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Peripheral Functionalization of Diruthenium Compounds via Heck Reactions

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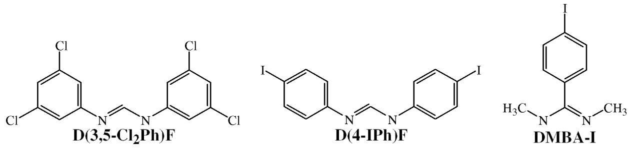
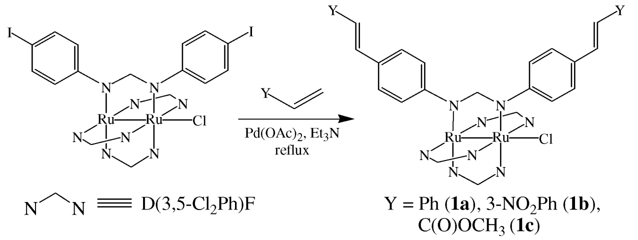
Summary: The coordination compounds $Ru_2Cl(L)_3(L')$, where L is D(3,5-Cl_2Ph)F and L′ is either D(4-IPh)F or DMBA-I, underwent Heck cross-coupling reactions with terminal olefins to afford compounds **1** *and* **2***; the organometallic compound trans-(PhC≡C)$_2$Ru$_2$(L)$_3$(DMBA-I) also underwent the Heck reaction under different conditions to yield compounds* **3***. Structural and voltammetric data indicated that the addition of peripheral olefins resulted in a minimal perturbation in both the coordination geometry around the Ru_2 center and the electronic properties of the Ru_2 species.*

Metal-catalyzed cross-coupling chemistry has become one of the most effective tools for organic and medicinal chemistry.[1] In addition to the recent development of the Buchwald−Hartwig reaction for catalytic C−N and C−O bond formation,[2] conventional C−C bond formation methodologies, namely Heck, Suzuki, Sonogashira, and Negishi reactions, have experienced a renaissance during the past decade.[3,4] In comparison, applications of cross-coupling methodology to coordination/organometallic compounds have remained largely unexplored, and only limited recent efforts have been focused on the utility of the Suzuki and Sonogashira reactions in materials preparation.[5] It has been noted in the course of developing organometallic molecular wires that Ru_2−alkynyl compounds are excellent chromophores and electrophores, and their incorporation into 1-D and 2-D hierarchical assemblies may lead to novel (opto)-electronic materials.[6] 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. The feasibility of both the peripheral Sonogashira coupling, a relatively mild reaction, and subsequent *click* reaction of Sonogashira derivatives was demonstrated recently.[7] Currently, we are extending peripheral modification chemistry to reactions that require harsher conditions and report herein the first successful Heck reactions[4] on inorganic/organometallic species.

Chart 1. Structures of Ligads L and L′



Scheme 1. Synthesis of Compounds 1



Y = Ph (**1a**), 3-NO_2Ph (**1b**), C(O)OCH_3 (**1c**)

The peripheral Heck modification is based on the $Ru_2(L)_3(L')$ scaffold,[7] where the auxiliary ligand L is *N,N′*-bis(3,5-dichlorophenyl)formamidinate (D(3,5-Cl_2Ph)F) and L′ is either *N,N′*-bis(4-iodophenyl)formamidinate (D(4-IPh)F) or *N,N′*-dimethyl-4-iodobenzamidinate (DMBA-I), as defined in Chart 1. The presence of one or two iodo substituents in L′ opens the door to a variety of cross-coupling reactions. The initial trial of the Heck reaction between $Ru_2(L)_3$(D(4-IPh)F)Cl and styrene was attempted in the presence of $Pd(OAc)_2$, $n$$Bu_4$NBr, and DMF reflux, which resulted in the decomposition of Ru_2 starting material. However, using Et_3N as both the solvent and base,the reaction of $Ru_2(L)_3$(D(4-IPh)F)Cl with 10 equiv of styrene resulted in the desired coupling product **1a** in 52% yield (Scheme 1).[8] Reactions using 3-nitrostyrene and methyl acrylate in place of styrene under the same conditions afforded compounds **1b**,**c**, respectively, illustrating the general utility of peripheral Heck reactions. While the high-spin ($S = {}^3/_2$) nature of compounds **1a**−**c** hinders their characterization by NMR spectroscopy, they were satisfactorily analyzed by MS and combustion analysis. Although the stereochemistry of added olefins could not be established via NMR, there was only one product detectable by TLC for each reaction, indicating the dominance of a single isomer. Furthermore, no peak around 1650 cm^{-1}, the expected ν(C=C) signal for a cis olefin,[9] could be located in the IR spectra of compounds **1** (Supporting Information), implying the predominance of trans isomers. The structural features of compound **1a** were established through

