



A Journal of the Gesellschaft Deutscher Chemiker

# Angewandte Chemie

GDCh

International Edition

[www.angewandte.org](http://www.angewandte.org)

## Accepted Article

**Title:** The Wolff-Rearrangement Reaction of Oxidatively Generated  $\alpha$ -Oxo Gold Carbenes: An Effective Approach to Silylketenes

**Authors:** Yang Zheng, Junqi Zhang, xinpeng Cheng, xinfang Xu, and Liming Zhang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

**To be cited as:** *Angew. Chem. Int. Ed.* 10.1002/anie.201814018  
*Angew. Chem.* 10.1002/ange.201814018

**Link to VoR:** <http://dx.doi.org/10.1002/anie.201814018>  
<http://dx.doi.org/10.1002/ange.201814018>

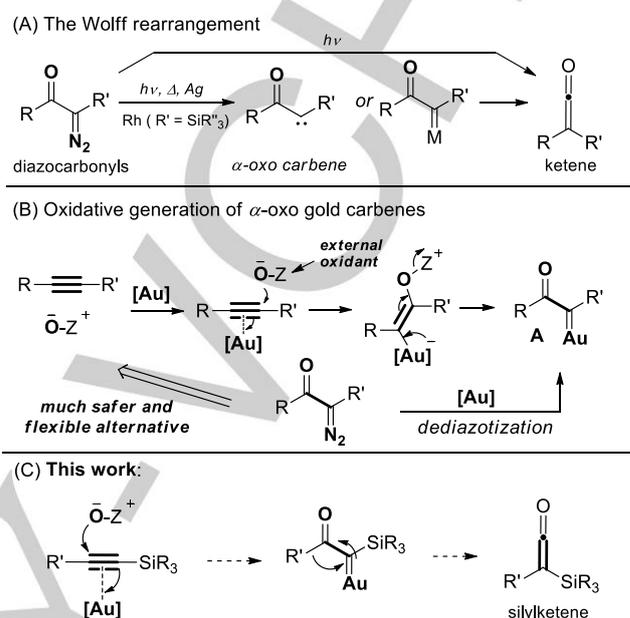
# The Wolff-Rearrangement Reaction of Oxidatively Generated $\alpha$ -Oxo Gold Carbenes: An Effective Approach to Silylketenes

Yang Zheng,<sup>[a,b]</sup> Junqi Zhang,<sup>[a]</sup> Xinpeng Cheng,<sup>[a]</sup> Xinfang Xu<sup>\*[b]</sup> and Liming Zhang<sup>\*[a]</sup>

**Abstract:** Gold-catalyzed oxidations of alkynes by *N*-oxides offer a direct access to reactive  $\alpha$ -oxo gold carbene intermediates from benign and readily available alkynes instead of hazardous diazo carbonyl compounds. Despite various versatile synthetic methods developed based on this strategy, one of the hallmarks of  $\alpha$ -oxo carbene/carbenoid chemistry, i.e., the Wolff rearrangement, has not been realized in this context. This study discloses the first examples that the Wolff rearrangement can be readily realized by  $\alpha$ -oxo gold carbenes oxidatively generated from TBS-terminated alkynes. The thus-generated silylketenes can be isolated pure or subsequently trapped by various internal or external nucleophiles in one pot to afford  $\alpha$ -silylated carboxylic acids, their derivatives or TBS-substituted allenes.

The Wolff rearrangement<sup>[1]</sup> is one of the classical transformations of  $\alpha$ -diazo ketones<sup>[2]</sup> and has been extensively studied and widely employed in organic synthesis (Scheme 1A).<sup>[3]</sup> The ketene generated in this powerful reaction is a reactive intermediate of exceptional synthetic value. The main drawback of the reaction, however, is the use of diazo ketone substrates, which are hazardous and potentially explosive but necessary to access highly reactive  $\alpha$ -oxo carbene/carbenoid or undergo concerted conversion (Scheme 1A).

