

Synthesis and Molecular Structure of (1,3-Dimethyl-4,5-dimethylimidazol-2-ylidene)Ag(I)(1,3-diphenyl-1,3-propanedionate) Complex

Min Chul Chung

Electronic Materials Team, Samsung Fine Chemicals R&D Center, 103-1, Moonji-Dong,
Yusung-Gu, Taejeon 305-380, Korea
Received December 21, 2001

Keywords : Silver, Imidazolylidene, β -Diketonate, Crystal structure.

Carbenes have played an important role in organic and inorganic chemistry. They are usually reactive and nucleophilic intermediates. After discovery of the organometallic carbene by Fischer *et al.*¹ and N-heterocyclic carbene by Wanzlick *et al.*² in the 1960s, the isolation and characterization of stable N-heterocyclic carbenes by Arduengo *et al.*³ has initiated a vast series of both experimental and theoretical new investigations. Research on stable carbenes is again a theme worldwide and presently the focus is not only on chemistry of the carbenes themselves, but also on their applications to other chemical systems.⁴

These nucleophilic carbenes can be used as ligands in organometallic chemistry. Since the first Hg(II) complexes with nucleophilic carbenes were prepared by Wanzlick *et al.*,⁵ numerous other complexes, *e.g.* of Cr(0), Fe(0), Cu(I), Ag(I), Au(I), Ni(0), Pt(0), Mo(0), W(0), Ni(0), Sm(II), Yb(II), Pd(II), Rh(I), Ir(I), Os(II) have been published.⁶ Complexes with carbene and β -diketonate reported that they can act as catalysts or precursors to transformations, such as nickel-catalyzed Grignard cross-coupling reaction of aryl-chloride, palladium-catalyzed Heck reaction.⁷ In general, metal complexes of N-heterocyclic carbenes are stable against heat, moisture, and oxygen. This paper is to describe the synthesis and the molecular structure of Ag(I) complex **2** with a N-heterocyclic carbene and 1,3-diphenyl-1,3-propanedionate ligand.

Experimental Section

All the manipulations of air-sensitive compounds were performed under N₂ atmosphere with the use of standard Schlenk technique. Solvents were distilled from Na-benzophenone or CaH₂. Elemental analysis was carried out by KRICT. 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene⁸ and 1,3-diphenyl-1,3-propanedionate-silver complex⁹ were prepared according to the literature methods.

Synthesis of 2: To a Schlenk flask containing 1,3-diphenyl-1,3-propanedionate-silver complex (749 mg, 2.262 mmol) was added THF (30 mL) and 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene (281 mg, 2.267 mmol) in that order at r.t. The reaction of insoluble silver complex with imidazolylidene gave soluble desired product. After stirring

for 1 hr, the reaction mixture was evaporated under vacuum and the residue was dissolved in CH₂Cl₂. The resulting solution was filtered with celite pad and the filtrate was evaporated. The crude product was washed with hexane. Recrystallization from CH₂Cl₂/toluene/hexane gave pale yellow crystals of complex **2** (825 mg, 1.81 mmol, 80%).

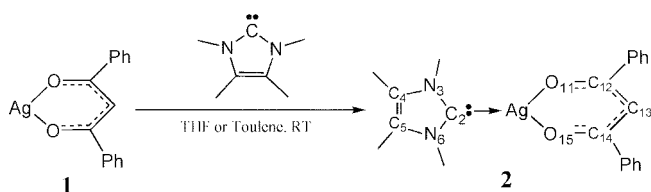
¹H-NMR (CH₂Cl₂): 3.75 [s, 6H, N(1,3)-CH₃], 2.14 [s, 6H, C=C(CH₃)], 6.45 [s, 1H, C-CH-C], 7.49, 7.89 [m, 10H, Ph]. ¹³C-NMR (CH₂Cl₂): 185.7 [s, O-C(Ph)-CH], 179.4 [s, C_{carbene}], 125.8 [s, (CH₃)C(N)=C], 127.4, 128.4, 130.2, 143.8 [Ph-ring], 93.1 [s, C(Ph)-CH-C(Ph)], 36.7 [s, N-CH₃], 9.5 [s, (CH₃)C(N)=]. FT-IR (KBr): 1425(s), 1466(s), 1507(s), 1566(s), 1605(s), 1645(sh) cm⁻¹. E.A. for C₂₂H₂₃O₂N₂Ag: Anal. (Cald); C, 56.93 (56.90); H, 5.11 (5.29).

