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Au(III)- versus Au(I)-induced cyclization: synthesis of 6-membered mesoionic carbene and acyclic (aryl)(heteroaryl) carbene complexes**

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Abstract

The Golden State: Selective 5-*exo*- and 6-*endo*-cyclizations of an alkynyl benzothioamide are achieved. The selectivity is controlled by the oxidation state of the gold precursor (+I or +III) yielding two new types of carbene ligand: an (aryl)(heteroaryl)carbene and a 6-membered mesoionic carbene.

Keywords

gold; cyclization; mesoionic carbenes; intermediates

In the last decade, gold complexes have been widely used as catalysts for promoting a variety of organic transformations.^[1] We have recently demonstrated that the gold-induced cyclization of heteroatom-substituted alkynes **A** and **B** provides the corresponding gold complexes **D**-[M] and **E**-[M], respectively (Figure 1).^[2,3] These complexes feature a recently discovered type of carbon-based ligand, namely a mesoionic carbene (MIC),^[4,5] in which a positive charge is delocalized throughout the ring atoms, and the formal negative charge is associated with a carbon atom of the ring. In contrast to their N-heterocyclic carbene (NHC) cousins, which are known as 4- to 8-membered rings,^[6] MICs have been so far limited mostly to the 5-membered series.^[7] We report herein the selective preparation of a cyclic 6-membered mesoionic carbene gold complex, as well as a very rare example of an acyclic (aryl)(heteroaryl)carbene gold complex. Both compounds are prepared from the same precursor, via an unusual gold induced 6-*endo-dig* ring closure process, and a more classical 5-*exo-dig* cyclization, respectively. The selectivity observed is dictated by the oxidation state of the gold promoter.

By analogy with the preparation of complexes **D**-[M] and **E**-[M], we envisioned that an alkyne of type **C** could undergo a 6-*endo-dig* cyclization, affording complex **F**-[M] featuring a thiopyryl-3-ylidene ligand (Figure 1). However, examination of the recent literature on gold catalysis showed that examples of 6-*endo-dig* cyclization are rare,^[8] and that the competitive 5-*exo-dig* cyclization is more likely to occur.^[9] The latter pathway would nonetheless yield a very rare example of carbene gold complex **G**-[M].

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In order to force a *cis* geometry between the alkyne and the thione of **C**, we chose a benzene fused system. 2-bromiodobenzene was cross-coupled with mesitylacetylene giving alkyne **1** in good yield (92%). Treatment of **1** with tert-butyllithium and subsequent addition of dimethylcarbamothioyl chloride afforded the desired alkynyl benzothioamide **2** (93% yield) (Scheme 1).

Compound **2** was first reacted with (tetrahydrothiophene)Au(I)Cl. The reaction proceeded cleanly in CH₂Cl₂; however, the ¹³C NMR spectrum of the product displayed peaks at 92.9 and 93.1 ppm, indicating that the alkyne moiety was still present and, consequently, that the expected cyclization did not occur. Nevertheless, slight but notable shifts in the ¹³C NMR spectrum indicated that the coordination of **2** to gold did take place. Single crystals were grown from a dichloromethane solution and an X-ray diffraction study revealed that **2** displaced the tetrahydrothiophene ligand yielding complex **3**, in which the sulfur atom is coordinated to the metal (Figure 2, left; Scheme 2).^[10]

Despite the aurophilicity of sulfur, we reasoned that the desired (MIC)Au(I) complex would be thermodynamically favored versus a (thioamide)Au(I) complex. After heating **3** at 40 °C for 16 hours, we observed the quantitative conversion to a new product. No alkyne carbon resonances were detected in the ¹³C NMR spectrum, and the CS resonance drastically shifted upfield, indicating that a cyclization process occurred. A single crystal X-ray diffraction study showed that it was complex **4**, resulting from the usually encountered 5-*exo-dig* cyclization^[1,9] (Figure 2, right).^[10] However, in contrast to previously reported studies on gold-mediated cyclization,^[11,12] this complex is better described as the (aryl) (heteroaryl)carbene complex **4** rather than the zwitterionic vinyl-gold complex **4'** (Scheme 2). The Au1–C1 bond length [1.990(11) Å] is shorter than in vinyl-gold complexes (2.04–2.06 Å),^[9a,12] and in the range observed for NHC-^[12] and MIC-gold complexes^[2a,5c,5g] (1.94–2.01 Å). Complex **4** is a very rare example of non-heteroatom substituted carbene-coinage metal complex.^[14]

