Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 359 (2006) 2859–2863

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis of new *mer*,*trans*-rhodium(III) hydrido-bis(acetylide) complexes: Structure of *mer*,*trans*-[$(PMe_3)_3Rh(C{\equiv}C–C_6H_4$-4-$NMe_2)_2H$]

Xunjin Zhu [a,b], Richard M. Ward [a], David Albesa-Jové [a], Judith A.K. Howard [a], Laurent Porrès [a], Andrew Beeby [a], Paul J. Low [a], Wai-Kwok Wong [b], Todd B. Marder [a,*]

[a] *Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK*

[b] *Department of Chemistry and Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Kowloon, PR China*

Received 18 October 2005; received in revised form 18 November 2005; accepted 23 November 2005

Available online 4 January 2006

Dedicated to Professor Brian James on the occasion of his 70th birthday, in recognition of his extensive contributions to inorganic chemistry and catalysis.

Abstract

Terminal alkynes (R–C≡C–H, *R* = 1-naphthyl, 9-anthryl, 4-$Me_2N–C_6H_4$–, or the longer analogue, 4-(4-$Me_2N–C_6H_4$–C≡C–)–C_6H_4–) react with [$Rh(PMe_3)_4Me$] at ambient temperature, with loss of methane and one PMe_3 ligand, to form the corresponding *mer*, *trans*-[$(PMe_3)_3Rh(C{\equiv}CR)_2H$] compounds in excellent yield. In this preliminary study, the synthesis and spectroscopic characterization of the four new compounds are reported, along with the single-crystal structure of the R = 4-$Me_2N–C_6H_4$ derivative.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Acetylide; Alkynyl; Luminescent; Hydride; Crystal structure

1. Introduction

The search for advanced materials with interesting properties has led to numerous investigations into inorganic and organometallic molecular materials [1]. A wide variety of transition metals with different nature, coordination geometry, coordination numbers, and oxidation states, and hence the number of d-electrons, can be employed. These, together with the diversity of ligand systems provide an extremely important and rich area of research in the field of materials science. The chemistry of transition metal acetylide complexes and polymers, in particular those with long sp carbon chains, has been the subject of much interest in recent years [1d,1e,1f], The linear geometry of the alkynyl unit, the rigidity of its structure, its extended π-electron delocalization and ability to interact with metal centers via d_π–p_π overlap make metal alkynyls versatile structural motifs for molecular wires [2–5], polymeric systems [6,7], catalysts for polymerisation [8–10], liquid crystals [11–14], organometallic catenanes [15], dendrimers [16,17], molecular scaffolds [18], luminescent materials [19–22], and as materials for nonlinear optics (NLO) [23–28]. Some systems have received more study than others and, in particular, those containing platinum or palladium [11,12,20,21,27,29–33], rhodium [13,34–36], iron and ruthenium [37–41], rhenium [5,19,42,43] and osmium [44] have received the bulk of the attention.

Some time ago, we reported the synthesis of rhodium acetylide complexes of the form *cis*-[$Rh(PMe_3)_4(H)(C{\equiv}CR)$]Cl [45], [$Rh(PMe_3)_4(C{\equiv}CR)$] [46], [$Rh(PMe_3)_4(C{\equiv}C$-*p*-$C_6H_4$-$C{\equiv}C)Rh(PMe_3)_4$] [47,48], *mer*,*trans*-[$(PMe_3)_3Rh(C{\equiv}CR)_2H$] [49] and related polyyne polymers [47]. Whereas we were previously able to prepare the unsymmet-

---

[*] Corresponding author. Tel.: +44 191 334 2037; fax: +44 191 384 4737.
E-mail address: todd.marder@durham.ac.uk (T.B. Marder).

0020-1693/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2005.11.030

rically substituted donor–acceptor *trans*-$[(PR_3)_2Pt(-C{\equiv}C-D)(-C{\equiv}C-A)]$ complexes necessary for useful second-order NLO effects [27,28] (others have recently investigated the mechanism of alkynyl exchange in these systems [50]), we were unsuccessful in synthesizing related unsymmetrical octahedral Rh(III) bis(alkynyls) in the absence of their symmetrical counterparts [47–49]. We therefore studied in detail the mechanism of formation of $[(PMe_3)_3Rh(C{\equiv}CR)_2H]$ via C–H oxidative addition including isomerization, alkynyl exchange, and hydride replacement by chloride [51]. In the process of this work, we discovered an unusual regioselective coupling of diynes to form luminescent 2,5-bis(arylethynyl)-3,4-bis(aryl)rhodacyclopentadienes [52]. This prompted us to re-explore the chemistry of the rhodium hydrido-bis(acetylide) complexes. In our previous studies, we had not observed luminescent behavior in such complexes. To this end, we prepared several new *mer*,*trans*-$[(PMe_3)_3Rh(C{\equiv}CR)_2H]$ complexes with aromatic substituents on the alkynyl groups. Although detailed studies of the photophysical properties (e.g., luminescence) of the new compounds are in progress, and will form the basis for a future paper, we report herein the synthesis and characterization of four new compounds in this series.

