Inorganic Chemistry

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Article

Gem-Diaurated Gold(III) Complexes: Synthesis, Structure, Aurophilic Interaction, and Catalytic Activity

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Cite This: *Inorg. Chem.* 2022, 61, 3508−3515

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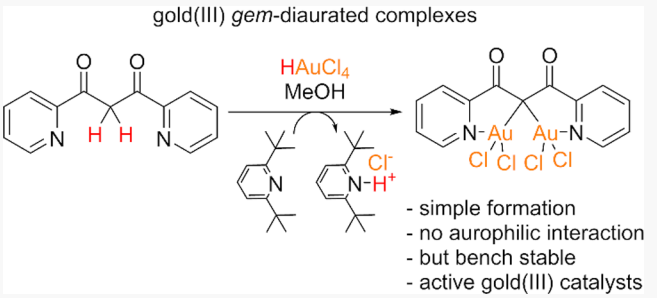
ABSTRACT: We present a protocol to synthesize air stable *gem*-diaurated gold(III) compounds from 1,3-diketones in a single cycloauration step with tetrachloroauric acid. So far related species were only accessible from phosphonium bis(ylide) ligands which hold the two gold atoms in close proximity. Lacking such a constraint, our compounds show the longest Au−Au distances of all *gem*-diaurated carbons, ranging from 3.26 to 3.32 Å. Modeling based on results of CCSD(T) calculations shows no stabilization by aurophilic interactions for our gold(III) systems, compared to 9.1 kcal/mol for gold(I) *gem*-diauration. This demonstrates no aurophilic interactions are needed for the isolation of air stable *gem*-diaurated gold(III) complexes. We show the new *gem*-diaurated gold(III) compounds are active in the gold-catalyzed phenol synthesis and highly active in the cycloisomerization of an *N*-propargylcarboxamide; here, we obtained the so far highest known TON of over 2500 per gold atom with respect to the oxazole formation.



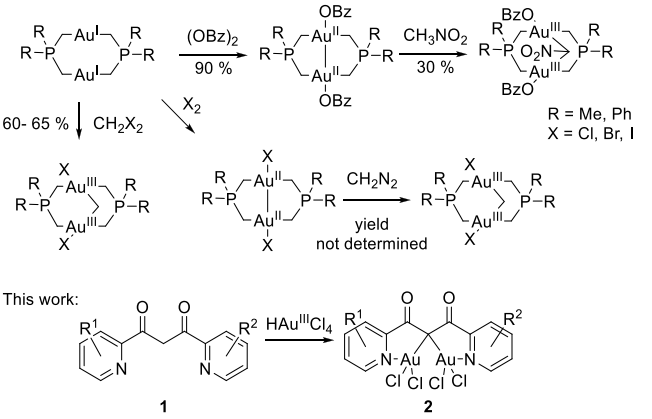
INTRODUCTION

A multitude of *gem*-diaurated gold(I) complexes was reported from as early as 1970 on.[1] This can be attributed to the effect of stabilizing aurophilic interactions between gold(I) centers.[2] The impact of these species was further boosted in 2009 by the discovery that they are also involved in catalytic processes.[3] They went into focus[4] either as catalyst sinks[5,6] or, in cases like dual gold catalysis, as active catalysts.[7] Thus, general procedures for their synthesis have been developed.[5,8]

In contrast, the only known *gem*-diaurated gold(III) complexes are based on phosphonium bis(ylide) ligands $[R_2P(CH_2)_2]^-$[9] (Scheme 1). In this system, the diauration is achieved by oxidative addition of a methylene unit to two gold(I) or gold(II) centers that are held in proximity by two phosphonium bis(ylide) ligands.[10] This strongly limits the structural variation; only derivatives based on the exchange of the halide ligands could be synthesized.[11] Only one *gem*-diaurated gold(III) complex has ever been investigated for its catalytic properties.[12]

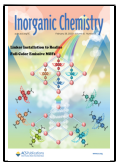
To develop a more direct and simple access to *gem*-diaurated gold(III) complexes, which is neither based on a phosphonium bis(ylide) ligand nor a change in the oxidation state of gold, we turned our attention to the 1,3-bis(2-pyridyl)-1,3-propanedione scaffold **1**. This already served as a ligand to various 3d metals,[13,14] some lanthanides[15] as well as late 4d and 5d metals[13,16] in a variety of binding modes enabled by its various donor sites. 1,3-Diketones have been *gem*-dimetalated with rhodium(II),[17] palladium(II),[18] mercury(II),[19] and gold(I).[20]

