Homogeneous Catalysis

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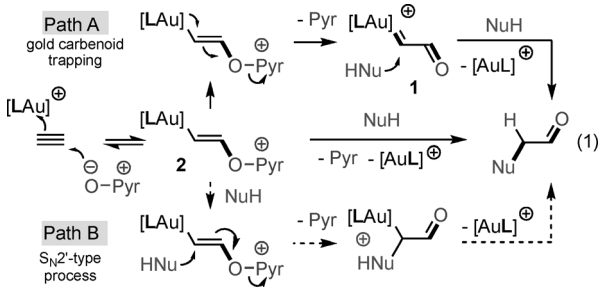
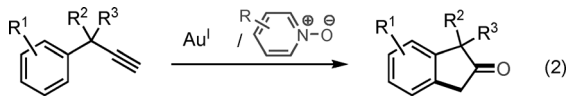
Biarylphosphonite Gold(I) Complexes as Superior Catalysts for Oxidative Cyclization of Propynyl Arenes into Indan-2-ones**

*Guilhem Henrion, Thomas E. J. Chavas, Xavier Le Goff, and Fabien Gagosz**

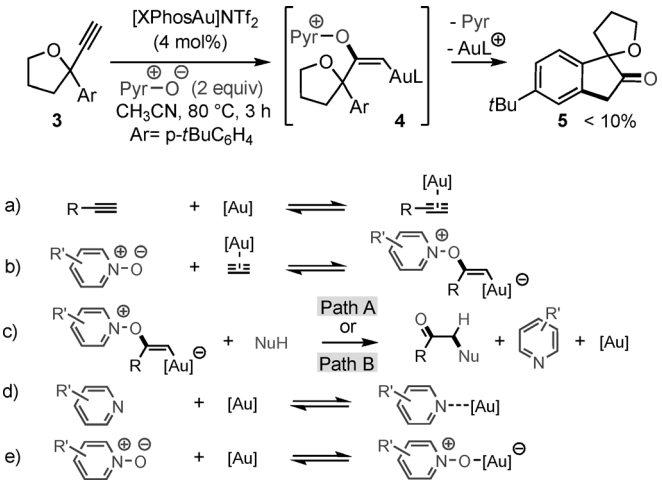
Gold-catalyzed alkyne oxidative reactions, involving the use of pyridine oxides as oxidants, have recently emerged as a new synthetic method to easily access a variety of functionalized molecules in a step-economical and efficient manner.[1] Most of the transformations reported so far have been proposed to proceed by the inter- or intramolecular trapping of the α-oxo gold carbenoid intermediate **1** [Eq. (1), path A].[1] However, an alternative S_N2'-type process, which would operate on the initially formed β-gold vinyloxypyridium intermediate **2**, could also be conceivable in some cases [Eq. (1), path B].[2] A large array of gold(I) complexes and pyridine oxides, possessing different electronic and steric properties, have been used in such transformations,[3] but no general rule can yet be defined regarding which gold catalyst/pyridine oxide couple would be the most efficient catalytic system for a given new transformation. This observation is relatively surprising when one considers that the formation of the putative α-oxo gold carbenoid intermediate **2** should, a priori, be dependent on the the electronic properties of both the gold catalyst and the pyridine oxide.



As part of our ongoing work in the field of gold catalysis,[4] we report herein a study which led us to develop a new class of gold(I) catalysts and a new pyridine oxide for the efficient oxidative cyclization of propynylarenes into indan-2-ones [Eq. (2)]. An alternative reactive intermediate to **1** and **2** is also proposed to account for the observed reactivity.



