

Note

Synthesis and characterization of bimetallic ruthenium complexes connected through linear (CH)₁₄ chain

Ping Yuan^a, Xiang-hua Wu^a, Guang-ao Yu^a, Dan Du^a, Sheng Hua Liu^{a,b,*}

^a Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China

Received 28 January 2007; received in revised form 15 April 2007; accepted 20 April 2007
Available online 6 May 2007

Abstract

Treatment of RuHCl(CO)(PPh₃)₃ with (3*E*,5*E*,7*E*,9*E*,11*E*)-HC≡C-(CH=CH)₅-C≡CH produces [RuCl(CO)(PPh₃)₂]₂[μ-(CH=CH)₇]. The later complex reacts with PMe₃ to give [RuCl(CO)(PMe₃)₃]₂[μ-(CH=CH)₇], the structure of which has been confirmed by X-ray diffraction. The through-space distance from one Ru to the other is 19.88 Å.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Bimetallic ruthenium complex; Polyenediyl bridge; Synthesis; Electrochemistry

1. Introduction

Bimetallic and polymetallic complexes with conjugated hydrocarbon ligands bridging metal centers are attracting considerable current interest [1,2]. Bimetallic complexes with polyynediyl bridges, M-(C≡C)_n-M', constitute the most fundamental class of carbon-based molecular wires and they have been proposed for construction of nanoscale electronic devices [2]. To date, C₁, C₂, C₃, C₄, C₅, C₆, C₈, C₁₀, C₁₂, C₁₆, and C₂₀, C₂₄, C₂₈ adducts have been isolated [2]. In contrast, few studies have been carried out with bimetallic complexes with polyenediyl bridges, despite the fact that many conjugated organic materials (e.g. polyacetylenes, push/pull stilbenes) have only sp² hybridized carbon in their backbones, and polyacetylenes have high electrical conductivity (up to 10⁵ Scm⁻¹) upon doping [3]. Linear monodisperse π-conjugated oligoenes R(CR'=CR'')_nR(R', R''=H or Me, R=Ar or CHO, n = 3, 5, ... up to 11) have been synthesized, and they have promising electronic and

optical properties [3]. Previously reported examples of (CH)_x-bridged bimetallic complexes are limited to a few of those with linear (CH)₂ [4], (CH)₄ [5–7], (CH)₅ [8], (CH)₆ [9,10], (CH)₈ [11] and (CH)₁₀ [12] bridges. In this report, We wish to report the synthesis, properties, and molecular structure of the first (CH)₁₄-bridged bi-ruthenium complexes, which features the longest sp² carbon chain bimetallic complexes synthesized and structurally characterized to date with the distance between the two metals 19.88 Å.