In 2010,<sup>[4]</sup> we reported that highly electrophilic  $\alpha$ -oxo gold carbene intermediates could be generated via intermolecular oxidation of benign alkynes instead of from hazardous diazo ketones (Scheme 1B).<sup>[5]</sup> The safety benefit of this strategy and the new approach to  $\alpha$ -oxo gold carbenes and their novel chemistry spurred a diverse range of subsequent studies by us<sup>[4-5, 6]</sup> and others,<sup>[7]</sup> which establish that the gold carbene intermediates or in some cases their precursors can undergo insertions into O-H,<sup>[4, 6a]</sup> N-H,<sup>[7i]</sup> B-H<sup>[7j]</sup> and even unactivated C-H bonds,<sup>[6f, 6g, 7a, 7d, 8]</sup> cyclopropanate alkenes<sup>[6d, 6e, 7g, 7h]</sup> including electron-deficient ones,<sup>[6e, 7g]</sup> electrophilic arene substitutions<sup>[6c, 7e]</sup> or Buchner reaction,<sup>[6h]</sup> and formation of ylides.<sup>[7i, 9]</sup> Despite of these advances, no Wolff-type rearrangement involving these oxidatively generated  $\alpha$ -oxo gold carbenes has been reported to date. Herein, we disclose a first example, which offers one-step access to stable yet versatile silyl ketenes from readily available TBS-terminated alkynes (Scheme 1C).



**Scheme 1. The Wolff rearrangement and our design.**

In 2015, we reported that acyl/acyl-substituted gold carbenes generated upon gold-catalyzed oxidation of enones undergo insertions into unactivated C-H bonds.<sup>[6f]</sup> In our effort to expand the C-H insertion chemistry, we examined as substrates silyl-terminated alkynes including silylated 3-phenyl-1-propyne **1**. As shown in Table 1, entry 1, with the silyl group of **1** as TBS, IPAuNTf<sub>2</sub> (5 mol %) as the catalyst and 8-isopropylquinoline *N*-oxide as the oxidant, the gold-catalyzed oxidation occurred smoothly overnight to deliver three identifiable products. Among them, the silylated indanone product **3** and its desilylated counterpart **2** were formed in 20% and <5% yield, respectively. The major product, formed in 75% NMR yield, is the  $\alpha$ -silylated 3-phenylpropionic acid **5**. We realized that this compound must be formed upon the hydration of the corresponding silylketene **4**. This result suggests the Wolff rearrangement occurred in the process. Critical to the success of the oxidation is the NHC ligand, as a range of phosphine-based ones including PPh<sub>3</sub>, JohnPhos, Mor-DalPhos, and BrettPhos were totally ineffective under the same reaction conditions (entry 2). Varying the catalyst counter anion from NTf<sub>2</sub><sup>-</sup> to SbF<sub>6</sub><sup>-</sup> (entry 3) or OTf<sup>-</sup> (entry 4) led to a lower yield of **5**. Other *N*-oxides were screened as well. While the use of 8-methylquinoline *N*-oxide also resulted in a lower yield of **5** (entry 5), those based on pyridine, however, were completely ineffective for this reaction (entry 6). In an attempt to obtain the ketene intermediate **4**, 4Å MS was added to the reaction to remove adventitious water. To our delight, the TBS ketene **4a** was indeed formed in 85% NMR yield and could be obtained upon column purification in 70% isolated yield (entry 7). Changing the TBS group in **1a** to smaller silyl groups such as TMS (entry 8), TES (entry 9) and Me<sub>2</sub>PhSi (entry 10) led to the formation of desilylated indanone **2** in >90% yield but none of

[a] Mr. Yang Zheng, Mr. Junqi Zhang, Mr. Xinpeng Cheng, and Prof. Dr. Liming Zhang  
Department of Chemistry and Biochemistry, University of California Santa Barbara, CA 93106, USA  
E-mail: [zhang@chem.ucsb.edu](mailto:zhang@chem.ucsb.edu)

[b] Mr. Yang Zheng, and Prof. Dr. Xinfang Xu  
Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science Soochow University, Suzhou 215123 (P.R. China)  
E-mail: [xinfangxu@suda.edu.cn](mailto:xinfangxu@suda.edu.cn)

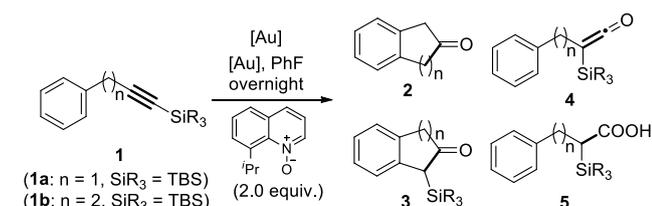
Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate))

