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Half-sandwich rhodium complexes containing both N-heterocyclic carbene and *ortho*-carborane-1,2-dithiolate ligands

Xu-Qiong Xiao, Guo-Xin Jin *

Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai 200433, China

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Abstract

A new route was used to synthesize half-sandwich rhodium complexes containing both N-heterocyclic carbenes (NHC) and carborane ligands. The rhodium carbene complexes $Cp^*Rh(L)[S_2C_2(B_{10}H_{10})]$ (Cp^* = pentamethylcyclopentadienyl, L = 1,3-dimethylimidazolin-2-ylidene; **4**) can be obtained from the reaction of $Cp^*Rh(L)Cl_2$ (**2**) with $Li_2S_2C_2(B_{10}H_{10})$ or from the reaction of $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ (**3**) with silver–NHC complex prepared by direct reaction of an imidazolium precursor and Ag_2O. Complexes **2** and **4** were characterized by IR, NMR spectroscopy, element analysis and X-ray structure analyses.

Keywords: Rhodium; N-heterocyclic carbenes (NHC); Carborane; Half-sandwich complexes; Molecular structures

1. Introduction

N-heterocyclic carbenes (NHC) have emerged as an important class of ligands in organometallic chemistry and homogenous catalysis due to their strong σ-donor electronic properties and ease of changing steric bulk in recent years [1,2]. Many efforts have been made in the design of NHC complexes bearing functionalized groups, including pyridine, picoline and lutidine [3]. Therefore, the design of NHC complexes containing new ligands is of important.

During the past decades, considerable attention has been devoted to metal complexes containing chelating 1,2-dicarba-*closo*-dodecarborane because of both their fundamental properties and wide-ranging potential applications [4]. Our group and Herherhold et al. have reported on the synthesis of 16-electron metal complexes and suggested that these complexes show rich coordination chemistry due to their unsaturation at a metal atom, which has allowed the addition reaction at the metal atom in a dichalcogenolato metal heterocycle [5]. Recently, our group has reported the synthesis of half-sandwich monometallic and dimetallic transition-metal complexes bearing both NHC and carborane ligands from the reaction of Ag carbene precursors and 16-electron "pseudo-aromatic" complexes $[Cp^*MS_2C_2(B_{10}H_{10})]$ (M = Rh, Ir) [6]. Herein, another strategy was used to synthesize rhodium carbene complexes containing both NHC and carborane ligands (Scheme 1).

2. Results and discussion

A solution of **1** in CH_2Cl_2 was added to the filtrate of 1,3-dimethylimidazolium iodide (L) and silver oxide, to afford yellow $Cp^*Rh(L)Cl_2$ (L = 1,3-dimethylimidozolin-2-ylidene, **2**) in a yield of 78%, which has been characterized by NMR, elemental analysis and X-ray structure analyses.

The ^1H NMR spectrum of complex **2** shows no signal at δ 10-11 ppm, where the imidazolium C_2–H signals of precursors were found ($\delta = 10.18$ ppm). The ^{13}C NMR spectroscopic data of **2** reveal that metalation of the carbene had occurred, as evidenced by presence of signals at $\delta = 164.9$ ppm (**2**) in the ^{13}C NMR spectrum, which is typical for the carbon of metal-carbene [7].

* Corresponding author. Tel.: +86 21 6564 3776; fax: +86 21 6564 1740.
E-mail address: gxjin@fudan.edu.cn (G.-X. Jin).

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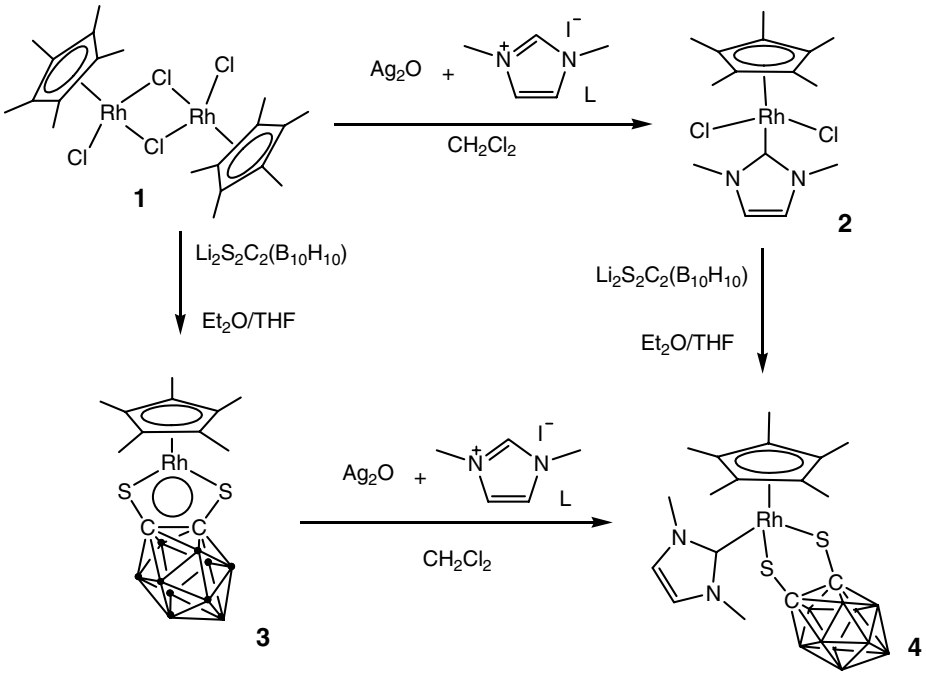

Scheme 1. Synthesis of complexes **2**–**4**.

