

# Pyridyl Gold(I) Alkynyls: A Synthetic, Structural, Spectroscopic, and Computational Study

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Planar neutral organometallic complexes have the potential to be exploited as building blocks for the construction of self-assembled nanoscale materials. We report the synthesis and first structural characterization of planar pyridyl gold(I) alkynyl complexes. Stable isolable complexes are only obtained when electron-rich pyridine ligands such as 4-(dimethylamino)pyridine or 4-aminopyridine are incorporated into the complexes. X-ray crystallography confirms that the pyridyl gold(I) alkynyls are neutral, linear, two-coordinate complexes. Furthermore, these gold(I) molecules form dimers in the solid state. However, no aurophilic interactions are observed to stabilize the solid-state structures. Density functional theory (DFT) calculations have been employed to model the electronic structure and thermodynamics of formation for selected complexes.

## Introduction

Planar organometallic complexes are beginning to show promise as building blocks for the construction of selfassembled nanoscale materials.<sup>1</sup> In particular, the synthesis of planar platinum(II) complexes containing  $\pi$ -conjugated ligands has received considerable attention, because these molecules are air- and water-stable and have the ability to self-assemble by exploiting a combination of metal-metal (Pt-Pt) and  $\pi$ - $\pi$  interactions.<sup>2</sup> The resulting cofacially

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stacked molecular aggregates often demonstrate interesting photophysical and photochemical properties due to orbital interactions between the  $\pi$  systems and metal ions of adjacent complexes. Che<sup>3</sup> and others<sup>4</sup> have used these planar platinum(II) building blocks to generate nanostructured materials with luminescent, semiconducting, liquid crystal-line, and gelating properties.

Like platinum(II), gold(I) is well-known to form metalmetal interactions in solution and the solid state. These aurophilic interactions can give rise to photophysical properties such as luminescence. Interest in these phenomena has led to the development of a range of gold(I)-containing materials.<sup>5</sup> One class of complexes that has been extensively studied in this regard (because they tend to form robust airand water-stable organometallic compounds) are the gold(I) alkynyl complexes.<sup>6</sup> The gold(I) alkyne fragment is most often found complexed to phosphine, carbene, or isonitrile

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# Article

two-electron-donor ligands, forming neutral linear twocoordinate complexes. However, the steric bulk associated with the phosphine and carbene ligands can prevent close contacts between adjacent Au(I) ions. Replacement of these bulky ligands with aromatic pyridinyl donor groups should lead to the formation of neutral planar pyridyl gold(I) alkynyl complexes such as **1a**. These pyridyl gold(I) alkynyl complexes could potentially be useful building blocks for the synthesis of nanoscale materials. The lack of steric hindrance around the Au(I) center should enable the two aromatic

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**Figure 1.** (a) Space-filling molecular model of **1a**. (b) Space-filling representation of a potential stacking arrangement of **1a** stabilized by Au–Au and  $\pi$ - $\pi$  interactions.

ligands to adopt a coplanar conformation, which would allow these organometallic fragments to assemble, through a combination of  $\pi$ - $\pi$  and Au(I)-Au(I) interactions, into linear supramolecular stacks (Figure 1). Recent literature provides support for this postulate: Lin et al. have demonstrated that the planar pyridine containing gold(I) cations [Au(py)<sub>2</sub>]<sup>+7</sup> and [(py)Au(carbene)]<sup>+8</sup> form linear stacks in the solid state, while Laguna et al. have shown that neutral [(py)Au(C<sub>6</sub>Cl<sub>5</sub>)]<sup>9</sup> complexes behave in an analogous manner.

We have a longstanding interest in metal–metal interactions<sup>10</sup> and have been exploring ways to exploit them to construct nanoscale materials. As part of that work, we report here the synthesis, properties, and structural characterization of pyridyl gold(I) alkynyl complexes. Additionally, density functional theory (DFT) calculations have been carried out in order to explain the observed thermodynamic and spectroscopic properties.

### **Experimental Section**

General Considerations. Ethynylbenzene, ethynylferrocene, AuCl(SMe<sub>2</sub>), 4-(dimethylamino)pyridine (4-dmap), and 4-aminopyridine (4-NH<sub>2</sub>Py) were purchased from commercial sources (Aldrich) and were used as received. NEt<sub>3</sub> was distilled over KOH prior to use. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. The compounds [(4-dmap)<sub>2</sub>Au]-[AuCl<sub>2</sub>], [(4-NH<sub>2</sub>Py)<sub>2</sub>Au][AuCl<sub>2</sub>], [(4-pic)<sub>2</sub>Au][AuCl<sub>2</sub>], and [(py)<sub>2</sub>Au][AuCl<sub>2</sub>] were synthesized by literature procedures.<sup>7</sup> As a precautionary measure, all reactions were carried out in the absence of light. NMR experiments were carried out on either a Varian 400-MR or a Varian 500 MHz VNMRS spectrometer operating at 298 K with chemical shifts referenced to residual solvent peaks (CDCl<sub>3</sub>, <sup>1</sup>H 7.26 ppm, <sup>13</sup>C 77.16 ppm;  $CD_3CN$ , <sup>1</sup>H 1.94 ppm, <sup>13</sup>C 1.32, 118.26 ppm;  $d_6$ -DMSO, <sup>1</sup>H 2.50 ppm). Chemical shifts are reported in parts per million (ppm) and coupling constants (J) in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, ttriplet, d = doublet, s = singlet, b = broad. ESI-MS analysis was carried out on methanol/dichloromethane solutions of the compound on a Bruker MicroTOF-Q spectrometer and IR

