Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 5710–5719
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Silver alkoxide and amino N-heterocyclic carbenes; syntheses and crystal structures

Ian S. Edworthy, Mark Rodden, Shaheed A. Mungur, Kate M. Davis, Alexander J. Blake, Claire Wilson, Martin Schröder, Polly L. Arnold *

School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, UK

Received 11 May 2005; accepted 6 July 2005
Available online 31 August 2005

Abstract

Silver(I) complexes of heterobidentate ligands that incorporate one or two N-heterocyclic carbene moieties coupled with an alcohol or amine group have been made by direct deprotonation of ligands of the form $[HOCR^1R^2CH_2(1\text{-}HC\{NCHCHNR\})][X]$, H_2L^1X ($X = Br$, I), $[H_2NR^1CHR^2CHR^2(1\text{-}HC\{NCHCHNR\})][Br]_2$ $H_3L^2X_2$ ($X = Cl$, Br), and $[H_2N\{CH_2CH_2(1\text{-}HC[NCHCHNMes])\}_2][X]_3$ $H_4L^3X_3$ ($X = Cl$, Br). Silver(I) oxide is sufficiently basic to deprotonate both the imidazolium and the alcohol functional groups of all but one of the L^1 ligand precursors, to afford rare examples of silver alkoxide complexes $[Ag(L^1)]$, stabilised by the soft donor carbene. Another complex of L^1 is characterised as the carbene alcohol adduct $[Ag(HL^1)_2I]$. The analogous reactions of silver(I) oxide with the amino imidazolium precursors afford silver aminocarbenes $[Ag(HL^2)Br]$ with the potentially bidentate L^2 ligand, and $[Ag(HL^3)X]$ ($X = Cl$, Br) with the potentially tridentate L^3 ligand. A single crystal X-ray diffraction study of the latter complex confirms that the neutral amine of the potentially tridentate L^3 ligand is unco-ordinated; instead the structure contains discrete chains of T-shaped silver bis(carbene) halide moieties that bridge to form a zig-zag 2-connected polymer. Protonolysis of two of the silver alkoxide and amino adducts, $[Ag(L^{1a})]$ and $[Ag(HL^{2a})Br]$, affords imidazolium complexes salts $[H_2L^{1a}][AgCl_2]$ and $[Ag(H_2L^{2a})Br][AgBr_2]$ that retain the Ag(I) centre as complex counterions. The single crystal X-ray structures of these salts have been determined and show the silver(I) cations are now incorporated into ladders or chains as silver(I) halo-anions, and a silver amine dative bond is present in the latter complex.

Keywords: Silver; Alkoxide; Carbene; N-ligand; Supramolecular; H-bonding

1. Introduction

N-heterocyclic carbenes (NHCs) are widely used as replacements for phosphines as supporting σ-bases in homogeneous late metal catalyst systems, and as rate accelerating additives in organic reactions catalysed by Lewis acidic metal cations [1–13]. Whilst almost all isolated NHCs are thermally stable indefinitely at room temperature, the strongly basic carbenes decompose in air, often rapidly. However, the silver(I) adducts, formed when an imidazolium precursor is deprotonated by basic silver(I) oxide or carbonate [14,15], are relatively air stable, yet sufficiently labile to be useful carbene transfer agents in solution [16–21]. We have been studying the chemistry of NHC ligands with an incorporated anionic functional group to allow us to isolate discrete carbene complexes of

---

* Corresponding author. Tel.: +44 0115 951 3437; fax: +44 0115 951 3563.
E-mail address: Polly.Arnold@Nottingham.ac.uk (P.L. Arnold).

doi:10.1016/j.jorganchem.2005.07.063

Lewis acidic transition metal cations and lanthanides. We have found that the Group 1 salts of both alkoxide, amide, and amino-functionalised NHC ligands can be readily synthesised to form kinetically inert complexes [4,22].

