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Short communication

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

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Abstract

New imidazolium salt, [*m*-$C_6H_4(CH_2ImMe)_2]Cl_2$ (**1**) was prepared by quaterization of *N*-methylimidazole with *m*-xylylene dichloride. A novel monocarbene silver dinulear complex, [*m*-$C_6H_4(CH_2ImMeAgCl)_2$] (**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 difficulties 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*-$C_6H_4(CH_2ImMe)_2]Cl_2$, and the silver–carbene complex [*m*-$C_6H_4(CH_2ImMeAgCl)_2$]. [*m*-$C_6H_4(CH_2ImMe)_2]Cl_2$ 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 ^{1}H-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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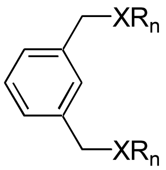


Plate 1. Pincer ligand.

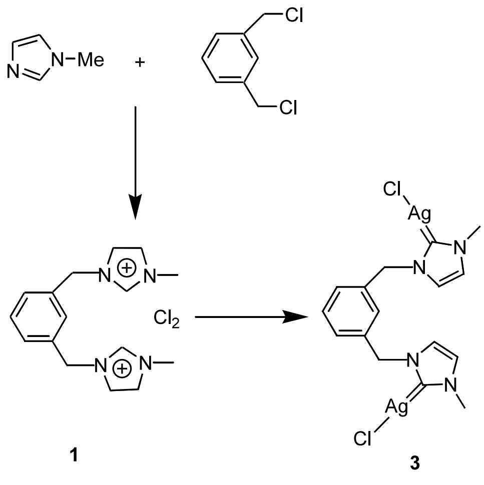
water. These two salts show very similar ^{1}H-NMR spectra, and the chemical shifts are consistent with those of the reported imidazolium salts [1] (Scheme 1).

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*-$C_6H_4(CH_2ImMeAgCl)_2$] (3)

Crystals suitable for X-ray crystallography were obtained by slow evaporation of the dichloromethane 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 $\beta = 92.128(3)°$ with the space group of *C*2/*c*. The dinulear silver complex is symmetric with a *C*2 axis passing through the C_6H_4 ring, and the asymmetric unit contains half of [*m*-$C_6H_4(CH_2ImMeAgCl)_2$]. 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.



Scheme 1.

The silver atoms are bi-coordinated with carbene carbon atoms and chloride ion, with the C1–Ag1 and Cl1–Ag1 bond distances of 2.068(3) and 2.3187(8) Å. The geometry at the Ag atom is virtually linear, with a Cl1–Ag–C1 bond angle of 176.25(8)°. 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 Ag(carbene)$_2$, the structurally characterized silver–carbene complexes consist of a linear [bis(carbene)Ag]$^+$ cation and a $[AgX_2]^-$ 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 [Ag(carbene)Br] in solution may occur [11,22]. Our successful characterization of **3** affords direct evidence. A few related compounds, [*o*-$C_6H_4(CH_2ImRAgCl)_2$] (R = ^{t}Bu, 2,4,6-$Me_3C_6H_2$, and ^{i}Pr), have been reported recently [22b].

As shown in Fig. 2, the molecule displays a chair-like conformation, with the intermolecular Ag···Ag contacts of 4.054 and 4.377 Å, and intermolecular Ag···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 Na[Ag(CN)$_2$] (3.71 Å) [28] and $K_2Na[Ag(CN)_2]_3$ (3.52 Å) [29]. It is important to note

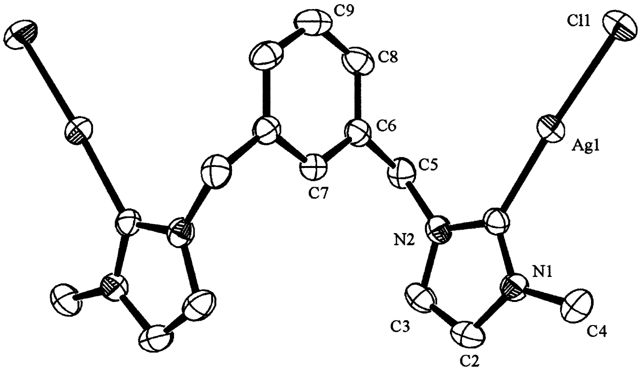


Fig. 1. An ORTEP view of [*m*-$C_6H_4(CH_2ImMeAgCl)_2$] (**3**) with the atom numbering scheme (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1
Selcted bond lengths (Å) and angles (°) for [*m*-$C_6H_4(CH_2ImMeAgCl)_2$] (**3**)

Bond lengths	
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)
Bond angles	
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)

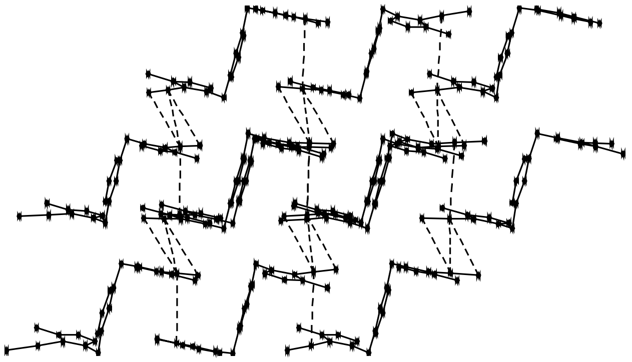


Fig. 2. Packing diagram of [*m*-$C_6H_4(CH_2ImMeAgCl)_2$] (**3**) viewed down the *b* axis.

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}–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-$C_6H_4(CH_2Im)_2$]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 C_3H_6O, 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}H-NMR (270.5 MHz, D_2O, ppm): δ 8.65 (s, NC*H*N, 2H), 7.23–7.30 (m, C_6H_4 and NC*H*C*H*N, 8H), 5.23 (s, CH_2, 4H), 3.70 (s, CH_3, 6H).

3.2. Preparation of [m-$C_6H_4(CH_2ImMe)_2$]$(BPh_4)_2$ (2)

A solution of $NaBPh_4$ (1.1 g, 3.21 mmol) in 10 ml of C_3H_6O was added to a suspension of [*m*-$C_6H_4(CH_2Im)_2$]Cl_2 (0.5 g, 1.47 mmol) in 30 ml of C_3H_6O. 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 $C_{64}H_{60}BN_4$: C, 84.77; H, 6.67; N, 6.18. Found: C, 84.69; H, 6.56; N, 6.19%. ^{1}H-NMR (270.5 MHz, C_3H_6O-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-$C_6H_4(CH_2ImMeAgCl)_2$] (3)

To a suspension of [*m*-$C_6H_4(CH_2ImMe)_2$]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 $C_{16}H_{18}Ag_2Cl_2N_4$: C, 34.75; H, 3.28; N, 10.13. Found: C, 34.66; H, 3.09; N, 10.01%. ^{1}H-NMR (270.5 MHz, $CDCl_3$, ppm): δ 6.76, 6.64 (both d, NCH, $J_{HH} = 1.62$ 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 × 0.17 × 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-$C_6H_4(CH_2ImMeAgCl)_2$] (**3**)

Compound	**3**
Empirical formula	$C_{16}H_{18}Ag_2Cl_2N_4$
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 × 0.19 × 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 [$I > 2\delta(I)$]	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).

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