Journal of Organometallic Chemistry 811 (2016) 8–13

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Chemistry of Rh-N,S heterocyclic carbene complexes

Dipak Kumar Roy, K. Yuvaraj, R. Jagan, Sundargopal Ghosh*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form
13 March 2016
Accepted 14 March 2016
Available online 17 March 2016

Keywords:
N,S heterocyclic carbene
Boratrane
Boron
Rhodium
Vinyl complex

ABSTRACT

Chloro-rhodaboratrane [(Cp*Rh)(L_2)BCl] **4** has been synthesized from rhodium N,S-heterocyclic carbene complex [(Cp*Rh)(L_2)(1-benzothiazol-2-ylidene)], **1**, (L = $C_7H_4NS_2$) and borane reagent $BHCl_2.SMe_2$. The Rh–B bond in **4** is buttressed between two benzothiazolyl units in [3.3.0] fashion. The presence of B–Cl bond allowed us to explore the chemistry of boratrane **4** at the boron centre. The reaction of ethynylmagnesium bromide with **4** yielded η^1-vinyl complex [Cp*RhBr(C_2H_2)L] **5**, containing a five membered metallaheterocycle. In an objective to abstract the chloride, alike borylene synthesis from haloboryl, we performed the reaction of **4** with $NaBAr^F{}_4$ that resulted the thiolato bridged bimetallic compound [Cp*Rh(μ-L)$_3$RhCp*][$BAr^F{}_4$] **6** (Ar^F: $C_6H_3(CF_3)_2$-3,5).

1. Introduction

Ever since the first report of crystalline *N*-heterocyclic carbene (NHC) [1], the chemistry of these complexes and their transition metal compounds has expanded rapidly due to their applications in catalysis [2–4]. Compare to diaminocarbenes with an *N*-heterocyclic ring, less attention has been paid to N,X-heterocyclic carbenes (X = O, S, P) as the free ligands are unstable and undergo an easy proton-catalyzed chemical equilibrium with their dimers [5,6]. On the other hand, in our laboratory, we have been exploring the reaction cyclopentadienylmetal chlorides with monoborane reagents as a general route to dimetallaboranes [7–14] which has allowed us to explore the systematic reaction chemistry of these clusters [15]. For example, [(Cp*RuCO)$_2B_2H_6$] had shown its potentiality for active cyclotrimerization catalyst [15a], a hydrogen rich tantalaborane had been used in C–H bond activation of arenes and heteroarenes [15b]. Similarly, to explore the reactivity of [(Cp*Rh)$_2B_3H_7$] with 2-mercaptobenzothiazole (2-mbz) ligand, we have structurally characterized Rh-N,S-heterocyclic carbene complex [(Cp*Rh)(L_2)(1-benzothiazol-2-ylidene)], **1**, (L = $C_7H_4NS_2$) for the first time [16]. The use of [Cp*$RhCl_2$]$_2$ as starting material led us to isolate compound **1** in good yield that further allowed us to explore its chemistry [17]. In this article, we present the reactivity of **1** with $BHCl_2 \cdot SMe_2$ that yielded a chloroboratrane [(Cp*Rh)(L_2)BCl] **4** and further its reactivity has been elaborated in order to functionalize the boron-chlorine bond.

