

# Copper-Catalyzed Huisgen [3+2] Cycloaddition of Gold(I) Alkynyls with Benzyl Azide. Syntheses, Structures, and Optical Properties

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The copper(I)-catalyzed Huisgen [3 + 2] cycloaddition is a general reaction encompassing wide ranges of organoazide and primarily terminal alkyne reacting partners. Strained internal alkynes can also undergo cycloaddition with azides. We report here that tetrakis(acetonitrile)copper(I) hexafluorophosphate catalyzes the [3 + 2] cycloaddition of (phosphine)- and (N-heterocyclic carbene)gold(I) alkynyls with benzyl azide. Isolated yields of up to 96% result. The reaction protocol broadly tolerates functionalities on the alkynyl reagent. Gold(I) triazolate products form with complete 1,4-regioselectivity. Some 15 new gold(I) triazolates are reported along with crystal structures of nine. Triazolate complexes bearing polycyclic aromatic substituents show dual singlet- and triplet-state luminescence from excited states localized on the aromatic fragment. Time-resolved emission experiments find long lifetimes consistent with triplet emission parentage. Absorption and emission transitions are analyzed with time-dependent density-functional theory calculations.

## Introduction

Gold commands attention in subfields ranging from nanomaterials<sup>1-3</sup> to catalysis,<sup>4-9</sup> and from cancer treatment<sup>10-12</sup> to energy recovery.<sup>13,14</sup> The (phosphine)- and (N-heterocyclic carbene)gold(I) fragments are at the center of much current research. These cations are isolobal with the proton;<sup>15</sup> unlike H<sup>+</sup>, they are soft Lewis acids whose properties derive partly

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from relativistic effects.<sup>16–18</sup> Formally two-coordinate gold(I) cations<sup>19–25</sup> are powerful catalysts that mediate a host of organic transformations, chiefly at unsaturated carbon.<sup>26–34</sup> The (phosphine)gold(I) thiosugar auranofin is the only orally

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ingestible gold(I) arthritis prodrug.35,36 Later observations show auranofin and other (phosphine)- and (carbene)gold(I) species to be toxic toward cancer cell lines *in vitro*; gold itself is the cytoactive component.<sup>37–40</sup> Very recent work by Teets and Nocera<sup>41</sup> shows that Au<sup>III</sup> and mixed-valence Au<sup>I</sup>-Au<sup>III</sup> complexes reductively eliminate elemental chlorine and bromine on photoexcitation of ligand-to-metal charge-transfer absorption bands. When photolysis proceeds without a halogen trap, a net energy-storing reaction is achieved. Clearly, the synthesis of gold-bearing molecules and materials is an inviting goal.

Research in this laboratory seeks selective auration of carbon skeletons to exploit the chemical and relativistic propensities of gold(I).<sup>42</sup> Direct attachment of gold to aromatic rings occurs on reacting arylboronic acids or pinacolboronate esters with gold(I) bromides.<sup>43</sup> (Phosphine)- or (Nheterocyclic carbene)gold(I) moieties displace boron while leaving other functionalities intact.<sup>44,45</sup>

Other reaction protocols have been sought that link gold to nonaryl carbon centers. Gold(I) alkynyls A are among the oldest organometallics.<sup>46–48</sup> They are most commonly prepared in reactions of (phosphine)- or (N-heterocyclic carbene)gold(I) halides with deprotonated alkynyl anions<sup>49,50</sup> and by ligand disruption of polymeric gold(I) acetylides  $^{51-54}$ or by proton interchange of gold acetylacetonate complexes

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with terminal alkynes.55-58 The resulting compounds are frequently stable in air; some are water-stable and even water-soluble.<sup>59</sup> Base deprotonations of terminal alkynes are incompatible with electrophilic and Brønsted acidic functional groups.



A report from this laboratory discloses a facile, room-temperature [3 + 2] cycloaddition reaction of (phosphine)gold(I) azides and terminal alkynes that forms carbon-bound (triazolato)gold(I) complexes  $\mathbf{B}$ .<sup>60</sup> This reaction is limited to terminal alkynes. In a related process, gold(I) alkynyls react with hydrazoic acid equivalents to yield the same triazolate complexes, although this reaction does not generate any net carbon-gold bonds. Organic (nonhydrolyzable) azides are unreactive toward (alkynyl)gold(I) species at room temperature or with heating.

This reaction, like alkynylgold(I) syntheses, adds no practicable functionality to the organogold product. A sensible objective is the synthesis of metallotriazolates C that unites alkyne precursors, gold, and functionalized azides. Triazoles C are the anticipated products of "gold click chemistry", the Huisgen [3 + 2] cycloaddition of gold(I) alkynyls and organic azides.

The copper-catalyzed [3 + 2] cycloaddition reaction of azides and alkynes<sup>61-63</sup> is now universally recognized for its synthetic power and experimental ease.<sup>64</sup> This reaction is the prototype of click chemistry, an exclusive subset of organic reactions that combine faithful reliability with ready execution and purification.<sup>65</sup> Triazole synthesis is heavily exergonic, releasing more than 20 kcal  $mol^{-1}$  of energy per product formed. The copper-catalyzed process selectively affords 1,4regioisomeric products, whereas the uncatalyzed thermal reaction produces a mixture of 1,4- and 1,5-isomers, eq 1.



Recent work has disclosed (pentamethylcyclopentadienyl)ruthenium(II) catalysts that afford wholly or predominately

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the 1,5-triazolate isomers.<sup>66–68</sup> The ruthenium-catalyzed variant produces triazolates from unstrained internal alkynes. Applications of these catalytic cycloadditions span materials synthesis,<sup>69–76</sup> bioconjugation,<sup>77–82</sup> and drug design.<sup>83,84</sup> The field has been reviewed frequently,<sup>85–89</sup> and activity shows no signs of subsiding. The vast majority of copper-catalyzed [3 + 2] cycloadditions involve terminal acetylenes, despite two observations of copper-catalyzed click cycloadditions to the symmetric alkyne 3-hexyne.<sup>90,91</sup>

The advent of click chemistry has produced terminalalkyne-bearing materials in profusion. We report here that gold(I) 1,4-triazolate products form regioselectively in high yields in the presence of copper(I) salts. This reaction represents an unusual instance of copper(I)-catalyzed cycloaddition of *internal*, unstrained alkynes. Several new gold triazolates luminesce and show triplet-state phosphorescence or dual singlet and triplet emission at room temperature. The excited states of gold(I) triazolates are discussed alongside results of density-functional theory calculations.

#### **Experimental Section**

All solvents were dried in an Mbraun solvent purification system with alumina columns. Reagents were obtained from

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commercial sources and were used as received. (PCy<sub>3</sub>)AuCl and (PPh<sub>3</sub>)AuCl were synthesized by a slight modification of the literature procedures (using toluene and Au(THT)Cl).<sup>92</sup> (SIPr)-AuCl was made according to the literature procedure.<sup>93</sup> Procedures for alkynylgold(I) complexes were done in air; these were prepared with methods described previously.<sup>94</sup> Microanalyses (C, H, and N) were performed by Robertson Microlit Laboratories, Inc. NMR spectra (<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}) were recorded on a Varian AS-400 spectrometer operating at 399.7 and 161.8 MHz, respectively. For <sup>1</sup>H NMR spectra, chemical shifts were determined from peaks of residual protiated solvent and are stated in parts-per-million relative to tetramethylsilane. For <sup>31</sup>P{<sup>1</sup>H} NMR spectra, chemicals shifts were determined relative to 85% aqueous H<sub>3</sub>PO<sub>4</sub>.<sup>95</sup>

