## Tetrahedron Letters 55 (2014) 2019-2021

Contents lists available at ScienceDirect

**Tetrahedron Letters** 

journal homepage: www.elsevier.com/locate/tetlet

# Silver perchlorate induced rearrangement of a tetraarylethene involving an apparent oxygen migration



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#### ARTICLE INFO

Article history: Available online 21 February 2014

Keywords: Rearrangement Silver perchlorate Crystal structure Dienone-phenol rearrangement Tetraarylethene

### ABSTRACT

An H-shaped tetraarylethene ligand was prepared and shown to react with silver perchlorate to produce a crystalline silver complex of a rearranged ligand. X-ray crystallography revealed that this involved the formation of a phenanthrene ring system with the apparent migration of an oxygen atom. We believe that this rearrangement proceeds via the intermediacy of a spirodienone.

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Metallosupramolecular chemistry<sup>1</sup> involves the use of bridging organic ligands and metal centres for the construction of 0, 1, 2 or 3D assemblies.<sup>2</sup> The use of silver(I) for such purposes has been particularly popular in recent years.<sup>3</sup> For some time now we have championed the use of the silver–alkene interaction as a useful synthon for access to novel metallosupramolecular assemblies.<sup>4</sup> For example, we showed that three isomeric divinylbenzenes reacted with silver(I) salts to give both discrete and polymeric species.<sup>5</sup>

Recently, we described the use of an H-shaped ligand **1** with four allyloxy arms as coordinating units for the construction of a molecular ladder that underwent double interpenetration to form the first example of an elusive metallosupramolecular topology.<sup>6</sup> We now report the synthesis and characterisation of a structurally related ligand **2** that, upon reaction with silver(I) perchlorate, undergoes an intriguing molecular rearrangement.

The potential ligand was prepared in a two-step procedure starting from 4,4'-dihydroxybenzophenone. McMurry coupling<sup>7</sup> generated a tetraarylethene, which was directly allylated,<sup>8</sup> as shown in Scheme 1, to give the four-armed ligand **2**. This was fully characterised<sup>9</sup> by <sup>1</sup>H and <sup>13</sup>C NMR, infrared spectroscopy, mass spectrometry, elemental analysis and the structure confirmed by X-ray crystallography (Scheme 1). It crystallises in the monoclinic space group P2<sub>1</sub>/*n* with a full molecule in the asymmetric unit.<sup>10</sup>



Reaction of **2** with silver(I) perchlorate in an acetone solution and slow evaporation of the solvent over two weeks furnished crystals of a silver complex<sup>11</sup> of the rearranged ligand **4**, as demonstrated by a single crystal X-ray structure determination. The crystal structure of this complex shows that it exists as a complicated 2D assembly, a section of which is shown in Figure 1. It crystallises in the triclinic space group P-1 and the asymmetric unit contains one full molecule of **4**. one and a half silver atoms, a coordinated water molecule and one and a half non-coordinated perchlorate anions.<sup>12</sup> All three remaining allyl arms of **4** are coordinated to silver, with bond lengths comparable to those in related silveralkene complexes.<sup>4,5,13</sup> The silver atoms are three- and fourcoordinate. The phenyl rings attached to the planar phenanthrene ring system are approximately orthogonal to that plane and experience edge-to-face  $\pi$ - $\pi$  interactions with a symmetry-related phenanthrene ring with separation distances of 3.613 and 3.664 Å.

In order to confirm that the crystal used was not a minor by-product in a mixture, we recorded the powder diffraction pattern of the bulk sample, which confirmed that the complex





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Scheme 1. Synthesis of 2, its X-ray crystal structure and rearrangement into 4.



