



Novel scorpionate-type triscarbene ligands and their silver and gold complexes

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ABSTRACT

New silver(I) carbene complexes were obtained starting from the *N*-heterocyclic carbene ligand precursors $\{[\text{HB}(\text{RImH})_3]\text{Br}_2\}$ (R = Bn, Mes and *t*-Bu) and $\{[\text{HC}(\text{MeImH})_3](\text{BF}_4)_3\}$, by treatment of the imidazolium salt with Ag_2O . Use of the tris-imidazolylborate precursors resulted in stable, well-characterized trimetallic complexes of general formula $\{\text{Ag}_3[\text{HB}(\text{RIm})_3]_2\}\text{Br}$, which were successfully employed as carbene transfer reagents in the synthesis of related gold(I) complexes by transmetalation. The silver complexes also proved to be active catalysts of the coupling of aryl iodides with terminal alkynes (the Sonogashira reaction), although related bimetallic silver complexes were found to exhibit enhanced reactivity.

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1. Introduction

An extremely useful and versatile class of ligands [1–3] is represented by *N*-heterocyclic carbenes (NHCs), first proposed by Wanzlick [4] and Öfele [5], and later isolated in the free state by Arduengo et al. [6]. Their chemical versatility not only implies a wide variety of structural diversity and coordination modes, but also a capability to form stable complexes with a large number of transition metals with different oxidation states.

Polydentate NHCs can provide new complexes with enhanced catalytic performances and higher stability [7–10]. Most of the poly-carbenes reported so far are neutral bidentate biscarbene ligands coordinated to transition metals such as Pd, Pt, Rh, Ru and Ir [10]. It is well recognized that chelating bis-NHCs are able to yield more stable metal complexes with interesting features that can provide fine tuning of topological properties such as steric hindrance, bite angles, chirality and fluxional behavior. In the preparation of chelating *N*-heterocyclic carbene complexes several methods have proved to be efficient, and these have been reviewed [1,2,7,8,11–15].

Whereas there are many studies describing the coordination of *pincer N*-heterocyclic carbene ligands [10] and a number of uncharged and flexible nitrogen-anchored poly-NHC ligands are

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known [8,16–26], the use of *anionic* NHCs is still scarce [27]. Recently, Siebert et al. [28,29] described the synthesis and characterization of the first anionic monocarbene imidazol-2-ylidenes, the 3-borane-1-alkylimidazol-2-ylidenes anions and their metal complexes [30]. The synthesis of monoanionic chelating dicarbene bis(imidazolylidene)borates, and their use as ligands in various homoleptic and heteroleptic palladium(II), platinum(II), gold(I) [31] and nickel(II) [32] complexes has been recently described. The first chelating triscarbene ligand with the topology of Trofimenko's tris(pyrazolyl)borate, tris(3-methylimidazolin-2-ylidene-1-yl)borate, has been introduced in 1995 by Fehlhammer and co-workers [33], together with its hexacarbene iron(III) and cobalt(III) complexes [34,35]; very recently, this ligand was found to form a trinuclear complex with copper(I) centers, which proved to be an active catalyst for C–N and C–O coupling reactions [36]. In 2005 Smith et al. [37] reported a new synthetic route that allows for the incorporation of bulkier substituents, and showed that a bulky tripodal tris(carbene)borate ligand, prepared from 1-*tert*-butylimidazole, is cleanly transferred to iron(II) by a magnesium reagent. Successively they have modified the tris(carbene)borate class of ligands to incorporate a phenyl group on the boron atom [38]. These bulky tris(carbene)phenylborate ligands are able to stabilize coordinatively unsaturated cobalt(II) centers [38] and to form cobalt(III) [39] and high-valent iron imido complexes [40]. More recently, the same authors have prepared and characterized the manganese(I) tricarbonyl complex of tris(carbene)phenylborate ligands prepared from 1-methylimidazole [41].

