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Communications

Monomeric Silver(I) *β*-Diketiminate Complexes

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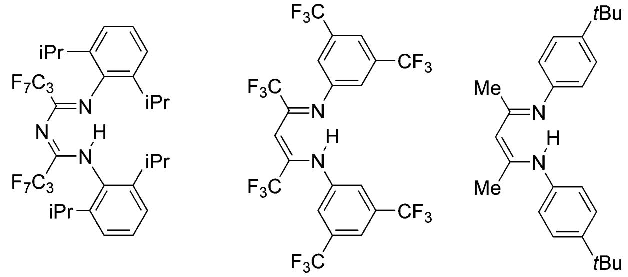
*Summary: New silver(I) β-diketiminate complexes have been prepared and characterized. Monomeric complexes with ethylene (**4**), triphenylphosphine (**5**), and IMes (IMes =1,3-dimesitylimidazol-2-ylidene) (**8**) as well as a dinuclear acetonitrile complex (**3**) were characterized by ^1H NMR, ^{13}C NMR, elemental analysis, and X-ray crystallography. These complexes are stable in the solid state at ambient temperature and inert atmosphere.*

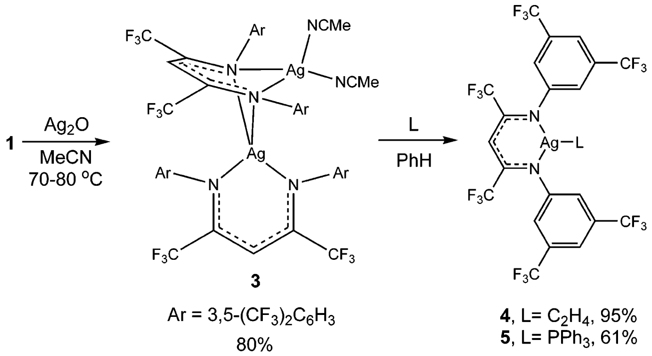
While monomeric β-diketiminate-copper complexes are well-studied and a number of them have been structurally characterized,[1] the corresponding derivatives of silver and gold remain unknown.[2] The problems preventing the synthesis of such complexes are the sensitivity to light, the oxidizing nature of silver(I),[3] and the ease of formation of coordination polymers and supramolecular complexes.[4] Closely related fluorinated triazapentadienyl complexes containing a $[N\{(C_3F_7)C(Dipp)N\}_2]$-silver(I) ligand (Figure 1, Dipp = 2,6-diisopropylphenyl) have recently been described.[5] In this case, the triazapentadienyl group behaves as a chelating bidentate ligand, forming monomeric complexes with silver in the presence of triphenylphosphine. However, it was observed that the $[N\{(C_3F_7)C(Dipp)N\}_2]$ ligand behaves as a κ^1-ligand, where the central nitrogen atom forms linear silver complexes in the presence of acetonitrile or *tert*-butylisocyanide. Shimokawa and Itoh have recently disclosed the synthesis and structural characterization of silver complexes supported by β-diketiminate ligands.[6] These complexes form both macrocyclic and polymeric structures. No monomeric complexes were observed. The silver ion was also shown to be easily reduced to the metal with the concurrent dimerization of the β-diketiminate ligands.



$[N\{(C_3F_7)C(Dipp)N\}_2]$ H **1** **2**

Figure 1. β-Diketimine ligands.

Scheme 1. General Synthetic Route for Fluorinated Silver *β*-Diketiminate Complexes



Silver complexes have found important applications in metal-mediated organic reactions.[7] Recently, several methods for silver-mediated functionalization of C−H bonds have been developed.[8] The characterization of new monomeric silver(I)−β-diketiminate complexes serves as an important stage in the further study of the chemistry of these species and their eventual applications.

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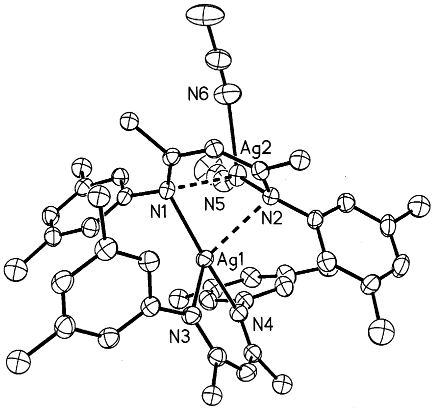

Figure 2. ORTEP view of the molecular structure of **3**. Thermal ellipsoids are drawn to encompass 40% probability. Hydrogens and fluorines are omitted for clarity. Selected bond distances (Å) and angles (deg): Ag(1)−N(1) 2.246(4), Ag(1)−N(2) 2.624(4), Ag(1)−N(3) 2.272(4), Ag(1)−N(4) 2.203(4), N(1)−Ag(1)−N(4) 149.88(16), N(1)−Ag(1)−N(3) 119.56(15), N(3)−Ag(1)−N(4) 88.03(16).

