

Short communication

Synthesis and crystal structure of *N*-heterocyclic carbene complex of silver

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Abstract

New imidazolium salt, $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]\text{Cl}_2$ (**1**) was prepared by quaterization of *N*-methylimidazole with *m*-xylylene dichloride. A novel monocarbene silver dinuclear complex, $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$ (**3**) was obtained by reacting **1** and Ag_2O in CH_2Cl_2 . The structure of **3** was determined by X-ray crystallography. The geometry around the Ag atoms in **3** is linear, and each Ag atom is bi-coordinated by a carbon and chloride ion. © 2002 Published by Elsevier Science B.V.

Keywords: Carbene; Imidazolium salts; Silver complex; X-ray structures

1. Introduction

Since the discovery of stable imidazoline-2-ylidenes, which was isolated and structurally characterized by Arduengo et al. in 1991 [1], much interest has been generated in the chemistry of both free heteroatom carbenes and the metal complexes of these ligands. Most recently, the synthesis and application of *N,N'*-dialkylimidazolium salts have been reviewed [2–4]. Heterocyclic carbenes derived from imidazolium ions form complexes with many transition metals; heterocyclic carbene complexes of Pd, Ni, Pt, Rh, Ru, Ag, and Au have been reported [3–24]. The late transition metal complexes have been employed as catalysts for Heck and Suzuki coupling reactions [5,6], copolymerization of ethene and CO [7], olefin metathesis [8], hydrogenation, hydroformylation, and hydrosilylation [9,10]. The use of silver and tungsten carbene complexes as carbene transfer reagent for the synthesis of Pd, Pt, Rh, and Au carbene complexes has been described [11,12]. Such a route affords a convenient method for the preparation of metal carbene complexes, and overcomes the diffi-

culties arising from the use of strong base to yield free heterocyclic carbenes.

It is noted that transition metal complexes containing XCX-coordinating pincer-type ligands (X = P, N, O, S, C coordinating atoms) have been receiving great attention, since these complexes are efficient catalysts for the C–C bond activation [25], the dehydrogenation of alkanes [26], and the C–C coupling reactions [27] (Plate 1).

We report here the preparation and characterization of new imidazolium salts $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]\text{Cl}_2$, and the silver–carbene complex $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$. $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]\text{Cl}_2$ is a precursor of a novel carbene ligand, which may potentially acts as a pincer bis-carbene ligand.

2. Results and discussion*2.1. Synthesis and ¹H-NMR spectra*

The imidazolium chloride, **1** was prepared by quaterization of *N*-methylimidazole with *m*-xylylene dichloride, and was obtained as white hygroscopic solid in a high yield. No satisfactory elemental analysis was obtained due to its severe hygroscopic property. The corresponding tetraphenylborate salt was obtained by mixing **1** and sodium tetraphenylborate in acetone or

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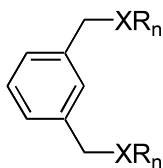


Plate 1. Pincer ligand.

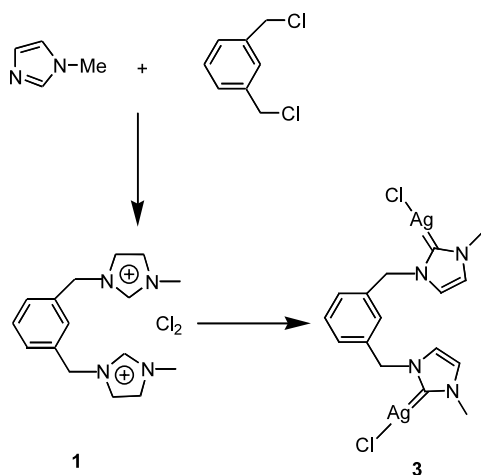
water. These two salts show very similar $^1\text{H-NMR}$ spectra, and the chemical shifts are consistent with those of the reported imidazolium salts [1] (Scheme 1).