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spectroscopy (KBr disks) on a Perkin-Elmer Spectrum BX FT-IR spectrometer. Melting points were determined on a Sanyo Gallenkamp apparatus and are uncorrected. Conductivity measurements were carried out on approximately  $1.0 \times 10^{-3}$ acetonitrile solutions of the complexes using a Suntex SC-170 conductivity meter. Microelemental analysis was carried out at the Campbell Microanalytical Laboratory at the University of Otago. FT-Raman spectra of PhC=CAu(4-dmap) (1b) and PhC≡CAu(4-NH<sub>2</sub>Py) (1c) were acquired in KBr and in the solution phase (CH<sub>3</sub>CN). The former was carried out using a Senterra dispersive Raman microscope (Bruker Optics, Ettlingen, Germany) using radiation from a 785 nm solid-state laser operating at 50 mW. An Olympus  $20 \times$  objective with a 50  $\mu$ m confocal pinhole was used to collect the Raman signal. In order to minimize irradiation time and thus sample degradation, 36 individual spectra were acquired in a  $6 \times 6$  geometry spaced over a 200  $\mu$ m grid, which were then coadded. KBr was used to absorb heating caused by the laser in order to minimize sample degradation. The solution-phase FT-Raman spectra were acquired using a Bruker Equinox 55 interferometer coupled with a FRA-106 Raman module and a D418T liquid-nitrogen-cooled germanium detector, controlled by the Bruker OPUS v5.5 software package. The spectra were acquired as 1024 coadded scans using 1064 nm radiation of a Nd:YAG laser operating at 360 mW. The resolution of all spectra is  $4 \text{ cm}^{-1}$ . UV-visible absorption spectra were acquired with a Jasco V-550 spectrophotometer. Steady-state emission spectra were acquired with a Perkin-Elmer LS-50 B luminescence spectrometer using an excitation wavelength of 280 nm. Excited-state emission and absorption transients were acquired using a LP920K transient absorption (TA) system by Edinburgh Instruments. Excitation was carried out using third-harmonic radiation (355 nm) from a Brilliant (Quantel) Nd: YAG laser operating at 5 Hz, and in TA mode, a Xe900 450W xenon arc lamp was used as the probe source. The photons were dispersed using a TMS300-A monochromator with a 1800 grooves/mm grating, recorded on a R928 (Hamamatsu) photomultiplier and transcribed on a TDS3012C (Tektronix) oscilloscope. The samples were in CH<sub>3</sub>CN solution and were thoroughly degassed with argon prior to the experiment. Cyclic voltammetric experiments in CH2Cl2 were performed at 20 °C on solutions degassed with nitrogen. A threeelectrode cell was used with a Cypress Systems 1.0 mm diameter Pt working electrode, Ag/AgCl reference electrode, and platinum-wire auxiliary electrode. The solution was  $\sim 10^{-3}$  M in electroactive material and contained 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] as the supporting electrolyte. Voltammograms were recorded with the aid of a Powerlab/4sp computer-controlled potentiostat. Potentials are referenced to the reversible formal potential (taken as  $E^{\circ} = 0.00 \text{ V}$ ) for the decamethylferrocenium/decamethylferrocene (Fc<sup>\*+/0</sup>) process,<sup>11</sup> where  $E^{\circ}$  was calculated from the average of the oxidation and reduction peak potentials under conditions of cyclic voltammetry. Under the same conditions,  $E^{\circ}$  calculated for Fc<sup>+/0</sup> was 0.55 V versus Fc<sup>\*+/0</sup>.

**Computations.** Density functional theory (DFT) calculations were carried out using the Gaussian 09 package (Gaussian, Inc.). Optimization and frequency calculations were both performed using the B3LYP functional with a variety of effective core potentials (ECPs) for the gold atom and the 6-31G(d) basis set for all other atoms. Time-dependent (TD) calculations were carried out on the optimized structures using the B3LYP and the Coulomb attenuated method (CAM) B3LYP functional<sup>12</sup> with the same basis sets described above. Solvent-based calculations were also performed, using the IEF-PCM method, which treats the solvent as a continuum containing the solute as a series of

interlocking spheres. All TD-DFT calculations were carried out this way, as the absorption spectra were also measured in the solution phase.

In order to ensure that calculated quantities are accurate, we calculated mean absolute deviations (MADs) between theoretical and experimental vibrational spectra. These are obtained by averaging the absolute difference in cm<sup>-1</sup> of the 5–10 most prominent experimental peaks to the corresponding calculated peaks in the spectral range 400–1800 cm<sup>-1</sup>; to account for dissimilar anharmonicities, peaks found in different regions of the spectra have to be scaled differently.<sup>13</sup> We calculated the scale factors to give the lowest MAD for each basis set.

The IR and Raman spectra were generated using a Lorentzian line shape with a half-width at half-maximum (HWHM) of 3 cm<sup>-1</sup>. The vibrational modes and molecular orbitals were visualized using Molden<sup>14</sup> and GaussView v5.0 (Gaussian, Inc.), respectively, after extraction from the output files using GaussSum.<sup>15</sup> Unambiguous assignment of vibrational modes from visual comparison of spectra was possible for most peaks.

General Procedure for the Preparation of Gold(I) Pyridyl Alkynes. To a solution of the gold(I) alkyne (1 equiv) in dichloromethane (10 mL) was added the substituted pyridine (1 equiv) and the solution stirred in a foil-covered flask at room temperature for 1.5 h. The solution was reduced in volume (ca. 5 mL) and, if required, filtered through a plug of Celite to remove any insoluble Au(0) material. Diethyl ether was added to the solution, resulting in the precipitation of the gold(I) alkynyl pyridyl complex as either an off-white or orange solid (60–73% yield). Full details and characterization data can be found in the Supporting Information.

X-ray Data Collection and Refinement. X-ray data for 2b and 1b were recorded with a Bruker APEX II CCD diffractometer at 89(2) K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by either direct methods (1b) using SIR97<sup>16</sup> or Patterson methods (2b) using SHELXL-97.<sup>17</sup> The resulting Fourier maps revealed the location of all other non-hydrogen atoms. Weighted full-matrix least-squares refinement on  $F^2$  was carried out using SHELXL-97.<sup>17</sup> For 2b all non-hydrogen atoms were refined anisotropically, but for 1b the poor data set meant only the gold atoms were able to be modeled anisotropically. In both cases, the hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. The residual electron density in both 1b and 2b is due to Fourier ripples around the gold atom (the peaks are approximately 1.2 Å from the gold).

X-ray data for 1c,d were collected at 123 K on a Rigaku Spider diffractometer equipped with a copper rotating anode X-ray source ( $\lambda = 1.54178$  Å) and a curved image plate detector. Structures were solved by direct methods and refined against  $F^2$  using anisotropic thermal displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined using a riding model (except where noted in the Supporting Information).

