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Article

Olefin Metathesis as an Inorganic Synthetic Tool: Cross and Ring Closing Metathesis Reactions of Diruthenium-Bound ω-Alkene-α-carboxylates

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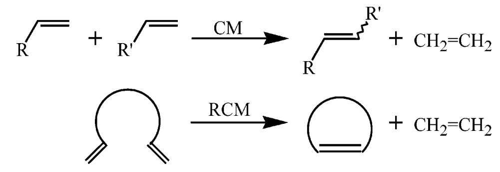
Diruthenium compounds containing one ω-alkene-α-carboxylate ligand, $Ru_2Cl(D(3,5\text{-}Cl_2Ph)F)_3(O_2C(CH_2)_nCH{=}CH_2)$ ($n = 1$ (**1a**) and 2 (**1b**)), were prepared from the reaction between $Ru_2Cl(D(3,5\text{-}Cl_2Ph)F)_3(O_2CCH_3)$ ($D(3,5\text{-}Cl_2Ph)F$ $=$ *N,N′*-bis(3,5-dicholorophenyl)formamidinate) and the corresponding ω-alkene-α-carboxylic acid. Compounds **1a** and **1b** both underwent olefin cross metathesis reactions catalyzed by $(Cy_3P)_2Cl_2Ru({=}CHPh)$ to afford the dimerized compounds $[Ru_2Cl(D(3,5\text{-}Cl_2Ph)F)_3]_2(\mu\text{-}O_2C(CH_2)_nCH{=}CH(CH_2)_nCO_2)$ ($n = 1$ (**2a**) and 2 (**2b**)). Similarly, diruthenium compounds containing two ω-alkene-α-carboxylate ligands, *cis*-$Ru_2Cl(D(3,5\text{-}Cl_2Ph)F)_2(O_2C(CH_2)_nCH{=}CH_2)_2$ ($n =$ 1 (**3a**), 2 (**3b**), and 3 (**3c**)), were prepared by substituting the acetate ligands in *cis*-$Ru_2Cl(D(3,5\text{-}Cl_2Ph)F)_2(O_2CCH_3)_2$ with the corresponding ω-alkene-α-carboxylate ligands. Compounds **3** exhibited different reactivity under olefin metathesis conditions: both **3b** and **3c** underwent the intramolecular ring closing reaction quantitatively to afford compounds *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2C(CH_2)_nCH{=}CH_2(CH_2)_nCO_2)Cl$ with $n = 2$ (**4b**) and 3 (**4c**), respectively, but **3a** displayed no metathesis reactivity. Molecular structures of compounds **1a/1b**, **2a/2b**, **3a/3b**, and **4b** were established via X-ray diffraction studies, confirming the formation of cross and ring closing metathesis products. Voltammograms of compounds **2** are nearly identical to those of compounds **1**, indicating the absence of electronic interactions mediated by the tether derived from olefin metathesis.

Introduction

Scheme 1. Cross (CM) and Ring Closing (RCM) Olefin Metathesis



Since its discovery in the 1950s, olefin metathesis has emerged as an indispensable synthetic tool for the construction of carbon−carbon bonds. The application of catalytic olefin metathesis ranges widely from organic and polymer synthesis to materials and surface sciences.[1] In comparison, the scope of catalytic olefin metathesis in the synthesis of coordination and organometallic compounds remains very limited.[2] Earlier studies by Rudler demonstrated that the W compounds of carbene ligands bearing alkene tails underwent ring closing metathesis (RCM, see Scheme 1) with $WOCl_4/Ph_2SiH_2$ as the catalyst.[3] The RCM method was subsequently applied to the high yield synthesis of [2]catenanes and molecular knots templated by Cu[4] and later on polypyridine macrocycles templated by Pt−pincer complexes.[5] Various metallocene-containing species including dendrimers, poly-

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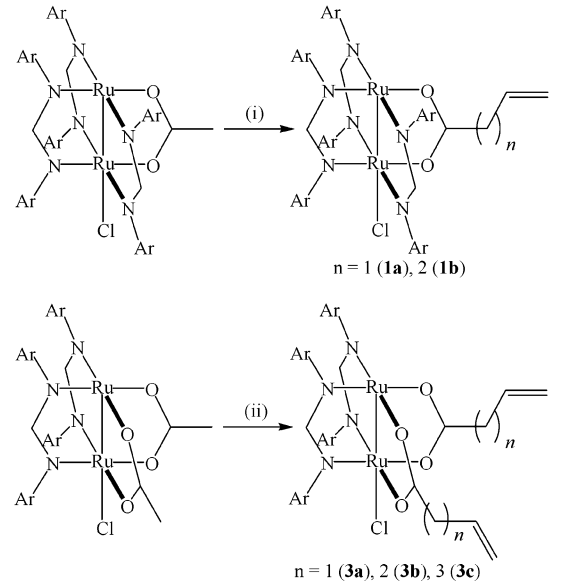
10.1021/ic070123l CCC: $37.00

Scheme 2. Preparation of Diruthenium-ω-alkene-α-carboxylate Compounds[a]

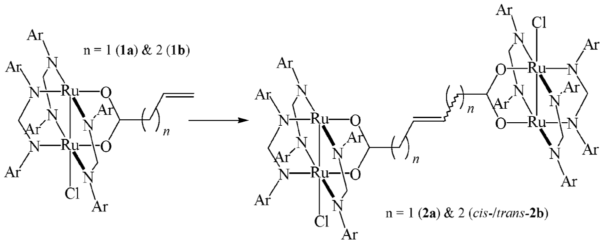


[a] Conditions: (i) 10 equiv of $HOOC(CH_2)_nCH{=}CH_2$, THF/MeOH (1/1), reflux; (ii) 2.2 equiv of $HOOC(CH_2)_nCH{=}CH_2$, toluene, reflux.

mers, and ansa-metallocenes have been prepared using either RCM, cross metathesis (CM, see Scheme 1), or ring opening metathesis polymerization reactions.[6] Polymers containing main group elements such as Sn and Si have also been prepared using the acyclic diene metathesis reaction (ADMET).[7] The most noteworthy are the creative efforts from the laboratory of Gladysz in applying RCM to a variety of metal compounds with phosphine ligands bearing terminal alkene, which resulted in novel compounds including sterically shielded linear Pt/Re−polyyne molecules and gyroscope-like molecules.[2,8,9]

