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Wire-like diruthenium σ-alkynyl compounds and charge mobility therein

Bin Xi, Tong Ren*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

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Abstract

Described in this short review is the chemistry of wire-like diruthenium σ-alkynyl species, which are promising building blocks for organometallic molecular wires. Two series of carbon-rich compounds have been studied: (a) polyyn-diyls with diruthenium capping units, and (b) bi-ferrocenes with a diruthenium alkynyl bridge. Investigations of both the charge transfer process across the polyyn-diyls and the role of diruthenium cores in enhancing charge mobility are achieved through X-ray structure determination, spectroscopic, voltammetric and spectroelectrochemical measurements. ***To cite this article: B. Xi, T. Ren, C. R. Chimie 12 (2009).***

Keywords: Diruthenium; Polyyn-diyl bridge; Molecular wire; Alkynyl organometallics

1. Introduction

The study of transition-metal σ-alkynyl complexes can be traced back to 1960s [1,2]. Since the mid-1980s, this area has attracted much more intense interests as evidenced by increasing numbers of research papers from approximately 200 to over 20,000 [3]. Compared with the pure organic conjugated systems [4,5], introduction of metal units into the polymeric or oligomeric systems may result in a broad range of improved properties including electronic communication (molecular wires) [6,7], nonlinear optical effects [8], luminescence and photoconductivity [9,10].

In the research of utilizing metal σ-alkynyl complexes as building blocks for molecular electronic devices, two types of metal alkynyl wires were proposed (Chart 1) [6,11]. Polyyn-diyls (C_{2n}) capped by two metal termini (type **I** in Chart 1) are very attractive prototypes of “organometallic molecular wires”. Many of the pioneering efforts focused on the design of type **I** wires featuring facile charge transfer across the *sp* carbon chain (polyyn-diyls), with [M] as CpFe(P−P) [12], CpRe(P)NO [13−15], $CpRu(P)_2$ [16], and $Mn(P{-}P)_2I$ [17] where P and P−P denote mono- and bidentate phosphines, respectively. Monodisperse oligomers (type **II** in Chart 1) could be better alternatives than dimers (**I**) on the aspects of controlling length and connecting to the outside world, from the practical applications point of view. However, some limitations preclude the possibility of many metal complexes as candidates for type **II** wires. To form oligomers, the metal units should be capable of forming bis-alkynyl complexes, and in addition, the selection of the metal center [M] is also critical to avoid insulating behavior [6,18]. Examples of

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* Corresponding author.
E-mail address: tren@purdue.edu (T. Ren).

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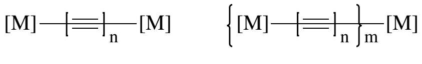
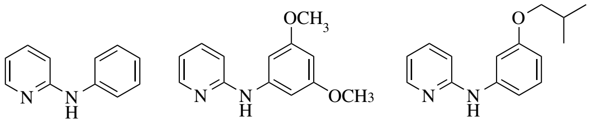


I II

Chart 1. Dimeric (**I**) and metallayne (**II**) wires.



ap **H-DiMeO*ap*** **H-iBuO*ap***

Chart 2. *N*,*N*′-bidentate ligands supporting the Ru_2 core.

well-characterized type **II** oligomers are rare, and those based on $Ru_2(DPhF)_4$-butadiynyl [19] and $Ru(P{-}P)_2{-}\sigma$-arylacetylide monomers [20,21] are noteworthy.

Our effort in developing organometallic molecular wires focuses on using diruthenium paddlewheel species as [M] [22–25], due to their attractive features including the controlled syntheses of the mono- and bis-alkynyl complexes, the stability toward ambient atmosphere and heat, the redox flexibility, and very small HOMO–LUMO gaps (1.2–1.5 eV) [26–34]. As excellent chromophores and electrophores, the diruthenium alkynyl complexes have been studied as promising building blocks for novel (opto)electronic materials [23].

