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Carbon−Gold Bond Formation through [3 + 2] Cycloaddition Reactions of Gold(I) Azides and Terminal Alkynes

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Carbon−gold bond formation propels a growing number of homogeneous catalyses, but the C−Au bond formation itself is comparatively underinvestigated. Reported here are C−Au bond-forming reactions that result from [3 + 2] cycloaddition of (triphenylphosphine)gold(I) azide to terminal alkynes. The reaction proceeds with the preformed azide complex or, in situ, by reaction of the corresponding gold(I) alkynyl with trimethylsilyl azide in the presence of protic solvents. This metal-mediated cycloaddition is analogous to the Huisgen dipolar addition of azides and alkynes and provides access to new classes of gold-bearing compounds and materials.

Introduction

Carbon−gold bond formation recurs as an essential step in a number of catalytic cycles, and organometallic catalysis with gold reagents is growing explosively.[1−4] However, rather little attention has been given to gold−carbon bond-forming steps per se.[5−7] The gold(I)−carbon bond is in many cases stable to air and water.[8−10] The (phosphine)gold(I) fragment is isolobal with H^+, and (phosphine)- or (N-heterocyclic carbene)gold(I) groups can act as functional groups in organic and other molecules in place of protons. Foreseeable applications include gold-driven catalysis, sensing,[11,12] metallopharmaceuticals design,[13,14] and X-ray contrast imaging,[15−17] among other possibilities.[18,19]

Metal-mediated cycloaddition chemistry is in an ascendancy with the re-emergence of the Huisgen dipolar cycloaddition of alkynes and azides,[20] in the context of copper catalysis and the Sharpless click chemistry.[16−36] These reactions are believed to

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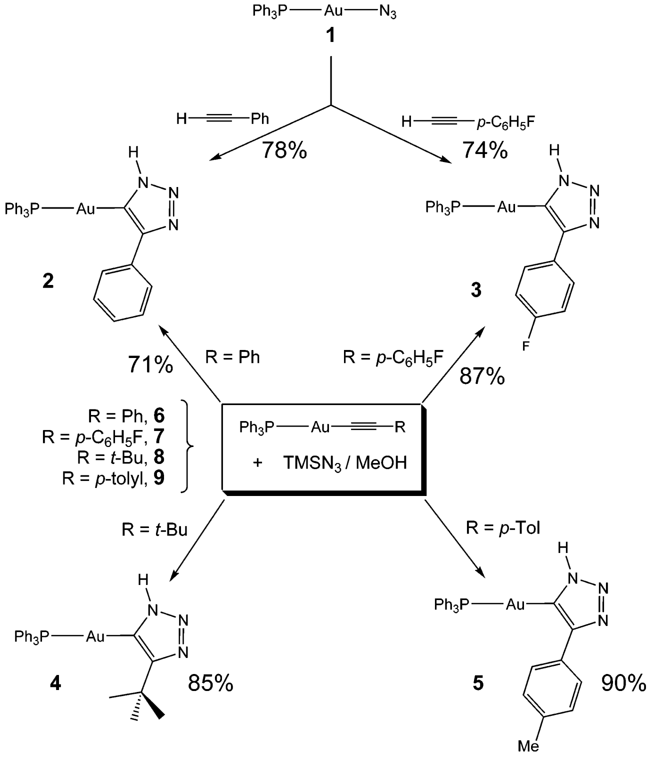
Scheme 1. Cycloaddition Reactions of Gold(I)[a]



[a] Isolated yields are indicated.

occur by formation of a three-coordinate copper(I) acetylide that reacts with an azide coligand, proceeding through a carbenoid intermediate to yield a C-bound copper(I) triazolate. Protonation at carbon affords the final 1,2,3-triazole.[24] The uncatalyzed reaction is concerted and can be induced by spatial confinement of alkynes and azides in enzyme active sites.[25]

Recent precedents affirm the stability of the bond between gold(I) and aryl or alkynyl carbon atoms in water.[8−10] We find that gold(I) is stably incorporated into organic molecules upon reaction of (triphenylphosphine)gold(I) azide (**1**) with terminal alkynes (Scheme 1). The reaction has clear potential for the synthesis of gold organometallics from accessible gold(I) azides. The cycloaddition superficially resembles the copper-catalyzed chemistry, except that the gold−carbon linkage in the products is hydrolytically stable and the organogold product is isolated.

