

# Application of 2,6-Diphenylpyridine as a Tridentate [C<sup>-</sup>N<sup>-</sup>C] Dianionic Ligand in Organogold(III) Chemistry. Structural and Spectroscopic Properties of Mono- and Binuclear Transmetalated Gold(III) Complexes

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The synthesis of a series of mono- and binuclear cyclometalated gold(III) complexes containing the tridentate C<sup>-</sup>N<sup>-</sup>C ligand (HC<sup>-</sup>N<sup>-</sup>CH = 2,6-diphenylpyridine) was developed using K[AuCl<sub>4</sub>] and the organomercury(II) compound Hg(C<sup>-</sup>N<sup>-</sup>CH)Cl as precursors. The molecular structures of [Au(C<sup>-</sup>N<sup>-</sup>C)(Spy-2)] (Spy-2 = 2-mercaptopyridine), [Au(C<sup>-</sup>N<sup>-</sup>C)PPh<sub>3</sub>]-ClO<sub>4</sub>, [Au<sub>2</sub>(C<sup>-</sup>N<sup>-</sup>C)<sub>2</sub>(μ-dppm)](ClO<sub>4</sub>)<sub>2</sub>, and [Au<sub>2</sub>(C<sup>-</sup>N<sup>-</sup>C)<sub>2</sub>(μ-dppe)](ClO<sub>4</sub>)<sub>2</sub> have been determined by X-ray crystallography. In the crystal lattice of [Au<sub>2</sub>(C<sup>-</sup>N<sup>-</sup>C)<sub>2</sub>(μ-dppm)](ClO<sub>4</sub>)<sub>2</sub> and [Au<sub>2</sub>(C<sup>-</sup>N<sup>-</sup>C)<sub>2</sub>(μ-dppe)](ClO<sub>4</sub>)<sub>2</sub>, interplanar separations of 3.4 Å are observed between the intramolecular [Au(C<sup>-</sup>N<sup>-</sup>C)] moieties, which imply the presence of weak π–π interactions. The torsion angle between the two [Au(C<sup>-</sup>N<sup>-</sup>C)] units in the former is 8.7°, while a larger angle (34.2°) is observed in the latter. In the absorption spectra, the binuclear complexes show a red shift for the absorption band in the near-visible region compared to the mononuclear analogues. This is attributed to π–π interactions between the intramolecular C<sup>-</sup>N<sup>-</sup>C ligands in solution. The new complexes are emissive at low temperatures (77 K) in acetonitrile.

## Introduction

While numerous organogold(III) complexes have been reported in the last 15 years,<sup>1</sup> accounts of their spectroscopic properties have seldom appeared. Recently, the cyclometalated derivatives [Au(L)Cl]<sup>+</sup>, where L is a tridentate carbanion of 2,9-diphenyl-1,10-phenanthroline<sup>2</sup> or 4'-(4-methoxyphenyl)-6'-phenyl-2,2'-bipyridine,<sup>3</sup> were found to be emissive, and the molecular structure of the former revealed stacking of pairs of [Au(L)Cl]<sup>+</sup> units in the solid state. In our endeavor to probe the intra- and intermolecular interactions of organogold(III) species, we initiated a program toward the preparation of binuclear face-to-face cyclometalated gold(III) complexes. Prominently, in the isoelectronic platinum(II) system, recent studies have highlighted the rich photophysical and photochemical properties of complexes supported by aromatic diimine and cyclometalated ligands.<sup>4</sup> The more electrophilic gold(III) ion should favor substrate-binding reactions, and in this context,

gold(III) complexes have potential applications as metal therapeutics for DNA binding. Indeed, metallointercalators for DNA bearing 2,2',2''-terpyridine (terpy) and cyclometalated 6'-phenyl-2,2'-bipyridine ligands ((C<sup>-</sup>N<sup>-</sup>N)<sup>-</sup>) have been described by Lippard and co-workers<sup>5</sup> and by our group.<sup>3</sup> In light of the reactivity displayed by gold(III) derivatives containing the neutral terpy and the (C<sup>-</sup>N<sup>-</sup>N)<sup>-</sup> carbanion, we envisaged that incorporation of the next logical tridentate ligand in the series, namely the dicarbanion (C<sup>-</sup>N<sup>-</sup>C)<sup>2-</sup> which would coordinate in a transmetalated fashion, would also yield photochemically interesting species.

Cyclometalated gold(III) complexes with one gold–carbon bond are typically supported by nitrogen-donor ligands.<sup>6–9</sup> There are many examples of *cis*-diorganogold(III),<sup>1,10</sup> -palladium(II), and -platinum(II)

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derivatives,<sup>10c,11</sup> cyclometalated or otherwise, but the C,C-*trans* arrangement is unknown for Au(III) and rare for Pd(II) and Pt(II) systems.<sup>12</sup> Employment of 2,6-diphenylpyridine as a tridentate trans-dianionic ligand was attempted by Selbin and co-workers<sup>13</sup> (for Pd(II)) and described by von Zelewsky and co-workers<sup>14</sup> (for Pt(II) and Pd(II)), but no crystal structures were reported. In this present study, we describe the synthesis and photophysical characteristics of a series of mono- and binuclear cyclometalated gold(III) derivatives which are, to the best of our knowledge, the first structurally characterized complexes to contain the tridentate (C<sup>∧</sup>N<sup>∧</sup>C)<sup>2-</sup> motif derived from 2,6-diphenylpyridine.

## Experimental Section

**General Procedures.** All starting materials were used as received from commercial sources, and the solvents were purified according to conventional methods.<sup>15</sup> K[AuCl<sub>4</sub>] (98%) was purchased from Aldrich Chemical Co. Hg(C<sup>∧</sup>N<sup>∧</sup>CH)Cl was prepared using published procedures.<sup>16</sup> UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer. Emission spectra were obtained on a SPEX Fluorolog-2 Model F11 fluorescence spectrophotometer. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra<sup>17</sup> were recorded on a DPX-300 Bruker FT-NMR spectrometer with chemical shifts (in ppm) relative to tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) and external H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Elemental analysis was performed by Butterworth Laboratories Ltd., Teddington, U.K.

