Inorganic Chemistry

Article

pubs.acs.org/IC

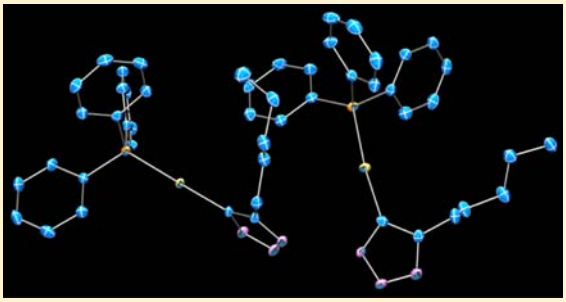
Azido, Triazolyl, and Alkynyl Complexes of Gold(I): Syntheses, Structures, and Ligand Effects

Thomas J. Robilotto, Nihal Deligonul, James B. Updegraff, III, and Thomas G. Gray*

Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, United States

Supporting Information

ABSTRACT: Gold(I) triazolyl complexes are prepared in [3 + 2] cycloaddition reactions of (tertiary phosphine)gold(I) azides with terminal alkynes. Seven such triazolyl complexes, not previously prepared, are described. Reducible functional groups are accommodated. In addition, two new (*N*-heterocyclic carbene)gold(I) azides and two new gold(I) alkynyls are described. Eight complexes are crystallographically authenticated; aurophilic interactions appear in one structure only. The packing diagrams of gold(I) triazolyls all show intermolecular hydrogen bonding between N-1 of one molecule and N-3 of a neighbor. This hydrogen bonding permeates the crystal lattice. Density-functional theory calculations of (triphenylphosphine)-gold(I) triazolyls and the corresponding alkynyls indicate that the triazolyl is a stronger *trans*-influencer than is the alkynyl, but the alkynyl is more electron-releasing. These results suggest that *trans*-influences in two-coordinate gold(I) complexes can be more than a simple matter of ligand donicity.

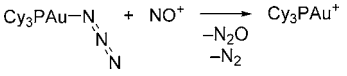


INTRODUCTION

The coinage metals in their +I oxidation states are often two-coordinate, notably gold.[1] The two-coordinate gold(I) fragment has re-emerged, mainly in organic synthesis,[2−11] but also for applications in medicine,[12−15] luminescence,[16−23] sensing,[24] and energy storage.[25] Gold(I) is metastable: the free ion disproportionates to gold(III) and two equivalents of the element in water.[26] Stability improves with a strong σ-donor ligand. (Isonitrile)gold(I) complexes are numerous,[27−34] but (organophosphine) and (*N*-heterocyclic carbene)gold(I) complexes dominate.[35−53] The resulting gold(I) compounds are frequently stable to air, water, and light, but are not necessarily monomeric.[54−56] Many (phosphine)- and (*N*-heterocyclic carbene)gold(I) complexes offer expedient combinations of crystallinity and solubility. These entities have far-flung catalytic applications.[57,58]

Gold-click chemistry seeks reliable gold-element bond-forming reactions that adhere to the standards of organic click chemistry.[59] Reactions should be operationally simple, high-yielding, and generate harmless byproducts, if any. Efforts in gold chemistry exploit the isolobality[60−62] of LAu^+ and H^+, where L is a σ-donor. The leading click reaction is certainly the copper-catalyzed azide−alkyne cycloaddition.[63−66] Several reactions of gold species are similar, an example being the reaction of gold(I) azides with isonitriles to afford *C*-tetrazolato complexes.[67] In 2007, work in this laboratory demonstrated [3 + 2] cycloaddition of (organophosphine)gold(I) azides to terminal alkynes.[68] This reaction functionalizes the termini of poly(benzyl ether) dendrimers with gold(I).[69] Also shown[68] was the related, formal addition of HN_3 to gold(I) alkynyls;[70] the azide source is Me_3SiN_3 in alcoholic media. Cycloaddition of gold(I) alkynyls and nonhydrolyzable azides proceeds in the presence of added copper. The solvate $[Cu(MeCN)_4]^+$ is effective,[71] but CuI or copper turnings are operationally superior.[72] Reactions done with copper turnings proceed in water/alcohol mixtures. Control experiments tell against a gold-catalyzed pathway, and no conversion was observed without added copper. Metzler-Nolte and collaborators have prepared (triazolato)gold(I) bioconjugates that surmount cisplatin resistance in a p53 mutant cancer cell line.[73] Veige and co-workers[74] report a double-gold click reaction where (triphenylphosphine)gold(I) azide and a (triphenylphosphine)-gold(I) alkynyl join to form a diaurated triazole with 1,5-regioselectivity. Reports from Hashmi and collaborators[75,76] describe cycloaddition reactions between gold(I) isonitriles and azomethine ylides that beget abnormal *N*-heterocyclic carbene complexes. (Tricyclohexylphosphine)gold(I) azide reacts instantly and exothermically with NO^+ to yield free (phosphine)-gold(I) cations without need of silver, thallium(I), or Brönsted acids, Scheme 1. We suggest that this redox-initiated synthesis of Cy_3PAu^+ ions is itself a click reaction. The resulting cations have been arrested with octaethylporphyrin to yield a genuine

Scheme 1. Silver-, Thallium-, and Brönsted-Acid Free Synthesis of a (Phosphine)gold(I) Cation from the Corresponding Azide

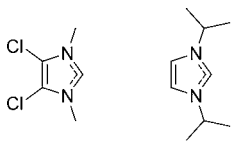


Received: June 8, 2013
Published: August 5, 2013

   dx.doi.org/10.1021/ic4014569 | *Inorg. Chem.* 2013, 52, 9659−9668

gold(I) porphyrin, with two gold centers in a sitting-atop position.[77] The combined result is the linking of LAu^{I} fragments to organic carriers to produce tags, prodrugs, and precatalysts.

Small *N*-heterocyclic carbenes have proven their value as tight-binding ligands. Youngs and co-workers have developed a variety of NHC-bound stabilizers of silver(I).[78−83] A number show appreciable antimicrobial activity.[84] Among these are 1,3-imidazole-2-ylidene and its 4,5-dichloro analogue (Cl_2NHC). Both gold(I) and silver(I) bis(carbene) complexes have been assayed against malignant human cell lines.[85,86] When assayed against a non-small cell lung cancer cell line, chloro-substituted complexes showed weaker action (higher inhibitory constants, IC_{50}) than nonhalogenated analogues. The ligand 1,3-diisopropylimidazol-2-ylidene (Pr_2^iNHC) is larger and lipophilic. It is similar to the 4,5-dimethyl analogue (Pr_2^iNHCMe_2) used by Holm and co-workers to stabilize cubane-type Co_4S_4 clusters[87] and all-ferrous $[Fe_4S_4(Pr_2^i NHCMe_2)_4]$ and $[Fe_8S_8(Pr_2^i NHCMe_2)_6]$.[88] In these assemblies, the carbene ligates tetrahedral metal centers at the vertices of clusters. The bis(carbene) complex $[(Pr_2^i NHC)_2Au]Cl$ has been evaluated in matched tumorigenic and nontumorigenic liver progenitor cell lines. Programmed cell death occurs selectively in the tumorigenic line, and evidence was presented for a mitochondrial mechanism of cytotoxicity.[89] The ligand Pr_2^iNHC has been bound to gold(I) peracetylthioglucose in place of triethylphosphine,[90] to produce a carbene analogue of auranofin.[91,92] The chloro complex (Pr_2^iNHC)AuCl has been examined as a precursor to gold nanoparticles.[93]



Cl_2NHC Pr_2^iNHC

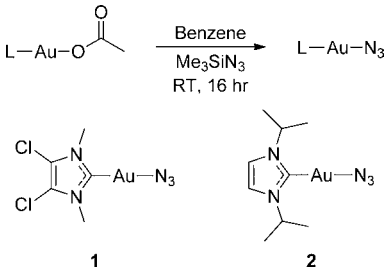
This work reports the synthesis of gold-click products and pertinent reagents. Our original disclosure[68] focused on triphenylphosphine complexes; here, complexes of tricyclohexylphosphine and the carbene ligands Cl_2NHC and Pr_2^iNHC are considered. Triazolyl products are bound through carbon, whereas reactants have gold−nitrogen bonds. Reactions proceed under mild conditions to yield air- and moisture-stable products. Some 11 new compounds are described, of which 8 are crystallographically characterized.