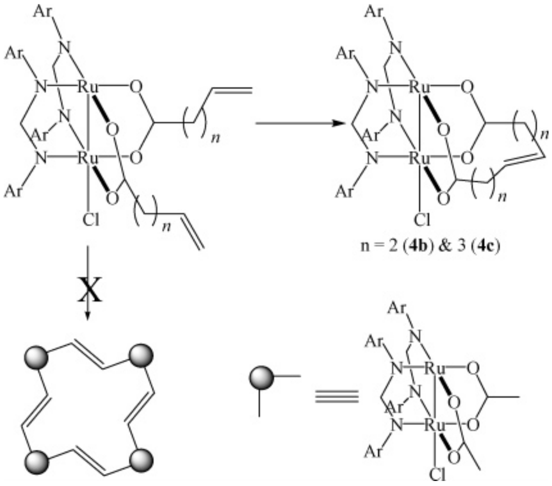
Our laboratory has been developing synthetic methods to covalently functionalize diruthenium compounds at the ligand periphery. The C−C bond formation reactions through either Sonogashira or Suzuki cross coupling were successfully executed with N,N′-bridging ligands bearing aryl iodo substituents.[10,11] Diruthenium compounds bearing a peripheral ethyne functional group, derived from Sonogashira coupling, can undergo further modifications including the Cu(I) catalyzed “click” reaction and oxidative homocoupling reactions.[12] It was communicated previously that diruthenium compounds containing a ω-alkene-α-carboxylate, namely, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(\mu\text{-}O_2C(CH_2)_nCH{=}CH_2)Cl$ ($n = 1$ (**1a**) and 2 (**1b**), $D(3,5\text{-}Cl_2Ph)F$ = *N,N′*-bis(3,5-dicholorophenyl)-formamidinate), underwent a cross metathesis reaction to yield dimeric structures (**2**).[13] Reported in this contribution are the detailed synthesis and characterization of compounds **1** and **2**, the ring closing metathesis reactions based on a new family of diruthenium species, *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2C(CH_2)_nCH{=}CH_2)_2Cl$ (($n = 1$ (**3a**), 2 (**3b**) and 3 (**3c**)).

Scheme 3. Cross Metathesis of MonoOlefin Compounds[a]



[a] Conditions: 5 mol % $(Cy_3P)_2Cl_2Ru({=}CHPh)$, CH_2Cl_2, reflux, overnight. Ar = 3,5-$Cl_2C_6H_3$.

Scheme 4. Metathesis of Diolefins[a]



[a] Conditions: 5 mol % $(Cy_3P)_2Cl_2Ru({=}CHPh)$, CH_2Cl_2, reflux, overnight.

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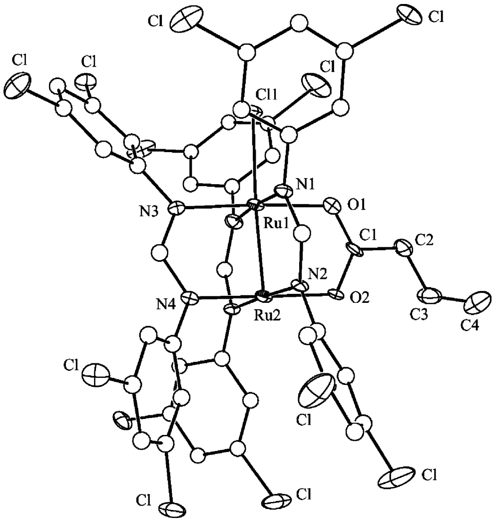

Figure 1. ORTEP plot of molecule **1a** at 30% probability level.

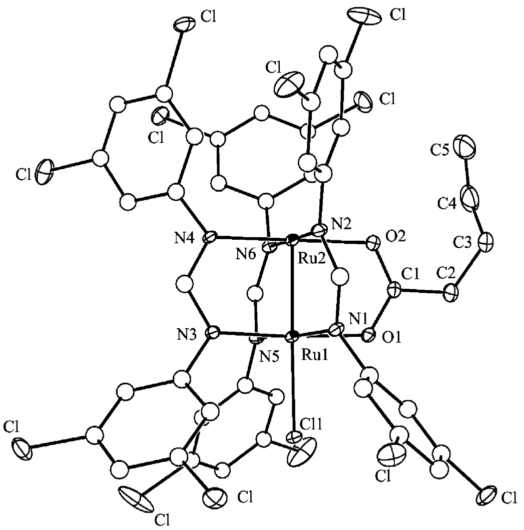

Figure 2. ORTEP plot of molecule **1b** at 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1a**, **1b**, *trans*-**2b**, and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$

	1a	**1b**	*trans*-**2b**	$Ru_2(D(3,5\text{-}Cl_2Ph)F)_3$ (OAc)Cl
Ru1−Ru2	2.321(2)	2.3131(4)	2.3285(9)	2.3220(7)
Ru1−Cl1	2.382(3)	2.3828(8)	2.382(2)	2.405(2)
Ru1−N1	2.102(11)	2.094(3)	2.076(6)	2.088(5)
Ru1−N3	2.068(10)	2.066(3)	2.071(7)	2.103(5)
Ru1−N5	2.073(12)	2.085(3)	2.080(6)	2.068(6)
Ru1−O1	2.060(9)	2.066(2)	2.059(6)	2.082(5)
Ru2−N2	2.051(12)	2.040(3)	2.052(7)	2.049(5)
Ru2−N4	2.032(11)	2.024(3)	2.023(6)	2.063(5)
Ru2−N6	2.035(12)	2.030(3)	2.051(6)	2.013(6)
Ru2−O2	2.045(9)	2.045(2)	2.040(6)	2.075(5)
C3−C4	1.29(2)			
C4−C5		1.356(9)		
C4−C4′			1.30(2)	
Ru2−Ru1−Cl1	176.13(11)	177.54(2)	173.98(6)	175.37(5)

