

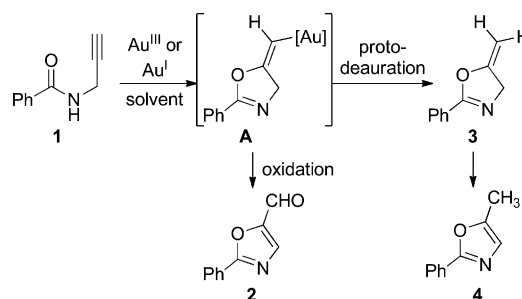
Characterization of Vinylgold Intermediates: Gold-Mediated Cyclization of Acetylenic Amides**

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Gold complexes show unusual affinity toward the carbon–carbon triple bond, thus activating it towards carbon, oxygen, and nitrogen nucleophiles. Therefore, various gold-catalyzed synthetic transformations involving carbon–carbon triple bonds have been developed in recent years,^[1] along with characterization of some reaction intermediates involved. In most cases, however, the gold-catalyzed reactions are interpreted with “suggested” mechanisms, as pointed out by Hashmi in a recent review article on the gold intermediates identified by direct observation and characterization.^[2] So far, a limited number of gold intermediates have been characterized by X-ray crystallography,^[3] including several vinylgold(I) species obtained from alkynes^[3a–f] or allenes,^[3g,h] and gem-digold(I) species from vinylboronic acids through an exchange reaction.^[3i,j]

During our study on a gold(I)/(III)-mediated intramolecular cyclization of an *N*-(propargyl)arylamides, we observed that the major product was a 2-oxazole-5-carboxaldehyde, an oxidation product of the vinylgold intermediate, rather than the compound(s) expected from a proto-deauration process.^[4] Vinylgold intermediates involved in various gold-catalyzed reactions are known to undergo proto-deauration in the presence of a proton source. The unexpected result drew our attention on the chemistry of vinylgold intermediates involved and thus prompted us to investigate the gold-mediated cyclization in detail with simple substrates, *N*-(propargyl)benzamides. Described herein is identification of the vinylgold(III) intermediates involved and their reaction pathways, all of which expands our present understanding on the vinylgold intermediates.

The treatment of *N*-(propargyl)benzamide (**1**) with an equimolar amount of AuCl₃ in acetonitrile/water (1:1 v/v) at room temperature for 1 hour produces the formyloxazole **2** as a major product, along with an unknown compound that was eventually characterized to be a dimerized product (see below). Neither the exomethylene oxazoline **3** or methyloxazole **4** is produced in any noticeable amounts, as determined by in situ NMR analysis. When a gold(I) species, AuCl (3 equiv), is used instead of AuCl₃, **2** becomes the predominant product (Scheme 1).



Scheme 1. Gold(I/III)-promoted cyclization reactions of *N*-(propargyl)-benzamide.

Hashmi and co-workers reported that **4** can be obtained in greater than 95 % yield from the AuCl₃-catalyzed cyclization of **1** in organic media.^[5a] They also noted that **3** could be obtained by addition of water to the corresponding vinylgold intermediate arising from **1** using a cationic gold(I) species and triethylamine in tetrahydrofuran (THF).^[3b]

We examined the product distribution in the above reaction in aqueous media for the different gold species in different amounts (see Table 1 in the Supporting Information). The results can be summarized as follows: 1) the formyloxazole **2** becomes the major product when more than one equivalent of the gold species is used; 2) under catalytic conditions, a hydration product becomes the major product,^[6] regardless of the catalyst used; 3) AuCl₃ and H[AuCl₄] behave similarly, whereas AuCl is required in excess to form **2**;^[7] 4) among the catalysts, only a cationic gold species ([PPh₃Au]OTf) produces the proto-deauration product **3** together with **2**.^[5c]