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(6) Ren, T. *Organometallics* **2005**, *24*, 4854.

(7) (a) Chen, W.-Z.; Ren, T. *Organometallics* **2004**, *23*, 3766. (b) Chen, W.-Z.; Ren, T. *Organometallics* **2005**, *24*, 2660. (c) Xu, G.-L.; Ren, T. *Organometallics* **2005**, *24*, 2564. (d) Xu, G.-L.; Ren, T. *Inorg. Chem.* **2006**, *45*, 10449. (e) Chen, W.-Z.; Ren, T. *Inorg. Chem.* **2006**, *45*, 8156.

(8) Preparation of **1a**. To a suspension of $Pd(OAc)_2$ (ca. 0.1 equiv) in Et_3N were added Ru_2(D(3,5-Cl_2Ph)F)$_3$(D(4-IPh)F)Cl (0.40 g) and styrene (5−10 equiv). The resultant mixture was refluxed under N_2 overnight. The product purification was effected via extraction and flash chromatography to yield 0.20 g of **1a** (52%). ESI-MS (*m/e*, based on ^{101}Ru): 1600, corresponding to $[M - Cl]^+$. Anal. Found (calcd) for $C_{68}H_{48}Cl_{13}N_8Ru_2$: C, 48.91 (49.92); H, 2.73 (2.71); N, 6.63 (6.85).

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10.1021/om7005408 CCC: $37.00

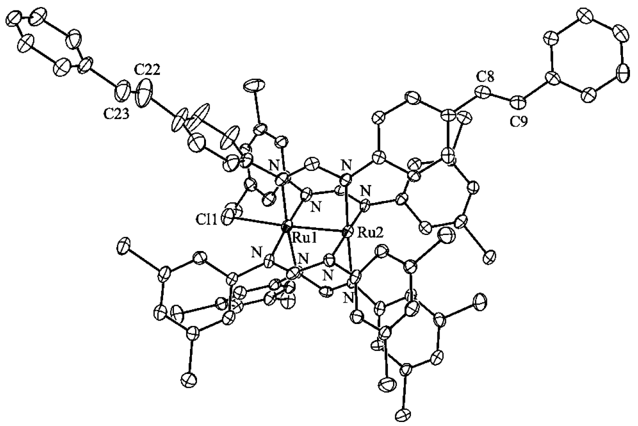


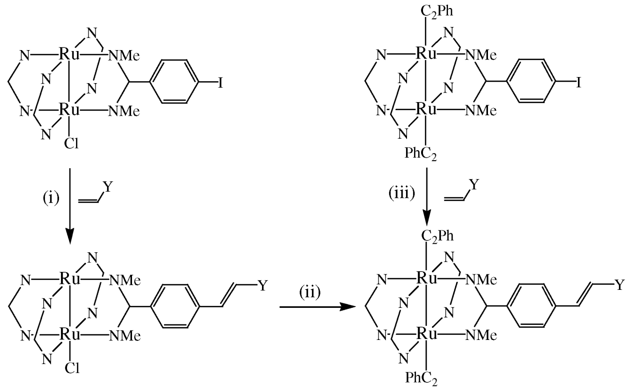
Figure 1. ORTEP plot of compound **1a** at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Ru1−Ru2, 2.331(1); Ru1−Cl1, 2.382(3); Ru−N(av), 2.072[6]; C8−C9, 1.20(1); C22−C23, 1.34(1).