[(SIPr)Au(1-benzyl-4-(2-naphthyl)triazolato)] (1). In a nitrogen-filled glovebox, [(SIPr)Au(2-ethynylnaphthalene)] (96.1 mg, 0.13 mmol) was suspended in 5 mL of acetonitrile. To this was added a mixture of benzyl azide (48 mg, 0.36 mmol) and [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (4.6 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h. Solvent was stripped under rotary evaporation. The remaining residue was extracted with benzene and filtered through Celite to yield a slightly yellow solution. Benzene was removed under rotary evaporation. Pentane was used to triturate the resultant residue, and an off-white powder was collected by filtration. Vapor diffusion of pentane into a benzene solution yielded colorless crystals. Yield: 103 mg (96%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$ (ppm) 9.12 (s, 1H), 8.16 (dd, 1H, J = 8.4 Hz, 2 Hz, 2-naphthyl), 7.83 (d, 1H, J = 7.6 Hz, 2-naphthyl), 7.60 (d, 1H, J =8 Hz, 2-naphthyl), 7.43 (d, 1H, J = 8.8 Hz, 2-naphthyl), 7.30 (t, 1H, J = 6.8 Hz, 2-naphthyl), 7.20-7.23 (m, 3H, 2-naphthyl, CH aromatic on SIPr), 7.00-7.03 (m, 3H, CH aromatic on benzyl), 6.98 (d, 4H, J=8 Hz, CH aromatic on SIPr), 6.78-6.80 (m, 2H, CH aromatic on benzyl), 5.02 (s, 2H, CH<sub>2</sub>-benzyl), 3.12 (s, 4H,  $CH_2$  imidazole), 2.90 (septet, 4H, J = 7.2 Hz,  $CH(CH_3)_2$ ), 1.25 (d, 12H, J = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.11 (d, 12H, J = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). UV-vis (THF):  $\lambda$  ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 257 (30700), 267 (28 200), 312 (16 800) nm. Anal. Calcd for C<sub>46</sub>H<sub>52</sub>AuN<sub>5</sub>: C, 63.37; H, 6.01; N, 8.03. Found: C, 63.58; H, 5.91; N, 8.07.

[(SIPr)Au(1-benzyl-4-tert-butyltriazolato)] (2). In a nitrogenfilled glovebox, [(SIPr)Au(tert-butylethynyl)] (75.7 mg, 0.11 mmol) was dissolved in 5 mL of acetonitrile. To this was added the mixture of benzyl azide (44 mg, 0.33 mmol) and [Cu(Me-CN)<sub>4</sub>]PF<sub>6</sub> (4.1 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h. Acetonitrile was then removed under rotary evaporation. The remaining residue was first triturated with pentane to yield a greenish powder. The powder was then redissolved in benzene and filtered through Celite. Benzene was removed from the filtrate by rotary evaporation. Pentane was used to triturate the residue, and an off-white powder was collected by filtration. Layering pentane onto a benzene solution yielded colorless crystals. Yield: 77.2 mg (85%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  (ppm) 7.11 (d, 2H, J = 7.6 Hz, CH aromatic SIPr), 6.98–6.99 (m, 3H, CH aromatic on benzyl), 6.96 (d, 4H, J = 8 Hz CH aromatic SIPr), 6.77-6.79 (m, 2H, CH aromatic on benzyl), 5.06 (s, 2H, CH<sub>2</sub>benzyl), 3.15 (s, 4H, CH imidazole), 2.89 (septet, 4H, J=7.2 Hz,  $CH(CH_3)_2$ ), 1.38 (s, 9H, tert-butyl), 1.33 (d, 12H, J = 6.8 Hz,  $CH(CH_3)_2$ , 1.13 (d, 12H, J = 6.8 Hz,  $CH(CH_3)_2$ ). Anal. Calcd for C<sub>40</sub>H<sub>54</sub>AuN<sub>5</sub>: C, 59.92; H, 6.79; N, 8.73. Found: C, 60.06; H, 6.74; N, 8.48.

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- (95) Abbreviations: Cy, cyclohexyl; NHC, N-heterocyclic carbene; SIPr, 1,3-bis(2,6-di-isopropylphenyl)-4,5-dihydroimidazol-2-ylidine; tht, tetrahydrothiophene.

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[(PPh<sub>3</sub>)Au(1-benzyl-4-carboxymethyltriazolato)] (3). In a nitrogen-filled glovebox, [(PPh<sub>3</sub>)Au(carboxymethylethynyl)] (84 mg, 0.15 mmol) was dissolved in 5 mL of acetonitrile. To this was added the mixture of benzyl azide (60 mg, 0.45 mmol) and [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (5.6 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h, after which solvent was evaporated. The remaining residue was first triturated with pentane to yield a greenish-brown powder. The powder was then redissolved in benzene and filtered through Celite. Benzene was removed by rotary evaporation. Pentane was used to triturate the resultant residue, and an off-white powder was collected by filtration. Layering pentane onto a benzene solution yielded colorless crystals. Yield: 67 mg (58%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 7.33–7.35 (m, 6H, CH aromatic), 7.07 (d, 3H, J = 7.6 Hz, CH aromatic), 6.84-6.97 (m, 14H, CH aromatic), 5.36 (s, 2H, CH<sub>2</sub>-benzyl),  $3.68 (s, 3H, CO_2CH_3)$ . <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  43.3 (s) ppm. IR (KBr): 1712 (vs,  $\nu_{C=0}$ ) cm<sup>-1</sup>. HR-MS (ES+): calcd m/z =676.1428 (M + H)<sup>+</sup>; found m/z = 676.1441. Anal. Calcd for C<sub>29</sub>H<sub>25</sub>AuN<sub>3</sub>O<sub>2</sub>P: C, 51.57; H, 3.73; N, 6.22. Found: C, 51.67; H, 3.75; N, 6.21.

[(PPh<sub>3</sub>)Au(1-benzyl-4-phenyltriazolato)] (4). In a nitrogenfilled glovebox, [(PPh<sub>3</sub>)Au(phenylethynyl)] (71 mg, 0.13 mmol) was dissolved in 5 mL of acetonitrile. To this was added the mixture of benzyl azide (51 mg, 0.38 mmol) and [Cu(MeCN)<sub>4</sub>]- $PF_6$  (4.7 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h. Solvent was removed by rotary evaporation. The remaining residue was first triturated with pentane to yield a greenish-brown powder. The powder was then redissolved in benzene and filtered through Celite. Benzene was removed from the filtrate by rotary evaporation. Pentane was used to triturate the resultant residue, and an off-white powder was collected by filtration. Layering pentane onto a benzene solution yielded colorless crystals. Yield: 60 mg (67%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 8.81 (d, 2H, J=7.2 Hz, CH aromatic), 7.27 (t, 2H, J=7.6 Hz, CH aromatic), 6.90-7.13 (m, 21H, CH aromatic), 5.50 (s, 2H, CH<sub>2</sub>-benzyl). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  43.9 (s) ppm. HR-MS (ES+): calcd  $m/z = 694.1686 (M + H)^+$ ; found m/z = 694.1670. Anal. Calcd for C<sub>33</sub>H<sub>27</sub>AuN<sub>3</sub>P: C, 57.15; H, 3.92; N, 6.06. Found: C, 57.05; H, 3.94; N, 6.05.

[(PPh<sub>3</sub>)Au(1-benzyl-4-(4-tolyl)triazolato)] (5). In a nitrogenfilled glovebox, [(PPh<sub>3</sub>)Au(4-tolylethynyl)] (66 mg, 0.11 mmol) was dissolved in 5 mL of acetonitrile. To this was added a mixture of benzyl azide (44 mg, 0.33 mmol) and [Cu(MeCN)<sub>4</sub>]- $PF_6$  (4.0 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h. Acetonitrile was removed by rotary evaporation. The remaining residue was first triturated with pentane to yield a greenish-brown powder. The powder was then redissolved in benzene and filtered through Celite. Benzene was removed by evaporation. Pentane was used to triturate the resultant residue, and an off-white powder was collected by filtration. Layering pentane onto a benzene solution yielded colorless crystals. Yield: 48 mg (58%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 8.23 (d, 2H, J = 6.8 Hz, CH aromatic), 7.16 (s, 2H, CH aromatic), 6.92-7.10 (m, 20H, CH aromatic), 5.50 (s, 2H, CH<sub>2</sub>-benzyl), 2.17 (s, 3H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.0 (s) ppm. HR-MS (ES+): calcd m/z =708.1843 (M + H)<sup>+</sup>; found m/z = 708.1860. Anal. Calcd for C<sub>34</sub>H<sub>29</sub>AuN<sub>3</sub>P: C, 57.72; H, 4.13; N, 5.94. Found: C, 57.57; H, 4.21; N, 5.79.

