Journal of Organometallic Chemistry xxx (2016) 1–8

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Carbon-rich dinuclear ruthenium bisallenylidene complexes

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ARTICLE INFO

Article history:
Received 13 February 2016
Received in revised form
8 June 2016
Accepted 9 June 2016
Available online xxx

Keywords:
Bisallenylidene
Ruthenium
Dinuclear complexes
Carbon-rich

ABSTRACT

Reactions of carbon-rich bispropargyl alcohols with two equivalents of the ruthenium precursor $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ and $NH_4[PF_6]$, respectively, result in dinuclear ruthenium bisallenylidene complexes $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2({=}C{=}C{=})(AC)({=}C{=}C{=})(PPh_3)_2(\eta^5\text{-}C_5H_5)Ru](PF_6)_2$ (**7**), $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2({=}C{=}C{=})(PC)({=}C{=}C{=})(PPh_3)_2(\eta^5\text{-}C_5H_5)Ru](PF_6)_2$ (**9**), $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2({=}C{=}C{=})(BAN)({=}C{=}C{=})(PPh_3)_2(\eta^5\text{-}C_5H_5)Ru](PF_6)_2$ (**10**), and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2({=}C{=}C{=})(IndFN)({=}C{=}C{=})(PPh_3)_2(\eta^5\text{-}C_5H_5)Ru](PF_6)_2$ (**11**) (polyaromatic moieties: AC = anthracene, PC = pentacene, BAN = bianthracene, IndFN = indenofluorene). These complexes show distinct spectroscopic and electronic properties, which could be investigated by cyclic voltammetry and UV/Vis/NIR spectroscopic measurements.

1. Introduction

Since the first discovery of allenylidene complexes by Fischer [1] and Berke [2], and later on, Selegue [3], who developed a straightforward method to obtain ruthenium allenylidene complexes by activation of propargyl alcohols, the interest in their synthesis and behavior rapidly increased. Transition metal allenylidene complexes, mainly ruthenium allenylidene complexes were comprehensively explored [4,5] and foremost, the carbon-rich complexes with polyaromatic substituents suggest a variety of potential applications [6–8]. Complexes bearing substituents like acene or pyrene groups are especially promising candidates for metal tuned FETs (field-effect transistors), “organic” metal semiconductor field effect transistors (OMESFETs), due to their ability of exchanging electrons. Moreover, because of their high extinction coefficients, potential applications in dye-sensitized solar cells (DSSCs) have been suggested [9,10].

Beside these mononuclear allenylidene complexes, dinuclear ruthenium complexes with π-conjugated bridges are of particular interest in order to investigate electronic communication between the metal centers [11–13]. Significant steps forward in the synthesis and characterization of these carbon-rich dinuclear bisallenylidene complexes have been mainly achieved by Zanello and coworkers [11] and Dixneuf and coworkers [13–17].

The metal based transformation of organic alkyne precursors, containing two terminal alkynes [17,18], as for example, the conversion of the diyne $HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH$ by $[RuCl_2(dppe)_2]$, leads to the bisvinylidene diruthenium derivative [17]. A “double activation” and subsequent elimination of water, on the other hand, is necessary to form bisallenylidene complexes [13]. Such complexes were obtained by the reaction of bispropargyl alcohols, separated by a carbon-rich unsaturated bridge [13]. Actually, larger trinuclear complexes are also accessible from organic spacers bearing propargyl alcohol moieties [11]. Regarding dinuclear complexes, Rigaut *et al.* published in 2004 the syntheses, electrochemical studies and specific behavior of new, stable bimetallic complexes, such as *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CR{-}T{-}CR{=}C{=}C{=}Ru(dppe)_2Cl]PF_6$ (R = H or Me, T = thiophene or aryl), containing two identical ruthenium fragments with various bisallenylidene bridges [12,14]. These complexes show one single reduction wave, which demonstrates the efficient connection of the metal centers through the allenylidene unit and the highly π-conjugated bridge.

Mantovani *et al.* presented in 2005 the behavior of bimetallic bisallenylidene complexes bearing multiconjugated organic spacers [11], working with the bis-α-alkynol organic spacer, 10,10′-diethynyl-10H,10′H-[9,9′-bianthracenylidene]-10,10′-diol (which is

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http://dx.doi.org/10.1016/j.jorganchem.2016.06.017
0022-328X/© 2016 Published by Elsevier B.V.