X-Ray Structure Determination. The pale yellow single crystal was obtained from CH₂Cl₂/toluene/hexane at -30 °C. Data were collected on a Siemens P4 diffractometer equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$) at 293 K. The unit cell dimensions were determined on the basis of 51 reflections in the range $4.67^\circ < \theta < 12.51^\circ$. Data were collected by ω -2 θ technique. Empirical absorption correction were applied to the intensity data. The standard direct method was used to position the heavy atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms (*Biso* = 1.2Beq or 1.5Beq). The structure was refined in a full matrix least-squares calculations on *F*². All computations were carried out with the SHELX-97 program package.¹⁰

Results and Discussion

Complex **2**, (1,3-dimethyl-4,5-dimethylimidazol-2-ylidene)-Ag(I)(1,3-diphenyl-1,3-propanedionate) as a pale yellow solid which is air stable in the solid state, had been prepared by the reaction of the (1,3-diphenyl-1,3-propanedionate)-silver, complex **1**, with 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene at room temperature in the THF (or toluene).

The reaction is easily confirmed by the ¹H-NMR of complex **2** which shows shifted-methyl peaks (C=C(CH₃)) in imidazol-2-ylidene ligand. The IR spectrum of complex **2** in the solid state contains a ν (C=O) band at 1566(s) cm⁻¹, a



$\nu(\text{C}=\text{C})$ band at $1645(\text{sh})\text{ cm}^{-1}$ in addition to the four vibration bands at $1425(\text{s}), 1466(\text{s}), 1507(\text{s}), 1605\text{ cm}^{-1}$. The CO stretching vibration of complex **2** was shifted by *ca.* 6 cm^{-1} ($1560 \rightarrow 1566\text{ cm}^{-1}$) compared to complex **1**.⁹ This shift is attributed to the ligand acting as a bidentate mode of diketonate-moiety, the following discussion on the structure should hold true for complex **2**. The $^1\text{H-NMR}$ spectrum of vinylidene group ($\text{C}_{12}\text{-C}_{13}\text{H-C}_{14}$) in acetonato-moiety in complex **2** showed a singlet at $\delta\ 6.45$. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum also showed a corresponding singlet at $\delta\ 93.1$ due to the vinylidene group ($\text{C}_{12}\text{-C}_{13}\text{H-C}_{14}$) in the diketonato ring. In the $^{13}\text{C-NMR}$, the C_2 carbon of the carbene ring shifted substantially upfield by *ca.* 33.3 ppm in the complex **2**. This upfield shift is consistent with that reported for bis(1,3-dimesitylimidazol-2-ylidene)silver(I) triflate, complex **3**,^{6b} the magnitude being almost the same (*cf.* $\Delta\delta\ 41.1$ for complex **3** relative to free 1,3-dimesitylimidazol-2-ylidene^{3c}). The ^{13}C resonance in **2** for $\text{C}_{4,5}$ shifts downfield by 3.3 ppm relative to the free carbene, similar to the behavior of complex **3**.^{6b}

A single crystal suitable for X-ray diffraction studies was grown by cooling at $-30\text{ }^\circ\text{C}$ in a CH_2Cl_2 /toluene/hexane solution of complex **2**. Molecular structure of **2** with atomic numbering scheme is shown in Figure 1. Details on crystal data and structure refinement for **2** are given in Table 1. The selected bond distances and bond angles are shown in Table 2.