X-ray diffraction, as shown in Figure 1, where the trans deposition of the added styrene fragments is clear. Metric parameters of **1a** (Supporting Information) revealed a Ru_2 coordination sphere identical with that of the parent compound $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(D(4\text{-}IPh)F)Cl$,[7d] which is consistent with a minimal electronic perturbation by the addition of peripheral olefins.

The successful application of Heck reactions at the periphery of $Ru_2(L)_3(D(4\text{-}IPh)F)Cl$ encourages further examination of peripheral Heck reactions of another type of Ru_2 compounds, i.e., $Ru_2(L)_3(DMBA\text{-}I)Cl$.[7e] Unfortunately, the reaction between $Ru_2(L)_3(DMBA\text{-}I)Cl$ and styrene under the conditions outlined in Scheme 1 only resulted in decomposition of the Ru_2 starting material. After screening of several sets of established conditions from the literature,[4] the combination of $Pd(OAc)_2$ and nBu_4NOAc[10] was found to be the most effective. Hence, $Ru_2(L)_3(DMBA\text{-}I)Cl$ reacted smoothly with styrene and vinyltrimethylsilane at room temperature in DMF to yield compounds **2a** (68%) and **2b** (78%), respectively, as shown in step i of Scheme 2.[11] Compound **2b** was converted to the axial phenylacetylide adduct **3b** via reaction with 6 equiv of LiCCPh under the conditions established previously (step ii in Scheme 2).[6] Similar to the case for the precursor compound ($Ru_2(L)_3(DMBA\text{-}I)Cl$), compounds **2** are also $S = {}^3/_2$ species and cannot be characterized with NMR spectroscopy. However, the X-ray structural determination of compound **2b** (Figure 2) clearly shows the added trimethylsilylvinyl group in a trans configuration.

We were also curious about the feasibility of Heck reactions on alkynylated diruthenium species, and *trans*-$(C_2Ph)_2Ru_2(L)_3(DMBA\text{-}I)$[7e] was selected for this study. It soon became clear that the aforementioned reaction conditions led only to the decomposition of the starting material via the cleavage of an Ru_2−alkynyl bond. However, *trans*-$(C_2Ph)_2Ru_2(L)_3(DMBA\text{-}I)$ reacted smoothly with styrene or methyl acrylate in the presence of $Pd(dba)_2$, KF, and nBu_4NCl at room temperature to yield compound **3a** (60%) or **3c** (51%), respectively (step iii in Scheme 2).[12] Products **3a**,**c**, both diamagnetic, were satisfactorily

Scheme 2. Preparation of Compounds 2 and 3[a]



Y = Ph (**2a**) and $SiMe_3$ (**2b**)

Y = Ph (**3a**), $SiMe_3$ (**3b**), C(O)OCH$_3$ (**3c**)

[a] Conditions: (i) $Pd(OAc)_2$, DMF, nBu_4NOAc, room temperature; (ii) 6 equiv of LiC_2Ph; (iii) $Pd(dba)_2$, toluene, nBu_4NCl, KF, room temperature.

