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Review

Complexes with protic (NH,NH and NH,NR) N-heterocyclic carbene ligands

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ABSTRACT

The review describes methods for the preparation of complexes bearing protic NHC ligands, i.e. NHCs featuring an NH,NH or NH,NR substitution pattern. The protic NHC ligands are easily functionalized at the ring nitrogen atoms after N–H deprotonation. Thus the introduction of various functional groups at the ring nitrogen atoms is possible giving access to new complexes with NHC ligands and even allowing the linkage of individual protic NHCs to give macrocyclic ligands with NHC donors. Selected applications for complexes bearing protic NHCs will be described.

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1. Introduction

The properties and applications of N-heterocyclic carbenes (NHCs) and their metal complexes have been intensively studied over the last twenty years. These efforts led to a variety of different NHC ligands, which exhibit different electronic or steric

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properties [1]. Several NHCs are used as organocatalysts [2]. An even greater number of NHC complexes have found application in catalysis [3]. More recently, NHC complexes have been employed for the preparation of OLEDs [4] or as metallodrugs [5]. Poly-NHC ligands have even been used for the generation of metallosupramolecular assemblies [6] and heterobimetallic complexes [7]. In NHC complexes, the NHC ligand is normally strongly bonded to the metal center based on the superb σ-donor properties of the NHC donor [8]. Due to their high stability, NHC complexes have developed into an important class of compounds in organometallic chemistry and they constitute an alternative to the widely used phosphine complexes.

Most of the known NHC complexes are prepared by in situ deprotonation of azolium cations in the presence of a metal precursor [1] or by a carbene transfer reaction from a suitable silver NHC complex [1,9]. Access to NHC complexes by coordination of a free NHC (sometimes generated by cleavage of its enetetramine dimer) to coordinatively unsaturated metal precursors is limited as it requires the isolation of the generally reactive NHCs or enetetramines [1,10]. The oxidative addition of azolium salts to low-valent transition metal centers has been studied in detail by Cavell and Yates [11] and this reaction constitutes an alternative access to NHC complexes. The oxidative addition of a C^2—X bond (X = halogen) to low-valent metal centers normally proceeds fast [11,12], but only few examples are reported for the oxidative addition of the C^2—H [11a,b], C^2—C [11b,13] or C^2—S [14] bond of azolium cations. The oxidative addition of C^2—X or C^2—H bonds of azolium cations becomes more feasible in the presence of an additional donor function at the azolium moiety, which can precoordinate thereby bringing the functionality for the oxidative addition in close proximity to the metal center [15].

The synthetic procedures described so far lead to NHC complexes of type **A** (Fig. 1) featuring "classical" NR,NR-substituted NHC ligands. In these complexes, the substitution pattern of the ring nitrogen atoms generally prevents a subsequent functionalization of the NHC ligand after complex formation. Such functionalization, however, is possible with complexes of types **B** and **C** (Fig. 1) featuring protic NHC ligands with an NH,Y (Y = NR, O, S) or an NH,NH-substitution pattern. The NH-functions in **B** and **C** can be deprotonated generating a strong *N*-nucleophile or *N*-base for subsequent reactions. Such a functionalization of the coordinated NHC ligand in complexes of types **B** and **C** by substitution of the NH proton yields complexes of type **A** with an NR,NR-substitution pattern [16]. In addition, the NH group of NH,O or NH,NEt-substituted NHC ligands are capable of forming hydrogen bonds to selected hydrogen bond acceptor molecules such as triphenylphosphine oxide [17] (Fig. 1, **D**) or dmpu (Fig. 1, **E**) [18].

The functionalization of complexes bearing protic NHCs offers multiple options for the introduction of N,N′-substituents. In addition, the recognition of hydrogen bond acceptors observed for complexes with protic NHC ligands (Fig. 1, **D** and **E**), bears potential for cooperative catalysis, as such hydrogen bonds could be utilized for substrate recognition and orientation in selected catalytic reactions. Until recently, only few complexes bearing protic NHC ligands have been described. Their potential utility in synthesis and catalysis has sparked new interest in these complexes. Access to complexes with protic NHCs is not possible using the synthetic methods for "normal" NHC complexes mentioned above. Recently, new synthetic protocols leading to complexes of types **B** and **C** have been developed. This account aims to summarize these recent efforts in the field together with a description of potential applications for complexes bearing protic NHCs.