The metal complexes of *N*-heterocyclic carbenes can be prepared by ligand substitution reactions by using free carbenes, which are accessible via deprotonation of the corresponding imidazolium salts [1–3,8]. A more convenient alternative is the direct reaction of the imidazolium salts with the metal compound containing basic ligands. By using the latter approach, a number of Ag, Ni, and Pd complexes have been prepared. A few *N*-heterocyclic carbene–silver complexes have been recently reported [11,22]. Indeed, the imidazolium chloride **1** was added to an Ag_2O suspension in CH_2Cl_2 at a ratio of 1:1 at room temperature to afford **3**. While the mixture was stirred overnight, the black Ag_2O solid disappeared and the silver–carbene complex was isolated in 94.5% yield after evaporation of the solvent. The solubility of compound **3** is poor in common organic solvents, but **3** is stable in air, and is only slightly light-sensitive.

Attempts to prepare the free carbene by deprotonation of the imidazolium salt **1** with either *t*-BuOK or KH was not successful, probably due to the high acidity of the methylene protons linking phenyl and imidazole rings.

2.2. Structure of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$ (**3**)

Crystals suitable for X-ray crystallography were obtained by slow evaporation of the dichloromethane



Scheme 1.

solution of the complex. Complex **3** crystallizes in the monoclinic unit cell of dimensions $a = 13.7315(19)$, $b = 8.7175(12)$, $c = 15.763(2)$ Å and $\beta = 92.128(3)^\circ$ with the space group of $C2/c$. The dinuclear silver complex is symmetric with a $C2$ axis passing through the C_6H_4 ring, and the asymmetric unit contains half of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$. An ORTEP drawing of the molecule and the numbering scheme is shown in Fig. 1. Selected bond lengths and angles are collected in Table 1.

The silver atoms are bi-coordinated with carbene carbon atoms and chloride ion, with the C1-Ag1 and C11-Ag1 bond distances of 2.068(3) and 2.3187(8) Å. The geometry at the Ag atom is virtually linear, with a C11-Ag-C1 bond angle of $176.25(8)^\circ$. These values are quite normal when compared to the corresponding values of other silver–carbene and silver–chloride complexes [11,22]. The planes of the imidazolato rings are approximately perpendicular to the phenyl ring with the dihedral angle of 83.88° . Generally, the central silver atoms in the reported silver–carbene complexes have a linear conformation of $\text{Ag}(\text{carbene})_2$, the structurally characterized silver–carbene complexes consist of a linear $[\text{bis}(\text{carbene})\text{Ag}]^+$ cation and a $[\text{AgX}_2]^-$ anion, which are linked via Ag–Ag interaction in their solid state [11,22]. It was suggested that the transfer of a carbene and a bromide bridge to form neutral $[\text{Ag}(\text{carbene})\text{Br}]$ in solution may occur [11,22]. Our successful characterization of **3** affords direct evidence. A few related compounds, $[o\text{-C}_6\text{H}_4(\text{CH}_2\text{ImRAgCl})_2]$ ($\text{R} = \text{'Bu}$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$, and 'Pr), have been reported recently [22b].

As shown in Fig. 2, the molecule displays a chair-like conformation, with the intermolecular $\text{Ag} \cdots \text{Ag}$ contacts of 4.054 and 4.377 Å, and intermolecular $\text{Ag} \cdots \text{Cl}$ of 3.690 Å. Thus these weak interactions led to the formation of three-dimensional networks. The Ag–Ag separations in **3** are remarkably longer than the Ag–Ag distance in $\text{Na}[\text{Ag}(\text{CN})_2]$ (3.71 Å) [28] and $\text{K}_2\text{Na}[\text{Ag}(\text{CN})_2]_3$ (3.52 Å) [29]. It is important to note