The heterocyclic products should be produced through the corresponding vinylgold intermediates. To characterize the vinylgold intermediates, we carried out in situ NMR analysis for an equimolar mixture of benzamide **1** (0.02–0.03 M) and AuCl₃ in CD₃CN at room temperature. Upon mixing the two components, two complexes were formed rapidly in a ratio of

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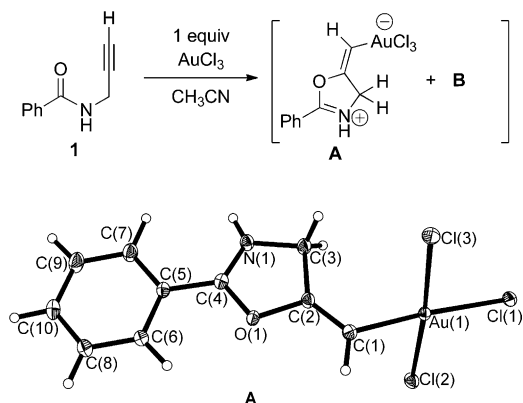
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1:2. By using [D]-**1**, we were able to confirm that the 5-*exo-dig* attack is dominant over the 6-*endo-dig* attack, as reported in the literature,^[3b] and in such a case, the *anti* addition occurs exclusively over the *syn* addition in the catalytic oxyauration reaction.^[5a] On the basis of these findings, we assigned the minor component to be the (*E*)-vinylgold(III) species **A**, which was later confirmed by crystal structure analysis (Scheme 2). The vinylgold(III) **A** was characterized through



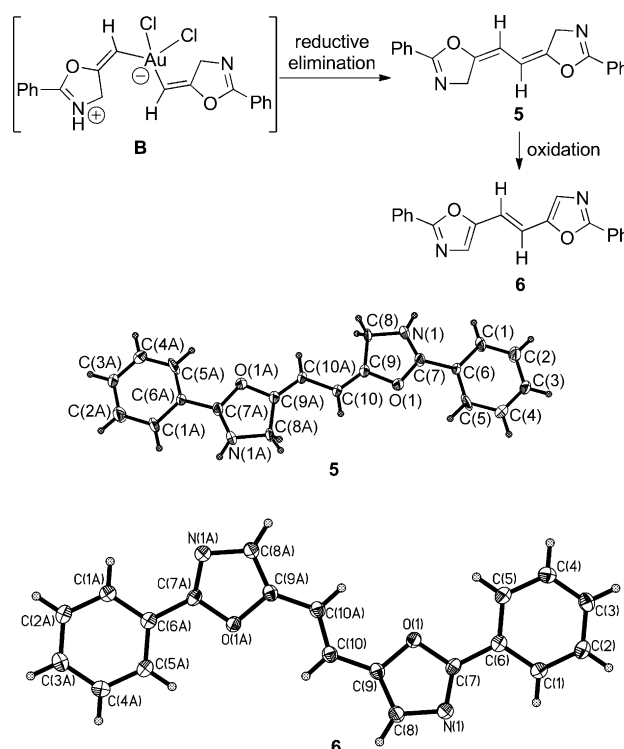
Scheme 2. AuCl₃-promoted cyclization of benzamide **1**. The structure of **A** is shown with thermal ellipsoids at 50% probability.

NMR spectroscopy by its vinylic proton at $\delta = 5.8$ ppm (triplet, $J = 3.0$ Hz) and methylene protons at $\delta = 5.0$ ppm (doublet, $J = 3.0$ Hz). The carbon atoms attached to the vinylic and methylene protons appeared at $\delta = 104.0$ and 49.6 ppm, respectively, in the ¹³C NMR spectrum. The other complex, **B**, exhibited chemical shifts similar to those of **A**, that is, showing only vinylic and methylene-type protons in addition to the aromatic ring protons: ¹H NMR: $\delta = 6.4$ (singlet, 1H), 5.1 ppm (singlet, 2H); ¹³C NMR: $\delta = 103.3$ and 49.4 ppm.