All ORTEP<sup>18</sup> diagrams have been drawn with 50% probability ellipsoids. Crystal data and collection parameters are given in Table 1. The CIF files CCDC 774529 (1b), CCDC 774532 (1c), CCDC 774530 (1d), and CCDC 774531 (2b) contain the

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<sup>(14)</sup> Schaftenaar, G.; Noordik, J. H. J. Comput.-Aided Mol. Des. 2000, 14 (2), 123–134.

<sup>(15)</sup> O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. J. Comput. Chem. 2008, 29 (5), 839–845.

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<sup>(18)</sup> Farrugia, L. J. J. Appl. Crystallogr. 1997, 30 (5, Pt. 1), 565.

## Table 1. Crystallographic Data for 1c,d and 2b

	1c	1d	2b
CCDC no.	774532	774530	774531
formula	$C_{13}H_{11}N_2Au$	$C_{14}H_{12}NAu$	$C_{19}H_{19}N_2FeAu$
formula wt	392.21	391.21	528.18
cryst syst, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a, A	6.15020(10)	6.393(2)	10.833(3)
b, Å	13.2177(2)	7.2809(3)	14.922(4)
c, Å	14.3392(10)	25.1246(9)	10.734(3)
α, deg	90	90	90
$\beta$ , deg	98.22(2)	97.161(12)	107.90(2),
$\gamma$ , deg	90	90	90
$V, Å^3$	1153.68(8)	1160.4(4)	1651.3(8)
Z	4	4	4
cryst size, mm; color, habit	$0.50 \times 0.12 \times 0.10;$ pale vellow, block	$0.16 \times 0.12 \times 0.01;$ colorless, plate	$0.21 \times 0.07 \times 0.02;$ orange, plate
$\rho_{\text{caled}}, \text{mg/mm}^3$	2.258	2.239	2.125
$\mu, \text{mm}^{-1}$	23.723	23.558	9.752
no. of rflns collected	3256	14 531	14 272
no. of indep rflns $(R_{int})$	1302 (0.2232)	2193 (0.0538)	2897 (0.1299)
no. of data/restraints/params	1302/91/158	2193/12/146	2897/0/199
goodness of fit on $F^{2^{\prime}}$	0.597	1.369	1.018
final R <sub>1</sub> and wR <sub>2</sub> indexes $(I > 2\sigma(I))$	0.0743. 0.1514	0.0369. 0.1127	0.0560, 0.1105
final $R_1$ and $wR_2$ indexes (all data)	0.0834, 0.1628	0.0425, 0.1191	0.1036, 0.1300
largest difference in peak and hole (e $Å^{-3}$ )	1.407 and -1.992	1.719 and -1.691	1.945 and -1.721

supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk/conts/ retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033).

### **Results and Discussion**

Synthesis. The synthesis of the pyridyl gold(I) alkynyl complex 1a has been reported previously. The complex was obtained by reacting the polymeric gold(I) alkynyl complex  $[Au(C \equiv CPh)]_n$  (1) with an excess of pyridine.<sup>19</sup> We set out to exploit this methodology to synthesize a family of pyridyl gold(I) alkynyl complexes 1a-f and 2a-d (Scheme 1, method a). The pyridyl ligands (3a-f, 1 equiv) were added to a suspension of  $[Au(C=CAr)]_n^{6a,20}$  (1 or 2; 1 equiv) in dichloromethane at room temperature, and the resulting reaction mixture was stirred for 1.5 h. With the two most electron-rich pyridine ligands, 4-(dimethylamino)pyridine (4-dmap, 3b;  $pK_a = 9.4$ ) and 4-aminopyridine (4-NH<sub>2</sub>Py, **3c**;  $pK_a = 9.11$ ), homogeneous solutions formed. After filtration to remove a small amount of insoluble Au(0), which had formed during the reaction, the addition of diethyl ether caused the precipitation of the pyridyl alkynyl complexes 1b,c and 2b,c in moderate yields (60-73%). However, the reactions of  $[Au(C \equiv CAr)]_n$  with the less basic amines 4-methylpyridine

(19) Coates, G. E.; Parkin, C. J. Chem. Soc. 1962, 3220-6.

Scheme 1. Synthesis of Mononuclear Au(I) Pyridyl Alkynyl Complexes<sup>a</sup>





(4-pic, **3d**;  $pK_a = 6.0^{21}$ ), 2,6-dimethylpyridine (2,6-lut, **3e**;  $pK_a = 6.7^{21}$ ), pyridine (py, **3a**;  $pK_a = 5.25^{21}$ ), 4,4'-bipyridine

<sup>(20) (</sup>a) Vicente, J.; Chicote, M. T.; Alvarez-Falcón, M. M.; Abrisqueta, M.-D.; Hernández, F. J.; Jones, P. G. Inorg. Chim. Acta 2003, 347, 67–74. (b) Siemeling, U.; Rother, D.; Bruhn, C. Organometallics 2008, 27 (24), 6419–6426. (c) Vicente, J.; Chicote, M.-T.; Alvarez-Falcon, M. M.; Jones, P. G. Organometallics 2005, 24 (24), 5956–5963. (d) The gold(I) alkynyl complexes used in this study were prepared by established methodologies.<sup>20a-c</sup> AuCl(SMe)<sub>2</sub> was reacted with the appropriate terminal alkyne (either ethynylbenzene or ethynylferrocene) in the presence of triethylamine, providing the gold(I) alkynyl complexes [Au(C=CPh)]<sub>n</sub> and [Au(C=CFc)]<sub>n</sub> in good yields. With the exception of the tetrameric tert-butyl complex [Au(C=CBut)]<sub>4</sub>, it is generally accepted that Au(I) alkynes are polymeric in nature, with the linear coordination geometry of the gold(I) center completed by  $\pi$ -electron donation from the alkyl group of a neighboring molecule. As a result, the gold alkynyl complexes tend to be insoluble in common organic solvents—such is the case for the phenyl derivative [Au(C=CPh)]<sub>n</sub>. The ferrocenyl derivative [Au(C=CFc)]<sub>n</sub>, however, shows much better solubility and dissolves readily in solvents such as dichloromethane.

