

# Synthesis and Molecular Structure of (1,3-Dimethyl-4,5-dimethylimidazol-2-ylidene)Ag(I)(benzoate)

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Silver, which has a bulk resistivity of  $1.59 \mu\Omega\text{cm}$  is the most conductive of all the metals and for this reason is potentially useful for high-speed microelectronics applications. For example, silver films on semiconductor device materials such as Si and  $\text{SiO}_2$ , are formed by chemical vapor deposition (CVD) of silver(I) carboxylates.<sup>1</sup> Various silver(I) carboxylates are readily synthesized from the reaction of  $\text{Ag}(\text{NO}_3)$  with carboxylic acid.<sup>2</sup> Whitcomb, *et al.* reported that the normal coordination sphere of the silver carboxylates comprises an eight-membered ring in which two silver atoms are bridged by the carboxylates.<sup>3b,3c</sup> Recently, Brammer, *et al.*<sup>3g</sup> reported that silver carboxylate dimers which are further coordinated by two neutral ditopic ligands gave the new building (square  $\rightarrow$  2D-network) through self-assembly of  $\text{Ag}_2(\text{RCO}_2)_2$ . Meanwhile, N-heterocyclic carbenes are two-coordinate carbon compounds that have two nonbonding electrons and no formal charge on the carbon.<sup>4</sup> These nucleophilic carbenes, Lewis bases, can be used as ligands in organometallic chemistry.<sup>5</sup> The carboxylate Ag(I) carbene complex is one of the candidates for CVD- and spin-on-glass (SOM) precursor. This paper describes the synthesis and the molecular structure of an Ag(I) complex derived from (1,3-dimethyl-4,5-dimethylimidazol-2-ylidene) Ag(I), complex **1**, with a benzoate.

## Experimental Section

All the manipulations of air-sensitive compounds were performed under  $\text{N}_2$  atmosphere, using the standard Schlenk technique. Solvents were distilled from Na-benzophenone or  $\text{CaH}_2$ . Elemental analysis was carried out by KRICT. FAB-MS was carried out by KBSI. 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene ligand<sup>4a,6</sup> and benzoate-silver complex<sup>2</sup> were prepared according to the literature method.

**Synthesis of complex 2:** To a Schlenk flask containing phenylacetate-silver complex **1** (819 mg, 3.5 mmol) was added toluene 50 mL and 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene (404 mg, 3.25 mmol) in that order at room temperature. The reaction insoluble of complex **1** with 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene gave soluble desired product. After stirring for 1 hr, the reaction mixture was evaporated under vacuum and the residue was dissolved

in dichloromethane. The resulting solution was filtered with celite pad and the filtrate was evaporated. The crude product was washed with hexane. Recrystallization from dichloromethane/toluene/hexane gave pale yellow crystals of complex **2** (975 mg, 2.76 mmol, 85%).

<sup>1</sup>H-NMR ( $\text{CD}_2\text{Cl}_2$ ): 3.70 [s, 6H, N- $\text{CH}_3$ ], 2.10 [s, 6H, C- $\text{CH}_3$ ], 7.38, 8.00 [m, 5H, Ph]. <sup>13</sup>C-NMR ( $\text{CD}_2\text{Cl}_2$ ): 176.9 [s, O-C(O)-Ph], 173.0 [s, C<sub>carbene</sub>], 126.2 [s, C=C(CH<sub>3</sub>)-N], 136.7, 130.8, 130.3, 128.2 [m, Ph], 36.9 [s, N- $\text{CH}_3$ ], 9.5 [s, C=C(CH<sub>3</sub>)-N], FT-IR (KBr): 1630, 1595, 1553, 1397  $\text{cm}^{-1}$ . FAB-MS (m/z): 354.9 [M-H]<sup>+</sup>. E.A. for  $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_2\text{Ag}$ : Anal. (Cald); C, 47.88 (47.54); H, 4.81 (4.85).

**X-ray Structure Determination. Crystal data:**  $\text{AgC}_{14}\text{H}_{17}\text{N}_2\text{O}_2$ ;  $M_r = 353.17$ , orthorhombic, space group  $Pbca$ ,  $a = 11.437(5)$ ,  $b = 8.149(3)$ ,  $c = 31.351(12)$  Å,  $V = 2922(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.379$  g  $\text{cm}^{-3}$ ,  $F(000) = 1424$ ,  $\mu(\text{Mo-K}\alpha) = 1.379$  mm<sup>-1</sup>,  $R_1 = 0.059$ ,  $wR_2 = 0.149$  for 2242 reflections [ $|F_o| > 2\sigma(F_o)$ ].