## COMMUNICATION

WILEY-VCH

the corresponding **4** and **5** was detected, while the bulkier TIPS group led to little reaction (entry 11). When the conditions of entry 7 was applied to the silylated 4-phenylbut-1-yne (i.e., **1b**, entry 12), to our surprise, the reaction was sluggish, and only 20% NMR yield of the expected silylketene **4b** was formed, while the rest of the starting material remained mostly unreacted. Upon further conditions optimization, it was found that increasing the catalyst loading to 10 mol % and introducing NaBARF<sub>4</sub> (10 mol %) as an additive significantly improved the substrate conversion to 89% (entry 13). The silylketene **4b** was obtained in 76% NMR yield and 60% isolated yields.

Table 1. Reaction optimization. [a]



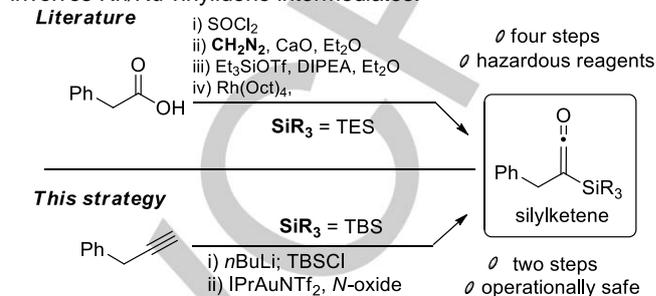
| Entry | 1 (n, SiR <sub>3</sub> )                | conditions   | Yield <sup>[b]</sup> (%) |    |                   |    |
|-------|---|--|--------------------------|----|-------------------|----|
|       |   |  | 2                        | 3  | 4                 | 5  |
| 1     | <b>1a</b> (1, TBS)                      | IPrAuNTf <sub>2</sub> (5%), 60 °C                        | <5                       | 20 | -                 | 75 |
| 2     | <b>1a</b> (1, TBS)                      | LAuNTf <sub>2</sub> <sup>[c]</sup> (5%), 60 °C           | NR <sup>[d]</sup>        |    |                   |    |
| 3     | <b>1a</b> (1, TBS)                      | IPrAuCl/AgSbF <sub>6</sub> (5%), 60 °C                   | <5                       | 28 | -                 | 65 |
| 4     | <b>1a</b> (1, TBS)                      | IPrAuCl/AgOTf (5%), 60 °C                                | <5                       | 25 | -                 | 60 |
| 5     | <b>1a</b> (1, TBS)                      | IPrAuNTf <sub>2</sub> <sup>[e]</sup> (5%), 60 °C         | -                        | 35 | -                 | 55 |
| 6     | <b>1a</b> (1, TBS)                      | IPrAuNTf <sub>2</sub> <sup>[f]</sup> (5%), 60 °C         | NR <sup>[d]</sup>        |    |                   |    |
| 7     | <b>1a</b> (1, TBS)                      | IPrAuNTf <sub>2</sub> (5%), 60 °C, 4 Å MS                | -                        | 10 | 85 <sup>[g]</sup> | <5 |
| 8     | <b>1-TMS</b> (1, TMS)                   | IPrAuNTf <sub>2</sub> (5%), 60 °C                        | >90                      | -  | -                 | -  |
| 9     | <b>1-TES</b> (1, TES)                   | IPrAuNTf <sub>2</sub> (5%), 60 °C                        | >90                      | -  | -                 | -  |
| 10    | <b>1-DMPS</b> (1, SiMe <sub>2</sub> Ph) | IPrAuNTf <sub>2</sub> (5%), 60 °C                        | >90                      | -  | -                 | -  |
| 11    | <b>1-TIPS</b> (1, TIPS)                 | IPrAuNTf <sub>2</sub> (5%), 60 °C                        | 10                       | -  | -                 | -  |
| 12    | <b>1b</b> (2, TBS)                      | IPrAuNTf <sub>2</sub> (5%), 60 °C, 4 Å MS                | -                        | -  | -                 | 20 |
| 13    | <b>1b</b> (2, TBS)                      | IPrAuNTf <sub>2</sub> (10%), 70 °C, NaBARF (10%), 4 Å MS | -                        | -  | 76 <sup>[h]</sup> | -  |

[a] Initial [**1a**] = 0.05 M. [b] NMR yields determined by using 1,3,5-trimethoxybenzene as the internal reference. [c] L = PPh<sub>3</sub>, JohnPhos, MorDalPhos, or BrettPhos. [d] the remaining starting material. [e] 8-Methylquinoline *N*-oxide instead used as the oxidant. [f] Various pyridine *N*-oxides as the oxidant. [g] 70% isolated yield. [h] 89% substrate conversion, and 60% isolated yield.

