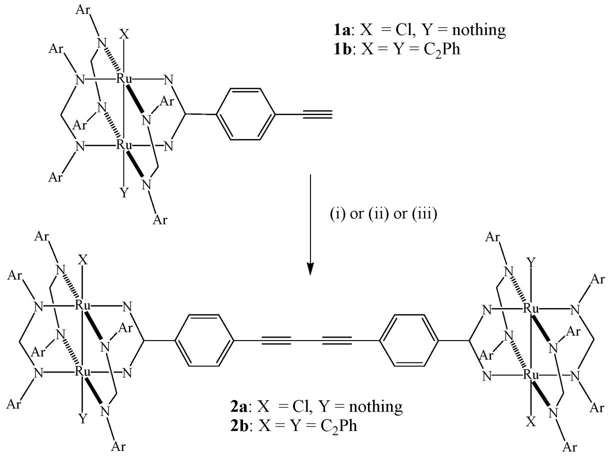
Scheme 1. Synthesis of Homodimers[a]



[a] Conditions: (i) **1a**, (0.05 g), THF (40 mL), excess TMEDA and CuCl, O_2 bubbling for ca. 1 h; yield of **2a**: 0.04 g, 80%; (ii) **1a**, (0.140 g), *trans*-$Pd(PPh_3)_2Cl_2$ (0.010 g), CuI (0.005 g), THF (15 mL), $^iPr_2NH$ (15 mL), stirring in air for 30 min, yield of **2a**: 0.12 g, 86%; (iii) **1b** (0.30 g), THF (40 mL), excess TMEDA, and CuCl, dry O_2 bubbling for 1 h, yield of **2b**: 0.12 g, 40%. Ar is 3,5-Cl_2Ph.

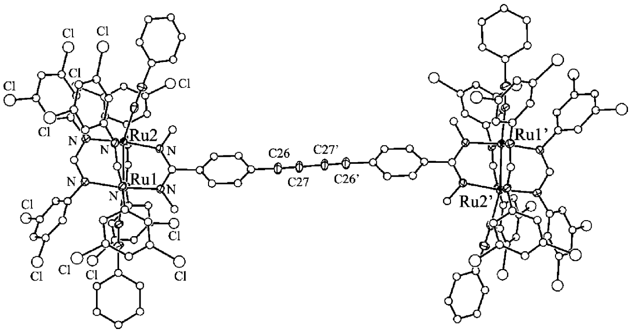


Figure 1. Structural plot of molecule **2b**. For clarity, H atoms were omitted. Both C and Cl atoms are shown as isotropic circles except acetylenic C atoms, which are shown as ellipsoids. Selected bond lengths (Å): Ru1−Ru2, 2.533(1); Ru−N(av), 2.057(7); C26−C27, 1.17(1); C27−C27′, 1.38(2).

the compound containing axial phenylacetylide, i.e., *trans*-$(PhC{\equiv}C)_2Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)$ (**1b**), which was converted to **2b** under Hay conditions in 40% yield. In addition to the observation of $[\mathbf{2b}]^+$ (3148) in MALDI-TOF-MS, the dimeric nature of **2b** was unambiguously verified by the determination of its crystal structure.[14] The structural plot of **2b** (Figure 1) clearly reveals both the butadiyne fragment (C26−C27−C27′−C26′) derived from the dimerization of **1b** and a "dumbbell" overall feature of **2b**.[14] Related by a crystallographic inversion center bisecting the C27−C27′ bond, two Ru_2 units in **2b** display a coordination geometry nearly identical with that of **1b**.[12] The middle PhC≡CC≡CPh fragment is rigorously coplanar (constrained by the inversion center), and it is canted at about 70° with respect to the adjacent amidinate (N−C−N) fragment, a feature also observed in the structure of **1b**.[12]

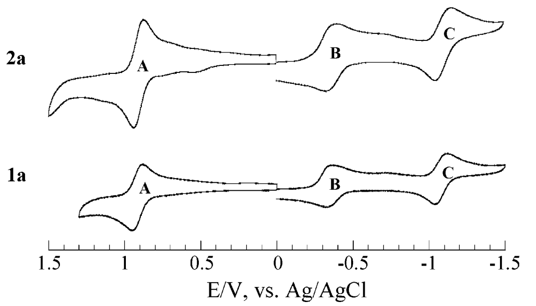


Figure 2. CVs of **1a** and **2a** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

