



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

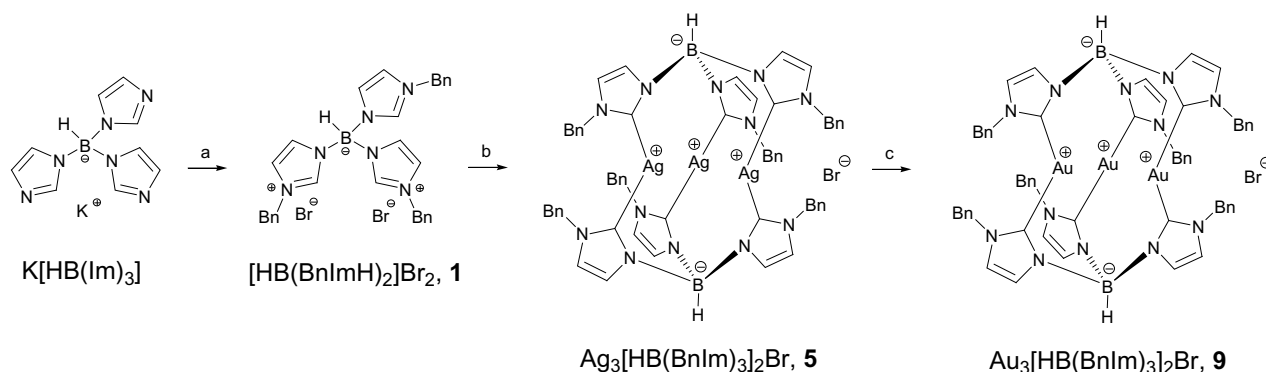
All reagents were purchased from Aldrich and used without further purification. The ligand $\text{K}[\text{HB}(\text{Im})_3]$ [46] was prepared in accordance with the literature method. The 1-mesitylimidazole [47] and the 1-*tert*-butylimidazole [48] were synthesized in accordance with the literature 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**)

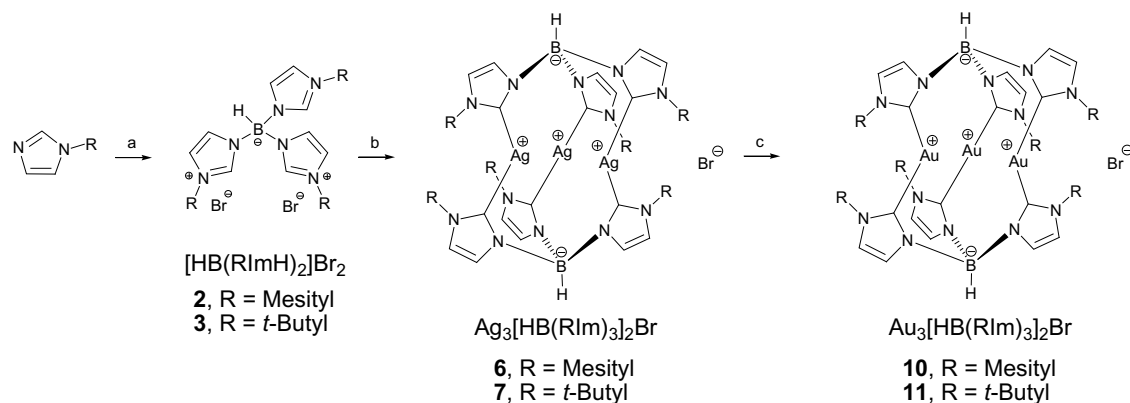
Benzylbromide (4.395 g, 25.7 mmol) was added to a chloroform solution (50 mL) of $\text{K}[\text{HB}(\text{Im})_3]$ (2.000 g, 7.9 mmol). The reaction mixture was stirred at room temperature for 24 h to give a light yellow solution and a white precipitate. The salt was removed by filtration and the volatiles 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**)