Scheme 1. Synthesis of *gem*-Diaurated Gold(III) Complexes Using Phosphonium Bis(ylide) Ligands[9,10] (Top) and the Approach Taken in This Work (Bottom)



Despite the comparison to gold(I) systems' expected weaker aurophilic interaction,[21] a 2-fold cycloauration of **1** with

Received: November 6, 2021
Published: February 18, 2022



https://doi.org/10.1021/acs.inorgchem.1c03479
Inorg. Chem. 2022, 61, 3508−3515

tetrachloroauric acid as the gold(III) source to form *gem*-diaurated gold(III) complexes proceeded readily.

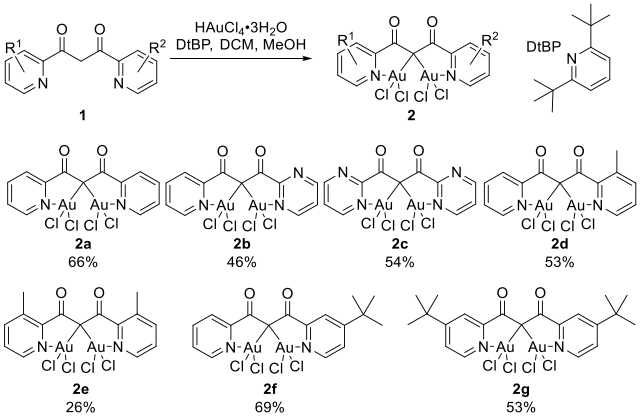
Seven derivatives were completely characterized, and accompanying quantum chemical calculations were conducted to elucidate a potential additional stabilizing contribution to an aurophilic interaction. Furthermore, we tested the catalytic activity of a representative of **2** in the phenol synthesis[22] and the cycloisomerization of an *N*-propargylcarboxamide.[23]

RESULTS AND DISCUSSION

The desired species **2a** simply precipitated from a methanolic solution of **1a** if treated with tetrachloroauric acid and base. After optimization of the reaction conditions to maximize yield and purity (see the SI for details), a yield of 66% was obtained for **2a** when 2,6-di-*tert*-butylpyridine (DtBP) was used as base and when **1a** was predissolved in DCM to give a more concentrated solution prior to the addition of methanol.

Next, we tested the optimized procedure for the *gem*-diauration of other diketones, which were obtained from readily available chemicals by short reaction sequences (see the SI for details). The optimized *gem*-diauration procedure yielded complexes **2a**–**2g** for all synthesized substrates (Scheme 2). **2b**–**2d** and **2f**–**2g** were obtained in moderate

Scheme 2. Synthesized *gem*-Diaurated Gold(III) Complexes

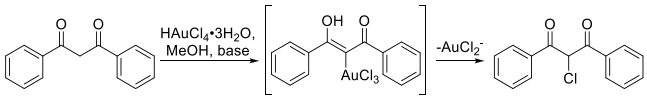


yields. A reason for the reduced yield of **2e** might be the low degree of enolization of the ligand. In chloroform, we found it to be 35% as compared to 65%–100% for the other investigated ligands (see NMR data in the SI). This renders **1e** less prone to electrophilic attack by gold, making the reaction less efficient. All *gem*-diaurated complexes are air-stable solids that can be stored at room temperature for several days (for more than six months at 8 °C). In DMSO, a slow decomposition is observed; this is especially fast for **2b** and **2c**, which both form noticeable gold mirrors after approximately 3 days.

It is noteworthy that we also tried to aurate benzoylmethane as representatives for a nonchelating ligand (Scheme 3). Depending on the employed reaction conditions, dibenzoylmethane was either chlorinated, or no reaction occurred.

This underlines the crucial role of a chelating ligand. Furthermore, the chlorination of dibenzoylmethane shows that an important decomposition pathway without chelating groups is the reductive elimination of the ligand under formation of a chlorine–carbon bond. A related process for the reaction of sodium acetylacetonate and tetrabutylammonium tetrachloroaurate(III), which yields tetrabutylammonium

Scheme 3. Reaction of Dibenzoylmethane with Tetrachloroaurate(III)



dichloroaurate(I), has already been reported.[24] The decreased stability of **2b** and **2c** may be attributed to the decreased donor strength of pyrimidines compared to pyridines. However, we could not detect any dichlorinated or monochlorinated ligands in ESI-MS samples of decomposed **2b** or **2c**.