Results and Discussion

Synthesis. The diruthenium compounds containing one or two ω-alkene-α-carboxylate ligands can be prepared by simple ligand exchange reactions. For example, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ readily reacted with $HO_2C(CH_2)_nCH{=}CH_2$ in excess ($n = 1$ and 2) under reflux in THF−MeOH to afford new compounds $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(\mu\text{-}O_2C(CH_2)_nCH{=}CH_2)Cl$ ($n = 1$, **1a**; 2, **1b**, Scheme 2). The crude products were further purified on a silica column to ensure the complete removal of some unidentified byproduct(s) that poison the metathesis catalyst. In contrast to the preparation of compounds **1**, reflux of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ with $HO_2C(CH_2)_nCH{=}CH_2$ in excess did not result in the anticipated *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2C(CH_2)_nCH{=}CH_2)_2Cl$ ($n = 1$, **3a**; 2, **3b**; 3, **3c**) in good yield. The accumulation of acetic acid during the reaction may prevent the reaction from completing. Nevertheless, compounds **3** were prepared in excellent yields by the combination of refluxing in toluene and the use of an acetic acid scrubbing apparatus described previously.[14] Similar to their precursors, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-n}(OAc)_nCl$ ($n = 1$ and 2), both **1** and **3** are $S = {}^3/_2$ molecules with effective magnetic moments ranging from 3.74 to 3.95 μ_B (μ_B is the Bohr magneton). The paramagnetisms persistent in compounds **1** and **3** and their metathetic derivatives **2** and **4** render their ^1H NMR spectra less useful, especially for the purpose of discerning the stereochemistry around the olefin function group.

Having incorporated either one or two ω-alkene-α-carboxylates into the coordination sphere of the diruthenium species, we were in position to investigate the feasibility of olefin metathesis reactions. Compound **1a** was refluxed in CH_2Cl_2 in the presence of $(Cy_3P)_2Cl_2Ru({=}CHPh)$, and a gradual buildup of a new compound, **2a**, was noted over a period of 5 days (Scheme 3). The dimeric nature of **2a** was confirmed by the observation of $[\mathbf{2a} - Cl_2]^+$ in MALDI-TOF-MS (2544). However, the conversion of **1a** to **2a** was only about 40%, despite several additions of fresh catalyst during the course of reaction. In contrast, refluxing compound **1b** under the same conditions resulted in a complete conversion of **1b** in 2 days to two new compounds that were similar in polarity ($R_f = 0.55$ and 0.45 in THF−hexanes, v/v: 1/5) and yielded the same $[\mathbf{2b} - Cl]^+$ peak in ESI-MS (2606). The new compounds are likely the cis-/trans-isomers, and the structural determination of the compound of $R_f = 0.45$ (see below) revealed a trans-configuration of the olefin bond derived from the CM reaction. It is interesting to note that the cross metathesis of the coordinated vinyl acetate in **1a** was slow and gave the trans-product only, while the reaction of the coordinated 4-pentenoate proceeded much faster and yielded a mixture of cis-/trans-products. Apparently, extension of the tether by a single methylene unit significantly reduces the steric strain imposed by the bulky diruthenium units during the CM reaction. Also critical is the use of chromatographically purified starting materials, as compounds **1** purified by recrystallization showed little or no reactivity under the same CM conditions. In comparison, the homodimerization reaction of acrylic acid was also classified as "slow" (15 h at 40 °C) with $(Cy_3P)(NHC)Cl_2Ru({=}CHPh)$ as the catalyst.[15] The effective magnetic mo-

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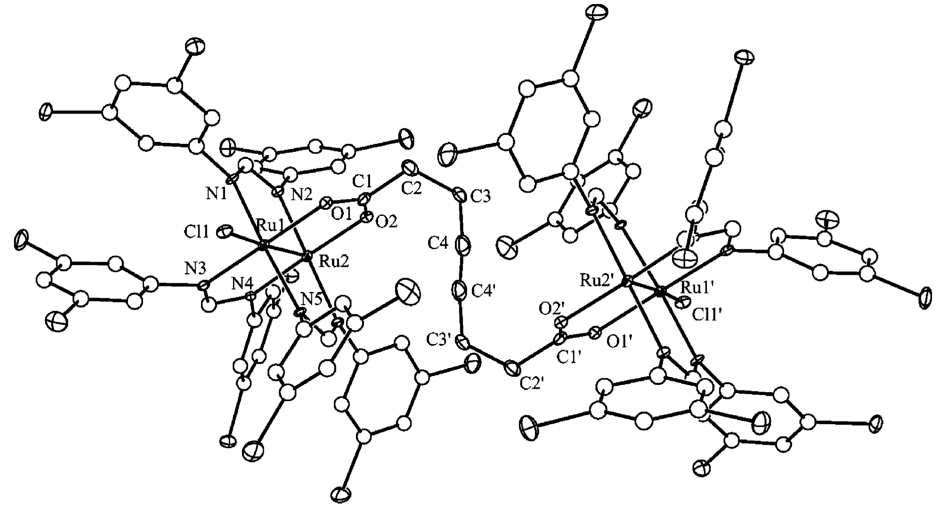


Figure 3. ORTEP plot of molecule *trans*-**2b** at 30% probability level.

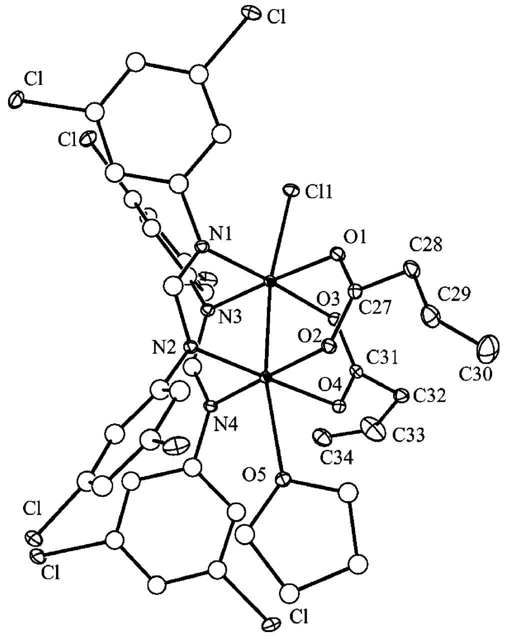


Figure 4. ORTEP plot of molecule **3a**·thf at 30% probability level.

