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Notes

Design and Synthesis of a Sterically Hindered Pyridine and Its Encapsulation of Silver(I) Cation

Eric Bosch*

Department of Chemistry, Southwest Missouri State
University, 901 South National Avenue,
Springfield, Missouri 65804-0089

Charles L. Barnes

Department of Chemistry, University of Missouri,
Columbia, Missouri 65211

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Introduction

Metallopyridine complexes are currently of intense interest because of their widespread use in the self-assembly of metallosupramolecular structures,[1,2] oligomers, polymers, and dendrimers.[3] On another level, silver salts are notoriously light-sensitive, and silver halides are often stabilized by complexation to N bases.[4] As the initial stage of our program to prepare light-stable organosilver polymers and dendrimers, we now describe the design and synthesis of a hindered pyridine and its encapsulation of silver(I) cation to form light-stable crystalline material.

Experimental Section

General. The ^{1}H NMR spectra were recorded at 200 MHz, and the ^{13}C NMR spectra were recorded at 50 MHz. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Materials. 2,6-Dibromopyridine, mesitylmagnesium bromide, *cis*-PtCl$_2$(PPh$_3$)$_2$, copper iodide (Aldrich), and silver triflate (Across) were used as received. The solvents tetrahydrofuran and hexane (Fisher) were distilled from calcium hydride, and dichloromethane (Fisher) was distilled from phosphorus pentoxide. The solvents were then stored under an argon atmosphere in Schlenk flasks.

Preparation of 2,6-Bis(2,4,6-trimethylphenyl)pyridine, 1. A solution of 3.05 g (12.8 mmol) of 2,6-dibromopyridine and PdCl$_2$(PPh$_3$)$_3$ in dry tetrahydrofuran was cooled to −10 °C in an ice/salt bath, and 28 mL of a 1.0 M solution of mesitylmagnesium bromide in tetrahydrofuran was added dropwise under an argon atmosphere. The pale yellow solution was allowed to warm to room temperature and then refluxed for 7 h. The solution was cooled, diluted with water, and extracted with ethyl acetate. The extract was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. The colorless solid was recrystallized from hexane as colorless plates (3.39 g, 84%). mp: 134 °C. ^{1}H NMR: δ 7.83 (t, $J = 7.7$ Hz, 1H), 7.24 (d, $J = 7.7$ Hz, 2H), 6.94 (s, 4H), 2.32 (s, 6H), 2.08 (s, 12H). ^{13}C NMR: δ 159.12, 137.07, 136.18, 135.50, 134.50, 127.08, 121.39, 20.01, 19.11. GC−MS *m/z* (relative intensity): 314 (M$^+$, 100%), 299 (5). Anal. Calcd for C$_{23}$H$_{25}$N: C, 87.57; H, 7.99. Found: C, 87.56; H, 8.02 (see Scheme 1).

Scheme 1. Synthesis of 2,6-Bis(mesityl)pyridine and the Complex with Silver Triflate

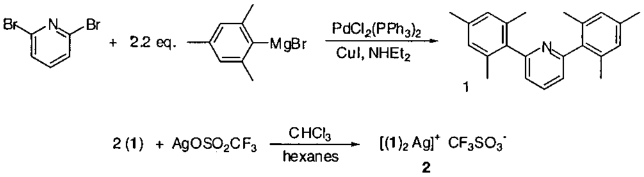

Table 1. Crystal Data and Structure Refinement for C$_{47}$H$_{50}$AgF$_3$N$_2$O$_3$S

formula	C$_{47}$ H$_{50}$ Ag F$_3$ N$_2$ O$_3$ S
fw	887.82
temp (K)	173(2)
λ (Å)	0.71073
cryst syst	monoclinic
space group	Cc
a (Å)	15.9744(10)
b (Å)	16.1255(10)
c (Å)	17.1825(11)
β (deg)	96.1910(10)
V (Å^3)	4400.3(5)
Z	4
ρ (mg/m^3)	1.340
μ (mm^{-1})	0.559
R1 ($I > 2\theta(I)$)	0.0344
wR2 (all data)	0.0848