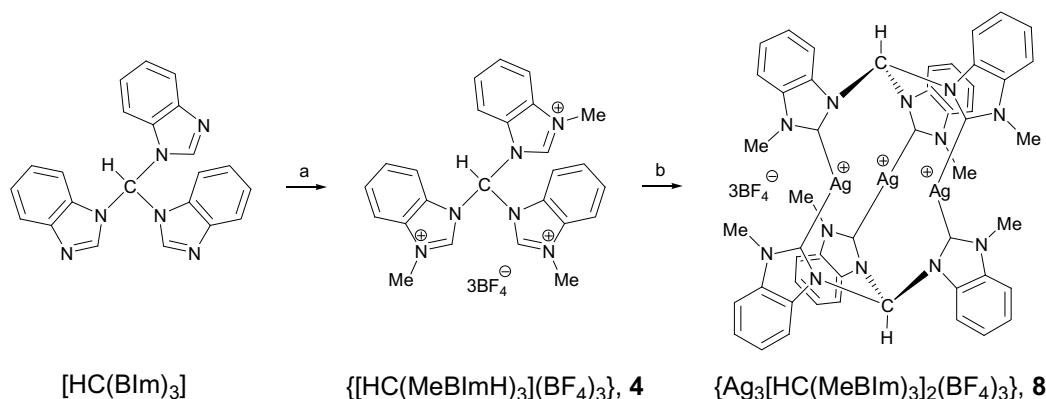
A 1 M dichloromethane solution of $(\text{CH}_3)_2\text{S}:\text{BHBr}_2$ (3.3 mL) was added to a dichloromethane solution (40 mL) of mesitylimidazole (2.000 g, 10.7 mmol). The reaction mixture was stirred at reflux for 24 h, then it was cooled to room temperature and the volatiles



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 .



Scheme 2. Preparation of **2**, **3**, **6**, **7**, **10** and **11**. Reaction conditions: (a) reflux, $(\text{CH}_3)_2\text{S}:\text{BHBr}_2$, CH_2Cl_2 ; (b) room temp, Ag_2O , CH_2Cl_2 ; (c) room temperature, $\text{Au}(\text{SMe}_2)\text{Cl}$, CH_2Cl_2 .



Scheme 3. Preparation of **4** and **8**. Reaction conditions: (a) room temp, $(\text{Me}_3\text{O})(\text{BF}_4)$, CH_2Cl_2 ; (b) room temp, Ag_2O , $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$.

were removed *in vacuo* to afford a brown hygroscopic solid. The solid was purified by re-crystallization from dichloromethane/diethyl ether (1/2), and dried at reduced pressure to give derivative **2** in 82% yield. ^1H NMR (CDCl_3 , 293 K): δ 2.05 (s, 18H, CH_3), 2.33 (s, 9H, CH_3), 6.99 (s, 6H, CH), 7.18 (s, 3H, 4-CH or 5-CH), 8.98 (s, 3H, 4-CH or 5-CH), 9.90 (s, 3H, 2-CH). ^{13}C NMR (CDCl_3 , 293 K): δ 17.75, 21.21 (CH_3), 120.86, 122.66, 124.45, 126.07, 129.96, 134.44, 140.83 (CH). IR (cm^{-1}): 3020w (CH), 2512w (BH), 1532s (C=C + C=N). ESI-MS (major positive-ions, CH_3OH), m/z (%): 285 (100) $[\text{HB}(\text{MesImH})_3]^{++}$, 650 (30) $[\{\text{HB}(\text{MesImH})_3\}\text{Br}]^+$. ESI-MS (major negative-ions, CH_3OH), m/z (%): 80 (100) $[\text{Br}]^-$, 810 (30) $[\{\text{HB}(\text{MesImH})_3\}\text{Br}_3]^-$. Anal. Calc. for $\text{C}_{36}\text{H}_{43}\text{BBr}_2\text{N}_6$: C, 59.20; H, 5.93; N, 11.51. Found: C, 59.07; H, 5.99; N, 11.29%.

2.2.3. $[\text{HB}(t\text{-BulmH})_3]\text{Br}_2$ (**3**)

A 1 M dichloromethane solution of $(\text{CH}_3)_2\text{S}:\text{BHBr}_2$ (2.9 mL) was added to a dichloromethane solution (40 mL) of 1-*tert*-butylimidazole (1.118 g, 9.0 mmol). The reaction mixture was stirred at reflux for 24 h, then it was cooled to room temperature and the volatiles were removed *in vacuo* to afford a white hygroscopic solid. The solid was purified by re-crystallization from dichloromethane/diethyl ether (1/2), and dried at reduced pressure to give derivative **3** in 78% yield. ^1H NMR (CDCl_3 , 293 K): δ 1.71 (s, 27H, CH_3), 7.32 (d, 3H, 4-CH or 5-CH), 8.42 (d, 3H, 4-CH or 5-CH), 9.75 (s, 3H, 2-CH). ^1H NMR (DMSO, 293 K): δ 1.58 (s, 27H, CH_3), 7.74 (d, 3H, 4-CH or 5-CH), 8.01 (d, 3H, 4-CH or 5-CH), 9.09 (s, 3H, 2-CH). ^{13}C NMR (DMSO, 293 K): δ 29.89 (CH_3), 59.68 ($\text{C}(\text{CH}_3)_3$), 122.01, 124.22, 137.61 (CH). IR (cm^{-1}): 3100sh, 3065w (CH), 2476w (BH), 1534m (C=C + C=N). ESI-MS (major positive-ions, CH_3OH), m/z (%): 192 (100) $[\text{HB}(t\text{-BulmH})_3]^{++}$, 464 (60) $[\{\text{HB}(t\text{-$