Recently, Hashmi, Nolan *et al.* reported an interesting switch of selectivity between 5-*exo-dig* and 6-*endo-dig* cyclization using two different (NHC)Au(I) complexes.^[8d] This prompted us to test other gold precursors, and we chose to simply change the oxidation state of the metal. A clean reaction was observed when Au(III)Cl₃ was added to **2**, and alkyne carbon resonances were absent in the ¹³C NMR spectrum, indicating that a cyclization process occurred. Indeed, when single crystals were obtained from a saturated acetone solution, an X-ray diffraction study proved that the desired 6-*endo-dig* cyclization took place, yielding the mesoionic carbene complex **5** (Figure 3; Scheme 2).^[10] The Au1–C1 bond length [2.077(7) Å] is considerably shorter than that observed for a (vinyl)Au(III)Cl₃ complex [2.2743(9) Å],^[9b] and slightly longer than for (NHC)Au(III)Cl₃ complexes (1.98–2.01 Å).^[15] The gold center features a weakly distorted square planar geometry (sum of angles = 359.9 °), and the 6-membered MIC ring is only slightly twisted, due to the proximity of the bulky mesityl substituent with the chloride on the gold center. Although NHCs are oxidized by Au(III)Cl₃^[16], preventing the direct synthesis of (NHC)Au(III) complexes, the formation of metallic Au(0) was never observed in the reaction leading to **5**. Interestingly, the reaction of **2** with HAu(III)Cl₄ also gave rise to complex **5** without the loss of purity or yield. This result demonstrates the robustness of **5** towards protodeauration.

In summary, we have shown that the regioselectivity of the gold-promoted cyclization of the alkynyl benzothioamide **2** is controlled by the oxidation state of the metal. Complex **4** is the first example of a diarylcarbene-gold complex, and more generally of a diarylcarbene-metal complex obtained without using a diazo precursor,^[14,17] or an oxidative addition process.^[18] In addition, **5** is the first metal complex featuring a non-nitrogen containing^[7] 6-membered mesoionic carbene. The availability of a variety of analogues of **2**, featuring different

heteroatoms, should allow for the preparation of numerous 6-membered MIC complexes. Both complexes **4** and **5** are very robust (m.p. **4** and **5**: 206 °C), a key feature for possible catalytic applications, which are under current investigation in our laboratories.

Experimental Section

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^1H , and ^{13}C NMR spectra were recorded on a Varian Inova 500 or Bruker 300 spectrometer at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus.