Figure 1. X-ray structure of a section of the 2D coordination polymer of the silver complex of rearranged ligand 4.

was the sole product (see Supplementary data). Indeed the <sup>1</sup>H NMR spectrum of the crystals dissolved in acetonitrile showed a single compound, the spectrum of which was assigned (Fig. 2) with the aid of 2D experiments. The dissolved crystals were decomplexed from the silver by passage through a column of silica, thereby allowing the isolation and characterisation of **4** itself.<sup>14</sup>

Only one compound has been reported with this carbon skeleton and oxygenation pattern, as a minor product in a palladiumcatalysed coupling reaction.<sup>15</sup> The rearrangement of **2** into **4** involves the loss of one allyl group, the formation of a C—C bond between two phenyl rings to generate the phenanthrene ring system and the apparent migration of an oxygen atom. We believe that this rearrangement proceeds through the intermediacy of dienone **3** (Scheme 1). Such spirodienones are known to form by



**Figure 2.** <sup>1</sup>H NMR spectrum of the crystals of the silver complex **4** dissolved in  $d_3$ -acetonitrile.

metal-catalysed rearrangement of 1,2-bis(4-alkoxyphenyl) precursors<sup>16,17</sup> and undergo dienone-phenol rearrangements into phenanthrenes<sup>18,19</sup> with selective migration of the alkenyl group.<sup>19</sup>

Reactions of **2** with other silver(I) salts did not induce this rearrangement and complexes of unrearranged **2** were able to be characterised.<sup>20</sup> In addition, a linear 1D coordination complex of **2** with silver perchlorate was formed in low yields by carrying out the reaction over a shorter timeframe in acetonitrile.<sup>20</sup>

In conclusion, the H-shaped ligand **2** was prepared in two steps and fully characterised, including an X-ray crystal structure. Reaction of **2** with silver perchlorate resulted in the isolation of crystals of a silver complex of the rearranged ligand **4**, involving an apparent oxygen migration. We believe that this reaction proceeds via the intermediate spirodienone **3**.

### Acknowledgments

We thank the University of Canterbury, College of Science, for a scholarship for S.W.K. and the RSNZ Marsden fund for generous financial support.

# Supplementary data

Supplementary data (X-ray powder diffraction figure and X-ray CIFs) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.02.026.

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9. *Data for* **2**: mp 46–48 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.46 (8H, br d, J = 3.0 Hz, H6), 5.26 (4H, dd, J = 10.5, 1.5 Hz, H8), 5.39 (4H, dd, J = 17.0, 1.5 Hz, H8'), 5.98–6.06 (4H, m, H7), 6.65 (8H, d, J = 8.5 Hz, H4), 6.92 (8H, br s, H3). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  68.65 (C6), 113.73 (C4), 117.59 (C8), 132.54 (C3), 133.34 (C7), 136.98 (C2), 138.42 (C1), 156.85 (C5). ESI-MS: found MH<sup>+</sup> = 557.2685; C<sub>38</sub>H<sub>37</sub>O<sub>4</sub> requires MH<sup>+</sup> = 557.2686. IR (cm<sup>-1</sup>): 3022, 2987, 2879, 2734, 2525, 1893, 1647, 1606, 1572, 1500, 1454, 1407, 1380, 1284, 1244, 1173, 1113, 996, 928, 863, 837, 800, 767, 745. Elem. Anal. Found: C, 82.17; H, 6.59. Calcd. for C<sub>38</sub>H<sub>36</sub>O<sub>4</sub>: C, 81.99; H, 6.52.