RESULTS AND DISCUSSION

(Azido)gold(I) Complexes. Syntheses of (azido)gold(I) complexes are similar to our earlier preparation of (tricyclohexylphosphine)gold(I) azide,[76,94] Scheme 2. Benzene solutions of the (carbene)gold(I) acetate are stirred with trimethylsilyl azide for 16 h, and azido complex **1** or **2** is isolated upon removal of solvent.

(Triazolyl)gold(I) Complexes. Treatment of a toluene suspension of (triphenylphosphine)gold(I) azide with 1-heptyne affords Ph_3PAu(*n*-pentyltriazole) complex **3**. The product formed as a precipitate that was washed repeatedly with toluene and recovered in 61% yield. In parallel reactions, the terminal alkynes cyclohexylacetylene, 1-ethynyl-4-methoxybenzene, and 3-aminophenylacetylene formed triazolyl complexes **4**−**6** in isolated yields of 67%, 59%, and 54%,

Scheme 2



1 **2**

respectively, Scheme 3. For solubility reasons, the products **4**−**6** were repeatedly washed with benzene instead of toluene. All reactions afforded clean triazolyl products after stirring for 72 h at room temperature. Reaction progress can be monitored by ^{31}P NMR. The $^{31}P\{^1H\}$ resonance of the starting material of (triphenylphosphine)gold(I) azide falls at δ 31.1 ppm in DMSO-d_6. During reaction, there is a steady decline of the starting material resonance with growth of a peak at ∼44−45 ppm for the corresponding triazolyls. Products **3**−**7** are white or off-white, air- and moisture-stable solids.

(Tricyclohexylphosphine)gold(I) complex **7**, Scheme 4, is analogous to **5**. The trialkylphosphine ligand enhances the solubility of the organometallic product compared to **5**. Precipitation occurred only on cooling to −78 °C. A white powder formed, and the supernatant was removed by decanting. The product was subsequently washed with cold pentane to afford clean **7** in 52% yield. Compound **7** is both air- and water-stable.

Complexes Bearing Coumarin Substituents. Coumarins are naturally occurring compounds first isolated from bean plants in the early 1800s, with many other varieties being found in a range of plant sources.[95] Complexes bearing coumarin moieties were pursued, in part to probe the functional group compatibility of cycloadditions within the coordination sphere of gold. The heterobicyclic benzo-α-pyrone core, although not delicate, is subject to attack by nucleophiles and reductants. Coumarins have biological applications as antibacterials, anticarcinogenics, and analgesics;[96] they are also anti-inflammatory drugs, antioxidants, and inhibitors of HIV protease.[97] Their photophysical properties make coumarins attractive as fluorescent tags and laser dyes.[98]

Reaction of **1** with 7-(propargyloxy)coumarin in toluene affords the derivatized complex, **9**, Scheme 4. Complex **9** readily precipitated and was washed with benzene to afford an off-white solid in 91% yield. The product persists in moist air over an extended period. Table 1 summarizes triazolyl products, reaction times, and isolated yields. The N-*H* ^{1}H NMR resonance of **9** appears at 14.05 ppm in DMSO-d_6.

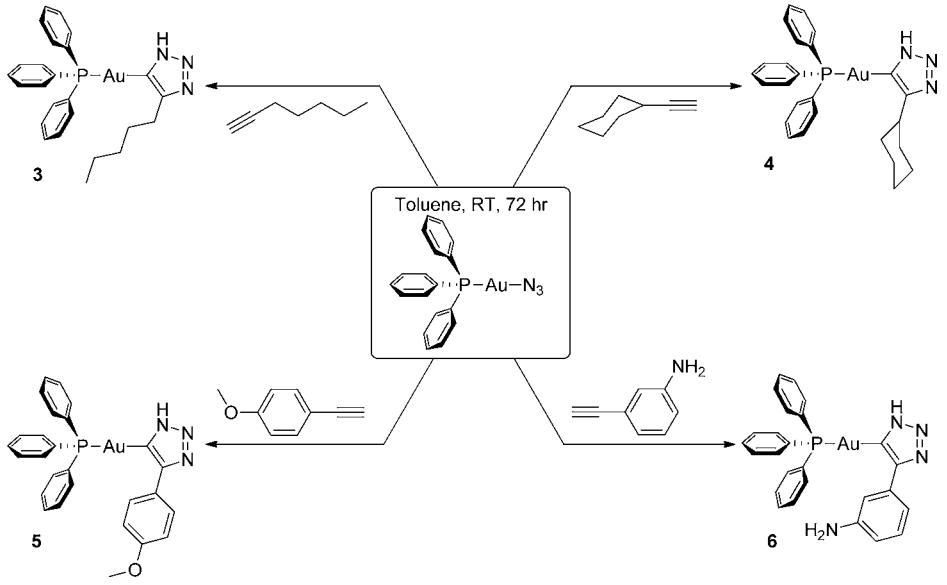
Gold(I) alkynyls bearing coumarins were also synthesized. Reactions proceeded as in Scheme 5. Interaction of Cy_3PAuCl or (Cl_2NHC)AuCl with a 7-substituted alkynylcoumarin and sodium *tert*-butoxide in 2-propanol furnished (alkynyl)gold species **10** and **11** in 72 and 85% isolated yields, respectively.

Crystal Structures. Eight complexes have been characterized crystallographically. All complexes show the two-coordinate, nearly linear geometry that is characteristic of gold(I). Table 2 sets out metric parameters involving gold. The Supporting Information summarizes crystallographic details.

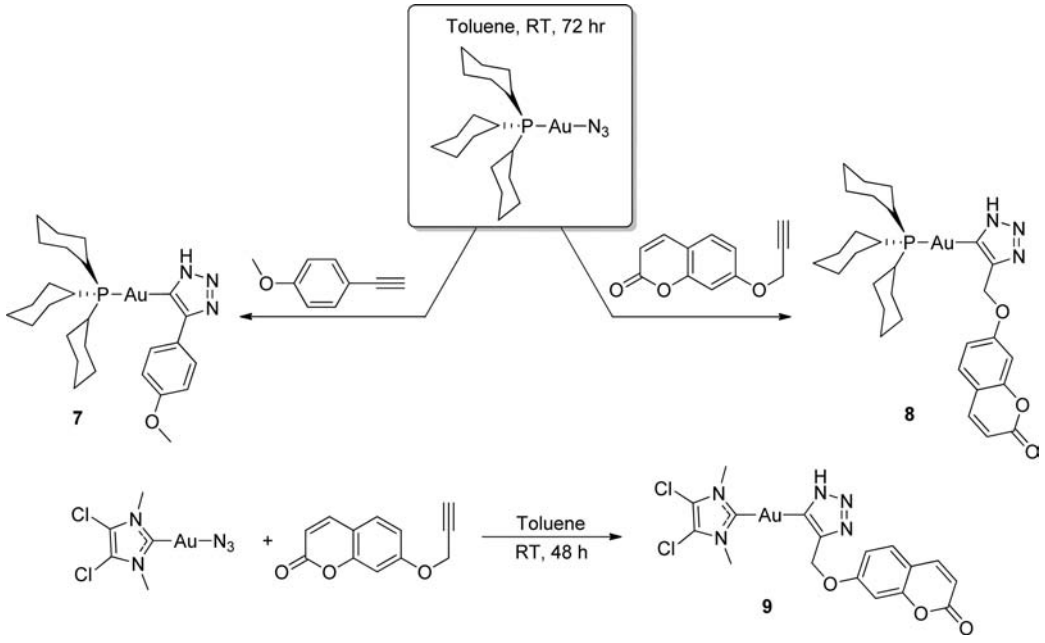
The structure of azide **1** appears as Figure 1. This compound crystallizes in the centrosymmetric space group *Pnma*; the carbene heterocycle, gold, and azide ligand rest on a mirror