Results and Discussion

Reaction of a toluene slurry of **1** with phenylacetylene cleanly affords the phenyltriazolate complex **2** in 78% isolated yield at room temperature. Similarly, reaction of **1** with (*p*-fluorophenyl)-acetylene yields the corresponding adduct **3** in 74% isolated yield. In a variant of this reaction, triazolato complexes can be generated from gold(I) alkynyls. Hence, (triphenylphosphine)-gold(I) phenylacetylide (**6**) reacts with trimethylsilyl azide at room temperature in the presence of methanol, affording **2** in 71% isolated yield. Neither starting material nor side products are evident by ^{31}P or ^{1}H NMR after 48 h. Similarly, reaction of the (*p*-fluorophenyl)acetylide complex **7** with trimethylsilyl azide affords **3** as the sole product in 87% isolated yield. Analogous reactions of *tert*-butylacetylide and *p*-tolylacetylide complexes with trimethylsilyl azide in the presence of CH_3OH cleanly delivers triazolates **4** and **5** in 85% and 90% isolated yields, respectively. All new compounds have been characterized by elemental analysis, multinuclear NMR, and X-ray diffraction crystallography.

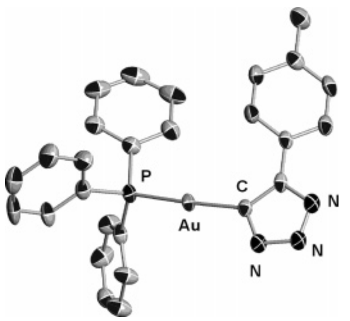


Figure 1. Crystal structure of **5**. Data were collected at 100 K; 50% probability ellipsoids are shown. Selected interatomic distances: C−Au, 2.027(5) Å; Au−P, 2.2710(13) Å; $C_{triazolato}$−N, 1.357(7) Å. Selected angle: P−Au−C, 175.01(15)°.

Diffraction-quality crystals were obtained by vapor diffusion of pentane into a saturated THF/toluene solution of **2** or into THF solutions of **3**−**5**. Figure 1 depicts the structure of compound **5**; the structures of **2**−**4** appear in the Supporting Information. In all instances, the 1,2,3-triazolato ligand is bound through carbon. An N−*H* resonance at δ ~14 ppm in the ^{1}H NMR spectrum confirms that the carbon-bound structure is maintained in solution. Gold−carbon lengths, which vary from 2.002(9) Å (**4**) to 2.027(5) Å (**5**), and the range of gold−phosphorus bond distances, 2.2641(15) and 2.2677(15) Å (**2**, both crystallographically independent molecules) to 2.279(2) Å (**4**), are normal. In all cases, the coordination geometry about gold is essentially linear, and the smallest C−Au−P angle (in one independent molecule of **2**) is 174.01(15)°. No intermolecular gold−gold interactions are observed in any of the structures.

Azide complex **1** was identified crystallographically among the products from (unoptimized) reactions targeting cycloaddition products **4** and **5**. In these reactions, the gold starting materials had been the acetylides. Nonhydrolyzable azides fail to react with gold(I) alkynyls under identical conditions. Also, internal alkynes do not react with **1**. These observations might suggest the intermediacy of **1** in the cycloaddition reactions documented here and elsewhere.[37−39] However, we cannot dismiss the possibility of gold(I) alkynyl intermediacy. All gold(I) cycloaddition products so far encountered are air- and water-stable.[40,41] Collectively these experiments suggest an essential stability of the carbon−gold bond that bodes favorably for materials and medicinal applications.[14,42,43]

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The foregoing results demonstrate that robust gold−carbon bonds form upon cycloaddition of (triphenylphosphine)gold(I) azide to terminal alkynes. The reaction occurs with purified **1** or with **1** prepared in situ from gold(I) alkynyls and trimethylsilyl azide in methanol. All reactions reported here yield carbon-bound cycloadducts. Studies of gold(I) cycloaddition reactions of other dipolarophiles and of more extensively functionalized alkynes are underway.

