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Preparation and Characterization of a Family of Ru$_2$ Compounds Bearing Iodo/Ethynyl Substituents on the Periphery

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A high-yield synthesis of mixed-bridging-ligand Ru$_2$ compounds, Ru$_2$(D(3,5-Cl$_2$Ph)F)$_{4-n}$(OAc)$_n$Cl [$n = 1$ (**1**) and 2 (**2**)] was developed, where D(3,5-Cl$_2$Ph)F is bis(3,5-dichlorophenyl)formamidinate. The acetate ligands in **1** and **2** can be quantitatively displaced with DMBA-I to yield Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(DMBA-I)Cl (**3**) and Ru$_2$(D(3,5-Cl$_2$Ph)F)$_2$(DMBA-I)$_2$Cl (**4**), respectively, where DMBA-I is *N*,*N*′-dimethyl-4-iodobenzamidinate. When compound **2** was treated with 1 equiv of HDMBA-I, a unique Ru$_2$ compound containing three different types of bidentate bridging ligands, *cis*-Ru$_2$(D(3,5-Cl$_2$Ph)F)$_2$(DMBA-I)(OAc)Cl (**5**), was obtained. Subsequent reactions between **3**/**4** and (trimethylsilyl)acetylene under Sonogashira coupling conditions resulted in Ru$_2$(D(3,5-Cl$_2$Ph)F)$_{4-n}$(DMBA-C$\equiv$CSiMe$_3$)$_n$Cl [$n = 1$ (**6**) and 2 (**8**)] in excellent yields, which were converted to the corresponding bis(phenylacetylide) compounds Ru$_2$(D(3,5-Cl$_2$Ph)F)$_{4-n}$(DMBA-C$\equiv$CSiMe$_3$)$_n$(C$\equiv$CPh)$_2$ [$n = 1$ (**7**) and 2 (**9**)]. Structural studies of several compounds provided insights about the change in Ru$_2$ coordination geometry upon the displacement of bridging and axial ligands. Voltammetric studies of these compounds revealed rich redox characteristics in all Ru$_2$ compounds reported and a minimal electronic perturbation upon the peripheral Sonogashira modification.

Introduction

Recent years have witnessed remarkable progresses in supramolecular assemblies based on bimetallic metal complexes.[1] 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.[1] In particular, significant electronic couplings mediated by ditopic linkers have been demonstrated in many M$_2$−linker−M$_2$ type systems with M = Mo or W,[2] revealing their potential utility as charge-transfer materials. The use of multivalent linkers that coordinate at the axial positions of Mo$_2$ and Ru$_2$ paddlewheel species also yields interesting two-dimensional hexagon and honeycomb assemblies.[3] The strong Lewis acidity of Rh$_2$(O$_2$CCF$_3$)$_4$ enables facile axial coordination by polycyclic aromatic hydrocarbons (PAHs), which has resulted in a vast array of solid-state Rh$_2$(O$_2$CCF$_3$)$_4$−PAH supramolecules.[4]

Scheme 1. Formation of a Dimeric Supramolecule via Reaction at Peripheral Sites

It is noteworthy that the aforementioned assemblies occur through coordination to metal center(s) at either the equatorial or axial sites, which modifies the electronic property of building blocks by a varying degree. Interested in retaining the electronic properties of building blocks during the assembly of supramolecules, we envision building blocks containing reactive functional groups away from the metal centers, which undergo homocoupling or cross-coupling to yield dimeric supramolecules through the formation of robust C−C bonds as outlined in Scheme 1. Metal-catalyzed cross-coupling reactions have become one of the most powerful synthetic tools in recent years, and frequently employed methods include Suzuki, Heck, Negishi, and Sonogashira reactions.[5] The Sonogashira reaction (alkyne cross-coupling)

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has the advantages of mild conditions and simple requirements on starting materials[6] and has been used in the preparation of push−pull zinc porphyrins,[7] tripodal ferrocene,[8] and dimers, trimers, and polymers of $[M(bpy)_3]^{2+}$ (M = Ru and Os)[9] and the extension of M−σ-ethynyls.[10] In an elegant and comprehensive study, Peng and co-workers have developed a set of polyoxometalates (POMs) bearing iodo/ethynyl-substituted organoimido groups, which were further converted into, under Sonogashira conditions, both the dimer of POMs and the main-chain POM polymers that exhibit interesting optoelectronic properties.[11]

Aiming at the realization of organometallic molecular wires, our laboratory has carried out extensive studies of Ru_2 complexes bearing one or two axial alkynyl ligands.[12] In addition to their ability to mediate efficient charge transfer,[13] these Ru_2 axial alkynyl species are both excellent electrophores and chromophores, which make them attractive building blocks for supramolecular electronic and optoelectronic materials. To minimize electronic perturbation, the assembly process should take place at the periphery of Ru_2 axial alkynyls instead of Ru_2 centers. Previously, we reported a series of $Ru_2(LL)_{4-n}(LL')_n$ type compounds, where LL′ is either an iodo-containing N,N′-bidentate ligand or its substitution surrogates, and the auxiliary ligand LL was exclusively DmAniF [bis(3-methoxyphenyl)formamidinate].[14−16] In this paper, we describe the synthesis and characterization of a new series of $Ru_2(LL)_{4-n}(LL')_n$ type compounds based on the auxiliary ligand D(3,5-Cl_2Ph)F [bis(3,5-dichlorophenyl)formamidinate].

Results and Discussion

Synthesis of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-n}(OAc)_nCl$ (n = 1 and 2). $Ru_2(LL)_{4-n}(LL')_n$ (n = 1 and 2) type compounds are generally prepared from $Ru_2(LL)_{4-n}(OAc)_n$ type starting materials. The first examples of these types of compounds were reported with LL as bis(*o*-alkoxyphenyl)formamidinate,[17] in which the crude product contains compounds of n ranging from 1 to 4 (!) and repeated cumbersome column purification was required. Much improved synthetic protocols became available in recent years with LL as DpAniF[bis(4-phethoxyphenyl)formamidinate],[18,19] DPhF (diphenylformamidinate),[20,21] and DmAniF.[15] Typical reaction conditions include the use of the HDArF ligand in slight excess, addition of Et_3N and LiCl, refluxing in THF between 12 and 24 h, and subsequent purification via either recrystallization or column chromatography. Upon reaction of $Ru_2(OAc)_4Cl$ with HD(3,5-Cl_2Ph)F in a 1:3 molar ratio under the aforementioned conditions, two compounds were isolated from the reaction mixture via chromatography and identified as $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ (**1**, 42%) and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ (**2**, 32%). To prepare **2** selectively, $Ru_2(OAc)_4Cl$ was reacted with 2 equiv of HD(3,5-Cl_2Ph)F, which always resulted in a mixture of **2** (major) and **1** (minor). It was found that the formation of **1** was reduced to a trace amount through both the elimination of the Et_3N additive and the addition of 2.2 equiv of the HD(3,5-Cl_2Ph)F ligand in portions.