dx.doi.org/10.1021/ic4014569 | *Inorg. Chem.* 2013, 52, 9659−9668

Scheme 3



Scheme 4



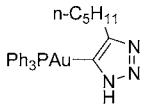
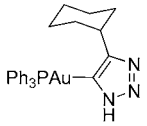
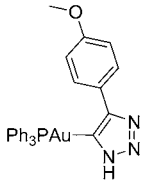
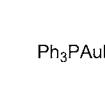
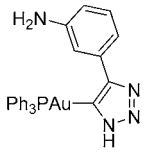
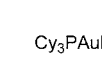
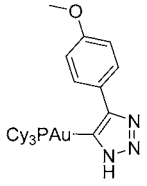
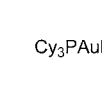
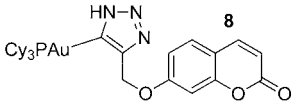
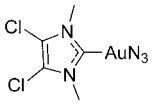
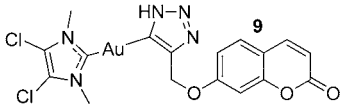
plane normal to the crystallographic *b*-axis. Neighboring gold(I) centers are in aurophilic contact at 3.40 Å apart. The gold-carbene carbon distance is similar to that (1.993(19) Å) of $(Cl_2NHC)AuCl$,[86] and to that in **2**. A thermal ellipsoid representation of **2** appears as Figure S1, Supporting Information. It is similar to **1**, even to the extent that **1** and **2** share the same space group. Compound **2** resides on a crystallographic mirror plane, except for the isopropyl methyls. Distances between gold and the bound azido nitrogens are 2.020(6) Å in **1** and 2.033(7) Å in **2**, but the difference is not statistically significant.[99] The closest approach of gold centers in **2** exceeds 3.8 Å, and the crystal structure does not show aurophilic interactions.

The essential structural features of triazolyls **3**–**7** are similar. All display linear gold(I) without aurophilic or π-stacking interactions. In no unit cell do molecules occupy special positions. Interatomic distances and angles involving gold, Table 2, are normal.[68−72] Complex **3** is representative. Its asymmetric unit, which contains two crystallographically independent molecules, appears as Figure 2a. Bond lengths to gold do not significantly differ between independent copies of the same molecule. A network of hydrogen bonds threads through the structure: N-1 and N-3 on an adjacent molecule are within hydrogen-bonding distance. The five triazolyl structures reported here all show this pattern of intermolecular hydrogen bonding. Figure 2b depicts the packing diagram of **3** viewed along *a*; hydrogen bonds are indicated.

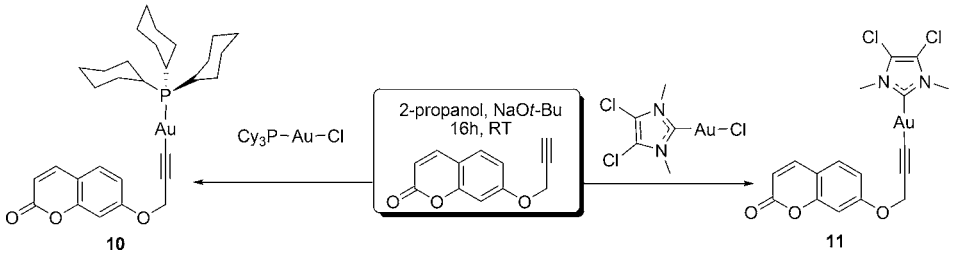
Figure 3 depicts the structure of alkynyl **11**. Diffraction-quality crystals of **11** grew in a saturated tetrahydrofuran (THF) solution layered with *n*-pentane, to which a drop (~20 μL) of benzene was added. Benzene of crystallization occurs in the asymmetric unit. Four molecules of **11** occupy the unit cell,

dx.doi.org/10.1021/ic4014569 | *Inorg. Chem.* 2013, 52, 9659−9668

Table 1. Synthesis of (Triazolyl)gold(I) Complexes

Gold(I) azide	Alkyne	Reaction time (h)	Product		Isolated yield
Ph_3PAuN_3		72		**3**	61%
Ph_3PAuN_3		72		**4**	67%
Ph_3PAuN_3		72		**5**	59%
Ph_3PAuN_3		72		**6**	54%
Cy_3PAuN_3		72		**7**	52%
Cy_3PAuN_3		48		**8**	66%
		48		**9**	91%

Scheme 5



but they are not crystallographically independent. There are no obvious intermolecular interactions. The nearest gold–gold approach exceeds 7 Å, despite the small *N*-heterocyclic carbene ligand. Geometric parameters involving gold, Table 2, are unexceptional,[70] as are those of the coumarin.[72]

Calculations. Gold(I) alkynyls[100−103] and triazolyls are closely related organometallics. With recent work in gold-click chemistry, terminal alkynes, organic azides, or premade gold(I) alkynyls can all embed gold in organic constructs. The electronic consequences of alkynyl vs triazolyl binding are immediate questions. We have performed density-functional theory computations on **3**, which is representative, and its corresponding alkynyl. Optimized metrics agree well with those of the two crystallographic modifications. The gold–phosphorus bond length *trans* to the triazolyl is computed to be longer (0.015 Å) than that opposite the alkynyl. Partial Kohn–Sham

dx.doi.org/10.1021/ic4014569 | *Inorg. Chem.* 2013, 52, 9659−9668

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

compound	Au−P	Au−$C_{carbene}$	Au−$C_{triazolyl}$	Au−$C_{alkynyl}$	∠P/C−Au−N/C
1		1.967(6)			175.5(2)
2		1.973(8)			178.6(3)
3	2.2913(6)		2.037(2)		178.85(7)
	2.2761(6)		2.014(2)		171.15(7)
4	2.273(3)		2.018(10)		177.4(3)
5	2.2798(12)		2.025(4)		175.20(12)
6	2.270(3)		2.019(11)		177.5(3)
	2.289(3)		2.032(10)		172.9(3)
	2.278(3)		2.049(10)		177.2(3)
7	2.2928(7)		2.047(3)		177.98(8)
	2.2883(8)		2.030(3)		178.24(8)
	2.2775(8)		2.023(3)		177.81(8)
11		2.013(5)		1.982(5)	177.3(2)

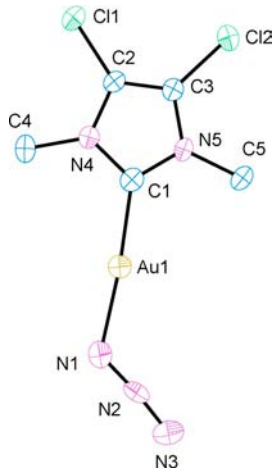


Figure 1. Thermal ellipsoid depiction of azido complex **1** (50% probability). An atom-labeling scheme is indicated. Hydrogen atoms are omitted for clarity.

orbital energy level diagrams appear in Figure 4, along with frontier orbital depictions. In both complexes, the highest-occupied Kohn−Sham orbital (HOMO) resides on the triazolyl or alkynyl ligand. The lowest unoccupied Kohn−Sham orbital (LUMO) mainly consists of phenyl p-functions on the capping PPh_3 ligand. The large HOMO−LUMO energy gaps agree qualitatively with the colorlessness of the pure compounds.

The triazolyl is a modestly stronger *trans*-influencer than the alkynyl. Work on *trans*-influences[104] in gold(I) complexes is not extensive. Jones and Williams,[105] on the basis of ^{35}Cl nuclear quadrupole resonance, find that σ-bonding dominates the *trans*-influences of chlorogold(I) complexes. A density-functional theory study[106] reiterates that *trans*-oriented ligand σ-orbitals compete for the same sd-hybrid orbital on gold.

