Research Article

Synthesis of Silver (I) Complexes of Iminoalkyl Functionalised *N*-Heterocyclic Carbenes

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A range of silver iminoalkyl imidazol-2-ylidene complexes have been isolated in good yield (50%–85%) and characterised by ¹H and ¹³C NMR spectroscopy. A single crystal X-ray diffraction structure determination of 1-{2-(benzylhydrylidene-amino)-ethyl}-3-benzyl imidazol-2-ylidene silver bromide indicated monodentate coordination of the ligand.

1. Introduction

N-heterocyclic carbenes such as imidazol-2-ylidenes have been established as an important class of ligands for transition metals. They typically have strong σ -donor properties but poor π -acceptor character and have been widely employed as alternative to phosphine ligands to stabilise transition metal complexes. Imidazol-2-ylidene ligands are conveniently prepared from the deprotonation of imidazolium salts. The use of Ag₂O to deprotonate imidazolium salts, developed by Lin and coworkers [1] has been widely employed as it gives silver imidazol-2-ylidene complexes that are effective carbene transfer agents and are much more stable than the free carbene [2]. The method is particularly useful when the imidazolium salt contains a base sensitive functional group. A diverse range of transition metal imidazol-2-ylidene complexes have been prepared from silver imidazol-2-ylidene complexes [3, 4].

Metal carbene complexes have been widely employed to catalyse Heck reactions, cross-coupling (such as Suzuki-Miyaura coupling) [5], and alkene metathesis reactions [6]. More recently, chiral mixed-donor ligands such as containing an *N*-heterocyclic carbene donor group have been reported to achieve high enantioselectivity in allylic alkylation [7], hydrogenation [8], and conjugate addition [9, 10]. In these cases the ligand is chelated to the metal via the imine and car-

bene donor groups. Previously, we have reported the synthesis of chiral iminoalkyl imidazolium salts and the generation of palladium imidazol-2-ylidene catalysts *via* deprotonation with silver oxide and carbene transfer to palladium [11]. In the latter work, the silver intermediates were not isolated or characterised. Here we report the isolation and characterisation of a range of silver iminoalkyl imidazol-2-ylidene complexes. These are of interest as they may be used as chiral catalysts for silver catalysed enantioselective reactions [12].

2. Experimental

The single crystal X-ray diffraction data were recorded on a Nonius CCD Kappa diffractometer (graphite-monochromated Mo K α radiation, λ = 0.71073 Å). Data were processed using program package WinGX, absorption correction MULTISCAN. Refinement was by using SHELXL-97. Crystallographic data of **2a** has been deposited with Cambridge Crystallographic Data centre, Deposition no. CCDC 726775. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

2.1. Preparation 1-{2-(benzylhydrylidene-amino)-ethyl}-3-benzylimidazol-2-ylidene of Silver (I) Bromide (2a**).** Silver oxide (I) (0.45 g, 1.93 mmol) was added to a solution of imidazolium salt (**1a**) (1.50 g, 3.36 mmol) in dichloromethane

TABLE 1: Synthesis of benzylhydrideneaminoalkyl imidazol-2-ylidene silver complexes **2a-2h**.

	R ¹	R ²	Product yield
1a	H	Bn	2a 79%
1b	Bn	Bn	2b 50%
1c	Me	Bn	2c 84%
1d	ⁱ Bu	Bn	2d 68%
1e	H	Ph	2e 78%
1f	Bn	Ph	2f 66%
1g	Me	Ph	2g 91%
1h	ⁱ Bu	Ph	2h 60%

(100 mL) in the presence 4 Å activated molecular sieves (4 g). The reaction mixture was protected from light and was refluxed for 2 days. The mixture was filtered through a layer of celite. The solvent was then removed under reduced pressure to give **2a** as a white solid (1.47 g, 79%); mp 157.5–162.1 °C; $\nu_{\text{C=N}}$: 1623 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz) δ_{H} 3.63 (t, 2H, $J = 5.3$ Hz), 4.39 (t, 2H, $J = 5.3$ Hz), 5.26 (s, 2H), 6.79–6.86 (m, 2H), 7.15–7.60 (m, 15H); ¹³C NMR (DMSO-d₆, 100 MHz) δ_{C} 52.1 53.9 (2C), 121.8, 122.4, 127.0, 127.3, 127.9, 128.5, 130.1, 135.6, 137.1, 138.6, 168.7 (1C, C=N), 179.8 (1C, C-Ag); Anal. found: C 54.26%, H 4.00%, N 7.64%; (C₂₅H₂₃N₃AgBr requires C 54.27%, H 4.19%, N 7.60%).