2. Synthesis of complexes with protic NHC ligands by tautomerization of azoles

2.1. Acid-catalyzed tautomerization

The acid-catalyzed tautomerization of imidazoles was first reported by Sundberg and Taube [19]. Upon treatment of ruthenium(II) complexes of type **1** bearing an N-bound imidazole ligand with acid, a rearrangement reaction of the heterocycle was observed. Complexes **2** with a C^2-bound NH,NH-NHC ligand were obtained. The NH,NH-substituted NHC ligand in **2** is strongly bound to the metal center and this arrangement tolerates the substitution of the H_2O ligand for a CO ligand giving complexes of type **3** [19b]. Even oxidation of the Ru^{II} to the Ru^{III} complexes of type **4** is possible without loss of the NH,NH-NHC ligand [19b] (Scheme 1).

Using a similar approach, Taube and co-workers also succeeded with the preparation of complexes with protic NHC ligands starting from alkylated xanthine derivatives [20]. The reaction proceeded by treatment of the xanthines with $[RuCl(NH_3)_5]^{2+}$ in the presence of zinc/amalgam, followed by addition of hydrochloric acid (Scheme 2, top), which led in an acid-induced tautomerization of the N-bound purine base to the C^8-bound NH,NR-NHC ligand. The subsequent oxidation in air gave the Ru^{III} complexes of type **5** [20].

In general, purine bases appear as suitable precursors for the preparation of NHC complexes, due to the presence of the imidazole moiety [21]. However, most of the known purine

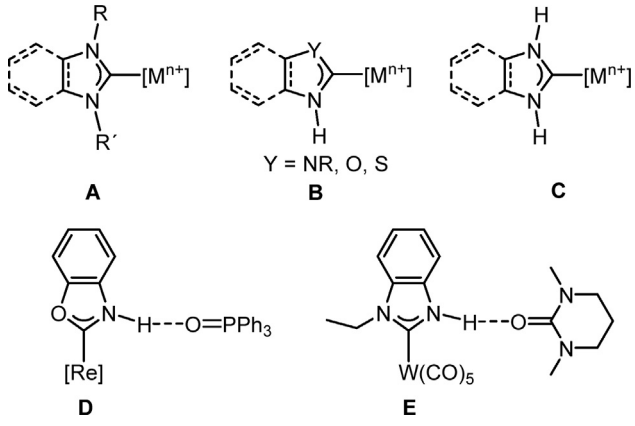
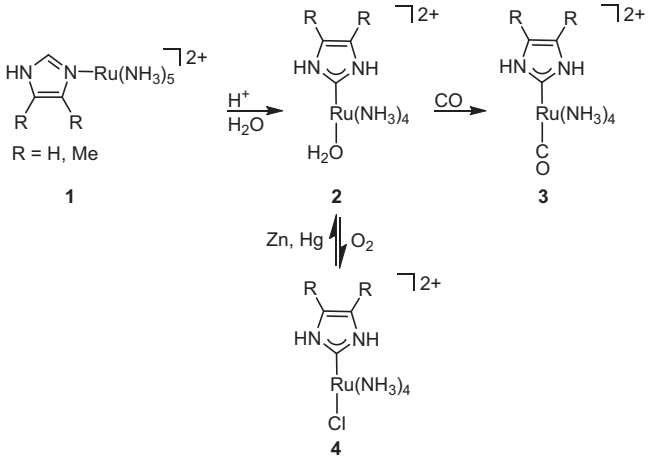


Fig. 1. Complexes **A**–**C** with NHC ligands featuring different substitution patterns and hydrogen bond formation observed for complexes bearing protic NHCs (**D** [17] and **E** [18]).



Scheme 1. Acid-induced tautomerization of N-coordinated imidazoles to NHC ligands [19].

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