

Straightforward Synthetic Access to *gem*-Diaurated and Digold σ,π -Acetylide Species**

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The advent of gold-mediated transformations has led to significant advances in organic synthesis.^[1] The majority of the synthetic/catalytic uses of gold catalysts rely on the well-documented ability of monomeric gold complexes to activate C–C multiple bonds or to form C–Au σ bonds which can be further functionalized. In contrast, the chemistry of dinuclear gold complexes, recently highlighted,^[2] remains relatively unexplored. Such complexes can activate organic molecules by the formation of either *gem*-diaurated or σ,π -activated alkyne complexes (Figure 1). We believe that the reactivity of

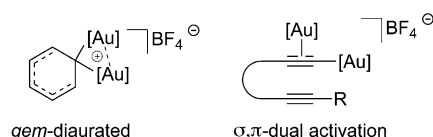


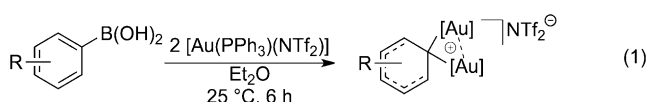
Figure 1. Example of *gem*-diaurated and σ,π -activated molecules.

such species could pave the way to exciting new gold-mediated reactions and also greatly increase the mechanistic understanding of gold catalysis. Thus, a robust and reliable synthesis of key digold complexes is central to achieve these goals. Therefore, we sought to develop a straightforward methodology leading to *gem*-diaurated and σ,π -acetylide species to permit further synthetic and mechanistic studies.

Geminally diaurated complexes have been known since the mid 1970s.^[3] For a long time they were considered to be mere curiosities. It was not until Gagné and co-workers observed and isolated a dinuclear gold species, more than 30 years after their original observation, that these began to attract the attention of the scientific community.^[4] The observation of these dinuclear gold complexes as intermediates in catalytic transformations has led researchers to question how gold truly interacts with organic molecules. This paradigm has brilliantly been shown by Hashmi et al. in

their recent contributions disclosing the role of gold acetylides and *gem*-diaurated species in organic transformations.^[5] For example, a change in selectivity between α and β isomers of a naphthalene derivative was observed depending on whether one or two gold centers interacted with the substrate.^[5a] Formation of both types of dinuclear gold species during catalytic transformations is more common than first thought, especially in reactions involving terminal alkynes.^[6] The number of publications highlighting these species is increasing as researchers become aware of their existence and actively attempt to identify them.

Several groups have contributed significantly to our understanding of the reactivity of both *gem*-diaurated and σ,π -acetylide species.^[4,7] While access to the latter class is relatively facile,^[6a,b] the formation of *gem*-diaurated compounds often involves tedious and circuitous procedures.^[8] It was not until Gray and co-workers developed a methodology to transmetalate arylboronic acids with $[\text{Au}(\text{PPh}_3)\text{Br}]$, using Cs_2CO_3 in isopropyl alcohol to form mononuclear gold species, that a door to milder procedures was opened.^[9] Recently, the group of Gray has progressed one step further and extended this methodology to the synthesis of $[\{\text{Au}(\text{PPh}_3)_2(\mu\text{-aryl})\}][\text{NTf}_2]$ species using 2 equivalents of the complex $[\text{Au}(\text{PPh}_3)(\text{NTf}_2)]$, which was reported by Gagosz and co-workers,^[10] in dry diethyl ether at room temperature [Eq. (1); Tf = trifluoromethanesulfonyl].^[11]

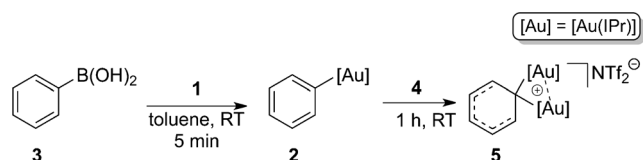


Despite the vast utility of N-heterocyclic carbene (NHC) ligands in homogenous catalysis in general^[12] and in gold catalysis,^[12a,b] in particular, only a handful of examples of *gem*-diaurated NHC species are known.^[5] Therefore, a mild and straightforward methodology leading to these species is needed. We recently reported the synthesis of mononuclear organogold complexes bearing NHC ligands in a rapid and efficient manner by transmetalation from boronic acids using a gold hydroxide species, $[\text{Au}(\text{IPr})(\text{OH})]$ (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).^[13] We thought that if we initially formed $[\text{Au}(\text{IPr})(\text{phenyl})]$ (**2**) by reacting **1** with phenyl boronic acid (**3**), the addition of the complex $[\text{Au}(\text{IPr})(\text{NTf}_2)]$ (**4**), reported by Gagosz, should form the *gem*-diaurated species $[\{\text{Au}(\text{IPr})_2(\mu\text{-phenyl})\}][\text{NTf}_2]$ (**5**; Scheme 1). As hypothesized, **5** was obtained in quantitative yield after 1 hour. Encouraged by this result, we envisioned a general one-step procedure leading to *gem*-diaurated