(bipy, **3f**;  $pK_a = 4.9^{21}$ ), and 4-cyanopyridine (4-CNPy, **3g**;  $pK_a = 1.86^{22}$ ) proceeded differently from those reported above. An excess (~6 equiv) of the pyridyl ligands (3a,d,e) was required to dissolve the  $[Au(C=CAr)]_n$  polymers and give homogeneous solutions, while refluxing a 100-fold excess of **3f**,g with  $[Au(C \equiv CPh)]_n$  in either dichloromethane or toluene failed to dissolve the polymeric starting materials. Addition of diethyl ether to the reaction mixtures containing the pyridyl ligands 3a,d,e resulted in the formation of microcrystalline materials. However, the attempted isolation of these pyridyl alkynyl complexes<sup>23</sup> by filtration and vacuum drying caused the colorless or orange solids to revert back to the initial polymeric materials, 1 (yellow) or 2 (red). Microanalysis of the isolated solids was consistent with [Au(C= $CAr)_{n}$ . Attempts to synthesize the analogous digold complexes from 1,3- or 1,4-substituted [AuC=CC<sub>6</sub>H<sub>4</sub>C=CAu]<sub>n</sub><sup>20c</sup> polymers failed even when an excess of the electron-rich pyridyl ligands were used.

Due to the difficulties encountered using method a, we examined an alternative approach for the synthesis of the pyridyl gold(I) alkynyl complexes (Scheme 1, method b). The known  $[Au(py')_2](AuCl_2)$  complexes<sup>7</sup> 4a-d were added to a dichloromethane solution containing one of the alkynes, 1 or 2, in the presence of triethylamine at room temperature. However, as with method a, only the pyridyl gold(I) alkynyl complexes that contained electron-rich pyridine ligands (1b,c and 2b,c) could be isolated. When the 4-pic- or py-containing  $[Au(py')_2](AuCl_2)$  complexes were used, the polymeric  $[Au(C \equiv$  $[CAr]_n$  materials 1 or 2 were isolated from the reaction mixtures in quantitative yields.

The results above suggest that the described synthetic approaches only provide stable isolable pyridyl gold(I) alkynyl complexes when strongly electron donating substituents (e.g., 4-dmap and 4-NH<sub>2</sub>Py) are present in the pyridyl ligands and this is supported by DFT calculations (vide infra). These very basic ligands are strong donor ligands and are able to readily displace the  $\pi$ -coordinated alkyne from the coordination sphere of the gold. When weaker pyridyl bases are employed as ligands (e.g., 3a,d-f) the N-donor strength is not of sufficient magnitude to displace the  $\pi$ -coordinated alkyne group. The pyridyl-containing gold(I) alkynyl complexes

are only formed when a large excess of these weaker donor ligands is present. Coates and Parkin report the isolation of the pyridine-containing complex 1a (which crystallized with free pyridine),<sup>19</sup> using a method similar to that which we have employed; however, in our hands we have been unable to isolate an appreciable quantity of 1a. In the presence of a large excess of the pyridyl ligands, the pyridine-containing complexes form in solution, as evidenced by positive ion ESMS,<sup>23</sup> and can be precipitated as white or orange solids, but when the solids are removed from the mother liquor and dried, the pyridyl ligands are lost and the polymeric  $[Au(C \equiv CAr)]_n$  starting materials regenerated.<sup>24</sup> This behavior is not uncommon for alkynyl complexes of the coinage metal group—for example, the complex  $PhC \equiv CCuNH_3$  is able to be isolated, but it is so unstable that the ammonia is lost when the complex is dried under a stream of nitrogen, affording the starting material [Cu(C=CPh)]<sub>n</sub>.<sup>25</sup> Likewise,  $iPrNH_2$  is lost from the unstable complex PhC=CAgNH<sub>2</sub>*i*Pr by pumping at room temperature.<sup>26</sup> Fortunately, the slow diffusion of diethyl ether into an acetone solution of  $[Au(C \equiv CPh)]_n$  and an excess of **3d** produced a small number of crystals (in a 5-10% yield) that were stable enough for single-crystal X-ray analysis (vide infra), but the poor yield obtained using this variation means that it is not a synthetically viable approach to these molecules. We postulate that the strong  $\sigma$  donation from the alkynyl ligand trans to the pyridyl ligand weakens the Au-py bond, rendering the pyridyl donor ligands labile. Due to this, the weakly bonded, less basic pyridyl ligands are readily lost from the complexes during the attempted isolation of the complexes.

The isolable mononuclear pyridyl compounds 1b, 2b, 1c, and 2c showed moderate stability in the solid state<sup>27</sup> but decompose in solutions of strongly coordinating solvents (e.g.,  $d_6$ -DMSO). All the isolable compounds were fully characterized by NMR (<sup>1</sup>H and <sup>13</sup>C) and IR spectroscopy, HRelectrospray mass spectrometry (ESMS), and elemental analysis. In addition, 1c,d and 2b were characterized by single-crystal X-ray diffraction (see below).

The <sup>1</sup>H NMR spectra of the gold complexes 1b, 2b, 1c, and 2c are in agreement with the proposed mononuclear structures. As an illustrative example, the <sup>1</sup>H NMR spectra (aromatic region) of PhC=CAu(4-dmap) (1b) is shown in Figure 2. Interestingly, the  $\beta$ -protons of the 4-dmap ligand are shifted downfield, as expected upon coordination to the gold(I) ion; however, the  $\alpha$ -protons are shifted upfield (Figure 2b). Similar behavior is observed in the gold(I) complex 4b, which is known to aggregate in solution;<sup>7</sup> as such, we postulate that this may be due to aggregation of the monomeric complexes in solution. Furthermore, the positions of the signals in the <sup>1</sup>H NMR spectra are very solvent dependent and the chemical shift of H<sub>3</sub> (the ortho proton on the phenyl ring) in different solvents suggests that the phenylalkyne moiety may be forming a weak C-H--- $\pi$  intermolecular interaction with the pyridine ligand on an adjacent complex in solution, as is observed in the solid-state structure of 1c (vide infra, Figure 4a).

