

Synthesis and reactivity of a novel hydridocobalt(III) complex containing trimethylphosphine and thiophenolato ligands

Guili Jiao, Xiaoyan Li ^{*}, Hongjian Sun, Xiaofeng Xu

School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China

Received 23 April 2007; received in revised form 13 June 2007; accepted 19 June 2007

Available online 27 June 2007

Abstract

The novel hydridocobalt(III) complex [*mer*-Co(H)(SPh)₂(PMe₃)₃] (**1**) was prepared by reaction of thiophenol with [Co(PMe₃)₃Cl], [Co(PMe₃)₄] and [Co(PMe₃)₄Me]. A dinuclear cobalt dithiophenolato complex [Co(PMe₃)₂(SPh)]₂ (**2**) was obtained from the reaction of thiophenol with [Co(PMe₃)₄Me]. Reaction of **1** with iodomethane afforded complex [Co(PMe₃)₃(I)₂] (**3**). Reaction of complex **2** with carbon monoxide gave a mononuclear dicarbonyl cobalt(I) complex [Co(PMe₃)₃(CO)₂(SPh)] (**4**). The crystal structures of **1–4** were determined by X-ray diffraction. Formation mechanism of **1** is discussed.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Hydridocobalt(III) complex; Trimethylphosphine; Thiophenol; Crystal structure

1. Introduction

Hyrido compounds of transition metals play an important role in synthetic and industrial processes. According to a widely accepted mechanism for the hydroformylation process given by Heck and Breslow, a hydridocobalt compound is regarded as a necessary precatalyst [1]. So far very few examples of hydridocobalt(III) complexes are known.

Metal thiolato complexes are known as ubiquitous biological electron-transfer mediators [2,3], yet complexes containing both phosphine and thiolato ligands have received relatively little attention and only a few reports are found in this area [4]. Interest in mono- and polynuclear transition-metal thiolates has undergone a remarkable increase in recent years [5]. Metal thiolate complexes are involved in fundamental catalytic (e.g. hydrodesulfurization [6]) and biological (e.g. iron–sulfur proteins [7]) processes. In particular, the study of sulfur–metal centers,

associated with several important features such as redox behavior, unusual geometries, stabilization of uncommon metal oxidation states, electron deficiency or abundance, can contribute to the understanding of structure, bonding and function of biologically important sulfur–metal sites [7]. Polyphosphine–transition-metal complexes with bis-sulfido coligands usually display good electron-transfer capability [8,9]. Recently, homogeneous nickel catalysts for the selective transfer of a single arylthio group in the catalytic hydrothiolation of alkynes were developed [10].

One of the difficulties in studying thiolate coordination chemistry is that RS[−] donors have a strong tendency to bridge metal ions acting as bidentate soft bases. If not controlled by coligands this can lead to the formation of aggregates or polymers of varying size which can be hard to study [11]. Control has been exerted by the use of bulky substituents and/or by the use of thiolate bearing electron-withdrawing groups. Bridging of thiolates is more easily controlled with aromatic RS[−] donors such as thiophenolates.

The main purpose of this study is to investigate the reactivity of the trimethylphosphine supported hydrido cobalt

^{*} Corresponding author. Tel.: +86 531 88361350; fax: +86 531 88564464.

E-mail address: xli63@sdu.edu.cn (X. Li).

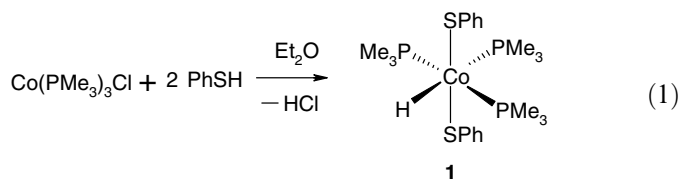
complex to thiophenol. At the same time some chemical properties of the thiophenolato hydrido cobalt complexes were studied. In this paper we report on recent studies of the chemistry of hydridocobalt(III) complexes. In this account reactions of thiophenol with $[\text{Co}(\text{PMe}_3)_3\text{Cl}]$, $[\text{Co}(\text{PMe}_3)_4]$, and $[\text{Co}(\text{PMe}_3)_4\text{Me}]$ are described. $[\text{mer-Co}(\text{H})(\text{SPh})_2(\text{PMe}_3)_3]$ (**1**) could be obtained from each of the starting materials. A dinuclear complex $[\text{Co}(\text{PMe}_3)_2(\text{SPh})_2]$ (**2**) was produced from the reaction of thiophenol with $[\text{Co}(\text{PMe}_3)_4\text{Me}]$. Reaction of **1** with iodomethane has been studied in detail. The reaction of the dinuclear complex **2** with carbon monoxide afforded the mononuclear dicarbonyl cobalt(I) complex **4**. The crystal structures of complexes **1–4** were determined by X-ray crystallography. The formation mechanism of **1** is proposed.

