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Spacer Flexibility in Bis(pyridyl) Ligands: Chelating Organosilicon Pyridylethynyl Ligands

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Two new bis(pyridylethynyl) ligands with organosilicon spacers have been synthesized. The ligands react readily with silver(I) to form crystalline complexes, both of which are revealed to be triflate-bridged dimers by X-ray crystallographic analysis. The complex with the flexible siloxane-based ligand possesses considerably less bond angle distortion.

Ethynylpyridine ligands have been extensively utilized in the synthesis of organometallic nonlinear optical materials and supramolecular frameworks.[1−10] A ligand of particular recent interest is 1,2-bis(2-pyridylethynyl)benzene, known to form complexes with Cu(I), Pd(II), Ag(I), and even Br^+.[1,6,11−15] Due to the rigid nature of this ligand, complexes are generally formed in which the two pyridine rings are directly opposed. Conceivably, replacing the benzene ring spacer between the pyridylethynyl moieties could lead to different coordination modes and new metal complex geometries. To this end, we have begun an investigation into the synthesis of new bis(pyridylethynyl) ligands in which the two pyridylethynyl moieties are separated by organosilicon spacers. The ready availability of different organosilicon starting materials should make it possible to easily vary the length and flexibility of the spacer unit, which in turn could affect the ligands' binding preferences. Furthermore, having the relatively bulky silyl group separated from the pyridine ring by a triple bond rather than directly attached[16−20] decreases potential steric interactions between the ligand and metal. Herein we report the synthesis of two new silicon-containing ligands, 1,3-bis(2-pyridylethynyl)-1,1,3,3-tetramethyldisiloxane (**L1**) and 1,2-bis(2-pyridylethynyl)-1,1,2,2-tetramethyldisilane (**L2**), and demonstrate their utility as ligands by isolating their complexes with silver(I). Unlike 1,2-bis(2-pyridylethynyl)benzene, ligands **L1** and **L2** complex with silver to form anion bridged dimers.

Ligands **L1** and **L2** were synthesized by the reaction of lithiated 2-ethynylpyridine[21] with 1,3-dichloro-1,1,3,3-tetramethyldisiloxane and 1,2-dichloro-1,1,2,2-tetramethyldisilane, respectively, in diethyl ether at −78 °C (Scheme 1). Ligand **L1** was obtained as a viscous oil and **L2** as a crystalline solid. Both ligands were fully characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, and ^{29}Si), IR spectroscopy, and differential scanning calorimetry.

Ag(I) complexes **ML1** and **ML2** were prepared by heating a stirred suspension consisting of a 1:1 mixture of AgOTf and **L1** or **L2** in dichloromethane until a clear solution was obtained. Layering the solution with hexane resulted in the formation of colorless crystals of the complexes (**ML1**, 32%; **ML2**, 29%) after cooling in a refrigerator for several days. Also formed during the cooling process were insoluble and thus far unidentified black products, presumably polymer. Both **ML1** and **ML2** are air-stable for a few days at ambient temperature, but gradually darken when exposed to light.

The ^1H NMR spectrum of **ML1** in $CDCl_3$ shows that the pyridyl proton signals are shifted considerably downfield compared to ligand **L1**, suggesting the coordination of the

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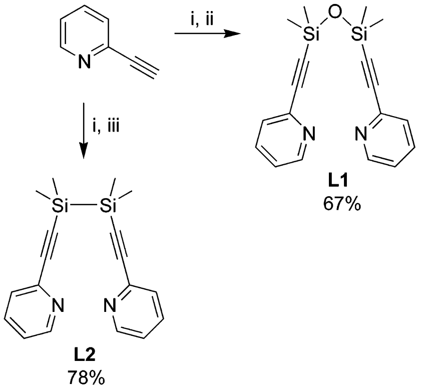
Scheme 1. Synthesis of Ligands **L1** and **L2**[a]



[a] (i) *n*-BuLi, diethyl ether, −78 °C; (ii) 1,3-dichloro-1,1,3,3-tetramethyldisiloxane; (iii) 1,2-dichloro-1,1,2,2-tetramethyldisilane.