The pale yellow single crystal was obtained from dichloromethane/toluene/hexane at  $-30$  °C. A single crystal suitable for structure determination was selected and mounted on a glass fiber tip. The diffraction data for the single crystal of this compound were collected at 298 K with a Bruker SMART CCD area detector diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using  $\omega$  scans with a scan width of  $0.3^\circ$  and a scan time of 5 sec per frame. Cell parameters were determined and refined using SMART software,<sup>7</sup> raw frame data were integrated using SAINT programs,<sup>8</sup> Empirical absorption correction was applied with the program SADABS.<sup>9a</sup> The data were corrected for  $Lp$  effects, but no correction for crystal decay was applied. The structure of the compound was solved and refined with SHELXS-97.<sup>9b</sup> Non-hydrogen atoms were refined by full-matrix least-square techniques with anisotropic displacement parameters. All hydrogen atoms were refined with isotropic displacement parameters. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition Nos. CCDC-185703). This data can be obtained free at [www.ccdc.cam.ac.uk/conts/retriving.html](http://www.ccdc.cam.ac.uk/conts/retriving.html).

## Results and Discussion

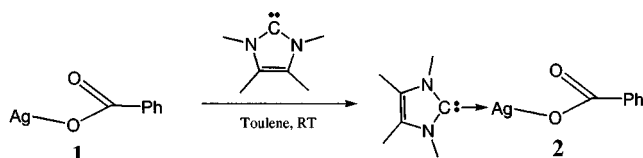
1,3-Dimethyl-4,5-dimethylimidazol-2-ylidene reacted

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smoothly with benzoate-silver complex **1** at room temperature in toluene to afford the corresponding complex **2**, a pale yellow, air-stable solid, in good yield (Scheme 1).

The reaction is easily confirmed by the  $^1\text{H-NMR}$  complex **2**, which shows shifted-methyl peaks ( $\text{C}=\text{C}(\text{CH}_3)$ ) in imidazolylidene ligand. The solid state structures of the complexes have been deduced from IR spectral information, with the most valuable data being the carbon-oxygen vibrations.<sup>3a,10</sup> Where the acetate is monodendate the divergence of  $\nu_{\text{asym.}}(\text{CO}_2)$  and  $\nu_{\text{sym.}}(\text{CO}_2)$ , compared with the free ion, is  $170\text{ cm}^{-1}$  up, and its divergence in bidentate complex is  $120\text{--}150\text{ cm}^{-1}$ . A divergence of  $\nu_{\text{asym.}}(\text{CO}_2)$  and  $\nu_{\text{sym.}}(\text{CO}_2)$  is expected due to a loss of equivalence of the C-O bonds.<sup>3a</sup> A stretching band of the  $\nu(\text{CO}_2)$  group of complex **2** appeared at  $1595$  (asymmetric) and  $1397$  (symmetric)  $\text{cm}^{-1}$ . The large IR  $\Delta$  ( $\nu_{\text{asym.}}(\text{CO}_2) - \nu_{\text{sym.}}(\text{CO}_2)$ ),  $198\text{ cm}^{-1}$  values are indicative of monodendate acetate groups. The following discussion on the structure should hold true for complex **2**.  $^1\text{H-NMR}$  spectrum of methyl peaks in imidazolylidene-moiety in complex **2** appeared at  $\delta$  3.70, 2.10.

In the  $^{13}\text{C-NMR}$ , the C(2) carbon of the carbene ring shifted substantially upfield by *ca.* 39.7 ppm in complex **2**.



Scheme 1

Table 1. Crystal data and structure refinement for complex 2

Empirical formula	$\text{C}_{14}\text{H}_{17}\text{AgN}_2\text{O}_2$
Formula weight	353.17
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbcu
Unit cell dimensions	$a = 11.437(5)$ Å $b = 8.149(3)$ Å $c = 31.351(12)$ Å
Volume	$2922(2)$ Å <sup>3</sup>
Z, Calculated density	8, 1.606 g/m <sup>3</sup>
Absorption coefficient	1.379 mm <sup>-1</sup>
F(000)	1424
Theta range for data collection	1.30 to 27.99 deg.
Limiting indices	$-10 \leq h \leq 14$ , $-9 \leq k \leq 10$ , $-40 \leq l \leq 35$
Reflections collected/unique	17157/3361 [R(int) = 0.0544]
Completeness to theta = 27.99	95.3%
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	3361/0/230
Goodness-of-fit on F <sup>2</sup>	1.105
Final R indices [I > 2σ(I)]	R1 = 0.059, wR2 = 0.149
R indices (all data)	R1 = 0.097, wR2 = 0.181
Extinction coefficient	0.0096(8)
Largest diff. peak and hole	2.278 and -1.027 e.Å <sup>-3</sup>