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Scheme 1. Synthesis of *gem*-diaurated species **5** using the gold hydroxide **1** and the complex **4**.

complexes using a digold hydroxide complex, such as $[\{Au(IPr)\}_2(\mu-OH)][BF_4]$ (**6**) as a synthon.^[15,16]

Initial reaction of **6** (1 equiv) with **3** (1 equiv) in CD_2Cl_2 at room temperature resulted in complete conversion of the starting materials and disappearance of the characteristic $\mu-OH$ signal (ca. $\delta = 0.4$ ppm)^[15a] of **6** within 30 minutes. The product was precipitated by the addition of pentane, collected by filtration, and dried under vacuum, thus affording a white powder in 96 % yield. Further characterization of the product by ^{13}C NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction studies confirmed the formation of $[\{Au(IPr)\}_2(\mu-phenyl)][BF_4]$ (**3a**; Figure 2a). In contrast to the monoaurated complex $[Au(IPr)(phenyl)]$ (**2**; Figure 2b),

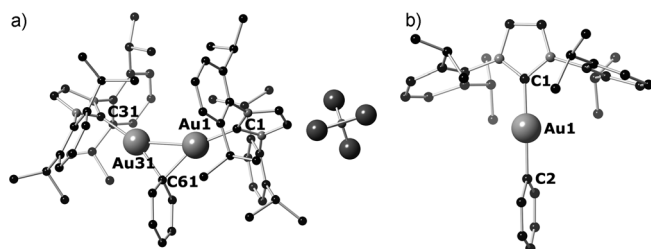
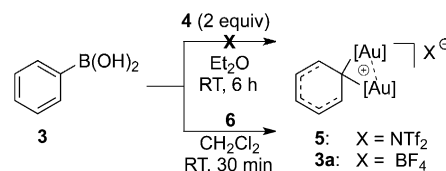


Figure 2. Molecular structures of a) **3a** and b) **2**. H atoms are omitted for clarity. Selected bond distances [Å] and angles [°] for **3a**: Au1–C1 2.017(8), Au1–C61 2.141(8), Au1–Au31 2.7697(8), Au31–C31 2.007(8), Au31–C61 2.122(8), Au31–Au1–C1 154.8(2), Au31–Au1–C61 49.2(2), C1–Au1–C61 155.6(3), Au1–Au31–C31 148.9(3) and C31–Au31–C61 160.6(3) and for **2** (range between three independent molecules): Au–C1 2.00(3)–2.06(3), Au–C2 2.01(3)–2.09(3) and C1–Au–C2 172.9(13)–178.1(11) and .

the diaurated species **3a** does not adopt the classical linear conformation for gold(I) complexes and presents $C_{carb}-Au-C_{phenyl}$ angles of $155.6(3)^\circ$ and $160.6(3)^\circ$. Most likely, this nonlinearity is due to the strong auriphilic interaction between the two gold centers and the steric hindrance of the carbene ligands. The Au–Au distance, 2.7697(8) Å, falls in the range of those reported in the literature (2.727–2.846 Å).^[5a] While the $C_{carb}-Au$ bond lengths are almost the same in **2** and **3a**, the $C_{phenyl}-Au$ bond lengths are slightly longer in **3a**. This is in agreement with the more cationic nature of **3a** and the three-center-two-electron system in the Au– C_{carb} –Au bond. If **3a** is compared to its phosphane congener $[\{Au(PPh_3)\}_2(\mu-phenyl)][NTf_2]$ significant differences can be noted. The latter presents the typical linear conformation for gold(I) complexes with a P–Au– C_{phenyl} angle of $175.70(8)^\circ$ and a shorter Au–Au distance of 2.7112(6) Å. As expected, the P–Au bond (2.2617(10) Å) is longer than the $C_{carb}-Au$ bond length. In contrast, the $C_{phenyl}-Au$ bond length is

slightly longer for the phosphane complex (2.153(4) Å) than for **3a**.^[11]

To compare the methodology of Gray and co-workers^[11] to the present route, the reaction between 2 equivalents of complex **4** with **3** under both sets of reaction conditions was carried out. No conversion to the desired product was observed when **4** was used, but the use of **6** under our initial conditions appears a very general protocol (Scheme 2).