A Dapprich−Frenking charge decomposition analysis[107] indicates that *alkynyls* are more electron-releasing than their respective triazolyls. This result is intuitive if the inductive effect of three triazolyl nitrogens outweighs the greater electronegativity of sp- vs sp^2-hybridized carbon. The triazolyl ligand of **3** donates 0.07 fewer electrons than the corresponding alkynyl. An attractive possibility is that the triazolyl ring is more π-acidic than the ethynyl moiety. Similar results prevail for the other (triphenylphosphine)gold(I) complexes, Table 3. The table also collects calculated Au−P bond distances. In all cases, the *triazolyl* is more *trans*-influencing by a small margin.

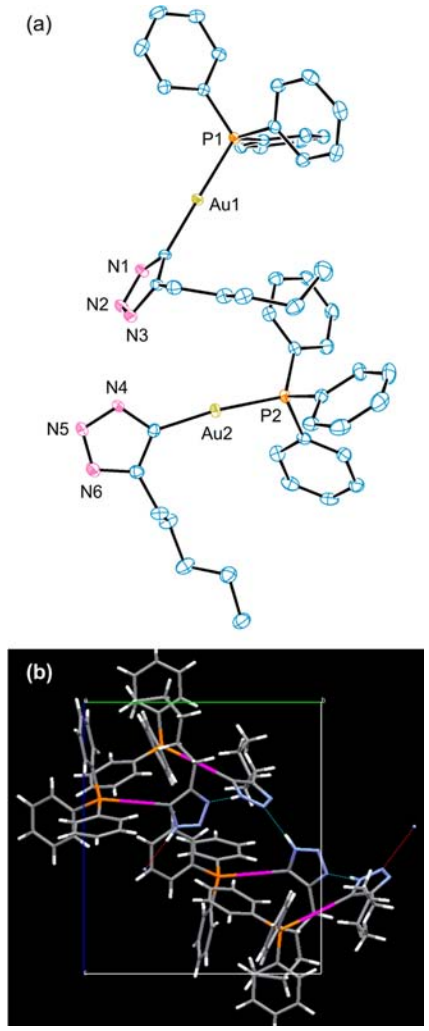


Figure 2. (a) Thermal ellipsoid depiction of triazolyl complex **3** (50% probability) showing two crystallographically independent molecules in the asymmetric unit (50% probability). A partial atom-labeling scheme is indicated. Hydrogen atoms are omitted for clarity; unlabeled atoms are carbon. (b) View of the unit cell along *a*. Dashed lines indicate intermolecular hydrogen bonds.

■ CONCLUSIONS

Gold-click chemistry, in one incarnation, yields triazolyl complexes from gold(I) azides and terminal alkynes. Earlier

dx.doi.org/10.1021/ic4014569 | *Inorg. Chem.* 2013, 52, 9659−9668

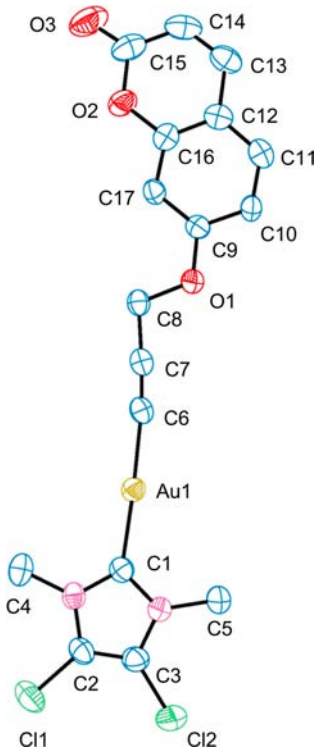


Figure 3. Thermal ellipsoid depiction of alkynyl complex **11** (50% probability). Benzene of crystallization (not shown) inhabits the unit cell. An atom-labeling scheme is indicated. Hydrogen atoms are omitted for clarity.

work from this laboratory shows that triazolyls can also be obtained from (phosphine)gold(I) alkynyls and azide ion, or its equivalents, in protic media.[68,69] Here, we enlarge the gold-click menagerie with (*N*-heterocyclic carbene)gold(I) azides, (phosphine)- and (carbene)gold(I) triazolyls, and functionalized gold(I) alkynyls. Crystal structures are included for eight new compounds. A recurrent hydrogen-bonding motif is described for *N*-protonated gold(I) triazolyls.

The four (triphenylphosphine)gold(I) triazolyls herein were chosen for density-functional theory calculations; **3** is a prototype. Computations have also been performed on the corresponding alkynyls. The calculations find that the triazolyl is a slightly better *trans*-influencer than the corresponding alkynyl, which is more electron-releasing. The stronger electron donation from the alkynyl carbon, despite its sp-hybridization, results from the electronegativity of the triazolyl nitrogens. The triazolyl ligands are more *trans*-influencing, but the difference is slight. These results caution against structural or reactivity generalizations for LAu^{I} without experimentation or preliminary calculations.

EXPERIMENTAL SECTION

Materials. Reagents were commercial in origin and were used without further purification unless indicated. Solvents were passed through activated alumina columns in an MBraun solvent purification system before use. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were collected on a Varian AS-400 spectrometer operating at 399.7 and 161.8 MHz, respectively. For ^{1}H NMR spectra, chemical shifts were determined relative to the solvent residual peaks. For $^{31}P\{^{1}H\}$ NMR, chemical shifts were determined relative to concentrated H_3PO_4. Microanalyses (C, H, and N) were undertaken by Robertson Microlit Laboratories. Mass spectrometry was performed at the University of Cincinnati Mass Spectrometry facility.

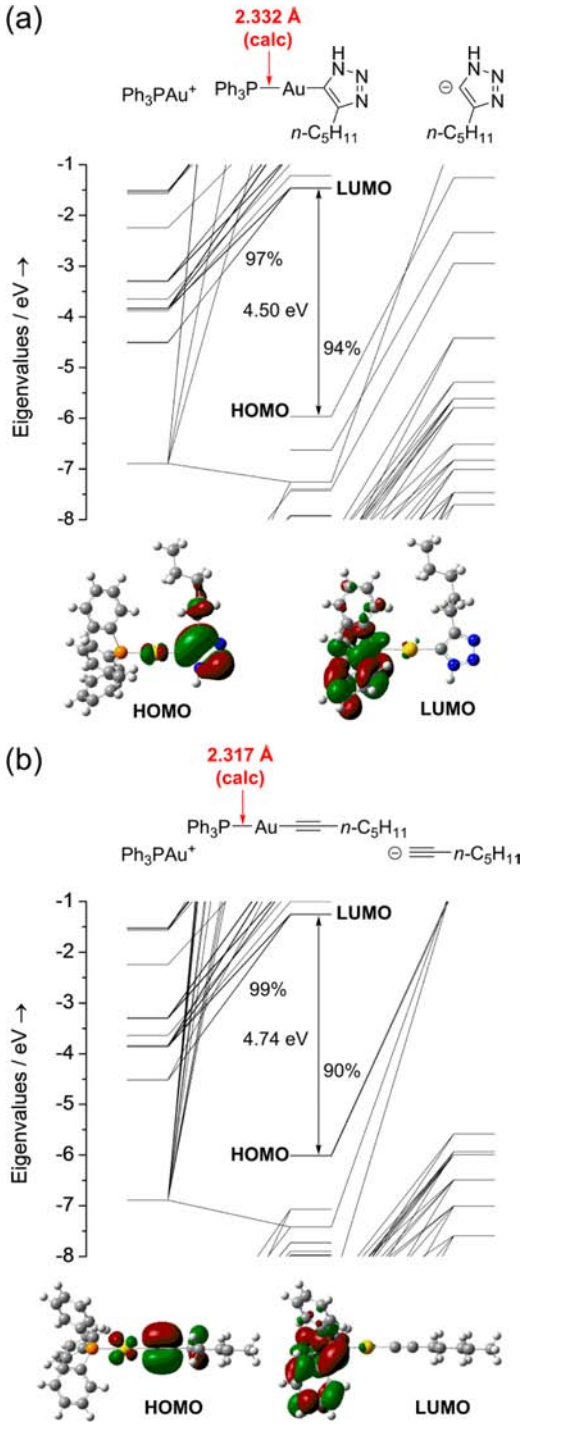


Figure 4. Frontier Kohn–Sham orbital energy level diagrams of (a) **3** and (b) its alkynyl analogue. Computed gold–phosphorus distances are indicated, and selected orbitals are inset (contour level 0.03 au). All calculations are gas-phase. Compositions of the HOMO and LUMO appear as percentages of fragment electron density.