[(PPh<sub>3</sub>)Au(1-benzyl-4-(4-fluorophenyl)triazolato)] (6). In a nitrogen-filled glovebox, [(PPh<sub>3</sub>)Au(4-fluorophenylethynyl)] (87.7 mg, 0.15 mmol) was dissolved in 5 mL of acetonitrile. To this was added the mixture of benzyl azide (60 mg, 0.45 mmol) and [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (5.6 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h. The resultant precipitate was collected by decanting the upper solution carefully. Solvent was removed from the upper solution under rotary evaporation. The remaining residue was

first triturated with pentane to yield a greenish-brown powder. The powder was then redissolved in benzene and filtered through Celite. Benzene was removed by rotary evaporation. Pentane was used to triturate the resultant residue, and an off-white powder was collected by filtration. The original white precipitate and the powder were combined as the product. Layering pentane onto a benzene solution yielded colorless crystals. Yield: 72 mg (66%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 8.71 (dd, 2H, J = 8 Hz, 5.6 Hz, CH aromatic), 6.89–7.13 (m, 22H, CH aromatic), 5.49 (s, 2H, CH<sub>2</sub>-benzyl). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.1 (s) ppm. HR-MS (ES+): calcd m/z = 712.1592 (M + H)<sup>+</sup>; found m/z = 712.1591. Anal. Calcd for C<sub>33</sub>H<sub>26</sub>AuN<sub>3</sub>PF: C, 55.71; H, 3.68; N, 5.91. Found: C, 55.83; H, 3.44; N, 5.82.

[(PPh<sub>3</sub>)Au(1-benzyl-4-(4-formylphenyl)triazolato)] (7). In a glovebox, in 2 mL of degassed 1,2-dichloroethane was suspended (PPh<sub>3</sub>)Au(4-formylphenylethynyl) (53 mg, 0.091 mmol). Benzyl azide (3 equiv, 36 mg, 0.27 mmol) in 2 mL of degassed acetonitrile was added, and to this solution was added [Cu-(MeCN)<sub>4</sub>]PF<sub>6</sub> (3.4 mg, 0.0091 mmol). The mixture was stirred for 12 h, and the solvent was removed in vacuo. The residue was triturated with pentane in the glovebox, causing separation of a solid, which was collected, dried, and extracted into benzene. The mixture was filtered through Celite, and the filtrate reduced to dryness by rotary evaporation. The residue was triturated with pentane, and the solid was collected and extracted into toluene and filtered. The filtrate was slowly evaporated in air; after several hours, a small amount of a light green material precipitated. After the toluene filtrate had evaporated to  $\sim 1 \text{ mL}$ , the suspension was filtered through Celite to remove the light green material, and pentane vapor was diffused. After 2-3 days, a light yellow crystalline solid had separated, which was collected and dried. Yield: 23 mg (35%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  9.72 (s, 1H, C<sub>6</sub>H<sub>4</sub>(CHO)), 8.88 (d, 2H, C<sub>6</sub>H<sub>4</sub>(CHO), J = 8.0 Hz), 7.66 (d, 2H,  $C_6H_4$ (CHO), J = 8.0 Hz), 6.87–7.21 (m, 20H), 5.47 (s, 2H,  $CH_2(C_6H_5)$ ) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ ):  $\delta$  43.7 (s) ppm. IR (KBr): 1693 (w,  $\nu_{C=0}$ ) cm<sup>-1</sup>. HR-MS (ES+): calcd m/z =722.1636 (M + H)<sup>+</sup>; found m/z = 722.1643. Anal. Calcd for C<sub>34</sub>H<sub>27</sub>AuN<sub>3</sub>OP: C, 56.60; H, 3.77; N, 5.82. Found: C, 56.39; H, 3.57; N. 5.78.

[(PPh<sub>3</sub>)Au(1-benzyl-4-(3-thienyl)triazolato)] (8). In a nitrogen-filled glovebox, [(PPh<sub>3</sub>)Au(3-thienylethynyl)] (68.7 mg) was dissolved in 5 mL of acetonitrile. To this was added the mixture of benzyl azide (49 mg) and [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (4.5 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h. Acetonitrile was removed by rotary evaporation. The remaining residue was first triturated with pentane to yield a greenish powder. The powder was then redissolved in benzene and filtered through Celite. Benzene was removed by rotary evaporation. Pentane was used to triturate the resultant residue, and an off-white powder was collected by filtration. Layering pentane onto a benzene solution yielded colorless crystals. Yield: 56 mg (66%). <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  (ppm) 8.32 (dd, 1H, J = 1.2 Hz, 4 Hz, 3-thienyl), 8.22 (dd, 1H, J = 1.2 Hz, 2.8 Hz, 3-thienyl), 7.18 (s, 2H, 3-thienyl, CH aromatic) 7.10-7.11 (m, 3H, CH aromatic), 6.90-7.00 (m, 16H, CH aromatic,  $P(C_6H_5)_3$ ), 5.48 (s, 2H, CH<sub>2</sub>-benzyl). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.3 (s) ppm. HR-MS (ES+): calcd m/z =700.1251 (M + H)<sup>+</sup>; found m/z = 700.1278. Anal. Calcd for C<sub>31</sub>H<sub>25</sub>AuN<sub>3</sub>PS: C, 53.22; H, 3.60; N, 6.01. Found: C, 53.37; H, 3.38; N, 5.81.

 $[(PPh_3)Au(1-benzyl-4-ferrocenyltriazolato)]$  (9).  $(PPh_3)Au-$ (ethynylferrocene) (77 mg, 0.11 mmol) was suspended in 5 mL of acetonitrile. To this was added the mixture of benzyl azide (45 mg, 0.33 mmol) and  $[Cu(MeCN)_4]PF_6$  (4.3 mg, 10 mol %) under stirring. The mixture was then stirred under argon at room temperature for 12 h. Acetonitrile was removed by rotary evaporation. The remaining residue was first triturated with pentane to yield a dark orange powder. The powder was then redissolved in benzene and filtered through Celite. Benzene was

then removed by rotary evaporation. Pentane was used to triturate the resultant residue, and an orange powder was collected by filtration. Layering pentane onto a benzene solution yielded orange crystals. Yield: 68 mg (73%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 7.26–7.31 (m, 8H, CH aromatic), 6.90–7.10 (m, 12H, CH aromatic), 5.52 (s, 2H, CH<sub>2</sub>-benzyl), 5.41 (t, 2H, J = 1.6 Hz, ferrocenyl), 4.15 (t, 2H, J = 1.6 Hz, ferrocenyl), 4.15 (t, 2H, J = 1.6 Hz, ferrocenyl), 4.10 (s, 5H, ferrocenyl). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.6 (s) ppm. Anal. Calcd for C<sub>37</sub>H<sub>31</sub>AuN<sub>3</sub>PFe: C, 55.45; H, 3.90; N, 5.24. Found: C, 55.18; H, 3.63; N, 5.18.

[(PCy<sub>3</sub>)Au(1-benzyl-4-trimethylsilyltriazolato)] (10). In 2 mL of acetonitrile was suspended (PCy<sub>3</sub>)Au(trimethylsilylethynyl) (91 mg, 0.16 mmol), and to this was added (in a glovebox) a 1 mL acetonitrile solution of benzyl azide (62 mg, 0.47 mmol). [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (5.8 mg, 0.016 mmol) was added to this suspension, and the resultant mixture was stirred for 12 h. The product, which had precipitated, was collected by filtration and recrystallized by diffusion of pentane vapor into a saturated benzene solution to yield analytically pure material. Yield: 26 mg (23%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.15–7.20 (m, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 6.93–7.02 (m, 3H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.66 (s, 2H, CH<sub>2</sub>-benzyl), 0.89–1.78 (m, 33H, C<sub>6</sub>H<sub>11</sub>), 0.73 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  58.1 (s) ppm. Anal. Calcd for C<sub>30</sub>H<sub>49</sub>AuN<sub>3</sub>PSi: C, 50.91; H, 6.98; N, 5.94. Found: C, 50.68; H, 7.25; N, 5.93.