Several interesting features are evident in the X-ray structure of complex **2**. The crystal packing structure observed in the complex **2** shows that the monomeric units are arranged

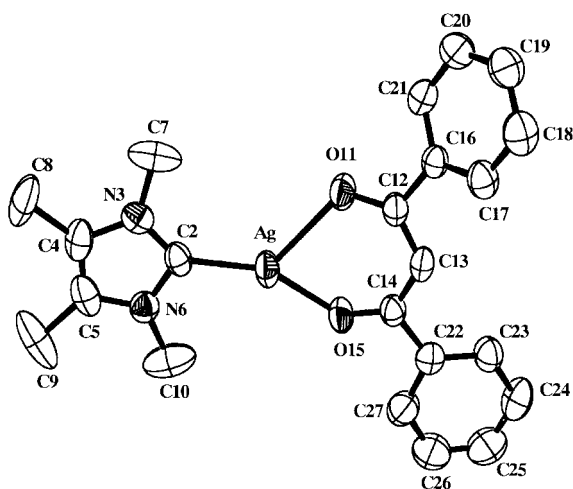


Figure 1. ORTEP drawing of **2** showing the atom-labeling scheme and 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

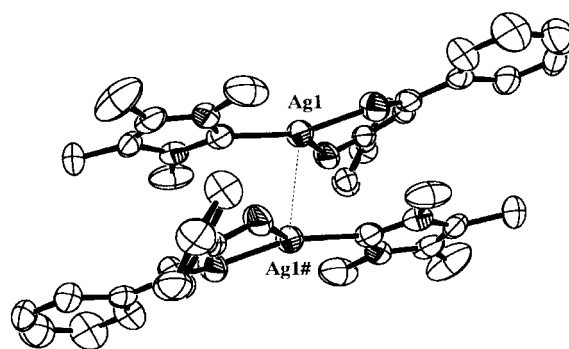


Figure 2. The dimeric nature of **2** showing the stack.

Table 1. Crystal data and structure refinement for compound **2**

| | |
|--------------------------------------|---|
| Empirical code | $\text{C}_{22}\text{H}_{23}\text{AgN}_2\text{O}_2$ |
| Formular weight | 455.29 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | $a = 7.9671(11)\text{ Å}$, $\alpha = 106.800(15)\text{ deg}$ $b = 11.625(2)$, $\beta = 93.298(12)\text{ deg}$ $c = 12.0479(18)$, $\gamma = 105.815(12)\text{ deg}$ |
| Volume | $1016.4(3)\text{ Å}^3$ |
| Z, calculated density | 2, 1.488 g/cm^3 |
| Absorption coefficient | 1.010 mm^{-1} |
| F(000) | 464 |
| Crystal size | $0.36 \times 0.18 \times 0.14\text{ mm}$ |
| Theta range for data collection | 1.79 to 27.49 deg |
| Index ranges | $-1 \leq h \leq 10$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$ |
| Reflections collected/unique | 5614/4613 [R (int) = 0.0368] |
| Completeness to $2\theta = 27.49$ | 98.7% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.9984 and 0.9198 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 4613/0/249 |
| Goodness-of-fit on F^2 | 0.977 |
| Final R indices [$I > 2\sigma(I)$] | $R1^a = 0.0642$, $wR2^b = 0.1437$ |
| R indices (all data) | $R1^a = 0.1941$, $wR2^b = 0.2438$ |
| Extinction coefficient | 0.017(2) |
| Largest diff. Peak and hole | 0.365 and -0.497 e.Å^{-3} |

$$^aR1 = \sum||F_o| - |F_c|| / \sum|F_o|. \quad ^b wR2 = \sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)]^{1/2}.$$