We describe here the first preparation and isolation of stable monomeric silver(I) complexes with β-diketiminate ligands. Two methods for stabilizing silver(I) complexes have been used: (1) the introduction of electron-withdrawing groups in the β-diketiminate ligands (**1**, Figure 1) and (2) the use of an N-heterocyclic carbene (NHC) as a supporting ligand for silver. This allows the isolation of an unfluorinated β-diketiminate silver−IMes complex. The use of fluorinated β-diketiminate ligands permits the isolation of acetonitrile, ethylene, and triphenylphosphine silver complexes.

Synthesis of Highly Fluorinated β-Diketiminate Silver Complexes. Compound **1** can be deprotonated by a slight excess of Ag_2O in warm acetonitrile (Scheme 1). Removal of the solvent under reduced pressure yields the acetonitrile complex **3** as a yellow-brown solid. Both the solid and its solutions in organic solvents are stable in the presence of light but decompose slowly when exposed to air for prolonged periods. The solid does not lose coordinated acetonitrile when stored under reduced pressure for 2 days at 50 °C. The ^{1}H NMR spectra of **3** taken in C_6D_6 display the resonance due to bound acetonitrile at 0.49 ppm. Interestingly, crystallographic examination of the yellow crystals of **3** grown from pentane−CH_2Cl_2 at −35 °C shows a well-defined dinuclear silver complex consistent with the stoichiometry implied by elemental analysis (Figure 2). The structure shows that two acetonitrile molecules are bound to one of the two silver ions in **3**. The Ag−N(nitrile) distances are 2.404 and 2.146 Å.[5] Analysis of the structure of **3** shows that two silver ions are arranged to assume a distorted T-shaped geometry. This complex is a convenient starting material for the synthesis of a variety of new silver complexes (vide infra). Interestingly, the ^{1}H spectrum is consistent with either a mononuclear solution structure or a fluxional process exchanging the ligands. No change in ^{1}H NMR (CD_2Cl_2) was observed upon cooling the sample to −80 °C.

Compound **3** undergoes ligand substitution with ethylene and PPh_3 in benzene solution to yield the new silver complexes **4** and **5**, respectively (Scheme 1). These complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, FT-IR, and elemental analysis (vide infra). An attempted preparation of the carbon monoxide complex by reacting a solution of **3** with gaseous CO led to the immediate formation of a silver mirror. No reaction was observed if **3** was combined with diphenylacetylene in CD_2Cl_2. The examination of ^{1}H NMR spectra of the reaction mixture indicated that replacement of the acetonitrile ligand in **3** by the sterically demanding alkyne did not occur. On the other hand, facile complexation of the less sterically demanding ethylene with silver, producing complex **4**, is noteworthy. Although several silver−ethylene complexes are known, only a few have been structurally characterized.[9] The yellow solid is stable at −35 °C under argon or at room temperature if stored under slight ethylene pressure. The ethylene ligand is quite labile when **4** is dissolved in dichloromethane or benzene. Although the complex survives NMR characterization, the solution of **4** will eventually precipitate silver metal on standing. Decomposition is avoided if an excess of ethylene is added to the solution of the complex. The ^{1}H NMR spectrum of **4** in C_6D_6 shows a resonance at 3.78 ppm that is assigned to the signal of the ethylene ligand protons.

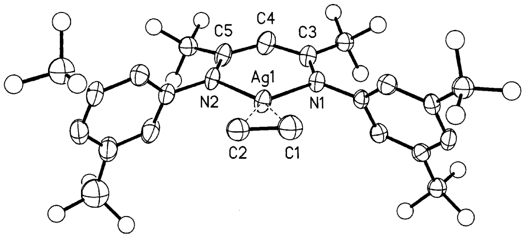

Figure 3. ORTEP view of the molecular structure of **4**. Thermal ellipsoids are drawn to encompass 40% probability. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)−C(2) 1.392(19), Ag(1)−C(1) 2.20(2), Ag(1)−C(2) 2.24(2), Ag(1)−N(1) 2.198(6), Ag(1)−N(2) 2.193(6), N(1)−Ag(1)−N(2) 88.9(2).