Synthesis of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-n}(DMBA\text{-}I)_nCl$ (n = 1 and 2). The labile acetate ligand(s) in $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-n}(OAc)_nCl$ can be easily displaced by a N,N′-bidentate ligand. As illustrated in Scheme 2, compounds **1** and **2** reacted with 2 and 4 equiv of HDMBA-I (*N*,*N*′-dimethyl-4-iodobenzamidine) to furnish $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}I)Cl$ (**3**; Scheme 3) and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}I)_2Cl$ (**4**), respectively, in quantitative yields (in situ). The retention of the cis arrangement in **4** is a clear indication that the spectator ligand D(3,5-Cl_2Ph)F is kinetically inert under the reaction conditions. When compound **2** was treated with 1 equiv of HDMBA-I, *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}I)(OAc)Cl$ (**5**) was obtained in 58% yield. The isolation of compound **5** is surprising because reactions between $Ru_2(OAc)_4Cl$ and HDMBA ligands in limited supplies (as low as 1 equiv) always yielded $Ru_2(DMBA)_4Cl_2$ and unreacted $Ru_2(OAc)_4Cl$.[22] It appears that the existence of

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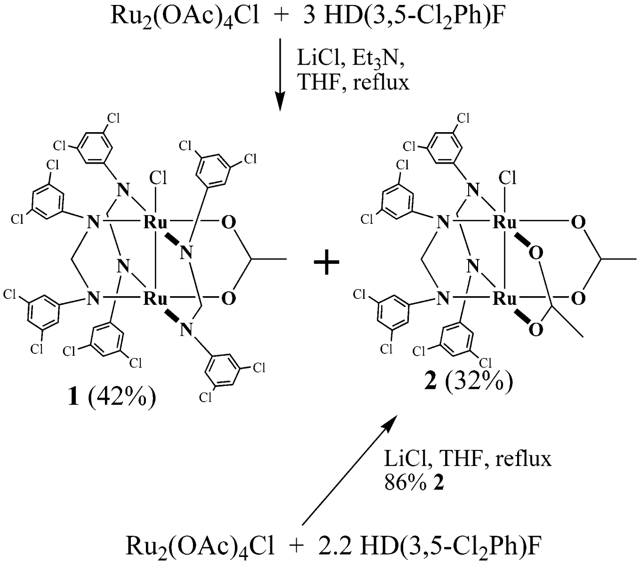
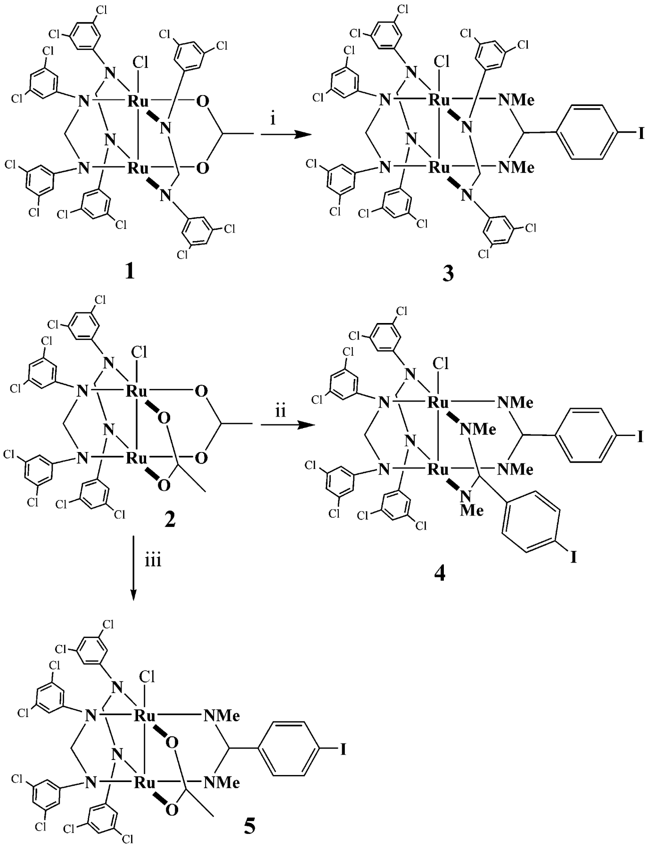
Scheme 2. Syntheses of Compounds **1** and **2**



Scheme 3. Syntheses of Iodo-Attached Ru_2 Compounds **3**−**5**[a]



[a] Conditions: (i) 2 equiv of *N*,*N*′-dimethyl-4- iodobenzamidine, LiCl, Et_3N; **3**, reflux 2 h, 86%. (ii) 4 equiv of *N*,*N*′-dimethyl-4- iodobenzamidine, LiCl, Et_3N, reflux 2 h; **4**, 85%. (iii) 1 equiv of *N*,*N*′-dimethyl-4-iodobenzamidine, LiCl, Et_3N; **5**, 58%.

DArF ligands slows down the substitution of OAc by DMBA-I and thus enables the formation of the partial substitution product **5**.

Synthesis of Alkynyl-Containing Ru_2 Compounds. It was demonstrated previously that $Ru_2(DmAniF)_{4-n}(DMBA\text{-}I)_nCl$ type compounds underwent Sonogashira cross-couplings with a variety of terminal alkynes HC≡CY (Y = SiR_3, Ph, and Fc) under mild reaction conditions: room temperature, a short reaction period, and common organic solvents.[14,15] In this study, $HC≡CSiMe_3$ was used as the exclusive substrate for cross-coupling because of the easy removal of the $SiMe_3$ group. As shown in Scheme 4, both compounds **3** and **4** reacted readily with $HC≡CSiMe_3$ under Sonogashira conditions to afford respectively the ethynylated compounds **6** and **8** in excellent yields. While Sonogashira coupling reactions of organic substrates typically require gentle heating, our coupling reactions occurred at room temperature, indicating the activation of the iodo substituent via coordination of the DMBA-I ligand to the Ru_2 center. Compounds **6** and **8** were readily converted to the axial phenylacetylide adducts **7** and **9** via the reaction with LiC≡CPh in excess.

Compounds **1**−**6** and **8** are Ru_2(II,III) species and have effective magnetic moments ranging from 3.7 to 3.9 μ_B at room temperature, which is consistent with a $S = {}^3/_2$ ground state. Compounds **7** and **9** are Ru_2(III,III) species and diamagnetic. All compounds reported herein are stable in an ambient atmosphere as both solids and solutions. The Me_3Si groups in compounds **6a**, **7a**, **8a**, and **9a** can be easily removed with K_2CO_3, as shown in Scheme 4.

Structures of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-n}(OAc)_nCl$ Type Compounds (*n* = 1 and 2). Molecular structures of compounds **1** and **2** were determined through single-crystal X-ray diffraction studies. ORTEP plots of **1** and **2** are shown in Figures 1 and 2, respectively, and some selected bond lengths and angles are listed in Table 1. The Ru−Ru bond lengths in **1** and **2** are 2.3219(4) and 2.3144(5) Å, respectively, which are between those reported for $Ru_2(O_2CR)_4Cl$ type (2.27−2.30 Å) and $Ru_2(DArF)_4Cl$ type compounds (2.34−2.39 Å).[23] Clearly, the Ru−Ru distance gradually increases as the number of DArF ligands increases in the $Ru_2(DArF)_{4-n}(OAc)_nCl$ type compounds. While Ru−O bond lengths in $Ru_2(O_2CR)_4Cl$ are within a narrow range of 2.02−2.03 Å, Ru−O bond lengths are ca. 2.08 and 2.05 Å in compounds **1** and **2**, respectively, reflecting the destabilization of the Ru−O bond by the *trans*-Ru−N bond (trans influence). In comparison with **1**, compound **2** has less steric crowding around the axial positions, which permits the coordination of H_2O in addition to the Cl ligand. Similar axial H_2O coordination was observed in the structures of $Ru_2(DpAniF)_2(OAc)_2Cl$[19] and $Ru_2(DmAniF)_2(OAc)_2Cl$.[15]