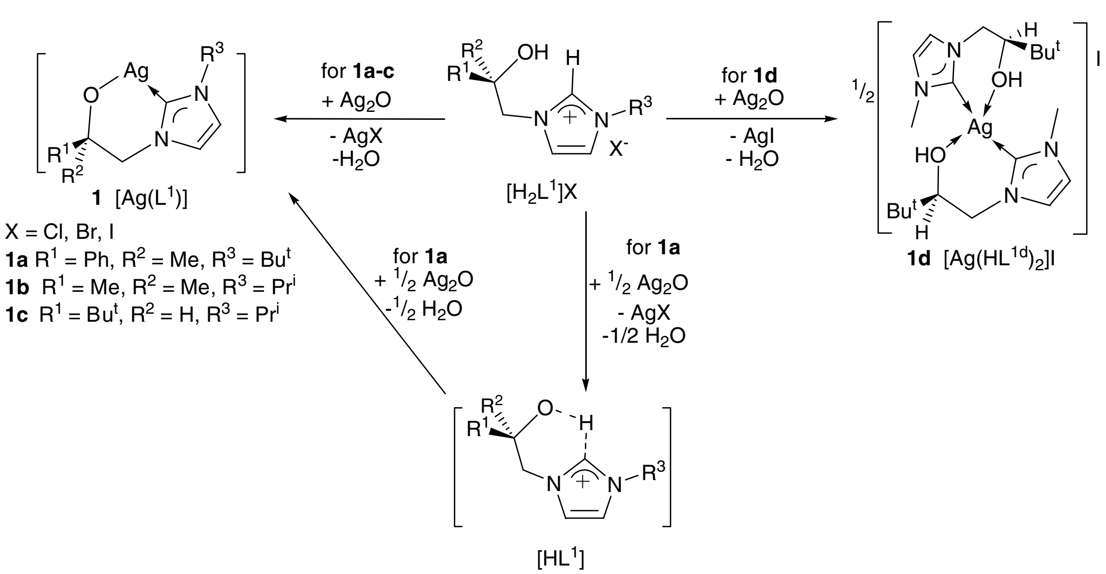
The synthesis of inert silver(I) carbene complexes that remain complexed in aqueous solvent systems, has recently been shown by Youngs et al. [23–25] to be an interesting new source of antimicrobial agents for medical applications. There are no simple silver alkoxides in the literature other than that of the tridentate alkoxy-dicarbene we have communicated, $[Ag\{OC(Ph)(CH_2\{1\text{-}C[NCHCHNBu^t])_2\}]_2$ [26]. Noting the potential for using such complexes as precursors for silver or silver oxide nanoparticles [27], homogeneous catalysts [11,28,29], and perceiving that silver complexes often show interesting structural [30,31], and optical properties [32,33], we have studied the complexation of silver(I) by bidentate alkoxide carbene ligands [4]. For comparison, we also report herein the results of studies on the complexation of silver(I) by bidentate amino-carbene ligands, and a new tridentate amino carbene, $[NH\{CH_2CH_2(C[NCHCHNMes])\}_2]$, the first with two NHC groups. A simple, one-pot route to the tridentate amino-carbene ligand is also described.

2. Results and discussion

2.1. Silver adducts of bidentate alkoxy carbene ligands

In turn, a sample of an alkoxide proligand – the non-halide containing zwitterionic $[HL^{1a}]$, or the imidazolium alcohol $[H_2L^{1b-d}]X$ (X = Cl, Br, or I) [4], was dissolved in dichloromethane, under a dinitrogen atmosphere, and a mixture of Ag_2O and activated 4 Å molecular sieves added. The black suspension was stirred for 12 h in the absence of light, during which time the suspended powder became a pale grey. The reaction mixture was filtered, and the volatiles removed under reduced pressure to afford the silver carbene $[AgOCR^1R^2CH_2(1\text{-}C\{NCHCHNR^3\})]$, $Ag(L^1)$, **1a**–**1c**, as colourless solids, in excellent yields, which could be recrystallised from dichloromethane/hexanes mixtures, Eq. (1). The reaction with $[H_2L^{1d}]I$ does not afford the alkoxide-carbene adducts. Instead, a bis(carbene-alcohol) silver(I) salt is isolated, $[AgOCHBu^tCH_2(1\text{-}C\{NCHCHNMe\})]I$, $[Ag(L^{1d})_2]I$, **1d**, which was recrystallised to purity from 1,2-dichloroethane. The proligands $[HL^{1a}]$, $[H_2L^{1c}]X$, and $[H_2L^{1d}]X$ were made and used as racemates; one diastereomer of **1d** has been drawn in Eq. (1).

For the three alkoxide complexes **1a**–**c** $^{13}C\{^1H\}$ NMR spectroscopy of the bulk material shows a high frequency carbene resonance, with no observed coupling to the silver nucleus. Thus, deprotonation of both the NHC and alcohol groups to afford complexes of the $[L^1]$ anion is achieved by the addition of silver oxide. The novelty of these products is in the fact that they are halide-free; NHC ligands studied to date have been almost exclusively those functionalised with neutral donor groups such as pyridyl or imine [16,19,21,34–37]. These tend to form cationic silver(I) bis(carbene) structures incorporating silver(I) polyhalo counteranions of the general form $[Ag(NHC)_2][AgX_2]$. Youngs et al. [38] have already



(1)

Synthesis of silver(I) adducts of L^1