- 10. Crystal data for **2**:  $C_{38}H_{36}O_4$ , FW 556.67, monoclinic, space group  $P_{2_1/n}$ , a = 9.2476(3), b = 24.8457(9), c = 13.2688(5)Å,  $\beta = 99.980(2)^\circ$ , V = 3002.55(18)Å<sup>3</sup>, F(000) = 1184, Z = 4, T = -158 °C,  $\mu$ (MoK $\alpha$ ) = 0.079 mm<sup>-1</sup>,  $D_{calcd} = 1.231$  g cm<sup>-3</sup>,  $2\theta_{max}$  54° (ApexII CCD area detector, MoK $\alpha$  radiation), GOF = 1.12, wR( $F^2$ ) = 0.1386 (all 6433 data), R = 0.0620 (5253 data with  $I > 2\sigma I$ ).
- 11. Yield 65%. Mp 95–97 °C. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  4.51 (4H, d, J = 5.0 Hz), 4.79 (2H, d, J = 5.5 Hz), 5.25–5.52 (6H, m), 6.02–6.10 (2H, m), 6.13–6.20 (1H, m), 6.78–6.82 (5H, m), 7.02–7.08 (5H, m), 7.17 (1H, d, J = 9.5 Hz), 7.31 (1H, d, J = 9.0 Hz), 8.11 (1H, s), 8.65 (1H, d, J = 9.5 Hz). IR (cm<sup>-1</sup>): 3093, 2870, 1611, 1527, 1497, 1454, 1424, 1367, 1327, 1281, 1225, 1197, 1178, 1042, 830, 780, 617. ESI-MS: Found MAg<sup>+</sup> = 621.1201; C<sub>35</sub>H<sub>30</sub>O<sub>4</sub>Ag requires MAg<sup>+</sup> = 621.1190.
- 617. ESI-MS: Foldid MAg = 0.21.1201; C<sub>33</sub>H<sub>30</sub>O<sub>4</sub>Ag requires MAg = 0.21.130. 12. Crystal data for the silver complex of 4: C<sub>70</sub>H<sub>64</sub>Ag<sub>3</sub>Cl<sub>3</sub>O<sub>22</sub>, FW 1687.17, triclinic, space group P-1, *a* = 9.4014(8), *b* = 12.8095(11), *c* = 15.4812(9)Å, *α* = 100.618(6), *β* = 106.646(6), *γ* = 104.621(7)°, *V* = 1660.9(2)Å<sup>3</sup>, *F*(000) = 852, *Z* = 1, *T* = -153 °C, *μ*(CuKα) = 8.811 mm<sup>-1</sup>, *D*<sub>calcd</sub> = 1.687 g cm<sup>-3</sup>, 2θ<sub>max</sub> 135° (Agilent Supernova area detector, CuKα radiation), GOF = 1.028, wR(F<sup>2</sup>) = 0.1514 (all 5991 data), *R* = 0.0564 (4724 data with *I* > 2*σI*).

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   *Data for* **4**: yield 63%. Mp 127–129 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.51 (4H, d,
- 44. Data for **4**: yield 63%. Mp 127–129 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.51 (4H, d, J = 5.1 Hz, H11, H16), 4.76 (2H, d, J = 4.3 Hz, H17), 5.51 (1H, d, J = 17.2 Hz, H19b), 5.41 (2H, d, J = 17.2 Hz, H13b, H14b), 5.35 (1H, d, J = 10.5 Hz, H19a), 5.29 (2H, d, J = 10.6 Hz, H13a, H14a), 6.14–6.19 (1H, m, H18), 6.03–6.11 (2H, m, H12, H15), 6.78–6.80 (4H, m, H1, H10), 6.89 (1H, s, H8), 7.00–7.02 (4H, m, H2, H9), 7.07 (1H, d, J = 9.0 Hz, H4), 7.19 (1H, d, J = 8.6 Hz, H7), 7.47 (1H, d, J = 9.4 Hz, H3), 8.06 (1H, s, H5), 8.56 (1H, d, J = 9.0 Hz, H6). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 68.71, 68.73, 69.10, 104.76, 111.29, 113.82, 113.97, 115.78, 115.88, 115.86, 117.68, 117.71, 117.94, 123.88, 124.59, 126.02, 129.52, 131.44, 131.89, 132.14, 132.22, 132.29, 133.30, 133.34, 134.04, 134.32, 137.71, 154.27, 156.97, 156.98, 157.28. IR (cm<sup>-1</sup>): 3093, 2870, 1716, 1647, 1608, 1575, 1506, 1456, 1421, 1281, 1173, 1107, 1013, 992, 916, 866, 828, 795, 777, 631. ESI-MS: found MH<sup>+</sup> = 515.2224; C<sub>35</sub>H<sub>3</sub>10<sub>4</sub> requires MH<sup>+</sup> = 515.2217. Elem. Anal. Found: C, 78.97; H, 5.81. Calcd. for C<sub>35</sub>H<sub>30</sub>O<sub>4</sub>·H<sub>2</sub>O: C, 78.92; H, 6.06.



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