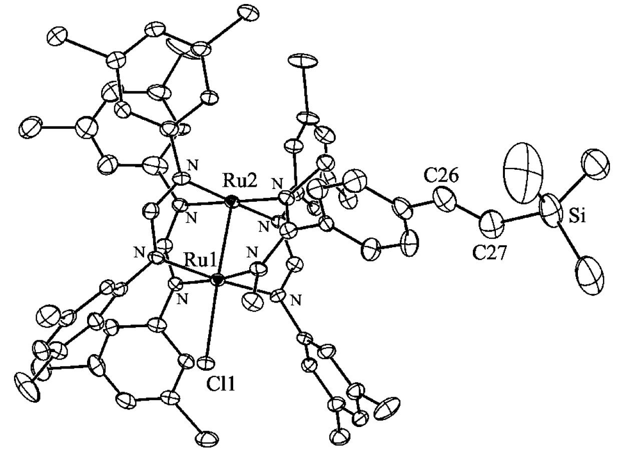


Figure 2. ORTEP plot of compound **2b** at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Ru1−Ru2, 2.318(1); Ru1−Cl1, 2.394(2); Ru−N(av), 2.074[7]; C26−C27, 1.33(2).

analyzed with ESI-MS and ^1H NMR techniques. Although the stereochemistry of the added olefin in compounds **3** could not be established via ^1H NMR, due to the overlap of olefin and phenylethynyl proton signals, the dominance of the trans isomer is confirmed by the absence of a $\nu(C{=}C)$ peak around 1650 cm^{-1} in the IR spectra of compounds **3** (Supporting Information). The trans configuration of the added methyl acrylate is also clear from the molecular structure of **3c** (Figure 3). Further structural comparison between compound **3c** and *trans*-$(C_2Ph)_2Ru_2(L)_3(DMBA\text{-}4\text{-}C_2H)$[7e] revealed identical Ru_2 core geometries within experimental errors, corroborating the minimal structural perturbation by peripheral substitution.

It was also of interest to us whether the electronic structure of Ru_2 species was altered upon the functionalization via Heck coupling. The degree of such electronic perturbation was primarily examined through the comparison of voltammetric behaviors of the Heck derivatives with those of the precursors. A typical comparison can be made for compound **2b** and

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[11] Preparation of **2a**. A mixture of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}I)Cl$ (0.20 g), styrene (10 equiv), nBu_4NOAc (3 equiv), $Pd(OAc)_2$ (0.1 equiv), and DMF (30 mL) was stirred over 4 Å molecular sieves under N_2 overnight. The product purification was effected via extraction and recrystallization to yield 0.13 g of **2a** (68%). ESI-MS (*m*/*e*, based on ^{101}Ru): 1451, $[M - Cl]^+$. Anal. Found (calcd) for $C_{56}H_{38}Cl_{13}N_8Ru_2\cdot THF$: C, 46.12 (46.25); H, 2.89 (2.98); N, 7.02 (7.19).

[12] Preparation of **3a**. A mixture of *trans*-$(C_2Ph)_2\text{-}Ru_2(D(3,5\text{-}Cl_2Ph)F)_3\text{-}(DMBA\text{-}I)$ (0.080 g), styrene (10 equiv), KF (2 equiv), nBu_4NCl (3 equiv), $Pd(dba)_2$ (0.1 equiv), and toluene (20 mL) was stirred under N_2 overnight for 4 days. The product purification was effected by recrystallization to yield 0.050 g of **3a** (60%). ESI-MS (*m*/*e*, based on ^{101}Ru): 1652, $[M]^-$. ^1H NMR: 8.16 (s, 1H, NC*H*N), 8.00 (s, 2H, NC*H*N), 7.85−7.81 (d, 2H, aromatic), 7.61−7.57 (d, 2H, aromatic), 7.46−6.61 (m, 35H, aromatic and vinyl H), 3.67 (s, 6H, NC*H*$_3$).