The design of NHCs with a tripod coordination is important because in octahedral complexes the *fac*-tricoordinate geometry should stabilise the metal complex, especially when the stability of the ligand–metal bond is high, while leaving three additional coordination sites for labile coligands, easily displaceable to yield mutually *cis* coordination sites available for catalytic activity. Metal complexes of these ligands should have quite different electronic properties from those of the tris(pyrazolyl)borates due to the very strong σ -donor nature of *N*-heterocyclic carbenes.

In this paper, we have synthesized new tripodal *N*-heterocyclic carbene ligand precursors and the related silver(I) carbene complexes (Schemes 1–3). The transmetalation from a silver(I) NHC complex, synthesized by treatment of the imidazolium salt with Ag_2O , is a useful coordination method in the preparation of chelating *N*-heterocyclic carbene complexes [42]; in most cases this procedure can be carried out under aerobic conditions, and the process has been successful with a variety of metals such as Au, Cu, Ni, Pd, Pt, Rh, Ir and Ru [43–45]. In the present paper we have used a similar approach to synthesize various gold(I) complexes by transmetalation reactions of the starting silver(I) derivatives. Finally, a preliminary screening of the catalytic potential of these and other silver(I) NHC complexes in C–C coupling reactions has been carried out.

2. Experimental

2.1. Material and methods

All syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C, H, N, S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. IR spectra were recorded from 4000 to 400 cm^{-1} with a Perkin–Elmer FT-IR Spectrum100. IR annotations used: br = broad, m = medium, mbr = medium broad, s = strong, sh = shoulder, w = weak. ^1H and ^{13}C NMR spectra were recorded on an Oxford-400 Varian spectrometer (400.4 MHz for ^1H and 100.1 MHz for ^{13}C). Chemical shifts for ^1H NMR spectra are relative to internal Me_4Si . ^{13}C NMR spectra were run with ^1H decoupling, and the chemical shifts are reported in ppm versus Me_4Si . NMR annotations used: br = broad, d = doublet, dd = double doublet, m = multiplet, s = singlet, sbr = broad singlet. Electrospray mass spectra (ESI-MS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using an acetone mobile phase. The compounds were added to the reagent grade methanol to give solutions of approximate concentration 0.1 mM.

These solutions were injected (1 μl) into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 $\mu\text{l min}^{-1}$, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 V and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all major species in this ESI-MS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the ISOPRO 3.0 computer program.

2.2. Synthesis

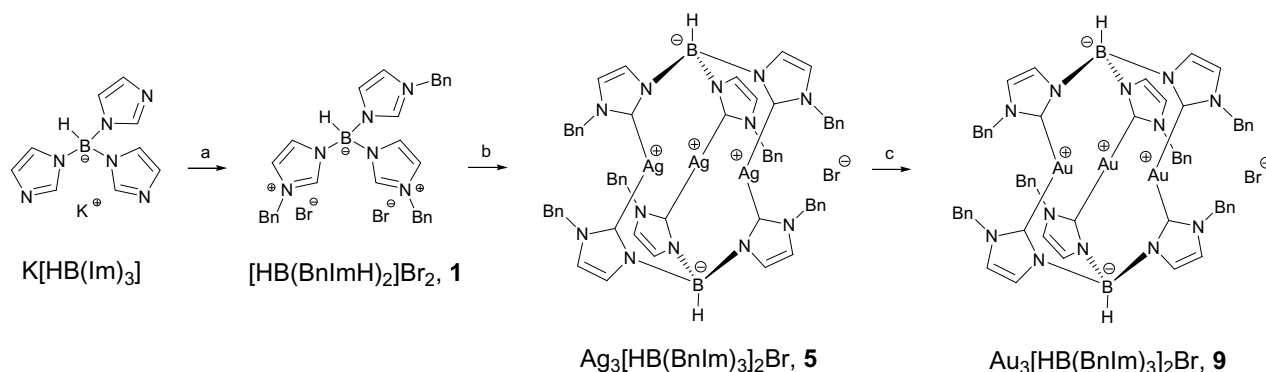
All reagents were purchased from Aldrich and used without further purification. The ligand $\text{K}[\text{HB}(\text{Im})_3]$ [46] was prepared in accordance with the literature method. The 1-mesitylimidazole [47] and the 1-*tert*-butylimidazole [48] were synthesized in accordance with the literature methods and purified by vacuum distillation. The imidazolium salt $\{[\text{HB}(t\text{-BulmH})_3]\text{Br}_2\}$ (**3**) was prepared modifying the synthetic procedure previously reported by Smith et al. [37]. Complexes $\{\text{Ag}_2[\text{CH}_2(\text{Melm})_2]_2(\text{PF}_6)_2\}$ (**12**) and $\{\text{Ag}_2[\text{CH}_2(n\text{-Bulm})_2]_2(\text{PF}_6)_2\}$ (**13**) were prepared following a literature procedure [49].