So far only a few vinylgold(I) intermediates have been characterized by X-ray crystallography as mentioned above,^[3a–f] but no of vinylgold(III) species have been characterized yet. Our efforts to obtain single crystals from the reaction mixture resulted in pale yellow prisms, the structure of which was resolved to be **A** by X-ray diffraction analysis. The crystal structure shows that the Au^{III} atom is coordinated to three chloride ligands in a typical square-planar geometry.^[8] The Au(1)–C(1) bond length is 2.004(19) Å and the C(1)–C(2) length is 1.311(3) Å. The five-membered ring is virtually planar and the C–C bond [C2–C3, 1.502(3) Å] is differentiated from that of the C=C bond of methyloxazole **4** [1.3401(18)].^[8] The gold atom has a formal negative charge; hence, the oxazoline nitrogen atom should be protonated to give a zwitterionic vinylgold species. The presence of the protonated oxazoline moiety was confirmed by the peaks in a ¹H NMR spectrum of a mixture containing **A** and **B** that correspond to an acidic proton; the peaks appear downfield as two broad singlets ($\delta = 10.6$ and 10.9 ppm), including the peaks corresponding to **B**.

The complex **B** is less soluble in acetonitrile than **A** and thus tends to precipitate at lower temperature. Therefore, it

can be enriched to a single component by a repeated precipitation process. In this way, a separate ¹H NMR spectrum for the major component, **B**, can be obtained. All our efforts to obtain a crystal structure of **B**, however, were unsuccessful because some of the crystals obtained were of low crystallinity and very fragile. Fortunately, we were able to obtain a reaction product from **B**, which provided us with valuable information on its structure. When an isolated sample of **B** was heated up to 50 °C in acetonitrile and slowly cooled to room temperature, needle-like crystals were obtained and identified to be the bis(oxazole) **6** by using ¹H NMR spectroscopy and X-ray diffraction analyses.^[8] We were also able to identify the bis(oxazoline) **5**, a precursor of **6**, by X-ray diffraction analysis (Scheme 3).^[8] These results



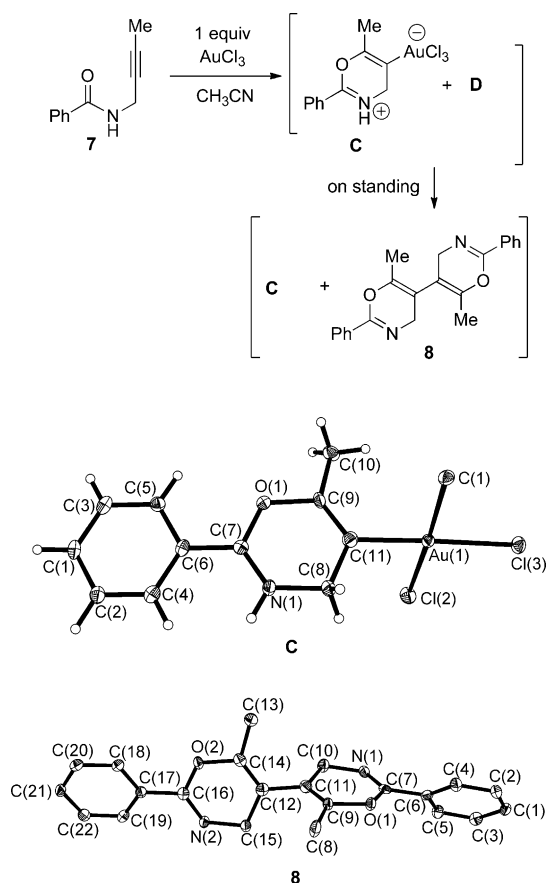
Scheme 3. Identification of the dimerized products, bis(oxazoline) **5** and bis(oxazole) **6**, formed from **B**. Structures of **5** and **6** in the solid state are shown with thermal ellipsoids at 50% probability (the counterions 2AuCl₄[−] in the case of **5** are omitted for clarity).

suggest that **B** is a divinylgold(III) species, the structure of which is assigned as shown in Scheme 3. This assignment is additionally supported by a crystal structure resolved for a dimeric vinylgold(III) species obtained from a similar reaction starting with a derivative of benzamide **1** (see below).