$\text{BulmH})_3\}\text{Br}]^+$. ESI-MS (major negative-ions, CH_3OH), m/z (%): 624 (100) $[\{\text{HB}(t\text{-BulmH})_3\}\text{Br}_3]^-$. Anal. Calc. for $\text{C}_{21}\text{H}_{37}\text{BBr}_2\text{N}_6$: C, 46.35; H, 6.85; N, 15.44. Found: C, 46.17; H, 6.83; N, 15.31%.

2.2.4. $[\text{HC}(\text{MeBImH})_3](\text{BF}_4)_3$ (**4**)

A solution of 1,1,1-tris(benzimidazol-1-yl)methane [50] (1.3 g, 3.6 mmol) in dichloromethane (15 mL) was added in small portions to a dichloromethane suspension (20 mL) of $(\text{Me}_3\text{O})(\text{BF}_4)$ (1.90 g, 12.8 mmol). The reaction mixture was stirred at room temperature for 24 h to give a light yellow solution and a white precipitate. The product was filtered and recrystallized from a mixture MeOH/water 95/5. Yield 50%. ^1H NMR (DMSO, 293 K): δ 4.14 (s, 9H, CH_3), 7.50–8.50 (m, 12H, CH_{BIm}), 10.08 (s, 3H, 2-CH), 10.65 (s, 1H, CH). ^{13}C NMR (DMSO, 293 K): δ 34.49 (CH_3), 73.19, 113.92, 114.64, 128.24, 128.37, 129.06, 132.35 (CH), 143.45 (2-CH). IR (cm^{-1}): 3094m (CH), 1618w, 1579m, 1460m, 1337m, 1259m, 1220m, 1034br, 753s. Anal. Calc. for $\text{C}_{25}\text{H}_{25}\text{B}_3\text{F}_{12}\text{N}_6$: C, 44.80; H, 3.73; N, 12.53. Found: C, 42.60; H, 3.39; N, 11.75%.

2.2.5. $\{\text{Ag}_3[\text{HB}(\text{Bnlm})_3]_2\text{Br}\}$ (**5**)

Ag_2O (2.700 g, 11.6 mmol) was added to a dichloromethane solution (50 mL) of $[\text{HB}(\text{BnlmH})_3]\text{Br}_2$ (5.000 g, 7.7 mmol). The reaction mixture was stirred at room temperature for 12 h. The resulting suspension was filtered through Celite and the solution was concentrated under vacuum and treated with diethyl ether (100 mL) to precipitate a microcrystalline white solid. It was filtered off, washed with diethyl ether and dried at reduced pressure. Yield 60%. M.p. 183–185 °C. ^1H NMR (CD_3OD , 293 K): δ 5.41 (s, 12H, CH_2), 7.02–7.33 (m, 30H, CH), 7.51 (d, 6H, 4-CH or 5-CH), 7.66 (d, 6H, 4-CH or 5-CH). ^1H NMR (DMSO, 293 K): δ 5.26 (s,

12H, CH₂), 7.00–7.40 (m, 30H, CH), 7.48 (d, 6H, 4-CH or 5-CH), 7.98 (d, 6H, 4-CH or 5-CH). ¹³C NMR (DMSO, 293 K): δ 56.71 (CH₂), 121.14, 121.57 (4-CH and 5-CH), 128.38, 129.07, 129.88, 138.92 (CH), 183.07 (dd, ¹J(C–¹⁰⁹Ag) = 202 Hz, ¹J(C–¹⁰⁷Ag) = 176 Hz, Ag–C). IR (cm⁻¹): 3105w, 3065w, 3029w (CH), 2434m, 2413m (BH), 1556m (C=C + C=N), 669w, 661w 636br, 616sh, 573m, 460m, 431br. ESI-MS (major positive-ions, CH₃OH), *m/z* (%): 1290 (100) [Ag₃{HB(Bnlm)₃}₂]⁺. Anal. Calc. for C₆₀H₅₆Ag₃B₂BrN₁₂: C, 52.59; H, 4.12; N, 12.27. Found: C, 52.84; H, 4.01; N, 12.00%.