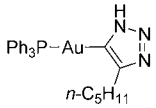
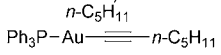
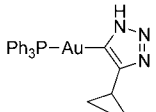
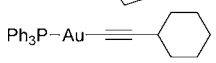
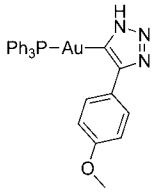
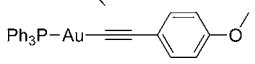
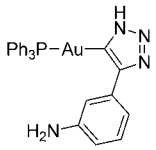
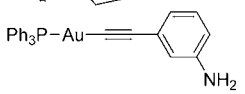
The (phosphine)- or (*N*-heterocyclic carbene)gold(I) azides used to synthesize triazolyl complexes were prepared as described previously.[76,93] (Phosphine)gold(I) chlorides and $(Pr^{i}_{2}NHC)AuCl$ were prepared according to literature procedures.[41]

Synthesis. ***Caution!*** *Metal azide complexes are potentially explosive, and due precautions should be taken.*

$(Cl_2NHC)AuCl$. In 10 mL of tetrahydrofuran was dissolved $(Cl_2NHC)AgI$ (102 mg, 0.255 mmol), followed by 85.0 mg (0.265 mmol) of (THT)AuCl. A white precipitate quickly formed. The

dx.doi.org/10.1021/ic4014569 | Inorg. Chem. 2013, 52, 9659–9668

Table 3. Calculated Triazolyl or Alkynyl Net Charge Transfer to (Triphenylphosphine)gold, from Dapprich−Frenking Charge Decomposition Analysis[a]

Complex		Calculated Au–P bond distance (Å)	Net charge donation to Ph_3PAu (electrons)
	**3**	2.332	0.93
	**3′**	2.317	1.00
	**4**	2.333	0.95
	**4′**	2.318	1.01
	**5**	2.331	0.91
	**5′**	2.318	0.97
	**6**	2.331	0.91
	**6′**	2.319	0.98

[a]Primes indicate alkynyl complexes.

solution mixture was stirred for 16 h, the solvent was filtered through a plug of Celite and then removed by rotary evaporation. A white solid remained that was washed with pentane (3 × 50 mL) and then vacuum-dried. Yield: 94 mg (93%). ^{1}H NMR ($CDCl_3$): δ 3.83 (s, 6H) ppm. Anal. Calcd for $C_5H_6AuN_2Cl_3$: C, 15.11; H, 1.52; N, 7.05. Found: C, 15.49; H, 1.53; N, 7.15%.

*(Cl_2NHC)AuN_3 (**1**).* To 15 mL of benzene was added (Cl_2NHC)-AuCl (155 mg, 0.390 mmol), and to this solution was added silver acetate (66.8 mg, 0.400 mmol), with formation of a gray precipitate. The solution was stirred for 16 h in the absence of light. The solution was filtered twice through a plug of Celite. To the filtrate 0.05 mL (3.80 mmol) of trimethylsilyl azide was added by syringe. There was no visible change. The solution was stirred for 16 h, the solvent removed by rotary evaporation, and the solid was triturated with pentane and collected. Yield: 144 mg (92%). ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 6H) ppm. IR (KBr): 2052 ($\nu_{as\ N=N=N}$, vs), 1286 ($\nu_{s\ N=N=N}$, w) cm^{-1}. Anal. Calcd for $C_5H_6AuN_5Cl_2$: C, 14.86; H, 1.50; N, 17.33. Found: C, 14.63; H, 1.53; N, 17.01%.

*(Pr_2^iNHC)AuN_3 (**2**).* To 15 mL of benzene was added (Pr_2^iNHC)-AuCl (99 mg, 0.258 mmol), and to this solution was added silver acetate (45 mg, 0.270 mmol). A gray precipitate quickly formed. The solution mixture was stirred for 16 h in the absence of light. The solution was filtered twice through Celite, and the filtrate was collected. To the filtrate was added 0.05 mL (3.80 mmol) of trimethylsilyl azide by syringe. There was no visible change. The solution was stirred for 16 h, the solvent removed by rotary evaporation, and the solid was triturated with pentane and collected. Yield: 83 mg (82%). ^{1}H NMR ($CDCl_3$): δ 6.97 (s, 2H, HC=C*H*), 4.97 (sept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 1.46 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$) ppm. IR (KBr): 2051 ($\nu_{as\ N=N=N}$, vs), 1285 ($\nu_{s\ N=N=N}$, w) cm^{-1}. Anal. Calcd For $C_9H_{16}AuN_5$: C, 27.63; H, 4.12; N, 17.90. Found: C, 27.54; H, 3.98; N, 17.65%.

*Ph_3PAu(n-pentatriazole) (**3**).* In 20 mL of toluene was suspended Ph_3PAuN_3 (122 mg, 0.24 mmol), and to this suspension was added 1-heptyne (100 μL, 0.76 mmol). The resultant suspension was stirred under argon for 72 h. The supernatant was decanted to yield a white solid. This solid was washed with toluene and *n*-pentane, and then vacuum-dried. Yield: 88 mg (61%). ^{1}H NMR (DMSO-d_6): δ 13.92 (s br, 1H, NH), 7.54−7.67 (m, 15H, CH), 2.68 (t, J = 7.6 Hz, 2H, CH_2), 1.70 (m, 2H, CH_2), δ 1.21−1.31 (m, 4H, CH_2), 0.75 (t, J = 6.8 Hz, 3H, CH_3) ppm. ^{31}P{^{1}H} NMR (DMSO-d_6): δ 45.0 ppm. Anal. Calcd for $C_{25}H_{27}AuN_3P$: C, 50.26; H, 4.56; N, 7.03. Found: C, 49.99; H, 4.52; N, 7.02%.

*Ph_3PAu(cyclohexyltriazole) (**4**).* In 10 mL of toluene was suspended Ph_3PAuN_3 (67 mg, 0.13 mmol), and to this suspension was added cyclohexylacetylene (50 μL, 0.38 mmol). The suspension was stirred under argon for 72 h. The resultant suspension was dried in vacuo to yield a white product. This solid was washed with benzene and *n*-pentane, and then vacuum-dried. Yield: 54 mg (67%). ^{1}H NMR (DMSO-d_6): δ 13.91 (s br, 1H, NH), 7.52−7.64 (m, 15H, CH), 2.79 (t, J = 11.6 Hz, 1H, CH), 1.05−1.98 (m, 10H, CH_2) ppm. ^{31}P{^{1}H} NMR (DMSO-d_6): δ 45.0 ppm. Anal. Calcd for $C_{26}H_{27}AuN_3P$: C, 51.24; H, 4.47; N, 6.89. Found: C, 50.94; H, 4.48; N, 6.74%.

*Ph_3PAu(4-methoxyphenyltriazole) (**5**).* To 10 mL of toluene was added Ph_3PAuN_3 (64 mg, 0.13 mmol), and to this suspension was added 1-ethynyl-4-methoxybenzene (50 μL, 0.21 mmol). The suspension was stirred under argon for 72 h, and was dried in vacuo to yield a white solid. The product was washed with benzene and *n*-

dx.doi.org/10.1021/ic4014569 | Inorg. Chem. 2013, 52, 9659−9668

pentane, and then vacuum-dried. Yield: 48 mg (59%). ^{1}H NMR (DMSO-d_6): δ 14.27 (s br, 1H, NH), 8.10 (d, J = 8.4 Hz, 2H, CH), 7.56−7.64 (m, 15H, CH), 6.91 (d, J = 8.4 Hz, 2H, CH), 3.78 (s, 3H, CH_3) ppm. ^{31}P{^{1}H} NMR (DMSO-d_6): δ 44.7 ppm. Anal. Calcd for $C_{27}H_{23}AuN_3OP$: C, 51.20; H, 3.66; N, 6.63. Found: C, 51.44; H, 3.92; N, 6.41%.