For all seven derivatives, the solid state molecular structures were obtained via single crystal X-ray diffraction (Figure 1).

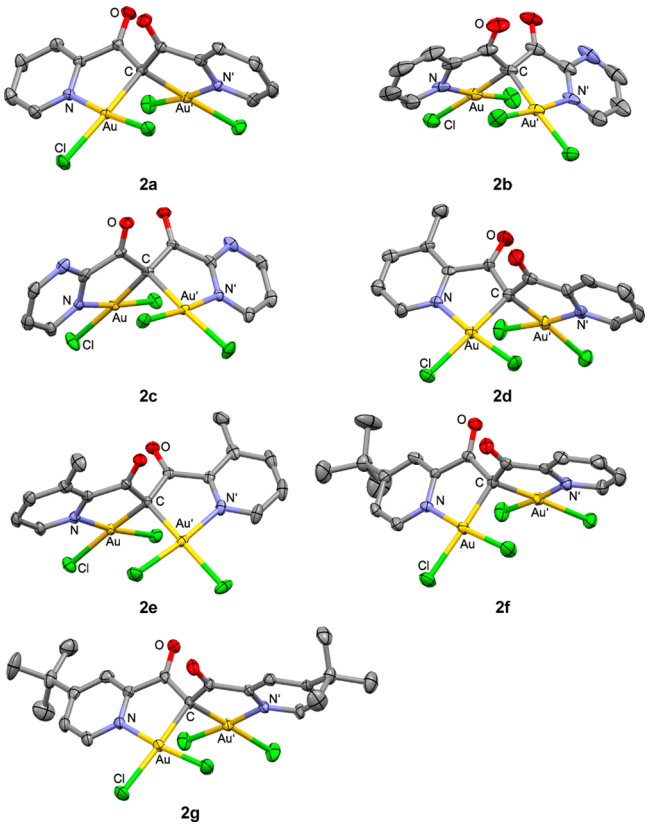


Figure 1. Solid state molecular structure of **2a**–**2g** obtained by single crystal X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity.

They can be regarded as gold(III) analogues of Schmidbaur's *gem*-diaurated acetylacetone 3,3-bis[(triphenylphosphine)-gold]pentane-2,4-dione **3**.[20] Since monoaurated 1,3-diketone derivatives are also known with gold(I) as well as gold(III),[25] **2a**–**2g** complete the set with the exception of a mixed gold(I) gold(III) diaurated diketone. The LAu^+ fragment is often seen as isolobal to a proton,[26] and their interchangeability can be interpreted as being caused by this relationship. The compounds synthesized herein confirm that the isolobality relationship can be extended to the LX_2Au^+ fragment.

In **2a**–**2g**, the bond lengths within the 1,3-diketone subunit (Table 1, see the SI for a more comprehensive compilation of characterization data) as well as the Au–C and the Au–N bond lengths are quite similar, and differences are typically below 0.04 Å. The larger deviations can be attributed to steric

https://doi.org/10.1021/acs.inorgchem.1c03479
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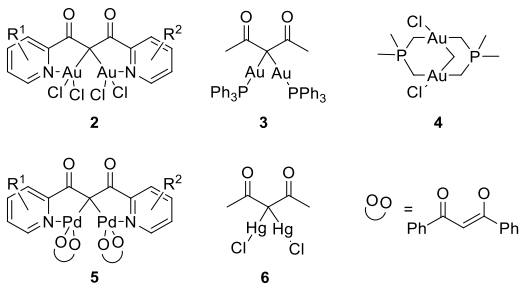
Table 1. Selected Structural Parameters for 2a−2g and the Related Literature-Known Complexes 3,[20] 4,[10] 5,[18] and 6[19]