[(PCy<sub>3</sub>)Au(1-benzyl-4-(4-biphenyl)triazolato)] (11). In 2 mL of acetonitrile in a glovebox was suspended [(PCy<sub>3</sub>)Au(4-biphenylethynyl)] (75 mg, 0.12 mmol), and to this suspension was added a 1 mL acetonitrile solution of 3 equiv (46 mg, 0.35 mmol) of benzyl azide. [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (4.3 mg, 0.012 mmol) was added to this suspension, and the resultant mixture was stirred for 12 h. An off-white solid was collected by filtration and washed twice with pentane and dried. This precipitate was analytically pure. Yield: 68 mg (75%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.97 (d, biphenyl, 2H, J = 8.4 Hz), 7.70 (d, biphenyl, 2H, J = 8.4 Hz), 7.60 (d, biphenyl, 2H, J = 7.2 Hz), 7.24 (t, biphenyl, 2H, J = 7.6 Hz), 7.11–7.21 (m, 5H), 5.61 (s, 2H, CH<sub>2</sub>-benzyl), 0.91–1.70 (m, 33H, C<sub>6</sub>H<sub>11</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  58.1 (s) ppm. UV–vis (2-MeTHF):  $\lambda$  ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 305 (18100) nm. Anal. Calcd for C<sub>39</sub>H<sub>49</sub>AuN<sub>3</sub>P: C, 59.46; H, 6.27; 5.33. Found: C, 59.18; H, 6.55; N, 5.61.

[(PCy<sub>3</sub>)Au(1-benzyl-4-(1-naphthyl)triazolato)] (12). In 1 mL of acetonitrile in a glovebox was suspended [(PCy<sub>3</sub>)Au(1ethynylnaphthalene)] (54 mg, 0.086 mmol), and to this suspension was added a 0.5 mL acetonitrile solution of 3 equiv (34 mg. 0.26 mmol) of benzyl azide. [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (3.2 mg, 0.0086 mmol) was added to this suspension, and the resultant mixture was stirred for 12 h. The acetonitrile was removed in vacuo, and pentane was added in air, allowed to soak for 2 h, and decanted. Ether was added and then removed by rotary evaporation. Repeating this process solidified the product residue. The solid was extracted into benzene and filtered through Celite, and pentane vapor was diffused into the saturated solution. After approximately 2 days, the mother liquor immersing the crystals that separated was decanted, and the crystals were washed with pentane and dried. The dry crystals were washed thoroughly twice with a small amount of very cold xylenes to remove a small amount of a red-brown residue, followed by a pentane and ether wash (small amount of ether). The light brown crystals were dried and collected. Yield: 25 mg (38%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.37 (d, 1H, J = 8.4 Hz), 8.32 (d, 1H, J = 7.2 Hz), 7.71 (t, 2H, J =7.2 Hz), 7.39 (t, 1H, J = 7.6 Hz), 7.20–7.35 (m, 4H), 7.08 (t, 2H, J = 7.6 Hz), 6.99–7.05 (m, 1H), 5.67 (s, 2H, CH<sub>2</sub>-benzyl), 0.70–1.60 (m, 33H, C<sub>6</sub>H<sub>11</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  57.7 (s) ppm. Anal. Calcd for C<sub>37</sub>H<sub>47</sub>AuN<sub>3</sub>P: C, 58.34; H, 6.22; N, 5.52. Found: C, 58.09; H, 6.51; N, 5.64.

 $[(PCy_3)Au(1-benzyl-4-(2-naphthyl)triazolato)]$  (13). In 2 mL of 1,2-dichloroethane in a glovebox was dissolved recrystallized (PCy<sub>3</sub>)Au(2-ethynylnaphthalene) (51 mg, 0.081 mmol). To this solution was added benzyl azide (3 equiv, 33 mg, 0.25 mmol) dissolved in 2 mL of acetonitrile, followed by CuI (2.3 mg,

Scheme 1. Copper-Catalyzed Gold(I) Triazolate Synthesis



0.012 mmol) with stirring. The resultant mixture was stirred 12 h under an inert atmosphere. The solvent was stripped in vacuo, and the residue soaked in pentane for several hours in the glovebox. The pentane was decanted, the residue was dried and then extracted into benzene, and ether was added (~1:1 v/v). The extract was filtered through Celite, and the solvent removed by rotary evaporation. Pentane was added and then removed by rotary evaporation to remove as much benzene as possible, in which the product is highly soluble. The crude material was taken back into the glovebox, extracted into a minimum of toluene, and filtered, and pentane vapor was diffused to cause separation of a crystalline solid, which was collected and dried. The solid appeared to be mildly sensitive to air and/or light. Yield: 39 mg (63%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  9.31 (s, 2-naphthyl, 1H), 9.08 (d, 2-naphthyl, 1H, J = 1.6, 8.4 Hz), 7.84 (t, 2-naphthyl, 2H, J = 8.8 Hz), 7.70 (d, 2-naphthyl, 1H, J = 8.0 Hz), 6.97–7.32 (m, 7H), 5.67 (s, 2H, CH<sub>2</sub>-benzyl),  $0.94-1.80 \text{ (m, 33H, C}_6H_{11}\text{) ppm. }^{31}P\{^1\text{H}\} \text{ NMR (C}_6D_6\text{): }\delta 57.9 \text{ (s) ppm. HR-MS (ES+): calcd } m/z = 762.3246 (M + H)^+; \text{ found}$ m/z = 762.3240. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  37.8 (s) ppm. UV-vis (2-MeTHF):  $\lambda$  ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 285 (16000), 301 (16300), 345 (2700) nm. Anal. Calcd for C<sub>37</sub>H<sub>47</sub>AuN<sub>3</sub>P: C, 58.34; H, 6.22; N, 5.52. Found: C, 58.10; H, 6.50; N, 5.51.

[(PCy<sub>3</sub>)Au(1-benzyl-4-(9-phenanthryl)triazolato)] (14). In 1 mL of acetonitrile in a glovebox was suspended [(PCy<sub>3</sub>)Au(9ethynylphenanthrene)] (68 mg, 0.10 mmol), and to this suspension was added a 1 mL acetonitrile solution of 3 equiv (40 mg, 0.10 mmol) of benzyl azide. To enhance solubility, 2 mL of 1,2dichloroethane was added. [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (3.7 mg, 0.010 mmol) was added to this suspension, and the resultant solution was stirred for 12 h. The solvent was removed in vacuo, and the residue soaked with pentane for several hours in a glovebox. The pentane was decanted and the dry residue was extracted into the minimum amount of benzene needed to dissolve the residue. Approximately one volume equivalent of ether was added, and the suspension was filtered through Celite. The filtrate was reduced to dryness by rotary evaporation, and the residue triturated with pentane. The powder was collected, extracted into a minimum of benzene, and filtered, and the material was recrystallized by vapor diffusion of pentane. Washing the recrystallized material thoroughly with cold benzene yielded analytically pure material. Yield: 31 mg (38%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 9.33-9.40 (m, 1H, 9-phenanthryl), 8.50-8.60 (m, 2H, 9-phenanthryl), 8.47 (s, 1H, 9-phenanthryl), 7.75 (d, 1H, 9-phenanthryl, J = 5.6 Hz), 7.33-7.45 (m, 6H), 7.00-7.14 (m, 3H), 5.72 (s, 2H,  $CH_2$ -benzyl), 0.80–1.80 (m, 33H,  $C_6H_{11}$ ) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  57.6 (s) ppm. UV-vis (2-MeTHF):  $\lambda$  ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 263 (14400), 311 (9300) nm. Anal. Calcd for C41H49AuN3P: C, 60.66; H, 6.08; N, 5.17. Found: C, 60.48; H, 5.93; N, 5.17.