Structures of DMBA-I-Containing Ru_2 Compounds. Among compounds containing the DMBA-I ligand, structures of **3** and **5** have been determined and some selected bond lengths and angles are included in Table 2. The molecular structure of **3**, shown in Figure 3, exhibits the expected feature of a DMBA-I ligand in place of the acetate in **1**. Upon substitution, the Ru−Ru bond is elongated from 2.3144(5) to 2.3276(8) Å, which is significantly shorter than that in $Ru_2(D(3,5\text{-}Cl_2Ph)F)_4Cl$ [2.368(1) Å].[24] As shown in Figure 4, the coordination sphere of compound **5** constitutes three sets of bidentate bridging ligands: two $D(3,5\text{-}Cl_2Ph)F$

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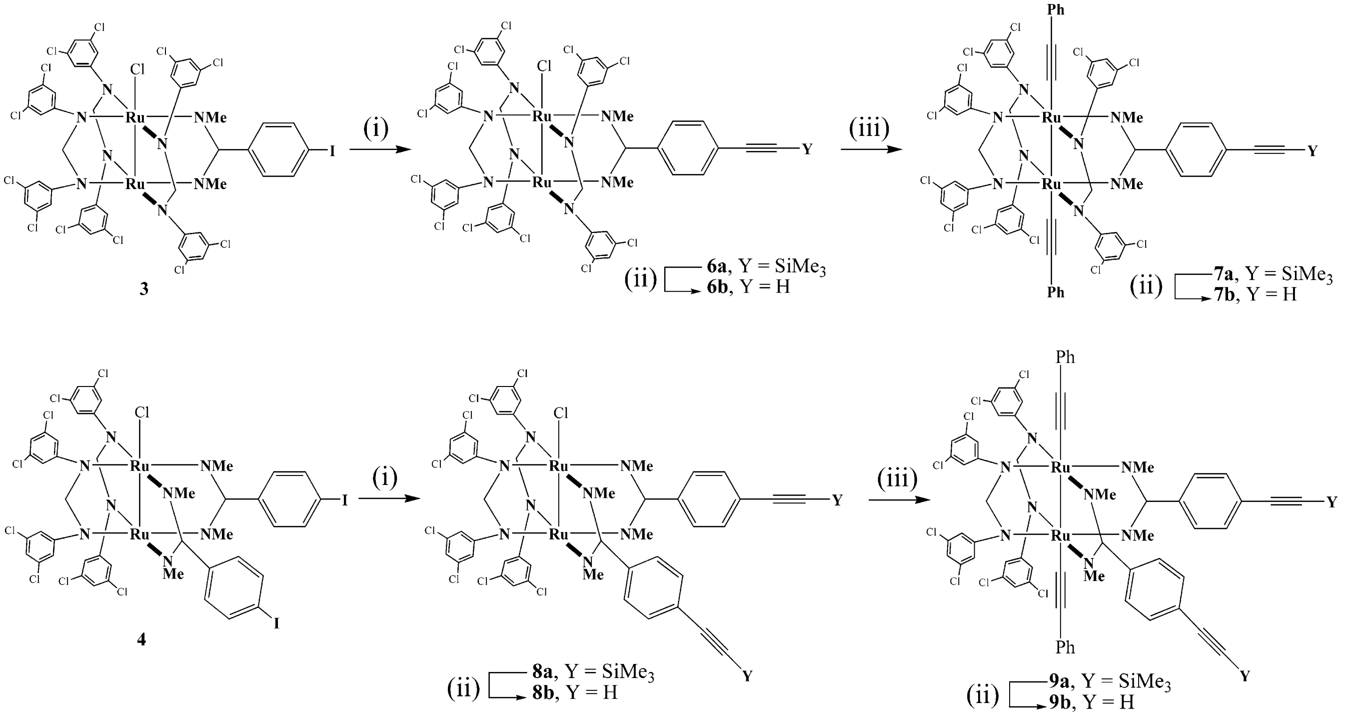
Scheme 4. Addition of Peripheral Ethynyl and Axial Alkynyl[a]



[a] Conditions: (i) HC_2TMS, *trans*-$Pd(PPh_3)_2Cl_2$, CuI, $^{i}Pr_2NH$, THF, rt. (ii) K_2CO_3, THF/methanol. (iii) 10 equiv of LiC_2Ph, THF.

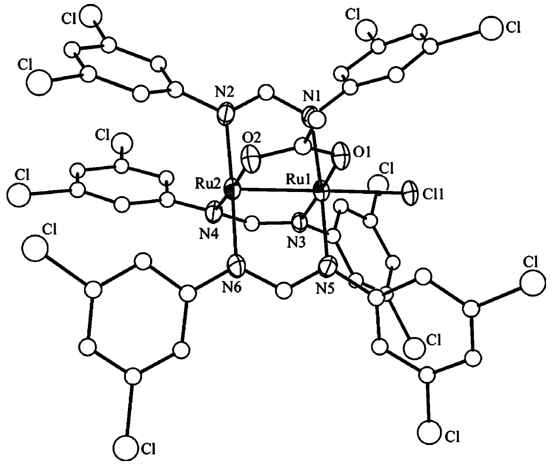


Figure 1. ORTEP representation of molecule **1** at 30% probability. All H atoms were omitted for clarity.

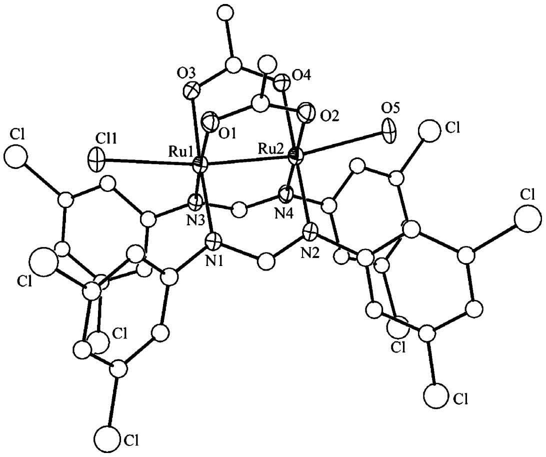


Figure 2. ORTEP representation of molecule **2** at 30% probability. All H atoms were omitted for clarity.

ligands in the cisoidal position, one DMBA-I ligand, and one carboxylate ligand. The Ru−Ru distance in **5** is 2.3186(8) Å and comparable to that in **3** [2.3144(5) Å]. As is clearly shown in Figure 4, compound **5** has very open axial positions when compared with **3** and, consequently, contains an axial H_2O molecule in addition to the nominal chloro axial ligand. It is interesting to note that both the Ru1−N5 and Ru2−N6 bonds are longer than the Ru1−N3 and Ru2−N4 bonds, a subtle consequence of the stronger trans influence of the DMBA-I ligand than DArF ligands.