**Synthesis. [Au(C<sup>∧</sup>N<sup>∧</sup>C)Cl] (1).** A mixture of K[AuCl<sub>4</sub>] (0.16 g, 0.43 mmol) and Hg(C<sup>∧</sup>N<sup>∧</sup>CH)Cl (0.20 g, 0.43 mmol) in acetonitrile (30 cm<sup>3</sup>) was refluxed for 24 h to afford a greenish yellow precipitate. The solid was filtered and washed with diethyl ether: yield 0.10 g, 50%. Anal. Calcd for C<sub>17</sub>H<sub>11</sub>N<sub>2</sub>AuCl: C, 44.22; H, 2.40; N, 3.03. Found: C, 44.31; H, 2.35; N, 3.29. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 8.21 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz), 7.99 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz), 7.89 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 7.70 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 7.43 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 7.31 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz); all C<sup>∧</sup>N<sup>∧</sup>C.

**[Au(C<sup>∧</sup>N<sup>∧</sup>C)(Meim-1)]ClO<sub>4</sub> (2(ClO<sub>4</sub>)).** 1-Methylimidazole (0.10 mL, 1.26 mmol) was added to a stirred suspension of complex **1** (0.05 g, 0.11 mmol) in acetonitrile (30 cm<sup>3</sup>). After 2 h, the solution became clear and excess LiClO<sub>4</sub> was added.

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(17) The poor solubility of complexes **1** and **3** in common deuterated solvents precluded their characterization by <sup>13</sup>C NMR spectroscopy.

After the mixture was stirred for a further 3 h, a yellow precipitate appeared which was collected and washed with diethyl ether. Recrystallization by diffusion of diethyl ether into an acetonitrile/dimethylformamide solution afforded yellow crystals: yield 0.04 g, 78%. Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>-AuCl: C, 41.50; H, 2.82; N, 6.91. Found: C, 41.55; H, 2.78; N, 7.05. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 8.28 (s, 1H, H(2)-im); 8.11 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz), 7.74 (m, 4H), 7.53 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz), 7.45 (d, 1H, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz), 7.38 (m, 4H), 7.04 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz), C<sup>∧</sup>N<sup>∧</sup>C and im; 3.96 (s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 169.3, 166.3 (C<sup>∧</sup>N<sup>∧</sup>C); 149.1 (im); 145.9 (C<sup>∧</sup>N<sup>∧</sup>C); 140.1 (im); 133.4, 133.1, 129.3 (C<sup>∧</sup>N<sup>∧</sup>C); 128.3 (im); 127.3, 125.0, 119.5 (C<sup>∧</sup>N<sup>∧</sup>C); 36.3 (Me).

**[Au(C<sup>∧</sup>N<sup>∧</sup>C)(Spy-2)] (3).** Triethylamine (0.10 mL, 0.72 mmol) was added to a stirred suspension of **1** (0.05 g, 0.11 mmol) and 2-mercaptopyridine (0.01 g, 0.11 mmol) in acetonitrile (30 mL). After 6 h, the resultant yellow precipitate was filtered, washed with diethyl ether, and recrystallized by the method used for complex **2**(ClO<sub>4</sub>): yield 0.03 g, 56%. Anal. Calcd for C<sub>22</sub>H<sub>15</sub>N<sub>2</sub>AuS: C, 49.26; H, 2.82; N, 5.22. Found: C, 49.20; H, 2.87; N, 5.27. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 8.20 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 8.00 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz), 7.90 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz), 7.50 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz), 7.45 (m, 3H), 7.25 (m, 4H), 6.98 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz), C<sup>∧</sup>N<sup>∧</sup>C and Spy.

**[Au(C<sup>∧</sup>N<sup>∧</sup>C)PPh<sub>3</sub>]ClO<sub>4</sub> (4(ClO<sub>4</sub>)).** The procedure was similar to that for **2**(ClO<sub>4</sub>), except **1** (0.05 g, 0.11 mmol) and triphenylphosphine (0.03 g, 0.11 mmol) were used: yield 0.05 g, 60%. Anal. Calcd for C<sub>35</sub>H<sub>26</sub>NO<sub>4</sub>AuClP: C, 53.35; H, 3.33; N, 1.78. Found: C, 53.51; H, 3.28; N, 1.67. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 8.16 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz), 7.81 (m, 13H), 7.60 (m, 6H), 7.23 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 6.87 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 6.16 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), C<sup>∧</sup>N<sup>∧</sup>C and PPh<sub>3</sub>. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 165.8, 164.8 (C<sup>∧</sup>N<sup>∧</sup>C); 151.9 (PPh<sub>3</sub>); 145.6 (C<sup>∧</sup>N<sup>∧</sup>C); 136.5 (d, J<sub>PC</sub> = 11.6 Hz, PPh<sub>3</sub>); 135.9, 134.8 (C<sup>∧</sup>N<sup>∧</sup>C); 132.0 (PPh<sub>3</sub>); 130.7 (d, J<sub>PC</sub> = 12.5 Hz, PPh<sub>3</sub>); 129.1, 127.6 (C<sup>∧</sup>N<sup>∧</sup>C); 124.8 (d, J<sub>PC</sub> = 67.8 Hz, Au-C); 119.6 (C<sup>∧</sup>N<sup>∧</sup>C). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 35.2.

**[Au<sub>2</sub>(C<sup>∧</sup>N<sup>∧</sup>C)<sub>2</sub>(μ-dppm)](ClO<sub>4</sub>)<sub>2</sub> (5(ClO<sub>4</sub>)<sub>2</sub>).** A mixture of **1** (0.10 g, 0.22 mmol) and bis(diphenylphosphino)methane (0.04 g, 0.11 mmol) in acetonitrile (40 mL) was stirred for 2 h. Excess LiClO<sub>4</sub> was then added to yield a yellow precipitate, which was filtered, washed with diethyl ether, and recrystallized by the method used for **2**(ClO<sub>4</sub>): yield 0.08 g, 50%. Anal. Calcd for C<sub>59</sub>H<sub>44</sub>N<sub>2</sub>O<sub>8</sub>Au<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub>: C, 49.36; H, 3.09; N, 1.95. Found: C, 49.40; H, 3.18; N, 1.83. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 8.04 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz), 7.88 (m, 8H), 7.64 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 7.47 (m, 16H), 6.97 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 6.58 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 6.41 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), C<sup>∧</sup>N<sup>∧</sup>C and PPh<sub>2</sub>; 5.28 (t, 2H, <sup>2</sup>J<sub>PH</sub> = 14.5 Hz, PCH<sub>2</sub>P). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 165.8, 164.2 (C<sup>∧</sup>N<sup>∧</sup>C); 151.1 (PPh<sub>2</sub>); 145.4, 137.0, 135.2 (C<sup>∧</sup>N<sup>∧</sup>C); 134.9 (d, J<sub>PC</sub> = 12.2 Hz, PPh<sub>2</sub>); 132.1 (PPh<sub>2</sub>); 130.7 (d, J<sub>PC</sub> = 10.7 Hz, PPh<sub>2</sub>); 129.4, 128.3 (C<sup>∧</sup>N<sup>∧</sup>C); 125.5 (d, J<sub>PC</sub> = 63.8 Hz, Au-C); 119.9 (C<sup>∧</sup>N<sup>∧</sup>C); 21.4 (t, J<sub>PC</sub> = 32.7 Hz, PCH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 25.8.

