Negishi Coupling—Expedient Formation of Biphenyls on the Periphery of Inorganic/Organometallic Diruthenium Species

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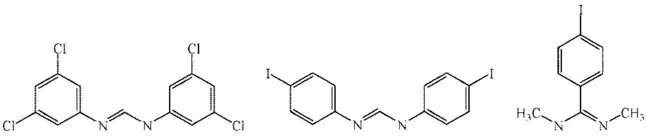
Received October 26, 2007

Summary: Negishi coupling is a facile, mild, and high-yield alternative to Suzuki coupling in the biphenyl formation at the periphery of diruthenium coordination and organometallic compounds.

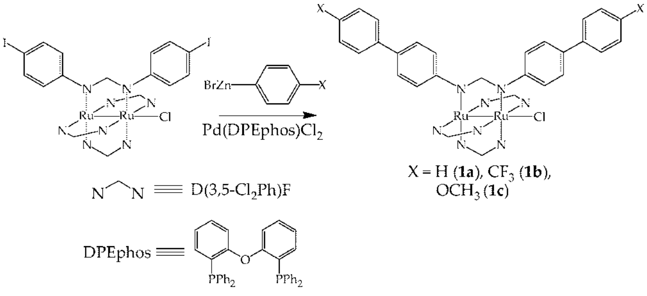
Carbon−carbon bond formation through metal catalyzed cross-coupling reactions[1] has become an indispensable synthetic tool for the organic, medicinal, and materials chemistry communities. Because of both the high reactivity and selectivity and mild reaction conditions, cross-coupling should be useful for the synthesis of inorganic/organometallic compounds, especially inorganic polymers, dendrimers, and supramolecules. The application of cross-coupling reactions in inorganic/organometallic synthesis, however, remains sparse. Limited efforts in recent years have been focused on the utility of the Sonogashira[2] and Suzuki[3] reactions in derivatizing metalloporphyrins and metal bi- and terpyridine complexes. A sustaining interest of one of our groups (Ren) has been the use of Ru_2−alkynyl compounds as molecular wires and active species in molecular devices, and the rich optical and electrochemical characteristics of Ru_2−alkynyl compounds are noteworthy.[4] Aiming at controlled assemblies through the formation of robust bonds, we have explored various cross-coupling reactions at the periphery of Ru_2 species, including the Sonogashira coupling and subsequent click reactions,[5,6] Suzuki coupling,[7] and Heck coupling.[8] Some of the aforementioned reactions invoked prolonged reflux in solvents with high boiling points, which can be a demanding reaction condition for Ru_2−alkynyl species. Recently, C−C bond formation reactions at the periphery of metallocenes and metal−bipy complexes were achieved under very mild conditions using the Negishi coupling method,[9] which encompasses the cross-coupling reactions between organic halides and organometallics including Zn, Al, and Zr with Pd/Ni catalysts.[10] Reported herein are the biphenyl formation reactions at the periphery of two different types of Ru_2 compounds using the Negishi method.

Chart 1. Structures of Ligands L and L′



D(3,5-Cl$_2$Ph)F **D(4-IPh)F** **DMBA-I**

Scheme 1. Synthesis of Compounds 1



X = H (**1a**), CF_3 (**1b**), OCH_3 (**1c**)

The peripheral modification is primarily based on the Ru_2L_3L' type compounds, where the auxiliary ligand L is *N*,*N*′-bis(3,5-dichlorophenyl)formamidinate (D(3,5-Cl_2Ph)F; Chart 1) and the reactive ligand L′ is either *N*,*N*′-bis(4-iodophenyl)formamidinate (D(4-IPh)F) or *N*,*N*′-dimethyl-4-iodobenzamidinate (DMBA-I). As shown in Scheme 1, the initial attempt was based on Ru_2(D(3,5-Cl_2Ph)F)$_3$(D(4-IPh)F)Cl (**A**), a Ru_2(II,III) species.[6] While Pd(DPEphos)Cl_2 was selected as the catalyst because of

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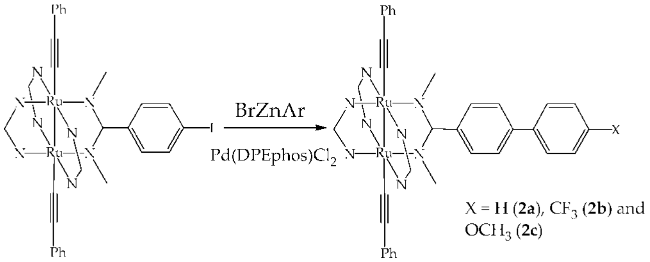
10.1021/om701083q CCC: $37.00

Table 1. Screening of Reaction Conditions[a] Based on $BrZnC_6H_4$-4-OCH_3

entry	amt of BrZnAr (equiv)	distribn (%)[b] **A**	mono	**1c**
1	1.2	50	40	10
2	2.2	40	40	20
3	4.0		trace	>95
4	8.0			100

[a] Conditions: **A**, 0.06 mmol; Pd(DPEphos)Cl_2, 0.007 mmol; 5 mL of THF, room temperature, 2 h. [b] Estimated from TLC.

