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Dimerization of Diruthenium Coordination Compounds via Olefin Metathesis

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Diruthenium compounds containing an 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 reactions 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 ω-alkene-α-carboxylic acids. Both compounds **1a** and **1b** undergo 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**)]. Molecular structures of compounds **1a**/**1b** and **2a**/**2b** were established by X-ray diffraction studies, which revealed the formation of *trans* product only in the case of shorter tether (**2a**) and a mixture of *cis-*/*trans* isomers in the case of longer tether (**2b**).

Introduction

Catalytic olefin metathesis, arguably one of the most important organic reactions discovered in the 20th century,[1] has found broad applications in organic and materials syntheses.[2,3] In comparison, there are only a limited number of applications of catalytic olefin metathesis in the synthesis of coordination and organometallic compounds.[4] Earlier studies by Rudler demonstrated that the W compounds of carbene ligands bearing alkene tails underwent ring-closing metathesis (RCM) with $WOCl_4/Ph_2SiH_2$ as the catalyst.[5] The RCM method was subsequently applied to the high-yield synthesis of Cu-templated [2]catenanes.[6] More recently, both the cross metathesis (CM) and RCM reactions have been utilized to prepare bridged metallocenes and pincer compounds.[7] The most noteworthy are the creative efforts from the laboratory of Gladysz in applying RCM to a variety of metal compounds with phosphane ligands bearing terminal alkene, which resulted in novel compounds including sterically shielded linear Pt–polyyne molecules and gyroscope-like molecules.[4,8]

Our laboratory has been developing methodologies to covalently modify diruthenium compounds at the ligand periphery, and Sonogashira and Suzuki cross couplings were successfully executed on N,N′-bridging ligands containing aryl iodo substituents.[9,10] Reported in this contribution is the synthesis of diruthenium compounds containing ω-alkenyl-α-carboxylate ligand, which subsequently undergoes cross metathesis reactions to afford a unique set of dimeric diruthenium compounds.

Results and Discussion

Our approach began with the preparation of diruthenium compounds containing ω-alkene-α-carboxylate. $Ru_2[D(3,5\text{-}Cl_2Ph)F]_3(OAc)Cl$ [$D(3,5\text{-}Cl_2Ph)F$ = *N*,*N′*-bis(3,5-dicholorophenyl)formamidinate][9,10] readily reacted with excess $HO_2C(CH_2)_nCH{=}CH_2$ (n = 1, vinylacetic acid; n = 2, 4-pentenoic acid) under reflux in THF/MeOH to afford the 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**) as purple crystalline materials, which were purified on silica column to ensure the complete removal of the unidentified by-products that might poison the metathesis catalyst. Although the paramagnetic nature of the compounds **1a**/**b** (S = 3/2) prevents the recording of NMR spectra, both **1a** and **1b** were analyzed satisfactorily and characterized by single-crystal X-ray diffraction. Structural plots of molecules **1a** and **1b** are shown in Figure 1 and Figure 2, respectively, and the similarity in Ru_2 coordination spheres among **1a**, **1b** and $Ru_2[D(3,5\text{-}Cl_2Ph)F]_3(OAc)Cl$[9,10] is clear from the comparison of both the structural plots and key geometric parameters including the averaged Ru–N and Ru–O bond lengths. Interestingly, the lengths of 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 structural flexibility of terminal olefins. Also noteworthy is the averaged Ru–O distance for **1a**/**b** (ca. 2.05 Å), which is significantly longer than those of $Ru_2(O_2CR)_4Cl$ (2.02–2.03 Å)[11] due to the *trans* influence of $D(3,5\text{-}Cl_2Ph)F$ ligand. Obviously, it is a concern whether such structural destabilization may translate into the lability

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of ω-alkene-α-carboxylate during the metathesis reaction (Scheme 1).

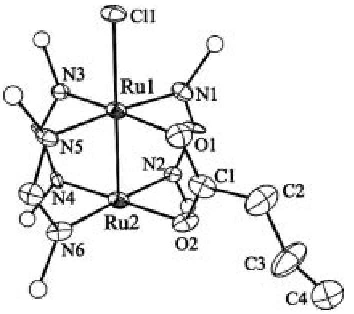


Figure 1. ORTEP plot of molecule **1a** at 40% probability level. All 3,5-Cl_2phenyl groups except for the *ipso*-carbon centers (shown as isotropic spheres) were removed for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Ru2 2.321(2), Ru1–Cl1 2.382(3), Ru–N(av.) 2.060(11), Ru–O(av.) 2.051(9), C3–C4 1.29(2), C2–C3–C4 128(2).