The <sup>13</sup>C NMR spectra of **1b**,**c** and **2b**,**c** exhibit resonances due to the C=C moiety between 95 and 110 ppm, values that are similar to those for other gold(I) alkynyl complexes.<sup>6</sup>

The C=C stretching band in the IR spectra (KBr) of the pyridyl gold alkynyl complexes was observed to range from

<sup>(21)</sup> Weast, R. C., Ed. CRC Handbook of Chemistry and Physics, 68th

ed.; CRC Press: Boca Raton, FL, 1987; 2464 pp. (22) Pham-Tran, N.-N.; Bouchoux, G.; Delaere, D.; Nguyen, M. T. J. Phys. Chem. A **2005**, 109 (12), 2957–2963.

<sup>(23)</sup> Positive ion ESMS of the reaction mixtures indicates that the pyridyl gold(I) alkynyl complexes are formed in solution; a series of peaks corresponding to  $[M + H]^+$ ,  $[M + Na]^+$ , and  $[M + K]^+$ , along with the cationic  $[Au(Py)_2]^+$  fragment ion, are observed.

<sup>(24) (</sup>a) At the request of a reviewer, we have attempted to obtain a  $^{1}$ H NMR spectrum of 1a. As stated in the text, we have been unable to isolate a solid sample of 1a, due to its instability; as such we have attempted to generate the compound in situ. A CDCl<sub>3</sub> solution of the DMAP complex 1b was treated with 1 equiv of pyridinium p-toluenesulfonate ([PyH<sup>+</sup>][OTs<sup>-</sup>]). This resulted in ligand exchange and the immediate formation of a white precipitate. The <sup>1</sup>H NMR spectrum of the resulting mixture shows peaks due to [DMAPH<sup>+</sup>][OTs<sup>-</sup>] and free pyridine. The insoluble white solid was isolated by filtration, and microanalysis confirmed that it was  $[Au(C \equiv CPh)]_n$  (1). These results suggest that 1a is formed in solution via ligand exchange and then rapidly decomposes to free pyridine and 1. This is completely consistent with our other data on the stability of 1a. Other workers have previously shown that treatment of DMAP-containing complexes with protonated pyridine leads to protonation of the more basic DMAP ligand and coordination of the Py donor group. See: (b) Leigh, D. A.; Lusby, P. J.; McBurney, R. T.; Symes, M. D. Chem. Commun. 2010, 46 (14), 2382-2384. (c), Crowley, J. D.; Leigh, D. A.; Lusby, P. J.; McBurney, R. T.; Perret-Aebi, L.-E.; Petzold, C.; Slawin, A. M. Z.; Symes, M. D. J. Am. Chem. Soc. 2007, 129 (48), 15085-15090.

<sup>(25)</sup> Nast, R.; Pfab, W. Chem. Ber. 1956, 89, 415-421.

<sup>(26)</sup> Blake, D.; Calvin, G.; Coates, G. E. Proc. Chem. Soc. 1959, 396-397. (27) In the solid state the complexes darken to a purple color (decompose) over a period of 2-3 months in the absence of light.



Figure 2. Partial <sup>1</sup>H NMR spectra (400 MHz, CD<sub>3</sub>CN, 298 K) of (a) the ligand 3b, (b) the gold(I) complex 1b, and (c) the gold(I) complex 4b.<sup>7</sup>

2116 to 2125 cm<sup>-1</sup>, which is similar to values for analogous primary and secondary amine containing gold(I) alkynyl compounds (2120–2134 cm<sup>-1</sup>) reported by Coates and Parkin.<sup>19</sup>

Positive-ion ESMS data also supported the formation of the neutral mononuclear structures, with the spectra dominated by a series of peaks corresponding to  $[M + H]^+$ ,  $[M + Na]^+$ , and  $[M + K]^+$ , along with the cationic  $[Au(Py)_2]^+$  fragment ion. The observation of the  $[Au(Py)_2]^+$ ion may indicate the presence of an equilibrium between the neutral monomeric [ArC=CAu(Py)] and the dimeric ion-paired species  $[Au(Py)_2][Au(C=CAr)_2]$  in solution, as is observed for the related [Au(Py)Cl] system.<sup>7</sup> However, the  $[Au(C=CAr)_2]^$ anion is not detected in negative ion ESMS experiments, and molar conductivity  $(\Lambda_M)$  values in acetonitrile are very low  $(6-7 \ \Omega^{-1} \ cm^2 \ mol^{-1})$ , suggesting that the complexes are nonelectrolytes.<sup>91</sup> In combination, these results indicate that the major gold(I) species present in solution are the neutral monomeric [ArC=CAu(Py)] complexes.

The electrochemistry of **2b** in dichloromethane solution was investigated using cyclic and square wave voltammetric techniques, and the results are presented in the Supporting Information. These show the predicted one-electron chemically reversible oxidation of the ferrocenyl group at  $E^{\circ} = 0.51$  V. This value compares well with values reported previously of 0.53 and 0.41 V for examples of platinum<sup>28</sup> and nickel<sup>29</sup> ferrocenyl acetylides, respectively.

**Molecular Structures.** X-ray crystallography was used to unequivocally determine the molecular structures of the pyridyl gold(I) alkynyl complexes **1c,d** and **2b** (Figure 3, Table 1), at least in the solid state. Each of the complexes crystallizes in a monoclinic space group  $(P2_1/c \text{ or } P2_1/n)$  with four molecules in the unit cell. The Au(I) ions are bound to a pyridyl and an alkynyl donor in the expected linear fashion (N-Au-C=C bond angles range from 173.7 to 179.8°). The Au-N bond



**Figure 3.** Molecular structures of **1c** (a, b), **1d** (c, d), and **2b** (e, f) as ORTEP diagrams. The thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **1c**: Au1–C1 = 1.952(11), Au1–N1 = 2.063(9), C1–C2 = 1.179(14); C1–Au1–N1 = 173.7(4), C2–C1–Au1 = 170.8(10). Selected bond lengths (Å) and angles (deg) for **1d**: Au1–C1 = 1.955(12), Au1–N1 = 2.069(10), C1–C2 = 1.219(17); C1–Au1–N1 = 179.8(4), C2–C1–Au1 = 178.9(11). Selected bond lengths (Å) and angles (deg) for **2b**: N1–Au1 = 2.044(11), C8–Au1 = 1.922(18), C8–C9 = 1.22(2); C9–C8–Au1 = 176.2(11), C8–Au1–N1 = 178.9(4).

lengths  $(2.025-2.069 \text{ Å})^{7-9}$  and Au-C=CAr  $(1.922-1.955 \text{ Å})^{5c,6c,6d,20b,20c,30}$  bond lengths are similar to those observed in other gold(I) complexes. Each of the molecules forms a dimer in the solid state. However, surprisingly, the dimers are not stabilized by gold(I)-gold(I) interactions.<sup>31</sup>

<sup>(28)</sup> McAdam, C. J.; Blackie, E. J.; Morgan, J. L.; Mole, S. A.; Robinson, B. H.; Simpson, J. *Dalton Trans.* **2001**, No. 16, 2362–2369.