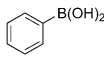
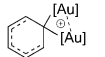
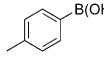
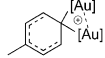
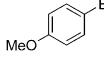
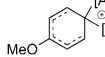
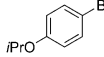
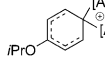
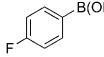
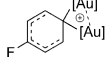
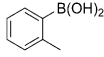
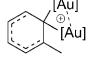
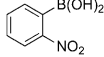
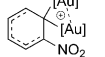
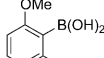
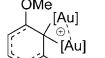
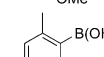
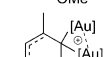
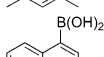
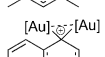
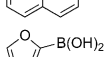
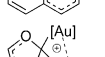
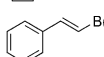
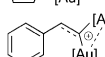
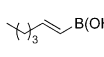
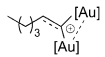
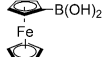
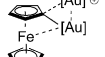
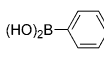
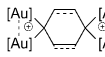
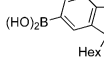
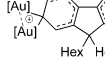
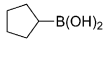
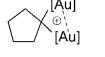
Scheme 2. Comparison between the methodology from Gray and co-workers and the one developed in this work.

Encouraged by these results, we proceeded to optimize the initial reaction conditions. Six different solvents were tested. No dramatic effect was observed and all reactions reached completion after 30 minutes. To further examine the scope of the method and for practical reasons, CH_2Cl_2 was selected as the operational solvent.^[17]

Different organometallic partners were also screened. The use of phenylboronic acid pinacol ester resulted in significantly slower transmetalation and 3 days were necessary to reach full conversion. Following our recent contribution on the transmetalation between $RSi(OMe)_3$ and **1**,^[18] we attempted to employ siloxanes to access *gem*-diaurated species. Unfortunately, under these reaction conditions, the monoaurated complex **2** was the main product. This may be due to the high temperature required for the transmetalation. Other transfer reagents are presently being explored.

With these results in hand, we proceeded to explore the substrate scope and limitations of the method (Table 1). Generally 1.1 equivalents of the boronic acid was sufficient to reach completion within a few hours. Most reactions afforded the desired product in excellent yields and various functionalities were tolerated, for example, methoxy, fluoro, and nitro groups. Phenylboronic acids with either electron-withdrawing (EWG) or electron-donating (EDG) groups at the *para* position required increased reaction times compared to those for **3** (Table 1, entries 1–5). Interestingly, reaction with *para*-isopropoxyphenylboronic acid (**9**) afforded the desired product **9a** in excellent yield, although 2 equivalents of the boronic acid were necessary for the reaction to go to completion (Table 1, entry 4). This result is a great improvement from previous literature reports which disclosed a 45 % yield.^[11] Surprisingly, a dramatic electronic effect was observed when EWGs or EDGs occupied the position *ortho* to the reactive center. While the use of EDGs resulted in the need for longer reaction times, the *ortho*-nitro substituent reduced this time to 45 minutes (Table 1, entries 6 and 7).^[19] The dramatically longer reaction times observed for 2,6-dimethoxyphenylboronic acid (**13**) could be explained by the electron-donating ability of the methoxy groups and the high steric congestion about the substrate reactive site (Table 1, entry 8). More

Table 1: Synthesis of *gem*-diaurated species.^[a]

	Boronic acid	<i>t</i> [h]	Product ^[b]	Yield [%]
1		3 0.5		3a 96
2		7 3		7a 89
3		8 3		8a 86
4		9 3		9a 96
5		10 3		10a 86
6		11 3		11a 89
7		12 0.75		12a 91 ^[c]
8		13 20		13a 91
9		14 2		14a 88
10		15 3		15a 88
11		16 2		16a 85
12		17 3		17a 97
13		18 20		18a 6 ^[c]
14		19 20		19a 0
15		20 20		20a 0
16		21 1		21a 87 ^[c]
17		22 20		22a 0