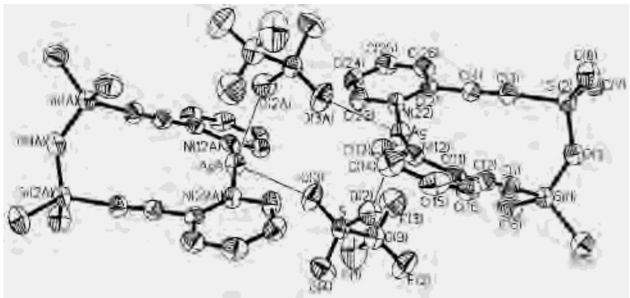


Figure 1. ORTEP of **ML1** (50% probability ellipsoids, hydrogens omitted for clarity).

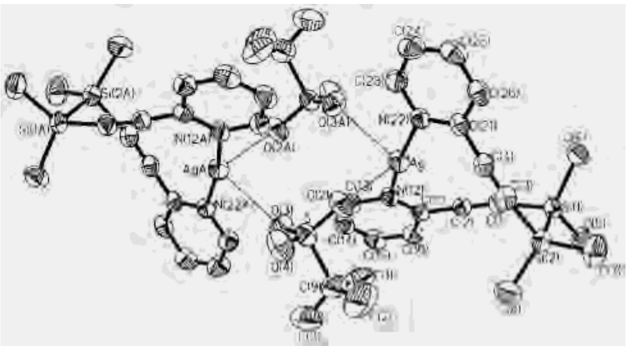


Figure 2. ORTEP of **ML2** (50% ellipsoids, hydrogens omitted for clarity).

ligands to silver. A similar deshielding effect is also observed in complex **ML2**. The methyl carbon atoms of the $Si(CH_3)$ groups in **ML1** and **ML2** are shifted slightly downfield at 1.63 and −3.98 ppm, respectively, in the ^{13}C NMR spectra. Slight shifts were also observed in the ^{29}Si NMR spectra of the complexes. Signals were observed at −14.0 ppm for **ML1** (−15.6 for **L1**) and at −36.1 ppm for **ML2** (−35.8 for **L2**).

The IR spectra for both complexes showed the characteristic band at 2168 cm^{-1} for carbon−carbon triple bond stretching. In complex **ML1**, a strong band for Si−O stretching is present at 1046 cm^{-1}. By virtue of the Si−Si bond present, ligand **L2** and the corresponding complex possess extended electron delocalization through the entire ligand framework. The UV−vis spectrum of **ML2** in THF exhibits two distinct absorption bands at 243 and 285 nm, indicative of Si−Si $\sigma-\pi$ conjugation[22] and pyridyl $\pi-\pi^*$ transitions, respectively.

X-ray single-crystal structural characterization of complexes **ML1** and **ML2** showed them to be dimers (Figures 1 and 2), both halves of which are crystallographically equivalent.[23] In the crystal systems of both complexes, each silver(I) is coordinated by two pyridyl nitrogen atoms from each ligand. Two additional coordination sites are occupied by oxygen atoms from two triflate bridges resulting in a distorted four-coordinate sawhorse arrangement around the silver(I) centers. Triflate bridges in silver(I) complexes are uncommon[24,25] and, to the best of our knowledge, unknown in pyridyl−silver complexes. Typically in these systems, a single oxygen atom of the triflate coordinates to silver.[26,27] The coordination of triflate to silver is reflected in the Ag−O bond lengths (**ML1**, Ag−O(2) = 2.621(3) Å, Ag−O(3) = 2.756(3) Å; **ML2**, Ag−O(2) = 2.605(2) Å, Ag−O(3) = 2.793(2) Å) compared to the longer Ag−O bond distances in weakly coordinated triflates.[7,18] The Ag−N average bond length of 2.18 Å is within the range of reported values[7,18,19,28] (**ML1**, Ag−N(12) = 2.193(3) Å, Ag−N(22) = 2.180(3) Å; **ML2**, Ag−N(12) = 2.184(2) Å, Ag−N(22) = 2.188(2) Å).