*Ph_3PAu(3-aminophenyltriazole) (**6**).* To 10 mL of toluene was added Ph_3PAuN_3 (74 mg, 0.14 mmol), and to this suspension was added 3-aminophenylacetylene (80 μL, 0.71 mmol). The suspension was stirred under argon for 72 h. The reaction mixture was dried in vacuo to yield a light orange product. The product was washed with benzene and *n*-pentane, and then vacuum-dried. Yield: 49 mg (54%). ^{1}H NMR (DMSO-d_6): δ 14.22 (s br, 1H, NH), 7.57−7.66 (m, 15H, CH), 7.43 (d, J = 7.6 Hz, 2H, CH), 7.39 (s, 1H, CH), 6.97 (t, J = 7.6 Hz, 1H, CH), 6.45 (d, J = 8.0 Hz, 1H, CH), 5.02 (s br, 2H, NH_2) ppm. ^{31}P{^{1}H} NMR (DMSO-d_6): δ 44.5 ppm. Anal. Calcd for $C_{26}H_{22}AuN_4P{\cdot}H_2O$: C, 49.07; H, 3.80; N, 8.80. Found: C, 49.40; H, 3.69; N, 8.70%.

*Cy_3PAu(4-methoxyphenyltriazole) (**7**).* In 5 mL of toluene was dissolved Cy_3PAuN_3 (125 mg, 0.241 mmol), and to this solution was added 1-ethynyl-4-methoxybenzene (120 μL, 0.50 mmol). The solution was stirred under argon for 72 h. The reaction mixture was cooled to near freezing in an acetone/dry ice bath. Upon cooling, a white solid precipitated. The supernatant was decanted while still cold. The white solid was washed repeatedly with *n*-pentane, vacuum-dried, and collected. Yield: 82 mg (52%). ^{1}H NMR (DMSO-d_6): δ 14.04 (s br, 1H, NH), 8.07 (d, J = 8.8 Hz, 2H, CH), 6.88 (d, J = 8.8 Hz, 2H, CH), 3.75 (s, 3H, CH_3), 2.45−1.12 (m, 33H, cyclohexyl) ppm. ^{31}P NMR (DMSO-d_6): δ 60.0 ppm. Anal. Calcd for $C_{27}H_{41}AuN_3OP$: C, 49.77; H, 6.34; N, 6.45. Found: C, 49.73; H, 6.15; N, 6.17%.

*Triazolyl **8**.* In 20 mL of toluene was dissolved Cy_3PAuN_3 (156 mg, 0.300 mmol), and to this solution was added 7-(propargyloxy)-coumarin (30.0 mg, 0.150 mmol). The reaction mixture was stirred under argon for 48 h. A pale yellow precipitate formed, which was collected and washed with benzene (3 × 10 mL) and then with pentane. The remaining light yellow solid was collected and dried. Yield: 71 mg (66%). ^{1}H NMR ($CDCl_3$): 11.51 (s br, 1H, NH), 7.62 (d, J = 9.2 Hz, 1H, CH), 7.34 (d, J = 8.4 Hz, 1H, CH), 7.04−7.96 (m, 2H, CH), 6.22 (d, J = 9.6 Hz, 1H, CH), 5.31 (s, 2H, Ar-OCH_2-tri), 0.85−2.30 (m, 33H, cyclohexyl) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 58.0 ppm. Anal. Calcd for $C_{30}H_{41}AuN_3O_3P$: C, 50.07; H, 5.74; N, 5.84. Found: C, 49.89; H, 5.54; N, 5.56%.

*Triazolyl **9**.* In 20 mL of toluene was dissolved **1** (80 mg, 0.198 mmol), and to the resulting solution was added 7-(propargyloxy)-coumarin (20.0 mg, 0.100 mmol). The solution was stirred under argon for 48 h. A pale white precipitate formed, which was collected and washed with benzene (3 × 10 mL) and then with pentane. The off-white solid was collected and dried. Yield: 54 mg (91%). ^{1}H NMR (DMSO-d_6): 14.05 (s br, 1H, NH), 7.93 (d, J = 9.6 Hz, 1H, CH), 7.56 (d, J = 8.8 Hz, 1H, CH), 7.25 (s, 1H, CH), 6.97 (dd, J = 2.4, 8.4 Hz, 1H, CH), 6.22 (d, J = 9.6 Hz, 1H, CH), 5.23 (s, 2H, Ar-OCH_2-tri), 3.78 (s, 6H, CH_3) ppm. Anal. Calcd for $C_{17}H_{14}AuCl_2N_5O_3$: C, 33.79; H, 2.34; N, 11.59. Found: C, 33.55; H, 2.47; N, 11.37%.

*Alkynyl **10**.* In 10 mL of 2-propanol was dissolved Cy_3PAuN_3 (55 mg, 0.105 mmol), and 7-(propargyloxy)coumarin (20.0 mg, 0.100 mmol). To the resulting solution was added sodium *tert*-butoxide (57 mg, 0.593 mmol). The solution was stirred under argon for 48 h, and a yellow precipitate formed. The yellow precipitate was collected by filtration and washed repeatedly with cold 2-propanol and then with pentane. The yellow-brown solid was then collected and dried in vacuo. Yield: 49 mg (72%). ^{1}H NMR ($CDCl_3$): δ 7.62 (d, J = 9.6 Hz, 1H, CH), 7.34 (d, J = 8.4 Hz, 1H, CH), 6.82−6.91 (m, 3H, CH), 6.63 (d, J = 2.4 Hz, 2H, CH), 6.59 (t, J = 2.4 Hz, 1H, CH), 6.23 (d, J = 9.2 Hz, 1H, CH), 5.03 (s, 2H, OCH_2), 4.74 (s, 2H, OCH_2), 1.22−2.08 (m, 33H, cyclohexyl) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 55.9 ppm. Anal. Calcd for $C_{30}H_{40}AuPO_3$: C, 53.26; H, 5.95. Found: C, 53.11; H, 6.31%.

*Alkynyl **11**.* In 10 mL of 2-propanol was dissolved (Cl_2NHC)AuCl (43 mg, 0.108 mmol) and 7-(propargyloxy)coumarin (20.0 mg, 0.100 mmol). To the resulting solution was added sodium *tert*-butoxide (53 mg, 0.551 mmol). The solution was stirred under argon for 48 h, and a light yellow precipitate evolved. The yellow precipitate was collected by filtration and was washed repeatedly with cold 2-propanol and then with pentane. The light yellow solid was then collected and dried in vacuo. Yield: 48 mg (85%). ^{1}H NMR ($CDCl_3$): δ .61 (d, J = 9.6 Hz, 1H, CH), 7.33 (d, J = 8.8 Hz, 1H, CH), 7.05 (d, J = 2.4 Hz, 1H, CH), 6.92 (dd, J = 2.4, 8.4 Hz, 1H, CH), 6.22 (d, J = 9.6 Hz, 1H, CH), 4.90 (s, 2H, Ar-OCH_2-tri), 3.79 (s, 6H, CH_3) ppm. Anal. Calcd for $C_{17}H_{13}AuCl_2N_2O_3{\cdot}1/2\ H_2O$: C, 35.81; H, 2.47; N, 4.91. Found: C, 35.67; H, 2.33; N, 4.78%.

Crystallography. Single-crystal diffraction studies proceeded on a Bruker AXS SMART APEX II CCD diffractometer using monochromatic Mo Kα radiation with the omega scan technique. Measurements were made at 100 K; samples were mounted on a mitogen tip using Paratone-N, then flash-frozen under a stream of nitrogen gas. The unit cells were determined using SMART and SAINT+. 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. Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in standard calculated positions and were refined with an isotropic displacement parameter 1.2 times that of the adjacent carbon.