Complexes **2b-2h** and **3a-3b** were prepared according to the same procedure.

2.2. Compound 2b. White solid; yield: 0.21 g, 50%; ¹H NMR (DMSO-d₆, 400 MHz) σ_{H} 2.89 (dd, 1H, $J = 8.8$ Hz, $J = 13.0$ Hz), 2.95 (dd, 1H, $J = 4.4$ Hz, $J = 13.0$ Hz), 3.60–3.75 (m, 1H), 4.31 (dd, 1H, $J = 2.6$ Hz, $J = 13.3$ Hz), 4.49 (dd, 1H, $J = 9.9$ Hz, $J = 13.3$ Hz), 5.05–5.25 (m, 2H), 5.66 (s, 1H), 5.68 (s, 1H), 6.90–7.52 (m, 20H); ¹³C NMR (DMSO-d₆, 100 MHz) δ_{C} 49.4, 54.2, 56.4, 64.8, 121.7, 122.9, 126.2, 126.4, 127.4, 127.6, 127.8, 128.0, 128.09, 128.13, 128.6, 129.7 (2C), 130.2, 132.6, 136.9, 137.9, 138.4, 168.4 (C=N), 179.8 (C-Ag); Anal. found: C 59.98%, H 4.18%, N 6.31% (C₃₂H₂₉N₃AgBr requires C 59.74%, H 4.54%, N 6.53%).

2.3. Compound 2c. White solid; yield: 0.47 g, 84%; mp 85.5–88.2 °C; ¹H NMR (DMSO-d₆, 400 MHz, 35 °C) δ_{H} 1.12 (d, 3H, $J = 6.6$ Hz), 3.57–3.69 (m, 1H) 4.17 (dd, 1H, $J = 2.9$ Hz, $J = 13.2$ Hz), 4.34 (dd, $J = 9.5$ Hz, $J = 13.2$ Hz), 5.05–5.40 (m, 2H), 6.54 (s, 1H), 6.56 (s, 1H), 7.50–7.60 (m, 15H); ¹³C NMR (DMSO-d₆, 100 MHz, 35 °C) δ_{C} 19.2, 54.1, 57.5, 58.4, 121.8, 122.7, 126.7, 127.4, 127.9, 128.0, 128.1 128.46, 128.53, 130.2, 135.6, 137.1, 138.4, 167.4 (C=N), 179.6 (C-Ag).

2.4. Compound 2d. White solid; yield: 0.25 g, 68%; ¹H NMR (DMSO-d₆, 400 MHz) δ_{H} 0.63 (d, 3H, $J = 6.4$ Hz), 0.76 (d, 3H, $J = 6.4$ Hz), 1.37–1.59 (m, 3H), 3.55–3.68 (m, 1H), 4.22–4.50 (m, 2H), 5.07–5.27 (m, 2H), 6.39 (s, 2H), 7.09–7.55 (m, 15H); ¹³C NMR (DMSO-d₆, 100 MHz) δ_{C} 22.6, 23.0, 23.9, 42.8, 54.1, 56.4, 60.8, 121.7, 122.9, 126.9 (2C), 130.0 (2C),

127.4, 127.9, 128.0, 128.1, 128.2, 128.5, 135.5, 136.8, 138.6, 167.7 (C=N), 179.9 (C-Ag).

2.5. Compound 2e. White solid; yield: 0.34 g, 78%; ¹H NMR (DMSO-d₆, 400 MHz) δ_{H} 3.67 (t, 4H, $J = 5.4$ Hz), 4.45 (t, 4H, $J = 5.4$ Hz), 6.29 (s, 2H), 7.10–7.53 (m, 15H); ¹³C NMR (DMSO-d₆, 100 MHz) δ_{C} 52.5, 53.9, 121.8, 123.4, 123.5, 126.9, 127.9, 128.0, 128.39, 128.43, 128.6 129.4, 129.5, 130.1, 135.6 (2C), 138.6 (2C), 139.6 (2C), 170.1 (C=N), 168.9 (C-Ag).