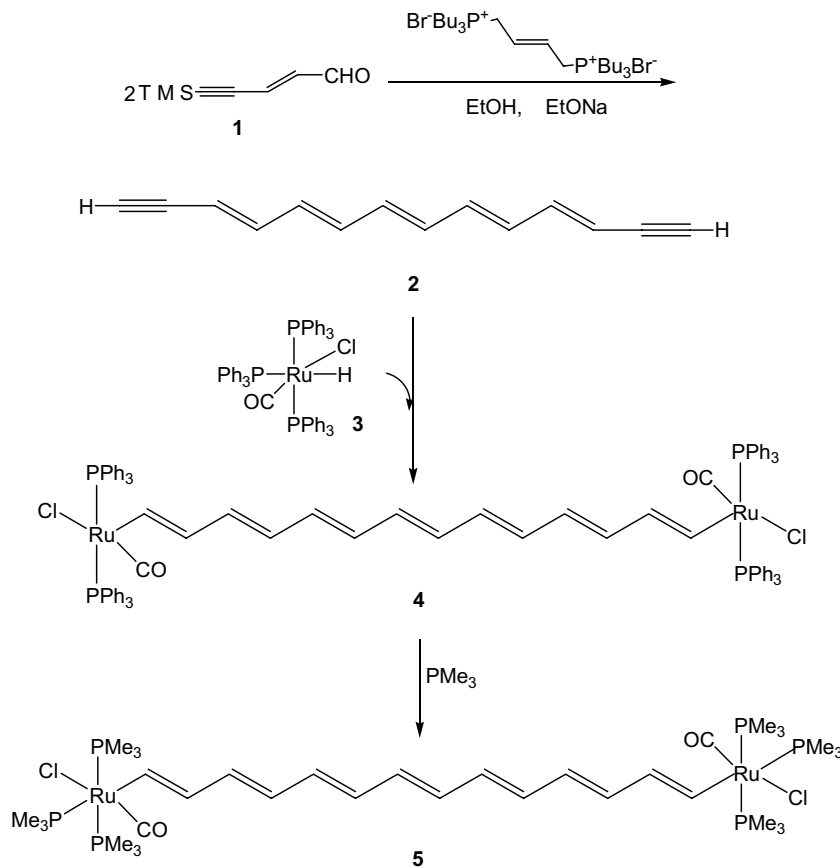
2. Results and discussion

2.1. Synthesis of metal complexes

As showed in Scheme 1, reaction of (*E*)-Me₃SiC≡CCH=CHCHO (**1**) [11] with BrBu₃PCH₂CH=CHCH₂PBu₃Br [13] in the presence of EtONa as the base produced the precursor compound **2**. The Me₃Si was hydrolysed in situ. We chose the tributylphosphonium bromide but not the triphenylphosphonium bromide to reduce the proportion of Z-isomer in the product during Wittig reaction [13]. The ¹H NMR spectrum of compound **2** (in CDCl₃) showed one

* Corresponding author.

E-mail address: chshliu@mail.ccnu.edu.cn (S.H. Liu).



Scheme 1.

$\equiv\text{CH}$ signal at 3.15 ppm and five $=\text{CH}$ signals at 5.61, 6.10, 6.37, 6.74, and 7.16 ppm.

Treatment of **2** with the ruthenium hydride complex $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (**3**) in dichloromethane produced the insertion product $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2]_2[\mu-(\text{CH}=\text{CH})_7]$ (**4**), which is sensitive to air. The ^{31}P NMR spectrum (in CD_2Cl_2) showed a singlet at 30.94 ppm, the chemical shift of which is typical for $\text{RuCl}(\text{CH}=\text{CHR})(\text{CO})(\text{PPh}_3)_2$ [14]. Treatment of **4** with PMe_3 produced the six-coordinated complex $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2[\mu-(\text{CH}=\text{CH})_7]$ (**5**), which is isolated through silica gel chromatography. The PMe_3 ligands in **5** are meridionally coordinated to ruthenium as indicated by the AM_2 pattern $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. In the ^1H NMR spectrum (in CD_2Cl_2), the vinyl proton signals were showed at 7.66 (Ru-CH), 6.32 (β -CH), 6.14 (γ , δ , ϵ , ζ -CH) and 5.83 (η -CH) ppm. In the ^{13}C NMR spectrum (in CD_2Cl_2), the CH signals were observed at 122.49 ($-\eta$ -CH), 129.82 (ζ -CH), 131.54 (ϵ -CH), 134.15 (δ -CH), 137.88 (γ -CH), 138.95 (β -CH) and 178.79 (Ru-CH) ppm.

2.2. Crystal structures of complex **5**

Crystal structure of **5** was confirmed by X-ray diffraction study. The molecular structure of complex **5** is depicted in Fig. 1. As shown in Fig. 1, complex **5** contains two ruthenium centers linked by a linear $(\text{CH})_{14}$ bridge,

The plane of the $(\text{CH})_{14}$ chain is slightly distorted with a S-shaped conformation, and the distance between the two metal centers is 19.88 Å. The linear $(\text{CH})_{14}$ bridge shows a single/double carbon-carbon bond alternation. All the olefinic double bonds are in trans geometry. Their double bonds have an average bond distance of 1.344 Å and the single bonds have an average bond distance of 1.435 Å. The difference in the average single and double bond distances is at 0.091 Å, which is similar to those in $\text{PhCH}=\text{CH}(\text{CH}=\text{CH})_2\text{CH}=\text{CHPh}$ (0.092 Å) [15]. The vinyl group of complex **5** is essentially co-planar with Cl-Ru-CO. The atoms Cl(1), Ru(1), C(10), O(10), C(1) and C(2) are in a plane with maximum deviation from the least-square plane of 0.037 Å for Ru(1). The coplanarity of vinyl group and CO is expected because stabilization due to interaction of CO and vinyl through metal centers is maximized in such a conformation [16].

2.3. Electrochemical study

The cyclic voltammogram of complex **5** exhibited two partially reversible oxidation waves at 0.30 and 0.50 V vs Ag/AgCl, as shown in Fig. 2 (The ferrocene/ferrocenium redox couple was located at 0.49 V under our experimental conditions). These two waves can be attributed to the formation of $[(\text{PMe}_3)_3(\text{CO})\text{ClRu}-(\text{CH}=\text{CH})_7-\text{RuCl}$

Download English Version:

<https://daneshyari.com/en/article/1326607>

Download Persian Version:

<https://daneshyari.com/article/1326607>

[Daneshyari.com](https://daneshyari.com)