**[Au<sub>2</sub>(C<sup>∧</sup>N<sup>∧</sup>C)<sub>2</sub>(μ-dppe)](ClO<sub>4</sub>)<sub>2</sub> (6(ClO<sub>4</sub>)<sub>2</sub>).** The procedure was similar to that for **5**(ClO<sub>4</sub>)<sub>2</sub>, except 1,2-bis(diphenylphosphino)ethane was used: yield 0.07 g, 45%. Anal. Calcd for C<sub>60</sub>H<sub>46</sub>N<sub>2</sub>O<sub>8</sub>Au<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub>: C, 49.71; H, 3.20; N, 1.93. Found: C, 49.57; H, 3.15; N, 1.90. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 8.04 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz), 7.94 (m, 8H), 7.58 (m, 8H), 7.49 (m, 8H), 7.39 (dd, 4H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz), 6.96 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 6.44 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 6.09 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), C<sup>∧</sup>N<sup>∧</sup>C and PPh<sub>2</sub>; 4.07 (s, 4H, PCH<sub>2</sub>CH<sub>2</sub>P). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 166.0, 164.1 (C<sup>∧</sup>N<sup>∧</sup>C); 151.6 (PPh<sub>2</sub>); 145.2, 135.8, 134.7 (C<sup>∧</sup>N<sup>∧</sup>C); 134.0 (t, J<sub>PC</sub> = 5.6 Hz, PPh<sub>2</sub>); 132.1 (PPh<sub>2</sub>); 130.7 (t, J<sub>PC</sub> = 6.2 Hz, PPh<sub>2</sub>); 129.1, 128.1 (C<sup>∧</sup>N<sup>∧</sup>C); 125.9 (d, J<sub>PC</sub> = 66.4 Hz, Au-C); 119.9 (C<sup>∧</sup>N<sup>∧</sup>C); 18.6 (t, J<sub>PC</sub> = 21.2 Hz, PCH<sub>2</sub>CH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 35.0.

**X-ray Crystallography.** Crystal data and details of collection and refinement are summarized in Table 1. All crystals

Table 1. Crystal Data

	<b>3</b>	<b>4</b> (ClO <sub>4</sub> )	<b>5</b> (ClO <sub>4</sub> ) <sub>2</sub> ·1.5(CH <sub>3</sub> ) <sub>2</sub> NCHO	<b>6</b> (ClO <sub>4</sub> ) <sub>2</sub> ·CH <sub>3</sub> CN
formula	[C <sub>22</sub> H <sub>15</sub> N <sub>2</sub> AuS]	[C <sub>35</sub> H <sub>26</sub> NAuP]ClO <sub>4</sub>	[C <sub>59</sub> H <sub>44</sub> N <sub>2</sub> Au <sub>2</sub> P <sub>2</sub> ] <sub>2</sub> (ClO <sub>4</sub> ) <sub>4</sub> ·3(CH <sub>3</sub> ) <sub>2</sub> NCHO	[C <sub>60</sub> H <sub>46</sub> N <sub>2</sub> Au <sub>2</sub> P <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·CH <sub>3</sub> CN
fw	536.40	787.99	3090.89	1490.88
color	yellow	yellow	yellow	yellow
cryst size, mm	0.15 × 0.08 × 0.30	0.15 × 0.10 × 0.25	0.20 × 0.15 × 0.40	0.20 × 0.15 × 0.30
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>a</i> (No. 14)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	<i>P</i> 2/ <i>c</i> (No. 13)
<i>a</i> , Å	7.686(2)	9.795(2)	17.429(6)	19.889(3)
<i>b</i> , Å	23.845(3)	10.081(2)	25.73(1)	15.157(3)
<i>c</i> , Å	9.546(2)	16.101(3)	14.500(6)	19.907(3)
α, deg		103.42(2)	103.57(3)	
β, deg	91.52(2)	101.29(2)	99.82(3)	101.87(2)
γ, deg		96.93(2)	103.23(3)	
<i>V</i> , Å <sup>3</sup>	1748.9(5)	1493.4(6)	5976(4)	5872(1)
<i>Z</i>	4	2	2	4
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	2.037	1.752	1.717	1.686
<i>μ</i> , cm <sup>-1</sup>	85.68	51.27	51.25	52.10
<i>F</i> (000)	1024	772	3032	2912
no. of unique data	3427	5669	17 665	10 692
no. of obsd data with <i>I</i> ≥ 3σ( <i>I</i> )	3061	4613	10 093	8200
no. of variables	235	388	1331	710
<i>R</i> <sup>a</sup>	0.035	0.028	0.051	0.037
<i>R<sub>w</sub></i> <sup>b</sup>	0.044	0.035	0.071	0.054
GoF, <i>S</i> <sup>c</sup>	1.61	1.54	2.19	1.62

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}, \quad ^c S = [\sum w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}.$$

were grown by slow diffusion of diethyl ether into acetonitrile/dimethylformamide solutions.