[(**PCy**<sub>3</sub>)**Au**(1-benzyl-4-(3-thienyl)triazolato)] (15). In a nitrogen-filled glovebox, a 2 mL acetonitrile solution of benzyl azide



(42 mg, 0.32 mmol) was added to a 2 mL 1,2-dichloroethane solution of [(PCy<sub>3</sub>)Au(3-thienylethynyl)] (61 mg, 0.10 mmol). To this solution was added [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (3.9 mg, 0.010 mmol), and the resultant mixture was stirred for 12 h. The solvent was removed in vacuo, and the residue was triturated with pentane in a glovebox. The pentane was decanted, and the dry residue was extracted into benzene/ether ( $\sim 1:1 \text{ v/v}$ ) and filtered through Celite. The filtrate was stripped of solvent by rotary evaporation, and the resultant residue soaked in copious pentane (30 mL). The pentane was removed by rotary evaporation, which dried the residue. The off-white solid was mixed thoroughly with toluene; the undissolved solid was washed with pentane and dried to yield 34 mg of pure product. Pentane vapor was diffused into the Celite-filtered toluene washing, and the crystalline mass that separated was washed with pentane and dried. This material was also pure by NMR and microanalysis. Combined yield: 54 mg (72%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta 8.35 \text{ (dd, 1H,}$ 3-thienyl, J = 1.2, 5.2 Hz), 8.28 (dd, 1H, 3-thienyl, J = 1.2, 3.2 Hz), 7.07 (dd, 1H, 3-thienyl, J=3.2, 4.8 Hz), 6.97-7.05 (m, 5H),

5.55 (s, 2H, CH<sub>2</sub>-benzyl), 0.90–1.64 (m, 33H, C<sub>6</sub>H<sub>11</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  58.3 (s) ppm. HR-MS (ES+): calcd  $m/z = 718.2659 (M + H)^+$ ; found m/z = 718.2661. Anal. Calcd for C<sub>31</sub>H<sub>43</sub>AuN<sub>3</sub>PS: C, 51.88; H, 6.04; N, 5.85. Found: C, 51.61; H, 6.09; N, 5.76.

[(PPh<sub>3</sub>)Au(1-adamantyl-4-(carboxymethyl)triazolato)] (17). In 2 mL of acetonitrile in a glovebox was suspended (PPh<sub>3</sub>)-Au(carboxylmethylethynyl) (16)<sup>96</sup> (66 mg, 0.12 mmol) and 1-azidoadamantane (67 mg, 0.38 mmol), and to this suspension was added 2 mL of 1,2-dichloroethane. [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (4.5 mg, 0.012 mmol) was added to this solution, and the resultant mixture was stirred for 72 h. The solvent was removed *in vacuo*, and the residue washed with pentane, dried, extracted into benzene, and filtered through Celite in a glovebox. The filtrate was reduced to dryness by rotary evaporation and triturated with pentane, and the solid that separated was

<sup>(96)</sup> Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. Aust. J. Chem. 1984, 37, 1163–1170.

Table 2. Crystanographic Data for Thazotatogolu(1) Complexes				
1	3	4	5	6
C46H52AuN5.C6H6	C <sub>29</sub> H <sub>25</sub> AuN <sub>3</sub> O <sub>2</sub> P	C <sub>33</sub> H <sub>27</sub> AuN <sub>3</sub> P	C <sub>34</sub> H <sub>29</sub> AuN <sub>3</sub> P·C <sub>6</sub> H <sub>6</sub>	C33H26 AuFN3P
1900.00	675.46	693.51	746.59	711.50
triclinic	monoclinic	monoclinic	monoclinic	monoclinic
$P\overline{1}$	$P2_1/c$	$P2_1/n$	$C_2/c$	$P2_1/c$
11.3686(11)	9.6041(7)	17.073(2)	24.504(4)	10.6315(13)
12.6375(13)	14.4554(10)	9.1697(13)	8.8512(14)	16.827(2)
16.3123(16)	18.4921(13)	17.541(2)	28.802(4)	15.2109(18)
103.1030(10)	. ,			
101.8910(10)	91.0140(10)	95.925(2)	100.730(2)	102.9620(10)
95.3870(10)				
2209.2(4)	2566.9(3)	2731.4(7)	6137.7(17)	2651.8(6)
2	4	4	8	4
1.428	1.748	1.686	1.616	1.782
100(2)	100(2)	100(2)	100(2)	100(2)
3.371	5.825	5.472	4.877	5.644
950	1320	1360	2952	1392
0.49  imes 0.47  imes 0.44	$0.22 \times 0.20 \times 0.11$	0.44  imes 0.43  imes 0.18	$0.46 \times 0.32 \times 0.10$	$0.36 \times 0.18 \times 0.16$
1.32, 26.94	1.79, 27.97	1.58, 27.75	1.44, 27.49	1.83, 27.11
24 345	30 741	31 466	35 642	27 379
9301	6109	6359	7047	5721
531	326	343	380	352
1.233	1.027	0.984	1.071	1.086
0.0248	0.0162	0.0286	0.0167	0.0399
0.0844	0.0363	0.1075	0.0389	0.1265
0.0258	0.0200	0.0339	0.0186	0.0434
0.0879	0.0374	0.1153	0.0397	0.1317
	$\frac{1}{\begin{array}{c} C_{46}H_{52}AuN_5\cdot C_6H_6\\ 1900.00\\ triclinic\\ P\overline{1}\\ 11.3686(11)\\ 12.6375(13)\\ 16.3123(16)\\ 103.1030(10)\\ 101.8910(10)\\ 95.3870(10)\\ 2209.2(4)\\ 2\\ 1.428\\ 100(2)\\ 3.371\\ 950\\ 0.49\times 0.47\times 0.44\\ 1.32, 26.94\\ 24345\\ 9301\\ 531\\ 1.233\\ 0.0248\\ 0.0844\\ 0.0258\\ 0.0879\\ \end{array}}$	$\begin{array}{c ccccc} 1 & 3 \\ \hline C_{46}H_{52}AuN_5\cdot C_6H_6 & C_{29}H_{25}AuN_3O_2P \\ 1900.00 & 675.46 \\ triclinic & monoclinic \\ \hline PI & P2_1/c \\ 11.3686(11) & 9.6041(7) \\ 12.6375(13) & 14.4554(10) \\ 16.3123(16) & 18.4921(13) \\ 103.1030(10) & \\ 101.8910(10) & 91.0140(10) \\ 95.3870(10) & \\ 2209.2(4) & 2566.9(3) \\ 2 & 4 \\ 1.428 & 1.748 \\ 100(2) & 100(2) \\ 3.371 & 5.825 \\ 950 & 1320 \\ 0.49 \times 0.47 \times 0.44 & 0.22 \times 0.20 \times 0.11 \\ 1.32, 26.94 & 1.79, 27.97 \\ 24345 & 30.741 \\ 9301 & 6109 \\ 531 & 326 \\ 1.233 & 1.027 \\ 0.0248 & 0.0162 \\ \hline 0.0844 & 0.0363 \\ 0.0258 & 0.0200 \\ \hline 0.0879 & 0.0374 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 2. Crystallographic Data for Triazolatogold(I) Complexes

	9	10	11	12
formula	C <sub>37</sub> H <sub>31</sub> AuFeN <sub>3</sub> P	C <sub>30</sub> H <sub>49</sub> AuN <sub>3</sub> PSi	C39H49AuN3P	C37H47AuN3P
fw	801.43	707.75	787.75	761.71
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\overline{1}$	$P2_{1}/c$
a, Å	23.71(2)	15.331(4)	10.7229(10)	12.2523(18)
b, Å	9.026(9)	10.891(3)	11.9560(11)	15.205(2)
<i>c</i> , Å	29.77(3)	19.294(5)	15.4679(14)	18.003(3)
α, deg			92.985(1)	
$\beta$ , deg	91.702(10)	104.821(2)	108.423(1)	108.110(1)
γ, deg			113.359(1)	
cell volume, Å <sup>3</sup>	6368(10)	3114.3(13)	1691.0(3)	3187.6(8)
Ζ	8	4	2	4
$D_{\rm calcd}, {\rm Mg}, {\rm m}^{-3}$	1.672	1.509	1.547	1.587
Т, К	100(2)	296(2)	100(2)	100(2)
$\mu$ , mm <sup>-1</sup>	5.138	4.836	4.429	4.696
F(000)	3152	1432	796	1536
cryst size, mm <sup>3</sup>	$0.35 \times 0.32 \times 0.10$	$0.27 \times 0.20 \times 0.11$	0.38 imes 0.18 imes 0.07	$0.37 \times 0.10 \times 0.10$
$\theta_{\min}, \theta_{\max}, \deg$	0.86, 27.50	1.37, 26.99	1.42, 26.96	1.75, 27.01
no. of reflns collected	54 0 27	31 641	18 921	34 007
no. of indep reflns	14 504	6594	6689	6108
no. of refined params	775	329	397	379
goodness-of-fit on $F^{2a}$	1.074	1.192	1.240	0.979
final <i>R</i> indices <sup><i>b</i></sup> $[I > 2\sigma(I)] R_1$	0.0216	0.0666	0.0265	0.0368
$wR_2$	0.0481	0.2055	0.0291	0.0415
$R$ indices (all data) $R_1$	0.0268	0.0817	0.0736	0.1179
$wR_2$	0.0545	0.2397	0.0797	0.1219