Experimental Section

The alkynylgold precursors were prepared according to a published procedure[44] or by the reaction of [(PPh$_3$)AuCl] with alkyne in methanol in the presence of sodium methoxide. All other solvents and reagents were used as received. Microanalyses (C, H, and N) were performed by Quantitative Technologies Inc. NMR spectra (^{1}H, ^{31}P) were recorded on a Varian AS-400 spectrometer. Mass spectrometry was performed at the Michigan State University Mass Spectrometry facility.

List of Compounds: [(PPh$_3$)Au(N$_3$)] (**1**); [(PPh$_3$)Au(phenyltriazole)] (**2**); [(PPh$_3$)Au((4-fluorophenyl)triazole)] (**3**); [(PPh$_3$)Au(*tert*-butyltriazole)] (**4**); [(PPh$_3$)Au(4-tolyltriazole)] (**5**); [(PPh$_3$)Au(phenylacetylide)] (**6**); [(PPh$_3$)Au((4-fluorophenyl)acetylide)] (**7**); [(PPh$_3$)Au(*tert*-butylacetylide)] (**8**); [(PPh$_3$)Au(4-tolylacetylide)] (**9**).

Synthesis of [(PPh$_3$)Au(N$_3$)] (1). This was prepared differently than the published procedure.[45] In 8 mL of toluene was suspended [(PPh$_3$)AuCl] (167 mg, 0.34 mmol), and to this suspension was added 1.05 equiv of [Tl(acac)] (108 mg, 0.35 mmol) with rapid formation of a white solid. After 4 h, the suspension was filtered through Celite, and to the filtrate was added a 1 mL toluene solution of trimethylsilyl azide (58 mg, 0.48 mmol); the solution became turbid. To this suspension was added 1 mL of methanol. The reaction mixture was stirred for 20 h to produce a suspension that was filtered through Celite, and the filtrate was concentrated to ∼3 mL in vacuo. Pentane was added to precipitate a white solid. Yield: 134 mg (79%). MS (FAB+): *m*/*z* 502.0743 (MH$^+$). Anal. Calcd for C$_{18}$H$_{15}$AuN$_3$P: C, 43.13; H, 3.02. Found: C, 43.13; H, 2.80. The IR spectral data matched those of an authentic sample.[46]

Synthesis of [(PPh$_3$)Au(phenyltriazole)]. To a 4 mL toluene solution of **6** (63 mg, 0.11 mmol) was added a 0.5 mL toluene solution of trimethylsilyl azide (26 mg, 0.21 mmol). The reaction mixture was stirred for 5 min, and 0.5 mL of methanol was added. The solution was stirred for 48 h and was then concentrated in vacuo to ∼2 mL. Pentane was added to precipitate a white solid. Yield: 48 mg (71%). ^{1}H NMR (DMSO-*d*$_6$): δ 14.34 (s br, 1H, NH), 8.22 (d, 2H, CH), 7.52−7.63 (m, 15H, CH), 7.35 (t, 2H, CH), 7.22 (t, 1H, CH) ppm. ^{31}P NMR (DMSO-*d*$_6$): δ 44.5 ppm. Anal. Calcd for C$_{26}$H$_{21}$AuN$_3$P: C, 51.75; H, 3.51; N, 6.96. Found: C, 51.35; H, 3.41, N, 6.80.