Silylketenes are isolable and valuable intermediates<sup>[10]</sup> for organic synthesis.<sup>[11]</sup> They are typically prepared via eliminations of  $\alpha$ -silylated carboxylic acids<sup>[12]</sup> and their derivatives,<sup>[13]</sup> thermolysis of alkoxy-2-silylacetylenes,<sup>[14]</sup> 1,3-silyl shift of (trimethylsiloxy)alkynes,<sup>[11]</sup> and the Wolff rearrangement of  $\alpha$ -diazo- $\alpha$ -silyl ketones.<sup>[15]</sup> The common drawback of these approaches is inefficient access to the corresponding substrates, which may require lengthy routes, use hazardous materials and/or exhibit limited scope. For example, in the Rh-catalyzed Wolff rearrangement approach show in the top half of Scheme 2,<sup>[15b]</sup> four steps<sup>[16]</sup> including the use of explosive diazomethane are necessary to deliver the silylketene product from phenylacetic acid. On the other hand, our oxidative gold catalysis offers a two-step and much safer route from likewise commercially available 3-phenylprop-1-yne (Scheme 2, the bottom half). Furthermore, in complicated molecule synthesis, a silyl group is usually employed as the terminal alkyne protecting group. As such, our approach to silyl ketenes would require only

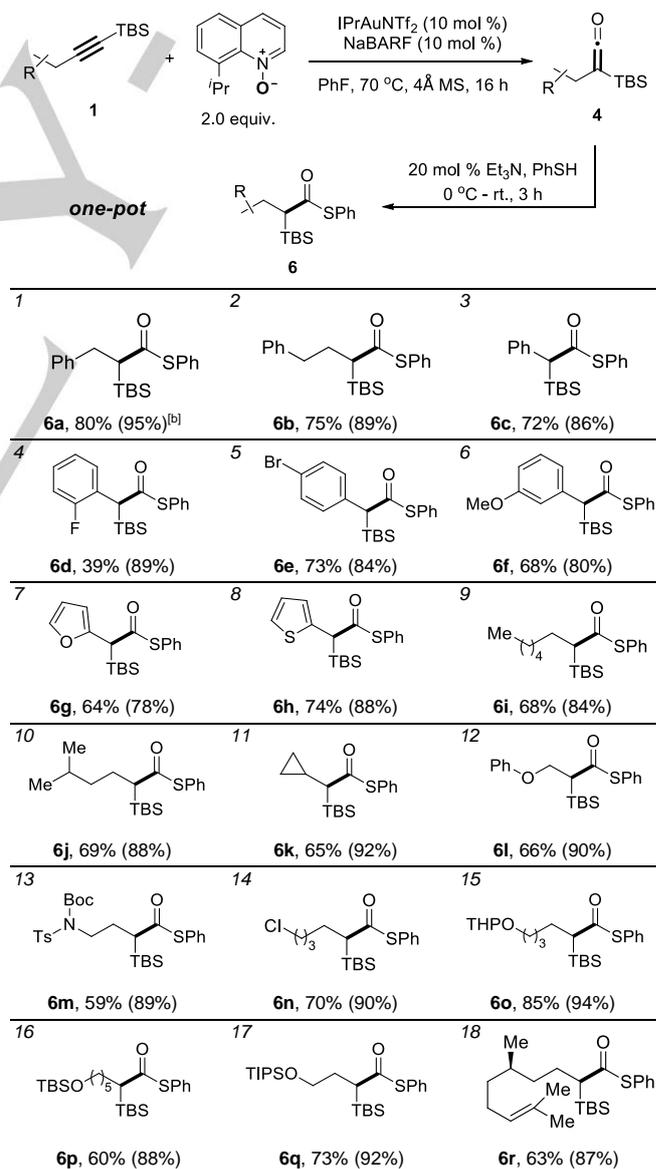
a single step. Notably, Rh- or Ru-catalyzed oxidative transformations of terminal alkynes to ketenes<sup>[17]</sup> have been reported. However, this gold-catalysis produces stable silylketene, which could be isolated or subsequently react with nucleophiles including those incompatible with the metal catalyst, thereby offering much enhanced synthetic flexibility and potentially broader reaction scopes; moreover, the mechanism of this reaction is distinctively different from these studies, which involves Rh/Ru vinylidene intermediates.