2. Results and discussion

2.1. Preparation of **1**

2.1.1. Reaction of $[\text{Co}(\text{PMe}_3)_3\text{Cl}]$ with thiophenol

$[\text{Co}(\text{PMe}_3)_3\text{Cl}]$ reacts with thiophenol giving the novel hydriocobalt(III) complex **1** according to Eq. (1). **1** forms yellow brown crystals from diethyl ether which decompose above 80 °C. In the IR spectra there is a conspicuous $\nu(\text{Co-H})$ absorption at 1977 cm^{-1} . The ^1H NMR spectrum indicates a pattern of PMe_3 signals expected for complex **1**: a virtual triplet for two *trans*- PMe_3 groups and a doublet for the single PMe_3 ligand. A doublet of triplets appears in the CoH region at -9.2 ppm with $^2J(\text{P}_{\text{cis}}, \text{H}) = 111.9$ Hz and $^2J(\text{P}_{\text{trans}}, \text{H}) = 69.6$ Hz (Fig. 1). ^{31}P NMR data clearly show two singlets (1:2) for three coordinated trimethylphosphine groups, one at -6.86 ppm for the singular PMe_3 and the other at 1.72 ppm for the two *trans*- PMe_3 ligands.



The molecular structure of **1** (Fig. 2) shows a hexa-coordinate cobalt atom surrounded by three P-donor atoms in a meridional configuration. Two thiophenolato donors S1, S2 are arranged in opposite positions. The angle S2-Co1-S1 of 177.38(4)° (Table 1) indicates the position of the hydrogen atom. Owing to the *trans*-influence of the hydrido ligand the distance Co1-P3 (2.2726(19) Å) is larger than Co1-P1 (2.2263(18) Å) and Co1-P2 (2.2266(19) Å).

To understand this mechanism the additional experiments were carried out (Scheme 1). Lithium thiophenolate obtained from the reaction of thiophenol with *n*-butyllithium reacted with $[\text{Co}(\text{PMe}_3)_3\text{Cl}]$ directly giving rise to dinuclear complex **2** without any evidence of formation of the tetra-coordinate cobalt(I) intermediate (route a). This result proves the low stability of this 16-valence-electron cobalt(I) intermediate. The dinuclear complex **2** with the interaction of thiophenol delivered complex **1** (route b). Complex **1** could also be prepared through one-pot reaction of lithium thiophenolate with $[\text{Co}(\text{PMe}_3)_3\text{Cl}]$ in the presence of thiophenol (route c).

2.1.2. Reaction of $[\text{Co}(\text{PMe}_3)_4]$ with thiophenol

The reaction of $[\text{Co}(\text{PMe}_3)_4]$ with thiophenol also yields complex **1** according to Eq. (2).

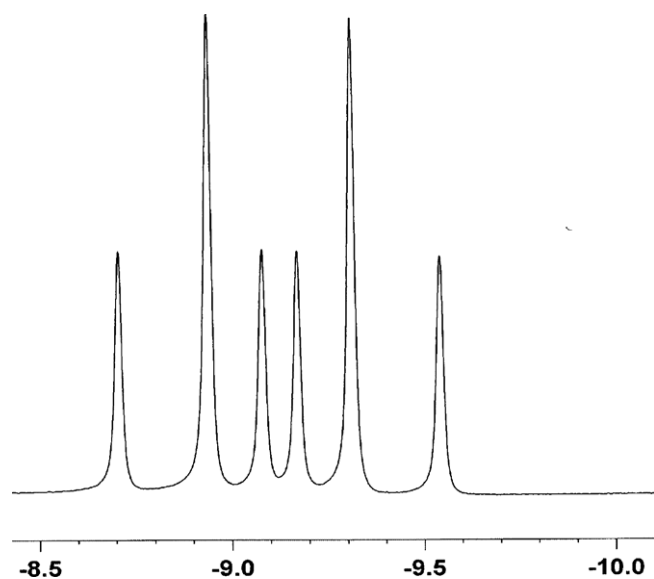


Fig. 1. The NMR spectrum of the hydrido ligand of **1**.

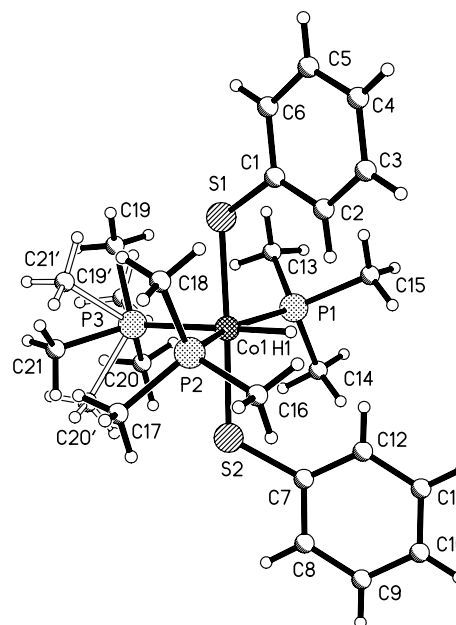


Fig. 2. Molecular structure of **1**.

Download English Version:

<https://daneshyari.com/en/article/1325045>

Download Persian Version:

<https://daneshyari.com/article/1325045>

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