

Communication

Sterically controlled formation of monodentate versus chelating carbene ligands from phenylhydrazine

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Abstract

Palladium-templated addition of phenylhydrazine to methylisocyanide led to a Chugaev-type chelating dicarbene–palladium complex that is an effective catalyst for Suzuki–Miyaura cross-coupling reactions of aryl bromides and activated aryl chlorides. In contrast, the use of isopropylisocyanide resulted in an unprecedented complex containing aminohydrinocarbene ligands, which was characterized by X-ray crystallography. The latter complex represents a possible intermediate in the formation of chelating carbene ligands.

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1. Introduction

Since the first report of a metal–carbene complex by Fischer and Maasböl in 1964 [1], heteroatom-stabilized carbene ligands have become ubiquitous in organometallic chemistry. Diaminocarbenes possess particularly favorable ancillary ligand properties, acting as powerful σ -donors without the electrophilic reactivity of Fischer-type carbenes [2]. This is exemplified by the imidazole-derived N-heterocyclic carbenes (NHCs) [3], which have received increasing attention following their isolation as free carbenes by Arduengo and co-workers [4]. The strong σ -donation of these ligands combined with their increased oxidative and thermal stability relative to phosphines have placed NHCs at the forefront of ligand design for organometallic catalysis [5]. Significant advances in catalytic activity for olefin metathesis [6] and

cross-coupling reactions [7,8] have already been achieved using NHC ligands, and opportunities exist for their application in a range of other synthetically useful reactions. Because each catalytic reaction has unique requirements for ligand steric and electronic properties, the search for new carbene ligand types that permit systematic tuning of these parameters is an important goal.

An overlooked but historically interesting class of bidentate diaminocarbene ligands is the “Chugaev-type” carbenes, which are formed by nucleophilic addition of hydrazines or diamines to metal-bound isocyanide ligands [9,10]. Platinum complexes of these ligands were reported as early as 1915 (a, Fig. 1), [9] though they were not recognized as carbenes until their structural characterization by Burke, Balch and Ene-mark in 1970 [11]. These chelating carbenes are intriguing candidates for catalyst development due to their similarity to acyclic diaminocarbenes [12], which have been reported to be stronger σ -donors than imidazole-based NHCs [13] but have not been substantially

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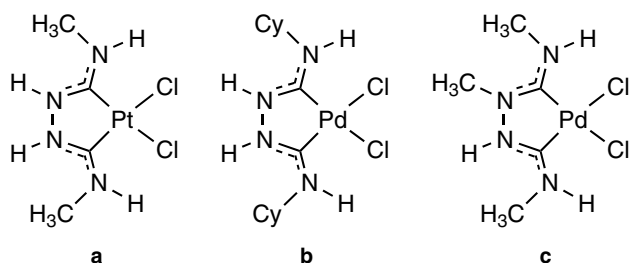
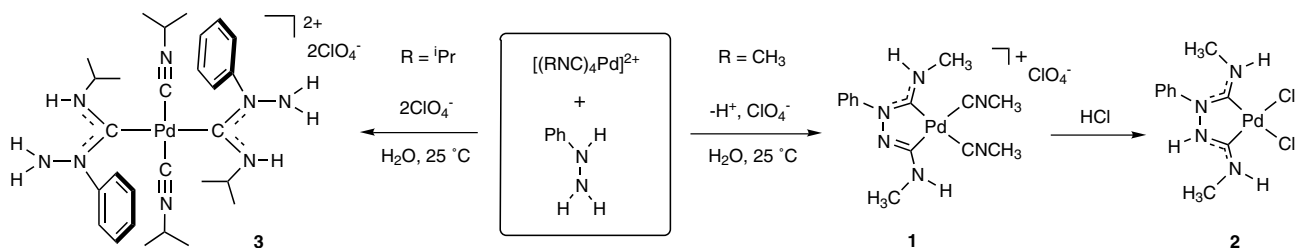


Fig. 1. Chugaev-type carbene complexes.

explored in catalysis. In addition, they have potential for systematic steric and electronic “tuning” by variation of the isocyanide and diamine backbone. Our initial studies showed that palladium–dicarbene complex **b** (Fig. 1) is a stable and active catalyst for Suzuki–Miyaura coupling of aryl bromides and electron-poor aryl chlorides, even under aerobic conditions [14]. Subsequently, systematic variation of ligand substituents and screening of the resulting catalyst “library” allowed identification of complex **c** as a more active catalyst with improved substrate scope [15]. This ability to optimize catalyst activity via systematic ligand modification is promising for the further development of Chugaev-type diaminocarbene complexes as ancillary ligands.