<sup>(29)</sup> Butler, P.; Gallagher, J. F.; Manning, A. R.; Mueller-Bunz, H.; McAdam, C. J.; Simpson, J.; Robinson, B. H. J. Organomet. Chem. **2005**, 690 (21–22), 4545–4556.

<sup>(30) (</sup>a) Gao, L.; Partyka, D. V.; Updegraff, J. B., III; Deligonul, N.; Gray, T. G. *Eur. J. Inorg. Chem.* 2009, No. 18, 2711–2719. (b) Siemeling, U.; Rother, D.; Bruhn, C. *Chem. Commun.* 2007, No. 41, 4227–4229. (c) Yip, S.-K.; Cheng, E. C.-C.; Yuan, L.-H.; Zhu, N.; Yam, V. W.-W. Angew. *Chem., Int. Ed.* 2004, *43* (37), 4954–4957.

<sup>(31)</sup> We also obtained the crystal structure of **1b** (see the Supporting Information). While we were readily able to determine the connectivity of **1b**, we have been unable to satisfactorily refine the data, despite collecting multiple data sets from several different crystals of reasonable quality. In all cases twinning was observed, which led to poor-quality diffraction data. As observed with the other structures, **1b** is a neutral linear two-coordinate complex that dimerizes in the solid state. In this case the formation of the dimer is stabilized by an Au(I)–Au(I) interaction (Au–Au distance 3.19 Å).



Figure 4. Ball-and-stick and space-filling representations of the solid-state dimers of 1c (a), 1d (b), and 2b (c).

# Article

The complex 1c forms a "head-to-tail" dimer that is stabilized by a C-H- $\pi$  interaction between the phenylacetylide group on one molecule of 1c and the 4-aminopyridine of the neighboring complex (Figure 4a). The phenylacetylide and 4-aminopyridine ligands of 1c are not coplanar as expected (Figure 3b), because the phenylacetylide ligand has to twist out of the plane in order to form the C-H- $\pi$ interaction. Although the gold(I) ions of the adjacent molecules are aligned, the Au(I)-Au(I) distance (3.705 Å) is outside of the range (2.5-3.5 Å) usually considered to constitute an aurophilic interaction (Figure 4a).<sup>5f</sup> In contrast, the phenylacetylide and 4-picoline ligands of 1d are essentially coplanar (Figure 3d). Two molecules of 1d are cofacially stacked in a "head-to-tail" orientation (Figure 4b), forming a dimer that is stabilized by a weak offset face-to-face  $\pi - \pi$  interaction<sup>32</sup> (centroid (4-pic)–centroid (4-pic) distance 3.945 Å) and a weak Au- $\pi$  interaction<sup>33</sup> (Aucentroid (4-pic) distance 4.074 Å,  $\alpha = 20.74^{\circ}$ ). In **2b** the planes of the ferrocenyl and 4-dmap ligands are almost orthogonal (the angle between the calculated mean planes is 77.12°, Figure 3e,f). Two molecules of 2b form a "head-totail" dimer that is supported by a weak lone-pair  $-\pi$  interaction (N-centroid distance 3.791 Å) between the lone pair of the NMe<sub>2</sub> group on one complex with the 4-dmap ligand of the adjacent molecule (Figure 4c).<sup>34</sup>

DFT and Spectroscopy. To provide further insight into the electronic and thermodynamic properties of the pyridyl gold(I) alkynyl complexes, we have carried out DFT calculations for compounds **1a**-c,g as well as a tetrameric model<sup>35</sup> of the  $[Au(C = CPh)]_n$  precursor, both in solvent and *in vacuo*. We have previously shown that vibrational spectroscopy is an excellent validation tool for gauging the effectiveness and accuracy of quantum-mechanical calculations, and for that reason frequency calculations were performed.<sup>36</sup> For example, the Raman activity of a molecule is closely related to the polarizability of the valence electrons, while correct modeling of the energies and reactivities is crucially dependent on the nature and energetics of these. As such, we screened for an appropriate basis set by comparing the calculated Raman spectra to the experimentally obtained spectrum (Supporting Information). A qualitative comparison of the calculated and measured Raman spectra of PhC≡CAu(4-dmap) (1b) is shown in Figure 5. The Raman spectrum is dominated by the C=C stretch at 2124 cm<sup>-1</sup> (not shown) and phenyl-based vibrations between 500 and  $1700 \text{ cm}^{-1}$ . 4-dmap peaks are observed at 767 and 1076 cm<sup>-1</sup>. It should be noted that while the solution-phase spectrum shows a very poor signal-to-noise ratio, several major peaks are observed at wavenumbers expected from the solid-state spectrum. An exception is the peak at  $1542 \text{ cm}^{-1}$ , which is shifted to  $1553 \text{ cm}^{-1}$  in solution. Table 2 shows the calculated mean absolute deviations (MADs) for compounds 1b,c, both



**Figure 5.** Measured FT-Raman spectra in MeCN and KBr and the calculated Raman spectrum scaled by 0.9750. Major peaks and equivalent calculated peaks are marked.

Table 2. MAD Values for PhC $\equiv$ CAu(4-dmap) (1b) and PhC $\equiv$ CAu(4-NH<sub>2</sub>Py) (1c) in Vacuo and in Solution<sup>*a*</sup>

	$MAD/cm^{-1}$				
	IR	Raman	C≡C	C≡C scaled	
<b>1b</b> ( <i>in vacuo</i> ) <b>1b</b> (in CH <sub>3</sub> CN)	6.5	7.0 7.0 7.0	59 43	18 1 26	
<b>1c</b> (in CH <sub>3</sub> CN)	/.0	7.4	35	20	

<sup>*a*</sup> The ECP used in all cases is LANL2DZ. The in vacuo calculations are compared with measurements carried out in KBr.  $C \equiv C$  refers to the use of a scale factor optimized in the 400–1700 cm<sup>-1</sup> region, while " $C \equiv C$  scaled" uses an alkyne-specific scale factor of 0.9568.