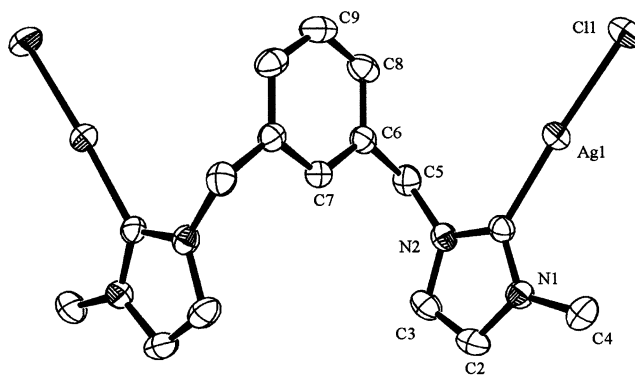


Fig. 1. An ORTEP view of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$ (**3**) with the atom numbering scheme (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$ (**3**)

<i>Bond lengths</i>	
Ag(1)–C(1)	2.068(3)
Ag(1)–Cl(1)	2.3187(8)
N(1)–C(1)	1.335(3)
N(1)–C(2)	1.376(4)
N(1)–C(4)	1.461(4)
N(2)–C(1)	1.349(3)
N(2)–C(3)	1.375(4)
N(2)–C(5)	1.468(4)
C(2)–C(3)	1.332(5)
<i>Bond angles</i>	
C(1)–Ag(1)–Cl(1)	176.25(8)
N(1)–C(1)–Ag(1)	126.60(19)
N(2)–C(1)–Ag(1)	128.6(2)
C(1)–N(1)–C(2)	110.8(2)
C(1)–N(1)–C(4)	124.1(2)
C(2)–N(1)–C(4)	125.1(3)
C(1)–N(2)–C(3)	110.8(2)
N(1)–C(1)–N(2)	104.8(2)
C(3)–C(2)–N(1)	107.1(3)
C(2)–C(3)–N(2)	106.5(3)

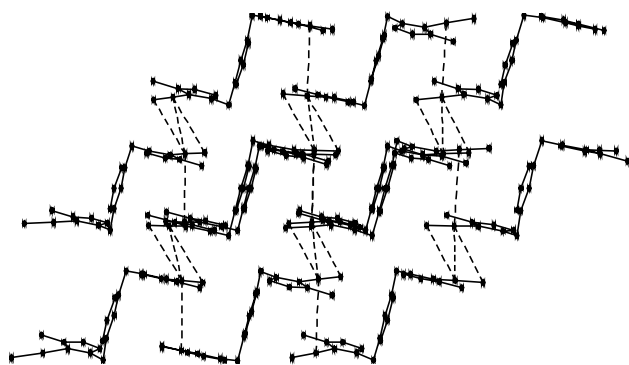


Fig. 2. Packing diagram of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$ (**3**) viewed down the *b* axis.

that Ag–Ag interactions have been emphasized in several recent articles in the literature, and the term *argentophilicity* has been adopted [30,31]. The *argentophilicity*, namely, the $d^{10}\text{--}d^{10}$ closed-shell attraction promotes the aggregation of silver(I) centers, which has been supported by recent spectroscopic and structural evidence.

3. Experimental

3.1. Preparation of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{Im})_2]\text{Cl}_2$ (**1**)

A mixture of *m*-xylylene dichloride (1.75 g, 10 mmol) and *N*-methylimidazole (3.28 g, 40 mmol) was heated at 60 °C for 2 h, giving white waxy product. It was treated with 20 ml of $\text{C}_3\text{H}_6\text{O}$, and the white hygroscopic solid

was obtained. Yield: 3.1 g (91.4%). Satisfactory elemental analysis was not obtained due to its heavily hygroscopic property. $^1\text{H-NMR}$ (270.5 MHz, D_2O , ppm): δ 8.65 (s, NCHN, 2H), 7.23–7.30 (m, C_6H_4 and NCHCHN, 8H), 5.23 (s, CH_2 , 4H), 3.70 (s, CH_3 , 6H).