<sup>*a*</sup> GOF =  $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ ; *n* = number of reflections, *p* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (||F_o| - |F_o|)/\sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)/(n-p)]^{1/2}$ ; *n* = number of reflections, *p* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (||F_o| - |F_o|)/\sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)/(n-p)]^{1/2}$ ; *n* = number of reflections, *p* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (||F_o| - |F_o|)/\sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)/(n-p)]^{1/2}$ ; *n* = number of reflections, *p* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (||F_o| - |F_o|)/\sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)/(n-p)]^{1/2}$ ; *n* = number of reflections, *p* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (||F_o| - |F_o|)/\sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_o^2)/(n-p)]^{1/2}$ ; *b* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (||F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>*b*</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>(b)</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>(b)</sup>  $R_1 = \sum (|F_o| - |F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>(b)</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>(b)</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>(b)</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w* = number of parameters refined. <sup>(b)</sup>  $R_1 = \sum (|F_o| - |F_o|)/\sum |F_o|$ ; *w*  $F_{\rm c}^{2})^{2}/\sum w F_{\rm o}^{4}]^{1/2}$ .

collected, dried, and recrystallized by vapor diffusion of pentane into a filtered, saturated chloroform solution. The resultant solid was extracted into benzene and filtered, and the benzene removed by rotary evaporation to yielded a residue, which was triturated with pentane. The resultant white solid was collected and dried. Yield: 18 mg (21%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  7.48–7.61 (m, 6H), 6.90-7.10 (m, 9H), 3.69 (s, 1H, CO<sub>2</sub>CH<sub>3</sub>), 2.70 (s, 6H, admantyl), 1.94 (s, 3H, adamantyl), 1.48 (s, 6H, adamantyl) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  42.5 (s) ppm. IR (KBr): 1705 (vs,  $\nu_{C=0}$ ) cm<sup>-1</sup>. HR-MS (ES<sup>+</sup>): calcd m/z = 720.2053 (M + H)<sup>+</sup>; found m/z = 720.2115.

X-ray Structure Determination. New compounds were crystallized by pentane diffusion into saturated benzene solutions. Single-crystal X-ray data were collected on a Bruker AXS SMART APEX II CCD diffractometer using monochromatic Mo K $\alpha$  radiation with the omega scan technique. The unit cells were determined using SMART^{97} and SAINT+.^{98}

<sup>(97)</sup> Bruker Advanced X-ray Solutions. SMART for WNT/2000 (Version 5.628); Bruker AXS Inc.: Madison, WI, 1997-2002. (98) Bruker Advanced X-ray Solutions. SAINT (Version 6.45);

Bruker AXS Inc.: Madison, WI, 1997-2003.

Data collection for all crystals was conducted at 100 K (-173.5 °C). All structures were solved by direct methods and refined by full matrix least-squares against  $F^2$  with all reflections using SHELXTL.<sup>99</sup> Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in standard calculated positions, and all hydrogen atoms were refined with an isotropic displacement parameter 1.2 times that of the adjacent carbon.

Computations. Spin-restricted density-functional theory computations were performed within the Gaussian 03 program suite.<sup>100</sup> Calculations employed the modified Perdew-Wang exchange functional of Adamo and Barone<sup>101</sup> and the original Perdew-Wang correlation functional.<sup>102</sup> Nonmetal atoms were described with the TZVP basis set of Godbelt, Andzelm, and coworkers.<sup>103</sup> Gold orbitals were described with the Stuttgart effective core potential and the associated basis set,104 which was contracted as follows: Au,  $(8s,6p,5d) \rightarrow [7s,3p,4d]$ .<sup>105</sup> Relativity with the Stuttgart ECP and its associated basis set is introduced with a potential term (i.e., a one-electron operator) that replaces the two-electron exchange and Coulomb operators resulting from interaction between core electrons and between core and valence electrons. In this way relativistic effects, especially scalar effects, are included implicitly rather than as four-component, one-electron functions in the Dirac equation. Geometries were optimized without imposed symmetry, and harmonic frequency calculations find all structures to be potential energy minima. Calculations on triplet states were spinunrestricted. Vertical excitation energies were calculated using a TDDFT implementation described by Scuseria and co-workers.<sup>106</sup> All calculated properties reported here include implicit THF solvation ( $\varepsilon = 7.58, 298.15$  K), which was incorporated in single-point calculations of the gas-phase geometries with To-masi's polarizable continuum model (PCM).<sup>107,108</sup> The stability of each converged density was confirmed by calculation of the eigenvalues of the A matrix.<sup>109,110</sup> Percentage compositions of

- (102) Perdew, J. P.; Wang, Y. Phys. Rev. B 1992, 45, 13244–13249.
- (103) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. Can. J. Chem. **1992**, *70*, 560–571.
- (104) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. J. Chem. Phys. 1987, 86, 866–872.
- (105) (a) Basis sets were obtained from the EMSL Office of Science Basis Set Exchange, https://bse.pnl.gov/bse/portal. (b) Feller, D. J. Comput. Chem. 1996, 17, 1571–1586. (c) Schuchardt, K. L.; Didier, B.
- T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. J. Chem. Inf. Model 2007, 47, 1045–1052.
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molecular orbitals, overlap populations, and bond orders between fragments were calculated using the AOMix program of Gorelsky.<sup>111,112</sup>

# **Results and Discussion**

Syntheses and Spectroscopy. Reaction of an (N-heterocyclic carbene)gold(I) 2-naphthyl alkynyl precursor with 3 equiv of benzyl azide in the presence of 10 mol % [Cu(Me-CN)<sub>4</sub>](PF<sub>6</sub>) at room temperature for 12 h affords triazolate 1 in quantitative yield by <sup>1</sup>H NMR, Scheme 1. Lower catalyst loadings lead to incomplete conversion after 12 h. <sup>1</sup>H NMR diagnoses product formation, through a downfield shift of the benzylic hydrogen resonances upon metalation. The benzylic protons of 1 resonate at  $\delta$  5.65 ppm in C<sub>6</sub>D<sub>6</sub> relative to tetramethylsilane; those of benzyl azide, at 3.66 ppm. Complex 1 is isolated in 96% yield by crystallization from benzene/pentane solutions. An X-ray diffraction crystal structure determination establishes its identity as the 1,4regioisomer, vide infra. Other triazolate complexes are prepared in like manner. Another copper(I) source, CuI, is also efficient in catalyzing the reaction, as specified in the synthesis of compound 13. Attempts at [3 + 2] cycloaddition of gold(I) alkynyls catalyzed by (THT)AuCl (THT = tetrahydrothiophene), AgOTf (OTf = triflate), or Cp\*RuCl(COD) $(Cp^* = \eta^5 - C_5 Me_5, COD = (1Z, 5Z) - cycloocta - 1, 5 - diene) \text{ pro-}$ duced no discernible product; starting materials were recovered.