compound	C−M [Å]	C−M′ [Å]	M−M′ [Å]	M−C−M′ [deg]
2a	2.0727(1)	2.0648(1)	3.3196(1)	106.70(15)
2b	2.082(4)	2.082(4)	3.2975(7)	104.7(3)
2c	2.084(4)	2.084(4)	3.3089(3)	105.1(3)
2d	2.043(8)	2.046(8)	3.2653(5)	106.0(4)
2e	2.054(3)	2.043(3)	3.2641(3)	105.62(13)
2f	2.053(5)	2.067(5)	3.3045(3)	106.7(2)
2g	2.074(4)	2.066(5)	3.3001(3)	105.7(2)
3	2.12	2.12	2.86	84.5
4	2.01	2.01	3.05	99
5	2.045(3)	2.051(3)	3.1056(3)	98.62(13)
6	2.11(4)	2.14(3)	3.31(1)	103(1)

reasons such as the repulsion between the ketones and methyl groups in **2d** and **2e** as well as packing effects in the crystal. A feature warranting further investigation is the large Au−Au distance ranging from 3.2641 to 3.3196 Å. Indeed according to the Cambridge Crystallographic Database, the Au−Au distance at *gem*-diaurated carbon atoms ranges from 2.675 to 3.143 Å.[27,28] Therefore, the Au−Au length of all complexes synthesized herein is longer than that at any previously known *gem*-diaurated carbon. We attribute this to the reduced aurophilic interaction between Au(III) atoms compared to Au(I) atoms.[21] The only known *gem*-diaurated gold(III) compounds are derivatives of **4**. The phosphonium bis(ylide) ligand facilitates their synthesis, but it also geometrically holds the gold atoms together in the final product, which explains the shorter Au−Au distance of 3.05 Å in **4** as compared to **2a−2g**. Nevertheless, the Au−Au distance in **4** is in the upper range of *gem*-diaurated carbons. This becomes especially apparent when **2a−2g** are compared to their gold(I) equivalent **3** which has a very short Au−Au distance of 2.86 Å. Regarding other metals, it is more meaningful to compare angles since different metals have different radii. The *gem*-dimetalated palladium complex **5** is based on the same ligand as **2**, and the palladium atoms have the same d^8 electron configuration as **2**. The M−C−M angle of **5** is 98.62°, which is only slightly smaller than that of **2** and similar to the M−C−M angle of 99° in **4**. One could assume that a weak metallophilic interaction is the result of a d^8 electronic configuration or a quadratic planar coordination with chelate[29] ligands. However, when considering the mercury complex **6** which has a linear coordination environment and d^{10} configuration like **3** but still a large Hg−C−Hg angle of 102.8°, this seems not to be the case.

To further investigate the difference of aurophilic interaction strengths between gold(I) and gold(III) in *gem*-diaurated compounds, we performed quantum chemical calculations with ORCA[30] based on the deformation energy of the Au−C−Au angle. It is known that aurophilic interactions are mostly based on dispersion, which is not accurately described by cheap local density functional theory but only expensive nonlocal wave function methods.[31] However, due to the size of the molecule, we could not completely rely on such highly accurate wave function methods. Nevertheless, we found that we could reproduce the Au−C−Au angle of **2a** and **3** reasonably well with the ωB97X-D3[32] density functional that employs a cheap empirical dispersion correction[33] (for the choice of density functional, validation, and details of the employed QM methods, see the SI). We used geometries obtained on the ωB97X-D3 level of theory to perform a minimal number of highly accurate wave function based single point calculations. For this, we employed coupled cluster calculations with singles, doubles, and perturbative triples CCSD(T), which is generally accepted as the gold standard,[34] within the DLPNO (Domain-based Local Pair Natural Orbital)[35] approximation. Furthermore, we extrapolated to the complete basis set to control for possible effects of an incomplete basis set.[36]

Figure 2 shows the calculated relative energies dependent on the Au−C−Au deformation angle. Next to **2a** we included **7** as