2.2.1. $\{[\text{HB}(\text{BnlmH})_3]\text{Br}_2\}$ (**1**)

Benzylbromide (4.395 g, 25.7 mmol) was added to a chloroform solution (50 mL) of $\text{K}[\text{HB}(\text{Im})_3]$ (2.000 g, 7.9 mmol). The reaction mixture was stirred at room temperature for 24 h to give a light yellow solution and a white precipitate. The salt was removed by filtration and the volatiles were removed *in vacuo* to afford a light yellow oil. The oil was dissolved in a minimum amount of CH_2Cl_2 (10 mL) and diethyl ether was added to give a white solid that was collected by filtration, washed with diethyl ether and dried at reduced pressure. Yield 85%. ^1H NMR (CD_3OD , 293 K): δ 5.44 (s, 6H, CH_2), 7.40–7.44 (m, 15H, CH), 7.54 (d, 3H, 4-CH or 5-CH), 7.62 (d, 3H, 4-CH or 5-CH), 9.02 (s, 3H, 2-CH). ^{13}C NMR (CD_3OD , 293 K): δ 54.03 (CH_2), 125.02, 125.45 (4-CH and 5-CH), 129.81, 130.43, 130.53, 135.54 (C_6H_5), 140.52 (2-CH). IR (cm^{-1}): 3103w, 3038m (CH), 2525m (BH), 1553m (C = C + C=N). ESI-MS (major positive-ions, CH_3OH), m/z (%): 243 (100) $[\text{HB}(\text{BnlmH})_3]^{+++}$, 566 (40) $[\text{HB}(\text{BnlmH})_3]\text{Br}^+$. ESI-MS (major negative-ions, CH_3OH), m/z (%): 726 (100) $[\text{HB}(\text{BnlmH})_3]\text{Br}_3^-$. Anal. Calc. for $\text{C}_{30}\text{H}_{31}\text{BBr}_2\text{N}_6$: C, 55.76; H, 4.84; N, 13.00. Found: C, 55.59; H, 4.80; N, 12.88%.

2.2.2. $\{[\text{HB}(\text{MeslmH})_3]\text{Br}_2\}$ (**2**)

A 1 M dichloromethane solution of $(\text{CH}_3)_2\text{S}:\text{BHBr}_2$ (3.3 mL) was added to a dichloromethane solution (40 mL) of mesitylimidazole (2.000 g, 10.7 mmol). The reaction mixture was stirred at reflux for 24 h, then it was cooled to room temperature and the volatiles



Scheme 1. Preparation of **1**, **5** and **9**. Reaction conditions: (a) room temperature, benzylbromide, CHCl_3 ; (b) room temperature, Ag_2O , CH_2Cl_2 ; (c) room temperature, $\text{Au}(\text{SMe}_2)\text{Cl}$, CH_2Cl_2 .

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