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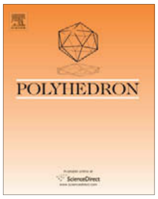

Preparation and characterization of diruthenium(II,III) compounds containing terminal olefin groups

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ABSTRACT

4-Vinylbenzoic acid reacted with $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ ($D(3,5\text{-}Cl_2Ph)F$ is *N,N′*-bis(3,5-dichlorophenyl)formamidinate) to yield $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3$(4-vinylbenzoate)Cl (**1**) and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2$(4-vinylbenzoate)$_2$Cl (**2**), respectively. $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ reacted with 5-hexenoic acid and 6-heptenoic acid to afford $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3$(5-hexenoate)Cl (**3**) and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3$(6-heptenoate)Cl (**4**), respectively. All new compounds were characterized using voltammetric and Vis–NIR spectroscopic techniques, and the structures of **1** and **2** were also established through X-ray single crystal diffractions.

1. Introduction

Organic molecules containing terminal olefin functionality are versatile building blocks that may undergo many useful transformations including the Heck type reactions [1] and olefin metathesis reactions [2]. One can easily imagine that metal compounds containing terminal olefin on the ligand periphery may undergo similar reactions [3]. Indeed, many elegant examples have been disclosed by the laboratory of Gladysz, where the olefin pendants of metal-bound phosphine ligands undergo both ring-closing and cross metathesis reactions [4]. Metal compounds containing peripheral olefin have been used as the substrates of Heck cross coupling reactions, leading to the formation of metallo supramolecules and metallo-conjugated polymers [3]. The other interesting utility of terminal olefin is its reaction with a hydride terminated silicon surface (Si–H) under photolytic conditions that results in the formation of a Si–C bond (Scheme 1). This type of reactions has been become an important tool for the modification of silicon surface with a molecular monolayer, a significant step toward the realization of CMOS-molecule hybrid devices [5,6].

Recent efforts from several laboratories including ours demonstrated the modular nature of bimetallic paddlewheel species with suitable peripheral functional groups, based on which dimeric, oligomeric and dendritic assemblies can be achieved [3,7–9]. Among previously reported studies are a series of diruthenium species containing one or two terminal olefins, namely $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(\mu\text{-}O_2C(CH_2)_nCH{=}CH_2)Cl$ ($n = 1$ and 2) and *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2C(CH_2)_mCH{=}CH_2)_2Cl$ ($m = 1$–3), where $D(3,5\text{-}Cl_2Ph)F$ is *N,N′*-bis(3,5-dichlorophenyl)formamidinate, and their cross metathesis and ring-closing metathesis reactions [10,11]. These diruthenium species are interesting from the device perspective because of both their rich redox characteristics and net molecular spin [6,12,13]. In order to modify Si surfaces with this type of diruthenium species, compounds with either rigid or extended hydrocarbon spacers are necessitated due to the size of Ru_2 head group. Reported in this contribution are the preparation and structural study of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}CH{=}CH_2)Cl$ (**1**, Scheme 2), *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}CH{=}CH_2)_2Cl$ (**2**), and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3\ (\mu\text{-}O_2C(CH_2)_nCH{=}CH_2)Cl$ ($n = 3$ (**3**) and 4 (**4**)).

2. Results and discussion

2.1. Synthesis

Preparative chemistry of compounds **1**–**4** is based on the $Ru_2(DArF)_{4-x}(\mu\text{-}O_2CMe)_xCl$ ($x = 1$ and 2) type synthons that have been developed by several laboratories [8,9,14]. As illustrated in Scheme 2, gentle reflux of $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(\mu\text{-}O_2CMe)Cl$ with 4-vinylbenzonic acid in excess afforded compound **1** in excellent yield. Carboxylate exchange reaction between $Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(\mu\text{-}O_2CMe)_2Cl$ and 4-vinylbenzonic acid required more rigorous conditions and the synthesis of **2** was achieved through reflux in toluene using a setup involving a micro Soxhlet extractor as described previously [15]. Preparations of compounds **3** and **4** are similar to that of **1** and both were obtained in good yields. Compounds **1**–**4** are all purple crystalline materials and yielded

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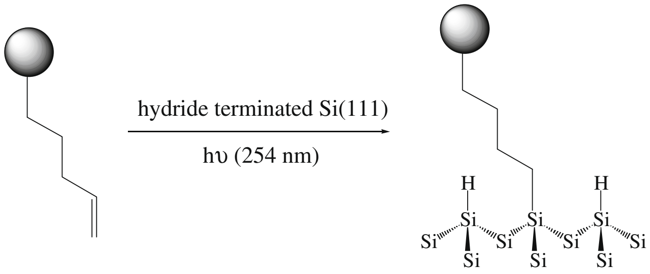


Scheme 1. Functionalization of Si surface with olefin-capped molecule (solid ball represent the head group).

satisfactory combustion analysis results. All four compounds are paramagnetic with the room temperature effective magnetic moments in a narrow range of 3.81–3.93 Bohr magneton, which is consistent with the presence of three unpaired electrons [12,16].