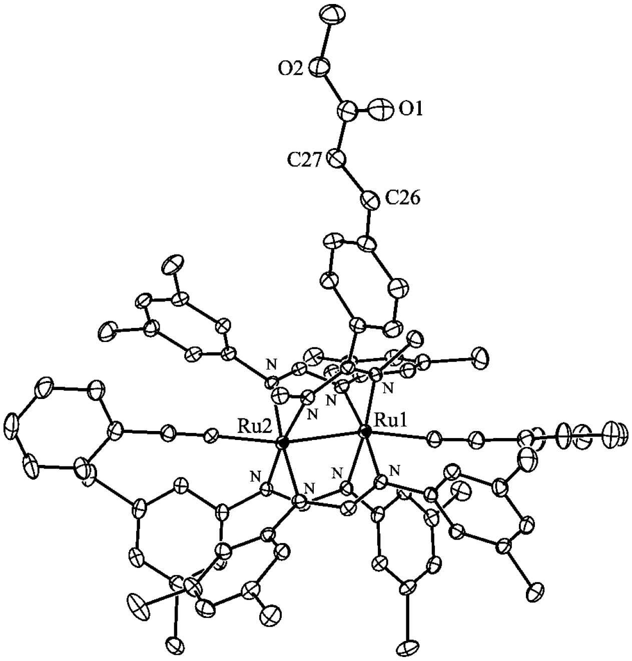

Figure 3. ORTEP plot of compound **3c** at the 30% probability level. Hydrogen atoms were omitted for clarity. ‘Selected bond lengths (Å): Ru1−Ru2, 2.5284(4); Ru−C$_{\alpha}$(av), 1.990[4]; Ru−N(av), 2.055[3]; C26−C27, 1.337(5).

$Ru_2(L)_3(DMBA\text{-}I)Cl$[7e] on the basis of their cyclic voltammograms (Figure 4), where the close resemblance between two compounds is obvious. Compound **2b** undergoes a 1e oxidation and two 1e reductions, just like $Ru_2(L)_3(DMBA\text{-}I)Cl$, and the electrode potentials of the corresponding couple are nearly identical between the two compounds. The latter feature indicates that both the nature of frontier orbitals of Ru_2 species and their energies are not perturbed by the olefin substitution on the periphery. This conclusion can be extended to compounds **1** and **3** (CVs provided in the Supporting Information) because of the similarity between Heck derivatives and their precursors in redox characteristics.

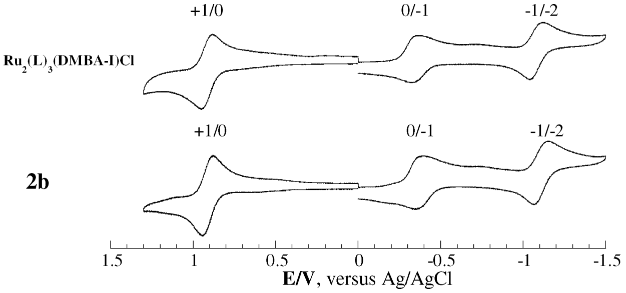

Figure 4. Cyclic voltammograms of compound **2b** and $Ru_2(L)_3$-(DMBA-I)Cl in 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

Our results demonstrated the feasibility of introducing an olefin functionality at the periphery of inorganic/organometallic species through Heck reactions under several sets of experimental conditions. On the other hand, the attempted Heck couplings on free ligands (HD(4-IPh)F and HDMBA-I) under similar reaction conditions did not yield the expected product (see the Supporting Information), further illustrating the advantage of performing cross-coupling reactions on the coordinated ligands. Peripheral addition of an olefin functionality has a minimal effect on the coordination geometry around the Ru_2 core and causes almost no changes in the redox and spectroscopic characteristics of the diruthenium compounds. The availability of bimetallic compounds with terminal olefins at peripheral positions may enable further transformations, such as homodimerization through metathesis,[13] heterodimerization through Heck coupling, and general assembly of polymetallic catalysts.[14] These possibilities are now being examined in our laboratory.

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Supporting Information Available: Text, figures, and tables giving details of the syntheses and characterizations of compounds **1**−**3** and CIF files giving X-ray crystallographic data for the structure determinations of compounds **1a**, **2b**, and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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