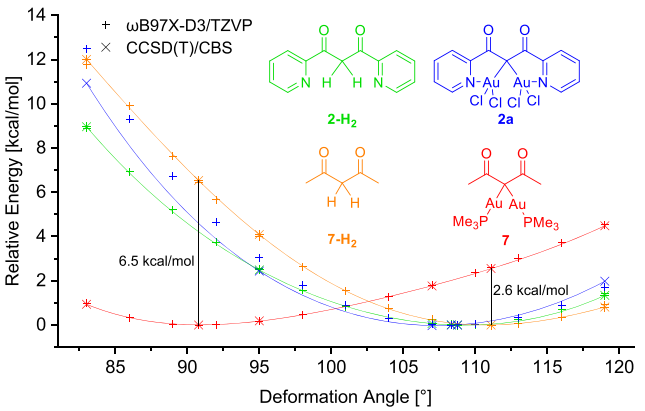


Figure 2. Potential energy curves for **2-H$_2$**, **2a**, **7-H$_2$**, and **7** calculated by DFT and CCSD(T). For all angles, geometries were optimized at the ωB97X-D3/TZVP level of theory. Single point calculations were undertaken at the CCSD(T)/CBS level of theory using these geometries. The colored lines are fourth order polynomial fits to the CCSD(T) energies. The vertical lines visualize the energy differences used to calculate the aurophilic interaction strength.

a reduced version of a *gem*-diaurated gold(I) complex **3** for the purpose of comparison. Similarly, we included the corresponding hydrogen-substituted molecules **2-H$_2$** and **7-H$_2$**. The energies obtained with the ωB97X-D3 functional agree mostly very well with the energies obtained by the CCSD(T) method. Only for **2a** the deviation grows to modest 2 kcal/mol at very small angles. It can be immediately seen that the potential curves for **7** and **7-H$_2$** differ significantly, while they are similar for **2a** and **2-H$_2$**, indicating a strong aurophilic interaction in **7** but not in **2a**. Furthermore, the potential curve of **7** is rather soft and unsymmetrical, as it features an almost constant slope at angles from 95° to 117° compared to the more harmonic potentials of **2-H$_2$**, **2a**, and **7-H$_2$**. This shape can also be attributed to the aurophilic interaction, similar to $I(AuI)_2^-$ which also shows a soft potential curve but with two minima.[37] Calculating the absolute aurophilic interaction energy is not possible without separating it from the strain energy incurred by the deformation of the Au−C−Au angle. This separation is

https://doi.org/10.1021/acs.inorgchem.1c03479
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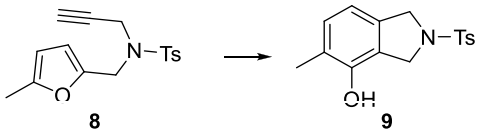
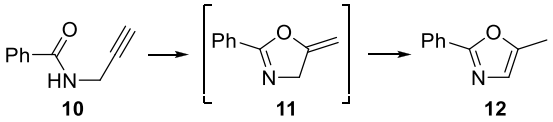
Table 2. Conducted Test Reactions to Test the Catalytic Ability of 2g, 2f, and 2c[c]





Entry	Catalyst [mol %]	Time	9	8	TON[a]	Entry	Catalyst [mol %]	Time	Molarity	12	11	10	TON[a]
1a	5 **2g**	3 d	81	0	8	1b	5 **2g**	3 d	0.03	93	0	0	9
2a	1 **2g**	7 d	72	0	36	2b	1 **2g**	3 d	0.03	99	0	0	50
3a	0.25 **2g**	6 d	40	51	80	3b	0.25 **2g**	16 d	0.03	81	2	0	162
						4b	0.1 **2g**	11 d	0.07	88	0	0	440
						5b	0.05 **2g**	16 d	0.07	88	1	1	880
4a	0.25 **2g**, 0.25 TFA	6 d	52	40	104	6b	0.08 **2g**, 0.08 TFA	8 d	0.1	89	0	2	1113
5a	0.25 **2g**, 0.25 $HNTf_2$	6 d	48	38	96								
6a	0.25 **2g**, 0.25 $AgNTf_2$	6 d	42	52	84	7b	0.08 **2g**, 0.08 $HNTf_2$	8 d	0.1	95	0	2	994
7a	0.25 **2g**, TFA 10 Equiv	0.5 h	45	22	90								
8a	0.25 **2g**, TFA 10 Equiv.	24 h	54	0	108	8b	0.015 **2g**, 0.015 TFA	8 d	0.1	77	4	1	2500
9a	0.25 **2g**, 10 Equiv. $HNTf_2$	8 d	0	0	0								
10a	0.25 TFA	1 d	0	100	0	9b	0.015 TFA	8 d	0.1	0	0	90	0
11a	0.25 $HNTf_2$	1d	0	99	0	10b	0.015 $HNTf_2$	7d	0.1	0	0	72	0
12a	0.25 $AgNTf_2$	1d	0	100	0	11b	10 Equiv. TFA	7d	0.1	0	0	0	0
13a	10 Equiv. TFA	1d	0	0	0								
14a	10 Equiv. $HNTf_2$	1d	0	0	0								
15a	10 Equiv. $AgNTf_2$	1d	0	0	0								
16a	5 **2f**, 5 TFA	2d	100	0	10	12b	5 **2f**, 5 TFA	5d	0.1	97	0	0	10
17a	0.25 **2f**, 0.25 TFA	15d	77	0	154	13b	0.05 **2f**, 0.05 TFA	16d	0.1	99	0	1	990
18a	5 **2c**[b], 5 TFA	5d	96	0	10	14b	0.015 **2f**, 0.015 TFA	32d	0.1	92	0	0	3067
19a	0.25 **2c**[b], 0.25 TFA	18d	84	0	168	15b	5 **2c**[b], 5 TFA	7d	0.1	84	0	0	8
						16b	0.5 **2c**[b], 0.5 TFA	8d	0.1	69	0	10	69
						17b	0.05 **2c**[b], 0.05 TFA	12d	0.1	10	66	22	100