We have sought Chugaev-type diaminocarbene ligands with steric bulk directed toward the metal center through the use of substituted hydrazines and bulky alkylisocyanides. This is important because increased bulk is thought to expedite product-forming reductive elimination steps in cross-coupling reactions [8]. Herein we report that palladium-templated addition of phenylhydrazine to isopropylisocyanide results in an unprecedented monodentate aminohydrazinocarbene ligand instead of the expected chelating dicarbene. The resulting carbene complex is mechanistically interesting, as it represents a likely intermediate in the formation of Chugaev-type carbenes that has not previously been observed. In contrast, the use of methylisocyanide gives rise to a chelating dicarbene complex that is an active precatalyst for Suzuki–Miyaura cross-coupling reactions. This effect of sterics on the type of carbene formed provides valuable insights for future ligand design efforts.



Scheme 1. Synthesis of chelating versus monodentate carbene complexes from phenylhydrazine.

2. Results and discussion

Sequential addition of methylisocyanide (4 equiv.) and phenylhydrazine (1 equiv.) to an aqueous solution of K_2PdCl_4 resulted in formation of a yellow solution, and a yellow precipitate was collected upon addition of excess LiClO_4 [16]. The ^1H NMR spectrum (CD_3CN) of this compound contains two NH resonances (δ 5.98, 4.82) and three CH_3 peaks (one unresolved) in addition to the phenyl resonances [16], diagnostic for a cationic complex containing two isocyanides and a deprotonated form of a Chugaev carbene ligand (**1**, Scheme 1). Such complexes are often the first products obtained in Chugaev carbene syntheses [11,14]. Complex **1** was readily converted into neutral (dicarbene) PdCl_2 **2** by dissolution in hot 3 M aqueous HCl [17]. Dicarbene complex **2** is characterized by three NH resonances (δ 11.32, 8.26, 7.95) and two CH_3 peaks in the ^1H NMR spectrum ($\text{DMSO}-d_6$) as well as the absence of isocyanide $\text{C}\equiv\text{N}$ stretches in the IR spectrum [17]. No crystals of **1** or **2** suitable for X-ray diffraction could be obtained. Thus, the differing stereochemistries of the terminal CH_3 groups nearest the phenyl group in **1** and **2** are assigned based on the reported structures of methylhydrazine-derived analogues [15,18], with a *trans* configuration for **1** and a *cis* configuration for **2**. However, the presence of two sets of phenyl and CH_3 peaks in the ^{13}C spectra of **1** and **2** suggests that both isomers of these compounds are in equilibrium in solution.

An identical procedure to that used to prepare **1**, but with isopropylisocyanide replacing methylisocyanide, afforded a colorless compound with different spectral signatures from **1** [19]. The ^1H NMR spectrum (CD_3CN) exhibited two NH resonances in a 1:2 ratio (δ 7.93, 4.66) as well as two distinct isopropyl groups, and only one carbene resonance was observed in the ^{13}C NMR (δ 182.1) [19]. An X-ray crystallographic analysis [20] revealed this complex to be a dication containing two *monodentate* carbene ligands and two isocyanides in a *trans* configuration (**3**, Scheme 1, Fig. 2). To the best of our knowledge, **3** is the first reported complex of an aminohydrazinocarbene ligand. A few examples of hydrazinocarbene ligands have been published, but these have alkynyl [21], alkenyl [22], or alkyl [23] groups as the second carbene substituent and more than one

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