2.6. Compound 2f. White solid; yield: 0.16 g, 66%; ¹H NMR (DMSO-d₆, 400 MHz) δ_{H} 3.20–3.35 (m, 2H), 3.60–3.80 (m, 1H), 4.10–4.25 (m, 1H), 4.30–4.45 (m, 1H), 6.69 (s, 2H), 7.10–7.90 (m, 20H); ¹³C NMR (DMSO-d₆, 100 MHz) δ_{C} 57.6 (2C), 58.4, 121.6, 123.5 (3C), 126.6, 127.9, 128.0, 128.3, 128.5, 129.6, 129.9, 130.1, 135.7 (2C), 138.5, 139.7, 167.4 (C=N), not vis. (1C, C-Ag).

2.7. Compound 2g. White solid 0.11 g, 91%; mp 85.0–87.4 °C; ¹H NMR (DMSO-d₆, 400 MHz) δ_{H} 1.20 (d, 3H, $J = 5.9$ Hz), 3.68–3.85 (m, 1H), 4.17–4.33 (m, 1H), 4.40 (dd, 1H, $J = 9.3$ Hz, $J = 13.4$ Hz), 6.75 (s, 2H), 7.25–7.62 (m, 14H), 7.83 (s, 1H); ¹³C NMR (DMSO-d₆, 100 MHz) δ_{C} 19.3 57.7, 58.5, 121.9, 123.5, 123.6, 126.6, 128.0, 128.1, 128.6, 129.7, 130.3, 135.7, 138.5, 139.6, 168.5, not vis. (1C, C-Ag).

2.8. Compound 2h. White solid; yield: 0.071 g, 60%; mp 68.2–70.5 °C; ¹H NMR (CDCl₃, 400 MHz) δ_{H} 0.70 (d, 3H, $J = 6.4$ Hz), 0.82 (d, 3H, $J = 6.4$ Hz), 1.40–1.63 (m, 3H), 3.73–3.87 (m, 1H), 4.22–4.45 (m, 2H), 6.57 (s, 1H), 6.59 (s, 1H), 7.10–7.65 (m, 15H); ¹³C NMR (CDCl₃, 100 MHz) δ_{C} 22.8, 23.2, 24.6, 43.1, 57.7, 61.2, 121.0, 123.2, 123.6 (2C), 126.9 (2C), 128.1 (2C), 128.38 (2C), 128.41 (2C), 128.7, 128.9, 129.8 (2C), 130.3, 135.9, 138.9, 139.6, 168.8 (C=N), 180.7 (C-Ag).

2.9. Compound 3a. White solid (0.27 g, 85%); ¹H NMR (CDCl₃, 400 MHz) δ_{H} 0.88 (d, 3H, $J = 6.6$ Hz), 0.93 (d, 3H, $J = 6.6$ Hz), 1.35–1.73 (m, 3H), 3.63–3.72 (m, 1H), 4.22 (dd, 1H, $J = 9.2$ Hz, $J = 13.6$ Hz), 4.34 (dd, 1H, $J = 3.7$ Hz, $J = 13.6$ Hz), 5.20 (d, 2H, $J = 9.2$ Hz), 7.07–7.44 (m, 9H), 7.54–7.62 (m, 2H), 8.04 (s, 1H), 10.19 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ_{C} 21.6, 23.5, 24.4, 42.1, 55.6, 57.2, 70.1, 120.4, 122.9, 128.2 (2C), 128.5 (2C), 128.6 (2C), 129.1, 129.1 (2C), 131.2, 135.5, 137.4, 161.6 (1C, N=CH-C₆H₅), 181.2 (1C, C-Ag).