The mother liquor was evaporated at reduced pressure; the resulting residue was treated with MeOH (0.5 mL), CH₂Cl₂ (0.5 mL) and diethyl ether (5 mL) to give an off-white solid, which was filtered and dried at reduced pressure. This second crop of isolated solid was identified as the bis-carbene byproduct {[Ag(Bnlm)₂AgBr₂]. Yield 30%. ¹H NMR (DMSO, 293 K): δ 5.30 (s, 8H, CH₂), 7.20–7.34 (m, 20H, CH), 7.54 (s, 4H, 4-CH and 5-CH). ¹³C NMR (DMSO, 293 K): δ 54.25 (CH₂), 122.56 (4-CH and 5-CH), 127.54, 128.00, 128.77, 137.26 (CH), carbene carbon not detected. ESI-MS (major positive-ions, CH₃OH), *m/z* (%): 604 (100) [Ag(Bnlm)₂]⁺. ESI-MS (major negative-ions, CH₃OH), *m/z* (%): 268 (100) [AgBr₂]⁻.

2.2.6. {Ag₃[HB(MesIm)₃]₂Br} (6)

Ag₂O (0.695 g, 3.0 mmol) was added to a dichloromethane solution (50 mL) of {[HB(MesImH)₃Br]₂} (1.462 g, 2.0 mmol). The reaction mixture was stirred at room temperature for 12 h. The resulting suspension was filtered through Celite and volatiles were removed *in vacuo* to afford a light brown hygroscopic solid. The solid was purified by re-crystallization from chloroform/diethyl ether (1/2), and dried at reduced pressure to give the colourless derivative **6** in 66% yield. M.p. 169–171 °C (dec.). ¹H NMR (CDCl₃, 293 K): δ 1.65 (s, 36H, CH₃), 2.41 (s, 18H, CH₃), 6.77 (s, 12H, CH), 6.90 (s, 6H, 4-CH or 5-CH), 7.46 (s, 6H, 4-CH or 5-CH). ¹³C NMR (DMSO, 293 K): δ 17.52, 21.48 (CH₃), 122.67, 123.21, 129.04, 134.73, 136.70, 137.85 (CH), 188.67 (dd, ¹J(C–¹⁰⁹Ag) = 207 Hz, ¹J(C–¹⁰⁷Ag) = 180 Hz, Ag–C). IR (cm⁻¹): 3118w (CH), 2457m (BH), 1556m (C=C + C=N), 649br, 635br, 582m, 560w, 539m, 527w. ESI-MS (major positive-ions, CH₃OH), *m/z* (%): 1459 (100) [Ag₃{HB(MesIm)₃}₂]⁺. Anal. Calc. for C₇₂H₈₀Ag₃B₂BrN₁₂: C, 56.20; H, 5.24; N, 10.92. Found: C, 56.02; H, 5.21; N, 10.75%.

2.2.7. {Ag₃[HB(*t*-Bulm)₃]₂Br} (7)

Ag₂O (0.695 g, 3.0 mmol) was added to a dichloromethane solution (50 mL) of {[HB(*t*-BulmH)₃Br]₂} (1.088 g, 2.0 mmol). The reaction mixture was stirred at room temperature for 12 h. The resulting suspension was filtered through Celite and volatiles were removed *in vacuo* to afford a light brown hygroscopic solid. The solid was purified by re-crystallization from chloroform/diethyl ether (1/2), and dried at reduced pressure to give the colourless derivative **7** in 60% yield. M.p. 175 °C (dec.). ¹H NMR (DMSO, 293 K): δ 1.63 (s, 54H, CH₃), 7.41 (s, 6H, 4-CH or 5-CH), 7.48 (s, 6H, 4-CH or 5-CH). ¹³C NMR (DMSO, 293 K): δ 31.50 (CH₃), 56.21 (C(CH₃)₃), 119.31, 120.52 (4-CH and 5-CH), 182.45 (dd, ¹J(C–¹⁰⁹Ag) = 197 Hz, ¹J(C–¹⁰⁷Ag) = 180 Hz, Ag–C). IR (cm⁻¹): 3131w (CH), 2456m (BH), 1533m (C=C + C=N), 727s, 684w. ESI-MS (major positive-ions, CH₃OH), *m/z* (%): 1086 (100) [Ag₃{HB(*t*-Bulm)₃}₂]⁺. Anal. Calc. for C₄₂H₆₈Ag₃B₂BrN₁₂: C, 43.26; H, 5.88; N, 14.41. Found: C, 43.02; H, 5.68; N, 14.20%.