## Literature



Scheme 2. Our strategy versus the reported.

Table 2. Substrate scope.

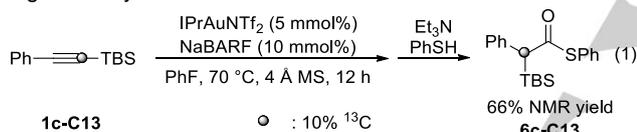


## COMMUNICATION

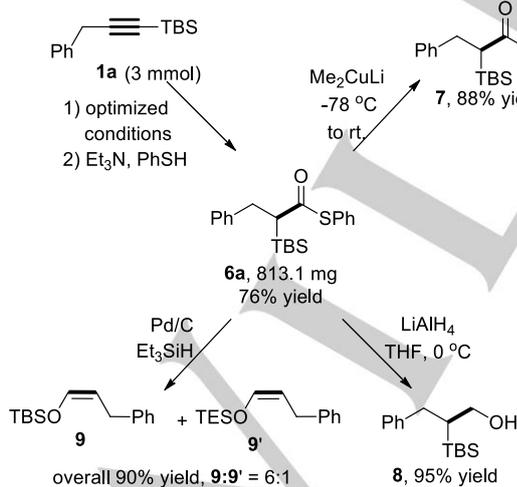
WILEY-VCH

[a] Isolated yield reported, and yield based on substrate conversion given in parentheses. [b] 5 mol % IPrAuNTf<sub>2</sub> and without NaBARF.

With the optimized conditions in Table 1, entry 13, we then set out to explore the reaction scope. To avoid isolating ketene products, which sometimes closely elude with 8-isopropylquinoline, we opted to convert it directly to the corresponding thioester in a one-pot process, which can be done readily in the presence of 20% Et<sub>3</sub>N as catalyst. As shown in Table 2, a phenyl group directly attached to or separated from the C-C triple bond by one or two methylene groups (entries 1-3) can be readily tolerated, and the  $\alpha$ -silylthioesters were formed efficiently in each case. The phenyl group in entry 3 could be substituted with halogens (entries 4 and 5) or MeO (entry 6) or replaced with heteroaryls (entries 7 and 8) with little impact on the reaction efficiency. The exception is entry 4, where an *o*-F group led to a low substrate conversion (44%). Substrates with nonfunctionalized alkyl chain (entries 9-11) or various functionalized ones (entries 12-18) also reacted smoothly. Of particular note is that the sensitive THP-protected HO group in entry 15 is tolerated, suggesting the mild nature of the reaction. It is important to point out that the yields based on substrate conversion were uniformly high in all the cases. The low or moderate isolated yields in some entries are due to the incomplete substrate conversion. Our attempts to drive the reaction to completion by adding more catalyst, extending the reaction time and/or heating it at a higher temperature led to little improvement. It is possible that the silyketene product inhibits the gold catalysis.



Mechanistically, our <sup>13</sup>C-labelling experiment (Eq. 1) established the alkyl/aryl migration instead of a silyl counterpart in this reaction.

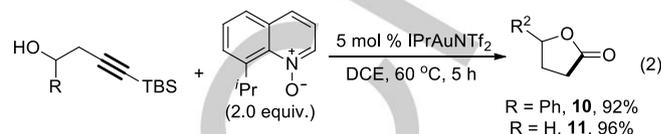


**Scheme 3.** Transformations of **6a**.

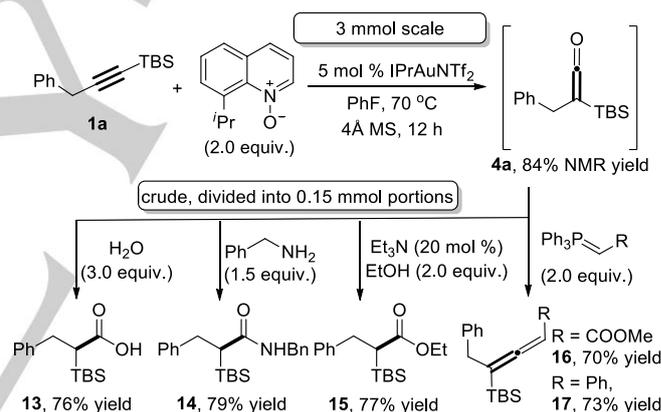
The synthetic utility of the  $\alpha$ -silylthioester products were examined by using **6a** as an example (Scheme 4). Firstly, it was prepared in a nearly gram-scale under the optimization conditions in an isolated yield comparable to that of a much smaller scale (see Table 2, entry 1). Its reaction with lithium dimethylcuprate afforded the  $\alpha$ -silylketone **7** in 88% yield. Its