For **3**, **4**(ClO<sub>4</sub>), and **6**(ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>CN, diffraction experiments were performed on a MAR diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The images were interpreted and intensities integrated using program DENZO.<sup>18</sup> The structures were solved by Patterson methods, expanded by Fourier methods (PATTY<sup>19</sup>), and refined by full-matrix least squares using the software package TeXsan<sup>20</sup> on a Silicon Graphics Indy computer. For **3**, one formula unit constitutes a crystallographic asymmetric unit. All 26 non-H atoms were refined anisotropically. Fifteen H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. For **4**(ClO<sub>4</sub>), one formula unit constitutes a crystallographic asymmetric unit. All 43 non-H atoms were refined anisotropically. A total of 26 H atoms at calculated positions were not refined. For **6**(ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>CN, one crystallographic asymmetric unit consists of one complex cation, one perchlorate anion, two half-perchlorate anions with chlorine atoms at special positions with an occupation number of 0.5, and one CH<sub>3</sub>CN solvent molecule. All 79 non-H atoms were refined anisotropically. A total of 49 H atoms at calculated positions were not refined.

For **5**(ClO<sub>4</sub>)<sub>2</sub>·1.5(CH<sub>3</sub>)<sub>2</sub>NCHO, the diffraction experiment was performed on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods (SIR92<sup>21</sup>), expanded by Fourier methods, and refined by full-matrix least squares using the software package TeXsan.<sup>20</sup> One crystallographic asymmetric unit consists of two independent complex cations, four perchlorate anions, and three solvent molecules.

(18) DENZO: Gewirth, D. (with the cooperation of the program authors Otwinowski, Z., and Minor, W.) In *The HKL Manual—A Description of Programs DENZO, XDISPLAYF, and SCALEPACK*; Yale University: New Haven, CT, 1995.

(19) PATTY: Beurskens, P. R.; Admiraal, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The *DIRDIF* Program System, Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.

(20) TeXsan: Crystal Structure Analysis Package; Molecular Structure Corp. The Woodlands, TX, 1985 and 1992.

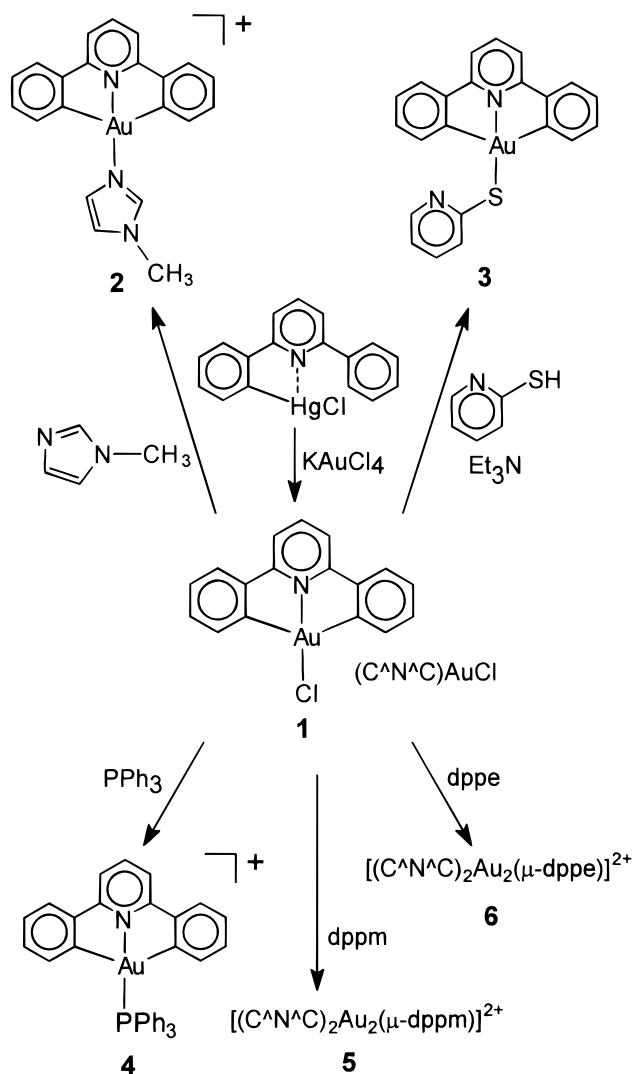
(21) SIR92: Altomare, A.; Casciarano, M.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

All non-H atoms of the complex cations and the four chlorine atoms of the perchlorate anions were refined anisotropically. The oxygen atoms of the perchlorate anions and the non-H atoms of the solvent molecules have large thermal motion and were refined isotropically. A total of 109 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were included in the calculation but not refined.

## Results and Discussion

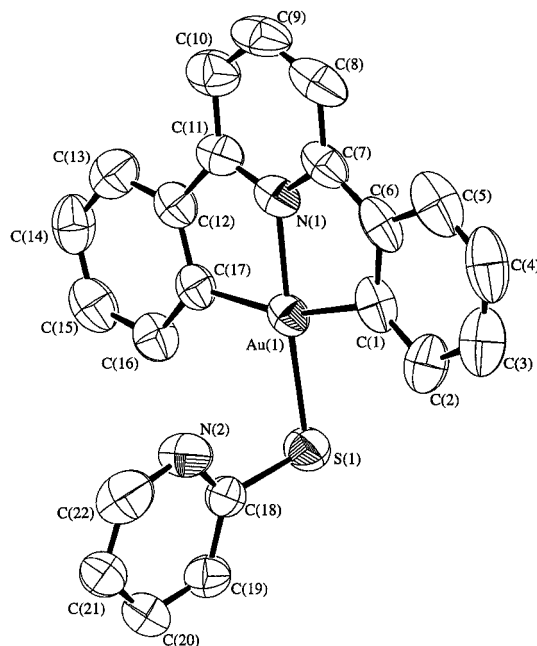
Formation of cycloaurated complexes can be effected by two methods.<sup>2,3,6–10</sup> Direct C–H activation of appropriate chelating ligands in the presence of AuCl<sub>4</sub><sup>-</sup> is usually performed at elevated temperatures. The alternative method of transmetalation using organomercury(II) or -tin(IV) reagents is often preferred, because the transformations are normally cleaner and can be achieved under ambient conditions. In this work, treatment of 2,6-diphenylpyridine with mercury(II) acetate followed by metathesis with LiCl yielded the organomercury(II) species Hg(C<sup>^N^</sup>CH)Cl,<sup>16</sup> and subsequent transmetalation with K[AuCl<sub>4</sub>] in refluxing acetonitrile gave [Au(C<sup>^N^</sup>C)Cl] (**1**). Complex **1** has low solubility in acetonitrile and is readily isolated from the reaction mixture. Facile displacement of the chloride group is achieved by reaction with the appropriate nitrogen, sulfur, and phosphorus ligands and allows for the derivatization of the [Au(C<sup>^N^</sup>C)] fragment (Scheme 1). For complex **2**, the 1-methylimidazole ligand presumably binds at the 3-*N* position due to steric constraints. The <sup>1</sup>H NMR spectra for **1–6**, although not fully assigned due to the large number of overlapping signals in the aromatic region, display the correct number of proton environments for each complex. The phosphorus-ligated species **4–6** are characterized by a single, sharp signal in their respective <sup>31</sup>P NMR spectra, and for **5** and **6**, this confirms that the two phosphine atoms of the bridging dpmm and dppe ligands respectively are chemically equivalent.