[a] Reaction conditions: [Au] (20 mg, 15.7 μmol, 1 equiv), boronic acid (1–2 equiv), CH₂Cl₂ (0.5 mL), RT. [b] Product isolated with BF₄[−] as the counterion. [c] Conversion as determined by ¹H NMR spectroscopy.

challenging architectures were then targeted. The use of 2-furanboronic acid (**16**) afforded the expected product in excellent yield after 2 hours (Table 1, entry 11). Access to vinyl *gem*-diaurated species was also investigated. Reactions with the *trans*-styreneboronic acid (**17**) needed 1.5 equivalents of the boronic acid to reach completion, but afforded the desired product in 97% yield (Table 1, entry 12). As observed by Fürstner and co-workers, this type of *gem*-diaurated species easily undergoes decomposition in CD₂Cl₂.^[7b] Unfortunately, attempts to extend this methodology to other vinylboronic acids, such as **18**, were unsuccessful, irrespective of the number of equivalents of starting material used (Table 1, entry 13). In contrast, reaction of 2 equivalents of the ferrocene derivative **19** with **6** afforded only the

mononuclear gold complex, while reaction with only 1 equivalent resulted in no conversion (Table 1, entry 14). The synthesis of bis(*gem*-diaurated) species was also attempted. While the reaction with the bis(boronic acid) **20** did not afford any product, regardless of the reaction time or number of equivalents of boronic acid used, reaction with **21** showed a 87% conversion into the desired product within 1 hour. Unfortunately, attempts to force the reaction to completion or to separate **21a** from **6** were unsuccessful. One last example was attempted using cyclopentylboronic acid (**22**), and, as expected, no reaction was observed (Table 1, entry 17).

All compounds shown in Table 1 were isolated and characterized by ¹H and ¹³C NMR spectroscopy, and yielded correct elemental analyses. It is worthwhile noting that previous phosphane analogues were reported without ¹³C NMR spectra of the complexes because attempts to identify the bridging *ipso*-carbon atom were unsuccessful.^[11] Very careful investigation of the carbene system using long delays and a large number of scans allowed us to identify the *ipso*-carbon atom by NMR spectroscopy for almost all products. To confidently assign structural features, HSQC and HMBP experiments were necessary. The chemical shifts for these *ipso*-carbon atoms appear between δ = 106.5 (**13a**) and 148.4 (**15a**) ppm for the phenyl derivatives, δ = 158.2 for **16a** and δ = 122.6 for the vinyl species **17a**. It was possible to grow suitable crystals for single-crystal X-ray diffraction (XRD) studies for compounds **7a**, **9a**, **10a**, **13a**, **15a**, and **17a** by slow diffusion of pentane into a saturated solution of the product in THF at 4 °C.^[20]

Once the effectiveness of our method for the synthesis of *gem*-diaurated species was demonstrated, we wondered if the methodology could be extended to the synthesis of σ,π-acetylide species, thereby extending the use of **6** as a synthon. Initial reaction of phenylacetylene (**23**) with **6** in CH₂Cl₂ at room temperature afforded the desired σ,π-acetylide species **23a** in excellent yield within 3 hours (Table 2, entry 1). The diaurated nature of compound **23a** was confirmed by XRD (Figure 3) as well as by comparison of the ¹H and ¹³C NMR data with that reported by Widenhoefer.^[6a,20] The reaction was then attempted with two additional substrates. These

Table 2: Synthesis of σ,π-acetylide species.^[a]

Table 1. Synthesis of 1,1-diaurated species.

$$\text{R}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{RT}]{\mathbf{6}} \text{R}-\text{C}(\text{Au})=\text{C}(\text{Au})-\text{H} \quad \text{BF}_4^-$$

	Alkyne	<i>t</i> [h]	Product ^[b]	Yield [%]
1		23 3		23a 92
2		24 18 ^[c]		24a 88
3		25 18 ^[c]		25a 89

[a] Reaction conditions: [Au] (20 mg, 15.7 μmol, 1 equiv), alkyne (1 equiv), CH₂Cl₂ (0.5 mL), RT. [b] Product isolated with BF₄[−] as the counterion. [c] Reaction times are not optimized.