LAH reduction yielded the  $\beta$ -silyl alcohol **8** nearly quantitatively. Under the standard Fukuyama reduction conditions,<sup>[18]</sup> the (*Z*)-silyl enol ethers **9** and **9'**, differing by the silyl group, were formed in a combined 90% yield instead of the expected aldehyde.

Besides trapping the silylketene intermediate with thiophenol, other internal or external nucleophiles can be employed. For example, the internal hydroxy group of the homopropargylic alcohol substrates readily trapped the ketene moiety to deliver  $\gamma$ -lactone **10** and **11** in 92% and 96% yield, respectively (Eq. 2). Of note is that the TBS group is not retained in the products.



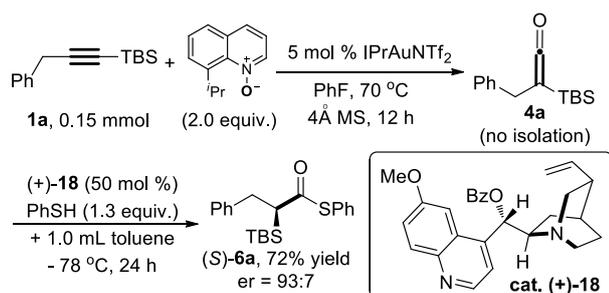
For trapping by other external nucleophiles, the silylketene **4a** was prepared on a 3-mmol scale without incident (Scheme 4). The crude reaction mixture was treated with several heteronucleophiles including water, benzylamine and ethanol.<sup>[15b, 16b]</sup> All the reactions proceeded smoothly to afford the carboxylic acid **13**, the carboxamide **14** and the ester **15**, respectively, in good yields. Of note is that the silyl group remained intact in the products. When phosphorus ylides were employed, the Wittig reactions led to synthetically valuable allenylsilanes **16** and **17** in 70% and 73% yield, respectively.<sup>[16b]</sup>



**Scheme 4.** One-pot trapping the silylketene **4a** by various external nucleophiles.

The formation of **6a** can be made enantioselective by following the protocol developed for trimethylsilylketenes and dimethylphenylsilylketenes by Simpkins.<sup>[19]</sup> As shown in Scheme 5, the crude *t*-butyldimethylsilylketene **4a** was treated with thiophenol (1.3 equiv.) and the (+)-quinine-derived **18** (50 mol %), and **6a** was isolated in 72% yield with an enantiomeric ratio of 93:7. The (*S*)-configuration of the major enantiomer is assigned based on the literature precedent.<sup>[19]</sup>

The enabling role of the TBS group in this oxidative Wolff rearrangement is likely multifaceted: a) it sterically and electronically directs the *N*-oxide attack at the distal C(sp); b) it sterically shields the highly electrophilic  $\alpha$ -oxo gold carbene carbon from inter-/intramolecular side reactions, thereby allowing the Wolff rearrangement to dominate. This rationale is consistent with the ineffectiveness of the smaller silyl groups (see Table 1, entries 8-10); c) a silyl group is known to offer less stability to an  $\alpha$ -carbocation than a methyl group but more than a hydrogen<sup>[20]</sup> and hence, the TBS group does not attenuate the reactivity of  $\alpha$ -oxo gold carbenes to a significant extent.



**Scheme 6.** Asymmetric trapping of the silylketene **1a**.

In conclusion, we have discovered the first examples of the Wolff rearrangement by oxidatively generated  $\alpha$ -oxo gold carbene species. The TBS group installed at the terminal alkyne is essential due to its steric shielding effect and electronic influence. The generated silylketenes are stable enough to be isolated or can be trapped by tethered HO groups or various external nucleophiles to afford  $\gamma$ -lactones,  $\alpha$ -silylated carboxylic acid and their derivatives, or TBS-substituted allenes. The trapping by thiophenol is also realized asymmetrically. This strategy avoids the typical use of hazardous diazo ketone substrates and provides a facile one- or two-step route to synthetically versatile yet isolable silylketenes from readily available alkyne substrates. It is anticipated this chemistry would further advance the applications of silylketene in organic synthesis.