The formation of the mono- and divinylgold species in the gold-mediated cyclization reaction was also observed when AuCl, instead of AuCl₃, was used, as indicated by the same NMR spectral patterns obtained for the crude reaction mixture (see the Supporting Information).

The oxidative dimerization of vinylgold species is a known process, as observed in several gold-catalyzed cyclization reactions.^[9] The corresponding vinylgold intermediates such as **B**, however, have remained elusive species.

To obtain additional information on the structure of **B**, we examined the same gold-promoted cyclization with *N*-(but-2-ynyl)benzamide (**7**). According to the previous study by Hashmi and co-workers,^[3b] the cyclization should proceed through the 6-*endo-dig* route for such an internal alkyne. An in situ NMR study for an equimolar mixture of benzamide **7** and AuCl₃ in CD₃CN at room temperature indicated that two organogold species, **C** and **D**, formed instantaneously in a ratio of 2:1, similar to the case involving benzamide **1** (Scheme 4). Both ¹H and ¹³C NMR analyses (see the Supporting Information) suggested that **C** is a monovinylgold species.



Scheme 4. Identification of the vinylgold intermediate **C** and the dimer product **D** in the gold-promoted cyclization of benzamide **7**. The structures of **C** and **D** in the solid state are shown with thermal ellipsoids at 50% probability (the counterion AuCl₂[−] in the case of **D** and solvent molecules are omitted for clarity).

Fortunately, we were able to obtain single crystals of **C** in the presence of **D**, by diffusion of water vapor into a solution of the reaction mixture in acetonitrile at room temperature. The resolved crystal structure confirmed that **C** is the vinylgold(III) species produced through the 6-*endo-dig* attack. Hashmi and co-workers characterized a crystal structure of the vinylgold(I) species formed through the 6-*endo-dig* attack.^[3b] The crystal structure of **C** shows that the Au^{III}Cl₃ moiety is in a typical square-planar geometry (Scheme 4), similar to that of **A**, with the bond lengths Au1-

C11 at 2.2743(9) Å, the neighboring C9-C11 at 1.322(6) Å, and the vinylic C8-C11 at 1.499(6) Å. **C** also exists as a stable zwitterionic form in which the nitrogen atom is protonated. Of particular note is that **C** is quite stable in aqueous media and does not undergo proto-deauration readily. Additionally, its solution in acetonitrile does not show any decomposition even after two weeks at room temperature.

In contrast to **C**, **D** was not stable and transformed into the organic dimer **8** after standing for seven hours at room temperature, as determined by NMR analysis. The intensity of the peaks for the methylene proton of **D** at δ = 4.44 ppm decreased, and a new peak appeared at δ = 4.32 ppm. In contrast to **D**, **C** remained unchanged during the ¹H NMR observation (see the Supporting Information). Colorless single crystals of the dimeric compound **8** were obtained from recrystallization of the final mixture containing **C** and **8** at −18°C; the crystal structure of **8** thus confirmed that it is the dimerized product that is produced from **D**.

Along with our efforts to obtain the crystal structures, we carried out extensive MS analyses for the reaction intermediates, **A/B** and **C/D**. An ESI-MS analysis (in the positive mode) for a 1:1 mixture of benzamide **1** and AuCl₃ in CD₃CN at room temperature (immediately after mixing) showed intensive peaks at *m/z* 548 and 550 (Figure 1), which were attributed to the divinylgold species **9** and its ³⁷Cl derivative, respectively.

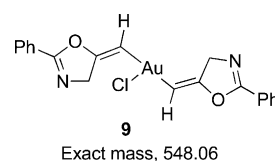


Figure 1. Divinylgold species **9** observed by ESI-MS.