Please cite this article in press as: S. Spörler, et al., Journal of Organometallic Chemistry (2016), http://dx.doi.org/10.1016/j.jorganchem.2016.06.017

also used in our present report). The dinuclear bisallenylidene complex *trans*,*trans*-[(dppe)$_2$RuCl(C$=$C$=$(BAN)$=$C$=$C)ClRu(dppe)$_2$](OTf)$_2$ was synthesized starting from the ruthenium mono-allenylidene complex *trans*-[(dppe)$_2$RuCl(C$=$C$=$C(BAN)C(OH)(C$\equiv$CH))]OTf [11]. The authors were able to establish electronic communication between the metal centers through the organic spacer via electrochemical measurements. Specifically, cyclic voltammetry provided evidence of a Ru(II)/Ru(III) oxidation and therefore, the formation of a delocalized mixed-valent Ru(II)/Ru(III) species. To characterize mixed-valent complexes, the classification of Robin and Day is usually applied [19]. In the case described by Mantovani *et al.* the partially delocalized positive charge between the two Ru centers is characteristic of a Robin-Day Class III complex [11,19].

Most recently, the development of metallic bisallenylidene complexes has been directed toward potential application in molecular scale electronic devices [12]. Moreover, such dinuclear bisallenylidene complexes could be promising for catalytic reactions or as building blocks in modern synthesis. Inspired by known examples of dinuclear bisallenylidene complexes, the search for new and larger π-conjugated bridges between the two allenylidene units seemed to be attractive to us. Thus, in this work, we report on cyclopentadienyl dinuclear bisallenylidene complexes [Ru(η^5-C$_5$H$_5$)(PPh$_3$)$_2$($=$C$=$C$=$)(Ar)($=$C$=$C$=$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)Ru](PF$_6$)$_2$ with various polyaromatic spacer ($=$Ar) between the allenylidene units.

2. Experimental

2.1. Methods and materials

All air-sensitive compounds were prepared under an atmosphere of dry nitrogen or argon using conventional Schlenk techniques. Given yields correspond to the purified products after column chromatography. Purchased solvents (*p.a.* grade, < 50 ppm H_2O) were degassed prior to use and stored under nitrogen or argon atmosphere. ^{1}H, ^{13}C, APT ^{13}C and ^{31}P NMR spectra were measured with a *Bruker AVANCE DPX300 NB*, a *Bruker AVANCE DRX400 WB*, a *Bruker AVANCE III HD 400 MHz*, or a *Bruker AVANCE III HD 600 MHz* instrument. For compounds **2** and **3**, NMR spectra were recorded on a *Bruker AVANCE 300* operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR), or on a *Bruker AVANCE 400* operating at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) at room temperature. The δ values are given in parts per million (ppm) relative to tetramethylsilane (^{1}H, ^{13}C) or to H_3PO_4 (^{31}P) as internal standard. The ^{13}C NMR signals were assigned based on APT (attached proton test) measurements. The signals were referenced according to the residual solvent peaks of the deuterated solvent. Coupling constants are reported as observed (±0.5 Hz). IR spectra were recorded with a *Varian EXCALIBUR FTS-3500 FT-IR spectrometer* in a KBr matrix or in CaF_2 cuvettes (0.2 mm) or with a *Varian-660 IR spectrometer* in ATR (attenuated total reflection) mode. For elemental analysis, *Euro EA 3000* (Euro Vector) and *EA 1108* (Carlo Erba) instruments were used ($\sigma = \pm 1\%$ of the measured content). Electrospray-ionization MS (ESI MS) measurements were performed on an *UHR-TOF Bruker Daltonik maXis plus 5G*, an ESI-ToF (time-of-flight) MS capable of resolution of at least 60.000 FWHM. Detection was in either the positive or negative ion mode, the source voltage was 2.8 kV. The flow rates were 180 μL/h. The drying gas (N_2), to aid solvent removal, was held at 180 °C and the spray gas was held at 20 °C. Mass spectra were obtained from a *Micromass Zabspec* (EI), *Bruker 9.4T Apex-Qe FTICR* (MALDI), *Agilent Technologies 6220 oaTOF* (ESI), *Bruker micro TOF II*, and *Bruker maxis 4G* (APPI, ESI) instruments. Melting points from DSC analysis are reported as the peak maxima, except in cases when the sample decomposed, in which case the onset temperature of the decomposition exothermic peak is reported, as well as the exothermic maxima corresponding to the decomposition. The data collection for the structure determination for structure **7** was carried out on an *Agilent Supernova A S2 (Dual)* diffractometer using an Atlas S2 CCD detector and Mova (Mo) X-ray sources (Mova, Mo-K$_\alpha$: $\lambda = 0.71073$ Å). A single crystal of **7** was coated with perfluoropolyether, picked with a glass fiber, and immediately mounted in the nitrogen cold gas stream of the diffractometer. The structure was solved by using direct methods and refined with full-matrix least squares against F^2 (olex2, Pro-Siemens SHELX-97) [20–22]. A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \max(F_o^2,0)]/3$. The hydrogen atoms were included in their calculated positions and refined in a riding model. The asymmetric unit of **7** consists of half a molecule **7** and a PF_6^- counter anion. Moreover, it contains one and a half disordered dichloromethane molecules. The structure pictures were prepared with the program Diamond 2.1e [23]. The UV/Vis/NIR spectra were performed with a *Varian Cary 5G* spectrometer. The spectra were recorded in CH_2Cl_2 and the measuring range is from 2000 nm up to 200 nm. The CV experiments were done using an *AUTOLAB PGSTAT 100*. A three-electrode cell was used, with a gold disk as working electrode, a platinum sheet counter electrode and a silver wire as a pseudo-reference electrode. The spectra were performed in CH_2Cl_2 solution (1.00 mM complex) containing 0.1 M *n*-Bu$_4$N[PF$_6$] as supporting electrolyte. All solutions were deoxygenated with N_2 before each experiment and a blanket of N_2 was used to cover the solution during the experiment. The potential values (E) were calculated using the following equation: $E = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. Potentials are referenced to the ferrocenium/ferrocene (Fc$^+$/Fc) couple used as an internal standard. 9,10-Diethynyl-9,10-dihydroanthracene-9,10-diol [24] (**1**) and 10,10'-diethynyl-10H,10'H-[9,9'-bianthracenylidene]-10,10'-diol [11] (**4**) were synthesized according to the literature. 6,13-Diethynyl-6,13-dihydropentacene-6,13-diol (**3**) was prepared based on adaptation of the route described by Lehnherr [25] and 6,12-diethynyl-6,12-dihydroindeno [1,2-b]fluorene-6,12-diol (**6**) was synthesized based on the diketone indeno[1,2-b]fluorene-6,12-dione [26].