Structures of Alkynyl-Containing Ru_2 Compounds. Compound **6a** is derived from the Sonogashira coupling reaction between compound **3** and $HC\equiv CSiMe_3$, and its structure (Figure 5) confirms the existence of peripheral $C\equiv CSiMe_3$. Compound **6b**, the desilylation product of **6a**, is shown in Figure 6. Ru−Ru bond distances in compounds **6a**, **6b**, and **3** (Table 3) range from 2.3166(7) to 2.3386(6) Å, reflecting the insensitivity of the Ru−Ru bond strength toward peripheral substituents. Compound **7b**, the bis(phenylacetylide) derivative of **6b**, has a drastically elongated Ru−Ru bond [2.5281(7) Å], which is consistent with a single bond between two Ru(III) centers (Figure 7).[12] The Ru−Ru−C1 [164.2(2)°] and Ru−Ru−C9 [161.6(2)°] angles significantly deviate from linearity, which are attributed to a second-order Jahn−Teller effect common among Ru_2(III,III) alkynyl compounds.[25]

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1** and **2**

1		**2**	
Ru1−Ru2	2.3220(7)	Ru1−Ru2	2.3267(7)
Ru1−N1	2.088(5)	Ru1−N1	2.051(4)
Ru1−N3	2.103(5)	Ru1−N3	2.063(4)
Ru1−N5	2.068(6)	Ru2−N2	2.031(4)
Ru2−N2	2.049(5)	Ru2−N4	2.030(4)
Ru2−N4	2.063(5)	Ru1−O1	2.053(3)
Ru2−N6	2.013(6)	Ru1−O3	2.054(3)
Ru1−O1	2.082(5)	Ru2−O2	2.048(3)
Ru2−O2	2.075(5)	Ru2−O4	2.043(3)
Ru1−Cl1	2.405(2)	Ru2−O5	2.362(3)
		Ru1−Cl1	2.480(1)
Ru2−Ru1−Cl1	175.37(5)	Ru2−Ru1−Cl1	171.52(3)
		Ru1−Ru2−O5	169.90(8)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **3** and **5**

3		**5**	
Ru1−Ru2	2.3276(8)	Ru1−Ru2	2.3186(8)
Ru1−N1	2.030(1)	Ru1−N1	2.056(1)
Ru1−N3	2.052(1)	Ru1−N3	2.058(1)
Ru1−N5	2.063(1)	Ru1−N5	2.116(1)
Ru1−N7	2.063(1)	Ru2−N2	2.031(1)
Ru2−N2	2.049(1)	Ru2−N4	2.064(1)
Ru2−N4	2.083(1)	Ru2−N6	2.069(1)
Ru2−N6	2.113(1)	Ru1−O1	2.078(1)
Ru2−N8	2.115(1)	Ru2−O2	2.035(1)
Ru1−Cl1	2.153(1)	Ru1−Cl1	2.523(1)
		Ru2−O3	2.371(1)
Ru2−Ru1−Cl1	178.41(4)	Ru2−Ru1−Cl1	174.99(3)
		Ru1−Ru2−O3	172.56(4)

Electrochemistry. As is often observed for Ru_2 paddlewheel species,[12] all compounds reported herein display rich and sometimes complicated redox chemistry. Cyclic voltammograms (CVs) measured for $Ru_2(DArF)_3(OAc)$ and $Ru_2(DArF)_3(DMBA)$ type compounds, namely, **1**, **3**, **6a**, and **7a**, are shown in Figure 8, and the tentative assignment of the observed couples is shown in Scheme 5. Compound **1** exhibits three Ru_2-based one-electron couples: one oxidation (B) and two reductions (C and D). The first reduction (C) is quasi-reversible because of the partial dissociation of an axial Cl^- ligand upon reduction, and the resultant species, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)$, is reoxidized at a more positive potential (E). Upon a second reduction (D), one or more ligands dissociated completely and rendered the couple irreversible. As derivatives of **1**, both $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3\text{-}(DMBA)Cl$ type compounds (**3** and **6a**) also exhibit one oxidation and two reductions with improved reversibility in

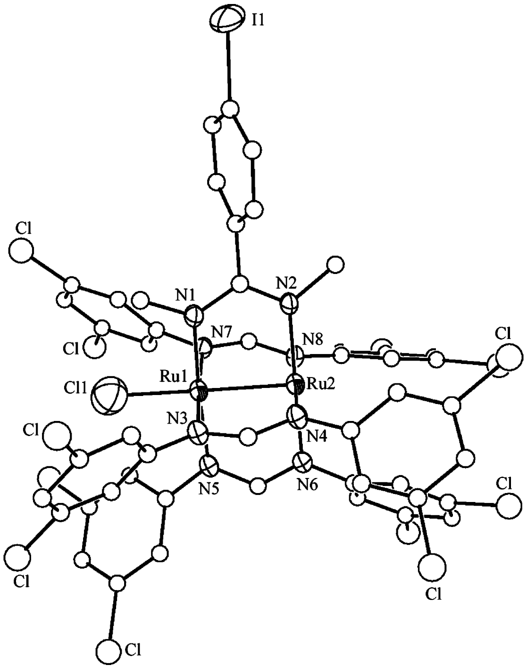


Figure 3. ORTEP representation of molecule **3** at 30% probability. All H atoms were omitted for clarity.

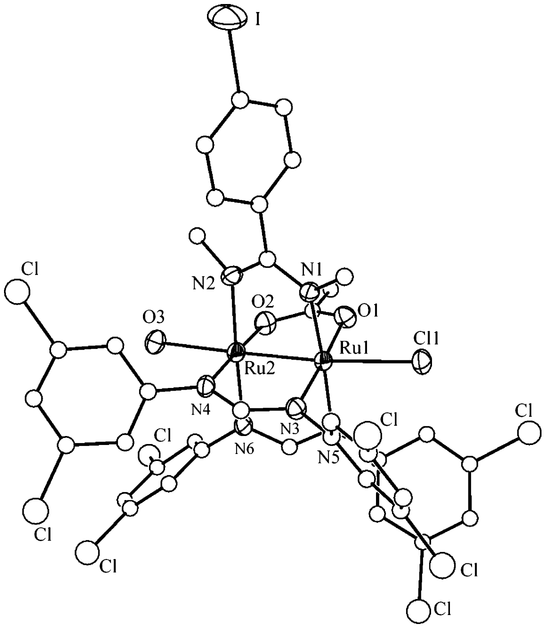


Figure 4. ORTEP representation of molecule **5** at 30% probability. All H atoms were omitted for clarity.

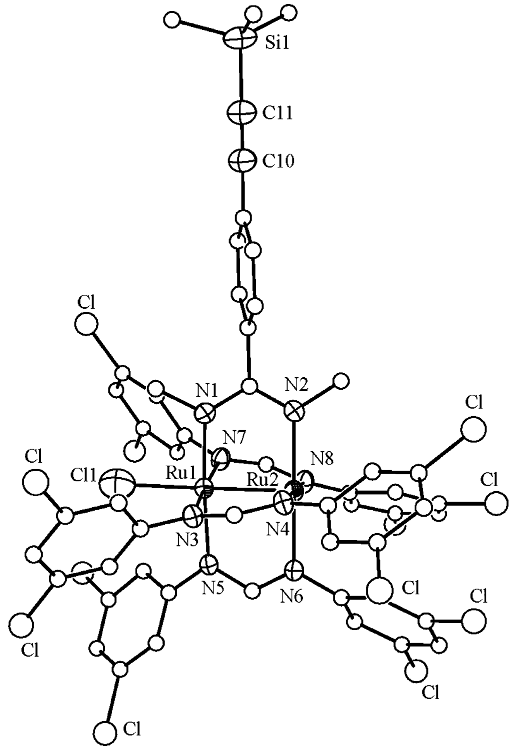


Figure 5. ORTEP representation of molecule **6a** at 30% probability.