2.2.8. {Ag₃[HC(MeBlm)₃]₂(BF₄)₃} (8)

Ag₂O (0.12 g, 0.5 mmol) was added to a dichloromethane/acetonitrile solution (7 mL/3 mL) of {[HC(MeBlmH)₃](BF₄)₃} (0.21 g, 0.31 mmol). The reaction mixture was stirred at room temperature for 5 h. The resulting suspension was filtered through Celite and volatiles were removed *in vacuo* to afford a off-white hygroscopic solid. Yield 30%. ¹H NMR (DMSO, 293 K): δ 3.91 (s, 9H, CH₃),

7.50–8.05 (m, 12H, CH_{BIm}), 9.83 (s, 1H, CH). The instability of the compound in solution prevents the obtainment of a ¹³C NMR spectra.

2.2.9. {Au₃[HB(Bnlm)₃]₂Br} (9)

A dichloromethane solution (30 mL) of Au(SMe₂)Cl (0.20 g, 0.68 mmol) was added dropwise to a dichloromethane solution of {Ag₃[HB(Bnlm)₃]₂Br} (0.31 g, 0.23 mmol). A white precipitate (AgBr) formed upon addition of the gold(I) salt. The mixture was stirred at room temperature for 2 h, and then filtered through Celite. The filtrate was concentrated under vacuum and treated with diethyl ether (20 mL) to give a white crystalline powder. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield 77%. M.p. 166–168 °C (dec.). ¹H NMR (DMSO, 293 K): δ 5.37 (s, 12H, CH₂), 7.15–7.30 (m, 30H, CH), 7.51 (d, 6H, 4-CH or 5-CH), 8.05 (d, 6H, 4-CH or 5-CH). ¹³C NMR (DMSO, 293 K): δ 52.98 (CH₂), 122.15, 122.73 (4-CH and 5-CH), 127.40, 127.76, 128.60, 137.03 (CH), 188.68 (Au–C). IR (cm⁻¹): 3115w, 3068w (CH), 2417mbr (BH), 1526m (C=C + C=N), 637br, 577m, 460br, 325w. ESI-MS (major positive-ions, CH₃OH), *m/z* (%): 1558 (100) [Au₃{HB(Bnlm)₃}₂]⁺. Anal. Calc. for C₆₀H₅₆Au₃B₂BrN₁₂: C, 44.01; H, 3.45; N, 10.26. Found: C, 43.84; H, 3.29; N, 10.07%.

2.2.10. {Au₃[HB(MesIm)₃]₂Br} (10)

A dichloromethane solution (50 mL) of Au(SMe₂)Cl (0.20 g, 0.68 mmol) was added dropwise to a dichloromethane solution of {Ag₃[HB(MesIm)₃]₂Br} (0.35 g, 0.23 mmol). A white precipitate (AgCl) formed upon addition of the gold(I) salt. The mixture was stirred at room temperature for 2 h, and then filtered through Celite. The filtrate was concentrated under vacuum and treated with diethyl ether (20 mL) to give a light brown powder. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum to give the colourless derivative **10**. Yield 71%. M.p. 192–194 °C. ¹H NMR (CDCl₃, 293 K): δ 1.65 (sbr, 36H, CH₃), 2.42 (sbr, 18H, CH₃), 6.80 (sbr, 12H, CH), 6.90 (br, 6H, 4-CH or 5-CH), 7.47 (br, 6H, 4-CH or 5-CH). ¹³C NMR (DMSO, 293 K): δ 16.80, 20.79 (CH₃), 122.42, 124.03, 128.29, 133.85, 135.98, 137.17 (CH), 190.44 (Au–C). IR (cm⁻¹): 3120w (CH), 2470m (BH), 1551br (C=C + C=N), 638m, 629w, 617m, 551m, 541w. ESI-MS (major positive-ions, CH₃OH), *m/z* (%): 1726 (100) [Au₃{HB(MesIm)₃}₂]⁺. Anal. Calc. for C₇₂H₈₀Au₃B₂BrN₁₂: C, 47.89; H, 4.47; N, 9.31. Found: C, 48.01; H, 4.54; N, 9.13%.