Computations. Spin-restricted density-functional theory calculations were executed in Gaussian 09 rev. A.02.[108] Geometries were fully optimized. Calculations employed the exchange and correlation functionals of Perdew, Burke, and Ernzerhof,[109] and the TZVP basis set of Godbelt, Andzelm, and co-workers for nonmetals.[110] For gold, the Stuttgart 97 effective core potential and basis set were used;[111] scalar relativistic effects are included implicitly. Harmonic frequency calculations returned real vibrational frequencies, except for the alkynyl **6′**, Table 3. A small imaginary frequency, 2.85i cm^{-1}, was calculated for substituent rotation about the axis of the carbon−carbon triple bond. The potential energy surface along this coordinate is very flat, and attempts to locate a true minimum failed. All calculations are gas-phase. Population analyses were performed with the AOMix-CDA software of Gorelsky.[112,113]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Thermal ellipsoid depictions of new compounds, table of crystallographic data, and optimized Cartesian coordinates; crystallographic files in .cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tgray@case.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation, Grant CHE-1057659 to T.G.G., and by an Ohio Third Frontier fellowship to T.J.R. The diffractometer at Case Western Reserve was funded by NSF Grant CHE-0541766. N.D. thanks the Republic of Turkey for a fellowship.

■ REFERENCES

(1) Carvajal, M. A.; Novoa, J. J.; Alvarez, S. *J. Am. Chem. Soc.* **2004**, *126*, 1465−1477.
(2) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395−403.
(3) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180−3211.
(4) Michelet, V.; Toullec, P. Y.; Genêt, J.-P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4268−4315.

(5) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326−3350.
(6) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239−3265.
(7) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351−3378.
(8) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208−3221.
(9) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232−5241.
(10) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2012**, *41*, 2448−2462.
(11) Brenzovich, W. E., Jr. *Angew. Chem., Int. Ed.* **2012**, *51*, 8933−8935.
(12) Tiekink, E. R. T. *Crit. Rev. Oncol. Hematol.* **2002**, *42*, 225−248.
(13) Hickey, J. L.; Ruhayel, R. A.; Barnard, P. J.; Baker, M. V.; Berners-Price, S. J.; Filipovska, A. *J. Am. Chem. Soc.* **2008**, *130*, 12570−12571.
(14) Bhabak, K. P.; Bhuyan, B. J.; Mugesh, G. *Dalton Trans.* **2011**, *40*, 2099−2111.
(15) Liu, W.; Gust, R. *Chem. Soc. Rev.* **2013**, *42*, 755−773.
(16) Che, C.-M.; Lai, S.-W. In *Gold Chemistry: Applications and Future Directions in the Life Sciences*; Mohr, F., Ed.; Wiley-VCH: Weinheim, Germany, 2009; pp 249−281.
(17) López-de-Luzuriaga, J. M. In *Modern Supramolecular Gold Chemistry*; Laguna, A., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 347−401.
(18) Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. In *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M., Fackler, J. P., Jr., Eds.; Plenum Press: New York, 1999; pp 195−226.
(19) Partyka, D. V.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2007**, *26*, 3279−3282.
(20) Gao, L.; Peay, M. A.; Partyka, D. V.; Updegraff, J. B., III; Teets, T. S.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2009**, *28*, 5669−5681.
(21) Vogt, R. A.; Peay, M. A.; Gray, T. G.; Crespo-Hernández, C. E. *J. Phys. Chem. Lett.* **2010**, *1*, 1205−1211.
(22) Vogt, R. A.; Gray, T. G.; Crespo-Hernández, C. E. *J. Am. Chem. Soc.* **2012**, *134*, 14808−14817.
(23) Elbjeirami, O.; Gonser, M. W. A.; Stewart, B. N.; Bruce, A. E.; Bruce, M. R. M.; Cundari, T. R.; Omary, M. A. *Dalton. Trans.* **2009**, 1522−1533.
(24) Luquin, A.; Bariáin, C.; Vergara, E.; Cerrada, E.; Garrido, J.; Matias, I. R.; Laguna, M. *Appl. Organomet. Chem.* **2005**, *19*, 1232−1238.
(25) Teets, T. S.; Nocera, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 7411−7420.
(26) Pacheco, E. A.; Tiekink, E. R. T.; Whitehouse, M. W. In *Gold Chemistry: Applications and Future Directions in the Life Sciences*; Mohr, F., Ed.; Wiley-VCH: Weinheim, Germany, 2009; pp 283−319.
(27) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, U.K., 1999.
(28) Balch, A. L. *Gold Bull.* **2004**, *37* (1−2), 45−50.
(29) Schneider, W.; Bauer, A.; Schmidbaur, H. *Organometallics* **1996**, *15*, 5445−5446.
(30) Schneider, D.; Schuster, O.; Schmidbaur, H. *Organometallics* **2005**, *24*, 3547−3551.
(31) Elbjeirami, O.; Yockel, S.; Campana, C. F.; Wilson, A. K.; Omary, M. A. *Organometallics* **2007**, *26*, 2550−2560.
(32) Elbjeirami, O.; Omary, M. A.; Stender, M.; Balch, A. L. *Dalton Trans.* **2004**, 3173−3175.
(33) Elbjeirami, O.; Omary, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 11384−11393.
(34) He, X.; Lam, W. H.; Zhu, N.; Yam, V. W.-W. *Chem.—Eur. J.* **2009**, *15*, 8842−8851.
(35) Laitar, D. S.; Müller, P.; Gray, T. G.; Sadighi, J. P. *Organometallics* **2005**, *24*, 4503−4505.
(36) Schmidbaur, H.; Schier, A. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Vol. 2, Section 2.05, pp 251−307.
(37) Partyka, D. V.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8188−8191.
(38) Gray, T. G. *Comments Inorg. Chem.* **2007**, *28*, 181−212.
(39) Tsui, E. Y.; Müller, P.; Sadighi, J. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8937−8940.
(40) Partyka, D. V.; Updegraff, J. B., III; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2009**, *28*, 1666−1674.
(41) Partyka, D. V.; Robilotto, T. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2008**, *27*, 28−32.
(42) Partyka, D. V.; Washington, M. P.; Gray, T. G.; Updegraff, J. B., III; Turner, J. F. II; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2009**, *131*, 10041−10048.
(43) Gao, L.; Deligonul, N.; Gray, T. G. *Inorg. Chem.* **2012**, *51*, 7682−7688.
(44) Partyka, D. V.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Inorg. Chem.* **2012**, *51*, 8394−8401.
(45) Partyka, D. V.; Teets, T. S.; Zeller, M.; Updegraff, J. B., III; Hunter, A. D.; Gray, T. G. *Chem.—Eur. J.* **2012**, *18*, 2100−2112.
(46) Burini, A.; Galassi, R.; Ricci, S.; Bachechi, F.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chem.* **2010**, *49*, 513−518.
(47) Heckler, J. E.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 5924−5928.
(48) Robilotto, T. J.; Bacsa, J.; Gray, T. G.; Sadighi, J. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 12077−12080.
(49) Lenker, H. K.; Gray, T. G.; Stockland, R. A., Jr. *Dalton Trans.* **2012**, *41*, 13274−13276.
(50) Nolan, S. P. *Acc. Chem. Res.* **2010**, *44*, 91−100.
(51) Shi, Y.; Ramgren, S. D.; Blum, S. A. *Organometallics* **2009**, *28*, 1275−1277.
(52) Manbeck, G. F.; Kohler, M. C.; Porter, M. R.; Stockland, R. A., Jr. *Dalton Trans.* **2011**, *40*, 12595−12606.
(53) Johnson, M. W.; Shevick, S. L.; Toste, F. D.; Bergman, R. G. *Chem. Sci.* **2013**, *4*, 1023−1027.
(54) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2008**, *37*, 1931−1951.
(55) Crespo, O. In *Modern Supramolecular Gold Chemistry*; Laguna, A., Ed.; Wiley-VCH: Weinheim, Germany, 2009; pp 65−129.
(56) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3−10.
(57) *Modern Gold Catalyzed Synthesis*; Hashmi, A. S. K., Toste, F. D., Eds.; Wiley-VCH: Weinheim, Germany, 2012.
(58) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Science* **2012**, *337*, 1644−1648.
(59) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.
(60) Raubenheimer, H. G.; Schmidbaur, H. *Organometallics* **2012**, *31*, 2507−2522.
(61) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711−724.
(62) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148−1155.
(63) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952−3015.
(64) Hein, J. E.; Fokin, V. V. *Chem. Soc. Rev.* **2010**, *39*, 1302−1315.
(65) Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057−3064.
(66) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599.
(67) Beck, W.; Burger, K.; Fehlhammer, W. P. *Chem. Ber.* **1971**, *104*, 1816−1825.
(68) Partyka, D. V.; Updegraff, J. B., III; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2007**, *26*, 183−186.
(69) Robilotto, T. J.; Alt, D. S.; von Recum, H. A.; Gray, T. G. *Dalton Trans.* **2011**, *40*, 8083−8085.
(70) Gao, L.; Partyka, D. V.; Updegraff, J. B., III; Deligonul, N.; Gray, T. G. *Eur. J. Inorg. Chem.* **2009**, 2711−2719.
(71) Partyka, D. V.; Gao, L.; Teets, T. S.; Updegraff, J. B., III; Deligonul, N.; Gray, T. G. *Organometallics* **2009**, *28*, 6171−6182.
(72) Heckler, J. E.; Deligonul, N.; Rheingold, A. L.; Gray, T. G. *Chem. Commun.* **2013**, *49*, 5990−5992.