Our investigations were initiated by a discovery made during our previous study on the oxidative cyclizations of alkynyl ethers.[2] It was indeed observed that treatment of the alkynyl derivative **3** with 4 mol% of [(XPhos)Au]NTf_2 in the presence of 2 equivalents of pyridine oxide led to the formation of the indan-2-one **5** as a side product (Scheme 1). This interesting transformation was supposed to involve the β-gold vinyloxypyridinium intermediate **4** which could then produce the C–H functionalization product **5** by following one of the two pathways depicted in Equation 1 (Path A or B). Given the synthetic importance of indan-2-ones (and their derivatives) and the restricted number of studies involving aromatic partners in such oxidative transformations,[1b,j] we decided to improve and extend this process. In this respect, we took into consideration a series of potential steps and equilibria (Scheme 1 a–e), which were postulated to influence the efficiency of the oxidative cyclization.



Scheme 1. Initial discovery and potential steps and equilibria influencing the efficiency of the transformation. Tf = trifluoromethanesulfonyl.

The commercially available and simpler 3-phenyl-1-propyne (**6a**) was chosen as a model substrate to determine the best catalytic conditions leading to the corresponding indan-2-one **7a**. The results of this optimization study are shown in Table 1. The substrate **6a** was initially treated with 4 mol% of [(XPhos)Au]NTf_2 and 2 equivalents of several halogenopyridine oxides (**8a–c**) which were previously shown to be suitable partners in a series of gold(I)-catalyzed oxidative processes (entries 1–3).[1h,k,p,q] The reactions were performed

[*] G. Henrion, T. E. J. Chavas, Dr. X. Le Goff, Dr. F. Gagosz
Département de Chimie, UMR 7652 and 7653 CNRS
Ecole Polytechnique
91128 Palaiseau (France)
E-mail: gagosz@dcso.polytechnique.fr

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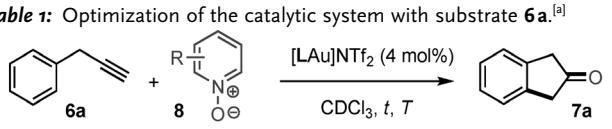
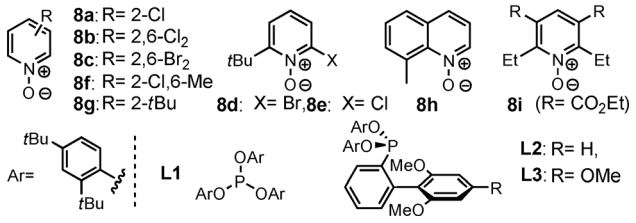
Table 1: Optimization of the catalytic system with substrate **6a**.[a]