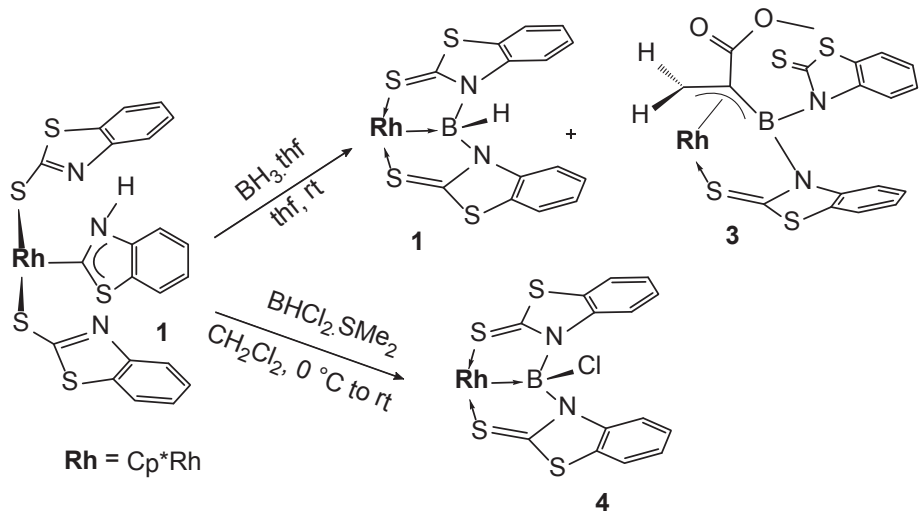
2. Results and discussion

2.1. Synthesis and characterization of chloroboratrane [(Cp*Rh)(L_2)BCl] 4

In our continuing research for alternative routes to various B-agostic complexes, recently we have shown Rh-N,S-heterocyclic carbene [(Cp*Rh)(L_2)(1-benzothiazol-2-ylidene)] **1**, (L = $C_7H_4NS_2$) as the effective precursor for various transition–metal boron complexes [16–18]. In particular, the treatment of $BH_3 \cdot$thf with **1** led to rhodaboratrane [(Cp*Rh)(L_2)BH] **2** and a rare type borataallyl complex [Cp*Rh(L)$_2$B{$CH_2C(CO_2Me)$}] **3** [18]. In probing these observations, we examined the reaction of **1** in the presence of excess $BHCl_2 \cdot SMe_2$ in CH_2Cl_2 in an objective to synthesize boratrane with B–Cl bond that can further be functionalized. Upon addition of $BHCl_2 \cdot SMe_2$ into ice cold CH_2Cl_2 solution of **1**, a rapid colour change from red to orange was observed (Scheme 1). After chromatographic separation that yielded a red crystalline solid **4** in 60% yield. The $^{11}B\{^1H\}$ NMR spectrum showed the presence of a sharp boron peak at δ = 17.4 ppm which is shifted down field compared to rhodaboratrane **1**. The coupled ^{11}B NMR did not show any broadening or splitting that suggests the absence of hydrogen attached to boron atom. The ^1H NMR hints the presence of one Cp* ligand and two equivalent benzothiazolyl rings. The identity of compound **4** was finally ascertained via X-ray crystallographic analysis to be a

* Corresponding author.
E-mail address: sghosh@iitm.ac.in (S. Ghosh).

http://dx.doi.org/10.1016/j.jorganchem.2016.03.012
0022-328X/



Scheme 1. Reactivities of Rh-N,S-heterocyclic carbene **1** with BH_3.thf to form previously reported **2** and **3** [18], and with $BHCl_2.SMe_2$ to form compound **4**.

rhodaboratrane with a B–Cl bond (Fig. 1). The ^{11}B and ^{1}H chemical shifts of **4** (Table S2), calculated using the gauge including atomic orbital (GIAO) and B3LYP functional, agreed well with the experimental values. This provides a firm test of the validity of the calculated electronic structure of **4**.

The molecular structure of **4** shows the presence of a direct metal–boron bond, which is further supported by two benzothiazolyl bridges (Fig. 1). The Rh-B distance of 2.119(5) Å is shorter than the first reported rhodaboratrane (2.132(6) Å) and **2** (2.139(10) Å) however, longer than the typical range seen in rhodiumboryl complexes (1.96–2.05 Å) [19], hence excludes boryl formulation. Pertinent optimized structural parameters are in well accord to the available X-ray parameters (Table S1). The natural bond orbital (NBO) analysis of compound **4** shows a strong covalent Rh-B interaction with Wiberg Bond Index (WBI) value of 0.67 (2.119 Å) and an area of charge concentration was observed along the Rh–B bond. The $B(ligand)_2$ fragment adopts a bicyclo[3.3.0] cage at a Rh centre anchoring a pentamethylcyclopentadienyl ligand. As expected from the ^{11}B and ^{1}H NMR study, the solid state structure showed that the absence of terminal hydrogen (BH_t) rather chlorine atom is attached to boron centre. The geometry at boron is distorted tetrahedral, whereas the geometry at the rhodium centre can be considered as pseudooctahedral with a pentamethylcyclopentadienyl ligand.

2.2. Reaction of chloroboratrane, *4* with ethynylmagnesium bromide

The presence of the B-Cl moiety in **4** inspired us to utilize it as a possible precursor for forming carbon–boron bond via Grignard reagents or organolithium compounds. The reaction of ethynyllithium led to some intractable products; however reaction of **4** with ethynylmagnesium bromide led to consumption of starting material (Scheme 2). The chromatographic work up allowed us to

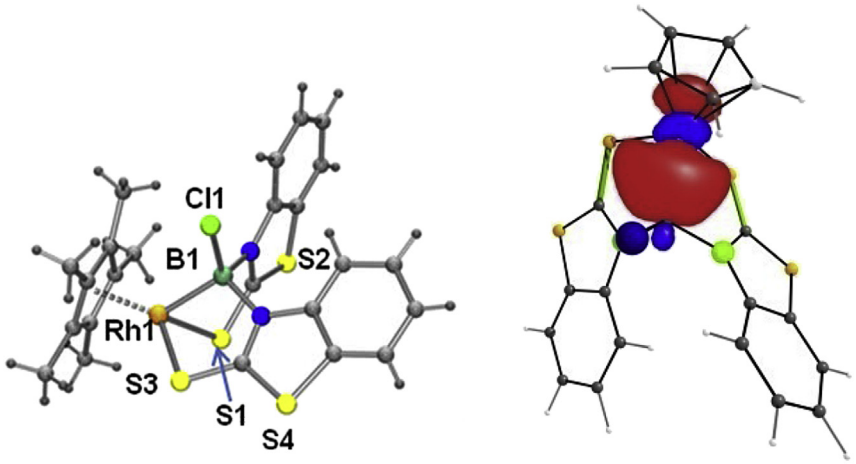


Fig. 1. (a) Molecular structure and labeling diagram of **4**. Selected bond lengths [Å] and angles [°]: Rh1–B1 2.119(5), Rh1–S3 2.3115(11), Rh1–S1 2.3369(11), Cl1–B1 1.866(5), S1–C1 1.686(4), S3–C8 1.682(5), N2–B1 1.581(5), N1–C1 1.326(5), N1–B1 1.595(5); B1–Rh1–S3 84.50(12), B1–Rh1–S1 79.15(13), S3–Rh1–S1 92.01(4), C1–N1–C2 112.3(3), N2–B1–N1 108.5(3), N2–B1–Cl1 104.0(3). (b) NBO demonstrating Rh-B coupling in **4**.