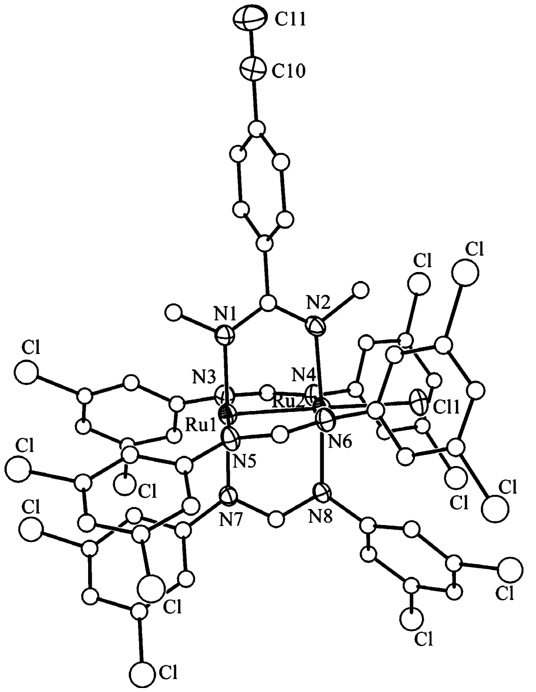


Figure 6. ORTEP representation of molecule **6b** at 30% probability.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds **6a**, **6b**, and **7b**

	6a	6b	7b	
Ru1−Ru2	2.3281(7)	2.3386(6)	Ru1−Ru2	2.5281(7)
Ru1−Cl1	2.2881	2.407(1)	Ru1−N1	2.030(4)
Ru1−N1	2.0484	2.042(4)	Ru1−N3	2.136(4)
Ru1−N3	2.0910	2.089(4)	Ru1−N5	2.065(4)
Ru1−N5	2.1148	2.126(4)	Ru1−N7	2.009(4)
Ru1−N7	2.0993	2.095(4)	Ru2−N2	1.987(4)
Ru2−N2	2.0400	2.016(4)	Ru2−N4	2.018(4)
Ru2−N4	2.0703	2.056(4)	Ru2−N6	2.077(4)
Ru2−N6	2.0685	2.075(4)	Ru2−N8	2.125(4)
Ru2−N8	2.0602	2.056(4)	Ru1−C1	1.993(5)
C10−C11	1.191(9)	1.203(8)	Ru2−C9	1.986(5)
			C1−C2	1.192(7)
			C9−C10	1.187(7)
			C26−C27	1.168(10)
Ru2−Ru1−Cl1	178.16(3)	177.69(4)	Ru2−Ru1−C1	164.2(2)
			Ru1−Ru2−C9	161.6(2)

general. While three aforementioned compounds are Ru_2(II,III) species, bis(phenylacetylide) adduct **7a** is a Ru_2(III,III) species and exhibits an irreversible oxidation (A), a reversible reduction (B), and a quasi-reversible reduction (C).

CVs measured for $Ru_2(LL)_2(LL')_2$ type compounds, namely, **2**, **4**, **8a**, and **9a**, are shown in Figure 9, and the observed couples can also be assigned based on Scheme 5. The CV of **2** consists of two reductions (C and D) and two irreversible oxidations (B1 and B2) of different currents. The presence of two oxidations in $[Ru_2(DPhF)_3Cl]_2[\mu\text{-}1,4\text{-}C_6H_4CO_2)_2]$ was noted by Jiménez-Aparicio and co-workers recently and rationalized with the fast association/dissociation of an axial H_2O ligand.[21] Axial coordination of H_2O in **2** was clearly revealed by an X-ray study (Figure 2), which may be responsible for the appearance of B1 and B2. The *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA)_2Cl$ type compounds **4** and **8a** exhibit CVs of the same type of redox couples as that of **2** but significantly improved reversibility that is attributed to the robustness of N,N′-bidentate ligands over carboxylates. Electrode potentials of corresponding couples in **4** and **8a** are identical within experimental errors, indicating a minimal electronic perturbation of the Ru_2 core by peripheral substituents. The oxidation couples B of compounds **4** and **8a** were cathodically shifted by 0.46 V from that of compound **2** and by 0.25 V from those of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA)$-Cl type compounds (**3** and **6a**), reflecting the strong donor

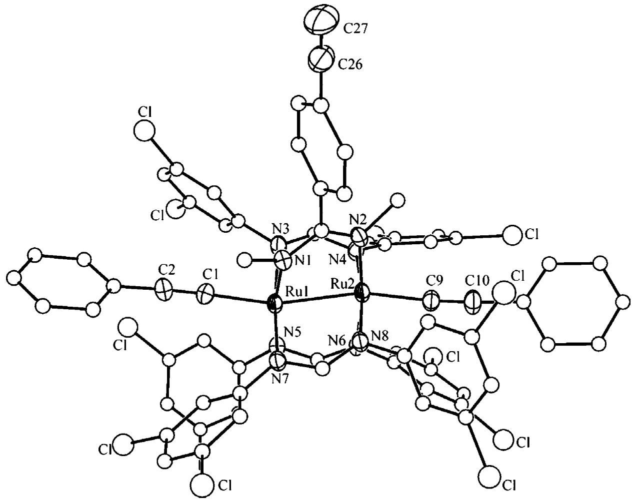


Figure 7. ORTEP representation of molecule **7b** at 30% probability.

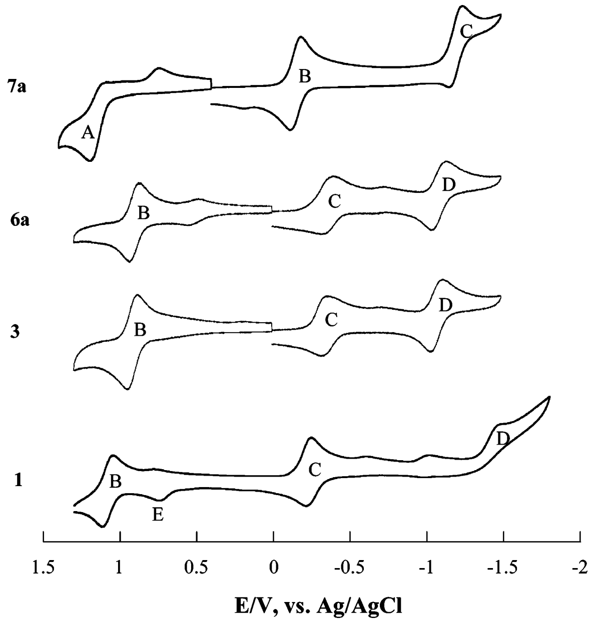
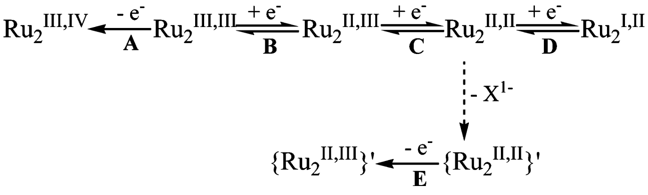


Figure 8. CVs of $Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_3(OAc)$ and $Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_3$-(DMBA) type compounds recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V s^{-1}.