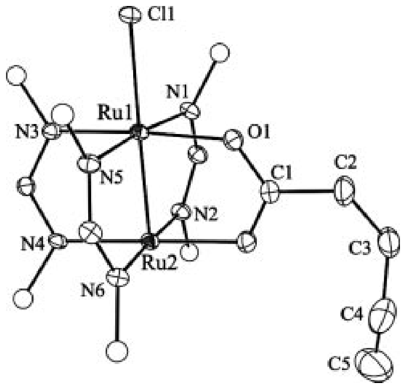
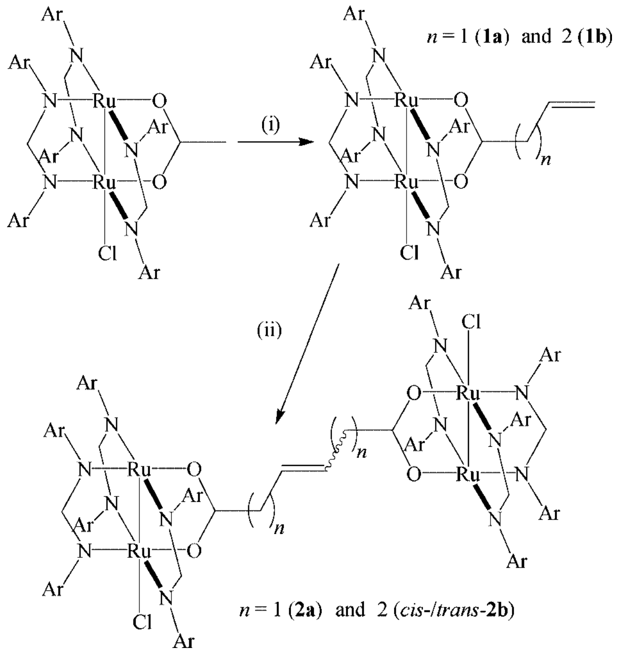


Figure 2. ORTEP plot of molecule **1b** at 40% probability level. All 3,5-Cl_2phenyl groups except for the *ipso*-carbon centers (shown as isotropic spheres) were removed for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Ru2 2.3131(4), Ru1–Cl1 2.3828(8), Ru–N(av.) 2.064(4), Ru–O(av.) 2.056(4), C4–C5 1.356(9), C3–C4–C5 120.3(6).



Scheme 1. (i) 10 equiv. $HOOC(CH_2)_nCH=CH_2$, THF/MeOH (1:1), reflux; ii) 5 mol-% $(Cy_3P)_2Cl_2Ru(=CHPh)$, CH_2Cl_2, reflux 2–5 d. Ar = 3,5-$Cl_2C_6H_3$.

Having incorporated ω-alkene-α-carboxylate into the coordination sphere of Ru_2 core, we were in position to investigate the feasibility of metathesis reactions. Compound **1a** was refluxed in CH_2Cl_2 in the presence of $(Cy_3P)_2Cl_2Ru(=CHPh)$ and a gradual build-up of a new compound **2a** was noted over a period of 5 d. The dimeric nature of **2a** was confirmed by both the observation of [**2a**-Cl_2]$^+$ in MALDI-TOF-MS (2544) and a preliminary X-ray study, the latter of which revealed the *trans* configuration of the olefin bridge.[12] 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 of compound **1b** under the same conditions resulted in a complete conversion of **1b** in 2 d to two new compounds that were similar in polarity (R_f = 0.55 and 0.45 in THF/hexanes, 1:5, v/v) and yielded the same [**2b**-Cl]$^+$ peak in ESI-MS (2606). The new compounds are obviously the *cis*/*trans* isomers, and the structural determination of the compound of R_f = 0.45 (Figure 3) 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 between the 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 homo-dimerization reaction of acrylic acid was also classified as "slow" (15 h at 40 °C) with $(Cy_3P)(NHC)Cl_2Ru(=CHPh)$ as the catalyst.[13]

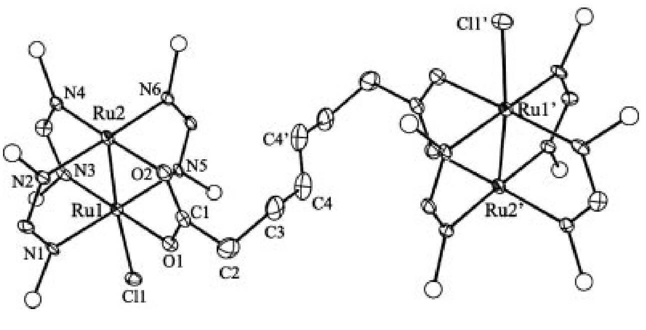


Figure 3. ORTEP plot of molecule *trans*-**2b** at 40% probability level. All 3,5-Cl_2phenyl groups except for the *ipso*-carbon centers (shown as isotropic spheres) were removed for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Ru2 2.329(1), Ru1–Cl1 2.382(2), Ru–N(av.) 2.059(7), Ru–O(av.) 2.050(6), C4–C4′ 1.30(2), C3–C4–C4′ 111(1).