[a]Turnover number per gold atom with respect to the formation of **9** or **12**. [b]Reaction conducted in CD_3CN with 1,4-dinitrobenzene as standard. [c]The phenol synthesis (left) and cycloisomerization of propargylcarboxamide (right). The phenol synthesis was conducted in a 0.03 M solution. Reactions were conducted in $CDCl_3$. Yields were determined against hexamethylbenzene as a ^1H NMR standard.

somewhat arbitrary since the two quantities will always change simultaneously due to the bridged geometry. Still, we think that the hydrogen-substituted molecules **7-H$_2$** and **2-H$_2$** are a natural choice for a reference system, as they are the most simple reference system and hydrogen is seen as isolobal[26] to gold. For **7**, this yields additional 6.5 kcal/mol strain energy and increases the aurophilic interaction from 2.6 kcal/mol to a total of 9.1 kcal/mol. Similar aurophilic interaction strengths have been obtained for non-*gem*-diaurated molecules.[38] For **2a**, we obtained negligible 0.01 kcal/mol, which is below the accuracy of our calculation method. This confirms that there is no significant aurophilic interaction in our *gem*-diaurated gold(III) complexes.

https://doi.org/10.1021/acs.inorgchem.1c03479
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Despite the fact that gold catalysis in its early stage was mostly based on gold(III) complexes,[39] gold(III) catalysis now is extremely underdeveloped compared to its gold(I) counterparts. This can be attributed to the easier synthesis and control of the coordination sphere of gold(I) complexes, and only recently a revival of gold(III) species for catalysis has taken place.[40] This enabled access to new reactivity through gold(I)/gold(III) redox cycles[41] or the better control over steric influence by the ligands due to its increased proximity to the substrate.[42]

We wanted to test if a *gem*-diaurated gold(III) complex could be used in catalysis. For this, we chose the phenol synthesis[22] as the first test reaction and the cycloisomerization of an *N*-propargylcarboxamide[23] as the second test reaction (Table 2). We started our investigation by employing **2g** as a catalyst since it has the highest general solubility of **2a**−**2g** and is therefore the easiest to handle as a stock solution. **2g** turned out to be an effective catalyst without any additive for both test reactions (entries 1a−3a and 1b−5b). For the first test reaction, only at catalyst loadings of 0.25 mol % the yield dropped below 40% (entry 3a), and for the second test reaction, catalyst loadings of 0.05 mol % still resulted in a yield of 88% (entry 5b). However, the required reaction time is very high for the latter. Therefore, we first investigated the effect of possible activators before further lowering the catalyst loading.