Single crystals suitable for X-ray crystallography of **2** were obtained by slow diffusion of hexane into dichloromethane solution of **2**. The metal centre of complex **2** adopts a distorted three-legged stool geometry (Fig. 1). The Rh–$C_{carbene}$ bond length (2.052(3) Å) are typical for Rh–C σ bonds with very little back-donation [8]. The bond angle C_{cent}–Rh–$C_{carbene}$ (C_{cent} is the central point of the Cp^*) is 126.2°, thus minimizing the repulsion between the Cp^* and the imidazole ring. The Rh–$C_{carbene}$ band is almost perpendicular to the Rh–Cl(1)–Cl(2) plane with an angle of 85.5°. As usual, the C–C distance in the imidazole unit is short (ca. 1.324(6) Å), which points to enhanced C=C double-bond character.

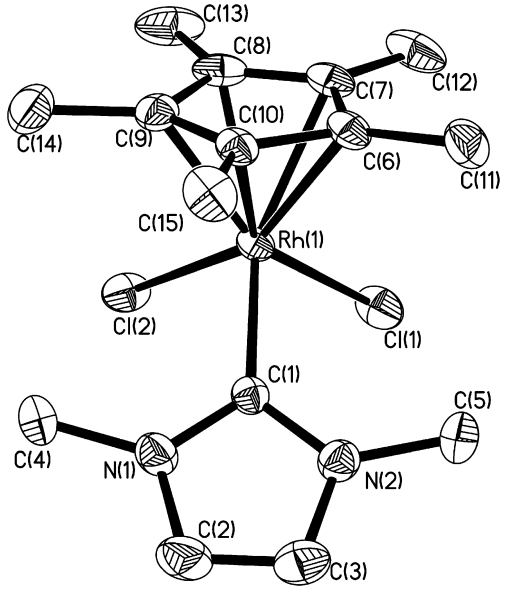

Fig. 1. Molecular structure of **2** (hydrogen atoms are omitted for clarity, ellipsoids set at the 30% probability level). Selected bond lengths (Å) and angles (°): Rh(1)–C(1) 2.052(3), Rh(1)–Cl(1) 2.4168(10), Rh(1)–Cl(2) 2.4232(11); C(1)–Rh(1)–Cl(1) 92.10(9), C(1)–Rh(1)–Cl(2) 94.08(9), Cl(1)–Rh(1)–Cl(2) 86.67(4), N(1)–C(1)–N(2) 103.6(3).

The complexes $Cp^*Rh(L)[S_2C_2(B_{10}H_{10})]$ (**4**) were obtained by treatment of **2** with the dilithium 1,2-dithiolate carborane cluster in THF solution or from the reaction of $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ (**3**) with silver–NHC complex prepared by direct reaction of an imidazolium precursor and silver oxide (Scheme 1).

The ^{1}H NMR spectrum of complex **4** also shows no signal at δ 10–11 ppm, which is typical for the imidazolium C_2–H signals of precursors. The ^{13}C NMR spectroscopic data of **4** exhibits signal at $\delta = 164.4$ ppm, which can be unequivocally assigned for the metal-carbene carbon. The ^{11}B NMR spectrum of **4** show signals at $\delta = -7.3$, -8.1, -8.7, -10.8, -11.6 ppm. The infrared spectrum of complexes **4** in the solid state exhibits intense B–H stretching of carborane at about 2580 cm^{-1}.

Single crystals suitable for X-ray crystallography of **4** were also obtained by slow diffusion of hexane into dichloromethane solution of **4**. The ORTEP diagram of **4** is presented in Fig. 2, which establishes that there is a pseudo mirror plane going through the Rh–$C_{carbene}$ bond. The metal centre is in a distorted octahedral environment with Cp^* as three-coordinated ligand, chelating *ortho*-carborane dithiolate and monodentate NHC. Due to the coordination of the carbene to the metal centre, the "*pseudo*-aromatic" metalladithiolate heterocyclic system is destroyed and bent with a dihedral angle (168.0°) along the S···S vector, compared to 180° in $[Cp^*RhS_2C_2(B_{10}H_{10})]$ [9]. The Rh–S distance (2.36 Å) at the formally 18-electron metal centre is