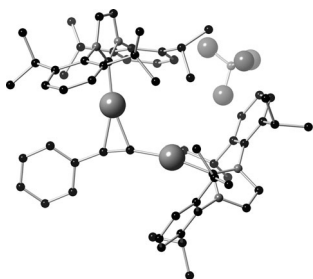


Figure 3. Molecular structure of **23a**. H atoms are omitted for clarity.

results are summarized in Table 2. All three complexes were obtained in excellent yields and both *para*- and *meta*-electron-donating substituents were tolerated (Table 2, entries 2 and 3).

In conclusion we have developed a new, mild, and straightforward methodology for the synthesis of *gem*-diaurated NHC species in excellent yields using $[\{\text{Au}(\text{IPr})_2(\mu\text{-OH})\}][\text{BF}_4]$ (**6**). This new synthetic protocol proves highly efficient for a wide range of phenyl derivatives bearing EWG, EDG, and sterically demanding substituents, as well as for vinyl and heteroaromatic species. This procedure fulfills the need for highly efficient methodologies for the synthesis of *gem*-diaurated NHC complexes. In addition, **6** could also be used to gain access to σ,π -acetylide species. We hope that this methodology will help in mechanistic studies to elucidate the role of dinuclear gold species in the ongoing “Gold Rush”. Ongoing work in our laboratories is aimed at addressing some of these fascinating questions.