*in vacuo* and in solution (CH<sub>3</sub>CN), and also includes C=C stretches scaled by a factor of 0.9568, as recommended by the NIST Computational Chemistry Comparison and Benchmark Database (CCCBD).<sup>37</sup> It appears that solvent-based calculations yield only a small improvement for peaks below 1700 cm<sup>-1</sup>; however, the C=C stretch is far better modeled and shows an excellent fit of experimental to calculated wavenumbers when alkyne-specific scale factors are used.

As the structure of PhC=CAu(4-dmap) (1b) is relatively simple and there is a direct connection of the  $C \equiv C$  bond to the Au atom, comparison of the calculated alkyne stretchingwavenumbers affords a useful test for the effectiveness of the various ECPs employed. The results can be found in the Supporting Information (Table S1 and Figure S11). While LANL2DZ showed the best performance overall when peaks below 1700 cm<sup>-1</sup> are considered, the C=C stretch is approximated rather poorly. However, this peak is easily assigned and thus perhaps less important in terms of identification of normal modes. Looking at intensity patterns in Figure S11, it is evident that most basis sets perform very similarly. The exception is the LANL1 ECPs, which generally show greatly diminished intensities of peaks with significant metal involvement. Overall, the results for most ECPs can be considered usable (i.e., MAD <  $10 \text{ cm}^{-1}$ ).<sup>38</sup>

<sup>(32) (</sup>a) Janiak, C. *Dalton Trans*. **2000**, No. 21, 3885–3896. (b) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans.* 2 **2001**, No. 5, 651–669.

<sup>(33)</sup> Tiekink, E. R. T.; Zukerman-Schpector, J. *CrystEngComm* **2009**, *11* (7), 1176–1186.

<sup>(34)</sup> Mooibroek, T. J.; Gamez, P.; Reedijk, J. CrystEngComm 2008, 10 (11), 1501–1515.

<sup>(35)</sup> To simplify the calculation, the polymeric gold precursor 1 was approximated by a tetrameric complex where the gold atoms bind endon to the alkyne group of a neighboring complex to give a square arrangement (see the Supporting Information).

<sup>(36)</sup> Walsh, P. J.; Gordon, K. C.; Lundin, N. J.; Blackman, A. G. J. Phys. Chem. A 2005, 109 (26), 5933-5942.

<sup>(37)</sup> Johnson, R. D., III. *NIST Computational Chemistry Comparison and Benchmark Database*; NIST Standard Reference Database Number 101 Release 15: http://cccbdb.nist.gov/, February **2010**.



Figure 6. UV-visible absorption (black) and emission (green) spectra of PhC $\equiv$ CAu(4-dmap) (1b) at 298 K in CH<sub>3</sub>CN. TD transitions calculated using B3LYP (orange) and CAM-B3LYP (blue) are overlaid. The emission units are arbitrary.

Table 3. Energy Change ( $\Delta E_{form}$ ) for the Reaction of the PyridylCompounds with the Gold Precursor, Listed in Descending Orderof Electron-Donating Ability

pyridyl gold(I) alkynyl complex	$\Delta E_{\rm form}$ in vacuo/kJ mol <sup>-1</sup>	pyridyl ligand p <i>K</i> a
PhC≡CAu(4-DMAP) (1b)	-4.5	9.40
$PhC \equiv CAu(4-NH_2Py)$ (1c)	-3.7	9.11
$PhC \equiv CAu(Py)(1a)$	5.8	5.25
$PhC \equiv CAu(4-CNPy) (1g)$	27.1	1.86

Having established the usefulness of LANL2DZ as an ECP for modeling the gold atoms in these compounds, we then used the single-point energies of the previously optimized structures to calculate the energies of formation  $(\Delta E_{\rm form})$  for the pyridyl gold(I) alkynyl complexes 1a-c,g (Table 3 and the Supporting Information). Consistent with the experimental data, the calculated energies of formation  $(\Delta E_{\rm form})$  indicate that the pyridyl gold(I) alkynyl complexes 1b,c, which contain the most electron-donating pyridyl ligands, are thermodynamically stable with respect to the reactants, whereas the complexes 1a,g, which contain less electron donating pyridyl ligands, are unstable with respect to the reactants (Table 3).

TD-DFT calculations were performed using the B3LYP and CAM-B3LYP methods; the results for PhC≡CAu(4dmap) (**1b**) are presented in Figure 6 and in the Supporting Information (Table S2). For both methods we employ the IEF-PCM solvent model. It should be noted that virtually the same transitions were calculated whether the solvated or *in vacuo* equilibrium geometry was considered. From Figure 6 it is evident that CAM-B3LYP overestimates transition energies for solvent calculations. While the occupied frontier orbitals calculated with B3LYP and CAM-B3LYP are almost identical, there are significant differences in the unoccupied or virtual orbitals (see Figure 7). Here, the B3LYP orbitals are calculated to be somewhat more delocalized over the entire molecule, whereas the CAM-B3LYP orbitals tend to be confined to one side of the molecule. This appears to be a manifestation of the modification of the Hartree–Fock (HF) exchange with increasing distance in CAM-B3LYP.<sup>12,39</sup> The more localized unoccupied molecular orbitals are expected to be of higher energies than their delocalized B3LYP counterparts, which is not inconsistent with the observed increase in transition energies.