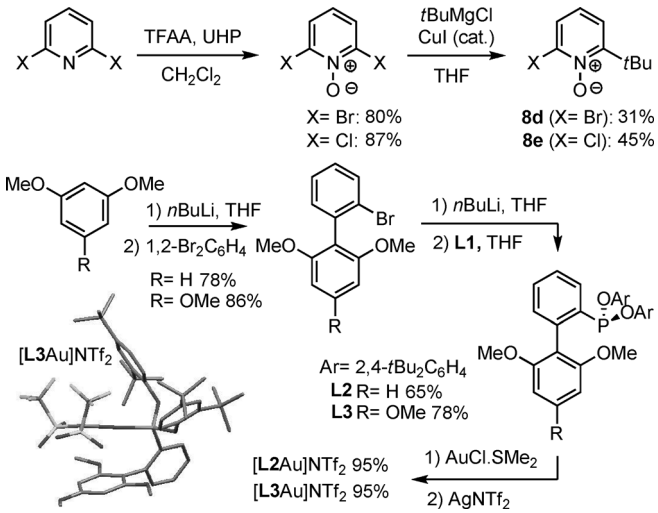


Entry	L	8	Equiv.	T [°C]	6a Conversion [%] 0.25 h	2 h	4 h	6 h	Yield [%][b]
1	XPhos	**8a**	2	20	16	18	19	20	15
2	XPhos	**8b**	2	20	20	23	23	24	18
3	XPhos	**8c**	2	20	20	25	26	26	22
4	XPhos	**8d**	2	20	5	26	45	59	45
5	XPhos	**8e**	2	20	8	40	60	70	55
6	XPhos	**8f**	2	20	7	9	10	11	9
7	XPhos	**8g**	2	20	7	12	13	15	11
8	XPhos	**8h**	2	20	5	12	13	15	10
9	Ph_3P	**8e**	2	20	3	12	18	25	17
10	RuPhos	**8e**	2	20	3	13	25	36	25
11	*t*BuXPhos	**8e**	2	20	9	46	76	86	71[c]
12	IPr	**8e**	2	20	3	11	14	16	10
13	**L1**	**8e**	2	20	21	37	44	50	42
14	**L2**	**8e**	2	20	41	73	79	80	61
15	**L3**	**8e**	2	20	50	90	100	100	80[d]
16	**L3**	**8e**	1.2	20	36	70	78	81	67
17	**L3**	**8e**	1.2	60	75	95	100	100	80[e]
18	Me_4*t*BuXPhos	**8i**	2	20	9	12	16	17	14

[a] Substrate concentration: 0.2 M. [b] Yield as determined by NMR spectroscopy. [c] After 22 h, yield of isolated product: 69%. [d] Yield of isolated product: 77%. [e] Yield of isolated product: 77%. IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, RuPhos = 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl, XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl.



in $CDCl_3$ at 20 °C and monitored by ^1H NMR spectroscopy for a 6 hour period. While disappointing in terms of yields (**7a** < 20%), these first results were, however, highly instructive. It was indeed observed that **6a** was converted to a minor extent (ca. 20%) during the early stage of the reaction (ca. 0.25 h) with very limited evolution afterwards. This rapid loss of catalytic activity was attributed to the possible complexation of the gold catalyst with the pyridine generated during the oxidative process (Scheme 1 d).[1q,5] This would hamper the gold activation of the alkyne (Scheme 1 a) and the subsequent nucleophilic addition of the pyridine oxide (Scheme 1 b).[6] We therefore sought an alternative pyridine oxide, thus reasonning that the replacement of one of the halogen atoms in **8a** and **8b** by a more sterically demanding group might help in disfavoring the coordination of the corresponding pyridine to the gold(I) complex. To validate this hypothesis, the 2-*tert*-butyl pyridine oxides **8d** and **8e** were synthesized in a straightforward manner (Scheme 2) and reacted with **6a**.[7]



Scheme 2. Syntheses of the pyridine oxides **8d,e** and gold(I) complexes [**L2**Au]NTf_2 and [**L3**Au]NTf_2. Hydrogen atoms have been omitted for clarity in the X-ray crystal structure of [**L3**Au]NTf_2. TFAA = trifluoroacetic anhydride, THF = tetrahydrofuran, UHP = urea–hydrogen peroxide.