Preparation of Silver Complex, 2. Silver triflate (70 mg, 0.27 mmol) and **1** (171 mg, 0.54 mmol) were placed in a dry Schlenk tube, and 2 mL of dry dichloromethane was added under an atmosphere of argon. The mixture was stirred until a homogeneous colorless solution was obtained, and then 2 mL of hexane was added. The solution was stirred and gently warmed until a clear homogeneous solution was obtained. The homogeneous solution was placed in a freezer at −5 °C for 1 week during which time large, colorless, cuboid crystals formed (185 mg, 77%). ^{1}H NMR (200 MHz): δ 8.15 (t, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 4H), 6.92 (s, 8H), 2.30 (s, 12H), 1.61 (s, 24H). ^{13}C NMR (50 MHz): δ 159.61, 140.55, 138.67, 135.36, 134.26, 128.02, 123.6, 20.12, 19.01. Anal. Calcd for C$_{47}$H$_{50}$AgF$_3$N$_2$O$_3$S: C, 63.58; H, 5.68; N, 3.15. Found: C, 63.12; H, 5.70; N, 3.15.

X-ray Crystallography. Table 1 lists the crystallographic data. Colorless crystals were grown from a chloroform/hexane solution, the solvents were removed, and the crystals were immediately protected from moisture under a layer of silicone oil. A crystal with dimensions 0.45 × 0.35 × 0.15 mm was used to collect 6414 unique reflections with $1.8° < \theta < 27.1°$. The structure was solved by direct methods and refined on F^2.[5] Hydrogen atoms were included in the calculated positions. Selected interatomic distances and angles are given in Table 2.

Results and Discussion

We reasoned that encapsulation of the silver cation could be accomplished in a linear bipyridyl complex provided that the

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(1) Sauvage, J.-P. *Transition Metals in Supramolecular Chemistry*; Wiley: Chichester, 1999.

(2) For a review of the application of higher oligopyridines in metallosupramolecular chemistry, see Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67.

(3) For a review of organometallic dendrimers see Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Lasado, J. *Coord. Chem. Rev.* **1999**, *193−195*, 395.

(4) Several patents describe the stabilization of silver salts by complexation to N bases. See, for example: (a) van den Zegel, M. E.; Kok, P. Eur. Pat. Appl. 201842, 1990. (b) Bloom, S. M.; Sachdev, K. G. U.S. Patent 80440, 1979.

(5) (a) Sheldrick, G. M. *SHELXS-97*: *Crystal Structure Solution*; University of Gottingen: Gottingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97*: *Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.

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Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsional Angles (deg) for **2**

Bond Distances			
Ag(1)−N(1)	2.128(5)	Ag(1)−N(2)	2.132(5)
Bond Angles			
N(1)−Ag(1)−N(2)	178.1(2)	C(1)−N(1)−Ag(1)	122.3(3)
C(5)−N(1)−Ag(1)	119.5(4)	C(24)−N(2)−Ag(1)	119.7(4)
C(28)−N(2)−Ag(1)	120.1(3)	N(1)−C(1)−C(6)	116.5(5)
N(1)−C(5)−C(12)	117.4(5)	N(2)−C(24)−C(35)	117.3(5)
N(2)−C(28)−C(29)	117.2(5)		
Torsional Angles			
N(1)−C(1)−C(6)−C(7)	−77.2(6)	N(1)−C(5)−C(12)−C(13)	103.6(6)
N(2)−C(24)−C(35)−C(36)	−89.1(6)	N(2)−C(28)−C(29)−C(30)	84.2(6)

pyridine N atom was flanked by aromatic groups orthogonal to the central pyridine ring. Pascal had earlier demonstrated that this arrangement was feasible with his elegant synthesis and X-ray structural characterization of a highly hindered 2,6-bis(decaphenylnaphthyl)pyridine.[6] Accordingly, we performed molecular modeling studies on a variety of simple substituted 2,6-diphenylpyridines. The extra steric bulk in 2,6-dimesitylpyridine forces the mesityl rings toward orthogonality with predicted dihedral angles between the mesityl and the pyridyl planes of 78.25 and 78.75°, respectively.[7−9] Accordingly, we proceeded to synthesize this molecule.