Table 2. Selected Bond lengths [Å] and angles [deg] for complex 2

Ag(1)-C(9)	2.064(6)	Ag(1)-O(1)	2.115(5)
Ag(1)-Ag(1)#1	3.2177(13)	O(1)-C(7)	1.273(9)
O(2)-C(7)	1.228(8)	N(8)-C(9)	1.339(7)
N(8)-C(12)	1.382(7)	N(8)-C(14)	1.447(8)
C(9)-N(10)	1.347(7)	N(10)-C(11)	1.384(7)
N(10)-C(13)	1.467(8)	C(11)-C(12)	1.340(9)
C(11)-C(16)	1.487(9)	C(12)-C(15)	1.491(9)
C(9)-Ag(1)-O(1)	165.2(2)	C(9)-Ag(1)-Ag(1)#1	69.99(15)
O(1)-Ag(1)-Ag(1)#1	115.41(15)	C(7)-O(1)-Ag(1)	111.4(5)
O(2)-C(7)-O(1)	124.9(6)	O(2)-C(7)-C(1)	120.6(6)
O(1)-C(7)-C(1)	114.5(6)	C(9)-N(8)-C(12)	110.9(5)
C(9)-N(8)-C(14)	124.9(6)	C(12)-N(8)-C(14)	124.2(5)
N(8)-C(9)-N(10)	104.9(5)	N(8)-C(9)-Ag(1)	124.9(4)
N(10)-C(9)-Ag(1)	130.2(4)	C(9)-N(10)-C(11)	111.0(5)
C(9)-N(10)-C(13)	124.6(6)	C(11)-N(10)-C(13)	124.3(5)
C(12)-C(11)-N(10)	106.2(5)	C(12)-C(11)-C(16)	131.7(6)
N(10)-C(11)-C(16)	122.0(6)	C(11)-C(12)-N(8)	106.9(5)
C(11)-C(12)-C(15)	130.7(7)	N(8)-C(12)-C(15)	122.4(7)

Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z+1.

This upfield shift is consistent with that reported for aryl-substituted carbene silver complex, complex **3**,<sup>11</sup> with the magnitude being almost the same (*cf.*  $\Delta\delta$  41.1 for complex **3** relative to free aryl-substituted carbene<sup>4c</sup>). The  $^{13}\text{C}$  resonance in **2** for C(4,5) shifted downfield by 3.65 ppm relative to the free carbene, similar to the behavior complex **3**.

A single crystal suitable for X-ray diffraction studies was grown by cooling at  $-30\text{ }^\circ\text{C}$  in a dichloromethane/toluene/hexane solution of complex **2**. The molecular structure of **2** with its atomic numbering scheme is shown in Figure 1. Details on crystal data and intensity are given in Table 1. The selected bond distances and bond angles are shown in Table 2. The acetate chelate ring is asymmetrical. The Ag(1)-O(1) bond distance, 2.115(5) Å, is slightly shorter than the typical 2.20-2.54 Å found in common  $[\text{Ag}(\mu\text{-O}_2\text{CR})_2]$  carboxylate dimers<sup>3b,3c</sup> and  $[(\text{L})\text{Ag}(\mu\text{-O}_2\text{CR})]$  carboxylate monomers.<sup>3d-f</sup> The other Ag(1)-O(2) distance in the chelate ring is a long 2.911(5) Å because the oxygen, O(2), is not bridged to the silver atom. The crystal packing structure observed in complex **2** shows that the monomeric units are arranged one above the other, and the distance between the two silver metals, Ag1...Ag#1, which is

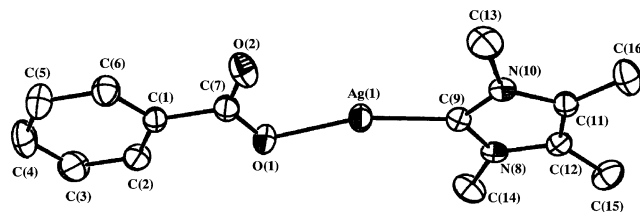


Figure 1. ORTEP drawing of **2** showing the atom-labeling scheme and 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

3.2177(13) Å, is similar to the 3.122(1) found in the terminally bound [Ag<sub>4</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>] complex. This distance is too long for significant interaction to occur between the metals.

The Ag-carbene bond length was 2.064 (6) Å which is almost the same bond lengths of biscarbene silver complex<sup>11</sup>: 2.067(4), 2.078(4) Å. The bond lengths of C(9)-N(8), C(9)-N(10), which were 1.339(7) and 1.347(7) Å, respectively, are within the expected range and comparable with those found in imidazol-2-ylidene ligands (1.34-1.37 Å).<sup>5</sup> The bond length of C(11)-C(12) of 1.340(9) Å is a carbon-carbon double bond. The FAB-MS spectrum of the product mixture is dominated by the complex **2** ion, [M-H]<sup>+</sup>, at m/z 354.9.

**Supplementary Material.** Tables of full bond distances and bond angles, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and torsion angles are available from the author.

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