2.10. Compound 3b. White solid (0.064 g, 77%); ¹H NMR (CD₂Cl₂, 400 MHz) δ_{H} 0.65 (d, 3H, $J = 6.3$ Hz), 0.72 (d, 3H, $J = 6.3$ Hz), 1.37–1.57 (m, 3H), 1.96 (s, 3H), 2.12 (s, 3H), 2.20 (s, 3H), 3.54–3.77 (m, 6H), 3.84–3.94 (m, 1H), 6.81 (s, 1H), 6.87 (s, 1H), 7.08 (s, 1H), 7.10 (s, 1H), 7.20–7.36 (m, 3H), 7.37–7.47 (m, 3H), 7.55–7.65 (m, 2H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ_{C} 17.7, 17.8, 20.8, 22.77, 22.83, 24.8, 43.2, 50.6, 51.2, 56.9, 58.9, 127.7 (2C), 128.2 (2C), 128.7 (4C), 129.5 (3C), 130.3 (1C), 135.7, 135.8, 135.9, 136.6, 138.6, 139.3, 167.9 (C=N), not vis. (1C, C-Ag).

TABLE 2: Crystal data and structure refinement.

	2a	
Empirical formula	C ₂₅ H ₂₃ Ag Br N ₃	
Formula weight	553.24	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$ (No. 2)	
Unit cell dimensions	a = 8.1675(2) Å	$\alpha = 92.909(2)^\circ$
	b = 8.6875(3) Å	$\beta = 92.682(2)^\circ$
	c = 16.5972(6) Å	$\gamma = 106.820(2)^\circ$
Volume	1123.49(6) Å ³	
Z	2	
Density (calculated)	1.64 Mg/m ³	
Absorption coefficient	2.69 mm ⁻¹	
F(000)	552	
Crystal size	0.25 × 0.20 × 0.10 mm ³	
Theta range for data collection	3.89 to 25.03°.	
Index ranges	−9 ≤ h ≤ 8, −10 ≤ k ≤ 10, −19 ≤ l ≤ 19	
Reflections collected	16098	
Independent reflections	3930 [R(int) = 0.043]	
Reflections with I > 2sigma(I)	3495	
Completeness to theta = 25.03°	98.9%	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	3930/0/363	
Goodness-of-fit on F ²	1.071	
Final R indices [I > 2sigma(I)]	R1 = 0.027, wR2 = 0.063	
R indices (all data)	R1 = 0.033, wR2 = 0.066	
Largest diff. peak and hole	0.42 and −0.53 e · Å ⁻³	

TABLE 3: Selected bond distances and angles for **2a**.

Angles (°)		Distances (Å)	
C(1)-Ag-Br	154.76(8)	Ag-C(1)	2.015(3)
C(1)-Ag-Br'	109.20(7)	Ag-Br	2.4969(3)
Br-Ag-Br'	95.823(11)	Ag-Br'	3.0549(4)
Ag-Br-Ag'	84.177(11)	N(1)-C(1)	1.353(4)
C(1)-N(1)-C(2)	111.1(2)	N(1)-C(2)	1.382(4)
C(1)-N(1)-C(4)	124.7(2)	N(1)-C(4)	1.460(4)
C(2)-N(1)-C(4)	124.0(3)	N(2)-C(1)	1.350(4)
C(1)-N(2)-C(3)	111.0(2)	N(2)-C(3)	1.392(4)
C(1)-N(2)-C(11)	125.1(2)	N(2)-C(11)	1.462(4)
N(2)-C(1)-Ag	129.5(2)	N(3)-C(13)	1.278(4)
N(1)-C(1)-Ag	126.19(19)

FIGURE 1: Synthesis of benzylhydrylideneaminoalkyl imidazol-2-ylidene silver complexes **2a-2h**.

FIGURE 2: Synthesis of benzylideneaminoalkyl imidazol-2-ylidene **3a** and imidazolin-2-ylidene silver complexes **3b**.

FIGURE 3: X-ray crystal structure of silver carbene complex **2a**.

FIGURE 4: X-ray crystal structure of **2a** showing weak interactions between monomers.