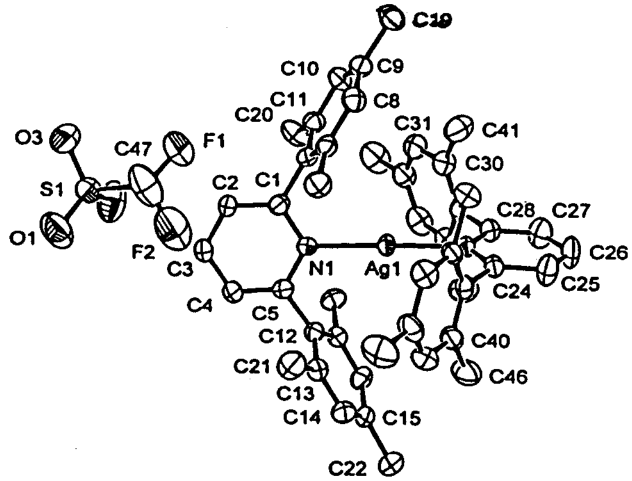

Figure 1. Perspective ORTEP[21] view of **2** ($C_{47}H_{50}AgF_3N_2O_3S$) with the H atoms omitted for clarity.

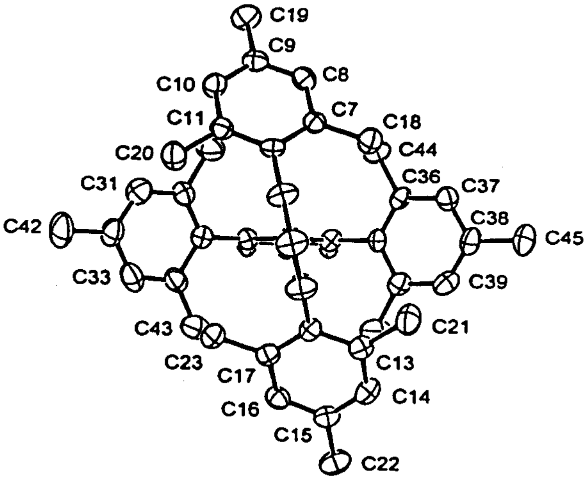

Figure 2. View along the N(1)−Ag(1)−N(2) axis showing the spatial orientation of the mesityl groups around the central silver cation with H atoms and the triflate anion omitted for clarity.

The palladium-catalyzed coupling reaction of 2,6-dibromopyridine with 2 equiv of mesitylmagnesium bromide in refluxing THF yielded 2,6-dimesitylpyridine in excellent isolated yield.[10] The complexation of silver(I) cation was accomplished by addition of a dichloromethane solution of the ligand to a stirred suspension of silver(I) triflate in dichloromethane. The complex was crystallized by dilution with hexane and then cooled. The crystals were hygroscopic and lost crystallinity rapidly (<10 min) when exposed to the atmosphere. The resultant white powder was, however, extremely stable in light and showed no darkening after exposure to room light for 6 months. Several resonances of the ligand 2,6-dimesitylpyridine were significantly shifted in the ^{1}H NMR spectrum of the complex as compared to the free ligand. In particular, the resonance of H4 on the pyridine is shifted downfield by 0.32 ppm, and the ortho methyl protons are shifted upfield by 0.47 ppm.[11] Furthermore, the resonances did not change on dilution of the complex from 0.23 to 0.01 M, indicating that the complex remained intact in this concentration range. Crystals of sufficient quality for X-ray structure analysis were grown by slow evaporation from a concentrated chloroform/hexane mixture and protected from moisture under silicone oil. A perspective drawing of the bis(pyridyl)/silver complex is shown in Figure 1. It is noticeable that the two pyridines form a linear complex with a N(1)−Ag(1)−N(2) angle of 178.1(2)°. Furthermore, the Ag(1)−N(1) and Ag(1)−N(2) bond distances of 2.128(5) and 2.132(5) Å, respectively, are within the normal range for linear silver(I)/pyridine complexes.[12] The steric bulk of the flanking mesityl groups prevent the pyridyl rings from being coplanar, and the dihedral angle between the two pyridyl planes is approximately 77°. It is noteworthy that less hindered pyridines such as 2,6-dimethylpyridine form a 2:1 complex with silver(I) in which the pyridyl rings are coplanar,[13] whereas complexation with more hindered and electronically repulsive substituents, for example, 2,6-diacetylpyridine, results in essentially orthogonal pyridine planes.[14,15] As expected, the mesityl moieties attached to each of the pyridines in **2** are almost orthogonal to the central pyridine ring.[16,17] The near-orthogonality of the pyridine/pyridine and mesityl/pyridine rings then combine to orient the mesityl groups around the central silver atom in such a way that they effectively encapsulate the silver(I) cation.[18] The spatial arrangement of the mesityl groups around the silver is clearly