Scheme 2. Negishi Modification of DMBA Compounds



X = H (**2a**), CF_3 (**2b**) and OCH_3 (**2c**)

its proven efficacy in promoting the Negishi coupling,[11] the optimum stoichiometry of organozinc reagents for *inorganic* Negishi modification was uncertain. Hence, a series of reactions using similar conditions but varying the stoichiometry of $BrZnC_6H_4$-4-OCH_3 were performed and the results are given in Table 1. It is clear from this table that the amount of the monoarylated intermediate was significant in both entries 1 and 2, and the conversion to the desired bis-arylated product (**1c**) was achieved with 4 equiv of $BrZnC_6H_4$-4-OCH_3 (1-fold excess). In practice, 8 equiv of $BrZnC_6H_4$-4-OCH_3 was used, and compound **1c** was isolated as a black crystalline material in a yield of 85%.[12] Reactions of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(D(4\text{-}IPh)F)Cl$ under similar conditions with either $BrZnC_6H_5$ or $BrZnC_6H_4$-4-CF_3 in large excess afforded either compound **1a** (60%) or **1b** (92%), respectively. Compound **1a** was also obtained in an improved yield (79%) when $BrZnC_6H_5$ was prepared from the corresponding Grignard reagent. Compound **1a** was previously prepared using the Suzuki coupling method in a lower yield (41%).[7] The new compounds **1b** and **1c** were analyzed satisfactorily with combustion analysis. They are both paramagnetic species with effective magnetic moments around 3.9 μ_B, which is consistent with an $S = {}^3/_2$ ground state.

The molecular structure of **1c** was established through a single-crystal X-ray diffraction study, and its structural plot is shown in Figure 1. The plot clearly revealed (1) the paddlewheel arrangement of N,N′-bidentate bridging ligands and (2) the 4-methoxyphenyls appended through the Negishi coupling reaction. Both the Ru−Ru and Ru−Cl bond lengths are typical for $Ru_2(DArF)_4Cl$ type compounds.[13] On the basis of both the structural and magnetic data, one can safely infer that the electronic structure of the Ru_2 core is not significantly altered upon biphenyl formation in compounds **1**.[14]

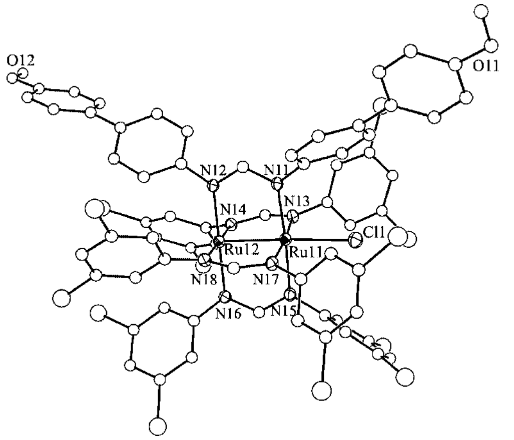


Figure 1. Structural plot of molecule **1c** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru11−Ru12, 2.3736(5); Ru11−Cl1, 2.4166(1); Ru11−N11, 2.084(4); Ru12−N12, 2.037(4); Ru11−N(DArF)$_{av}$, 2.095; Ru12−N(DArF)$_{av}$, 2.055; Ru12−Ru11−Cl1, 175.09(4).

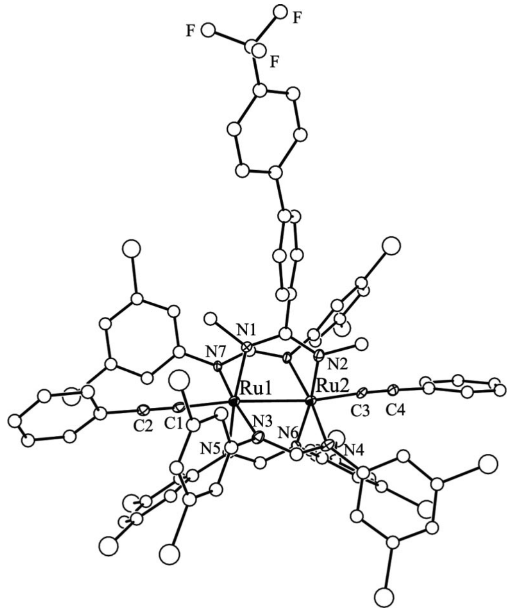


Figure 2. Structural plot of molecule **2b** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Ru2, 2.5271(9); Ru1−C1, 1.967(5); Ru2−C3, 1.977(5); Ru1−N1, 2.029(4); Ru2−N2, 1.980(4); Ru−N(DArF)$_{av}$, 2.067[4]; Ru2−Ru1−C1, 162.49(14); Ru1−Ru2−C3, 160.42(14).