In the negative ESI-MS mode, the cluster peaks observed at *m/z* 461.0 and 463.0 were attributed to the deprotonated form of **A** (C₁₀H₈AuCl₃NO, exact mass 459.93) having different isotopes (C₁₀H₇DAuCl₃NO and C₁₀H₇DAu³⁵Cl₂³⁷ClNO, respectively). Both data sets also supported the formation of the mono- and divinylgold species. We found that deposition of metal gold during the mass analysis contaminated the instrument; hence, we carried out MALDI-TOF MS analysis for the mixture of **C** and **D**. A freshly prepared sample showed an intense peak at *m/z* 345, which corresponded to the protonated form of **8**; in this case, peaks that represent vinylgold species were observed but as minor fragments.

It was difficult to obtain single crystals of less stable **D** from a mixture containing **C** because **C** crystallizes out first and, furthermore, **D** has low stability in organic solvents. After many attempts, we were able to identify single crystals of **D** whose structure was resolved by X-ray diffraction analysis. **D** is a *cis*-dichlorobis(vinylloxaziny)gold species, as shown in Figure 2. The cocrystal of AuCl₄[−] indicates that both the oxaziny nitrogen atoms are protonated to balance the charge. To the best of our knowledge, this is the first divinylgold intermediate characterized by X-ray diffraction analysis. On the basis of this result, we have assigned the

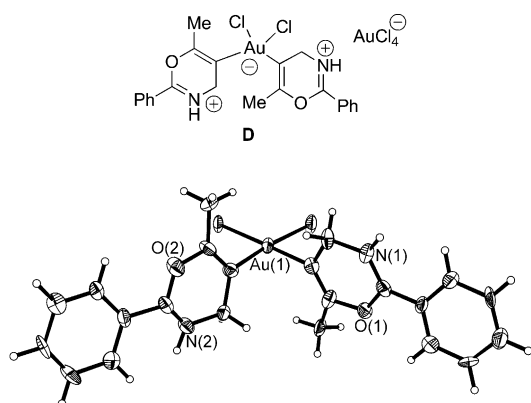
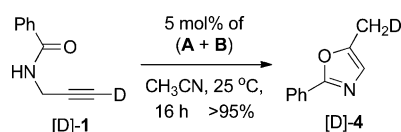


Figure 2. Structure of **D** in the solid state. Thermal ellipsoids shown at 50% probability. A counterion (AuCl_4^-) is omitted for clarity.

structure of **B** as the corresponding divinyldigold(III) species (Scheme 3). Before obtaining the crystal structure of **D**, we suspected that **B** might be a dimerized species of **A**, a divinyldigold species in which two **A** species are bridged through two chlorine ligands. Further experiments, however, indicate that there is no exchange reaction between **A** and **B** or between **C** and **D**; the results exclude the possibility of **B** as a divinyldigold species.

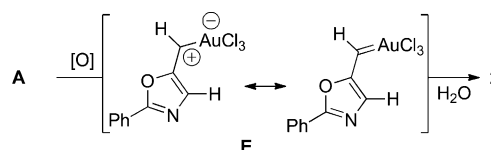
To examine whether **B** could be formed from **A**, we followed NMR spectral changes for a mixture of benzamide **1** and AuCl_3 in a ratio of 3:2 in CD_3CN at room temperature. We know that, under the stoichiometric and dilute (0.3 M of benzamide **1**) reaction conditions, only **A** and **B** form instantly in a ratio of 1:2, with no benzamide **1** left.^[10] Under the substoichiometric reaction conditions, we observed **A**, **B**, and benzamide **1** in an approximate ratio of 1:4:3. This result indicates that the divinyldigold **B** is not produced by a possible reaction between **A** (or its dissociated form) and benzamide **1**. If it were the latter case, we could not observe the unreacted benzamide under the substoichiometric reaction conditions. The distribution ratio also did not change when the temperature of the mixture was raised to 40 °C. A similar behavior was also observed in the case of benzamide **7**. The divinyldigold intermediate seems to be formed by a 1:2 coordination between AuCl_3 and the benzamide starting material through the propargylic group, although the mechanism is not clear at present.