Copper-catalyzed cycloaddition of azides to gold(I) alkynyls tolerates a range of functionalities on the alkynylgold(I) reactant, Table 1. Triazolate complexes bearing alkyl and trialkylsilyl (compounds 2, 10), an ester (3), polycyclic hydrocarbon substituents (1, 12-14), phenyl groups and substituted benzene rings (4-7, 11), ferrocenyl (9), and thienyl (8, 15) readily form from (alkynyl)gold(I) precursors. New compounds are characterized by nuclear magnetic resonance spectroscopy and combustion analysis; X-ray crystal-structure determinations of 1, 3-6, and 9-12 are reported. Gold(I) triazolate complexes are isolated by crystallization, and yields are somewhat wide-ranging; that of 10 is below 30%. An expectation of crystalline products suggested the choice of benzyl azide in this work. Preliminary experiments indicate that other azides also undergo coppercatalyzed cycloaddition with gold(I) alkynyls. For example, 1-azidoadamantane reacts with alkynyl 16 to yield the alkyl triazolate:



Purification of **17** requires repeated washings and crystallization, and its isolated yield is 21%, despite <sup>31</sup>P NMR

<sup>(99)</sup> Bruker Advanced X-ray Solutions. *SHELXTL* (Version 6.10); Bruker AXS Inc.: Madison, WI, 2000.

<sup>(100)</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian 03, Revision D.01; Gaussian, Inc.: Wallingford, CT. 2004.

<sup>(101)</sup> Adamo, C.; Barone, V. J. Chem. Phys. 1998, 108, 664-675.

 <sup>(111)</sup> Gorelsky, S. I. AOMix: Program for Molecular Orbital Analysis; York University: Toronto, 1997, http://www.sg-chem.net.
 (112) Gorelsky, S. I.; Lever, A. B. P. J. Organomet. Chem. 2001, 635,

<sup>(112)</sup> Gorelsky, S. I.; Lever, A. B. P. J. Organomet. Chem. 2001 187–196.



**Figure 1.** Crystal structures (100 K) of representative gold(I) triazolates: (a) **1**; (b) **11**. Hydrogen atoms are omitted for clarity; 50% probability thermal ellipsoids are shown. A partial numbering system appears; unlabeled atoms are carbon.



Figure 2. Room-temperature absorption (blue) and emission spectra (red, 312 nm excitation) of 1 in THF.

spectra that indicate quantitative product. Attempted reactions of gold(I) alkynyls with phenyl azide led to recovery of starting reagents with no evidence of product formation.

Table 2 compiles crystallographic data. Intermolecular aurophilic interactions,<sup>113</sup> where gold atoms approach within 3.5 Å of each other, are absent from the new structures, nor do packing diagrams of the new complexes indicate intermolecular  $\pi - \pi$  interactions. Metric data are similar to those of related organogold complexes.<sup>43,45</sup> Except for **9**, a single gold complex inhabits each asymmetric unit, in some cases with benzene of crystallization. The asymmetric unit of **9** contains two crystallographically independent molecules.

The structures of 1 and 11, Figure 1, are representative. For 1, the gold-triazolato carbon bond distance is 2.015(3) Å and is nearly identical to the gold-carbone carbon length of 2.018(3) Å. For comparison, the gold-carbon bond in (Ph<sub>3</sub>P)-Au(4-tolyltriazole) measures 2.027(5) Å;<sup>60</sup> here a triazole nitrogen binds hydrogen, rather than an organic substituent. In the

(113) Schmidbaur, H.; Schier, A. Chem. Soc. Rev. 2008, 37, 1931–1951.

Table 3. Luminescence Maxima (273  $\pm$  2 K) of Emissive Compounds in THF Solution

compound	$\lambda_{\rm ex} ({\rm nm})$	$E_{\rm em}$ (nm)
1	312	383, 498, 536, 579
11	325	363, 489, 522
12	325	390, 534, 570
13	325	390, 494, 533
14	325	385, 531, 561

Table 4. Emission Lifetimes  $\tau$  and Quantum Yields  $\phi_{em}$  of Luminescent Compounds in 2-MeTHF Solution (room temperature) or Glass (77 K)

compound	$T(\mathbf{K})$	$E_{\max}$ (nm)	$\lambda_{\rm em}  ({\rm nm})^a$	$\tau$ (ms)	$\varphi_{\rm em}$
1	295	497			0.00092
1	77		495	19.1	
11	295	522			0.0014
11	77		515	0.260	
12	295	530			0.0025
12	77		540	0.277	
13	295	532			0.0016
13	77		490	5.06	
14	295	531			0.0028
14	77		540	0.401	

<sup>a</sup>Wavelength at which emission lifetime data were collected.

structure of a two-coordinate (triphenylphosphine)gold(I) allenoate complex, Hammond and co-workers report a 2.036(5) Å C–Au bond.<sup>114</sup> Such bond lengths are expected for gold-(I)–carbon single bonds.<sup>115,116</sup> Gold(I) is two-coordinate and virtually linear; the C<sub>triazolate</sub>–Au–C<sub>carbene</sub> angle is 175.06(13)°. The triazolate and naphthyl ring systems are nearly coplanar; the dihedral angle between their (non-hydrogen-atom) mean planes is 5.50°. The triazolate linker moves gold nearer the naphthyl fragment than in its alkynyl precursor. In **1**, gold is 3.593(4) Å from the nearest naphthyl carbon atom;

<sup>(114)</sup> Liu, L.-P.; Mashuta, M. S.; Hammond, G. B. J. Am. Chem. Soc. 2008, 130, 17642–17643.

<sup>(115)</sup> Fañanás-Mastral, M.; Aznar, F. Organometallics 2009, 28, 666-668.

<sup>(116)</sup> Shi, Y.; Ramgren, S. D.; Blum, S. A. Organometallics 2009, 28, 1275–1278.



**Figure 3.** Kohn–Sham orbital correlation diagram of model complex **1**'. Fragments are the (N-heterocyclic carbene)gold(I) fragment (left) and the naphthyl triazolate ligand, right (mpwpw91/Stuttgart ECP and basis on Au; TZVP on nonmetal atoms); implicit THF solvation is included through a polarizable continuum model. Right: plots of selected orbitals (contour level 0.03 au).

Table 5. Calculated Energies, Orbital Compositions, and Oscillator Strengths *f* of Allowed Transitions beyond 300 nm for 1' Dissolved in

no.	E(nm)	E(eV)	f	assignment
1	376.4	3.29	0.0992	HOMO→LUMO+1 (+80%), HOMO→LUMO (11%), HOMO→LUMO+2 (+7%)
2	367.5	3.37	0.0816	HOMO→LUMO (+56%), HOMO→LUMO+1 (+14%), HOMO−1→LUMO (+12%), HOMO→LUMO+2 (8%)
3	334.0	3.71	0.0025	HOMO-2→LUMO (+96%)
4	332.1	3.73	0.2242	HOMO $\rightarrow$ LUMO+2 (+56%), HOMO-1 $\rightarrow$ LUMO (17%), HOMO $\rightarrow$ LUMO (+14%)
5	318.7	3.89	0.0418	HOMO-1→LUMO+1 (+83%), HOMO-1→LUMO (6%)
6	309.5	4.01	0.1480	HOMO $\rightarrow$ LUMO+3 (+46%), HOMO-1 $\rightarrow$ LUMO (30%), HOMO $\rightarrow$ LUMO+2(8%)
7	304.6	4.07	0.0009	HOMO−3→LUMO (+98%)

in (SIPr)Au(2-ethynylnaphthalene), it is 4.621(5) Å away.<sup>94</sup> Metric parameters of **11** are similar.

Triazolate complexes bearing polycyclic aromatic hydrocarbon fragments are luminescent. The 2-naphthyl-substituted triazolate 1 is typical. A combined absorption and emission spectrum of 1 in tetrahydrofuran solvent appears in Figure 2. The excitation spectrum of 1 parallels the absorption trace. Absorption sets in near 400 nm. A prominent absorption maximizes at 312 nm,  $\varepsilon = 16\,600 \text{ M}^{-1} \text{ cm}^{-1}$ ; a shoulder is apparent at 325 nm. Higher-energy absorption peaks occur between 250 and 275 nm.

Excitation of 1 at 312 nm elicits dual emission at room temperature. The shorter-wavelength emission peaks are at 383 nm; the vibronic structure is partly resolved. This higherenergy emission is unquenched on exposure to air. We attribute the unquenched emission to ligand-centered fluorescence. A longer-wavelength,  $O_2$ -quenchable emission rises near 475 nm. The vibronic structure is clearly resolved with maxima at 498, 536, and 579 nm, corresponding to an average separation of 1400 cm<sup>-1</sup>. These vibronic spacings suggest that ring-deformation modes are activated in the excited states. Similar structure occurs in the triplet-state emission of naphthalene embedded in sandwich adducts with trinuclear gold<sup>117,118</sup> and in the free hydrocarbon.<sup>119</sup> Table 3 collects room-temperature emission maxima of luminescent complexes in THF (tetrahydrofuran) solution.