**Crystal Structures.** This account features the first examples of *trans*-diorganylgold(III) complexes to be

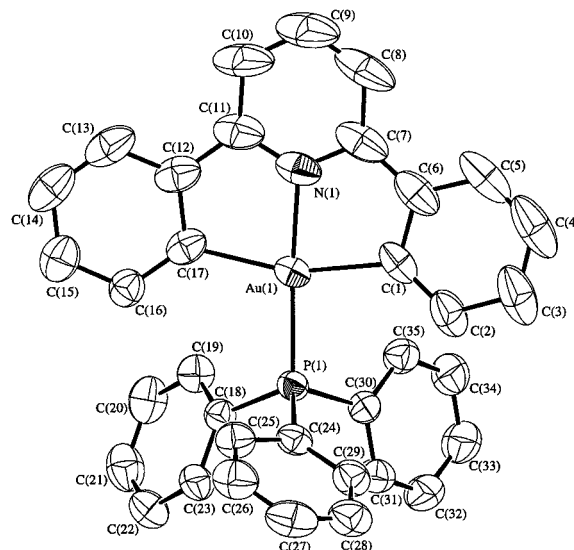
Scheme 1<sup>a</sup>

<sup>a</sup> All reactions in acetonitrile.

characterized by X-ray crystallography. Perspective views of **3**–**6** are shown in Figures 1–4, respectively. Selected bond distances and angles are listed in Table 2. The observed gold–carbon distances in the mono- (mean 2.093 Å) and binuclear (mean 2.119 Å) derivatives are noticeably longer than those in related cycloaurated complexes with trans chloride ligands (e.g.  $[\text{Au}(\text{L})\text{Cl}_2]$ : L = 4,4-dimethyl-2-phenyl-2-oxazoline,<sup>9b</sup> 2.040(8) Å; L = 2-(2-pyridylcarbonyl)phenyl,<sup>9a</sup> 2.033(7) Å), which in turn are more elongated than those with trans pyridine groups (e.g.  $[\text{Au}(\text{L})\text{Cl}]^+$ : L = 2,9-diphenyl-1,10-phenanthroline,<sup>2</sup> 2.017(7) Å; L = 6-CMe<sub>2</sub>Ph-2,2'-bipyridine,<sup>9c</sup> 2.009(6) Å). This trend is in accordance with the relative trans influences in the order  $\text{py} < \text{Cl}^- < \text{C}_6\text{H}_5^-$ . In contrast, the gold–N(pyridyl) contacts in these structures are comparable. The respective angles between the trans aryl carbon atoms in **3**–**6** (range 158.3(7)–161.9(3)°) are significantly deviated from linearity. This is attributed to the tethered nature of the phenyl substituents with respect to the pyridine ring, which evidently restricts the bite angle. The gold–sulfur bond length of 2.296(2) Å in **3** is very similar to those in the gold(I) complexes  $\text{Au}(\text{8-S-quinoline})(\text{PPh}_3)$



**Figure 1.** Perspective view of  $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{Spy-2})]$  (**3**) (50% probability ellipsoids).



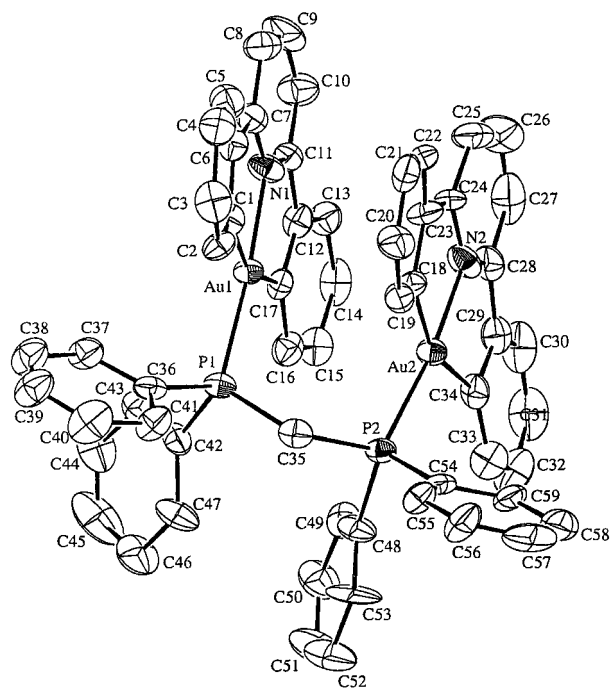
**Figure 2.** Perspective view of  $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{PPh}_3]^+$  (**4**) (50% probability ellipsoids).

(2.296(8) Å)<sup>22</sup> and  $[\text{Au}_2(\mu\text{-S}(\text{CH}_2)_3\text{S})(\mu\text{-dppm})]$  (2.281(4) and 2.288(3) Å).<sup>23</sup> In **4**, the Au(1)–P(1) distance (2.283(1) Å) resembles that in  $[\text{AuCl}\{2\text{-}(2\text{-pyridylmethyl})\text{-phenyl}\}(\text{PPh}_3)]\text{BF}_4$  (2.311(3) Å).<sup>9a</sup> No intermolecular face-to-face stacking interactions are apparent in **3** and **4**.