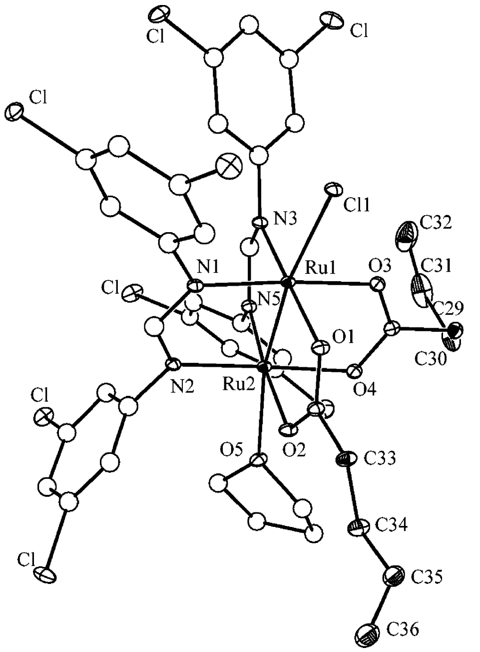


Figure 5. ORTEP plot of molecule **3b**·thf at 30% probability level.

ments of compounds **2a** and *cis-/trans-***2b** were estimated to be approximately 5.6 μ_B, which is close to the spin-only theoretical value of two noninteractive $S = {}^3/_2$ centers (5.48 μ_B).

The success of CM reactions with compounds **1** encouraged the examination of metathetic behavior of compounds **3**, where two terminal olefins in cis-arrangement might yield a macrocycle should an intermolecular CM reaction take place. Compound **3a**, however, showed no reactivity with either $(Cy_3P)_2Cl_2Ru(=CHPh)$ or $(Cy_3P)(NHC)Cl_2Ru(=CHPh)$ under the conditions outlined in Scheme 4. On the other hand, both compounds **3b** and **3c** were converted to new compounds **4b** and **4c** quantitatively under the same metathesis conditions (Scheme 4). Compounds **4b** and **4c** were identified as the ring closing metathesis (RCM) products based on the observation of [**4b** − Cl]$^+$ (1038) and [**4c** − Cl]$^+$ (1067) in ESI-MS and structural characterization of **4b**, the latter of which also revealed a trans-configuration of the olefin bridge. Lack of metathetic activity of compound **3a** is likely attributed to the fact that a single methylene tether between the carboxylate and olefin is simply too short. Our results for compounds **3b** and **3c** clearly indicate that the intramolecular RCM product is kinetically preferred. This is consistent with the conclusion from the earlier studies of mononuclear compounds bearing diolefins by Gladysz and co-workers.[8]

Molecular Structures. Single crystals of X-ray quality were obtained for compounds **1a**, **1b**, **2b**, **3a**, **3b**, and **4b**, and molecular structures of these compounds were determined through X-ray diffraction studies. The ORTEP plots of molecules **1a** and **1b** are shown in Figures 1 and 2, respectively. The similarity in Ru_2 coordination spheres among compounds **1a**, **1b**, and their precursor $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ is clear from the comparison of both the structural plots and key geometric parameters, including the Ru−N and Ru−O bond lengths listed in Table 1. The Ru−Ru bond lengths of compounds **1a** (2.321(2) Å) and **1b**

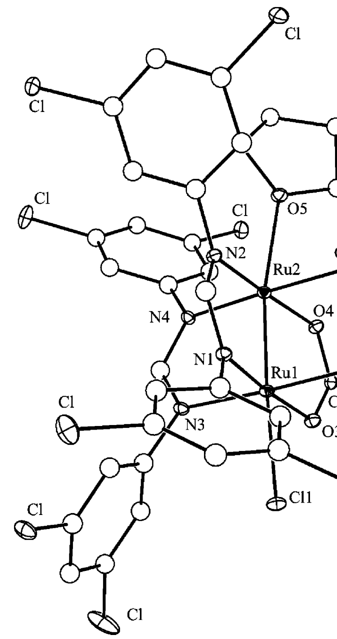


Figure 6. ORTEP plot of molecule **4b**·thf at 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **3a**, **3b**, **4b**, and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$

	3a	**3b**	**4b**	$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$
Ru1−Ru2	2.3210(2)	2.3227(2)	2.3222(3)	2.3267(7)
Ru1−N1	2.0576(16)	2.034(2)	2.030(2)	2.051(4)
Ru1−N3	2.0465(16)	2.028(2)	2.032(2)	2.063(4)
Ru2−N2	2.0270(16)	2.053(2)	2.048(3)	2.031(4)
Ru2−N4	2.0318(16)	2.058(2)	2.041(2)	2.030(4)
Ru1−O1	2.0474(13)	2.035(1)	2.048(2)	2.053(3)
Ru1−O3	2.0713(14)	2.048(1)	2.045(2)	2.054(3)
Ru2−O2	2.0376(13)	2.071(1)	2.065(2)	2.048(3)
Ru2−O4	2.0490(13)	2.048(1)	2.060(2)	2.043(3)
Ru2−O5	2.4165(13)	2.402(1)	2.403(2)	2.362(3)
Ru1−Cl1	2.4648(5)	2.4605(5)	2.4547(7)	2.480(1)
C29−C30	1.303(4)			
C33−C34	1.226(6)			
C31−C32		1.313(4)	1.41(1)	
C35−C36		1.346(6)		
Ru2−Ru1−Cl1	170.10(1)	170.51(1)		171.52(3)
Ru1−Ru2−O5	168.65(3)	168.27(4)		169.90(8)

(2.313(1) Å) are almost identical to that of $Ru_2(D(3,5\text{-}Cl_2\text{-}Ph)F)_3(OAc)Cl$ (2.322(1) Å), consistent with the invariance of electronic structures upon the substitution of acetate by ω-alkene-α-carboxylate. Interestingly, the lengths of the terminal olefin, 1.29(2) Å for C3−C4 in **1a** and 1.356(9) Å for C4−C5 in **1b**, differ significantly, which may be attributed to the positional disorder caused by the structural flexibility of terminal olefins. Also noteworthy is the averaged Ru−O distance for **1a/b** (approximately 2.05 Å), which is significantly longer than those of $Ru_2(O_2CR)_4Cl$ (2.02−2.03 Å)[16] due to the trans-influence of the $D(3,5\text{-}Cl_2\text{-}Ph)F$ ligand.