Of particular note is that when benzamide [D]-**1** was treated with a catalytic amount (5 mol%) of a preformed mixture of **A** and **B**, the vinylgold complexes undergo proto-deauration to afford **4** via **3**, as determined by ^1H NMR spectroscopy (Scheme 5). Therefore, it is apparent that the substrate facilitates the proto-deauration step in this gold-catalyzed cyclization reaction in aprotic media. Once vinyl-



Scheme 5. Substrate-assisted proto-deauration. Vinylgold-catalyzed conversion of [D]-**1** into [D]-**4**.

gold species such as **A** and **B** are generated, they are chemically stable in aprotic media if there are no promoters such as **1** or others for the proto-deauration.^[11] However, in aqueous media, the stable vinylgold species can follow new reaction pathways such as the formation of the formylloxazole **2**. Previously, we tentatively suggested a gold-mediated hydration of vinylgold **A** as a possible mechanism for the introduction the formyl group in **2**. A high level of molecular calculation has been carried out, which suggests that the AuCl_3 -mediated hydration of vinylgold **A** is less probable owing to its high activation energy. An alternative route may involve a gold carbenoid intermediate **E** (Scheme 6), which could be produced through an oxidation process ($\text{Au}^{\text{III}} \leftrightarrow \text{Au}^{\text{I}} + \text{Au}^0$) to produce **2** in the presence of water. Gold carbenoids have been assumed to be intermediates in various transformations but they have rarely been characterized.^[12] Additional studies are necessary to characterize the mechanism suggested.



Scheme 6. A gold carbenoid route for **A** to form formylloxazole **2** via **E**.

In summary, we have characterized key vinylgold(III) intermediates in the gold-mediated cyclization reactions of *N*-(propargyl)benzamides. Both mono- and divinyldigold(III) complexes are instantaneously produced in comparable ratios upon the treatment of the *N*-(propargyl)benzamides with an equimolar amount of AuCl_3 in acetonitrile at room temperature. The structures of the vinylgold intermediates have been identified by NMR, MS, and X-ray diffraction analyses. Two crystal structures of two different monovinyldigold(III) complexes and one crystal structure of a divinyldigold(III) complex have been resolved. We have also identified that the monovinyldigold intermediate from *N*-(prop-2-ynyl)benzamide does not undergo the proto-deauration reaction even in the presence of water. However, it does produce 2-phenyloxazole-5-carbaldehyde, an oxidation product of the vinylgold intermediate, probably through a gold(III) carbenoid intermediate. The proto-deauration of the vinylgold intermediates takes place upon the addition of the *N*-(propargyl)benzamides. The divinyldigold intermediates are not as stable as the corresponding monovinyldigold species and thus, on standing they produce the corresponding dimerized organic compounds, which were identified by NMR and X-ray diffraction analyses. These results expand our present understanding of the vinylgold intermediates in the gold-catalyzed addition reactions, the presumed proto-deauration process, and new reaction pathways of the vinylgold species.