In the structure of *trans*-**2b**, there is a crystallographic inversion center that bisects the C4–C4′ bond and relates one half of the molecule to the other half. The structural features of the diruthenium unit in **2b** bear close resemblance to those of **1a/b**. Also obvious from Figure 3 is the formation of 1,8-dicarboxy-4-octene from the cross metathesis of **1b**.

When two identical metallic centers are tethered covalently, an obvious question is whether two centers are corporative (electronically coupled) or modular (electronically independent). 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 CVs. of **1a** and **2a** are shown in Figure 4. Similar to the parent compound $Ru_2[D(3,5-Cl_2Ph)F]_3(OAc)Cl$, compound **1a** underwent a reversible oxidation (**A**) and a quasireversible reduction (**B**) in the potential window shown. The dimeric derivative **2a** displayed a nearly identical CV, except that the peak currents were roughly doubled. Similar comparison can be made between compounds **1b** and **2b**. Clearly, two diruthenium units remain modular in compounds **2**. Further corroborating the modular feature, 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 (see supporting information).

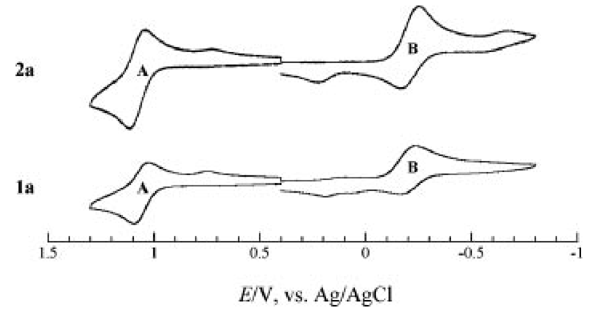


Figure 4. Cyclic voltammograms of **1a** and **2a** recorded in 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

Conclusions

Formation of compounds **2a/b** from **1a/b** are the first examples of cross metathesis of coordinated ω-alkene-α-carboxylate to the best of our knowledge,[2] and represents a novel 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,[14] and supramolecules of Ru_2 units linked with both di-/tricarboxylates and other ditopic ligands have also been reported.[15] In most cases, the assemblies occur via the coordination to M_2 centers by pre-formed 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, we also envision the possibilities of macrocyclization through intra- and 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 pentenoic acid were purchased from ACROS, silica gel was purchased from Merck, and $(Cy_3P)_2Cl_2Ru(=CHPh)$ was purchased from Aldrich. $Ru_2[D(3,5-Cl_2Ph)F]_3(OAc)Cl$ was prepared as reported earlier.[9] Magnetic susceptibility was measured at 294 K with a Johnson Matthey Mark-I Magnetic Susceptibility Balance. Elemental analysis was performed by Atlantic Microlab, Norcross, GA. Visible absorption spectra were recorded with a Cary300 UV/Vis spectrophotometer. Cyclic voltammograms were recorded in 0.2 M $(n\mathrm{Bu})_4NPF_6$ solution (THF, N_2-degassed) with 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 (vs. Ag/AgCl) under the experimental conditions.

Preparation of $Ru_2[D(3,5-Cl_2Ph)F]_3(\mu-O_2CCH_2CH{=}CH_2)Cl$ (1a): A mixture of $Ru_2[D(3,5-Cl_2Ph)F]_3(OAc)Cl$ (200 mg, 0.15 mmol), vinylacetic acid (10 equiv.), THF (20 mL) and methanol (20 mL) was refluxed in air overnight. The solvent was removed and the residue was washed repeatedly with H_2O and hexanes. Further purification was carried out on a silica column (THF/hexanes, 1:5) to yield a purple crystalline material (170 mg, 81 %). UV-Vis: λ_{max} (ε, $M^{-1}cm^{-1}$) = 520 (11,200) nm. $C_{43}H_{26}Cl_{13}N_6O_2Ru_2{\cdot}THF$ (1393.84): calcd. C 40.50, H 2.46, N 6.03; found C 40.36, H 2.48, N 6.13. χ_{mol} (corrected) = $6.40{\cdot}10^{-3}$ emu, μ_{eff} = 3.90 BM. 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.

Preparation of $Ru_2[D(3,5-Cl_2Ph)F]_3(\mu-O_2CCH_2CH_2CH{=}CH_2)Cl$ (1b): Synthesis of **1b** was similar to that of **1a** with vinylacetic acid being replaced by pentenoic acid. Yield 87 %. UV-Vis: λ_{max} (ε, $M^{-1}cm^{-1}$) = 520 (10,400) nm. $C_{44}H_{28}Cl_{13}N_6O_2Ru_2$ (1335.76): calcd. C 39,56, H 2.11, N 6.29; found C 39.96; H 2.19, N 6.39. χ_{mol} (corrected) = $6.55{\cdot}10^{-3}$ emu, μ_{eff} = 3.95 BM. 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.

