

# Chiral, bridged bis(imidazolin-2-ylidene) complexes of palladium <sup>☆</sup>

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Dedicated to Prof. Dr. Gerhard Erker on the occasion of his 60th birthday.

## Abstract

Varieties of chiral, bridged bisimidazolium salts as well as the synthesis of palladium complexes of general formula  $[bridge\{NC(H)=C(H)N(R^*)C\}_2PdBr_2]$  with the corresponding chelating N-heterocyclic carbene ligands is reported. This is the first systematic study of chiral bis(imidazolin-2-ylidene)palladium(II) complexes bearing chiral groups on the endocyclic nitrogens. Structural proof of such a chiral palladium(II) complex is presented by way of an X-ray diffraction study of complex **3a**.

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**Keywords:** Chelating ligands; Chiral ligands; Bisimidazolium salts; Palladium

## 1. Introduction

N-Heterocyclic carbenes have become universal ligands in organometallic and inorganic coordination chemistry [1,2]. The bond between the N-heterocyclic carbene and the metal centre of a complex can be best described as a dative  $\sigma$ -bond as the M–C distance falls comfortably in the range of typical single M–C bond lengths (X-ray diffraction) [3,4]. Metal complexes of imidazolin-2-ylidenes have attracted considerable attention as homogeneous catalysts [2]. For example, complexes of ruthenium and palladium show excellent catalytic properties for olefin metathesis and C–C coupling reactions [5]. In contrast to the corresponding phosphine complexes, ligand dissociation is not favored in NHC complexes [6]. This eliminates the need for an excess of ligand [7], and makes them possible candidates for asymmetric catalysis [8,9]. Thus, a sub-

stantial amount of work on the preparation of chiral NHC ligands has been published [10], following our report of the first chiral NHC-complex employed in homogeneous catalysis [4]. The rigidity of chelating chiral carbene ligands is expected to result in higher optical inductions in asymmetric reactions relative to two non-chelating ligands. Such ligands can be constructed, for example, by a bridged bis(imidazolin-2-ylidene) ligand, a well known framework for achiral NHC ligands [11–17]. The complexes with chelating carbene ligands are presumably highly thermal stable because of the chelating effect.

The preparation of chelating ligands of N-heterocyclic carbenes, in order to impart higher air- and moisture stability to palladium centers, is receiving nowadays much attention [18,19]. We and others have published chelated palladium NHC complexes which can be used in C–C coupling reactions [13,15,20–22]. For example, some methylene-bridged bis(imidazolium) salts, in combination with  $Pd(OAc)_2$ , were equally efficient as the non-bridged biscarbene complexes in the Suzuki coupling reaction with aryl chlorides as substrates [23,24] and the bridged biscarbene complexes even achieve the C–H activation of methane [25]. In the first part of the present article, a variety of

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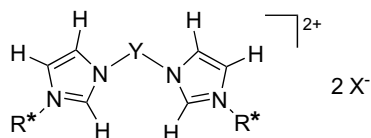


Fig. 1. R\*-substituted (R\* = chiral alkyl group) imidazolium salts with Y-bridging groups (Y = bridging moiety).

new bis(imidazolium) salts will be presented. We will focus on the variation of the bridging group Y and the substituents R\* (Fig. 1).

## 2. Results and discussions

### 2.1. General synthesis of chiral imidazole derivatives

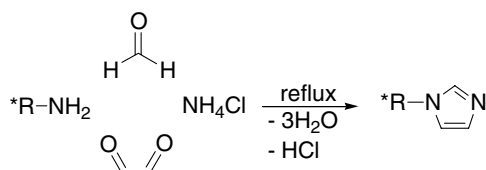
The substituted imidazole precursors are accessible via an one-pot synthesis route according to Gridnev and Mihaltseva (Scheme 1) [26].

The products can be purified by extraction, recrystallization or distillation. Via this synthesis two new chirally modified imidazoles, 1-(R)-(phenylethyl)imidazole **1a** [27], and 1-(R)-(1'-naphthylethyl)imidazole **1b**, could be synthesized without racemization and with retention of the (R)-configuration employing commercially available chiral amines.