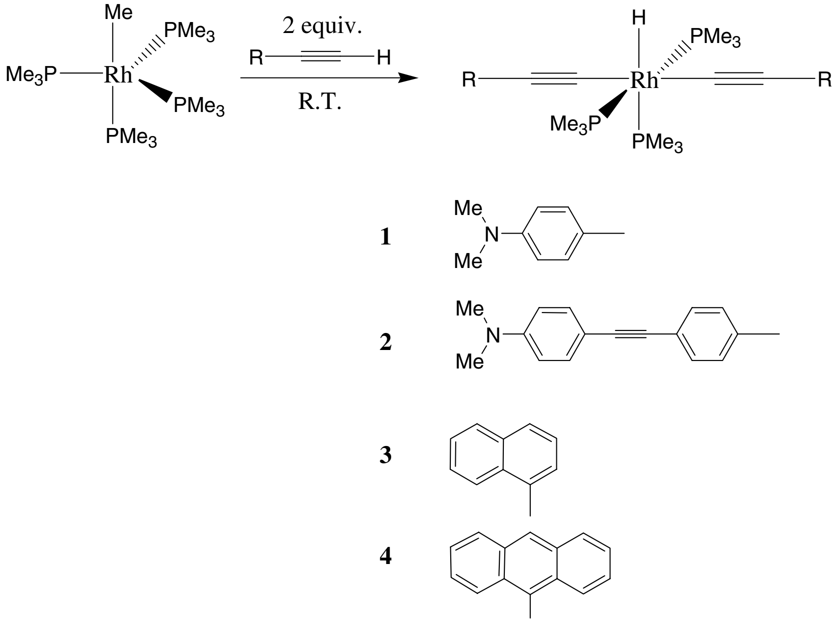
2. Results and discussion

2.1. Synthesis

The complexes *mer*,*trans*-$[(PMe_3)_3Rh(-C{\equiv}CR)_2H]$ (*R* = 1-naphthyl, 9-anthryl, 4-$Me_2N-C_6H_4$ or (4-$Me_2N-C_6H_4-C{\equiv}C-)-C_6H_4-$) were formed cleanly from reaction of $[(PMe_3)_4RhMe]$ with the corresponding terminal alkynes (Scheme 1). The initial step of the reaction is the elimination of methane and the formation of the trigonal bipyramidal complex $[(PMe_3)_4Rh(-C{\equiv}CR)]$, a reaction that has been shown to take place at temperatures as low as −78 °C [51]. This intermediate reacts with a second equivalent of alkyne via oxidative addition of the $\equiv$CH bond with loss of one PMe_3 ligand to give the thermodynamic product *mer*,*trans*-$[(PMe_3)_3Rh(-C{\equiv}CR)_2H]$. Once formed, *mer*,*trans*-$[(PMe_3)_3Rh(-C{\equiv}CR)_2H]$ complexes are configurationally stable [51].

2.2. Characterization

The ^1H NMR spectra of the complexes show the expected virtual triplet and doublet resonances respectively at ca. 1.4–1.5 and 1.1–1.3 ppm for the mutually *trans* PMe_3 groups and the one *trans* to H, aromatic resonances for naphthyl, anthryl and para-phenylene fragments and a hydride at ca. −9 ppm which is split into a doublet with a large coupling ($^2J_{H-P(trans)} = 194$ Hz) and then further split into two apparent quartets with a smaller coupling ($^2J_{H-P(cis)} = {}^1J_{H-Rh} = 18$ Hz) confirming the geometry of this species as the *mer*,*trans*-isomer. In the ^{31}P NMR, the PMe_3 groups thus give rise to a doublet of doublets and a doublet of triplets with $^1J_{Rh-P}$ values of ca. 93 and 76 Hz, and $^2J_{P-P}$ values are 26–27 Hz for P *trans* to P and P *trans* to H, respectively. The IR spectra of the complexes **1**–**4** show $\upsilon_{C\equiv C}$ bands in the range 2087–2066 and υ_{Rh-H} in the range 1978–1930 cm^{-1}. Interestingly, while most samples for elemental analyses were prepared and sealed in a glove box, compound **3** was also submitted in air, and a relatively reasonable analysis on that sample was obtained indicating that, in the solid state, it is not very air-sensitive.



Scheme 1.

Download English Version:

https://daneshyari.com/en/article/1313026

Download Persian Version:

https://daneshyari.com/article/1313026

Daneshyari.com