Synthesis of complexes **3** and **4**

CH_2Cl_2 (10 mL) was added to a Schlenk tube loaded with benzothioamide **2** (210 mg, 680 mmol) and (tht)AuCl (220 mg, 680 mmol), and the mixture was stirred for 14 hours. The reaction mixture was filtered and the filtrate was evaporated under vacuum. The residue was recrystallized from a saturated solution of dichloromethane. Complex **3** was obtained as orange crystals (240 mg, 65 % yield). m.p. 200 °C (dec); ^1H (300 MHz, CDCl_3) δ 2.26 (s, 3H, $\text{CH}_3^{\text{para}}$), 2.38 (s, 6H, $\text{CH}_3^{\text{ortho}}$), 3.21 (s, 3H, NCH_3), 3.58 (s, 3H, NCH_3), 6.86 (s, 2H, CH_{ar}), 7.30–7.36 (m, 3H, CH_{ar}), 7.38–7.40 (m, 1H, CH_{ar}); ^{13}C (75 MHz, CDCl_3) δ 21.2 (CH_3), 21.4 (CH_3), 44.6 (NCH_3), 46.1 (NCH_3), 92.9 ($\text{C}\equiv\text{C}$), 93.1 ($\text{C}\equiv\text{C}$), 118.9 (C^{q}), 119.1 (C^{q}), 125.9 (CH_{ar}), 127.8 (CH_{ar}), 128.8 (CH_{ar}), 130.1 (CH_{ar}), 132.5 (CH_{ar}), 138.8 (C^{q}), 140.1 (C^{q}), 143.2 (C^{q}), 197.7 ($\text{C}=\text{S}$). A CH_2Cl_2 solution of **3** was heated at 40 °C for 16 hours. The solvent was evaporated under vacuum. The residue was recrystallized by layering pentane on top of a saturated solution of dichloromethane/THF (1:1). Complex **4** was obtained as yellow crystals (238 mg, quant.). m.p. 206 °C (dec); ^1H (500 MHz, $\text{dmsol}-d_6$) δ 2.08 (s, 6H, $\text{CH}_3^{\text{ortho}}$), 2.24 (s, 3H, $\text{CH}_3^{\text{para}}$), 3.41 (s, 3H, NCH_3), 3.88 (s, 3H, NCH_3), 6.86 (s, 2H, CH_{ar}), 7.67 (t, $J = 8.0$ Hz, 1H, CH_{ar}), 7.91 (t, $J = 8.0$ Hz, 1H, CH_{ar}), 8.34 (d, $J = 8.0$ Hz, 1H, CH_{ar}), 10.03 (d, $J = 8.0$ Hz, 1H, CH_{ar}); ^{13}C (125 MHz, $\text{dmsol}-d_6$) δ 20.0 (CH_3), 20.6 (CH_3), 46.5 (NCH_3), 50.1 (NCH_3), 127.9 (CH_{ar}), 128.6 (CH_{ar}), 131.1 (CH_{ar}), 135.6 (CH_{ar}), 144.7 (C^{q}), 145.4 (C^{q}), 166.9 (C^{q}), 174.2 (C^{q}), 179.8 (C^{q}).

Synthesis of complex **5**

THF (10 mL) was added at room temperature to a solid mixture of benzothioamide **2** (175 mg, 0.57 mmol) and gold(III) precursor (AuCl_3 : 173 mg; HAuCl_4 : 305 mg, 0.57 mmol) under an atmosphere of argon. The reaction mixture was stirred for 16 hours, and was allowed to decant. The supernatant was removed via cannula filtration, and the resulting yellow solid was washed with diethyl ether and dried under vacuum. The residue was recrystallized from a saturated solution of acetone. Complex **4** was obtained as pale yellow crystals (275 mg, 79 % yield). m.p. 206 °C; ^1H (500 MHz, $\text{dmsol}-d_6$) δ 2.33 (s, 6H, $\text{CH}_3^{\text{ortho}}$), 2.34 (s, 3H, $\text{CH}_3^{\text{para}}$), 3.62 (br s, 3H, NCH_3), 3.91 (br s, 3H, NCH_3), 7.04 (s, 2H, CH_{ar}), 7.85 (t, $J = 8.0$ Hz, 1H, CH_{ar}), 8.15 (t, $J = 8.0$ Hz, 1H, CH_{ar}), 8.25 (d, $J = 8.0$ Hz, 1H, CH_{ar}), 8.63 (d, $J = 8.0$ Hz, 1H, CH_{ar}); ^{13}C (125 MHz, $\text{dmsol}-d_6$) δ 20.8 (CH_3), 45.8 (br, NCH_3), 50.3 (br, NCH_3), 120.9 (C^{q}), 125.7 (C^{q}), 128.3 (CH_{ar}), 128.7 (CH_{ar}), 128.8 (CH_{ar}), 129.3 (C^{q}), 130.3 (C^{q}), 133.2 (CH_{ar}), 134.9 (CH_{ar}), 138.5 (C^{q}), 139.6 (C^{q}), 140.6 (C^{q}), 176.4 (C^{q}).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

