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Diruthenium σ-iminophenylacetylide complexes from on-complex Schiff base condensation☆

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Six diruthenium(II,III) compounds of the formula $Ru_2(ap)_4-(C\equiv C-C_6H_4-4-N=CH-4'-C_6H_4-R)$ (*ap* as 2-anilinopyridinate, **3**) and $Ru_2(ap)_4-(C\equiv C-C_6H_4-3-N=CH-4'-C_6H_4-R)$ (**4**), where R is H (**a**), Br (**b**) or CHO (**c**), were prepared from the condensation reactions between $Ru_2(ap)_4(C\equiv C-C_6H_4-4/3-NH_2)$ (**1**/**2**) and an appropriate aldehyde. X-ray structural studies of compounds **3a** and **3b** revealed minimal changes upon the formation of the imine bond in the coordination sphere of the Ru_2 core with respect to the parent compounds. Voltammetric measurements show that compounds **3a**/**b** and **4a**/**b** exhibit four one electron redox processes: an oxidation of Ru_2, two reductions of Ru_2, and a reduction of the imine group. Both compounds **3c** and **4c** also undergo a fourth reduction attributed to the aldehyde functional group.

1. Introduction

Metal alkynyl and alkenyl complexes have been investigated as the building blocks for molecular wires [1–4], non-linear optical chromophores [5], and photovoltaic materials [6]. Significant intermetallic couplings, a prerequisite for molecular wires, have been realized in many bimetallic/trimellic species bridged by polyynyls, and recent examples include those based on Fe [7], Ru [8,9], W [10] and Ru_2 [11,12]. Furthermore, molecular wire/switch characteristics of metal-polyyne species have been demonstrated through the current–voltage (I–V) measurement at the single or few molecule level [13–17]. Although examples of compounds bridged by polyenyl ($-(CH)_x-$) are sparse in comparison with those by polyynyl, the extensive work on both the $Ru-(CH)_x-Ru$ type compounds by Liu and Jia [18–20] and the $Fe-(CH)_x-Fe$ type by Sponsler [21,22] revealed electronic couplings comparable to or even stronger than those based on polyynyl bridges.

In contrast to the aforementioned successes based on polyynyl and polyenyl ligands, organometallic compounds containing hetero-atoms in the conjugated pathway are far less common. Revealing the potential of the latter type compounds, Frisbie and coworkers recently reported that oligophenyleneimines (OPI) are efficient charge carriers in the donor–bridge–acceptor (D–B–A) scheme. Charge transfer was found to be mediated by tunneling at short distances (up to 4 nm), and by hopping at extended distances (4–8 nm) with an exceptionally small attenuation constant β of 0.09 $Å^{-1}$ ($R = R_0e^{-\beta L}$; R and L are molecular resistance and length, respectively) [23]. Accordingly, there is an interest in the use of an OPI ligand attached to $[M]-C\equiv C-R$, which may lead to interesting charge transfer characteristics.

Chemistry of diruthenium compounds began with the synthesis of diruthenium(II,III) tetracarboxylate by Stephenson and Wilkinson [24] and subsequent structure determination by Bennett, Caulton and Cotton [25]. While the research during the ensuing 40+ years has focused on the structure and bonding [26,27], recent years have witnessed new development in molecular magnetism [28–31], small molecule activation [32,33] and catalysis [34–36]. Described in this contribution, as the first step toward organometallic wires containing an imine moiety, are the preparation of compounds **3** and **4** (Scheme 1) by the condensation reaction between $[Ru_2(ap)_4]-(C\equiv C-C_6H_4-4/3-NH_2)$ (compounds **1**/**2**) [37] and arylaldehydes and their characterization.

2. Results and discussion

2.1. Synthesis

Two distinctive methods have been employed in the synthesis of M–C≡C-aryl compounds with an imine bond: the Au [38] and Ni [39] compounds were prepared from the reaction between a metal

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☆ We wish to dedicate this contribution to Ken Caulton, a dear colleague and early contributor to the diruthenium chemistry, on the occasion of his 70th birthday.

