



Synthesis, coordination chemistry and reactivity of transition metal complexes supported by a chelating benzimidazolylidene carboxylate ligand



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ABSTRACT

To construct the framework for a chelating, anionic benzimidazole-based N-heterocyclic carbene (NHC) ligand (**1**[−]), N-(3,5-dimethylphenyl)benzimidazole was reacted with 2-bromoacetic acid to yield the corresponding benzimidazolium [1H₂][Br]. Double deprotonation followed by metallation of [1H₂][Br] with Ag₂O produced the Ag–NHC complex [Ag(**1**)]_n (**2**), which exhibited good solubility in organic solvents despite its multinuclear nature. Crystallographic analysis of **2** revealed a dodecametallic structure (*n* = 12) comprising mononuclear [Ag(**1**)] and dinuclear [Ag₂(**1**)₂] subunits, the latter of which featured close Ag···Ag contacts. Transmetalation of **1**[−] from Ag to Ru via the reaction of [RuCl(η⁶-cymene)(μ-Cl)]₂ with **2** afforded the Ru–NHC complex [RuCl(**1**)(η⁶-cymene)] (**3**), which demonstrated catalytic activity for transfer hydrogenation of C=O, C=N and C=C bonds using isopropanol as the H₂ source.

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1. Introduction

N-heterocyclic carbenes (NHCs) have served as ligands for transition metals for nearly 50 years, beginning with the imidazolylidene-supported mercury(II) and chromium(0) complexes reported by Wanzlick [1] and Öfele [2], respectively, in 1968 (Fig. 1). Early NHCs such as these did not feature bulky N-substituents, and Wanzlick had previously demonstrated that the free NHCs were unstable with respect to dimerization to their corresponding tetraaza alkenes [3]. In 1991, Arduengo prepared the first stable free NHC by using sterically-encumbering adamantyl N-substituents [4]. Since then, NHCs have become widely used ligands for transition metals in applications ranging from conventional catalysis [5] to solar energy harvesting [6] to hydrogen storage [7] to antitrypanosomal therapy [8].

Archetypal NHCs function as neutral (L-type) ligands and thus often substitute other L-type ligands in metal complexation reactions [9]. Typically, L-type ligands undergo exchange in an equilibrium process determined by their relative affinities for a metal center, where ligand exchange can be driven to completion, even if not thermodynamically favorable, by removing one equilibrium component from solution (e.g., precipitation, gas evolution, etc.).

For example, substitution of a carbonyl ligand in [Cr(CO)₆] by an NHC is exothermic, albeit not always by a sufficient amount to afford complete conversion, thus [Cr(CO)₅(NHC)] formation can be facilitated by the loss of CO(g) [10]. Similarly, the dithiolene complex [W(CO)₂(S₂C₂Me₂)₂] rapidly undergoes substitution by one NHC to afford [W(CO)(NHC)(S₂C₂Me₂)₂], but no additional substitution to give [W(NHC)₂(S₂C₂Me₂)₂] occurs even in the presence of excess NHC [11]. Conversely, the reaction of [Ni(CO)₄] with an NHC to produce [Ni(CO)₃(NHC)] or [Ni(CO)₂(NHC)] can be reversed with CO(g) at sufficiently high pressures [12]. In contrast, L-type ligand exchange with even a substitutionally inert anionic (X-type) ligand can be effected exogenously via silver(I) salts, Brønsted acids, Lewis acids or alkylating reagents. Isocyanide substitution of X-type ligands, for example, can be achieved via abstraction with AgPF₆ [13], CF₃SO₃H [14], B(C₆F₅)₃ [15], or [Et₃O][BF₄] [16], respectively, to create an open coordination site. However, X-type ligand abstraction with one of these classes of reagents may alter the overall charge of the complex and be accompanied by undesired changes in its properties (e.g., decreased organic solubility of ionic salts versus neutral compounds).

Alternatively, coordination of a negatively-charged NHC via X-type ligand abstraction can be achieved without the possible complications of altering the overall charge on the complex. If the anionic functional group can also bind to the metal, NHC coordination will be enhanced due to the chelate effect. To minimize protonation-induced dissociation by water or protic solvents,

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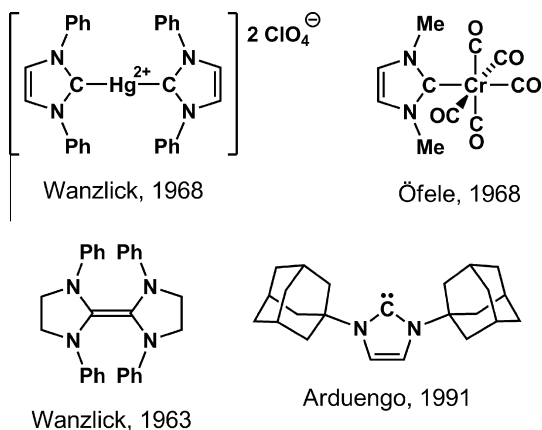


Fig. 1. Pioneering work with N-heterocyclic carbenes.