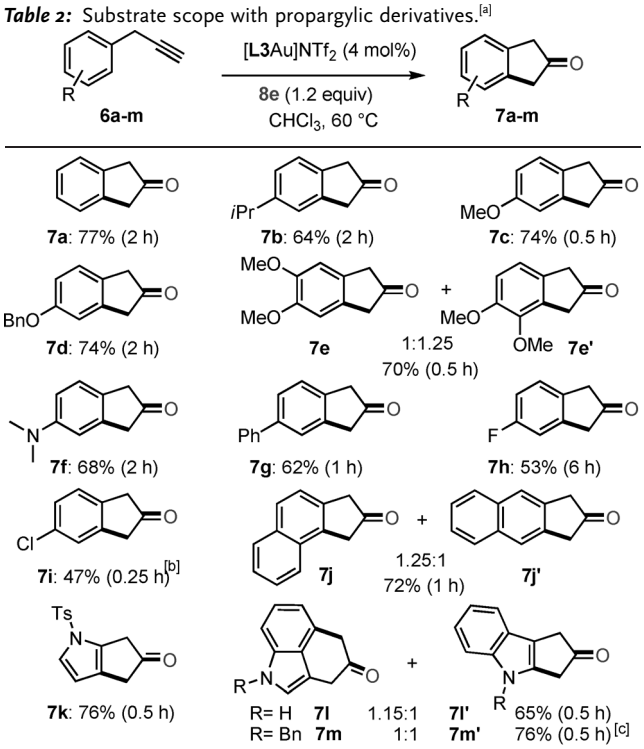
Gratifyingly, we observed in both cases an initially slower but gradual formation of **7a** with the conversion of **6a** reaching a maximum of 70% in the case of the pyridine oxide **8e** (Table 1, entries 4 and 5).[8] The combination of the chloride atom and the *tert*-butyl group in **8e** proved crucial, as reactions with the pyridine oxides **8f** (replacement of the *tert*-butyl group by a methyl) or **8g** (removal of the chloride atom) led to poor conversions of **6a**. The same observation was made in the case of the quinoline oxide **8h**, a commonly used partner in a series of oxidative processes (entry 8).[1a,d,f,i,m,n,l] The pyridine oxide **8e** was retained as the oxidizing agent and a screening of various gold catalysts was then performed to optimize both the conversion of **6a** and the yield of **7a** (entries 9–13). Generally, the conversion could not be improved except when the [(*t*BuXPhos)Au]NTf_2 complex was used as the catalyst (entry 11). In this case, the conversion attained was 86% after 6 hours and **7a** was formed in 71% yield as determined by NMR spectroscopy. We were however particularly surprised by the result obtained in the case of the [**L1**Au]NTf_2 gold complex possessing a phosphite ligand (entry 13).[9] We initially expected it to be a poor catalyst because its high electrophilicity combined with its limited steric crowding around the gold center (%V_{Bur} = 32.3)[1b,10] should favor the coordination to the pyridine by-product. Unexpectedly, not only a respectable 50% conversion of **6a** was obtained after 6 hours, but the conversion after 0.25 h (21%) was the best of all the catalysts screened (entry 13 versus entries 5 and 9–12). This result led us to conclude that the net oxidative cyclization process (Scheme 1 a–c) is kinetically favored by the use of gold catalysts possessing electron poor ligands.[11] We therefore decided to design new gold(I) catalysts which possess ligands combining both the electron deficient character of the phosphite **L1** and the steric bulk of the biaryl moiety in the *t*BuXPhos ligand (%V_{Bur} = 54.9).[1b,10] Such catalysts should indeed favor a high reaction rate while

limiting their coordination with the pyridine by-product. Biarylphosphonite ligands appeared to be promising candidates as they would fulfill the above-mentioned electronic and steric requirements. The new biarylphosphonite gold(I) complexes [**L2**Au]NTf_2 and [**L3**Au]NTf_2 were therefore synthesized by a convenient and efficient four-step procedure (Scheme 2),[7,12,13] and their catalytic activity evaluated (Table 1, entries 14 and 15). We were delighted to observe that, as expected, these complexes exhibit a superior reactivity with increased initial reaction rates. [**L3**Au]NTf_2, from which **L3** was calculated to have a $\%V_{Bur}$ value of 54.5 (similar to that of *t*BuXPhos),[14] was shown to be the most active catalyst (entry 15).[15] In this case, **6a** was completely consumed after only 4 hours and **7a** could be isolated in an enhanced 77% yield. The experimental conditions could be further improved: working with only 1.2 equivalents of **8e**[16] at 60°C furnished **7a** with the same 77% yield (entries 16 and 17). It is noteworthy that the combination of [(Me_4*t*BuXPhos)Au]NTf_2 with **8i**, which was shown by the group of Zhang to be optimal for the related oxidative cyclization of propargyl aryl ethers, was mostly inefficient in our case (entry 18).[1b]