## Acknowledgements

Y.Z. thanks the China Scholarship Council for a scholarship. We thank NIGMS R01GM123342 for financial support and NIH shared instrument grant S10OD012077 for the purchase of a 400 MHz NMR spectrometer.

**Keywords:** the Wolff rearrangement • gold catalysis •  $\alpha$ -oxo carbenes • silylketene • alkyne

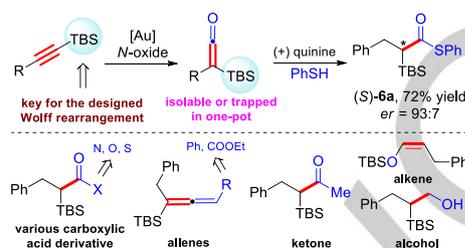
- [1] For a review, see: W. Kirmse, *Eur. J. Org. Chem.* **2002**, 2002, 2193-2256.
- [2] For reviews, see: (a) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire, M. A. McKerverey, *Chem. Rev.* **2015**, *115*, 9981-10080; (b) T. T. Tidwell, *Angew. Chem. Int. Ed.* **2005**, *44*, 5778-5785.
- [3] A. D. Allen, T. T. Tidwell, *Chem. Rev.* **2013**, *113*, 7287-7342.
- [4] L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258-3259.
- [5] For reviews, see: (a) L. Zhang, *Acc. Chem. Res.* **2014**, *47*, 877-888; (b) L. Zhang, in *Contemporary Carbene Chemistry* (Eds.: R. A. Moss, M. P. Doyle), John Wiley & Sons, **2013**; (c) Z. Zheng, Z. Wang, Y. Wang, L. Zhang, *Chem. Soc. Rev.* **2016**, *45*, 4448-4458; (d) J. Xiao, X. Li, *Angew. Chem., Int. Ed.* **2011**, 7226-7236.
- [6] For selected studies, see: (a) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550-8551; (b) L. Ye, W. He, L. Zhang, *Angew. Chem., Int. Ed.* **2011**, *50*, 3236-3239; (c) Y. Wang, K. Ji, S. Lan, L. Zhang, *Angew. Chem., Int. Ed.* **2012**, *51*, 1915-1918; (d) K. Ji, L. Zhang, *Org. Chem. Front.* **2014**, *1*, 34-38; (e) K. Ji, Z. Zheng, Z. Wang, L. Zhang, *Angew. Chem., Int. Ed.* **2015**, *54*, 1245-1249; (f) Y. Wang, Z. Zheng, L. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 5316-5319; (g) Z. Zheng, L. Zhang, *Org. Chem. Front.* **2015**, *2*, 1556-1560; (h) K. Ji, L. Zhang, *Adv. Synth. Catal.* **2017**, *360*, 647-651.
- [7] For selected studies, see: (a) K. Ji, X. Liu, B. Du, F. Yang, J. Gao, *Chem. Commun.* **2015**, 51, 10318-10321; (b) C. Shu, L. Li, Y.-F. Yu, S. Jiang, L.-W. Ye, *Chem. Commun.* **2014**, 50, 2522-2525; (c) C. Shu, L. Li, X.-Y. Xiao, Y.-F. Yu, Y.-F. Ping, J.-M. Zhou, L.-W. Ye, *Chem. Commun.* **2014**, 50, 8689-8692; (d) P. Nösel, L. N. dos Santos Comprido, T. Lauterbach, M. Rudolph, F. Rominger, A. S. K. Hashmi, *J. Am. Chem. Soc.* **2013**, *135*, 15662-15666; (e) G. Henrion, T. E. J. Chavas, X. Le Goff, F. Gagosz, *Angew. Chem., Int. Ed.* **2013**, *52*, 6277-6282; (f) J. Fu, H. Shang, Z. Wang, L. Chang, W. Shao, Z. Yang, Y. Tang, *Angew. Chem., Int. Ed.* **2013**, *52*, 4198-4202; (g) D. Vasu, H.-H. Hung, S. Bhunia, S. A. Gawade, A. Das, R.-S. Liu, *Angew. Chem., Int. Ed.* **2011**, *50*, 6911-6914; (h) D. Qian, J. Zhang, *Chem. Commun.* **2011**, 47, 11152-11154; (i) M. Chen, Y. Chen, N. Sun, J. Zhao, Y. Liu, Y. Li, *Angew. Chem., Int. Ed.* **2015**, 1200-1204; (j) J.-M. Yang, Y.-T. Zhao, Z.-Q. Li, X.-S. Gu, S.-F. Zhu, Q.-L. Zhou, *ACS Catal.* **2018**, *8*, 7351-7355.