The coordination number and geometry of silver(I) complexes vary widely although linear complexes are the most common.[26] In **ML1** and **ML2**, the pyridine rings about the silver centers are distorted from a linear coordination geometry with N−Ag−N bond angles of 168°. Such bending of the N−Ag−N bond from a linear geometry could be due to the influence of the triflate bridging ligands.

Although both ligands form dimers with Ag(I), the difference in flexibility between the two spacers is apparent on examination of the various bond angles in the complexes. Ligand **L1** benefits not only from having an extra atom in its chain, but also from the well-documented flexibility of the Si−O−Si linkage.[29] Despite this built-in flexibility, complex **ML1** does reveal elements of strain. The Si−O−

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(23) **ML1**: $C_{38}H_{40}F_6N_4O_8S_2Si_4Ag_2$, formula weight 1186.96, space group $P\bar{1}$, $a = 9.117(1)$ Å, $b = 10.123(1)$ Å, $c = 14.956(1)$ Å, $\alpha = 103.419(6)°$, $\beta = 97.560(4)°$, $\gamma = 109.066(7)°$, $V = 1236.3(2)$ Å^3, $Z = 1$, $d = 1.594$ Mg/m^3, $\mu = 1.046$ mm^{-1}. **ML2**: $C_{38}H_{40}F_6N_4O_6S_2Si_4Ag_2$, formula weight 1154.96, space group $P\bar{1}$, $a = 8.9282(4)$ Å, $b = 10.6108(7)$ Å, $c = 14.3566(7)$ Å, $\alpha = 102.897(5)°$, $\beta = 97.614(4)°$, $\gamma = 107.907(4)°$, $V = 1231.5(1)$ Å^3, $Z = 1$, $d = 1.557$ Mg/m^3, $\mu = 1.045$ mm^{-1}. Both sets of data were collected on a Bruker P4 diffractometer at room temperature, Mo Kα, 2θ 3.5−50.0°. A ψ scan was carried out for absorption correction. The structure was solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL program package (Sheldrick, G. M., *SHELXTL* (1990), Bruker Analytical X-Ray Systems, Inc.). Each dimeric molecule possesses a center of symmetry. All non-H atoms were anisotropically refined, while H atoms were constrained with a riding model. The final refinement parameters R_1 [$I > 2\sigma(I)$] = 0.031, 0.035, and wR_2 [all data] = 0.080, 0.093 for **ML2** and **ML1**, respectively.

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Si bond angle of 137.89(18)° is higher than the corresponding angle in hexamethylcyclotrisiloxane (125.0(5)°),[30] yet is considerably lower than the Si−O−Si bond angle in the linear disiloxane $Me_3SiOSiMe_3$ (148.8(2)°).[31] Additionally, the observed bond angle is significantly lower than those calculated for the free ligand using a Hartree−Fock/3-21G* low-energy conformation search[32] (170−179°). Evidence for strain in **ML1** is also apparent from the Si−C≡C bond angles, which deviate slightly from 180° (C(4)−C(3)−Si(2), 172.4(3)°, and C(2)−C(1)−Si(1), 178.6(4)°).

As expected with the less flexible **L2**, complex **ML2** is considerably more strained to accommodate the silver center. The Si−C≡C bond angles are further deviated from linearity (C(2)−C(1)−Si(1), 168.2(3)°, and C(4)−C(3)−Si(2), 169.5(3)°). Furthermore, the Si−Si−C(alkyne) bond angles are significantly bent from an idealized tetrahedral geometry (C(1)−Si(1)−Si(2), 99.42(11)°, and C(3)−Si(2)−Si(1), 99.99(12)°). The Si−Si bond length of 2.3539(14) Å is similar to that of known disilanes.[33,34]

In conclusion, we have prepared two representatives of a new class of silicon-based bis(pyridylethynyl) ligands. The structure of the ligand affects the strain of the resulting complex, which in turn may conceivably be exploited for further reaction. We are currently synthesizing other organosilicon ligands with spacers of varying length and stiffness, and examining their metal complexation behavior. The results of this work will be reported in due course.

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Supporting Information Available: Synthetic details for **L1**, **L2**, **ML1**, and **ML2**. ORTEP diagrams and packing diagrams for **ML1** and **ML2**. Crystallographic data for **ML1** and **ML2** in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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