The dimer of "dimers" formed from Mo_2/W_2 units linked by a dicarboxylate has been studied extensively by the laboratories of Cotton and Chisholm,[15−17] and the electronic coupling was detected with voltammetric techniques at $d_{M_2-M_2}$ (defined as the distance between centroids of the M_2 units) up to 16 Å.[16] To examine the possible coupling between two Ru_2 units in **2a**, a cyclic voltammogram (CV) of **2a** was measured and compared with that of **1a** in Figure 2. The CV of **1a** features three *one-electron* couples: a reversible oxidation **A**, an irreversible reduction **B**, and quasireversible reduction **C**.[12] The CV of **2a** is nearly identical with that of **1a** except that the peak currents are doubled. Clearly, two equivalent Ru_2 units behave as completely independent redox centers and give rise to three *two-electron* couples. A similar comparison can be made between the CVs of compounds **1b** and **2b** (Supporting Information). The absence of a significant cooperative interaction in **2** may be attributed to the extended separation between two Ru_2 units: the $d_{M_2-M_2}$ of molecule **2b** is 20.49 Å. The nature of orbital interactions along the superexchange pathway is also a factor: the δ orbital (highest occupied molecular orbital) of the Mo_2/W_2 moiety has a strong overlap with the empty $\pi^*(O_2C-)$ orbital of the dicarboxylate bridge,[16,17] while the empty $\pi^*(N-C-N)$ of the amidinate bridge is too high in energy to interact with the valence orbitals on the Ru_2 core.

One of the advantages of a modular approach is the possibility of cross-coupling of two chemically *different* modules, which results in an unsymmetric dimer. To illustrate such chemical selectivity, the Sonogashira coupling reaction between a pair of known compounds $Ru_2Cl(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}I)$[12] (**3**) and $Ru_2Cl(DmAniF)_3(DMBA\text{-}4\text{-}C_2H)$[11] (**4**) was tested (Scheme 2). It was found that the success of coupling reaction depends on the choice of organic bases: use of $^iPr_2NH$ only led to a trace amount of the desired heterodimer **5,** while most of the starting material **4** was homodimerized. On the other hand, homodimerization was

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(14) X-ray diffraction data for crystal **2b** were collected on a Bruker SMART1000 CCD diffractometer using Mo Kα at 300 K. Crystal data for $\mathbf{2b}\cdot 6THF\cdot 2CH_3OH$: $C_{146}H_{82}Cl_{24}N_{16}O_5Ru_4$, fw = 3395.36, monoclinic, *C*2/*c*, $a = 56.510(9)$ Å, $b = 13.073(2)$ Å, $c = 23.723(4)$ Å, $\beta = 104.31(2)°$, $V = 16981(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.284$ g cm^{-3}. Of 37 942 reflections measured, 12 202 were unique ($R_{int} = 0.108$). Least-squares refinement based on 6647 reflections with $I \geq 2\sigma(I)$ and 783 parameters led to convergence with final R1 = 0.071 and wR2 = 0.186.

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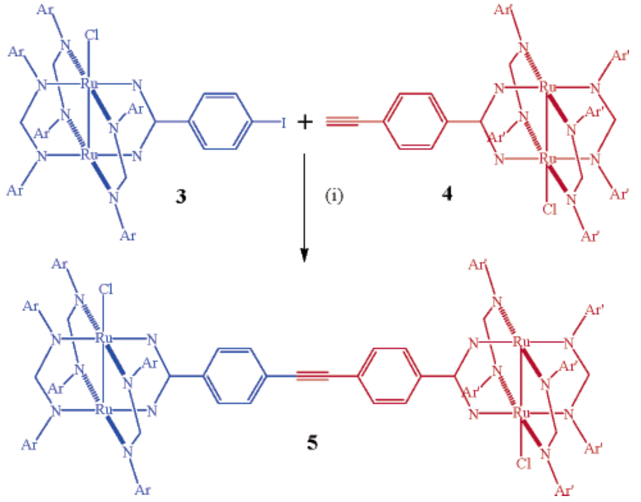
Scheme 2. Synthesis of Heterodimers[a]



[a] Conditions: (i) **3** (0.20 g), **4** (0.14 g), *trans*-Pd(PPh$_3$)$_2$Cl$_2$ (0.01 g), CuI (0.005 g), ^{i}Pr$_2$NEt (10 mL), and THF (20 mL) was stirred under N$_2$ at room temperature for 4 h, yield of **5**, 0.15 g, 52%, Ar = 3,5-Cl$_2$Ph, Ar′ = 3-MeOPh.

