Gold Complexes

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Gold(III)- versus Gold(I)-Induced Cyclization: Synthesis of Six-Membered Mesoionic Carbene and Acyclic (Aryl)(Heteroaryl) Carbene Complexes[**]

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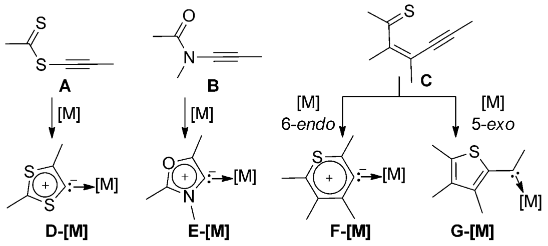
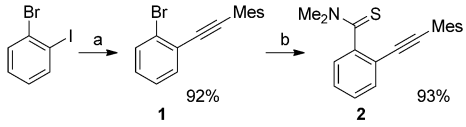
In the last decade, gold complexes have been widely used as catalysts for promoting a variety of organic transformations.[1] We have recently demonstrated that the gold-induced cyclization of heteroatom-substituted alkynes **A** and **B** provides the corresponding gold complexes **D**-[**M**] and **E**-[**M**], respectively (Scheme 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 to exist as 4- to 8-membered rings,[6] MICs have been mostly limited so far 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 by an unusual gold induced 6-*endo-dig* ring closure process and by a more classical 5-*exo-dig* cyclization, respectively. The selectivity observed is dictated by the oxidation state of the gold promoter.



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

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 (Scheme 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**].

To force a *cis* geometry between the alkyne and the thione of **C**, we chose a benzene fused system. 2-bromoiodobenzene 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 2).



Scheme 2. Synthesis of alkynyl benzothioamide **2**. Reagents and conditions: a) HC≡CMes, [PdCl$_2$(PPh$_3$)$_2$], CuI, NEt$_3$, 16 h, RT; b) *t*BuLi, Et$_2$O, 15 min, −78 °C, then ClC(S)NMe$_2$, Et$_2$O, 2 h, −78 °C→RT; Mes = 2,4,6-trimethylphenyl.

Compound **2** was first reacted with [(tht)Au^{I}Cl] (tht = tetrahydrothiophene). The reaction proceeded cleanly in CH$_2$Cl$_2$; however, the ^{13}C NMR spectrum of the product showed peaks at $\delta = 92.9$ 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 ^{13}C 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 1, left; Scheme 3).[10]

Despite the aurophilicity of sulfur, we reasoned that the desired MIC–Au^{I} complex would be thermodynamically favored over a thioamide–Au^{I} complex. After heating **3** at 40 °C for 16 h, we observed the quantitative conversion into a new product. No alkyne carbon signals were detected in the ^{13}C NMR spectrum, and the CS signal shifted drastically upfield, indicating that a cyclization process occurred. A single-crystal X-ray diffraction study showed that it was

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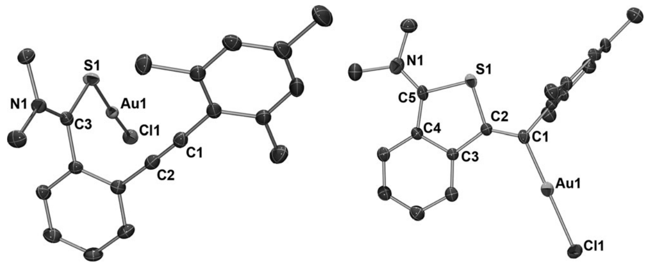


Figure 1. Structures of **3** (left) and **4** (right) in the solid state. Ellipsoids are set at 50% probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3**: C1-C2 1.192(4), Au1-Cl1 2.2795(7), S1-Au1 2.2547(7), C3-S1 1.714(3), 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); C1-Au1-Cl1 179.0(4).

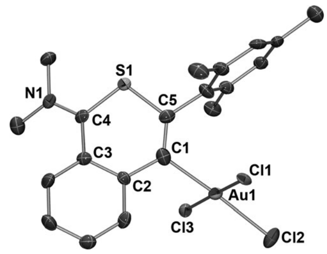
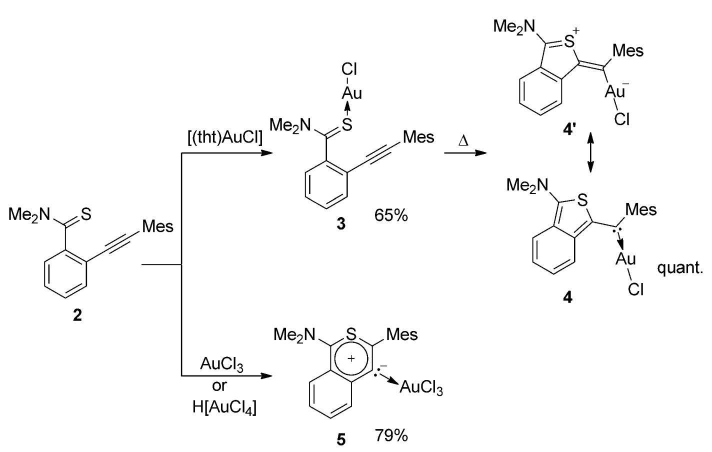