2. Ru_2 polyyn-diyls

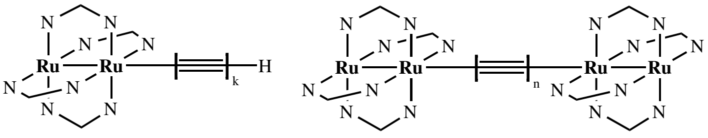
Our investigation of diruthenium alkynyl compounds of a paddlewheel motif demonstrated that σ-alkynyl compounds of $[Ru_2L_4]$ have good charge mobility along the axial direction. Ru$_2$(II,III) based wire-like compounds (type **I**) with n up to 10 have been prepared with various supporting ligands (L). Compounds of long polyyn-diyl segments are desired for better understanding of the electron coupling within the type **I** molecules and the distance dependence of H_{ad} (adiabatic electronic coupling elements).

The *N*,*N*′-bidentate bridging ligands (L) utilized in supporting the Ru_2 core include 2-anilinopyridinate (*ap*) and its anilino-substituted derivatives, 2-(3,5-dimethoxyanilino)pyridinate (DiMeO*ap*), and 2-(*i*-butoxyanilino)pyridinate (*i*BuO*ap*) (Chart 2). Using *ap* as the auxiliary ligand, type **I** compounds with *n* up to 6 were prepared and studied [35,36]. Both of the modified *ap* ligands afford significantly improved solubility in common organic solvents [37,38], and facilitate the preparation of type **I** compounds with *n* up to 10, and the access to compounds of odd *n* as well.

2.1. Monomers and dimers

Wire-like molecules $[Ru_2L_4]_2(\mu\text{-}C_2)$, $[Ru_2L_4]_2(\mu\text{-}C_4)$ and $[Ru_2L_4]_2(\mu\text{-}C_6)$ (L = DiMeO*ap*, compounds **A1–A3**; L = *ap*, compounds **A1′–A3′**) were synthesized through anion metathesis between $[Ru_2L_4]{-}Cl$ and $LiC_{2n}Li$ [35,36]. However, this technique became impractical with longer polyyn-diyl ligands, due to the instability of $LiC_{2n}Li$ with $n \geq 4$. Hence, the longer type **I** compounds ($n \geq 4$) were prepared through the Glaser oxidative coupling [39] of their corresponding “half” molecules which are the monomer type in Chart 3.

The mono-adduct with $k = 2$ was prepared from a reaction between $[Ru_2L_4]{-}Cl$ and LiC_4SiMe_3. After the removal of terminal protection group $-SiMe_3$ (K_2CO_3, THF/MeOH), a two-carbon sp chain extension reaction was achieved by the Glaser oxidative coupling [39] of $[Ru_2L_4]{-}C_4H$ and excess $HC{\equiv}CSiMe_3$ (*Hay* conditions: O_2, cat. CuCl, TMEDA and acetone) to give $[Ru_2L_4]{-}C_6SiMe_3$ (monomer with $k = 3$). However, extending this sequence to longer monomers ($k = 4$ and 5) was unsuccessful with the problem of increasing tendency for homo-coupling of $[Ru_2L_4]{-}C_{2k}H$ during the reaction. The *Cadiot–Chodkiewicz* (Cadiot for short) coupling method [39] was successfully employed by Gladysz and coworkers to extend $Re{-}(C{\equiv}C)_n{-}$ chains [40], which involved the formation of a copper alkynyl complex intermediate. As shown in Scheme 1, the extension of $Ru_2{-}(C{\equiv}C)_k{-}$ monomers ($k > 2$) under *Cadiot* conditions was achieved with significantly



$[Ru_2L_4](C_{2k}H)$ mono-adduct **$[Ru_2L_4](\mu\text{–}C_{2n})[Ru_2L_4]$** bridge complex

Chart 3. Diruthenium mono-alkynyl building block and wire-like bridge compound.