one above the other. The two ligands in complex **2** stack in a 'head-to-tail' manner which results in contacts between two silver metals (Figure 2). This is accounted for by the steric hindrance of phenyl group in the β -diketonato ring and the distance between the two silver metals ($\text{Ag1} \cdots \text{Ag1\#}$) is 3.000 Å . It seems that between two silver metals in complex **2** is slightly bonding interaction as a Van der Waals bond (Ag , $r = 1.441\text{ Å}$). It is dimer-like unit. The carbene moiety in complex **2** is located at the same plane with respect to the (β -diketonato)silver plane. But the two-phenyl group in β -diketonato-moiety is slightly twisted as an up and down formation. The carbene-Ag bond length is $2.085(10)\text{ Å}$ which shows almost the same bond length of biscarbene silver complex^{6b}: $2.067(4)$, $2.078(4)\text{ Å}$.

Table 2. Selected bond lengths [Å] and angles [deg] for compound **2**

| | | | |
|-------------------|-----------|--------------------|-----------|
| Ag(1)-O(15) | 2.036(8) | Ag(1)-O(11) | 2.562(5) |
| Ag(1)-C(2) | 2.085(10) | Ag(1)-Ag(1)# | 3.000(10) |
| C(2)-N(3) | 1.337(12) | C(2)-N(6) | 1.361(11) |
| N(3)-C(4) | 1.390(12) | N(3)-C(7) | 1.451(11) |
| C(4)-C(5) | 1.319(13) | C(4)-C(8) | 1.497(13) |
| C(5)-N(6) | 1.352(12) | C(5)-C(9) | 1.517(14) |
| N(6)-C(10) | 1.449(12) | O(11)-C(12) | 1.266(9) |
| C(12)-C(13) | 1.411(12) | C(13)-C(14) | 1.393(12) |
| C(14)-O(15) | 1.241(9) | | |
| O(15)-Ag(1)-C(2) | 155.7(4) | O(15)-Ag(1)-O(11) | 79.1(3) |
| C(2)-Ag(1)-O(11) | 121.8(4) | O(15)-Ag(1)-Ag(1)# | 114.4(4) |
| C(2)-Ag(1)-Ag(1)# | 76.5(3) | O(11)-Ag(1)-Ag(1)# | 100.1(3) |
| N(3)-C(2)-N(6) | 102.7(8) | N(3)-C(2)-Ag(1) | 140.9(8) |
| N(6)-C(2)-Ag(1) | 116.4(8) | C(2)-N(3)-C(4) | 112.3(9) |
| C(2)-N(3)-C(7) | 121.6(10) | C(4)-N(3)-C(7) | 126.1(11) |
| C(5)-C(4)-N(3) | 105.2(9) | C(5)-C(4)-C(8) | 134.1(12) |
| N(3)-C(4)-C(8) | 120.6(13) | C(4)-C(5)-N(6) | 108.2(9) |
| C(4)-C(5)-C(9) | 127.6(13) | N(6)-C(5)-C(9) | 124.1(13) |
| C(5)-N(6)-C(2) | 111.5(9) | C(5)-N(6)-C(10) | 125.9(11) |
| C(2)-N(6)-C(10) | 122.5(10) | C(12)-O(11)-Ag(1) | 119.6(6) |
| O(11)-C(12)-C(13) | 128.0(9) | C(14)-C(13)-C(12) | 125.5(8) |
| O(15)-C(14)-C(13) | 127.2(10) | C(14)-O(15)-Ag(1) | 138.1(7) |

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

During the refinement it was found that silver metal is disordered. The mean length of Ag-O bond in complex **2** is 2.249 Å, which is similar with typical Ag-O bond distance in silver diketonates (typically 2.35-2.64 Å).¹⁰ The bond lengths of C₁₂-C₁₃(1.411(12) Å), C₁₃-C₁₄(1.393(12) Å) are almost the same. They are between those of sp²-sp² single bond and carbon-carbon double bonds suggesting the delocalization of π-electrons over O₁₁-C₁₂-C₁₃-C₁₄-O₁₅ in the diketonato ligand.

