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Peripheral covalent modification of diruthenium compounds – New approach toward robust molecular architectures

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Abstract

This short review describes the carbon–carbon bond formation chemistry at the periphery of inorganic/organometallic diruthenium species. The types of reactions applicable include the Sonogashira, Suzuki, Negishi and Heck cross-couplings. The structural, spectroscopic and voltammetric studies revealed that these peripheral modifications have exerted a minimal perturbation on the electronic structures of the diruthenium species. ***To cite this article: T. Ren, C. R. Chimie 11 (2008).***

Keywords: Diruthenium; Peripheral reactions; Cross-coupling

1. Introduction

Metal catalyzed homo- and cross-coupling reactions are among the most effective tools for organic and medicinal chemistry [1,2]. Ru and Mo catalyzed olefin metathesis reactions have become an indispensable arsenal for the synthesis of delicate molecular targets of pharmaceutical and materials interests [3]. Conventional C–C bond formation (between sp/sp^2 carbons) methodologies have also experienced a renaissance during the last decade [4,5]. In comparison, applications of coupling methodologies to coordination/organometallic compounds have remained largely unexplored and limited. Recent efforts have focused on the utility of the Sonogashira [6] and Suzuki [7] reactions in derivatizing metallo-porphyrins, metal bi-/ter-pyridine complexes and metal-alkynyl compounds.

During the course of developing organometallic molecular wires, we noticed that Ru_2-alkynyl compounds are excellent chromophores and electrophores, and hence promising building blocks for novel (opto)-electronic materials [8]. Further exploration of the materials' potential of Ru_2-alkynyl species necessitates controlled assemblies of these building blocks without significantly altering their (opto)electronic properties. Cross-coupling reactions at the periphery of Ru_2-alkynyls are appealing tools for such assemblies owing to the formation of robust C–C bonds and chemical selectivity therein. Described in this short review are our recent efforts in both the development of appropriate Ru_2-precursors and execution of ensuing coupling reactions including the Sonogashira, Suzuki, Heck and Negishi types.

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2. Ru_2-species as cross-coupling substrates

Aryl halides, especially aryl iodides, are the most common substrates for cross-coupling reactions. Hence, iodo substituents were introduced via the preparation of $Ru_2L_{4-x}L'_x$ ($x = 1$ or 2) type compounds, where auxiliary ligand L is a diarylformamidinate (DArF), and L′ is an iodo-containing ligand, either *N*,*N*′-dimethyl-4-iodobenzamidinate (DMBA-I) or *N*,*N*′-di(4-iodophenyl)formamidinate (D(4-IPh)F) (Chart 1). The selective formation of $Ru_2L_{4-x}L'_x$ relies on the high yield syntheses of both the $Ru_2(DArF)_3(OAc)Cl$ and $Ru_2(DArF)_2(OAc)_2Cl$ type compounds. DArFs are used as ancillary ligands due to their inertness toward substitution and good solubility of the resultant Ru_2 complexes in common organic solvents. The first examples of such compounds were reported in 1999 [9], and further explorations by several groups [10–13] demonstrated that $Ru_2(DArF)_3(OAc)Cl$ can be prepared on a multi-gram scale. As shown in Scheme 1, a typical preparation of $Ru_2(DArF)_3(OAc)Cl$ involves refluxing $Ru_2(OAc)_4Cl$ with 3 equiv of HDArF in THF, and subsequent recrystallization or column purification results in analytically pure material. This simple route works well with a range of DArF ligands such as *N*,*N*′-di(3-methoxyphenyl)formamidinate (DmAniF) [11,12] and *N*,*N*′-di(3,5-dichlorophenyl)formamidinate (D(3,5-Cl_2Ph)F) [13]. Preparation of $Ru_2(DArF)_2(OAc)_2Cl$ type compounds (Scheme 1) is similar to that of $Ru_2(DArF)_3(OAc)Cl$, but requires lower reaction temperatures [12,13]. Both the $Ru_2(DArF)_3(OAc)Cl$ and $Ru_2(DArF)_2(OAc)_2Cl$ type compounds are paramagnetic $S = 3/2$ species and their structures were established through single crystal X-ray diffraction studies (Fig. 1), which revealed the *cis*-configuration of the $Ru_2(DArF)_2(OAc)_2Cl$ type compounds.

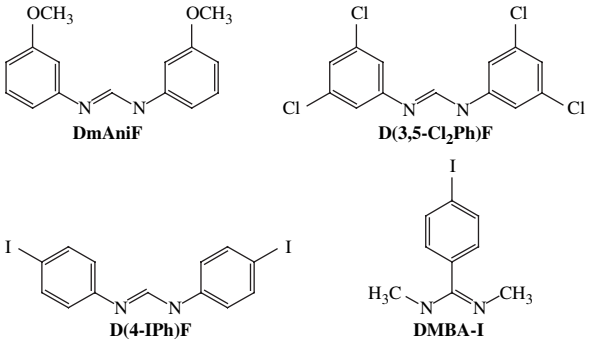
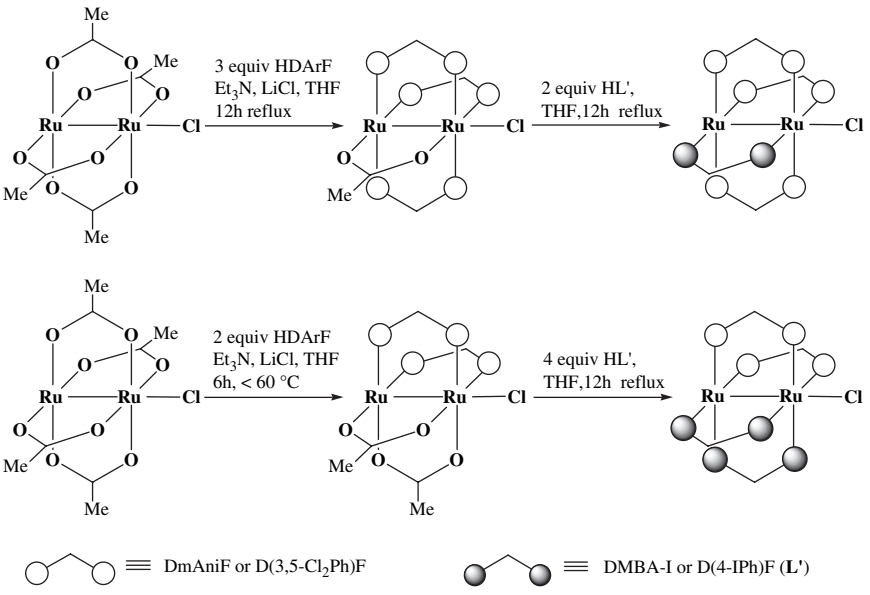


Chart 1. Structures of ligands L and L′.

Also shown in Scheme 1, the $Ru_2(DArF)_{4-x}(OAc)_x Cl$ ($x = 1$ and 2) type compounds undergo smooth ligand displacement reactions with a different *N*,*N*′-bidentate ligand, L′, to yield the $Ru_2(DArF)_{4-x}(L')_x Cl$ type compounds. L′ can be either DMBA-I or D(4-IPh)F, and contains one or two peripheral iodo substituents that enables further modification. The $Ru_2(DArF)_{4-x}(L')_xCl$ type compounds also undergo reactions with LiC_2R (R as Ph or C_2SiMe_3, in excess) to afford the corresponding axial alkynyl derivatives *trans*-$[Ru_2(DArF)_{4-x}(L')_x](C_2R)_2$. As shown in Fig. 2, structural studies of the derivatized $Ru_2(L)_2(L')_2$ type



Scheme 1.