2.2.11. {Au₃[HB(*t*-Bulm)₃]₂Br} (11)

A dichloromethane solution (50 mL) of Au(SMe₂)Cl (0.20 g, 0.68 mmol) was added dropwise to a dichloromethane solution of {Ag₃[HB(*t*-Bulm)₃]₂Br} (0.27 g, 0.23 mmol). A white precipitate (AgCl) formed upon addition of the gold(I) salt. The mixture was stirred at room temperature for 2 h, and then filtered through Celite. The filtrate was concentrated under vacuum and treated with diethyl ether (20 mL) to give a light brown powder. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum to give the colourless derivative **11**. Yield 71%. M.p. 236 °C dec. ¹H NMR (CDCl₃, 293 K): δ 1.82 (s, 54H, CH₃), 7.02 (d, 6H, 4-CH or 5-CH), 7.16 (s, 6H, 4-CH or 5-CH). ¹³C NMR (DMSO, 293 K): δ 31.86 (CH₃), 57.38 (C(CH₃)₃), 118.42, 129.72 (4-CH and 5-CH), 187.39 (Au–C). IR (cm⁻¹): 3137w (CH), 2466br (BH), 1558m, 1532m (C=C + C=N). ESI-MS (major positive-ions, CH₃OH), *m/z* (%): 1353 (100) [Au₃{HB(*t*-Bulm)₃}₂]⁺. Anal. Calc. for C₄₂H₆₈Au₃B₂BrN₁₂: C, 41.42; H, 4.59; N, 10.08. Found: C, 41.25; H, 4.32; N, 10.25%.

2.3. Catalysis

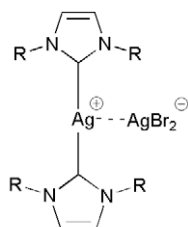
General procedure for the catalytic tests. An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged

with aryl halide (0.25 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol, 1.2 equiv.) and 0.008 mmol catalyst (10 mol% silver). The tube was closed with a rubber septum, evacuated and filled with argon. Phenylacetylene (33 μ L, 0.3 mmol, 1.2 equiv.) and solvent (2 mL) were subsequently injected, and the tube was placed in an oil bath preheated at 110 °C. The reaction mixture was stirred at 110 °C for 24 h, after which it was cooled to room temperature and diluted with 5 mL dichloromethane. The resulting suspension was filtered and the solvent was removed under vacuum to give a brown solid. The reaction yield was determined by ¹H NMR spectroscopy.

3. Results and discussion

3.1. Syntheses

The *N*-heterocyclic carbene ligand precursor salt, {[HB(BnImH)₃]Br₂} (1), has been synthesized in chloroform solution via alkylation with benzyl bromide of the starting compound potassium tris-(imidazol-1-yl)borate K[HB(Im)₃] (Scheme 1). The bulky {[HB(MesImH)₃]Br₂} (2), and tris(*tert*-butyl-imidazol-3-ium-1-yl)hydroborate, {[HB(*t*-BulmH)₃]Br₂} (3), were synthesized by a similar synthetic path to that reported for the preparation of ionic liquid imidazole-based “boronium” ions [51]. Three equivalents of 1-*tert*-butylimidazole or 1-mesitylimidazole were heated in refluxing dichloromethane with (CH₃)₂S:BHBr₂ (Scheme 2). Compounds 1–3 are hygroscopic solids; they are soluble in methanol, DMSO and chlorinated solvents and insoluble in water, diethyl ether and *n*-hexane. The related compound 4, {[HC(MeBImH)₃](BF₄)₃}, was synthesized by simple methylation of 1,1,1-tris(benzimidazol-1-yl)methane with Meerwein’s salt (Me₃O)(BF₄) (Scheme 3). Compound 4 possesses a CH bridge and is therefore precursor for a neutral triscarbene ligand. The silver(I) complexes {Ag₃[HB(BnIm)₃]₂Br} (5) (Scheme 1), {Ag₃[HB(MesIm)₃]₂Br} (6), and {Ag₃[HB(*t*-Bulm)₃]₂Br} (7) (Scheme 2), were prepared in dichloromethane solution via deprotonation of the imidazolium salts 1–3 with Ag₂O. The complexes were obtained analytically pure in good yields. Remarkably, during the preparation of complex 5 we were able to isolate and identify a mononuclear NHC–silver(I) complex [52,53] with two *N,N*-dibenzylimidazolynylidene carbene ligands bearing AgBr₂[−] as counterion (Scheme 4) as byproduct of the reaction. Similar byproducts were detected also in the preparation of the other complexes by ESI-MS. We are currently investigating the mechanism by which such byproducts could form. Reaction of the benzimidazolium salt 4 with Ag₂O yields a white solid, identified as the tricationic, trinuclear silver(I) complex 8. Product 8 is, however, unstable, as indicated by the progressive darkening of the solid and by the fact that we were unable to obtain satisfactory elemental analyses, so that this behaviour prevents the study of the subsequent transfer reaction to gold. Owing to the tripodal nature of the uninegative carbene ligands, they likely give rise to metallacycles [(L)₂(μ-Ag)₃] (L = carbene ligand),



