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氮杂环卡宾银碘化物$[Ag(MEIm)_2]^+[AgI_2]^-$的合成、结构与催化性能 (MEIm=1-methyl-3-ethyl-imidazolyl)

王志国* 边清泉 黄宝美 邓 毅 刘思曼
(绵阳师范学院化学与化学工程学院,绵阳 621000)

摘要:常温下(MEIm)$^+$I$^-$(MEIm=1-methyl-3-ethyl-imidazolyl)与 Ag_2O 按照物质的量比为 1:2 在 DMSO 中反应成功的合成了线型氮杂环卡宾银碘化物$[Ag(MEIm)_2]^+[AgI_2]^-$,化合物通过了元素分析,^{1}H NMR,X-ray 衍射表征。配合物属于单斜晶系,空间群为 $C2/m$,a=1.592 5(4) nm,b=0.679 07(14) nm,c=0.927 1(2) nm,β=110.247(5)°,V=0.940 7(4) nm^3,M_r=689.86,Z=8,D_c=2.436 g·cm^{-3},μ(Mo $K\alpha$)=5.36 mm^{-1},F(000)=640,R=0.036,wR=0.105。配合物由阴阳离子对构成,配阳离子中 2 个卡宾碳原子与银原子呈线型结构。目标化合物对 *L*-lactide 的聚合具有高的催化活性。

关键词:氮杂环;卡宾;银;晶体结构;催化性能
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Synthesis, Crystal Structure and Catalytic Behavior of Linear *N*-heterocyclic Carbene Silver $[Ag(MEIm)_2]^+[AgI_2]^-$ (MEIm=1-methyl-3-ethyl-imidazolyl)

WANG Zhi-Guo* BIAN Qin-Quan HUANG Bao-Mei DENG Yi LIU Si-Man
(*Department of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang, Sichuan* 621000, *China*)

Abstract: The title complex $[Ag(MEIm)_2]^+[AgI_2]^-$ (MEIm=1-methyl-3-ethyl-imidazolyl) has been synthesized by the reaction of Ag_2O with (MEIm)$^+$I$^-$ in a 1:2 molar ratio at room temperature in DMSO, and characterized by elemental analysis, ^{1}H NMR and single-crystal X-ray diffraction analysis. It crystallizes in monoclinic system, space group $C2/m$ with a=1.592 5(4) nm, b=0.679 07(14) nm, c=0.927 1(2) nm, β=110.247(5)°, V=0.940 7(4) nm^3, M_r=689.86, Z=8, D_c=2.436 g·cm^{-3}, μ(Mo $K\alpha$)=5.36 mm^{-1} and F(000)=640. The structure was refined to R=0.036 6 and wR=0.142 6 for 728 observed reflections with $I>2\sigma(I)$. The cation has a typical linear conformation of $[Ag_{(carbine)2}]^+$ with a C-Ag-C angle of 180°. The catalytic behavior of the title complex has been investigated, the results indicate the title complex has a highly catalytic activation for *L*-lactide polymerization. CCDC: 843657.

Key words: *N*-heterocyclic carbene; carbene; silver; crystal structure; catalytic behavior

Silver and other transition metal *N*-heterocyclic carbene complexes have been played important role in the development of metal carbene systems for transmetalation reactions. The silver oxide is the most commonly used metal base for the purposes. Recent review dealing with silver *N*-heterocyclic carbenes were published by Arnold[1], Lin and Vasam[2]. The product molecular structure differs depending upon reaction conditions and the imidazolium salt used. To date, a variety of structures of *N*-heterocyclic carbene silver complexes have been reported, which include mononuclear complexes with one or two carbenes

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*通讯联系人。E-mail:wangzhiguo224865@163.com

coordinated to Ag(Ⅰ), halide-bridged dinuclear complexes, multinuclear and polymeric *N*-heterocyclic carbene silver complexes, ect.[3-10]. In silver *N*-heterocyclic carbene complexes of anionic iodide, the ions $[AgI_3]^{2-}$, $[Ag_2I_4]^{2-}$, $[Ag_4I_8]^{4-}$, $[Ag_4I_6]^{2-}$ were found in the literature[11], but no ion $[AgI_2]^-$ has been reported. Meanwhile, the catalytic behavior of the title complex for *L*-lactide polymerization has been investigated. Here we report the preliminary results.

1 Experimental

1.1 General procedures

The manipulations for *L*-lactide polymerization were performed in a purified argon atmosphere using standard Schlenk techniques. Toluene and THF were degassed and distilled from sodium benzophenone ketyl under argon prior to use, $(MEIm)^+I^-$ was prepared according to the literature[12]. The melting point was determined in a sealed argon filled capillary tube and uncorrected. The elemental analyses of C, H and N were performed by the direct combustion on a Carlo-Erba EA-1110 instrument, ^1H NMR spectra were obtained in C_6D_6 (400 MHz). The polydispersity were obtained by Waters 1515 gel permeation chromatography (GPC).