Scheme 5. Assignments of Observed Ru_2-Based Redox Couples[a]



[a] X stands for the axial ligand.

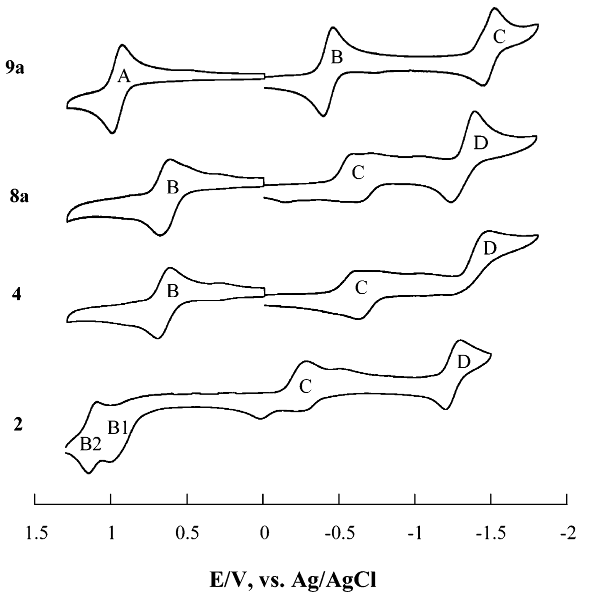


Figure 9. CVs of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_2(OAc)_2$ and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_2(DMBA)_2$ type compounds recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V s^{-1}.

nature of DMBA ligands. Both compounds **4** and **8a** are less stable toward reduction than compounds **3** and **6a**, as shown by the irreversibility of couples C. Clearly, $Ru_2(LL)_2(LL')_2$-Cl type compounds are less redox-robust than $Ru_2(LL)_3(LL')$-Cl type compounds. The bis(phenylacetylide) compound **9a**, a Ru$_2$(III,III) species, displays a well-behaved CV with one reversible oxidation (A) and two reversible reductions (B and C). The electrode potentials are cathodically shifted by at least 220 mV from those of the corresponding couples in $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}C_2TMS)(C_2Ph)_2$ (**7a**). The reversibility of the oxidation couple (A) depends on the number of DMBA ligands: compound **7a** contains one DMBA ligand and the oxidation (A) is irreversible, resembling those of $Ru_2(DArF)_4(C_2Y)_2$ type compounds.[25,26] Compound **9a** has two DMBA ligands and its oxidation (A) is reversible, analogous to those of $Ru_2(DMBA)_4(C_2Y)_2$ type compounds.[27]

Conclusion

$Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_{4-n}(O_2CMe)_nCl$ (n = 1 and 2) type compounds were prepared and further derivatized to yield Ru$_2$ compounds containing peripheral iodo and ethynyl substituents. The latter compounds are of interest as building blocks for both homo- and heterodimeric supramolecular molecules. Moreover, functional dendrons can be covalently grafted onto the periphery of those building blocks through various organic coupling reactions such as Heck and *Click* reactions. Promising preliminary results have been obtained and will be reported soon.

Experimental Section

(Trimethylsilyl)acetylene and phenylacetylene were purchased from GFS Chemicals, silica gel was purchased from Merck, and CuI and *trans*-$Pd(PPh_3)_2Cl_2$ were purchased from Strem Chemicals. Ligands HD(3,5-Cl_2Ph)F and HDMBA-I were prepared from modified literature procedures.[28] 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. Cyclic and differential pulse 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-C working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode. The concentration of Ru$_2$ 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 $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ (1) and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ (2). A round-bottomed flask was charged with $Ru_2(OAc)_4Cl$ (1.0 g, 2.11 mmol), *N*,*N*′-bis(3,5-dichlorophenyl)formamidine (2.11 g, 6.33 mmol), LiCl (0.50 g), Et$_3$N (2 mL), and 60 mL of THF. The mixture was gently refluxed overnight. After cooling to room temperature, the reaction mixture was filtered through a silica gel pad to get rid of excess LiCl. The mixture was further purified with a silica column (THF/hexanes = 1/9 to 1/1) to yield 1.15 g of **1** (42% based on Ru) and 0.69 mg of **2** (32% based on Ru).

Data for 1. FABMS (*m*/*e*, based on ^{101}Ru): 1261 [M − Cl]$^+$. Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 515 (5260). Anal. Found (calcd) for $C_{41}H_{24}ClN_6O_2Ru_2$: C, 38.04 (38.01); H, 1.68 (1.87); N, 6.48 (6.49). χ_{mol}(corrected) = 6.35 × 10^{-3} emu, μ_{eff} = 3.89 μ_B. CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: B, 1.078, 0.065, 0.703; C, −0.222, 0.054, 0.772; E_{pc}(D), −1.484; E_{pa}(E), 0.736.

Data for 2. FABMS (*m*/*e*, based on ^{101}Ru): 988 [M − Cl]$^+$. Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 515 (5260). Anal. Found (calcd) for $C_{32}H_{24}Cl_9N_4O_5Ru_2$ (**2**·0.5THF): C, 35.85 (36.20); H, 2.44 (2.66); N, 5.02 (5.28). χ_{mol}(corrected) = 5.99 × 10^{-3} emu, μ_{eff} = 3.78 μ_B. CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: E_{pa}(B1), 1.000; $E_{1/2}$(B2), 1.281; E_{pc}(C), −0.304; D, −1.270, 0.141, 0.468.

Method B To Prepare 2. A round-bottomed flask was charged with $Ru_2(OAc)_4Cl$ (0.47 g, 1.0 mmol), 1.1 equiv of *N*,*N*′-bis(3,5-dichlorophenyl)formamidine (0.37 g, 1.1 mmol), excess of LiCl, and 40 mL of THF. The mixture was gently refluxed for 1 h, and at that point, another 1.1 equiv of *N*,*N*′-bis(3,5-dichlorophenyl)formamidine was added to the reaction mixture. After refluxing under N$_2$ overnight, the mixture was cooled to room temperature and filtered through silica gel to get rid of excess LiCl. Thin-layer chromatography indicates that compound **2** is the major product. The purification is the same as that above. Yield: 0.88 g (86%).

Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}I)Cl$ (3). A mixture of **1** (1.2 g, 0.93 mmol), *N*,*N*′-dimethyl-4-iodobenzamidine (0.38 g, 1.40 mmol), LiCl (0.20 g), Et$_3$N (2 mL), and THF (40 mL) was refluxed overnight, with the color of the reaction mixture changing from dark purple to green. The reaction mixture was filtered through silica gel. After solvent removal, the residue was purified from recrystallization (THF/hexanes = 1/9) to yield a green crystalline material (1.2 g, 86%). FABMS (*m*/*e*, based on ^{101}Ru): 1511 [M$^+$]. Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 473 (8280), 581 (3580). Anal. Found (calcd) for $C_{48}H_{31}Cl_{13}N_8IRu_2$·THF: C, 39.46 (39.48); H, 2.22 (2.49); N, 7.42 (7.08). χ_{mol}(corrected) = 6.41 × 10^{-3} emu, μ_{eff} = 3.91 μ_B. CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: B, 0.915, 0.061, 0.992; C, −0.343, 0.068, 0.785; D, −1.077, 0.080, 0.863.