3. Results and Discussion

The synthesis of iminoalkyl imidazolium salts **1a-1h** has been previously reported. The imidazolium salt **1a** was deprotonated by silver (I) oxide in dry CH_2Cl_2 under

reflux, in the presence of activated 4 Å molecular sieves [13, 14]. The reaction was carried out in the dark to prevent photodecomposition of the silver complex. After 2 days, the achiral silver imidazol-2-ylidene complex **2a** was obtained in good yield (79%). The method was subsequently extended to the preparation of chiral silver imidazol-2-ylidene complexes **2b-2h** from chiral iminoalkyl *N*-benzyl, *N*-phenyl imidazolium bromide salts **1b-1h** (Figure 1). The yields ranged from 45% to 91% (Table 1). The steric bulk of the R^1 substituent appears to have a significant effect on the yield of the reaction, for $\text{R}^1 = \text{H}$ or Me yields are in the range 78%–91% whilst for $\text{R}^1 = \text{Bn}$, tBu they are in the range 50%–68%. This is consistent with the observation of Lin et al. that yields of silver complex formation are dependent on steric hindrance around the imidazolium salt [15].

The silver carbene transfer agent (**3a**) was prepared as the reduced steric bulk of a benzylideneamino-donor group has been linked to improved selectivity in palladium catalysed allylic alkylation [7, 16]. In addition, the imidazolin-2-ylidene silver complex (**3b**) is of interest as the unsaturated imidazolin-2-ylidene is considered a stronger σ -donor ligand and hence could enable greater electronic differentiation of a coordinated allyl group when **3b** is employed as a carbene transfer agent in palladium catalysed allylic alkylation. This should result in greater enantioselectivity (Figure 2).

The deprotonation of imidazolium salts **1a-1h** was evidenced by the disappearance of imidazolium C_1 proton singlet in the ^1H NMR spectra between 9 and 10 ppm. The coordination of the carbene carbon to the Ag(I) centre was characterised by ^{13}C NMR. ^{13}C NMR analysis confirmed conservation of the imine double bond, with the quaternary carbon signals observed between 168.5 and 170.1 ppm. The characteristic C_1 carbon signals of **2a-2h** were generally shifted up field from c.a. 136 ppm for imidazolium compounds, to c.a. 180 ppm for the carbene with no measurable coupling with silver. The carbene carbon signals were generally not detected for chiral silver iminoalkyl *N*-phenylimidazol-2-ylidene complexes **2e-2h**. The lack of Ag(I)- ^{13}C coupling is indicative of labile nature in silver complexes [17], Danopoulos [13] and Douthwaite [16] reported similar structural and spectroscopic observations

for chiral silver iminoalkyl *N*-substituted imidazol-2-ylidene complexes. Diastereotopic methyl groups in compounds derived from leucine (**2d**, **2h**) gave a rise to doublet of doublets in the ^1H NMR spectra.

The deprotonation of *N*-functionalised imidazolium halides and their coordination to Ag(I) can lead to a variety of structures, including: ion pairs, mononuclear neutral complexes, halide bridged complexes, bridged tetranuclear complexes, or bis carbene complexes. Single crystals of **2a** were grown by slow diffusion of diethyl ether into a saturated equivolume solution of $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. The single crystal X-ray diffraction structure determination indicated compound **2a** was a mononuclear neutral complex with monodentate coordination of the imino-alkyl)imidazol-2-ylidene ligand (Table 2, Figure 3). However, there is evidence of weak interactions between monomers across an inversion centre (Figure 4).

X-ray crystallographic data of **2a** indicates that the distance between the imine nitrogen (N(3)) and the Ag atom (3.402 Å) is significantly longer than that between the carbene carbon (C(1)) and Ag (2.105 Å) (Table 3). Although the imine nitrogen is directed toward the Ag atom, the two atoms are too far away to significantly interact. The structure of **2a** with no imine N(3)-Ag coordination, is in agreement with the general trend of silver to form linear and low coordinate complexes [9]. The orientation of the imine moiety away from the metal centre is assumed to be due to steric hindrance.

4. Conclusion

A range of silver iminoalkyl imidazole-2-ylidene complexes have been synthesised and characterised. The single crystal X-ray diffraction study of **2a** reveals a neutral mononuclear structure in which the imine donor group is not coordinated to the silver. Further work will be aimed at synthesising palladium iminoalkyl imidazole-2-ylidene complexes using these new compounds as carbene transfer agents.

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