The coordinated ethylene in **4** is kinetically labile in solution. Saturating the C_6D_6 solution of **4** with ethylene at room temperature causes the coalescence of the peak at 3.78 ppm and that of the unbound ethylene. This observation is indicative of a fast dynamic exchange between bound and free ethylene at room temperature.

Single crystals of **4** suitable for X-ray structure determination were grown from ethylene-saturated benzene solution layered with pentane at room temperature. The ORTEP diagram of complex **4** is shown in Figure 3. The solid-state structure of **4** shows an ethylene ligand coordinated to silver in a typical η^2-fashion. Ethylene is coplanar with the β-diketiminate ligand, and the ligand chelates the silver ion with a bite angle of 88.9(2)°. The planar arrangement of ethylene ligands has been reported also for another Ag−ethylene complex.[9b] The ethylene C=C distance is 1.392(19) Å, which is slightly lengthened compared to the C=C distance of free ethylene (1.337 Å).[10] The Ag−C(ethylene) distances for **4** are 2.20(2) and 2.24(2) Å.

The preparation of **5** was accomplished by stirring **3** with 1 equiv of triphenylphosphine in benzene. The solutions of this complex in benzene or dichloromethane are stable at room temperature for several days. Complex **5** can be recrystallized from hot heptane, and the solution yields yellow crystals upon cooling. The ^{31}P NMR of **5** in CD_2Cl_2 at −50 °C shows an overlapping doublet centered at δ 16.48 ($J_{(Ag-P)}$ = 632.05 Hz) and δ 16.49 ($J_{(Ag-P)}$ = 720.29 Hz) corresponding to $^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ resonances. The $^1J(^{109}Ag-^{31}P)/^1J(^{107}Ag-$

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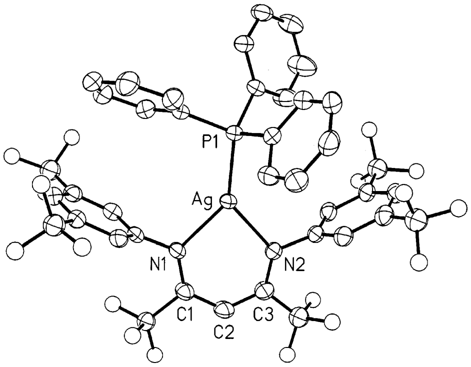
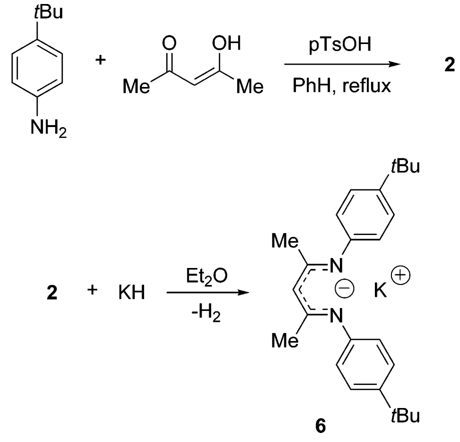


Figure 4. ORTEP view of the molecular structure of **5**. Thermal ellipsoids are drawn to encompass 40% probability. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Ag−P(1) 2.3401(11), Ag−N(1) 2.240(3), Ag−N(2) 2.232(3), N(1)−Ag−N(2) 85.03(13), C(1)−C(2)−C(3) 128.5(4).

Scheme 2. Synthesis of 2 and 6



^{31}P) ratio is found to be 1.14, which is close to the characteristic ratio of 1.15 reported by Muetterties.[11]

A single crystal of complex **5** grown from warm heptane was subjected to X-ray structure determination, and the ORTEP diagram of the monomeric structure is shown in Figure 4. Complex **5** possesses a Y-shaped trigonal planar geometry. The Ag−P distance of 2.34 Å is typical for several structurally characterized Ag(I)−PPh$_3$ complexes.[5,12]