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}I)_2Cl$ (4). A mixture of **2** (0.2 g, 0.20 mmol), HDMBA-I (0.22 g, 0.80 mmol),

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LiCl (0.10 g), Et_3N (1 mL), and THF (40 mL) was refluxed overnight, with the color of the reaction mixture changing from dark purple to green. On cooling to room temperature, the reaction mixture was filtered through silica gel. After solvent removal, the residue was purified via recrystallization from THF/hexanes (1/9) to yield a green crystalline material (0.21 g, 85%). Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 442 (6000), 547 (2060), 654 (1400). χ_{mol}(corrected) $= 6.83 \times 10^{-3}$ emu, $\mu_{eff} = 3.83\ \mu_B$. Anal. Found (calcd) for $C_{44}H_{38}N_8Cl_9I_2Ru_2$: C, 36.57 (36.35); H, 2.47 (2.63); N, 7.62 (7.71). CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: B, 0.664, 0.077, 0.850; E_{pc}(C), −0.612; E_{pc}(D), −1.480.

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}I)(O_2CMe)$-Cl (5). A mixture of **2** (0.20 g, 0.20 mmol), H-DMBA-I (0.05 g, 0.20 mmol), 20 mL of THF, and excess of LiCl and Et_3N was refluxed under Ar for 1 h. The color of the reaction mixture changed from purple to brown. The purification of the desired product was carried out by a silica column (THF/hexanes = 1/5 to 1/2). Yield: 0.14 g (58%). FABMS 1022 [M − Cl]$^+$. χ_{mol}(corrected) $= 6.48 \times 10^{-3}$ emu, $\mu_{eff} = 3.93\ \mu_B$. Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 475 (5030). Anal. Found (calcd) for $C_{37}H_{31}N_6Cl_9IO_2Ru_2$·THF: C, 37.11 (37.54); H, 2.64 (3.00); N, 6.53 (6.41).

Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2TMS)Cl$ (6a). A mixture of **3** (1.2 g, 0.79 mmol), *trans*-$Pd(PPh_3)_2Cl_2$ (0.1 g, 0.14 mmol), CuI (0.05 g, 0.26 mmol), $^iPr_2NH$ (20 mL), THF (20 mL), and (trimethylsilyl)acetylene (0.5 mL) was stirred at room temperature overnight. After solvent removal, the residue was dissolved in a THF/hexanes (1/5) solution and filtered through silica gel. The filtrate was allowed to stand, and needlelike crystals were harvested over 2 days. Yield: 0.88 g (75%). FABMS (*m*/*e*, based on ^{101}Ru): 1442 [M$^+$ − Cl]. Anal. Found (calcd) for $C_{56}H_{48}Cl_{13}N_8Ru_2Si$·THF: C, 44.09 (44.11); H, 2.80 (3.12); N, 7.30 (7.22). χ_{mol}(corrected) $= 6.04 \times 10^{-3}$ emu, $\mu_{eff} = 3.79\ \mu_B$. Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 473 (8190), 573 (3560). CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: B, 0.903, 0.062, 0.998; C, −0.358, 0.082, 0.741; D, −1.096, 0.097, 0.917.

Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)Cl$ (6b). Compound **6a** (0.35 g, 0.24 mmol) was dissolved in 30 mL of THF/methanol (20 mL/10 mL), to which 500 mg of K_2CO_3 was added. After being stirred at room temperature for 2 h, the mixture was filtered through a 2-cm silica gel pad. Removal of the solvent afforded **6b** as a brown microcrystalline material, which was further purified via recrystallization from THF/hexanes (1/9). Yield: 0.22 g (65%). FABMS (*m*/*e*, based on ^{101}Ru): 1409 [MH$^+$]. Anal. Found (calcd) for $C_{50}H_{36}Cl_{13}N_8Ru_2$·THF: C, 43.74 (43.70); H, 2.73 (2.90); N, 7.51 (7.55).

Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2TMS)(C_2Ph)_2$ (7a). To 40 mL of THF containing 0.4 g of **6a** was added 10 equiv of PhCCLi, and the mixture was stirred at room temperature for 30 min, during which time the solution became dark red. O_2 was bubbled through the reaction mixture for 15 min, and the mixture was filtered through a silica gel pad. After solvent removal, the residue was purified via recrystallization from THF/methanol to yield 0.22 g of a dark-red crystalline material (46%). ^1H NMR: δ 8.16 (s, 1H, NC*H*N), 7.99 (s, 2H, NC*H*N), 7.82−7.78 (d, 2H, aromatic), 7.24−6.48 (m, 30H, aromatic), 3.62 (s, 6H, NCH_3), 0.32 (s, 18H, Si(CH_3)$_3$). Anal. Found (calcd) for $C_{69}H_{54}Cl_{12}N_8Ru_2Si$: C, 50.55 (50.20); H, 3.05 (3.30); N, 6.85 (6.79). Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 520 (15 320), 900 (sh). CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: E_{pa}(A), 1.197; B, −0.154, 0.071, 0.860, E_{pc}(C), −1.247.

Preparation of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)(C_2Ph)_2$ (7b). Compound **7a** (0.15 g, 0.09 mmol) was dissolved in 30 mL of THF/methanol (20 mL/20 mL), to which 500 mg of K_2CO_3 was added. After stirring at room temperature for ca. 1 h, the mixture was purified via recrystallization from THF/methanol to yield 0.07 g (49%) of dark-red material. FABMS (*m*/*e*, based on ^{101}Ru): 1577 [M$^+$]. ^1H NMR: δ 8.18 (s, 1H, NC*H*N), 8.00 (s, 2H, NC*H*N), 7.84−7.80 (d, 2H, aromatic), 7.30−6.60 (m, 30H, aromatic), 3.63 (s, 6H, NCH_3).

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2TMS)_2Cl$ (8a). A mixture of **4** (0.5 g, 0.34 mmol), *trans*-$Pd(PPh_3)_2Cl_2$ (0.1 g, 0.14 mmol), CuI (0.05 g, 0.26 mmol), $^iPr_2NH$ (20 mL), THF (20 mL), and (trimethylsilyl)acetylene (0.5 mL) was stirred at room temperature overnight. After solvent removal, the residue was dissolved in a THF/hexanes (1/4) solution and filtered through silica gel. The filtrate was collected, and after the solvent was removed, the residue was recrystallized from ethyl acetate/hexanes (1/7) to yield a gray/green crystalline material. Yield: 0.37 g (78%). ESIMS 1367 [M − Cl]$^+$. χ_{mol}(corrected) $= 5.89 \times 10^{-3}$ emu, $\mu_{eff} = 3.75\ \mu_B$. Anal. Found (calcd) for $C_{54}H_{56}N_8Cl_9Ru_2Si_2$·THF: C, 47.05 (47.50); H, 4.08 (4.40); N, 7.43 (7.64). Vis−near-IR: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 444 (9100), 650 (2520). CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: B, 0.652, 0.070, 0.829; E_{pc}(C), −0.592; D, −1.262, 0.172, 0.706.