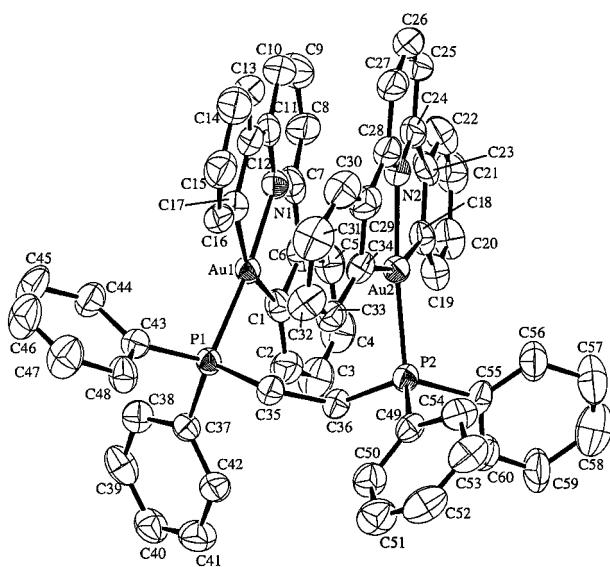
For the binuclear derivatives **5** and **6**, the dihedral angle between the two intramolecular  $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$  planes is 4.6 and 5.7°, respectively; in other words, the  $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$  moieties are virtually parallel to each other. The average interplanar distance between these two planes is 3.40 Å for **5** and 3.44 Å for **6**, which is further than the upper limit for Au⋯Au interactions (2.5–3.2 Å<sup>1</sup>). However,  $\pi$ -stacking interactions are

(22) Tzeng, B. C.; Chan, C. K.; Cheung, K. K.; Che, C. M.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1997**, 135.

(23) Dávila, R. M.; Elduque, A.; Grant, T.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* **1993**, *32*, 1749.



**Figure 3.** Perspective view of molecule A in  $[\text{Au}_2(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})_2-(\mu\text{-dppm})]^{2+}$  (**5**) (40% probability ellipsoids).



**Figure 4.** Perspective view of  $[\text{Au}_2(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})_2(\mu\text{-dppe})]^{2+}$  (**6**) (50% probability ellipsoids).

possible, since  $\pi$ - $\pi$  interactions in planar aromatic hydrocarbons can occur up to 3.8 Å and are indeed most favorable at around 3.4 Å.<sup>24</sup> It is notable that the average interplanar separations are almost identical for **5** and **6**, even though an additional methylene group is incorporated into the bridging diphosphine ligand of the latter. One significant difference between the structures of **5** and **6** is the respective torsion angle between the two intramolecular  $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$  units (defined by the dihedral angle between the  $\text{Au}(1)-\text{Au}(2)-\text{C}(9)$  and  $\text{Au}(1)-\text{Au}(2)-\text{C}(26)$  planes), which is 8.7° in **5** while a larger angle (34.2°) is observed in **6**. To achieve maximum overlap of the  $\pi$  orbitals, the two  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  ligands should stack in a face-to-face manner. However,

(24) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

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

Complex 3			
Au(1)-S(1)	2.296(2)	Au(1)-N(1)	2.003(5)
Au(1)-C(1)	2.078(6)	Au(1)-C(17)	2.086(7)
S(1)-Au(1)-N(1)	176.5(1)	S(1)-Au(1)-C(1)	99.3(2)
S(1)-Au(1)-C(17)	98.7(2)	N(1)-Au(1)-C(1)	80.7(3)
N(1)-Au(1)-C(17)	81.2(2)	C(1)-Au(1)-C(17)	161.9(3)
Au(1)-S(1)-C(18)	101.8(2)		
Complex 4(ClO <sub>4</sub> )			
Au(1)-P(1)	2.283(1)	Au(1)-N(1)	2.036(4)
Au(1)-C(1)	2.099(5)	Au(1)-C(17)	2.107(5)
P(1)-Au(1)-N(1)	174.5(1)	P(1)-Au(1)-C(1)	97.6(1)
P(1)-Au(1)-C(17)	102.2(1)	N(1)-Au(1)-C(1)	79.9(2)
N(1)-Au(1)-C(17)	80.6(2)	C(1)-Au(1)-C(17)	159.9(2)
Complex 5(ClO <sub>4</sub> ) <sub>2</sub> ·1.5(CH <sub>3</sub> ) <sub>2</sub> NCHO			
Molecule A			
Au(1)-P(1)	2.297(4)	Au(1)-N(1)	2.040(1)
Au(1)-C(1)	2.100(2)	Au(1)-C(17)	2.100(2)
Au(2)-P(2)	2.287(4)	Au(2)-N(2)	2.010(1)
Au(2)-C(18)	2.120(2)	Au(2)-C(34)	2.140(2)
P(1)-Au(1)-N(1)	175.3(5)	P(1)-Au(1)-C(1)	98.3(5)
P(1)-Au(1)-C(17)	103.0(5)	N(1)-Au(1)-C(1)	80.1(7)
N(1)-Au(1)-C(17)	78.8(7)	C(1)-Au(1)-C(17)	158.7(7)
P(2)-Au(2)-N(2)	173.9(5)	P(2)-Au(2)-C(18)	95.5(5)
P(2)-Au(2)-C(34)	103.1(5)	N(2)-Au(2)-C(18)	83.1(7)
N(2)-Au(2)-C(34)	78.9(8)	C(18)-Au(2)-C(34)	160.8(7)
Molecule B			
Au(3)-P(3)	2.305(4)	Au(3)-N(3)	2.040(1)
Au(3)-C(60)	2.120(2)	Au(3)-C(76)	2.130(2)
Au(4)-P(4)	2.291(5)	Au(4)-N(4)	2.050(1)
Au(4)-C(77)	2.160(2)	Au(4)-C(93)	2.130(2)
P(3)-Au(3)-N(3)	175.8(5)	P(3)-Au(3)-C(60)	97.3(5)
P(3)-Au(3)-C(76)	104.1(5)	N(3)-Au(3)-C(60)	80.6(6)
N(3)-Au(3)-C(76)	78.2(6)	C(60)-Au(3)-C(76)	158.3(7)
P(4)-Au(4)-N(4)	172.8(4)	P(4)-Au(4)-C(77)	95.6(5)
P(4)-Au(4)-C(93)	105.1(6)	N(4)-Au(4)-C(77)	80.5(7)
N(4)-Au(4)-C(93)	79.4(7)	C(77)-Au(4)-C(93)	158.6(7)
Complex 6(ClO <sub>4</sub> ) <sub>2</sub> ·CH <sub>3</sub> CN			
Au(1)-P(1)	2.281(2)	Au(1)-N(1)	2.030(6)
Au(1)-C(1)	2.114(7)	Au(1)-C(17)	2.116(7)
Au(2)-P(2)	2.280(2)	Au(2)-N(2)	2.019(6)
Au(2)-C(18)	2.099(7)	Au(2)-C(34)	2.099(7)
P(1)-Au(1)-N(1)	174.9(2)	P(1)-Au(1)-C(1)	102.4(2)
P(1)-Au(1)-C(17)	96.9(2)	N(1)-Au(1)-C(1)	80.5(3)
N(1)-Au(1)-C(17)	80.6(3)	C(1)-Au(1)-C(17)	160.4(3)
P(2)-Au(2)-N(2)	174.5(2)	P(2)-Au(2)-C(18)	97.9(2)
P(2)-Au(2)-C(34)	101.4(2)	N(2)-Au(2)-C(18)	80.4(3)
N(2)-Au(2)-C(34)	80.8(3)	C(18)-Au(2)-C(34)	160.2(3)