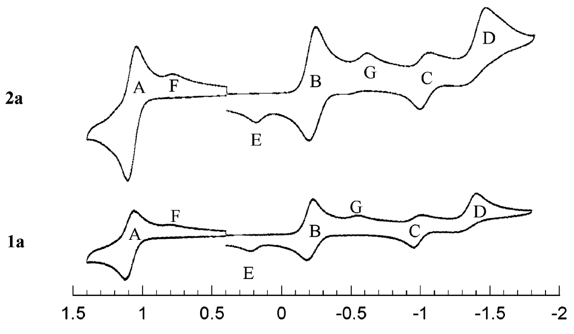


Figure 7. Cyclic voltammograms of **1a** and **2a** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

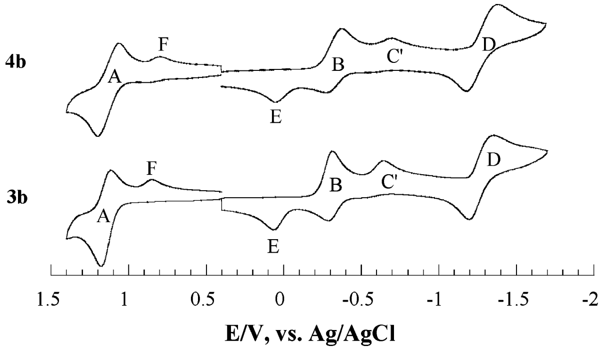
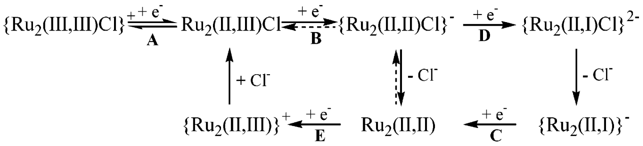


Figure 8. Cyclic voltammograms of compounds **3b** and **4b** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

Scheme 5. Assignments of Observed Ru_2-Based Redox Couples in Compounds **1/2**



Molecular structure of *trans*-**2b** is shown in Figure 3, where a crystallographic inversion center bisects the C4−C4′ bond and relates one-half of the molecule to the other half. Also collected in Table 1, the geometric parameters of the diruthenium unit in molecule **2b** bear close resemblance to those of molecules **1a/b**. It is obvious from Figure 3 that a 1,8-dicarboxy-4-octene bridge formed from the CM reaction of **1b**. The trans-configuration of the olefin derived from the CM reaction, though not obvious from Figure 3, is implied by the crystallographic inversion symmetry. Repeated efforts to obtain single crystals of X-ray quality for the cis-isomer of **2b** failed. A preliminary diffraction study of compound **2a** revealed the trans-configuration for the CM-derived olefin, and a structural plot of **2a** can be found in the Supporting Information.[17]

Molecular structures of compounds **3a**, **3b**, and **4b** have also been determined via single-crystal X-ray diffraction studies, and their structural plots are shown in Figures 4, 5, and 6, respectively. Both **3a** and **3b** retain the cis- ligand arrangement of the precursor compound *cis*-$Ru_2(D(3,5\text{-}Cl_2\text{-}Ph)F)_2(OAc)_2Cl$, reflecting the substitution inert nature of the $D(3,5\text{-}Cl_2Ph)F$ ligand. Structural data of compound **3a**

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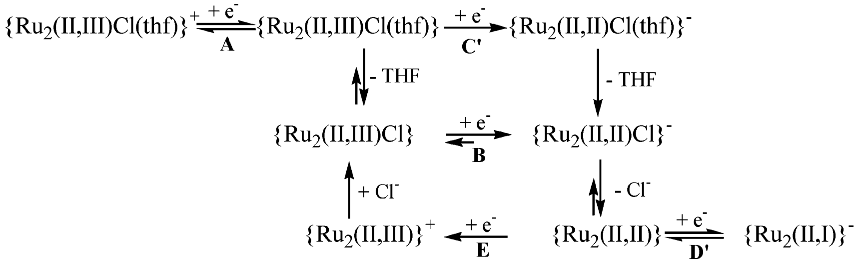
(16) Angaridis, P. In *Multiple Bonds between Metal Atoms*; Cotton, F. A., Murillo, C. A., Walton, R. A., Eds.; Springer Science and Business Media, Inc.: New York, 2005.

(17) Data collection on a crystal of **2a** revealed a triclinic cell of $a = 10.904$ Å, $b = 12.883$ Å, $c = 25.466$ Å, $\alpha = 101.615°$, $\beta = 97.314°$, $\gamma = 106.175°$, $V = 3299.6$ Å^3, and the dimer of dimers framework. However, the quality of data set was poor, and the least-squares refinement did not yield a structure of publishable figures of merit.

Scheme 6. Assignments of Observed Ru_2-Based Redox Couples in Compounds **3**/**4**



also shed light on the absence of metathetic reactivity: the distance between the C28 and C32 atoms is 5.79 Å, which is significantly longer than the span of a C−C═C−C fragment (the sum of two C−C and one C═C bond lengths is only about 5.5 Å). Selected bond lengths and angles of compounds **3a**, **3b**, **4b**, and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ are collected in Table 2, where the similarity in Ru_2 coordination geometry among all compounds is clear. A feature common to compounds **3a**, **3b**, and **4b** is the presence of an axial thf ligand that is absent in compounds **1** and **2**, reflecting the reduced steric crowding around the axial positions in the former compounds. Coordination to the second axial site in the more crowded $Ru_2(DArF)_3(O_2CR)$ and $Ru_2(DArF)_4$ type compounds is possible but limited to small/linear ligands such as water molecules[18] and phenyl acetylides.[19,20] The trans-configuration of the bridge olefin in the RCM product is clearly shown in Figure 6.