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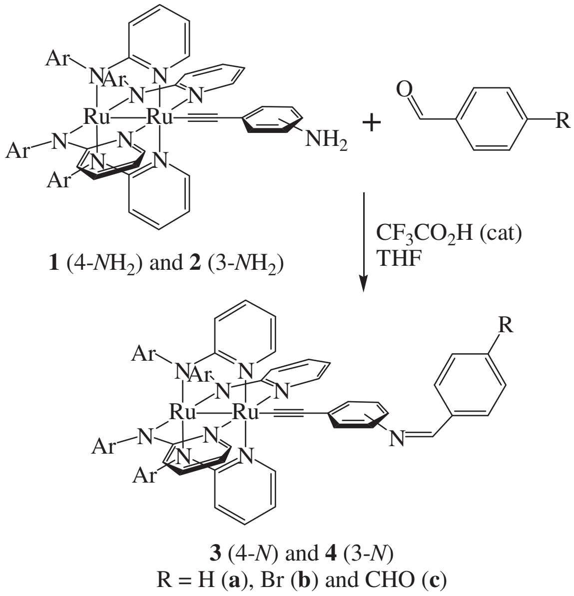

Scheme 1. Ru2-alkynyls with imine substituent.

precursor and an alkynyl ligand already containing an imine, while the Pt compound was prepared from the condensation reaction between a primary amine and a Pt precursor containing the acetylide ligand –C≡C–C_6H_4–CHO [40]. With the $[Ru_2(ap)_4]$–(C≡C–C_6H_4–4/3–NH_2) type compounds (**1**/**2**) already prepared by us [37], it is conceivable to prepare the imine containing derivative via Schiff base condensation with a substituted benzaldehyde. The condensation reaction occurred without a catalyst under reflux conditions (in either THF or toluene), but degradation products were present. A “solvent-free” technique was also tested and found to be productive, but proved difficult to reach completion [41]. Purification of the imine derivatives using silica columns was also accompanied with substantial degradation. In order to improve the yield of the desired imine product and hence minimize unnecessary purification, acids were tested as catalysts. The reactions with strong acids, HCl and HNO_3, were too fast to be controlled and resulted in considerable degradation. The reaction with acetic acid was slow and degradation would occur before the reaction reached completion. The most prominent degradation product arose due to cleavage of the Ru–C bond resulting in a green compound, likely $Ru_2(ap)_4(OH)$, even with the use of freshly distilled THF. Eventually, complete conversion was achieved in THF using trifluoroacetic acid as described in Scheme 1. While the reaction progress was typically monitored by TLC, FT-IR was useful in regards to the loss of the NH_2 peak at 3200 cm^{-1} and appearance of a peak representing the C=N stretch at 1620 cm^{-1}, which are two clear indicators of the completion of the reaction. Recrystallization in THF:MeOH yielded the desired product as a dark green crystalline material in yields between 55 and 75%. Compounds **3** and **4** are all paramagnetic with effective magnetic moments between 3.55 and 3.72 μ_B, which are consistent with a ground state of $S = 3/2$.