The aforementioned successes prompted a further examination of Negishi coupling on other diruthenium species. *trans*-$(PhC{\equiv}C)_2[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}I)]$ (**B**)[6] was chosen because of its high oxidation state, namely Ru_2(III,III), and the presence of two σ-phenylacetylides. Compound **B** reacts smoothly with the organozinc reagent BrZnAr (large excess) in the presence of Pd(DPEphos)Cl_2 at room temperature to afford *trans*-$(PhC{\equiv}C)_2[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_6H_4\text{-}4'\text{-}X)]$ in good yield (Scheme 2; **2a**, X = H, 47%; **2b**, X = CF_3, 79%; **2c**, X = OMe, 75%).[15]

Compounds **2** are dark red-purple crystalline materials and are diamagnetic; they were characterized satisfactorily by both

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[12] *Synthesis of* $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(D(4\text{-}MeOPh\text{-}Ph)F)Cl$ (**1c**): $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(D(I\text{-}Ph)F)Cl$ (0.13 mmol), 4-bromozincanisole (1.0 mmol), and Pd(DPEphos)Cl_2 (0.014 mmol) were stirred in 10 mL of THF at room temperature for 1 h under a nitrogen atmosphere. The reaction mixture was filtered through a 2 cm silicon gel pad and subsequently purified on a silica column with hexanes−THF (10:2 v/v) to yield 180 mg of a black crystalline solid (85% based on Ru). Data for **1c** are as follows. Anal. Found (calcd) for $C_{66}H_{44}Cl_{13}N_8O_2Ru_2 \cdot 2C_4H_8O$: C, 49.72 (49.70); H, 3.32 (3.38); N, 6.54 (6.27).

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^{1}H NMR and combustion analysis. In addition, compound **2c** was successfully crystallized, and its molecular structure is shown in Figure 2. Obvious from the plot are (1) the overall paddlewheel arrangement of the N,N′-bridging ligands, (2) the 4′-$\mathrm{CF_3C_6H_4}$ group appended to the DMBA ligand, and (3) the presence of axial phenylacetylide ligands. Both the Ru−Ru (2.5271(9) Å) and Ru−C bond lengths (1.967(5) and 1.977(5) Å) are similar to the corresponding parameters reported for *trans*-$\mathrm{(PhC{\equiv}C)_2[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4'\text{-}C{\equiv}CH)]}$ (2.53 and 1.99 Å).[6] Also worthy of note is the significant deviation of the Ru−Ru−C bond angle (about 161°) from linearity, which is attributed to a second-order Jahn–Teller distortion common among $\mathrm{Ru_2}$(III,III) species.[16]

In this contribution, we have demonstrated that the Negishi coupling method is applicable to biphenyl formation at the periphery of both coordination and organometallic compounds. Furthermore, this method is expedient (2 h or less), uses very mild conditions (room temperature), and gives high yields, hence making it superior to the Suzuki method.[7] Structural and other physical properties appear to indicate that the peripheral modification derivatives **1** and **2** have electronic structures very similar to those of their parent compounds **A** and **B**, respectively. Of course, the scope of Negishi coupling is not limited to biphenyl formation, and it may be extended to the formation of C−C(sp^2) bonds (Heck-like) and C−C(sp) bonds (Sonogashira-like). These reactions are being explored in our (Ren) laboratory.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (Grant Nos. CHE 0715404 to T.R. and CHE 0309613 to E.N. and Grant No. CHE 0541766 to Case Western Reserve University for the purchase of an X-ray diffractometer) and Purdue University.

Supporting Information Available: Text and figures giving details of the synthesis and characterization data for compounds **1** and **2** and CIF files giving X-ray crystallographic data for the structure determination of compounds **1c** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) *Synthesis of trans-*$\mathit{(PhC{\equiv}C)_2[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}Ph)]}$ *(**2a**).* *trans*-$\mathrm{(PhC{\equiv}C)_2[Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}I)]}$ (100 mg, 0.06 mmol) was stirred with $\mathrm{BrZnC_6H_5}$ (0.5 mmol) and Pd(DPEphos)$\mathrm{Cl_2}$ (5 mg, 0.007 mmol) in 5 mL of THF for 2 h at room temperature. The reaction mixture was filtered through a 2 cm silicon gel pad, and the filtrate was purified on a silica column with hexanes−THF (20:1 v/v) to yield **2a** as a black crystalline solid (50 mg, 45% based on Ru). Data for **2a** are as follows. Anal. Found (calcd) for $\mathrm{C_{70}H_{46}Cl_{12}N_8Ru_2.3H_2O}$: C, 49.99 (50.02); H, 3.26 (3.12); N, 6.58 (6.67); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.17 (s, 1H, −NCHN), 8.00 (s, 2H, −NCHN), 7.90 (s, 2H, aromatic), 7.72–7.33 (m, 5H, aromatic), 7.17–6.93 (m, 22H, aromatic), 6.70–6.61 (m, 8H, aromatic), 3.68 (s, 6H, Me−NCN−Me).

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