In summary, the reaction of the β-diketonate-silver complex with N-heterocyclic carbene gave monovalent Ag complex **2**, which is air and moisture stable for periods of months in the solid state. The X-ray crystallographic structure of the complex showed that the two ligands are on the same plane.

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.

Acknowledgment. Author thanks Prof. Sung Kwon Kang, Chemistry department at Chungnam National University, for his assistance with the X-ray crystallography analysis.

References

- Fisher, E. O.; Maasböl, A. *Angew. Chem. Int. Ed. Engl.* **1964**, *580*.
- Wanzlick, H. W. *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75.
- (a) Arduengo III, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo III, A. J. *USP* **5,077,414**, 1991. (c) Arduengo III, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (d) Arduengo III, A. J.; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812. (e) Arduengo III, A. J.; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027. (f) Arduengo III, A. J.; Davidson, F.; Dais, H. V. R.; Goerlich, J. R.; Khasnis, D.; Mashall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *119*, 12742. (g) Arduengo III, A. J.; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375. (h) Arduengo III, A. J.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523. (i) Arduengo III, A. J. *Acco. Chem. Res.* **1999**, *32*(11), 913.
- (a) Regitz, M. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*(7), 725. (b) Sauers, R. R. *Tetrahedron Letters* **1996**, *37*(2), 149. (c) Herrmann, W. A.; Köcher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162. (d) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972. (e) Frison, G.; Sevin, A. *J. Phys. Chem. A* **1999**, *103*, 10998. (f) Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. *Chem. Eur. J.* **1999**, *5*(6), 1931. (h) Hahn, F. E.; Wittenbecher, L.; Van, D. L.; Fröhlich, R. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*(3), 541.
- Wanzlick, H. W. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141.
- (a) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F.; Tuaupe, H. *J. Am. Chem. Soc.* **1994**, *116*, 4391. (b) Arduengo III, A. J.; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (c) Bonati, F.; Burini, A.; Pietron, B. R.; Bovio, B. *J. Organomet. Chem.* **1989**, *375*, 147. (d) Arduengo III, A. J.; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391. (e) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdweck, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177. (f) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdweck, E.; Priermeier, T.; Kiprof, P. *J. Organomet. Chem.* **1995**, *498*, 1. (g) Kuhn, N.; Kratz, T.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1994**, *470*, C8. (h) Schumann, H.; Glanz, M.; Winterfield, J.; Hemling, H.; Kuhn, N.; Kratz, T. *Chem. Ber.* **1994**, *127*, 2369. (i) Herrmann, W. A.; Elison, M.; Fisher, J.; Köcher, C.; Artus, G. R. *J. Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2317. (j) Herrmann, W. A.; Elison, M.; Fisher, J.; Köcher, C.; Artus, G. R. *J. Chem. Eur. J.* **1996**, *2*, 772.
- (a) Böhm, V. P. W.; Weskamp, T.; Gstttmayr, C. W. K.; Herrmann, W. A. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 1602. (b) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165.
- Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.
- Wakeshima, I.; Ohgi, H.; Kijima, I. *Synth. React. Inorg. Met.-Org. Chem.* **1993**, *23*(9), 1507.
- Sheldrick, G. M. *SHELXL97. Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
- (a) Lin, W.; Warren, T. H.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 11644. (b) Xu, C. Y.; Cirbitt, T. S.; Hampden-Smith, M. J.; Kostas, T. T.; Duesler, E. N.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **1994**, 2841. (c) Yuan, Z.; Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Can. J. Chem.* **1994**, *72*, 1605. (d) Bailey, B.; Corbitt, T. S.; Hampden-Smith, M. J.; Duesler, E. N.; Kostas, T. T. *Polyhedron* **1993**, *12*, 1785. (e) Edwards, D. A.; Harker, R. M.; Mahon, M. F.; Molloy, K. C. *J. Mater. Chem.* **1999**, *9*, 1771.