The most common activators in gold catalysis are silver salts like $AgNTf_2$. However, we found no significant influence for our catalyst system in the phenol synthesis (entry 6a), and *N*-propargylcarboxamides are known to react with silver salts.[43] Hence, we focused on an alternative strategy to activate gold catalysts by protonation of basic ligands which, for example, has been applied for IPrAuMe[44] and IPrAuOH.[45] We tested this mode of activation with trifluoroacetic acid (TFA) and bis(trifluoromethanesulfonyl)imide ($HNTf_2$) as **2g** likely can be activated by protonation of a pyridine or the central carbon. Due to the comment of a reviewer, we investigated this assumption by mixing **2g** only with an excess of TFA. No other signals than those belonging to **2g** and TFA were present in a ^{1}H NMR making this assumption unlikely. Still as discussed below, we found positive effects of the acid additives. An alternative explanation could be a speedup of the protodeauration step. Especially for the reaction of **10** to **11**, protodeauration has been found to be rate limiting.[46]

For our first test reaction, TFA or $HNTf_2$ slightly increases the yield to 52% (entry 4a) or 48% (entry 5a) if employed in an equimolar amount to the catalyst. Interestingly, if a large excess of 10 equiv of TFA was added, the reaction was complete within hours instead of days, and the yield increases further to 56% (entries 7a and 8a). However, this comes at the cost of decomposition of the starting material which was completely consumed. When only small equimolar amounts of acid were added to the catalyst, no significant decomposition took place.

The effect of acid additives was much more pronounced for the second test reaction (entries 6b−8b). Together with an increased concentration, the reaction was complete within 8 days even at a very low catalyst loading of 0.015 mol %. When TFA (amount equivalent to the catalyst) was employed, the yield was still 77%, resulting in a turnover number (TON) of 2500 per gold atom (entry 8b). This is much higher than the highest TON that has been achieved for this reaction which is 340 at a catalyst loading of 0.34 mol %.[47]

The catalytic tautomerization of **11** to **12** is a unique property of gold(III) catalysts.[48] For the formation of the tautomer **11**, KitphosAuNTf$_2$ type catalysts[49] reach TONs up to 980 at a catalyst loading as low as 0.1 mol %.[50] SPhosAuCO$_2$CF$_3$ reaches a TON of 1563 at a catalyst loading of 0.05 mol % in the formation of **11**.[51]

If one does not accept major educt decomposition (entries 13a, 14a, 11b), **2g** performed best together with amounts of TFA equimolar to the catalyst. Therefore, we tested more of our *gem*-diaurated gold(III) complexes using the catalyst and equimolar amounts of TFA as activator.

2a, **2b**, **2d**, and **2e** are insoluble in any common deuterated solvent that is typically employed for gold catalysis, but **2f** and **2c** are slightly soluble in $CDCl_3$ and CD_3CN, respectively. Therefore, we also tested these catalysts in the respective solvents. **2f** and **2c** are similar competent catalysts to **2g** in both test reactions at high catalyst loadings (entries 16a, 18a, 12b, and 15b). At lower catalyst loadings, **2f** gives for both test reactions slightly higher yields and TONs than **2g** but needs much more time for complete conversion (entries 17a and 14b). **2c** also performs similarly to **2f** with respect to the first test reaction (entry 19a) but is an incompetent catalyst at low catalyst loading for the second test reaction (entry 17b). Reasons for this might be the neutralization of TFA by the pyrimidine rings or acetonitrile and low stability of **2c** in solution.

CONCLUSION

In conclusion, we offer a new and simple protocol to synthesize *gem*-diaurated gold(III) compounds in a single cycloauration step. This approach complements the phosphonium bis(ylide) ligand which holds the two gold atoms in close proximity. The Au−Au distance in **2a** to **2g** is the longest of all *gem*-diaurated compounds up to date indicating no stabilization by aurophilic interactions. We confirmed this by modeling with high level CCSD(T) calculations. Our example demonstrates that no aurophilic interactions are needed for the isolation of air stable *gem*-diaurated gold(III) complexes. Furthermore, we demonstrated the representatives **2c**, **2f**, and **2g** to be active gold catalysts reaching the highest TON up to date in our second example.

The easy formation and catalytic capability of *gem*-diaurated gold(III) complexes suggest that these compounds might play a similar important role in gold(III) catalysis as their gold(I) counterparts. Therefore, we hope that our simple protocol for gold(III) *gem*-diauration will be adopted for the synthesis of more gold(III) *gem*-diaurated complexes and further boost investigation of *gem*-diaurated gold(III) compounds in catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03479.

Detailed experimental procedures, compound characterization, and details and validation of employed computational methods (PDF)

Accession Codes

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https://doi.org/10.1021/acs.inorgchem.1c03479
Inorg. Chem. 2022, 61, 3508−3515

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.F.W. thanks the Hector Fellow Academy for support. The authors acknowledge the support by the state of Baden-Württemberg through bwHPC.

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