References

1. For recent reviews, see: Hashmi ASK. *Gold Bull.* 2004; 37:51. Hashmi ASK. *Chem Rev.* 2007; 107:3180. [PubMed: 17580975] Fürstner A, Davies PW. *Angew Chem.* 2007; 119:3478. *Angew Chem Int Ed.* 2007; 46:3410. Gorin DJ, Toste FD. *Nature.* 2007; 446:395. [PubMed: 17377576] Jimenez-Nunez E, Echavarren AM. *Chem Commun.* 2007:333. Hashmi ASK. *Catal Today.* 2007; 122:211. Li Z, Brouwer C, He C. *Chem Rev.* 2008; 108:3239. [PubMed: 18613729] Arcadi A. *Chem Rev.* 2008; 108:3266. [PubMed: 18651778] Jimenez-Nunez E, Echavarren AM. *Chem Rev.* 2008; 108:3326. [PubMed: 18636778] Gorin DJ, Sherry BD, Toste FD. *Chem Rev.* 2008; 108:3351. [PubMed: 18652511] Patil NT, Yamamoto Y. *Chem Rev.* 2008; 108:3395. [PubMed: 18611054] Diez-Gonzalez S, Nolan SP. *Acc Chem Res.* 2008; 41:349. [PubMed: 18281951] Shen HC. *Tetrahedron.* 2008; 64:3885. Widenhoefer RA. *Chem Eur J.* 2008; 14:5382. [PubMed: 18442031] Fürstner A. *Chem Soc Rev.* 2009; 38:3208. [PubMed: 19847352] Hashmi ASK, Ramamurthi TD, Rominger F. *Adv Synth Catal.* 2010; 352:971. Rudolph M, Hashmi ASK. *Chem Soc Rev.* 2012; 41:2448. [PubMed: 22182942]
2. a) Ung G, Mendoza-Espinosa D, Bouffard J, Bertrand G. *Angew Chem.* 2011; 123:4301. *Angew Chem Int Ed.* 2011; 50:4215. b) Ung G, Frey GD, Schoeller WW, Bertrand G. *Angew Chem.* 2011; 123:10097. *Angew Chem Int Ed.* 2011; 50:9923. c) Ung G, Bertrand G. *Chem Eur J.* 2012; 18:12955. [PubMed: 22961643]
3. Ung G, Mendoza-Espinosa D, Bertrand G. *Chem Commun.* 2012; 48:7088.
4. For reviews on MICs and related species, see: Schuster O, Yang L, Raubenheimer HG, Albrecht M. *Chem Rev.* 2009; 109:3445. [PubMed: 19331408] Albrecht M. *Chem Commun.* 2008; 31:3601. Arnold PL, Pearson S. *Coord Chem Rev.* 2007; 251:596. Albrecht M. *Chimia.* 2009; 63:105. Melaimi M, Soleilhavoup M, Bertrand G. *Angew Chem.* 2010; 122:8992. *Angew Chem Int Ed.* 2010; 49:8810. Martin D, Melaimi M, Soleilhavoup M, Bertrand G. *Organometallics.* 2011; 30:5304. [PubMed: 22707843]
5. For our contribution to the MICs chemistry, see: Lavallo V, Dyker CA, Donnadiou B, Bertrand G. *Angew Chem.* 2008; 120:5491. *Angew Chem Int Ed.* 2008; 47:5411. Fernandez I, Dyker CA, DeHope A, Donnadiou B, Frenking G, Bertrand G. *J Am Chem Soc.* 2009; 131:11875. [PubMed: 19645451] Aldeco-Perez E, Rosenthal AJ, Donnadiou B, Parameswaran P, Frenking G, Bertrand G. *Science.* 2009; 326:556. [PubMed: 19900893] Ung G, Bertrand G. *Chem Eur J.* 2011; 17:8269. [PubMed: 21656597] Guisado-Barrios G, Bouffard J, Donnadiou B, Bertrand G. *Angew Chem.* 2010; 122:4869. *Angew Chem Int Ed.* 2010; 49:4759. Bouffard J, Keitz BK, Tonner R, Guisado-Barrios G, Frenking G, Grubbs RH, Bertrand G. *Organometallics.* 2011; 30:2617. [PubMed: 21572542] Mendoza-Espinosa D, Ung G, Donnadiou B, Bertrand G. *Chem Commun.* 2011; 47:10614.
6. For NHCs with different ring sizes, see: Hahn FE, Jahnke MC. *Angew Chem.* 2008; 120:3166–3216. *Angew Chem Int Ed.* 2008; 47:3122–3172. Dröge T, Glorius F. *Angew Chem.* 2010; 122:7094–7107. *Angew Chem Int Ed.* 2010; 49:6940–6952. Lu WY, Cavell KJ, Wixey JS, Kariuki B. *Organometallics.* 2011; 30:5649.
7. Examples of pyridinylylidene ligands are known, see ref. 4a.
8. See for examples: Nevado C, Cárdenas DJ, Echavarren AM. *Chem Eur J.* 2003; 9:2627. [PubMed: 12794906] Genin E, Toullec PY, Antoniotti S, Brancour C, Genêt JP, Michelet V. *J Am Chem Soc.* 2006; 128:3112. [PubMed: 16522069] Ritter S, Horino Y, Lex J, Schmalz HG. *Synlett.* 2006:3309. Hashmi ASK, Schuster AM, Gaillard S, Cavallo L, Poater A, Nolan SP. *Organometallics.* 2011; 30:6328. Barabé F, Levesque P, Korobkov I, Barriault L. *Org Lett.* 2011; 13:5580. [PubMed: 21916520]
9. See for examples: Hashmi ASK, Schuster AM, Rominger F. *Angew Chem.* 2009; 121:8396. *Angew Chem Int Ed.* 2009; 48:8247. Egorova OA, Seo H, Kim Y, Moon D, Rhee YM, Ahn KH. *Angew Chem.* 2011; 123:11648. *Angew Chem Int Ed.* 2011; 50:11446.