Electrochemistry. When two identical metallic centers are tethered covalently, an obvious question is whether two centers are cooperative (electronically coupled) or modular (electronically uncoupled). To investigate the effect of dicarboxylate bridges, the redox properties of compounds **1a/b** and **2a/b** were examined with cyclic voltammetric (CV) measurements, and the cyclic voltammograms of **1a** and **2a** are shown in Figure 7. It is clear from Figure 7 that the dimeric derivative **2a** displayed a cyclic voltammogram nearly identical to that of **1a**, except that the peak currents were roughly doubled in the former. The same comparison can be made between compounds **1b** and **2b** (Supporting Information). Clearly, two diruthenium units remain modular (electronically uncoupled) in compounds **2**. Both compounds **1** and **2** absorb intensely at 520 nm, and the molar extinction coefficients of the latter are about twice of that of the former, for further corroboration of the modular feature.

It is also clear from Figure 7 that both compounds **1a** and **2a** exhibit very complicated cyclic voltammograms. A plausible mechanism accounting for major features observed is outlined in Scheme 5. The reversible oxidation A is clearly the $Ru_2(III,III)/Ru_2(III,II)$ couple, and the quasireversible reduction (B) is the $Ru_2(III,II)/Ru_2(II,II)$ couple with the axial Cl^- intact. When the cathodic sweep is extended to a more negative region, the axial Cl^- starts to dissociate, and the complete dissociation occurs upon the second reduction (D). On the return sweep, the $Ru_2(II,I)$ species free of axial Cl^- is reoxidized to $Ru_2(II,II)$ species free of axial Cl^- at E_{pa}(C). The latter either is further oxidized to $Ru_2(II,III)$ at E_{pa}(E) or undergoes Cl^- rebound to yield $\{Ru_2(II,II)Cl\}^-$ that is oxidized at E_{pa}(B). Some low current events (F and G) remain unaccounted for in this mechanism and cannot be discerned without more elaborate study.

The cyclic voltammograms of compound **3b** and its RCM derivative **4b** are shown in Figure 8, where their resemblance and complexity are easy to notice. The assignment of the observed couples is given in Scheme 6, and the consideration of the axial thf ligand that is found in the structures of both **3** and **4** is important. The anodic region features a quasireversible oxidation (A) attributed to the $Ru_2(III,II)/Ru_2(II,II)$ couple. It is likely that the axial thf is quite labile, which results in an equilibrium shown in the middle of Scheme 4. Since the Ru_2 with axial thf is more electron rich, the first (B) and second (C′) reductions are assigned as the $Ru_2(III,II)/Ru_2(II,II)$ couples from the species without and with axial thf, respectively. The axial thf quickly dissociates on the formation of $Ru_2(II,II)$, and the axial Cl^- ligand gradually dissociates on extending the cathodic sweep to the more negative region. The Ru_2 species is already free of the axial Cl^- ligand on the second reduction, which renders the couple D′ quasireversible. On the backward sweep, the equilibrium nature of the rebound of Cl^- results in the appearance of peaks at both E_{pa}(B) and E_{pa}(E). Similar ECE (electrochemical−chemical−electrochemical) mechanisms have been proposed to rationalize complex voltammograms recorded for both $Ru_2(DArF)_4Cl$ and $Ru_2(DArF)_{4-n}(OAc)_nCl$ types compounds.[18,19,21]

Conclusions

In conclusion, both the CM and RCM type reactions have been realized on the Ru_2 compounds bearing ω-alkene-α-carboxylate ligands, and those reactions represent a new approach in applying olefin metathesis to inorganic chemistry. Supramolecules consisting of a pair of Mo_2 units linked by a dicarboxylate linker have been extensively studied by the laboratory of Cotton,[22] and supramolecules of Ru_2 units linked with both di-/tricarboxylates and other ditopic ligands

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have also been reported.[18,23] In most cases, the assemblies occur via the coordination to M_2 centers by preformed di/tricarboxylate linkers. Clearly, the metathesis method developed here may be utilized as a novel alternative for the preparation of the M_2 supramolecules. In addition to the simple dimerization and intramolecular cyclization, we also envision the possibilities of macrocyclization through intermolecular metathesis and ring opening polymerization based on Ru_2-containing scaffolds, which are being explored in our laboratory.

Experimental Section

General. Vinylacetic acid and 4-pentenoic acid were purchased from ACROS, silica gel was purchased from Merck, and $(Cy_3P)_2Cl_2Ru({=}CHPh)$, $(Cy_3P)(NHC)Cl_2Ru({=}CHPh)$, and 5-hexenoic acid were purchased from Aldrich. $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ were prepared as reported earlier.[11] Magnetic susceptibilities were measured at room temperature using either a Johnson Matthey Mark-I magnetic susceptibility balance or the Evans method[24] in $CDCl_3$ on a Varian Mercury 200 NMR spectrometer. Elemental analysis was performed by Atlantic Microlab, Norcross, GA. Visible absorption spectra were recorded on a Cary300 UV−vis spectrophotometer. Cyclic voltammograms were recorded in a 0.2 M $(n\text{-}Bu)_4NPF_6$ solution (THF, N_2-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode. The concentration of diruthenium species was always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.582 V (versus Ag/AgCl) under the experimental conditions.

Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(\mu\text{-}O_2CCH_2CH{=}CH_2)Cl$ (1a). A mixture of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ (200 mg, 0.15 mmol), vinylacetic acid (0.13 mL, 1.5 mmol), THF (20 mL), and methanol (20 mL) was refluxed in air overnight. Solvents were removed, and the residue was washed repeatedly with H_2O and hexanes to yield a dark red solid. Further purification was carried out on a silica column (THF/hexanes = 1/5) to yield a purple crystalline material (170 mg, 81%). Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 520, 11 200. Anal. for $C_{43}H_{26}Cl_{13}N_6O_2Ru_2{\cdot}THF$, found (calcd): C, 40.50 (40.36); H, 2.46 (2.48); N, 6.03 (6.13). χ_{mol}(corrected) = 6.40×10^{-3} emu/mol, $\mu_{eff} = 3.90\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.092, 0.066, 0.676; B, −0.208, 0.044, 0.704; C, −0.992, 0.084, 2.205; E_{pc}(D), −1.444; E_{pa}(E), 0.230.

Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(\mu\text{-}O_2CCH_2CH_2CH{=}CH_2)Cl$ (1b). Synthesis of **1b** was similar to that of **1a** with vinylacetic acid being replaced by pentenoic acid. Yield, 87%. Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 520, 10 400. Anal. for $C_{44}H_{28}Cl_{13}N_6O_2Ru_2$, found (calcd): C, 39.96 (39.56); H, 2.19 (2.11); N, 6.39 (6.29). χ_{mol}(corrected) = 6.55×10^{-3} emu/mol, $\mu_{eff} = 3.95\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.105, 0.065, 0.585; B, −0.215, 0.039, 0.742; C, −0.992, 0.084, 2.206; E_{pc}(D), −1.444; E_{pa}(E), 0.230.

Preparation of $[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3]_2(\mu\text{-}O_2CCH_2CH{=}CH_2CH_2CO_2)Cl_2$ (2a). To a CH_2Cl_2 solution of **1a** (300 mg in 80 mL) was added 9 mg of $(Cy_3P)_2Cl_2Ru({=}CHPh)$ (5 mol %), and the resultant solution was refluxed under N_2 for 5 days. The reaction progress was monitored by TLC (THF/hexanes = 1/5), and the product **2a** with an R_f of 0.45 was detected. The purification of **2a** was effected by silica column chromatography (THF/hexanes = 1/7 to 1/5). Yield: 120 mg, 40%. MALDI-TOF-MS, 2544, [**2a** − Cl_2]$^+$. Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 520, 22 800. Anal. for $C_{84}H_{56}Cl_{26}N_{12}O_4Ru_4{\cdot}THF$, found (calcd): C, 39.25 (39.33); H, 1.95 (2.10); N, 6.51 (6.25). $\mu_{eff} = 5.73\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.075, 0.061, 0.699; B, −0.212, 0.043, 0.715; C, −1.013, 0.066, 3.402; E_{pc}(D), −1.456; E_{pa}(E), 0.190.

Preparation of $[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3]_2(\mu\text{-}O_2CCH_2CH_2CH{=}CH_2CH_2CH_2CO_2)Cl_2$ (*cis*-2b and *trans*-2b). To a CH_2Cl_2 solution of **1b** (320 mg in 80 mL) was added 10 mg of $(Cy_3P)_2Cl_2Ru({=}CHPh)$ (5 mol %), and the resultant solution was refluxed under N_2 for 2 days. The metathesis products *cis*-**2b**/*trans*-**2b** with R_f of 0.55 and 0.45, respectively, were detected. Compounds *cis*-**2b**/*trans*-**2b** were partially separated by chromatography (THF/hexanes = 1/7 to 1/5). Combined yield: 191 mg (60%).

Data for *trans*-2b. ESI-MS, 2606, [**2b** − Cl]$^+$. Vis-NIR, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 520, 22 400. Anal. for $C_{86}H_{52}Cl_{26}N_{12}O_4Ru_4{\cdot}THF$, found (calcd): C, 40.16 (39.81); H, 2.26 (2.23); N, 6.52 (6.19). $\mu_{eff} = 5.61\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.070, 0.071, 0.500; B, −0.220, 0.061, 0.726; C, −1.010, 0.091, 2.506; E_{pc}(D), −1.510; E_{pa}(E), 0.186.

Data for *cis*-2b. ESI-MS, 2606, [**2b** − Cl]$^+$. Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 520, 23 100. Anal. for $C_{86}H_{52}Cl_{26}N_{12}O_4Ru_4{\cdot}THF$, found (calcd): C, 39.89 (39.81); H, 2.11 (2.23); N, 6.39 (6.19). $\mu_{eff} = 5.54\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.073, 0.082, 0.536; B, −0.223, 0.074, 0.695; C, −1.010, 0.092, 2.454; E_{pc}(D), −1.504; E_{pa}(E), 0.203.

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2CCH_2CH{=}CH_2)_2Cl$ (3a). A 100 mL round-bottom flask was charged with *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ (200 mg, 0.20 mmol), vinylacetic acid (0.04 mL, 0.44 mmol), and 40 mL of toluene. The flask was mounted with a MicroSoxhlet extractor containing a thimble filled with K_2CO_3. The reaction mixture was refluxed in air for 4 h. Solvent was then removed, and the residue was washed repeatedly with H_2O and hexanes to yield a dark red solid. Further purification was carried out on a silica column (THF/hexanes = 1/2) to yield a purple crystalline material (158 mg, 75%). Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 529, 4400. Anal. for $C_{34}H_{24}Cl_9N_4O_4Ru_2{\cdot}H_2O$ (1091.81), found (calcd): C, 37.20 (37.40); H, 2.47 (2.40); N, 4.86 (5.13). $\mu_{eff} = 3.74\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.153, 0.060, 0.628; B, −0.285, 0.036, 0.397; E_{pc}(C), −0.618; D, −1.253, 0.136, 0.635; E_{pa}(E), 0.078.

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2CCH_2CH_2CH{=}CH_2)_2Cl$ (3b). Synthesis of **3b** was similar to that of **3a** with vinylacetic acid being replaced by 4-pentenoic acid. Yield, 85%. Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 530, 3900. Anal. for $C_{36}H_{28}Cl_9N_4O_4Ru_2{\cdot}THF$, found (calcd): C, 40.92 (40.98); H, 3.09 (3.04); N, 4.77 (4.79). $\mu_{eff} = 3.84\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.147, 0.056, 0.557; B, −0.301, 0.027, 0.475; E_{pc}(C′), −0.644; D, −1.273, 0.162, 0.904; E_{pa}(E), 0.063.

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2CCH_2CH_2CH{=}CH_2)_2Cl$ (3c). Synthesis of **3c** was similar to that of **3a** with vinylacetic acid being replaced by 5-hexenoic acid. Yield, 76%. Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 531 3100. Anal. for $C_{38}H_{32}Cl_9N_4O_4Ru_2{\cdot}THF$, found (calcd): C, 41.97 (41.82); H, 3.35 (3.30); N, 4.66

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Table 3. Crystal Data for Compounds **1a**, **1b**, *trans*-**2b**, **3a**, **3b**, and **4b**