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- [1] a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; b) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; c) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; d) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766–1775; e) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; f) A. S. K. Hashmi, C. Hubbert, *Angew. Chem.* **2010**, *122*, 1026–1028; *Angew. Chem. Int. Ed.* **2010**, *49*, 1010–1012; g) M. Bandini, *Chem. Soc. Rev.* **2011**, *40*, 1358–1367; h) T. C. Boorman, I. Larrosa, *Chem. Soc. Rev.* **2011**, *40*, 1910–1925; i) O. Debléds, E. Gayon, E. Vrancken, J.-M. Campagne, *Beilstein J. Org. Chem.* **2011**, *7*, 866–877.
- [2] A. Gómez-Suárez, S. P. Nolan, *Angew. Chem.* **2012**, *124*, 8278–8281; *Angew. Chem. Int. Ed.* **2012**, *51*, 8156–8159.
- [3] A. N. Nesmeyanov, E. G. Perevalova, K. I. Grandberg, D. A. Lemenovskii, T. V. Baukova, O. B. Afanassova, *J. Organomet. Chem.* **1974**, *65*, 131–144.
- [4] D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem.* **2009**, *121*, 5843–5846; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733–5736.
- [5] a) A. S. K. Hashmi, I. Braun, M. Rudolph, F. Rominger, *Organometallics* **2012**, *31*, 644–661; b) A. S. K. Hashmi, I. Braun, P. Nösel, J. Schädlich, M. Wietek, M. Rudolph, F. Rominger, *Angew. Chem.* **2012**, *124*, 4532–4536; *Angew. Chem. Int. Ed.* **2012**, *51*, 4456–4460; c) A. S. K. Hashmi, M. Wietek, I. Braun, P. Nösel, L. Jongbloed, M. Rudolph, F. Rominger, *Adv. Synth. Catal.* **2012**, *354*, 555–562; d) A. S. K. Hashmi, M. Wietek, I. Braun, M. Rudolph, F. Rominger, *Angew. Chem.* **2012**, *42*, 10785–10789; *Angew. Chem. Int. Ed.* **2012**, *51*, 10633–10637.
- [6] a) T. J. Brown, R. A. Widenhoefer, *Organometallics* **2011**, *30*, 6003–6009; b) A. Grirrane, H. Garcia, A. Corma, E. Álvarez, *ACS Catal.* **2011**, *1*, 1647–1653; c) A. Simonneau, F. Jaroschik, D. Lesage, M. Karanik, R. Guillot, M. Malacria, J.-C. Tabet, J.-P. Goddard, L. Fensterbank, V. Gandon, Y. Gimbert, *Chem. Sci.* **2011**, *2*, 2417–2422; d) T. J. Brown, D. Weber, M. R. Gagné, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2012**, *134*, 9134–9137; e) D. Weber, M. Gagné, *Chem. Sci.* **2012**, DOI: 10.1039/C2SC21281A.
- [7] a) P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 4517–4526; b) G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem.* **2010**, *122*, 8644–8648; *Angew. Chem. Int. Ed.* **2010**, *49*, 8466–8470; c) T. N. Hooper, M. Green, C. A. Russell, *Chem. Commun.* **2010**, *46*, 2313–2315; d) A. Himmelsbach, M. Finze, S. Raub, *Angew. Chem.* **2011**, *123*, 2676–2679; *Angew. Chem. Int. Ed.* **2011**, *50*, 2628–2631; e) D. Weber, T. D. Jones, L. L. Adduci, M. R. Gagné, *Angew. Chem.* **2012**, *124*, 2502–2506; *Angew. Chem. Int. Ed.* **2012**, *51*, 2452–2456; f) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370–412; g) L. Ye, Y. Wang, D. H. Aue, L. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 31–34; h) J. Roithová, Š. Janková, L. Jašíková, J. Váňa, S. Hybelbauerová, *Angew. Chem.* **2012**, *124*, 8503–8507; *Angew. Chem. Int. Ed.* **2012**, *51*, 8378–8382.
- [8] a) H. Schmidbaur, Y. Inoguchi, *Chem. Ber.* **1980**, *113*, 1646–1653; b) R. Usón, A. Laguna, E. J. Fernández, A. Mendia, P. G. Jones, *J. Organomet. Chem.* **1988**, *350*, 129–138; c) K. I. Grandberg, V. P. Dyadchenko, *J. Organomet. Chem.* **1994**, *474*, 1–21; d) T. y. V. Baukova, L. G. Kuz'mina, N. y. A. Oleinikova, D. A. Lemenovskii, A. L. Blumenfel'd, *J. Organomet. Chem.* **1997**, *530*, 27–38; e) O. Schuster, A. Schier, H. Schmidbaur, *Organometallics* **2003**, *22*, 4079–4083; f) K. A. Porter, A. Schier, H. Schmidbaur, *Organometallics* **2003**, *22*, 4922–4927; g) M. Osawa, M. Hoshino, D. Hashizume, *Dalton Trans.* **2008**, 2248–2252.
- [9] D. V. Partyka, M. Zeller, A. D. Hunter, T. G. Gray, *Angew. Chem.* **2006**, *118*, 8368–8371; *Angew. Chem. Int. Ed.* **2006**, *45*, 8188–8191.
- [10] N. Mézailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005**, *7*, 4133–4136.
- [11] J. E. Heckler, M. Zeller, A. D. Hunter, T. G. Gray, *Angew. Chem.* **2012**, *124*, 6026–6030; *Angew. Chem. Int. Ed.* **2012**, *51*, 5924–5928.
- [12] a) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; b) S. P. Nolan, *Acc. Chem. Res.* **2011**, *44*, 91–100; c) S. Gaillard, C. S. J. Cazin, S. P. Nolan, *Acc. Chem. Res.* **2012**, *45*, 778–787.
- [13] S. Dupuy, L. Crawford, M. Bühl, A. M. Z. Slawin, S. P. Nolan, *Adv. Synth. Catal.* **2012**, *354*, 2380–2386.
- [14] L. Ricard, F. Gagosz, *Organometallics* **2007**, *26*, 4704–4707.
- [15] a) S. Gaillard, J. Bosson, R. S. Ramón, P. Nun, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2010**, *16*, 13729–13740; b) R. S. Ramón, S. Gaillard, A. Poater, L. Cavallo, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2011**, *17*, 1238–1246.
- [16] **6** can be easily synthesized following three different routes: 1) reaction of **1** with 0.5 equiv of a strong acid, for example, HBF₄, HOTf, etc.; 2) chloride abstraction of [Au(NHC)Cl] by a silver salt and subsequent addition of water; or 3) mixing equimolar amounts of Gagosz' complex **5** and **1**. For more information see ref. [15].
- [17] Details concerning solvent optimization can be found in the Supporting Information. CH₂Cl₂ was filtered through basic alumina prior to use to remove residual traces of HCl.

- [18] S. Dupuy, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2012**, *18*, 14923–14928.
- [19] ¹³C NMR spectra and elemental analysis could not be recorded for **13a** because of the rapid decomposition of the diaurated complex into the monoaurated one.
- [20] CCDC 905570 (**2**), 905571 (**3a**), 905572 (**7a**), 905573 (**9a**), 905574 (**10a**), 905575 (**13a**), 905576 (**15a**), 905577 (**17a**) and 905578 (**23a**) 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.
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