[(PPh$_3$)Au(4-fluorophenyltriazole)]. To a 4 mL toluene solution of **7** (79 mg, 0.14 mmol) was added a 0.5 mL toluene solution of trimethylsilyl azide (32 mg, 0.26 mmol). This was stirred for 5 min, and 0.5 mL of methanol was added. The colorless solution was stirred for 48 h and concentrated to approximately half the original volume in vacuo, at which point it was a suspension. Pentane was added to complete precipitation of a white solid, which was collected, washed with pentane, and dried. Yield: 74 mg (87%). ^{1}H NMR (DMSO-*d*$_6$): δ 14.34 (s br, 1H, NH), 8.20 (dd, 2H, CH), 7.55−7.68 (m br, 15H, CH), 7.17 (t, 2H, CH). ^{31}P NMR (DMSO-*d*$_6$): δ 44.5 ppm. Anal. Calcd for C$_{26}$H$_{20}$AuFN$_3$P: C, 50.25; H, 3.24; N, 6.76. Found: C, 50.05; H, 3.03; N, 6.70.

[(PPh$_3$)Au(*t*-butyltriazole)]. In 3 mL of toluene was dissolved **8** (69 mg, 0.13 mmol), and to this was added a 0.5 mL toluene solution of trimethylsilyl azide (22 mg, 0.18 mmol). This solution was stirred for 5 min, and 0.5 mL of methanol was added. This solution was stirred for 24 h, and 0.03 mL of *tert*-butylacetylene was added. The resultant solution was stirred for an additional 48 h and concentrated in vacuo to ∼2 mL. Pentane was added to complete precipitation of a white solid, and the suspension was cooled to −20 °C to maximize precipitation. The solid was collected and dried. Yield: 63 mg (85%). ^{1}H NMR (DMSO-*d*$_6$): δ 13.94 (s br, 1H, NH), 7.56−7.63 (m br, 15H, CH), 1.40 (s, 9H, C(CH$_3$)$_3$). ^{31}P NMR (DMSO-*d*$_6$): δ 44.7 ppm. Anal. Calcd for C$_{24}$H$_{25}$AuN$_3$P: C, 49.41; H, 4.32; N, 7.20. Found: C, 49.25; H, 4.12; N, 6.96.

[(PPh$_3$)Au(4-tolyltriazole)]. To a 4 mL toluene solution of **9** (100 mg, 0.17 mmol) was added a 0.5 mL toluene solution of trimethylsilyl azide (32 mg, 0.26 mmol). This was stirred for 15 min, and 0.5 mL of methanol was added. The colorless solution was stirred for 72 h and concentrated to ∼2 mL in vacuo, and pentane was added to complete precipitation of a white solid, which was collected and dried. Yield: 97 mg (90%). ^{1}H NMR (DMSO-*d*$_6$): δ 14.28 (s br, 1H, NH), 8.09 (d, 2H, CH), 7.56−7.68 (m, 15H, CH), 7.14 (d, 2H, CH), 2.28 (s, 3H, CH$_3$) ppm. ^{31}P NMR (DMSO-*d*$_6$): δ 44.5 ppm. Anal. Calcd for C$_{27}$H$_{23}$AuN$_3$P: C, 52.52; H, 3.75; N, 6.81. Found: C, 52.42; H, 3.48; N, 6.71.

Synthesis of 2 from [(PPh$_3$)Au(N$_3$)]. In 3 mL of toluene was suspended [(PPh$_3$)Au(N$_3$)] (35 mg, 0.070 mmol), and to this suspension was added a 1 mL toluene solution of phenylacetylene (10 mg, 0.098 mmol). The resultant suspension was stirred under argon for 48 h and filtered. The filtrate was concentrated in vacuo to ∼0.5 mL, and pentane was added to precipitate a white solid, which was collected and dried. The ^{1}H and ^{31}P NMR spectra of this material in DMSO-*d*$_6$ matched the spectra for **2**. MS (FAB+): *m*/*z* 604.1217 (MH$^+$).

Synthesis of 3 from [(PPh$_3$)Au(N$_3$)]. In 4 mL of toluene was suspended [(PPh$_3$)Au(N$_3$)] (61 mg, 0.12 mmol), and to this suspension was added a 1 mL toluene solution of (4-fluorophenyl)acetylene (21 mg, 0.17 mmol). The resultant suspension was stirred under argon for 48 h and concentrated in vacuo to half its original volume. Pentane was added to complete precipitation of a white solid, which was collected and dried. The ^{1}H and ^{31}P NMR spectra of this material in DMSO-*d*$_6$ matched the spectra for **3**. MS (FAB+): *m*/*z* 621.1117 (MH$^+$).