$\pi$ - $\pi$  repulsive interactions disfavor an eclipsed geometry, and the most stable orientation results in a twist of around 45°, which optimizes the  $\pi$ -stacking.<sup>24</sup> The experimental value observed in **6** approaches this, and many examples have been found in biological systems.<sup>25</sup> The greater rigidity of the dppm ligand in **5** limits twisting of the two  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  ligands so that only a small torsion angle is evident. Hence, the crystal structures of **5** and **6** are good models for illustrating  $\pi$ -stacking interactions in organometallic complexes.

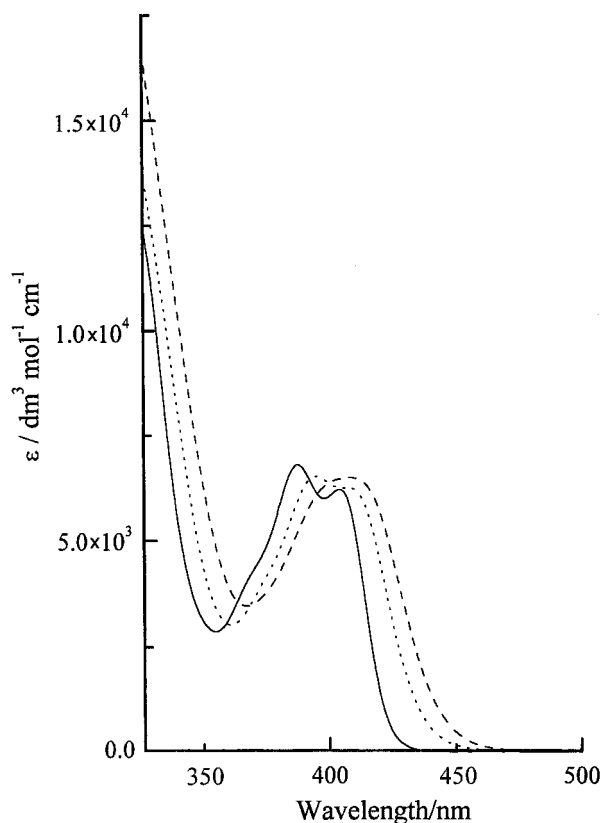
**Absorption and Emission Data.** The UV-vis absorption and emission data for complexes **1-6** are summarized in Table 3. For the mononuclear complexes, there is a characteristic absorption with vibronic

(25) (a) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984; pp 132-140. (b) Langlet, J.; Claverie, P.; Caron, F.; Boeue, J. C. *Int. J. Quantum Chem.* **1981**, *19*, 299. (c) Claverie, P. In *Intermolecular Interactions. From Diatomics to Biopolymers*; Pullman, B., Ed.; Wiley: Chichester, U.K., 1978; pp 69-306. Rein, R. *Ibid.*, pp 307-362.

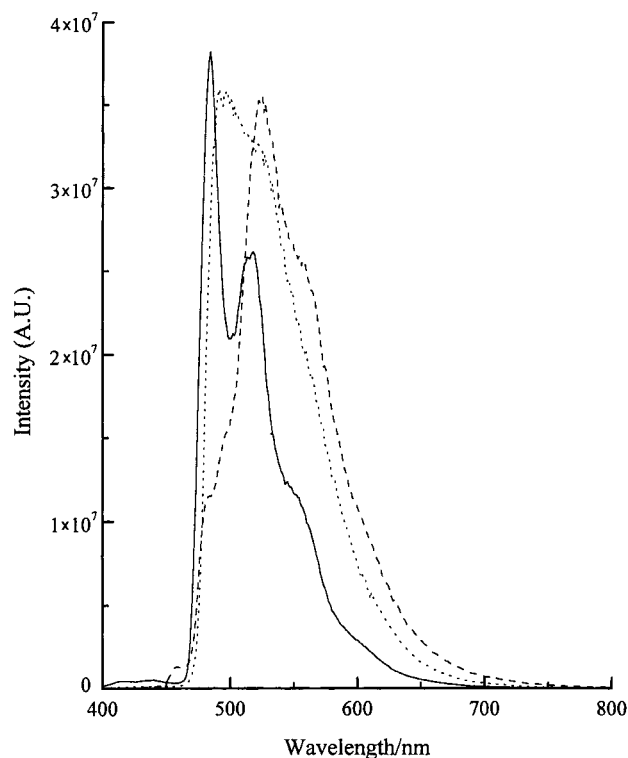
**Table 3. UV-Vis Absorption and Emission Data in Acetonitrile**