Synthesis of an Unfluorinated *β*-Diketiminate Silver Complex. By adapting a literature procedure, ligand **2** can be obtained by refluxing a mixture of 1,4-pentanedione with 2.2 equiv of 4-*tert*-butylaniline in benzene with catalytic amounts of *p*-toluenesulfonic acid (Scheme 2).[13] Following the success in the synthesis of a number of silver complexes based on fluorinated *β*-diketiminate ligands, attempts were made to prepare the unfluorinated analogues. Initial reactions to form silver complexes from the *β*-diketiminate **6** and silver salts (AgOTf, AgNO$_3$, AgCl) resulted in immediate precipitation of silver metal. A strategy was used where a silver salt was first coordinated with a neutral ligand, followed by metathesis reaction with the *β*-diketiminate salt **6**. Silver salts such as PPh$_3$-AgNO$_3$, PPh$_3$AgCl, Me$_2$SAgNO$_3$, COD-AgNO$_3$, (Pyr)AgNO$_3$, and (IMes)AgCl (**7**)[14] were explored as potential sources of stabilized silver. These salts were reacted with either the sodium or potassium salt of the *β*-diketiminate ligand using different conditions. Only one reaction yielded promising results. The (NHC)AgCl salt proved effective in forming stable unfluorinated *β*-diketiminate silver complexes that could be isolated in good yields. Reaction of (IMes)AgCl with **6** in dichloromethane or toluene at 0 °C yielded the silver complex **8** as a pale yellow solid in 61% yield (Scheme 3). Using THF instead of dichloromethane led to precipitation of silver metal. Complex **8** is partially soluble in hydrocarbon solvents but may be washed free of undesired contaminants with cold pentane and can be recrystallized from a benzene−heptane mixture. Slow decomposition of **8** in solution was observed if manipulations were performed at ambient temperature. The dichloromethane solution of the unfluorinated complex is stable only below 0 °C. At room temperature, silver mirror is formed within minutes. In contrast, the benzene solutions are stable at room temperature for several days.

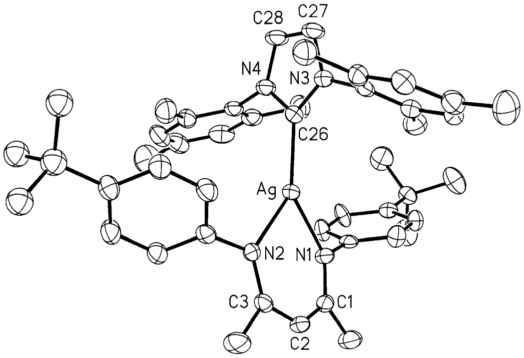
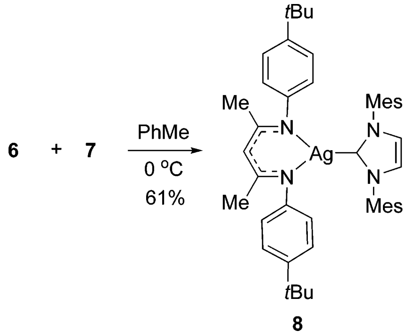


Figure 5. ORTEP view of the molecular structure of **8**. Thermal ellipsoids are drawn to encompass 40% probability. Selected bond distances (Å) and angles (deg): Ag−C(26) 2.076(5), Ag−N(1) 2.234(5), Ag−N(2) 2.246(4), C(27)−C(28) 1.340(8), C(1)−C(2)−C(3) 131.9(5), N(3)−C(26)−N(4) 103.4(4).

Scheme 3. Synthesis of 8



Single crystals of **8** grown from dichloromethane solution were analyzed by X-ray crystallography (Figure 5). Inspection of the ORTEP diagram indicates that **8** is monomeric in the solid state. The Ag−C(carbene) distance of 2.076(5) Å is slightly longer than the Ag−C(carbene) distance (2.056(7) Å) reported for **7**.[14] The resonance of the C(carbene) could not be located in the ^{13}C NMR spectrum of **8**. This is characteristic also for other Ag(NHC) complexes.[14,15]

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In conclusion, new silver(I) β-diketiminate complexes have been prepared and characterized. The structures of a silver(I)−ethylene, −acetonitrile, and −triphenylphosphine complexes supported by fluorinated β-diketiminate ligands and silver(I)−IMes supported by an unfluorinated β-diketiminate ligand were determined by X-ray crystallography. At present, investigations of the reactivity of these complexes are underway and will be reported later.

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Supporting Information Available: Experimental procedures and X-ray crystallographic data for **3**, **4**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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