Preparation of $[Ru_2[D(3,5-Cl_2Ph)F]_3]_2(\mu-O_2CCH_2CH{=}CH_2CH_2CO_2)Cl_2$ (2a): $(Cy_3P)_2Cl_2Ru(=CHPh)$ (5 mol-%, 9 mg) was added to **1a** (300 mg) in 80 mL of dry CH_2Cl_2 . The resulting solution was refluxed under N_2 for 5 d. The reaction progress was monitored by TLC (THF/hexanes, 1:5, same below) and the product **2a** was detected; R_f = 0.45 . The purification of **2a** was performed by a silica column chromatography (THF/hexanes, 1:7 to 1:5). Yield: 120 mg, 40 %. MALDI-TOF-MS: *m*/*z* = 2544, $[\mathbf{2a}\text{-}Cl_2]^+$. UV-Vis: λ_{max} (ε, $M^{-1}cm^{-1}$) = 520 (22,800) nm. $C_{84}H_{56}Cl_{26}N_{12}O_4Ru_4{\cdot}THF$ (2687.51): calcd. C 39.33, H 2.10, N 6.25; found C 39.25, H 1.95, N 6.51. 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.

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

Data for *cis*-2b: ESI-MS: *m*/*z* = 2606, $[\mathbf{2b}\text{-}Cl]^+$. UV-Vis: λ_{max} (ε, $M^{-1}cm^{-1}$) = 520 (23,100) nm. $C_{86}H_{52}Cl_{26}N_{12}O_4Ru_4{\cdot}THF$ (2715.57): calcd. C 39.81, H 2.23, N 6.19; found C 39.89, H 2.11, N 6.39.

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.

Data for *trans*-2b: ESI-MS: m/z = 2606, [**2b**-Cl]$^+$. Vis/NIR: λ_{max} (ε, $\text{M}^{-1}\,\text{cm}^{-1}$) = 520 (22,400) nm. $C_{86}H_{52}Cl_{26}N_{12}O_4Ru_4$·THF (2715.57): calcd. C 39.81, H 2.23, N 6.19; found C 40.16, H 2.26, N 6.52. 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.

X-ray Structural Studies: Crystal data for **1a**·C_6H_{14}: $C_{49}H_{40}Cl_{13}N_6O_2Ru_2$, M = 1407.86, triclinic, space group $P\bar{1}$, a = 16.297(1) Å, b = 16.413(1) Å, c = 23.067(2) Å, α = 78.848(2)°, β = 70.724(2)°, γ = 74.988(3)°, V = 5585.6(7) Å^3, Z = 4, D_c = 1.674 g cm^{-3}, R_1 = 0.0557 [$I > 2\sigma(I)$], wR_2 = 0.2139 (all data), T = 100(2) [K]. **Crystal Data for 1b:** $C_{44}H_{28}Cl_{13}N_6O_2Ru_2$, M = 1335.78, triclinic, space group $P\bar{1}$, a = 11.5633(5) Å, b = 14.8987(6) Å, c = 15.7020(7) Å, α = 104.820(2)°, β = 99.830(2)°, γ = 94.748(2)°, V = 2553.94(19) Å^3, Z = 2, D_c = 1.753 g cm^{-3}, R_1 = 0.034 [$I > 2\sigma(I)$], wR_2 = 0.080 (all data), T = 150(1) K, Data were collected to a maximum 2θ of 55.0°. **Crystal Data for *trans*-2b:** $C_{86}H_{60}Cl_{26}N_{12}O_4Ru_4$, M = 2651.44, triclinic, space group $P\bar{1}$, a = 11.8156(3) Å, b = 17.4357(5) Å, c = 24.9434(7) Å, α = 101.488(2)°, β = 92.864(2)°, γ = 92.053(2)°, V = 5023.9(2) Å^3, Z = 2, D_c = 1.753 g cm^{-3}, R_1 = 0.0794 [$I > 2\sigma(I)$], wR_2 = 0.1938 (all data), T = 100(2) K.

CCDC-616302 (for **1a**), -616285 (for **1b**) and -616303 (for *trans*-**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ORTEP plots of **1a**, **1b**, *trans*-**2b**, skeletal plot of *trans*-**2a**, Vis/NIR absorption spectra of compounds **1a** and **2a**, and CVs of compounds **1b** and **2b**.

Acknowledgments

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[12] Data collection on a crystal of **2a** revealed a triclinic cell of a = 10.904, b = 12.883, c = 25.466 Å, α = 101.615, β = 97.314, γ = 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. See the supporting information for the plot of the preliminary structure.

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