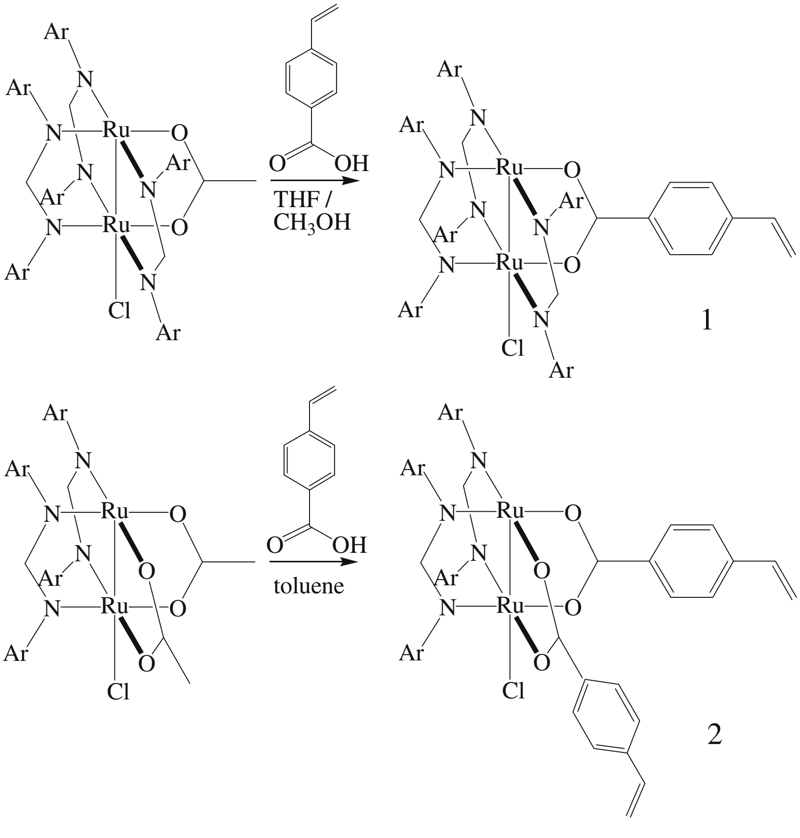
2.2. Molecular structures

Both compounds **1** and **2** crystallize in the space group $P\bar{1}$, and the asymmetric unit contains a complete diruthenium molecule in each case. The structural plot of **1**, Fig. 1, reveals the presence of three D(3,5-Cl_2Ph)F ligands and one 4-vinylbenzoate around the diruthenium core. The coordination sphere of the Ru_2 unit is completed with a chloro and a water ligand in the axial positions, which were disordered over both axial sites and refined with 50% occupancy each for Cl and O (labeled as Cl′ in Fig. 1). Hence, the Ru–Cl′ distance is shorter than the Ru1–Cl1 bond in **2** but longer than the Ru–O(OH_2) distance in Ru_2(D(3,5-Cl_2Ph)F)$_2$(μ-O_2CMe)$_2$Cl(H_2O) (2.362 Å) [9]. It is clear from the structural plot of **2** (Fig. 2) that the coordination sphere of the Ru_2 unit consists of two D(3,5-Cl_2Ph)F and two 4-vinylbenzoate bridging bidentate ligands in a *cis*-arrangement, and a chloro and an ethanol axial ligands.

Listed in Table 1 are the selected bond lengths and angles data for compounds **1** and **2**. The Ru–Ru bond length in **1** (2.3381(4) Å) is slightly longer than that in the precursor Ru_2(D(3,5-Cl_2Ph)F)$_3$(μ-O_2CMe)Cl (2.3220(7) Å), and the shortness of Ru–Ru bond in the latter is attributed to the absence of axial water ligand [9]. The Ru–Ru bond length in **2** (2.319(2) Å) is slightly shorter than that of Ru_2(D(3,5-Cl_2Ph)F)$_2$(μ-O_2CMe)$_2$Cl(H_2O) (2.327 Å) [9], reflecting the weak ligating ability of ethanol in comparison with water. The equatorial Ru–O and Ru–N bond lengths are all in good agreement with those of related compounds reported earlier [9,11].

2.3. Voltammetry

Similar to other Ru_2(DArF)$_{4-x}$(carboxylate)$_x$ type compounds, compounds **1**–**4** display cyclic voltammograms (CV, Fig. 3) with rich features. Common to all compounds are three Ru_2-centered one-electron events: the quasi-reversible oxidation (**A**), quasi-reversible reduction (**B**), and subsequent irreversible reduction (**D**) as illustrated in Scheme 3. It is clear from Table 2 that the mono-carboxylate species **1**, **3** and **4** have nearly identical electrode potentials. Interestingly, the voltammetric characteristic of the dicarboxylate species **2** is comparable to those of the other three compounds, except that the couple **D** of **2** is anodically shifted. Additional features such as peaks **C** and **E** are related to the dissociation/association of the chloro ligand (Scheme 3), as discussed in our prior study of related species [11]. Peaks **F** and **G** are also prevalent and could be related to the dissociation/association of axially bound solvent molecule, although there is no concrete evidence supporting this speculation.



Scheme 2. Preparation of diruthenium-4-vinylbenzoate compounds.