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(6) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1997**, *38*, 7.

(7) Geometry optimization performed with SPARTAN PC Plus at the AM1 level.

(8) Indeed, the phenyl rings are twisted out of planarity in the parent 2,4,6-triphenyl pyridine: Ondracek, J.; Novotny, J.; Petru., M.; Lhotak, P.; Kuthan, J. *Acta Crystallogr., Sect. C* **1994**, *50*, 1809.

(9) The X-ray crystal structure of the closely related 1,3-dimesityl benzene has been determined. Niemeyer, H.; Power, P. P. *Organometallics* **1997**, *16*, 3258.

(10) Negishi, E.; Takahashi, T.; King, A. O. *Org. Synth.* **1988**, *66*, 67.

(11) Macomber, R. S. *A Complete Introduction to Modern NMR Spectroscopy*; Wiley: New York, 1998; pp 168−171.

(12) See, for example, the parent silver(I)/dipyridine complex in Menchetti, S.; Rossi, G.; Tazzoli, V. *Rend. Ist. Lomb. Accad. Sci. Lett. A: Sci. Mat. Fis. Chim. Geol.* **1970**, *104*, 309.

(13) (a) Perchlorate and nitrate salts: Engelhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 117. (b) Tetrafluoroborate salt: Horn, E.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1987**, *40*, 761. 5.

(14) Silong, S.; Engelhardt, L. M.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 1381.

(15) The pyridyl rings in the parent complex, silver(I) dipyridine nitrate monohydrate, are slightly twisted from coplanarity, see ref 12.

(16) The interplanar angles between the mesityl groups and the pyridines to which they are bonded are approximately 78, 77, 83, and 86°.

demonstrated by viewing the molecule along the N(1)−Ag(1)−N(2) axis as shown in Figure 2, which clearly shows how the silver cation is protected in the middle of the complex.[19]

In conclusion, we have prepared a novel, light-stable, bis(pyridyl)/silver(I) complex where the silver cation is encapsulated by suitably positioned mesityl rings. We are currently exploring the application of this idea to the encapsulation of other metal cations and to the preparation of light-stable conjugated silver/pyridyl polymers and dendrimers.[20]

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Supporting Information Available: X-ray crystallographic file in CIF format for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) A similar approach was used by Power et al. in their elegant studies of a variety of metal/arene σ-complexes using flanking mesityl and 2,4,6-triisopropylbenzene groups to stabilize their systems. For a review, see Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem*. **1999**, *44*, 1.

(18) For a different approach to the encapsulation of silver(I), see de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1991**, *30*, 3103.

(19) Interestingly, the spatial orientation of the aromatic rings in the structure presented here is strikingly similar to the diaryl/mercury complex bis(2,6-dimesitylphenyl) mercury(II) reported by Niemeyer and Power in ref 9.

(20) (a) Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotochin, S. V. *Science* **1996**, *271*, 1095. (b) Manners, I. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 1602. See also: Saalfrank, R. W.; Demleitner, B. *Transition Metals in Supramolecular Chemistry*; Wiley: Chichester, 1999; Chapter 1.

(21) Farrugia, L. J. *J. Appl. Crystallogr*. **1997**. *30*, 565.