- [8] S. Bhunia, S. Ghorpade, D. B. Huple, R.-S. Liu, *Angew. Chem., Int. Ed.* **2012**, *51*, 2939-2942.
- [9] S. K. Pawar, C.-D. Wang, S. Bhunia, A. M. Jadhav, R.-S. Liu, *Angew. Chem., Int. Ed.* **2013**, *52*, 7559-7563.
- [10] D. M. George, R. L. Danheiser, in *Science of Synthesis, Vol. 23*, Thieme Chemistry, **2006**, p. 53.
- [11] (a) P. J. Kocięński, B. Pelotier, J.-M. Pons, H. Prideaux, *J. Chem. Soc. Perkin. T1* **1998**, 1373-1382; (b) J.-M. Pons, P. Kocięński, *Tetrahedron Lett.* **1989**, *30*, 1833-1836; (c) A. Pommier, J.-M. Pons, P. J. Kocięński, L. Wong, *Synthesis* **1994**, 1294-1300.
- [12] G. A. Olah, A.-h. Wu, O. Farooq, *Synthesis* **1989**, 1989, 568-568.
- [13] A. S. Kostyuk, Z. G. Boyadzhian, V. N. Zaitseva, V. N. Sergeev, N. I. Savel'eva, Y. I. Baukov, I. F. Lutsenko, *J. Gen. Chem. USSR (Engl. Transl.)* **1979**, *49*, 1346.
- [14] E. Valenti, M. A. Pericas, F. Serratos, *J. Org. Chem.* **1990**, *55*, 395-397.
- [15] (a) R. Brückmann, K. Schneider, G. Maas, *Tetrahedron* **1989**, *45*, 5517-5530; (b) S. P. Marsden, W.-K. Pang, *Chem. Commun.* **1999**, 1199-1200.
- [16] (a) V. Pace, G. Verniest, J.-V. Sinisterra, A. R. Alcántara, N. De Kimpe, *J. Org. Chem.* **2010**, *75*, 5760-5763; (b) S. P. Marsden, P. C. Ducept, *Beilstein Journal of Organic Chemistry* **2005**, *1*, 5.
- [17] (a) I. Kim, C. Lee, *Angew. Chem., Int. Ed.* **2013**, *52*, 10023-10026; (b) Y. Wang, Z. Zheng, L. Zhang, *Angew. Chem., Int. Ed.* **2014**, *53*, 9572-9576.
- [18] H. Tokuyama, S. Yokoshima, T. Yamashita, L. Shao-Cheng, L. Leping, T. Fukuyama, *J. Braz. Chem. Soc.* **1998**, *9*, 381-387.
- [19] A. J. Blake, C. L. Friend, R. J. Outram, N. S. Simpkins, A. J. Whitehead, *Tetrahedron Lett.* **2001**, *42*, 2877-2881.
- [20] J. B. Lambert, *Tetrahedron* **1990**, *46*, 2677-2689.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

The Wolff rearrangement is observed for the first time upon gold-catalyzed oxidation of terminally TBS-substituted alkyne. The silyl group is essential for this reaction, and the generated silylketenes are stable and can be isolated or subsequently trapped in a variety of manners to afford  $\gamma$ -lactones,  $\alpha$ -silylated carboxylic acids and their derivatives, or silylallenes.



Yang Zheng, Junqi Zhang,  
Xinpeng Cheng, Xinfang  
Xu\* and Liming Zhang\*

Page No. – Page No.

The Wolff-  
Rearrangement Reaction  
of Oxidatively Generated  
 $\alpha$ -Oxo Gold Carbenes:  
An Effective Approach to  
Silylketenes

Accepted Manuscript