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2Cl$ (8b). Compound **8a** (0.20 g, 0.14 mmol) was dissolved in 30 mL of ethyl acetate/methanol (20 mL/10 mL), to which 0.2 g of K_2CO_3 was added. After stirring at room temperature for 20 min, the mixture was filtered through a 2-cm silica gel pad to remove excess K_2CO_3. Removal of the solvent afforded **8b** as a green material, which was further purified by recrystallization (ethyl acetate/hexanes = 1/6). Yield: 0.33 g (90%). FABMS (*m*/*e*, based on ^{101}Ru): 1211 [M$^+$ − Cl]. Anal. Found (calcd) for $C_{48}H_{40}N_8Cl_9Ru_2$: C, 46.67 (46.12); H, 2.89 (3.23); N, 9.00 (8.96).

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2TMS)_2$-$(C_2Ph)_2$ (9a). To a THF solution containing 0.29 g of **8a** (0.21 mmol) was added 5 equiv of PhCCLi. After stirring under N_2 for 15 min, O_2 was bubbled through the reaction mixture. The product was purified by chromatography (ethyl acetate/hexanes = 1/10). Yield: 0.24 g (75%). UV−vis: λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 518 (14 350), 912 (1580). ^1H NMR: δ 8.00 (s, 2H, NC*H*N), 7.7.0−6.78 (m, 30H, aromatic), 3.37 (s, 12H, NCH_3), 0.303 (s, 18H, Si(CH_3)$_3$). Anal. Found (calcd) for $C_{70}H_{66}N_8Cl_8Ru_2Si_2$·THF: C, 54.51 (54.41); H, 4.24 (4.57); N, 6.87 (6.86). CV [$E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$]: A, 0.971, 0.065, 0.917; B, −0.418, 0.064, 0.956; D, −1.477, 0.066, 0.731.

Preparation of *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2(C_2Ph)_2$ (9b). Compound **9a** (0.20 g) was dissolved in 20 mL of THF and 10 mL of methanol, to which was added an excess of K_2CO_3. After stirring for 30 min, the solution was filtered through silica gel. Removal of the solvent afforded a dark-red powder, **9b**. Yield: 0.13 g (75%). ^1H NMR: δ 8.00 (s, 2H, NC*H*N), 7.72−6.78 (m, 30H, aromatic), 3.38 (s, 12H, NCH_3), 3.22 (s, 2H, C_2*H*).

X-ray Data Collection, Processing, and Structural Analysis and Refinement. Single crystals were grown via slow evaporation of a hexanes/ethyl acetate solution (**1**) or a THF/hexanes solution (**2**, **3**, and **5**). The X-ray intensity data were measured at 300 K on a Bruker SMART1000 CCD-based X-ray diffractometer system using Mo Kα (λ = 0.710 73 Å). Thin plates of dimensions 0.20 × 0.10 × 0.04 mm^3 (**1**), 0.14 × 0.08 × 0.06 mm^3 (**2**), 0.18 × 0.10 × 0.01 mm^3 (**3**), 0.31 × 0.12 × 0.01 mm^3 (**5**), 0.28 × 0.0.21 × 0.06 mm^3 (**6a**), 0.27 × 0.25 × 0.10 (**6b**), and 0.42 × 0.30 × 0.08 mm^3 (**7b**) were used for X-ray crystallographic analysis (Table 4). Crystals were cemented on a quartz fiber with epoxy glue. Data were measured using ω scans of 0.3°/frame such that a hemisphere (1271 frames) was collected. No decay was indicated for any of

Table 4. Crystal Data for Compounds **1**−**3**, **5**, **6a**, **6b**, and **7b**

	1$\cdot{}^1/_2C_6H_{14}\cdot$EtOAc	**2**$\cdot H_2O\cdot$2THF	**3**$\cdot$2THF	**5**	**6a**$\cdot{}^1/_2C_6H_6\cdot$THF	**6b**	**7b**$\cdot{}^1/_2C_6H_{14}\cdot$THF
formula	$C_{48}H_{24}Cl_{13}N_6O_4Ru_2$	$C_{38}H_{21}Cl_9N_4O_7Ru_2$	$C_{56}H_{31}Cl_{13}IN_8O_2Ru_2$	$C_{45}H_{27}Cl_9IN_6O_5Ru_2$	$C_{60}H_{40}Cl_{13}N_8ORu_2Si$	$C_{50}H_{32}Cl_{13}N_8Ru_2$	$C_{73}H_{57}Cl_{12}N_8ORu_2$
fw	1411.72	1166.78	1637.78	1379.82	1580.08	1407.83	1689.81
space group	$C2$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	29.0204(15)	11.247(3)	12.8766(9)	15.416(2)	13.2166(12)	11.6248(10)	14.444(2)
b, Å	14.8456(8)	12.382(2)	13.0643(9)	22.943(4)	14.0803(14)	15.1656(13)	14.451(2)
c, Å	13.4913(7)	18.534(5)	21.5652(14)	17.110(4)	18.807(3)	32.409(3)	18.962(3)
α, deg		77.32(2)	107.493(1)		89.144(7)		93.125(11)
β, deg	100.314(1)	73.25(2)	91.9230(1)	113.033(14)	87.640(14)	100.0340(10)	99.824(11)
γ, deg		72.070(13)	104.573(1)		80.432(10)		106.141(9)
V, Å^3	5718.5(5)	2327.3(10)	3325.2(4)	5568.9(18)	3448.1(7)	5626.2(8)	3724.4(10)
Z	4	2	2	4	2	4	2
T, °C	27	27	27	27	27	27	27
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1.640	1.665	1.636	1.646	1.522	1.662	1.507
μ, mm^{-1}	0.53	1.212	1.486	1.575	1.004	1.198	0.885
R1	0.043	0.041	0.063	0.055	0.053	0.048	0.048
wR2	0.102	0.099	0.170	0.134	0.143	0.113	0.123

the six data sets in the re-collection of the first 50 frames at the end of each data collection. The frames were integrated with the Bruker *SAINT* software package[29] using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using *SADABS* supplied by George Sheldrick.

Structures were solved and refined using the Bruker *SHELXTL* (version 5.03) software package[30] in the space groups $C2$ for **1**, $P\bar{1}$ for **2**, **3**, **6a**, and **7b**, and $P2_1/c$ for **5** and **6b**. Positions of all non-H atoms of Ru_2 moieties were revealed by direct methods. In the case of crystal **1**, the asymmetric unit contains one independent molecule, half of a hexane solvate molecule, and one ethyl acetate solvate molecule. Crystal **2** displayed an asymmetric unit containing one independent molecule, two THF solvate molecules, and one H_2O molecule coordinated to the axial position. Crystals **3** and **5** both contain asymmetric units containing one independent molecule and two THF solvate molecules. In the case of crystal **6a**, the asymmetric unit contains one independent molecule, one THF solvate molecule, and half of a benzene solvate molecule. In the case of crystal **6b**, the asymmetric unit contains one independent molecule. In the case of crystal **7b**, the asymmetric unit contains one independent molecule, one THF solvate molecule, and one H_2O. With all non-H atoms being anisotropic and all H atoms in the calculated position and riding mode, the structure was refined to convergence by a least-squares method on F^2, *SHELXL-93*, incorporated in *SHELXTL.PC V 5.03*.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structural determination of compounds **1**−**3**, **5**, **6a**, **6b**, and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) *SAINT V 6.035 Software for the CCD Detector System*; Bruker-AXS Inc.: Madison, WI, 1999.

(30) *SHELXTL 5.03 (WINDOW-NT Version), Program library for Structure Solution and Molecular Graphics*; Bruker-AXS Inc.: Madison, WI, 1998.