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- [1] For reviews, see: a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; b) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; c) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403; d) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; e) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; f) E. Jiménez-Núñez, A. Echavarren, *Chem. Commun.* **2007**, 333–346; g) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; h) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; i) E. Jiménez-Núñez, A. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; j) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; k) N. T. Patil, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 3395–3442; l) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766–1775; m) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1782.
- [2] A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360–5369; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241.
- [3] a) J. A. Akana, K. X. Bhattacharyya, P. Müller, J. O. Sadighi, *J. Am. Chem. Soc.* **2007**, *129*, 7736–7737; b) A. S. K. Hashmi, M. Schuster, F. Rominger, *Angew. Chem.* **2009**, *121*, 8396–8398; *Angew. Chem. Int. Ed.* **2009**, *48*, 8247–8249; c) X. Zeng, R. Kinjo, B. Donnadiou, G. Bertrand, *Angew. Chem.* **2010**, *122*, 954–957; *Angew. Chem. Int. Ed.* **2010**, *49*, 942–945; d) Y. Chen, D. Wang, J. L. Petersen, N. G. Akhmedov, X. Shi, *Chem. Commun.* **2010**, 6147–6149; e) A. S. K. Hashmi, A. M. Schuster, F. Rominger, *Adv. Synth. Catal.* **2010**, *352*, 971–975; f) Y. Zhu, B. Yu, *Angew. Chem.* **2011**, *123*, 8479–8482; *Angew. Chem. Int. Ed.* **2011**, *50*, 8329–8332; g) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642–17643; h) D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem.* **2009**, *121*, 5843–5846; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733–5736; i) E. Y. Tsui, P. Müller, J. P. Sadighi, *Angew. Chem.* **2008**, *120*, 9069–9072; *Angew. Chem. Int. Ed.* **2008**, *47*, 8937–8940; j) G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem.* **2010**, *122*, 8644–8648; *Angew. Chem. Int. Ed.* **2010**, *49*, 8466–8470; k) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592–597; l) R. L. LaLonde, W. E. Brenzovich, Jr., D. Benitez, E. Tkatchouk, K. Kelley, W. A. Goddard III, F. D. Toste, *Chem. Sci.* **2010**, *1*, 226–233.
- [4] a) O. A. Egorova, H. Seo, A. Chatterjee, K. H. Ahn, *Org. Lett.* **2010**, *12*, 401–403; b) Concurrently, Jou et al. also reported the same observation; see: M. J. Jou, X. Chen, K. M. K. Swamy, H. N. Kim, H.-J. Kim, S.-g. Lee, J. Yoon, *Chem. Commun.* **2009**, 7218–7220.
- [5] a) A. S. K. Hashmi, J. P. Weyrauch, W. Frey, J. W. Bats, *Org. Lett.* **2004**, *6*, 4391–4394; b) A. S. K. Hashmi, M. Rudolph, S. Schymura, J. Visus, W. Frey, *Eur. J. Org. Chem.* **2006**, 4905–4909; c) J. P. Weyrauch, A. S. K. Hashmi, A. Schuster, T. Hengst, S. Schetter, A. Littmann, M. Rudolph, M. Hamzic, J. Visus, F. Rominger, W. Frey, J. W. Bats, *Chem. Eur. J.* **2010**, *16*, 956–963.
- [6] a) Y. Fukuda, K. Utimoto, *J. Org. Chem.* **1991**, *56*, 3729–3731; b) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem.* **1998**, *110*, 1475–1478; *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1418.
- [7] AuCl disproportionates into Au^{III} and Au⁰ in water; hence, more than an equivalent amount gave better results: a) R. Kissner, G. Welti, G. Geier, *J. Chem. Soc. Dalton Trans.* **1997**, 1773–1777.