Time-resolved measurements at 77 K find that the emissions near 475 nm last from hundreds of microseconds to tens of milliseconds. Table 4 collects luminescence lifetimes and quantum yield data. Emission persists the longest for 1; its lifetime is 19.1 ms (77 K). The long lifetimes indicate triplet-state luminescence brought about by the heavy atom

<sup>(117)</sup> Mohamed, A. A.; Rawashdeh-Omary, M. A.; Omary, M. A.; Fackler, J. P., Jr. *Dalton Trans.* **2005**, 2597–2602.

<sup>(118)</sup> Omary, M. A.; Mohamed, A. A.; Rawashdeh-Omary, M. A.; Fackler, J. P., Jr. *Coord. Chem. Rev.* **2005**, *249*, 1372–1381.

<sup>(119)</sup> Lakowicz, J. Principles of Fluorescence Spectroscopy; Kluwer/ Plenum: New York, 1999.



∠C<sub>triazole</sub>-Au-C<sub>carbene</sub>: **175.06(13)°**, 178.3°, *178.9*°

Figure 4. Selected optimized geometric parameters of singlet and triplet 1', with comparisons to the crystal structure of 1. Bond distances, where indicated, are between non-hydrogen atoms. Legend: Gold, yellow; carbon, gray; nitrogen, blue; white, hydrogen; boldface type, crystal structure of 1; sans serif, calculated geometry of singlet 1'; blue italics, calculated geometry of triplet 1'.

effect of gold. Quantum yields are in a range typical of ligand-centered luminescence. The large number of available rotors, some owing to the benzyl substituents, all contribute to nonradiative decay.<sup>120</sup> The new compounds, all diamagnetic, lend themselves to density-functional theory calculations of the first several excited states.

**Computations.** Density-functional theory (DFT) calculations were undertaken to determine the orbital origins of the new compounds' absorption and emission. Calculations were conducted on 1', where methyls substitute for the *N*-2,6-diisopropylphenyl groups and the triazolate benzyl substituent of **1**. Geometry optimization converged to an energy minimum, as verified by a harmonic frequency calculation.

Figure 3 depicts a partial Kohn–Sham orbital energylevel diagram of 1'. The calculations include implicit THF solvation through the polarized continuum model (PCM) of Tomasi and co-workers.<sup>107,108</sup> The calculations predict a sizable gap (2.970 eV) between filled and unfilled levels. Consistent with this prediction, naphthyl triazolate complexes 1 and 13 are colorless when isolated and in solution.

Plots of selected orbitals appear at right in the figure. Percentages of ligand character are indicated, in terms of electron density.<sup>121</sup> The naphthyl-triazolate ligand dominates the frontier orbitals of 1'. The highest occupied Kohn–Sham orbital (HOMO) and the HOMO–1 are more than 97% localized on the naphthyl-triazolate fragment. The lowest unoccupied Kohn–Sham orbital (LUMO) resides almost entirely on the naphthalene fragment. In contrast, the LUMO+1 is nearly three-quarters (N-heterocyclic carbene)gold(I)-based (23.9% gold); the rest derives from the triazolate ligand.

Time-dependent density-functional theory (TDDFT) calculations were applied to the optical spectroscopy of 1'. Table 5 collects orbital compositions of allowed transitions beyond 300 nm, along with their calculated oscillator

(121) Mulliken, R. S. J. Chem. Phys. 1955, 23, 1833–1840.

strengths. Transitions are mostly composed of one-electron promotions that mingle through configuration interaction. The first singlet-singlet transition, calculated at 376 nm, consists of an excitation from the HOMO to the LUMO+1 (but with other contributions). It can be described as a ligand-to-(metal-ligand) charge transfer from the naphthyl triazolate to the (carbene)gold(I) fragment. The second allowed transition is calculated at 368 nm. It consists of more than four one-electron transitions in configuration interaction; the major contributor (56%) is a LUMO HOMO excitation. The most intense transition, based on oscillator strength, is computed at 332 nm. It is a majority (56%) LUMO+2←HOMO transition, with LUMO←HOMO-1 (17%) and LUMO HOMO (14%) character. The extensive configuration interaction among the first several singlet-singlet transitions hinders a succinct description of them. Suffice it to say that those involving the HOMO-1, HOMO, LUMO, or LUMO+2 have substantial participation from the naphthyl moiety.

Spin-unrestricted geometry optimization of the triplet excited state converged on a structure closely similar to the ground-state geometry. A harmonic frequency calculation finds the optimized triplet to be an energy minimum. Calculated bond distances and angles show good agreement with crystallographic values. The near-linearity of the  $C_{carbene}$ -Au- $C_{triazole}$  linkage is reproduced, as is the near-coplanarity of the triazole and naphthyl rings. Figure 4 compares calculated ground- and triplet-state metrics to the crystal structure of 1. The triplet-state structure is minimally distorted relative to the (singlet) ground state.

## Conclusion

In summary, gold(I) alkynyls undergo copper-catalyzed click chemistry with benzyl azide. Reactions proceed with 1,4-regioselectivity, affording triazolate products that retain both azide and alkynyl substituents. This reaction contrasts with our earlier noncatalytic reaction in protic solvents,<sup>60</sup> where a hydrolyzable azide reacts with (alkynyl)gold(I)

<sup>(120)</sup> Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006; p 953.

species in a net [3 + 2] cycloaddition of HN<sub>3</sub> across the carbon-carbon triple bond. Nine new gold(I) triazolates are structurally characterized. In no case are intermolecular aurophilic interactions observed. Gold(I) triazolates bearing photoactive substituents exhibit dual luminescence. Both singlet- and triplet-state emissions are observed. Phosphorescence suggests a pseudoexternal heavy-atom effect, where gold promotes intersystem crossing to reach an emissive, ligand-centered triplet state.<sup>122</sup> Vibronic splittings indicate that ring deformation modes are activated in the lowest triplet state. Density-functional theory calculations on a representative naphthyl-triazolate complex find the frontier orbitals to lie mostly on the conjugated triazolate ligand. The first several optically allowed transitions have both intraligand and ligand-to-metal character; configuration interaction is extensive.

The copper-mediated [3 + 2] cycloaddition is part of an emerging trend where gold(I) alkynyls react with other organometallics or with substrates under metal-ion catalysis. Blum and co-workers<sup>116</sup> report that PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> catalyzes the *syn*-carboauration of electrophilic alkynes, with crystal structures of two gold-bearing products. Fañanás-Mastral and Aznar<sup>115</sup> describe carbene-transfer reactions from chromium or tungsten centers to (N-heterocyclic carbene)gold(I) cations generated *in situ* by dehalogenation of the corresponding (NHC)gold(I) chloride with AgSbF<sub>6</sub>; one

(123) Liu, L.-P.; Hammond, G. P. *Chem. Asian J.* **2009**, *4*, 1230–1236. (124) Allred, A. L. J. Inorg. Nucl. Chem. **1961**, *17*, 215–221.

organogold product is crystallographically characterized. Hammond and co-workers<sup>114,123</sup> find that cyclization results upon reaction of (triphenylphosphine)gold(I) cations with carboethoxy-substituted allenes. Ring-closure affords fivemembered lactones with exocyclic carbon–gold bonds. One representative is crystallographically authenticated.

The results herein demonstrate that metal alkynyls support copper-catalyzed cycloaddition with organic azides. It is noteworthy that the phosphine and N-heterocyclic carbene fragments are isolobal with the proton. Standard Pauling electronegativities<sup>124</sup> suggest that the carbon–gold  $\sigma$ -bond is nonpolar. The copper-based protocol described here readily attaches gold to azide-bearing materials now available from recent efforts in click chemistry. Investigations of these aurated materials are underway.

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**Supporting Information Available:** Thermal ellipsoid projections for **3**–**6**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(122)</sup> Turro, N. J. In *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; pp 191–195.