Both methods calculated the lowest energy transition as a transfer of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO); however, with B3LYP it appears that a HOMO/ HOMO-1  $\rightarrow$  LUMO+1 transition also contributes. The HOMO  $\rightarrow$  LUMO transition can also be described as a  $\pi \rightarrow \pi^*$  transition, where the  $\pi$  and  $\pi^*$  orbitals are phenylbased and delocalized, respectively (Figure 7). This transition is measured in the absorption spectrum at 279 nm, with a red shoulder at ca. 291 nm; this represents a good approximation by the B3LYP calculation, which shows peaks at 276 and 280 nm. It is also comparable to the UV-visible spectra of PhC=CAu(PPh<sub>3</sub>)<sup>40</sup> and 4-pyC=CAu(PPh<sub>3</sub>).<sup>41</sup> One might expect that the intuitively predicted ground- and excitedstate orbitals would appear as Au-alkynyl-based and pyridyl-based, respectively, and that orbital scrambling is responsible for the deviation observed.<sup>42</sup> A single-point tripletstate calculation carried out on the ground-state geometry of the complex shows that the lowest energy singly occupied molecular orbital is located across the Au-alkynyl-phenyl portion of the complex, while several higher-energy MOs are pyridyl-based. A higher energy band observed at 258 nm has been calculated by B3LYP TD-DFT as a transition solely originating from the HOMO-1 orbital and terminating on the LUMO and LUMO+1 orbitals, which is represented as a  $\pi_{4-\text{dmap}} \rightarrow \pi^*_{\text{delocalized}}$  electron transfer by the molecular orbital pictures (Figure 7). A weak feature is also observed at ca. 360 nm. This could be due to a spin-forbidden direct excitation of the triplet state; however, no corresponding peaks could be observed in the photoluminescence spectrum. The absorption spectrum (Supporting Information) of the compound FcC≡CAu(4-dmap) (2b) shows a peak at 281 nm  $(\varepsilon = 36 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1})$  and shoulders at ca. 427 nm  $\epsilon = 1.6 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  and 350 nm ( $\epsilon = 3.6 \times 10^3 \text{ L}$  $mol^{-1}$  cm<sup>-1</sup>). The energies of these are consistent with ferrocene d-d transitions previously found at 416 and 325 nm<sup>43</sup> and suggest limited interaction between Fc and the residual molecule, as indicated by the electrochemical measurements on 2b.

Solution-phase emission spectra were acquired for PhC $\equiv$  CAu(4-dmap) (1b) and compound 2b at excitation wavelengths of 280 nm. The former is weakly emissive, showing a peak at 421 nm with some fine structure (see Figure 6), while the latter shows no detectable emission from 400 to 800 nm. We assign the 421 nm band observed for PhC $\equiv$ CAu(4-dmap) (1b) as a triplet excited-state emission. The absorption– emission peak-to-peak separation is ca. 12 000 cm<sup>-1</sup>, which is significantly larger than for singlet-state emission investigated by Gao et al. on a similar compound.<sup>30a</sup> Furthermore,

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Figure 7. Frontier orbitals of PhC≡CAu(4-dmap) (1b), as calculated by CAM-B3LYP and B3LYP DFT methods.

the gap between the lowest energy triplet state and the ground state has been calculated at 2.913 eV *in vacuo*, which corresponds to a wavelength of 426 nm and is not inconsistent with the observed data.<sup>44</sup> The fine-structure spacing is 1200 cm<sup>-1</sup>, which is comparable to skeletal ring-stretching modes observed in the FT-IR and FT-Raman spectra. The lack of emission observed for compound **2b** is due to intramolecular quenching by the ferrocenyl moiety, which is not uncommon.<sup>45</sup>

When the samples were subjected to time-resolved emission measurements, no transients could be detected for either  $PhC \equiv CAu(4-NH_2Py)$  (1c) or  $PhC \equiv CAu(4-dmap)$  (1b). This may be due to low absorbance at the pump wavelength (355 nm) leading to very limited excited-state population, coupled with weak emission; transient absorption data were observed. These transient signals showed lifetimes of  $45(\pm 7)$ ns for PhC=CAu(4-NH<sub>2</sub>Py) (1c) and 22( $\pm$ 5) ns for PhC= CAu(4-dmap) (1b). Despite thorough degassing using argon, sample degradation was observed for both compounds, but as it was more severe for the former, only a small data set could be collected. The photolability of the samples meant that only a cursory transient absorption spectrum could be collected for PhC≡CAu(4-dmap) (1b). This revealed two transient absorption peaks, centered at ca. 500 and 680 nm, both showing a 22 ns lifetime. Unfortunately, sample degradation precluded experiments with extended acquisition times, from which we may have been able to observe weak phosphorescence decay.

### Conclusions

We have synthesized and structurally characterized a family of pyridyl gold(I) alkynyl complexes. The described synthetic approaches only provide stable isolable complexes when electron-rich pyridyl ligands such as 4-(dimethylamino)pyridine and 4-aminopyridine are incorporated into the complexes. In the solid state the pyridyl gold(I) alkynyl complexes form dimers; however, somewhat surprisingly none of the structures are stabilized by aurophilic interactions. Electronic absorption spectroscopy exhibited peaks at ca. 280 nm for compounds 1b and 2b. It was found that DFT calculations using B3LYP and the 6-31G(d) and LANL2DZ basis sets for "light atoms" and gold, respectively, are adequate in modeling the vibrations and electronic transitions. Little improvement could be observed upon varying the effective core potential; similarly, using the CAM-B3LYP functional for time-dependent calculations did not yield a better approximation to the absorption spectra. Triplet emission observed for compound 1b at 421 nm was quenched in the ferrocenecontaining compound 2b. DFT calculations support the experimental finding that only the pyridyl gold(I) alkynyl complexes that contain very electron rich pyridine ligands are thermodynamically stable with respect to the reactants. The limited structural diversity and stability issues associated with these molecules along with the absence of Au(I)-Au(I) interactions in the solid-state structures suggests that it will be difficult to exploit these molecules as supramolecular synthons for the construction of self-assembled nanoscale materials.

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Supporting Information Available: Text, figures, tables, and CIF files giving full experimental descriptions and spectroscopic data for 1b,c and 2b,c, crystallographic data for 1b,c and 2b,c along with figures and packing diagrams, and additional computation data and figures showing the optimized structures. This material is available free of charge via the Internet at http:// pubs.acs.org. Crystallographic data for 1b,c and 2b,c are also available from the Cambridge Crystallographic Database (CCDC 774529–774532).

<sup>(44)</sup> This quantity was obtained by comparison of TD-DFT calculations using the B3LYP method of the singlet and triplet states, using singlet and triplet geometries, respectively.

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