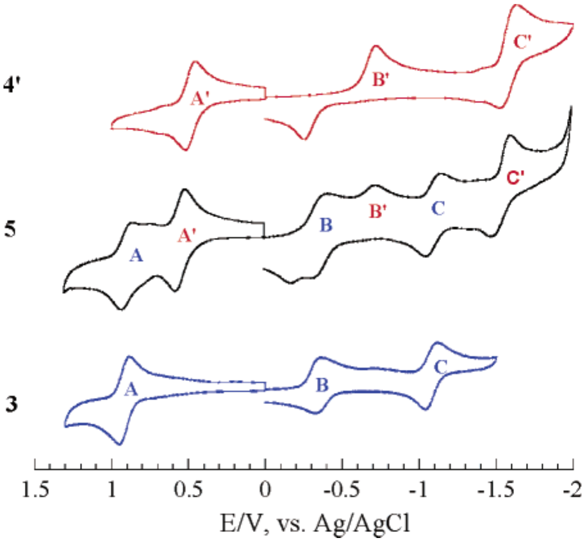


Figure 3. CVs of compounds **3**, **4′**, and **5** recorded in a 0.20 M THF solution of Bu$_4$NPF$_6$ at a scan rate of 0.10 V/s.

minimized with the use of ^{i}Pr$_2$EtN, and the heterodimer **5** was obtained with a yield of 52% after chromatographic purification. Compound **5** was converted to the corresponding axial alkynyl derivative [*trans*-(Me$_3$SiC$_4$)$_2$Ru$_2$(D(3,5-Cl$_2$-Ph)F)$_3$](*μ*-*N*,*N′*,*N″*,*N‴*-DMBA-C$_2$-DMBA)[*trans*-(Me$_3$SiC$_4$)$_2$-Ru$_2$(DmAniF)$_3$] (**6**) via the reaction with 10 equiv of LiC$_4$SiMe$_3$. Although crystallizations of compounds **5** and **6** remain unsuccessful, they were positively identified from MALDI-TOF-MS ([**5**]$^+$, 2556) and electospray ionization (ESI)-MS ([**6**]$^+$, 2970) data and yielded satisfactory combustion analysis data.

The redox behavior of heterodimer **5** is naturally enticing because of the presence of two nonequivalent redox centers. The CV of compound **5** (Figure 3) appears very complicated with six one-electron couples, and one may naively assume the appearance as evidence for electronic coupling between two Ru$_2$ centers. However, careful comparison with the CVs of **3** and **4′** [**4′** is Ru$_2$Cl(DmAniF)$_3$(DMBA-4-C$_2$Si^{i}Pr$_3$)] revealed that three couples of compound **5**, namely, **A**, **B**, and **C**, have electrode potentials very close to those of the corresponding couples of **3**, while the remaining three couples, i.e., **A′**, **B′,** and **C′**, have electrode potentials close to those of **4′**. Similar to the case of symmetric compound **3**, two Ru$_2$ centers in **5** are not strongly coupled. Further examination of the electrode potential data (Supporting Information) also revealed that the **A′**, **B′**, and **C′** couples in compound **5** were anodically shifted from those in compound **4′**, while the **A**, **B**, and **C** couples in **5** were cathodically shifted from those in **3**. These subtle shifts (less than 70 mV) are indicative that compound **5** is a weakly coupled push−pull pair: the very electron-deficient Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$ end [the Hammett constant (σ) of the 3,5-Cl$_2$ substituent is 0.74][18] draws a small amount of electron density from the electron-*richer* Ru$_2$Cl(DmAniF)$_3$ end [σ(3-MeO) = 0.12], hence the cathodic shift of Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$-based couples, and vice versa.

In summary, the utility of peripheral modification in preparing a simple dimer of “dimers”, especially the unsymmetric dimer, has been demonstrated. In addition to an extensive array of two- and three-dimensional motifs uncovered by the laboratory of Cotton,[4] a number of interesting motifs, including honeycomb/Kagomé nets and cuboctahedral cages, have been reported.[19] Inspired by these beautiful examples, we envision the assembly of two-dimensional supramolecules including triangles, squares, and networks in the near future, for which a set of cis-difunctional building blocks has already been developed.[11,12]

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Supporting Information Available: Detailed synthesis and characterization of compounds **2a**, **2b**, **5**, and **6** and X-ray crystallographic files in CIF format for the structural determination of compound **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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