R = Benzyl, Mesityl or *t*-Butyl

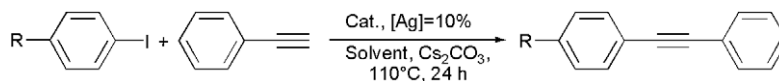
Scheme 4. Ag(I)-NHCs obtained from reaction media.

in which every silver atom is coordinated to two imidazol-2-ylidene rings, belonging to two different triscarbene units, each one therefore coordinating in η^1 fashion. The resulting complexes 5–7 are cationic, monomeric and organic-soluble. Complexes 5–7 have been used to synthesize the homoleptic gold(I) complexes 9–11 by transmetalation reaction with Au(SMe₂)Cl in dichloromethane solution. Similar types of complexes have been obtained with bidentate bis(carbene) ligands [54,55]. The formation of trinuclear complexes 5–11 reflects the tripodal nature of the *N*-heterocyclic carbene donor ligands and the tendency of group 11 metal ions to form linear, two-coordinate complexes [16,17,19,56].

3.2. Spectroscopy

The ligands 1–3 and the metal derivatives 5–11 have been characterized by analytical and spectral data. The infrared spectra carried out on the solid samples showed all the expected bands for the ligands and the silver(I) or gold(I) moieties: weak absorptions in the range 3020–3137 cm^{−1} are due to the azolyl ring C–H stretchings and medium to strong absorptions at 1526–1558 cm^{−1} are related to ring “breathing” vibrations. In the infrared spectra of tris(imidazolyl)borate ligands 1–3 the B–H stretching vibrations appear in the range 2476–2525 cm^{−1}. Interestingly, on going from the imidazolium salts 1–3 to the carbene complexes 5–7 and 9–11, a red shift of the ν (BH) feature is always observed.

The ¹H and ¹³C NMR data reflect significant changes in going from the imidazolium salts to the carbene complexes. In particular the ¹H NMR spectra of the complexes 5–11 showed the disappearance of the diagnostic 2-CH imidazolium resonances in the 1–4 ligands at 9.02, 9.90, 9.09 and 10.08 ppm, respectively. The formation of the silver(I) carbene complexes 5–7 was confirmed by the appearance of the 2-C resonance of the imidazol-2-ylidene as double doublets at 183.07, 188.67 and 182.45 ppm, respectively, due to coupling of 2-C with the two spin 1/2 isotopes of silver. The individual couplings to the two isotopes of silver were well resolved in the spectra (¹J(C–¹⁰⁹Ag) = 197–207 Hz, ¹J(C–¹⁰⁷Ag) = 176–180 Hz), and they are in the range of the values for ¹⁰⁷Ag and ¹⁰⁹Ag coupling constants found in similar silver(I) *N*-heterocyclic carbenes [44,52,53]. Unfortunately, the relative instability of complex 8 prevents the obtainment of a ¹³C NMR spectrum. In the ¹³C NMR spectra of the gold(I) complexes 9–11 the 2-C resonance of the imidazol-2-ylidene appeared as singlet in the range 187.39–190.44 ppm; the chemical shift value for the carbene carbons is in good agreement with the carbene carbon chemical shifts of similar dinuclear bis(carbene)gold species [31,54,55]. Mass spectra (ESI-MS) of all the new compounds have been recorded (Section 2). The general appearance of the molecular ions followed by characteristic fragmentations supports the structural assignments. The structure of the imidazolium salts 1–3 was confirmed by the presence of peaks at *m/z* 243, 285 and 192, due to the species [HB(RImH)₃]⁺⁺ in the positive ion mode electrospray ionization mass spectra, together with minor peaks at *m/z* 566, 650 and 464 due to the aggregates {[HB(RImH)₃]Br}⁺ (R = Bn, Mes and *t*-Bu). The negative ion mode electrospray ionization mass spectra of 1–3 were dominated by peaks due to the species {[HB(RImH)₃]Br₃}[−] (R = Bn, Mes and *t*-Bu). The structure of the silver(I) complexes 5–7 was confirmed by the presence in their positive-ion mass spectra of peaks at *m/z* 1290, 1459 and 1086 due to the trinuclear species [Ag₃{HB(RIm)₃]₂}⁺. Analogously the positive ion mode electrospray ionization mass spectra of the gold(I) compounds 9–11 were dominated by peaks due to the trinuclear species [Au₃{HB(RIm)₃]₂}⁺. No fragment ions were observed for the pure complexes, showing that the silver(I) and gold(I) complexes were stable under the conditions of the electrospray ionization and detection.