10. CCDC 901815 (3), 901816 (4), and 901817 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
11. For reviews and recent examples on the isolation of gold intermediates, see: Hashmi ASK. *Gold Bull.* 2009; 42:275. Hashmi ASK. *Angew Chem.* 2010; 122:5360. *Angew Chem Int Ed.* 2010; 49:5232. Liu LP, Hammond GB. *Chem Soc Rev.* 2012; 41:3129. [PubMed: 22262401] Hashmi ASK, Braun I, Nösel P, Schädlich J, Wietek M, Rudolph M, Rominger F. *Angew Chem.* 2012; 124:4532. *Angew Chem Int Ed.* 2012; 51:4456. Hashmi ASK, Wietek M, Braun I, Nösel P, Jongbloed L, Rudolph M, Rominger F. *Adv Synth Catal.* 2012; 354:555.
12. See for examples: Liu LP, Xu B, Mashuta MS, Hammond GB. *J Am Chem Soc.* 2008; 130:17642. [PubMed: 19055329] Shi Y, Ramgren SD, Blum SA. *Organometallics.* 2009; 28:1275. Weber D, Tarselli MA, Gagné MR. *Angew Chem.* 2009; 121:5843. *Angew Chem Int Ed.* 2009; 48:5733. Zeng X, Kinjo R, Donnadiou B, Bertrand G. *Angew Chem.* 2010; 122:954. *Angew Chem Int Ed.* 2010; 49:942. Döpp R, Lothschütz C, Wurm T, Pernpointer M, Keller S, Rominger F, Hashmi ASK. *Organometallics.* 2011; 30:5894.
13. a) de Frémont P, Scott NM, Stevens ED, Nolan SP. *Organometallics.* 2005; 24:2411. b) Jahnke MC, Paley J, Hupka F, Weigand JJ, Hahn FE. *Z Naturforsch, B: Chem Sci.* 2009; 64:1458. c) Alcarazo M, Stork T, Anoop A, Thiel W, Fürstner A. *Angew Chem.* 2010; 122:2596. *Angew Chem Int Ed.* 2010; 49:2542. d) Hashmi ASK, Lothschütz C, Böhling C, Hengst T, Hubbert C, Rominger F. *Adv Synth Catal.* 2010; 352:3001. e) Hashmi ASK, Lothschütz C, Graf K, Häffner T, Schuster A, Rominger F. *Adv Synth Catal.* 2011; 353:1407. f) Dunsford JJ, Cavell KJ, Kariuki BM. *Organometallics.* 2012; 31:4118. g) Pellei M, Gandin V, Marinelli M, Marzano C, Yousufuddin M, Dias HVR, Santini C. *Inorg Chem.* 2012; 51:9873. [PubMed: 22946642] h) Sato T, Hirose Y, Yoshioka D, Oi S. *Organometallics.* 2012; 31:6995.
14. For an example of diarylcarbene copper complex, see: Dai X, Warren TH. *J Am Chem Soc.* 2004; 126:10085. [PubMed: 15303885]
15. a) Gaillard S, Slawin AMZ, Bonura AT, Stevens ED, Nolan SP. *Organometallics.* 2010; 29:394. b) Pazicky M, Loos A, Ferreira MJ, Serra D, Vinokurov N, Rominger F, Jakel C, Hashmi ASK, Limbach M. *Organometallics.* 2010; 29:4448.
16. de Frémont P, Singh R, Stevens ED, Petersen JL, Nolan SP. *Organometallics.* 2007; 26:1376.
17. a) Dötz KH, Pfeiffer J. *Chem Commun.* 1996:895. b) Pfeiffer J, Dötz KH. *Organometallics.* 1998; 17:4353.
18. Sugawara S, Kojima S, Yamamoto Y. *Chem Commun.* 2012; 48:9735.