(73) Köstler, S. D.; Alborzinia, H.; Can, S.; Kitanovic, I.; Wölfl, S.; Rubbiani, R.; Ott, I.; Riesterer, P.; Prokop, A.; Merz, K.; Metzler-Nolte, N. *Chem. Sci.* **2012**, *3*, 2062−2072.
(74) Del Castillo, T. J.; Sarkar, S.; Abboud, K. A.; Veige, A. S. *Dalton Trans.* **2011**, *40*, 8140−8144.
(75) Hashmi, A. S. K.; Riedel, D.; Rudolph, M.; Rominger, F.; Oeser, T. *Chem.—Eur. J.* **2012**, *18*, 3827−3830.
(76) Manzano, R.; Rominger, F.; Hashmi, A. S. K. *Organometallics* **2013**, *32*, 2199−2203.
(77) Partyka, D. V.; Robilotto, T. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Proc. Natl. Acad. Sci., U.S.A.* **2008**, *105*, 14293−14297.
(78) Melaiye, A.; Simons, R. S.; Milsted, A.; Pingitore, F.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *J. Med. Chem.* **2004**, *47*, 973−977.
(79) Melaiye, A.; Sun, Z.; Hindi, K.; Milsted, A.; Ely, D.; Reneker, D. H.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **2005**, *127*, 2285−2291.
(80) Kascatan-Nebioglu, A.; Melaiye, A.; Hindi, K.; Durmus, S.; Panzner, M. J.; Hogue, L. A.; Mallet, R. J.; Hovis, C. E.; Coughenour, M.; Crosby, S. D.; Milsted, A.; Ely, D. L.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *J. Med. Chem.* **2006**, *49*, 6811−6818.
(81) Hindi, K. M.; Siciliano, T. J.; Durmus, S.; Panzner, M. J.; Medvetz, D. A.; Reddy, D. V.; Hogue, L. A.; Hovis, C. E.; Hilliard, J. K.; Mallet, R. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *J. Med. Chem.* **2008**, *51*, 1577−1583.
(82) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Chem. Rev.* **2009**, *109*, 3859−3884.
(83) Wright, B. D.; Shah, P. N.; McDonald, L. J.; Shaeffer, M. L.; Wagers, P. O.; Panzner, M. J.; Smolen, J.; Tagaev, J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Dalton Trans.* **2012**, *41*, 6500−6506.
(84) Kascatan-Nebioglu, A.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Coord. Chem. Rev.* **2007**, *251*, 884−895.
(85) Siciliano, T. J.; Deblock, M. C.; Hindi, K. M.; Durmus, S.; Panzner, M. J.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2011**, *696*, 1066−1071.
(86) Schuh, E.; Pflüger, C.; Citta, A.; Folda, A.; Rigobello, M. P.; Bindoli, A.; Casini, A.; Mohr, F. *J. Med. Chem.* **2012**, *55*, 5518−5528.
(87) Deng, L.; Bill, E.; Wieghardt, K.; Holm, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 11213−11221.
(88) Deng, L.; Holm, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 9878−9886.
(89) Jellicoe, M. M.; Nichols, S. J.; Callus, B. A.; Baker, M. V.; Barnard, P. J.; Berners-Price, S. J.; Whelan, J.; Yeoh, G. C.; Filpovska, A. *Carcinogenesis* **2008**, *29*, 1124−1133.
(90) Baker, M. V.; Barnard, P. J.; Berners-Price, S. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2005**, *690*, 5625−5635.
(91) Ho, S. Y.; Tiekink, E. R. T. In *Metallotherapeutic Drugs & Metal-based Diagnostic Agents: The Use of Metals in Medicine*; Gielen, M., Tiekink, E. R. T., Eds.; Wiley: New York, 2005; pp 507−528.
(92) Shaw, C. F., III The Biochemistry of Gold. In *Gold: Progress in Chemistry, Biotechnology, and Technology*; Schmidbaur, H., Ed.; Wiley: New York, 1999; pp 259−308.
(93) Vignolle, J.; Tilley, T. D. *Chem. Commun.* **2009**, 7230−7232.
(94) Partyka, D. V.; Robilotto, T. J.; Updegraff, J. B., III; Zeller, M.; Hunter, A. D.; Gray, T. G. *Organometallics* **2009**, *28*, 795−801.
(95) Sethna, S. M.; Shah, N. M. *Chem. Rev.* **1945**, *36*, 1−62.
(96) Deana, A. A.; Stokker, G. E.; Schultz, E. M.; Smith, R. L.; Cragoe, E. J., Jr.; Russo, H. F.; Watson, L. S. *J. Med. Chem.* **1983**, *26*, 580−585.
(97) Kostova, I. *Curr. Med. Chem. Anticancer Agents* **2005**, *5*, 29−46.
(98) Xu, B.; Yang, J.; Jiang, X. S.; Wang, Y. L.; Sun, H.; Yin, J. *J. Mol. Struct.* **2009**, *917*, 15−20.
(99) Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination: A Practical Guide*; Wiley-Interscience: New York, 1989; pp 404−405.
(100) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley & Sons Ltd.: Chichester, U.K., 1999; pp 647−746.
(101) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541−3547.
(102) Vicente, J.; Chicote, M.-T.; Alvarez-Falcon, M. M.; Bautista, D. *Organometallics* **2004**, *23*, 5707−5712.
(103) Stockland, R. A.; Kohler, M. C.; Guzei, I. A.; Kastner, M. E.; Bawiec, J. A.; Labaree, D. C.; Hochberg, R. B. *Organometallics* **2006**, *25*, 2475−2485.
(104) For a general discussion of *trans*-influences in square-planar d^8 complexes, see: Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Longman: Essex, U.K., 1999; pp 95−98.
(105) Jones, P. G.; Williams, A. F. *Dalton Trans.* **1977**, 1430−1434.
(106) Sokolov, A. Yu.; Sizova, O. V. *Russ. J. Gen. Chem.* **2010**, *80*, 1223−1231.
(107) Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352−9362.
(108) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
(109) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.
(110) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560−571.
(111) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866−872.
(112) Gorelsky, S. I. *AOMix, Program for Molecular Orbital Analysis*, version 6.5; University of Ottawa: Ontario, Canada, 2011; http://www.sg-chem.net.
(113) Gorelsky, S. I.; Lever, A. B. P. *J. Organomet. Chem.* **2001**, *635*, 187−196.