complex	UV-vis <sup>a</sup>	emission <sup>b</sup>
	$\lambda, ^c \text{ nm } (\epsilon, ^d \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	$\lambda_{\text{max}}, ^c \text{ nm}$
[Au(C <sup>^N</sup> ^A <sup>^C</sup> )Cl] ( <b>1</b> )	280 (40 000), 310 (21 000); 383, 400 (6100)	485
[Au(C <sup>^N</sup> ^A <sup>^C</sup> )(Meim-1)]ClO <sub>4</sub> ( <b>2</b> (ClO <sub>4</sub> ))	275 (30 000), 308 (18 000); 384, 403 (6800)	485
[Au(C <sup>^N</sup> ^A <sup>^C</sup> )(Spy-2)] ( <b>3</b> )	280 (30 000), 310 (24 000); 384, 404 (6300)	483
[Au(C <sup>^N</sup> ^A <sup>^C</sup> )PPh <sub>3</sub> ]ClO <sub>4</sub> ( <b>4</b> (ClO <sub>4</sub> ))	276 (30 000), 307 (18 000); 386, 403 (6700)	484
[Au <sub>2</sub> (C <sup>^N</sup> ^A <sup>^C</sup> ) <sub>2</sub> ( $\mu$ -dppm)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>5</b> (ClO <sub>4</sub> ) <sub>2</sub> )	273 (50 000), 306 (30 000); 400–416 (6500)	524
[Au <sub>2</sub> (C <sup>^N</sup> ^A <sup>^C</sup> ) <sub>2</sub> ( $\mu$ -dppe)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>6</b> (ClO <sub>4</sub> ) <sub>2</sub> )	280 (30 000), 302 (24 000); 393–408 (6500)	491

<sup>a</sup> At room temperature. <sup>b</sup> At 77 K; nonexponential decays were observed, and lifetimes were in the range 10<sup>-5</sup>–10<sup>-4</sup> s. <sup>c</sup> Error  $\pm 2$  nm. <sup>d</sup> Error  $\pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

**Figure 5.** Characteristic UV-vis absorption bands of **4** (—), **5** (---), and **6** (···) in acetonitrile at 298 K.

structure at 380–405 nm ( $\epsilon > 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). The vibronic progression (*ca.* 1200  $\text{cm}^{-1}$ ) is in close agreement with the skeletal vibrational frequency of the C<sup>^N</sup>^A<sup>^C</sup> ligand. Importantly, the  $\lambda_{\text{max}}$  value of this absorption band for **1–4** is constant despite the different auxiliary ligands. This excludes the possibility of ligand-to-metal and ligand-to-ligand charge transfer transitions (LMCT and LLCT, respectively). The electrophilic nature of Au(III) also eliminates the feasibility of a metal-to-ligand charge transfer transition (MLCT). The characteristic absorption is therefore tentatively assigned to a metal-perturbed intraligand (IL) transition. Notably, this absorption band is shifted to longer wavelengths for the binuclear species **5** and **6** (Figure 5). No Au(III)···Au(III) interaction is apparent from the crystal structures; thus, this observation cannot be credited to a metal–metal-to-ligand charge-transfer transition (MMLCT).<sup>4b,f</sup> The red shift for the binuclear complexes is ascribed to excimer character arising from  $\pi$ – $\pi$  interactions between intramolecular C<sup>^N</sup>^A<sup>^C</sup> ligands. As evident from the structural parameters, the two C<sup>^N</sup>^A<sup>^C</sup> moieties are oriented in a face-to-face fashion whereby overlapping of the  $\pi$  and  $\pi^*$  orbitals can occur.

**Figure 6.** Emission spectra of **4** (—), **5** (---), and **6** (···) ( $\lambda_{\text{ex}} = 350 \text{ nm}$ ) in acetonitrile at 77 K.

Hence, the low-energy absorption band in **5** and **6** is attributed to a IL transition displaying excimer character. In solution, since the bridging ligand in **5** (dppm) is shorter than that in **6** (dppe), the interplanar separation in the former is intrinsically shorter and thus a stronger  $\pi$ – $\pi$  interaction and larger red shift is plausible.

Luminescent gold(III) complexes are rare in the literature. Complexes **1–6** are emissive at low temperatures in acetonitrile but not at room temperature. The frozen-state (77 K) emission of the mononuclear complexes show well-resolved vibronic structures with spacing in the 1100–1300  $\text{cm}^{-1}$  range, which correlates with the skeletal vibrational frequency of the tridentate C<sup>^N</sup>^A<sup>^C</sup> ligand. The emission spectra of **1–4** are very similar, demonstrating as in the absorption data that different auxiliary ligands do not alter the emission maxima. By comparing the emission spectra with those of the free and protonated forms of 2,6-diphenylpyridine, we tentatively infer that the emission originates from a metal-perturbed  $^3\pi\pi^*$  state.<sup>2,3</sup> We also contend that this assignment is more appropriate for the emitting state of the analogous derivatives [Pt<sup>II</sup>(C<sup>^N</sup>^A<sup>^C</sup>)L] (L = SET<sub>2</sub>, py, pyrazine), rather than MLCT with ligand-centered character, as originally suggested by von

Zelewsky and co-workers.<sup>14a</sup> The emission maxima of **5** and **6** are also red-shifted, as in the absorption spectra (Figure 6). This is presumably due to their excimer character which derives from the effects of  $\pi$ - $\pi$  interactions.

**Summary.** A new class of mono- and binuclear cyclometalated gold(III) complexes bearing the trans dicarbanion of 2,6-diphenylpyridine was prepared.  $\pi$ -Stacking interactions and corresponding geometry are apparent in the crystal structures of  $[\text{Au}_2(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})_2(\mu\text{-dppm})](\text{ClO}_4)_2$  and  $[\text{Au}_2(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})_2(\mu\text{-dppe})](\text{ClO}_4)_2$ , although no  $\text{Au}\cdots\text{Au}$  interactions are observed. The photophysical properties of the new compounds have been examined. The characteristic absorption band near the visible region for the mononuclear species is tentatively assigned to a metal-perturbed intraligand transition, while the red shifts for the binuclear deriva-

tives are proposed to be the consequences of  $\pi$ - $\pi$  interactions. Emission is observed for all complexes at low temperatures (77 K) and is attributed to a metal-perturbed  $^3\pi\pi^*$  state.

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**Supporting Information Available:** Tables of crystal data, atomic coordinates, calculated coordinates, anisotropic displacement parameters, and bond lengths and angles for **3**, **4**( $\text{ClO}_4$ ), **5**( $\text{ClO}_4$ ) $\cdot$ 1.5( $\text{CH}_3$ ) $_2$ NCHO, and **6**( $\text{ClO}_4$ ) $\cdot$ CH $_3$ CN (66 pages). Ordering information is given on any current masthead page.

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