3.2. Preparation of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2](\text{BPh}_4)_2$ (**2**)

A solution of NaBPh_4 (1.1 g, 3.21 mmol) in 10 ml of $\text{C}_3\text{H}_6\text{O}$ was added to a suspension of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{Im})_2]\text{Cl}_2$ (0.5 g, 1.47 mmol) in 30 ml of $\text{C}_3\text{H}_6\text{O}$. The resulted colorless solution was filtered through cellite and the filtrate was concentrated to 10 ml. The white solid was obtained by addition of 20 ml Et_2O . Yield: 1.21 g (91.7%). Anal. Calc. for $\text{C}_{64}\text{H}_{60}\text{BN}_4$: C, 84.77; H, 6.67; N, 6.18. Found: C, 84.69; H, 6.56; N, 6.19%. $^1\text{H-NMR}$ (270.5 MHz, $\text{C}_3\text{H}_6\text{O-}d_6$, ppm): δ 8.26 (s, NCHN, 2H), 7.48–6.74 (m, NCH and phenyl, 48H), 5.32 (s, NCH_2 , 4H), 3.76 (s, NCH_3 , 6H).

3.3. Preparation of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$ (**3**)

To a suspension of $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMe})_2]\text{Cl}_2$ (0.339 g, 1.0 mmol) in 50 ml of CH_2Cl_2 was added Ag_2O (0.231 g, 1.0 mmol). The mixture was stirred until Ag_2O dissolved. The resulted colorless solution was filtered and concentrated to 3 ml. The white solid was afforded by addition of 20 ml of Et_2O . Yield: 0.52 g (94.5%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the CH_2Cl_2 solution. Anal. Calc. for $\text{C}_{16}\text{H}_{18}\text{Ag}_2\text{Cl}_2\text{N}_4$: C, 34.75; H, 3.28; N, 10.13. Found: C, 34.66; H, 3.09; N, 10.01%. $^1\text{H-NMR}$ (270.5 MHz, CDCl_3 , ppm): δ 6.76, 6.64 (both d, NCH, $J_{\text{HH}} = 1.62$ Hz, each 2H), 6.72 (s, phenyl, 1H), 6.55–6.49 (m, phenyl, 3H), 4.53 (s, NCH_2 , 4H), 3.00 (s, NCH_3 , 6H).

3.4. X-ray structure determination

Prismatic single crystal with dimensions $0.26 \times 0.17 \times 0.12$ mm for **3** was covered with polyfluoroether, and mounted on a glass fiber. Data were collected on a Siemens SMART CCD diffractometer by using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct method and refined by full-matrix least-squares techniques [32,33]. All hydrogen atoms were geometrically fixed and allowed to ride on their attached atoms. Table 2 summarizes the crystal data collection and refinement parameters.

Table 2

Crystal data and structure refinement for $[m\text{-C}_6\text{H}_4(\text{CH}_2\text{ImMeAgCl})_2]$ (**3**)

Compound	3
Empirical formula	$\text{C}_{16}\text{H}_{18}\text{Ag}_2\text{Cl}_2\text{N}_4$
Formula weight	552.98
Temperature (K)	293.2(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	13.7315(19)
b (Å)	8.7175(12)
c (Å)	15.763(2)
β (°)	92.128(3)
V (Å ³)	1885.6(5)
Z	4
D_{calc} (Mg m ⁻³)	1.948
Crystal size (mm)	$0.28 \times 0.19 \times 0.16$
θ range (°)	2.59–27.49
Reflections collected	5348
Reflections unique (R_{int})	2145 (0.0206)
Data/restraints/parameters	2145/0/112
R_1, wR_2 [$I > 2\sigma(I)$]	0.0290, 0.0797
R_1, wR_2 (all data)	0.0360, 0.0835
Goodness-of-fit	1.065

4. Supplementary material

Additional data of the X-ray structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 169826 for compound **3**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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