1.2 Synthesis of $[Ag(MEIm)_2]^+[AgI_2]^-$

Ag_2O (0.464 g, 2 mmol) was added to a solution of $(MEIm)^+I^-$ (0.954 g, 4 mmol) in DMSO (50 mL). The solution became clear after stirring for 3 h at room temperature. The volume of the solution was reduced to 20 mL under vacuum. The residue was filtered and the resulting solution was kept at the room temperature for a few days. Colorless crystals of title compound were obtained after slow evaporation (1.17g. 85%). m.p.: 369 K (dec). ^1H NMR ($CDCl_3$) 3.63(s, 6H, CH_3), 3.85(s, 4H, CH2), 6.89 (s, 4H, CH), 1.54 (s, 6H, CH_3) ppm. Anal. Calcd.(%): C, 20.06; H, 2.86; N,8.01; found (%): C, 20.01; H, 2.79; N,8.05.

1.3 General procedure for *L*-lactide polymerization

The $[Ag(MEIm)_2]^+[AgI_2]^-$ (27.8 mg, 40 μmol) and 1-pyrenebutanol (5.94 mg, 20 μmol) was added to solution of *L*-lactide (577.6mg, 4mmol) in dry toluene (2.9 mL). The mixture was heated to 50 ℃ and stirred for 8 h. The mixture was cooled to room temperature, 4 mL of THF was added, and the solution was added dropwise to stirring hexanes to precipitate the polymer. The polymer was washed with hexanes, filtered, and dried. Yield (548 mg, 95%).

1.4 Structure determination

A colorless crystal with dimensions of 0.15 mm×0.14 mm×0.13 mm was sealed in a thin-walled glass capillary filled with argon for X-ray diffraction studies. Intensity data were collected on a Rigaku Mercury CCD area detector equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. A total of 2 296 reflections were collected in the range of $2.34° \leqslant \theta \leqslant 25°$ by using an ω scan mode at 296 K, of which 899 (R_{int}=0.020) were independent. 728 observed reflections with $I>2\sigma(I)$ were used in the structure refinement. The structure was solved by direct methods. Non-hydrogen atoms were determined with successive difference Fourier syntheses. The hydrogen atoms were located at the calculated positions. The anisotropic thermal parameters for the non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2. The final refinement converged to R=0.036 and wR=0.142 6 ($w=1/[\sigma^2(F_o^2)+(0.106\,5P)^2+1.456\,8P]$, where $P=(F_o^2+2F_c^2)/3$), $(\Delta/\sigma)_{max}<0.001$, S=1.03, ρ_{max}=940 and ρ_{min}=−1 050 e·nm^{-3}. The programs for structure solution and refinement are SHELXS-97[13] and SHELXL-97[14], respectively.

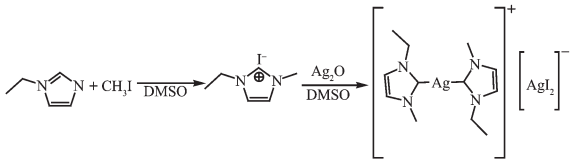
CCDC: 843657.

2 Results and discussion

2.1 Crystal structure of the title complex

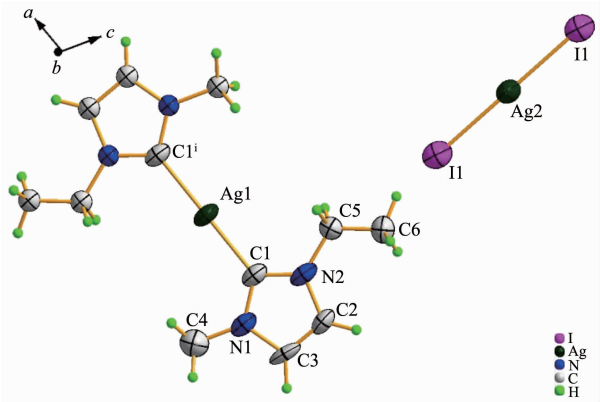
Reaction of Ag_2O with **2** equiv of $(MEIm)^+I^-$ in DMSO at room temperature gave a light yellow solution. After workup, the title complex was isolated as colorless crystals in 85% yield (Scheme 1). The composition of the title complex was confirmed by elemental analysis and ^1H NMR, and its definitive structure was determined by X-ray diffraction.

The molecular structure of the title complex is



Scheme 1

shown in Fig.1. The details crystallographic data were collected in Table 1, The selected bond lengths and bond angles are given in Table 2.



Symmetric codes: [i] 1–*x*, *y*, 2–*z*; [ii] 1–*x*, *y*, –*z*; Displacement ellipsoids at the 30% probability level

Fig.1 View of the title complex

As shown in Fig.1, the crystal structure of the title complex is composed of $[Ag(MEIm)_2]^+$ cations and $[AgI_2]^-$ anions. It was known that the type of anionic complexes $[Ag_mI_n]^{(n-m)-}$ formed is strongly influenced by the countercation and the nature of the halide[11]. In the case of iodide, the ions $[AgI_3]^{2-}$, $[Ag_2I_4]^{2-}$, $[Ag_4I_8]^{4-}$, $[Ag_4I_6]^{2-}$ have been reported. Thus $[AgI_2]^-$ is a new anionic $[Ag_mI_n]^{(n-m)-}$ complex form.