In order to synthesize a library of chirally modified bridged imidazolium salts, we used a general synthetic procedure. Two equivalents of the imidazole were dissolved in THF and transferred to an ACE pressure tube. One equivalent of the corresponding dibromo compound was added and the resulting mixture was heated. The purification of the air stable hygroscopic colorless to pale brown products was achieved by washing the obtained solids with THF [28]. The product was dried under high vacuum. It is remarkable that the synthesis of chiral imidazolium salts occurs without racemization of the chiral centers; the (R)-configuration is maintained in each case. To the best of our knowledge these are the first enantiomerically pure chiral, bridged bisimidazolium salts with the chirality introduced at the N-atoms reported to date [15]. Table 1 gives an overview of the prepared bis(1,3-azolium) salts.

### 2.2. Synthesis of chiral bis(carbene)palladium(II) complexes

The neutral bis(carbene)palladium(II) bromide complexes **3a–3f** were prepared via an adaptation of our



Scheme 1. Synthesis of substituted imidazoles.

Table 1  
Chelating imidazolium salts as carbene (NHC) precursors

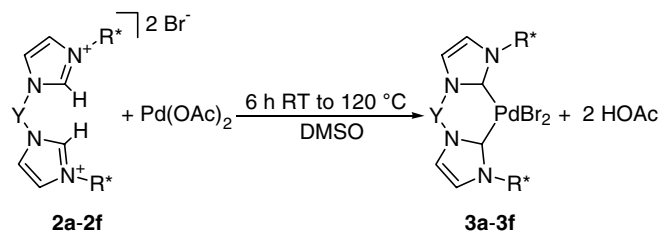
Azolium salt	R*	Y	Yield [%]
<b>2a</b>	(R)-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	-CH <sub>2</sub> -	49
<b>2b</b>	(R)-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	<i>o</i> -Xylene	83
<b>2c</b>	(R)-CH(C <sub>10</sub> H <sub>7</sub> )CH <sub>3</sub>	<i>o</i> -Xylene	76
<b>2d</b>	(R)-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	<i>m</i> -Xylene	97
<b>2e</b>	(R)-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	<i>p</i> -Xylene	93
<b>2f</b>	(R)-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	2,6(CH <sub>2</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)	80
<b>2g</b>	(R)-CH(C <sub>10</sub> H <sub>7</sub> )CH <sub>3</sub>	2,6(CH <sub>2</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)	75

straightforward procedure, avoiding the formation of free carbenes as intermediates [13], which utilizes longer reaction times and milder temperatures to increase yields of the palladium complexes, particularly when chiral substituents are present in the bridged bis(imidazolium) salt precursors. Thereon, the bis(imidazolium) salt and Pd(OAc)<sub>2</sub> were stirred in DMSO overnight at room temperature. After this, slow heating over a period of 6 h not reaching more than 120 °C afforded the bis(carbene)palladium(II) complexes **3a–3f** without racemization of the chiral groups (Scheme 2). The synthesized complexes are depicted in Fig. 2.

### 2.3. X-ray crystal structure of complex **3a**

The molecular structure of the square-planar Pd(II) complex **3a** in the solid state is shown in Fig. 3. Selected bond lengths and angles are denoted in the figure caption. The crystal structure of complex **3a** shows the biscarbene ligand chelating the palladium(II) center in a *cis*-arrangement with a boat conformation being observed for the six-membered C<sub>3</sub>N<sub>2</sub>Pd ring. The remaining two coordination sites of the distorted square planar coordinated palladium center are occupied by bromine anions.

The Pd–C distances (1.974(3), 1.992(3) Å) fall comfortably within the range found for the dicationic and neutral chelating bis(carbene)palladium(II) complexes [*cis*-CH<sub>2</sub>



Scheme 2. Synthesis of chiral bis(carbene)palladium(II) complexes.

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