- [8] Crystal data for **A** (C₁₀H₉N₁O₁Cl₃Au₁): *M* = 462.50, monoclinic, space group *P*2₁/*c* (No. 14); *a* = 9.7219(6), *b* = 8.4971(5), *c* = 14.9538(9) Å, β = 97.364(3)°, *V* = 1225.11(13) Å³, *Z* = 4, *T* = 100(2) K, $\mu(\lambda=0.71073 \text{ Å})$ = 12.394 mm⁻¹, ρ_{calc} = 2.508 g cm⁻³, 59124 reflections measured, 10447 unique (*R*_{int} = 0.0472), *R*₁ = 0.0287, *wR*₂ = 0.0542 (*I* > 2σ(*I*)), *R*₁ = 0.0434, *wR*₂ = 0.0573 (all data), GOF = 1.058. Crystal data for **C** (C₁₁H₁₁AuCl₃N O₃): *M* = 508.52, triclinic, space group *P* $\bar{1}$ (No. 2), *a* = 7.8236(3), *b* = 9.2952(4), *c* = 10.9315(4) Å, α = 75.575(2), β = 79.595(2), γ = 84.014(3)°, *V* = 755.77(5) Å³, *Z* = 2, *T* = 100(2) K, $\mu(\lambda=0.71073 \text{ Å})$ = 10.264 mm⁻¹, ρ_{calc} = 2.235 g cm⁻³, 29010 reflections measured, 7798 unique (*R*_{int} = 0.0728), *R*₁ = 0.0465, *wR*₂ = 0.0666 for 5508 reflections (*I* > 2σ(*I*)), *R*₁ = 0.0837, *wR*₂ = 0.0760 (all data), GOF = 0.997. Crystal data for **D** (C₂₈H₃₁Au₂Cl₆N₅O₂): *M* = 1076.21, orthorhombic, *Pca*2₁ (No. 29), *a* = 23.6666(14), *b* = 11.8359(8), *c* = 24.6210(13) Å, *V* = 6896.7(7) Å³, *Z* = 8, *T* = 100(2) K, $\mu(\lambda=0.71073 \text{ Å})$ = 8.998 mm⁻¹, ρ_{calc} = 2.073 g cm⁻³, 64521 reflections measured, 13790 unique (*R*_{int} = 0.1264), *R*₁ = 0.0638, *wR*₂ = 0.1299 for 8285 reflections (*I* > 2σ(*I*)), *R*₁ = 0.1312, *wR*₂ = 0.1541 (all data), GOF = 1.026. Synthetic procedures and crystal data for other organic compounds (**4**, **5**, **6**, and **8**) are provided in the Supporting Information. CCDC 801793 (**A**), 801792 (**4**), 806020 (**6**), 806021 (**5**), 813810 (**C**), 813809 (**8**), and 837674 (**D**) 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.
- [9] a) For a recent review, see: H. A. Wegner, *Chimia* **2009**, *63*, 44–48; b) A. S. K. Hashmi, M. C. Blanco, D. Fisher, J. W. Bats, *Eur. J. Org. Chem.* **2006**, 1387–1389; c) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem.* **2009**, *121*, 3158–3161; *Angew. Chem. Int. Ed.* **2009**, *48*, 3112–3115.
- [10] See the Supporting Information for the NMR spectral data. Under the stoichiometric but more concentrated conditions ($\geq 0.054 \text{ M}$ of benzamide **1**), a third species (ca. 14%, from the NMR integration) appeared together with **A** and **B**; this unknown compound also seems to be a vinylgold species, as inferred from the characteristic vinyl proton at δ = 5.76 ppm. Under both the stoichiometric and dilute conditions at –20 °C, **A** and **B** were formed in a ratio of 1:1; hence **A** is preferentially formed at lower temperature over **B** (**A**/**B** = 1:2 at 25 °C).
- [11] During preparation of this manuscript, Zhu and Yu also reported that the proto-deauration of a vinylgold(I) species does not proceed in protic solvent (MeOH or EtOH); they used triflic acid to promote the protodeauration in a catalytic reaction. See Ref. [3f].
- [12] a) A. Correa, N. Marion, L. Fensterbank, M. Malacria, S. P. Nolan, L. Cavallo, *Angew. Chem.* **2008**, *120*, 730–733; *Angew. Chem. Int. Ed.* **2008**, *47*, 718–721; b) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482–486; c) L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258–3259; d) For a mini-review on gold α -oxo carbenoids, see: J. Xiao, X. Li, *Angew. Chem.* **2011**, *123*, 7364–7375; *Angew. Chem. Int. Ed.* **2011**, *50*, 7226–7236.