Figure 2. Structure of **5** in the solid state. Ellipsoids are set at 50% probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1-Cl1 2.3286(14), Au1-Cl2 2.3602(17), Au1-Cl3 2.3048(15), Au1-C1 2.077(7), C1-C2 1.462(9), 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 3. Reactivity of **2** towards $\mathrm{Au^{I}}$ and $\mathrm{Au^{III}}$ complexes. tht = tetrahydrothiophene.

complex **4**, resulting from the usually encountered 5-*exo-dig* cyclization[1,9] (Figure 1, 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 3). The Au1−C1 bond (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[13] and MIC gold complexes[2a,5c,g] (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–$\mathrm{Au^{I}}$ 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 $\mathrm{Au^{III}Cl_3}$ was added to **2**, and alkyne carbon signals were absent in the ^{13}C NMR spectrum, indicating that a cyclization process had 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 2; Scheme 3).[10] The Au1−C1 bond (2.077(7) Å) is considerably shorter than that observed for a [(vinyl)$\mathrm{Au^{III}Cl_3}$] complex (2.2743(9) Å),[9b] and slightly longer than for [(NHC)$\mathrm{Au^{III}Cl_3}$] complexes (1.98–2.01 Å).[15] The gold center features a weakly distorted square planar geometry (sum of angles = 359.9°), and the six-membered MIC ring is only slightly twisted, which is due to the proximity of the bulky mesityl substituent with the chloride on the gold center. Although NHCs are oxidized by $\mathrm{Au^{III}Cl_3}$,[16] preventing the direct synthesis of NHC–$\mathrm{Au^{III}}$ complexes, the formation of metallic $\mathrm{Au^{0}}$ was never observed in the reaction leading to **5**. Interestingly, the reaction of **2** with H[$\mathrm{Au^{III}Cl_4}$] 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] Furthermore, **5** is the first metal complex featuring a non-nitrogen-containing[7] six-membered mesoionic carbene. The availability of a variety of analogues of **2** that feature different heteroatoms should allow for the preparation of numerous six-membered MIC complexes. Both complexes **4** and **5** are very robust (m.p. **4** and **5**: 206 °C), which is 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. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500 or Bruker 300 spectrometer at 25 °C. 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 h. 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); ^{1}H (300 MHz, $CDCl_3$) $\delta = 2.26$ (s, 3 H, C$H_{3\mathrm{para}}$), 2.38 (s, 6 H, C$H_{3\mathrm{ortho}}$), 3.21 (s, 3 H, NCH_3), 3.58 (s, 3 H, NCH_3), 6.86 (s, 2 H, CH_{ar}), 7.30–7.36 (m, 3 H, CH_{ar}), 7.38–7.40 ppm (m, 1 H, CH_{ar}); ^{13}C (75 MHz, $CDCl_3$) $\delta = 21.2$ (CH_3), 21.4 (CH_3), 44.6 (NCH_3), 46.1 (NCH_3), 92.9 ($C{\equiv}C$), 93.1 ($C{\equiv}C$), 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 ppm ($C{=}S$). A CH_2Cl_2 solution of **3** was heated at 40 °C for 16 h. 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); ^{1}H (500 MHz, [D_6]DMSO) $\delta = 2.08$ (s, 6 H, C$H_{3\mathrm{ortho}}$), 2.24 (s, 3 H, C$H_{3\mathrm{para}}$), 3.41 (s, 3 H, NCH_3), 3.88 (s, 3 H, NCH_3), 6.86 (s, 2 H, CH_{ar}), 7.67 (t, $J = 8.0$ Hz, 1 H, CH_{ar}), 7.91 (t, $J = 8.0$ Hz, 1 H, CH_{ar}), 8.34 (d, $J = 8.0$ Hz, 1 H, CH_{ar}), 10.03 ppm (d, $J = 8.0$ Hz, 1 H, CH_{ar}); ^{13}C (125 MHz, [D_6]DMSO) $\delta = 20.0$ (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 ppm (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 the gold(III) precursor ($AuCl_3$: 173 mg; H[$AuCl_4$]: 305 mg, 0.57 mmol) was added under an atmosphere of argon. The reaction mixture was stirred for 16 h, and was allowed to decant. The supernatant was removed by 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; ^{1}H (500 MHz, [D_6]DMSO) $\delta = 2.33$ (s, 6 H, C$H_{3\mathrm{ortho}}$), 2.34 (s, 3 H, C$H_{3\mathrm{para}}$), 3.62 (br s, 3 H, NCH_3), 3.91 (br s, 3 H, NCH_3), 7.04 (s, 2 H, CH_{ar}), 7.85 (t, 1 H, CH_{ar}), 8.15 (t, $J = 8.0$ Hz, 1 H, CH_{ar}), 8.25 (d, $J = 8.0$ Hz, 1 H, CH_{ar}), 8.63 ppm (d, $J = 8.0$ Hz, 1 H, CH_{ar}); ^{13}C (125 MHz, [D_6]DMSO) $\delta = 20.8 = (CH_3)$, 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 ppm (C^q).

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