2.2. 6,13-Bis((trimethylsilyl)ethynyl)-6,13-dihydropentacene-6,13-diol (2)

To a solution of trimethylsilylacetylene (870 mg, 8.85 mmol) in dry, deoxygenated THF (20 mL) at −78 °C was added *n*-BuLi (2.5 M in hexanes, 3.42 mL, 8.56 mmol). The solution was stirred for 30 min at −78 °C and was transferred into a solution of pentacenequinone (1.20 g, 2.95 mmol) in dry, deoxygenated THF (20 mL) via a cannula. The mixture was stirred for 18 h at room temperature and saturated aq NH_4Cl (100 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic phases were washed with brine (100 mL), dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. Further purification was achieved by column chromatography (silica gel, CH_2Cl_2/hexanes) (3:1 v/v) ($R_f = 0.13$) and then recrystallized from *n*-pentane at −15 °C to provide **2** as a colorless solid (685 mg, 46%). **Mp** = 244–246 °C; **^{1}H NMR** (300 MHz, CDCl$_3$): $\delta = 8.58$ (s, 4H, PC), 7.94–7.91 (m, 4H, PC), 7.55–7.52 (m, 4H, PC), 3.65 (s, 2H, OH), 0.20 (s, 18H, TMS) ppm. **^{13}C NMR** (100 MHz, CDCl$_3$): $\delta = 136.1$ (PC), 133.1 (PC), 128.2 (PC), 126.9 (PC), 125.8 (PC), 106.9 (C$\equiv$**C**(TMS)), 93.5 (**C**$\equiv$C(TMS)), 69.7 (C–OH), 0.32 (TMS); **ESI HRMS** *m/z* = 487.1910 [M–OH]$^+$ calcd for $C_{32}H_{31}OSi_2$, 527.1834 [M+Na]$^+$ calcd for $C_{32}H_{32}NaO_2Si_2$; **IR** (ATR): $\tilde{\nu} = 3537$ (OH), 3054 (CH$_{Aryl}$), 2957 (CH$_3$), 2169 (CH$_3$) cm^{-1}.

Please cite this article in press as: S. Spörler, et al., Journal of Organometallic Chemistry (2016), http://dx.doi.org/10.1016/j.jorganchem.2016.06.017