Scheme 5. General procedure for arylation of phenylacetylene.

3.3. Catalysis

Recently there has been a surge of interest in the application of silver salts and complexes as catalysts for fine chemical synthesis [57]. In particular, a recent report highlights the possibility to use such metal species as catalyst in the coupling of aryl halides with terminal alkynes (the Sonogashira reaction) [58]. This reaction is routinely performed using a palladium-based catalyst [59], but efficient palladium-free systems would obviously be much more interesting for economical reasons, related both to the higher cost of palladium as well as to the difficulties in removing the metal from the reaction product. Indeed, it is a common industrial practice to avoid, whenever possible, the use of Pd catalysts in the last steps of the synthesis of a complex molecule.

We set out to evaluate the potential of our silver(I) triscarbene complexes as catalysts for the reaction outlined in Scheme 5. The reaction conditions were chosen according to those found to be optimal in [59]. For comparison, we also included in the study the silver(I) dicarbene complexes **12** and **13** (Scheme 6), whose preparation has been previously reported in the literature [49]. Results of the catalytic screening of the various complexes are reported in Table 1.

In principle, two side reactions potentially affecting selectivity can occur in this system beside the Sonogashira reaction, namely homocoupling of the aryl halide or of the alkyne. Interestingly, it turned out that in the case of the polycarbene–silver complex catalysts the solvent has a decisive influence in determining the selectivity of the reaction. In fact, aryl halide homocoupling was

exclusively observed in DMSO, whereas use of *N,N*-dimethylformamide (DMF) as the reaction solvent yielded exclusively the Sonogashira product; the only exception to this behaviour was complex **8**, which in DMSO yielded equal amounts of the Sonogashira product and of the aryl halide homocoupling product. The reason for this unexpected reversal in selectivity are currently being investigated. The reaction yields were, however, quite low, even with the activated 4-iodoacetophenone substrate: best results were obtained with the dicarbene complex **12**, which beside 4-iodoacetophenone was also able to activate the less reactive 4-iodoanisole. For sake of comparison, simple AgI was reported to convert both substrates with >90% yield in the Sonogashira reaction with phenylacetylene under similar reaction conditions [58].

4. Conclusions

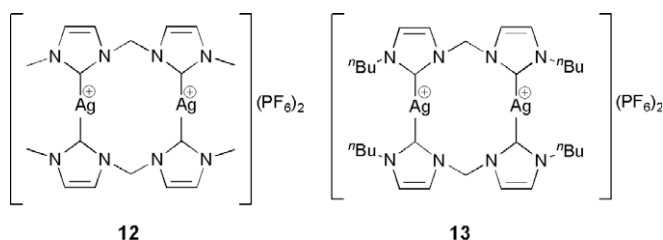
In this paper, we have synthesized novel silver(I) carbene complexes starting from the tripodal *N*-heterocyclic carbene ligand precursors {[HB(RImH)₃]Br₂} (R = Bn, Mes and *t*-Bu) and {[HC(Me-BImH)₃](BF₄)₃}. Use of the tris-imidazolylborate precursors resulted in stable, well-characterized trimetallic complexes of general formula {Ag₃[HB(RIm)₃]₂}Br, which were successfully employed as carbene transfer reagents in the synthesis of related gold(I) complexes by transmetalation reaction with Au(SMe₂)Cl. 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. The silver complexes proved to be active catalysts of the coupling of aryl iodides with terminal alkynes (the Sonogashira reaction), although bis(imidazolynylidene)methanes silver(I) dicarbene complexes were found to exhibit enhanced reactivity.

Acknowledgment

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Scheme 6. Bis(imidazolynylidene)methanes silver(I) dicarbene complexes employed as catalysts in this work.

Table 1
Catalytic results

Catalyst	Solvent	R	Yield (%) ^a	
			Sonogashira	Aryl halide homocoupling
5	DMF	CH ₃ CO	17	0
6	DMF	CH ₃ CO	0	0
6	DMSO	CH ₃ CO	0	35
7	DMF	CH ₃ CO	0	0
7	DMSO	CH ₃ CO	0	12
8	DMSO	CH ₃ CO	15	15
12	DMF	CH ₃ CO	71	0
12	DMSO	CH ₃ CO	0	33
12	DMF	CH ₃ O	24	0
13	DMF	CH ₃ CO	12	0

Reaction conditions: 0.25 mmol aryl halide, 0.3 mmol phenylacetylene, 0.3 mmol Cs₂CO₃, 0.008 mmol catalyst (10 mol% silver), 2 mL solvent, 110 °C, 24 h.

^a Yields determined by ¹H NMR.

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