	1a·C_6H_{14}	**1b**	*trans*-**2b**	**3a**·THF	**3b**·THF	**4b**·THF
formula	$C_{49}H_{40}Cl_{13}N_6O_2Ru_2$	$C_{44}H_{28}Cl_{13}N_6O_2Ru_2$	$C_{86}H_{60}Cl_{26}N_{12}O_4Ru_4$	$C_{38}H_{32.5}Cl_9N_4O_5Ru_2$	$C_{40}H_{36}Cl_9N_4O_5Ru_2$	$C_{42}H_{40}Cl_9N_4O_6Ru_2$
fw	1407.86	1335.78	2651.44	1146.37	1173.92	1217.97
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	16.297(1)	11.5633(5)	11.8156(3)	11.1616(7)	11.3739(4)	10.9030(3)
b, Å	14.8987(6)	14.8987	17.4357(5)	12.8807(8)	12.6997(4)	25.1518(9)
c, Å	23.067(2)	15.7020(7)	24.9434(7)	17.4883(11)	17.7184(8)	17.9937(6)
α, deg	78.848(2)	104.820(2)	101.488(2)	108.2980(10)	108.329(2)	
β, deg	70.724(2)	99.830	92.864(2)	108.2980(10)	96.638(2)	107.625(2)
γ, deg	74.988(3)	74.988	92.053(2)	97.3280(10)	106.7400(10)	
V, Å^3	5585.6(7)	5585.6(7)	5023.9(2)	109.8980(10	2265.90(15)	4702.8(3)
Z	4	2	2	2	2	4
T, K	100(2)	150(1)	100(2)	100(2)	100(2)	100(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calc}, g cm^{-3}	1.674	1.753	1.753	1.758	1.721	1.720
GOF on F^2	1.018	1.369	1.224	1.047	1.027	1.021
R, wR2	0.056, 0.214	0.042, 0.110	0.079, 0.194	0.023, 0.063	0.026, 0.068	0.039, 0.085

(4.70). $\mu_{eff} = 3.94\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.145, 0.034, 0.581; B, −0.296, 0.066, 0.342; E_{pc}(C′), −0.672; D, −1.291, 0.183, 0.677; E_{pa}(E), 0.067.

Preparation of *cis*-Ru_2(D(3,5-Cl_2Ph)F)$_2$(*μ*-$O_2CCH_2CH_2CH{=}CH_2CH_2CH_2CO_2$)Cl (4b). To a CH_2Cl_2 solution of **3b** (40 mg in 50 mL) was added 2 mg of $(Cy_3P)_2Cl_2Ru({=}CHPh)$, and the resultant solution was refluxed under N_2 overnight. The purification of **4b** was effected by a silica column chromatography (THF/hexanes = 1/2). Yield, 33 mg, 83%. ESI-MS, 1038, [**4b** − Cl]$^+$. Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 529, 34 500. Anal. for $C_{34}H_{24}Cl_9N_4O_4Ru_2$·0.5THF, found (calcd): C, 38.96 (39.01); H, 2.54 (2.60); N, 5.05 (4.92). $\mu_{eff} = 3.99\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.128, 0.136, 0.643; B, −0.329, 0.106, 0.512; E_{pc}(C′), −0.699; D, −1.289, 0.200, 0.816; E_{pa}(E), 0.049.

Preparation of *cis*-Ru_2(D(3,5-Cl_2Ph)F)$_2$(*μ*-$O_2CCH_2CH_2CH_2CH{=}CH_2CH_2CH_2CO_2$)Cl (4c). To a CH_2Cl_2 solution of **3c** (140 mg in 50 mL) was added 5 mg of $(Cy_3P)_2Cl_2Ru({=}CHPh)$, and the resultant solution was refluxed under N_2 overnight. The purification of **4c** was effected by a silica column chromatography (THF/hexanes = 2/5). Yield, 113 mg, 83%. ESI-MS, 1067, [**4c** − Cl]$^+$. Vis, λ_{max} (nm), ϵ (M^{-1} cm^{-1}): 529, 4200. Anal. for $C_{36}H_{28}Cl_9N_4O_4Ru_4$·THF, found (calcd): C, 40.92 (40.83); H, 3.09 (3.10); N, 4.77 (4.72). $\mu_{eff} = 3.65\ \mu_B$. Cyclic voltammogram [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 1.130, 0.107, 0.646; B, −0.303, 0.080, 0.339; E_{pc}(C′), −0.678; D, −1.286, 0.185, 0.712; E_{pa}(E), 0.064.

Attempted RCM Reaction of 3a. (1) To a CH_2Cl_2 solution of **3a** (20 mg in 50 mL) was added 2 mg of $(Cy_3P)_2Cl_2Ru({=}CHPh)$, and the resultant solution was refluxed under N_2 overnight. No new product was detected by TLC. Another 2 mg of catalyst was added, and reflux continued overnight. No reaction occurred. (2) To a toluene solution of **3a** (20 mg in 50 mL) was added 2 mg of $(Cy_3P)_2Cl_2Ru({=}CHPh)$, and the resultant solution was refluxed under N_2 for 3 days. No new product was detected by TLC. (3) To a CH_2Cl_2 solution of **3a** (20 mg in 50 mL) was added 2 mg of $(Cy_3P)(NHC)Cl_2Ru({=}CHPh)$, and the resultant solution was refluxed under N_2 for 7 days. No new product was detected by TLC.

X-ray Data Collection, Processing, and Structure Analysis and Refinement. Single crystals of compounds **1a**, **1b**, *trans*-**2b**, **3a**, **3b**, and **4b** were all grown via slow evaporation of THF/hexanes solutions. Crystals were mounted on Mitogen tips using Paratone-N that was then frozen under a stream of N_2. Data collection was carried out at 100 K using a Bruker AXS APEX II CCD area detector. Data processing/reduction was performed using the APEX2 crystallographic suite (Bruker, 2004 software contains SAINT+, SADABS, etc.). Refinement was carried out on F^2 using full-matrix least-square refinement. Hydrogen atoms were placed at calculated positions using isotropic displacement parameters of 1.5 (methyl) and 1.2 (all others) times that of the adjacent atom. Table 3 summarizes the crystal data from compounds **1a**, **1b**, *trans*-**2b**, **3a**, **3b**, and **4b**.

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Supporting Information Available: Visible spectra of compounds **1**−**4**, voltammograms of compounds **1b**, **2b**, **3a**, **3c**, and **4c**, skeletal plot of the preliminary structure of **2a**, and X-ray crystallographic files in CIF format for compounds **1a**, **1b**, *trans*-**2b**, **3a**, **3b**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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