X-ray Structure Determination. Compound **2** was crystallized by diffusion of pentane into a saturated THF/toluene solution. Compounds **3**−**5** were crystallized by diffusion of pentane into saturated THF solutions. Single-crystal X-ray data for compounds **2**−**5** were collected on a Bruker AXS SMART APEX CCD diffractometer using monochromatic Mo Kα radiation with the ω-scan technique. The unit cell was determined using SMART and SAINT+.[47] The crystals of **3** undergo a phase change between about −20 and −30 °C, associated with a breakup of the crystals; data for **3** were therefore collected at 260 K (−13.5 °C). The data collections of **2**, **4**, and **5** were 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.[48] Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. Compound **2** exhibits two independent gold complexes as well as very large voids within the structure filled with ill-defined THF solvate molecules (715 Å^3 per asymmetric unit or 13 vol %). Three THF molecules per asymmetric unit had been identified in the

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Table 1. Crystallographic Data for Gold Triazoles 2−5

	2	**3**	**4**	**5**
formula	$C_{26}H_{21}AuN_3P$	$C_{26}H_{20}AuFN_3P$	$C_{27}H_{23}AuN_3P$	$C_{24}H_{25}AuN_3P$
fw	603.39	621.39	617.42	583.41
cryst syst	monoclinic	tetragonal	tetragonal	tetragonal
space group	$P2_1/c$	$P4_3$	$P4_3$	$P4_3$
a, Å	14.797(4)	12.8693(3)	13.7355(5)	13.0753(8)
b, Å	22.554(7)			
c, Å	17.371(5)	20.2649(14)	12.5315(9)	13.0705(12)
β, deg	109.840(5)			
cell vol, Å^3	5453(3)	2427.1(1)	2364.2(2)	2234.6(3)
Z	8	4	4	4
D_{calcd}, Mg m^{-3}	1.470	1.700	1.735	1.734
T, K	100(2)	100(2)	100(2)	100(2)
μ, mm^{-1}	5.469	6.152	6.310	6.670
F(000)	2336	1200	1200	1184
cryst size, mm	0.055 × 0.121 × 0.543	0.25 × 0.26 × 0.60	0.15 × 0.20 × 0.25	0.12 × 0.32 × 0.39
θ_{min}, θ_{max}, deg	1.46, 28.28	1.58, 28.28	2.10, 28.28	2.20, 30.43
no. of rflns collected	54 125	25 118	22 982	17 060
no. of indep rflns	13 523	5991	5949	4658
no. of refined params	559	289	293	265
goodness of fit on F^2 [a]	1.022	1.075	1.099	0.827
final R indices[b] ($I > 2\sigma(I)$)				
R1	0.0421	0.0225	0.0342	0.0382
wR2	0.1003	0.0529	0.0851	0.0713
R indices (all data)				
R1	0.0603	0.0253	0.0360	0.0653
wR2	0.1070	0.0541	0.0866	0.0757

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$; n = number of reflections, p = number of parameters refined. [b] R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

difference Fourier map, but a tentative refinement showed that the molecules are ill-defined, partially disordered, and quite diffuse, and no meaningful and stable refinement could be achieved. Thus, the structure was refined with omission of the solvate molecules and the diffuse sections of the unit cell were "squeezed out" using the program Platon.[49] The N−H hydrogen atoms of all three structures were localized in the difference density Fourier map. The N−H distance of **4** was refined and restrained to be 0.8 Å within a standard deviation of 0.2; the other three N−H distances were placed in calculated positions using an AFIX 43 command. All other hydrogen atoms were placed in standard calculated positions, and all hydrogen atoms were refined with an isotropic displacement parameter 1.5 (CH_3) or 1.2 (all others) times that of the adjacent carbon or nitrogen atom.

Crystallographic data for **2**−**5** are given in Table 1.

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Supporting Information Available: Figures showing the structures of **2**−**4** and CIF files giving crystallographic data for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(49) Spek, A. L. Platon for Windows; Delft, The Netherlands, 2003.