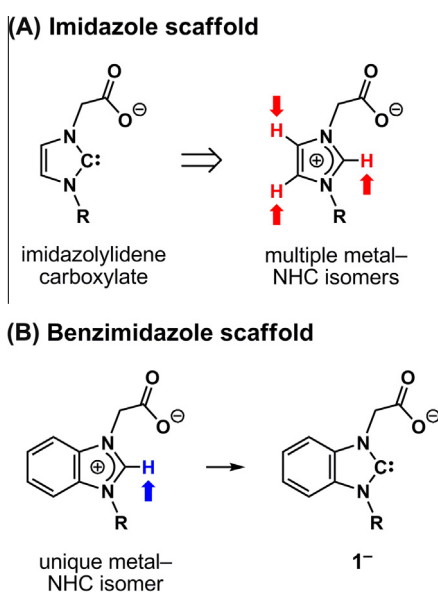


Fig. 2. Comparison of imidazolylidene and benzimidazolylidene carboxylate ligand scaffolds.

this anionic group should be weakly basic. Transition metal complexes supported by NHC ligands bearing carboxylate or sulfonate moieties are known, but relatively few feature the NHC and carboxylate [17] or sulfonate [18] both coordinated to the transition metal. Chelating imidazolylidene-based NHCs with acetate side chains (Fig. 2A), for example, have been shown to afford ruthenium and palladium complexes stable to air and atmospheric moisture. One possible complication with a chelating imidazolylidene scaffold is that multiple chemically-inequivalent protons in the imidazolium precursor could give rise to a mixture of multiple different metal–NHC regioisomers [19]. These “abnormal” NHC–metal complexes are typically only obtained following deprotonation of an imidazolium with a strong base (e.g. ^tBuLi), but Meyer has recently shown that a Pd(OAc) moiety was already coordinated to the ligand in an adjacent site sterically predisposed to remove that proton [20]. In contrast, a benzimidazolium will only be deprotonated at the 2-position and not afford such mixtures (Fig. 2B). We therefore sought to synthesize a benzimidazolylidene with a chelating carboxylate side-chain (**1**[−]), study its transition metal coordination chemistry and explore the reactivity of these complexes, the results of which are presented herein.

2. Experimental

2.1. Materials and methods

N-(3,5-dimethylphenyl)benzimidazole was prepared as previously described [21]. All other materials and solvents were of reagent quality and used as received. ¹H and ¹³C[¹H] NMR spectra were recorded using a Bruker 500 MHz spectrometer. Chemical shifts δ (in ppm) for ¹H and ¹³C NMR are referenced to SiMe₄ using the residual protio-solvent as an internal standard [22]. For ¹H NMR: CDCl₃, 7.26 ppm; DMSO-*d*₆, 2.50 ppm. For ¹³C NMR: CDCl₃, 77.16 ppm; DMSO-*d*₆, 39.52 ppm. Coupling constants (*J*) are expressed in hertz (Hz). Infrared spectra were recorded on a Thermo Nicolet IR200 spectrometer with 4 cm^{−1} resolution. Elemental analyses were performed at Atlantic Microlab, Inc. (Norcross, GA). All syntheses and purifications were performed under ambient conditions unless specified otherwise. Syntheses requiring an inert atmosphere were performed under an N₂ atmosphere using standard Schlenk or glovebox techniques. When required, solvents were dried and deoxygenated using an Innovative Technologies solvent purification system, and then stored over molecular sieves (3 Å) in a drybox.

2.2. Crystal structure data acquisition and structure determination

Single crystals of [1H₂][Br] and **3** were immersed in Paratone-N oil at room temperature and mounted on glass fibers using epoxy glue. To protect crystals of **2** from rapid desolvation, those crystals were transferred from the solvent into cold, viscous Paratone-N oil, mounted on a glass fiber, and immediately cooled to 200 K under a stream of cold nitrogen. Intensity data on all crystals were collected under nitrogen at 200 K with Mo K α radiation ($\lambda = 0.71073$ Å) on a Rigaku AFC8S diffractometer equipped with a Mercury CCD area detector and controlled using the CRYSTALCLEAR software package [23]. A crystal-to-detector distance of 27 mm was used for [1H₂][Br] and **3**, whereas the data collection for **2** required a crystal-to-detector distance of 42 mm accompanied by a detector swing of 12 degrees to resolve the diffraction profile and retain appropriate resolution limits. Data were corrected for absorption as well as Lorentz and polarization effects using the REQAB subroutine of CRYSTALCLEAR [24]. The structures were solved by direct methods and subsequently refined using the SHELXTL software package [25] and checked for higher symmetry using the PLATON program suite [26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions using a riding model and assigned thermal parameters equal to either 1.5 (methyl hydrogen atoms) or 1.2 (non-methyl hydrogen atoms) times the thermal parameters of the atoms to which they were attached. For **3**, a partially-occupied solvent molecule was identified from the difference electron density map and included in the refinement. In the case of **2**, several solvent molecules could be identified from the difference map, and other highly disordered solvent molecules were modeled using the SQUEEZE tool of PLATON (see footnote, Table S1). Crystal data, intensity collection and refinement parameters for [1H₂][Br], **2** and **3** are summarized in the Supporting information (Tables S1).

2.3. Syntheses

2.3.1. Synthesis of 2-(3-{3,5-dimethylphenyl}-benzimidazol-1-ium-1-yl)acetate hydrobromide [1H₂][Br]

2-Bromoacetic acid (947 mg, 6.82 mmol) and N-(3,5-dimethylphenyl)benzimidazole (1.50 g, 6.75 mmol) were dissolved with 20 mL of toluene in a heavy-walled flask equipped with a stir bar. The flask was then sealed and the clear, dark orange-brown

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