2.2. X-ray structures of **3a** and **3b**

The molecular structures of **3a** and **3b** were determined by X-ray single crystal diffraction and their structural plots are presented in Figs. 1 and 2, respectively. Both display similar coordination geometry around the diruthenium core consistent with previously studied $Ru_2(ap)_4$–C≡CR type compounds [2,37,42–52]. The *ap* ligands are in a (4,0)-arrangement around the Ru_2 core with the pyridine nitrogen bonding to Ru1 and all aniline nitrogens bonding to Ru2. The Ru1–Ru2 (2.324 (6) Å) bond is nearly identical to other $Ru_2(II,III)(ap)_4$ compounds accounting for experimental error. The Ru1–C1 (2.110 (6) Å) bonds of **3a**/**b** are slightly longer than prior $Ru_2(ap)_4$–CC–C_6H_4–R compounds (2.08 (1) Å) [53]. The C1–C2 bond shows little deviation from a standard C≡C at 1.186 (6) and 1.196 (6) Å for **3a** and **3b**, respectively, and is within experimental error compared to **1**. The C2–C3 distance of **3a**/**b** (avg. 1.445 [9] Å) is slightly shorter than **1** (1.48 (1) Å) likely due to the decreased electron donating ability of the imine compared to the terminal amino. An increase in the C=N–C bond angle from 117.7 (8)° for **3a** to 121.0 (6)° for **3b** is likely electronic in origin from the bromine substitution as a packing diagrams did not reveal any intermolecular interactions. Also noteworthy is that the imine bond is coplanar with the second phenyl (derived from aryl aldehyde) in both **3a** and **3b**, and this plane has an approximate 40° dihedral angle in respect to the first phenyl ring (acetylide bonded). The coplanarity between imine and aldehyde-derived phenyl ring is also true in the prior examples of imino-phenylacetylide complexes [38–40] (Table 1).

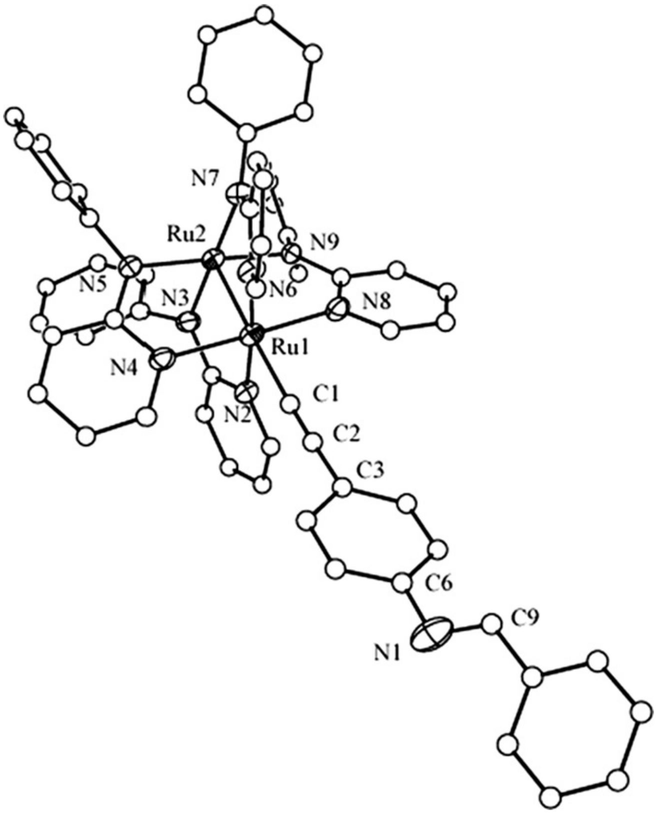

Fig. 1. Structural plot of compound **3a**. Hydrogen atoms were omitted for clarity.

2.3. UV–Vis–NIR

The Vis–NIR absorption spectra of **3** and **4** were recorded in CH_2Cl_2 (Figs. 3 and 4) with peaks at *circa* 460 and 755 nm, which are similar to those of related $Ru_2(ap)_4$(C≡CR)-type compounds from prior studies [2,37,47,49,50,54]. Based on a previous TD-DFT study of the model compounds for **1** and **2** [54], the high energy band arises from the transition of π(C≡C) to δ*(Ru–Ru), while the low energy band is due to a combination of the π(Ru–N) and π(Ru–Ru) to δ*(Ru–Ru). For the low energy band, minimal differences in peak position and intensity exist between **3** and **4** since this transition originates from the equatorial coordination sphere that is the same