The structure of the title complex is similar to the reported complex [15] consisted of $[[CH_3\{C(NCHCHN)CH_3\}]_2Ag]^+$ and $[Ag_4I_6]^{2-}$, both of them have no interaction between the anionic silver-halide cluster and the silver NHC complex, but different from the silver NHC complex consisted of $[AgI_3]^{2-}$, $[Ag_2I_4]^{2-}$, $[Ag_4I_8]^{4-}$[11], which have interaction between the anionic silver-halide cluster and the silver NHC complex. The geometry at the Ag(1) atoms is linear, which is bi-coordinated by two carbene carbon atoms with C-Ag-C ideal angle of 180°, comparable with other examples of linear $[Ag(carbine)_2]^+$ complexes[8].

The two imy ring planes are essentially coplanar for the torsion angles between the two NHC rings is 180° . Comparison of the title complex with 1,3-

Table 1　Crystallographic data and structure refinement parameters for title complex

Empirical formula	$[Ag(MEIm)_2]^+[AgI_2]^-$	*F*(000)	640
Formula weight	689.86	Calculated density / ($g\cdot cm^{-3}$)	2.436
Temperature / K	296	Absorption coefficient / mm^{-1}	5.36
Wavelength / nm	0.071 073	θ range for data collection / (°)	2.7~27.6
Crystal system	Monoclinic	Limiting indices	$-18 \leqslant h \leqslant 18, -5 \leqslant k \leqslant 8, -10 \leqslant l \leqslant 10$
Space group	*C*2/*m*	Observed reflections ($I>2\sigma(I)$)	728
a / nm	1.592 5(4)	Reflections collected / unique	2 296 / 899
b / nm	0.679 07(14)	Refinement method	Full-matrix least-squares techniques on F^2
c / nm	0.927 1(2)	Data / restraints / parameters	899 / 15/ 65
β / (°)	110.247(5)	Goodness-of-fit on F^2	1.028
Volume / nm^3	0.940 7(4)	Final *R* indices	R_1=0.036 6, wR_2=0.125 2
Z	8	*R* indices (all data)	R_1=0.045 7, wR_2=0.142 6

Table 2　Selected bond lengths (nm) and bond angles (°)

I(1)-Ag(2)	0.258 31(10)	Ag(1)-C(1)	0.207 9(8)	N(1)-C(1)	0.135 6(12)
Ag(1)-C(1)[i]	0.207 9(8)	Ag(2)-I(1)[ii]	0.258 31(10)	C(3)-C(2)	0.135 3(15)
C(1)-Ag(1)-C(1)[i]	180.0	C(3)-N(1)-C(4)	125.1(8)	N(1)-C(1)-N(2)	104.0(7)
I(1)-Ag(2)-I(1)[ii]	180.0	C(1)-N(2)-C(5)	122.2(8)	N(1)-C(1)-Ag(1)	127.4(7)
C(1)-N(1)-C(3)	111.3(8)	C(1)-N(2)-C(2)	111.8(8)	N(2)-C(1)-Ag(1)	128.6(6)
C(1)-N(1)-C(4)	123.5(8)	C(2)-N(2)-C(5)	126.0(9)	C(2)-C(3)-N(1)	106.3(8)

Symmetric codes: [i] 1–*x*, *y*, 2–*z*; [ii] 1–*x*, *y*, –*z*.

dimesityl-*N*-heterocyclic carbene-silver(I)[15] and 1,3-diferrocenyl-*N*-heterocyclic carbenes silver[16] suggests that substituents in complexes 1,3-dimesityl-*N*-heterocyclic carbene-silver(I) and 1,3-diferrocenyl-*N*-heterocyclic carbenes silver result in the rotation of the NHC rings to alleviate steric collisions. The title complex does not have the steric constraints and therefore is able to form the planar system.

Both of the Ag-C bond distances lengths are 0.208 1 nm, which are consistent with other reported silver-carbene complexes[4-6]. The Ag(2) atom adopts linear geometry with C-Ag-C angle of 179.99°. The Ag-I bond distance (0.258 34(9) nm) is relatively shorter than the reported complexe $[Ag(carbene)_2]_2[Ag_2I_4]$ (0.283 13(15), 0.278 39(15) nm)[10].

2.2 Catalytic properties

The activity of the 1-ethyl-3-methylimidazolium carbene silver chloride as catalysts for lactide polymerization has been reported[17]. The structure of the title complex is similar to the reported complex, in order to further understand the catalytic activity of the complexes, the catalytic activity of $[Ag(MEIm)_2]^+[AgI_2]^-$ has been investigated, the results show the title complex can catalyze the polymerization of *L*-lactide at 50 ℃, which gives 95% conversion after 8 h, to give polymer of M_n=26 130 and polydispersity (M_w/M_n=1.17) by gel permeation chromatography (GPC). Compared with the 1-ethyl-3-methylimidazolium carbene silver chloride, the target compound has high catalytic activity for lactide polymerization, this may be due to small bond energy (Ag-Br) in title complex and more easily generate carbene.

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