Figure 1.

Previously reported transition-metal induced cyclization of ethynyl dithiocarbamate **A** and ynamide **B** to the corresponding 1,3-dithiol-5-ylidene **D** and oxazol-4-ylidene **E** complexes. Alkyne **C**, as a potential precursor of the thiopyryl-3-ylidene ligand **F** or carbene gold complex **G**.

Figure 2.

Structure of **3** (left) and **4** (right) in the solid state. Ellipsoids are drawn at 50% probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°]: **3**: C1–C2 = 1.192(4), Au1–Cl1 = 2.2795(7), S1–Au1 = 2.2547(7), C3–S1 = 1.714(3), C3–N1 = 1.306(3), S1–Au1–Cl1 = 174.03(2); **4**: Au1–Cl1 = 2.307(3), Au1–C1 = 1.990(11), C1–C2 = 1.325(15), C2–C3 = 1.457(15), C3–C4 = 1.436(14), C4–C5 = 1.426(15), C2–S1 = 1.781(11), C5–S1 = 1.733(11), C5–N1 = 1.299(14), S1–Au1–Cl1 = 179.0(4).

Figure 3.

Structure of **5** in the solid state. Ellipsoids are drawn at 50% probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°]: Au1–Cl1 = 2.3286(14), Au1–Cl2 = 2.3602(17), Au1–Cl3 = 2.3048(15), Au1–C1 = 2.077(7), C1–C2 = 1.462(9), C3–C2 = 1.432(9), C3–C4 = 1.455(9), C1–C5 = 1.308(10), S1–C5 = 1.754(7), S1–C4 = 1.734(7), N1–C4 = 1.325(8), Cl1–Au1–Cl2 = 90.10(6), Cl3–Au1–Cl2 = 91.41(6), C1–Au1–Cl1 = 93.34(19), C1–Au1–Cl3 = 85.01(19), C5–C1–C2 = 124.0(7).

Scheme 1.

Synthesis of alkynyl benzothioamide **2**. Reagents and conditions: a) HC≡CMes, PdCl₂(PPh₃)₂, CuI, NEt₃, 16 hours, r.t.; b) *t*BuLi, Et₂O, 15 min, -78 °C then ClC(S)NMe₂, Et₂O, 2 hrs, -78 °C to r.t.; Mes = 2,4,6-trimethylphenyl.

Scheme 2.

Reactivity of **2** towards Au(I) and Au(III) complexes. tht = tetrahydrothiophene.