The reaction scope was next examined using the optimal catalytic conditions noted in entry 17, of Table 1: 4 mol% of [**L3**Au]NTf_2 and 1.2 equivalents of **8e** in $CHCl_3$ at 60°C. We first focused on the use of aromatic and heteroaromatic substrates without a subsituent on the propargylic position (Table 2). A series of these derivatives (**6a**–**m**) were smoothly converted in less than 2 hours into the corresponding cyclized prodcuts **7a**–**m**, which were isolated in moderate to good yields (53–77%). This transformation exhibits an interesting functional group compatibility since various alkyl (**6b,l,m**), aryl (**6g**), ether (**6c**–**e**), amine (**6f**), and halide (**6h**–**i**) substituents on the aromatic nucleus were tolerated. Interestingly, no noticeable loss of reactivity was observed with **6f**, bearing a Lewis basic dimethylamino group which susceptible to coordination with the gold catalyst. It is also noteworthy that this chemistry could be applied to heteroaromatic substrates (**6k**–**m**), thus representing a useful alternative to the previously reported hazardous use of α-diazo acetonyl derivatives.[17] A limitation was found with the chloro derivative **6i**, for which a modified catalytic system must be used.[18]

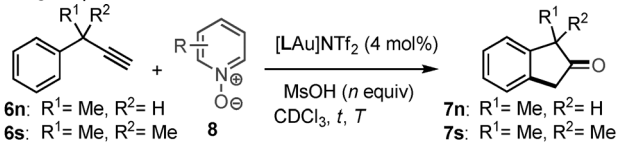
We also attempted to react substrates which were either mono- or disubstituted at the propargylic position. Under the previously optimized catalytic conditions, the monomethyl-substituted substrate **6n** reacted slowly (3 h) to furnish **7n** in a moderate yield of 56% upon isolation (Table 3, entry 1), while the dimethyl-substituted substrate **6s** did not react at all. This reduced or even complete loss of reactivity was tentatively attributed to the bulky **8e**, which would disfavor its addition to the gold-activated alkyne when substituents are present on the propargylic position (Scheme 1b). We therefore decided to employ a less bulky pyridine oxide (2 equiv) and methanesulfonic acid (1.2 equiv) to trap the pyridine by-product and therefore disfavor its coordination with the catalyst.[1c,e,i,p,q] Among the different pyridine oxides screened (Table 3) **8k**, possessing a bromo substituent at the 3-position, gave the best results both in terms of yield and reaction rate

Table 2: Substrate scope with propargylic derivatives.[a]



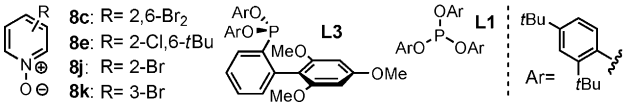
[a] Substrate concentration: 0.2 M. Yields of isolated products. Reaction time in parentheses. [b] Reaction run with **8c** (2 equiv), MsOH (1.2 equiv) at 20°C. [c] Reaction run at 20°C.

Table 3: Optimization of reaction conditions with **6n** and **6s**.[a]



Entry	Substrate	L	8 (equiv)	*n*	*T* [°C]	*t* [h]	Yields [%][b]	
1	**6n**	**L3**	**8e** (1.2)	0	60	3	56	(62)
2	**6n**	**L3**	**8c** (2)	1.2	20	0.5	–	(56)
3	**6n**	**L3**	**8j** (2)	1.2	20	0.5	–	(61)
4	**6n**	**L3**	**8k** (2)	1.2	20	0.5	64	(67)
5	**6n**	**L1**	**8k** (2)	1.2	20	2	–	(53)
6	**6s**	**L3**	**8e** (1.2)	0	60	12	0	(0)
7	**6s**	**L3**	**8c** (2)	1.2	60	6	–	(21)
8	**6n**	**L3**	**8j** (2)	1.2	60	1	–	(59)
9	**6s**	**L3**	**8k** (2)	1.2	60	0.5	67	(70)
10	**6s**	**L1**	**8k** (2)	1.2	60	1	–	(62)

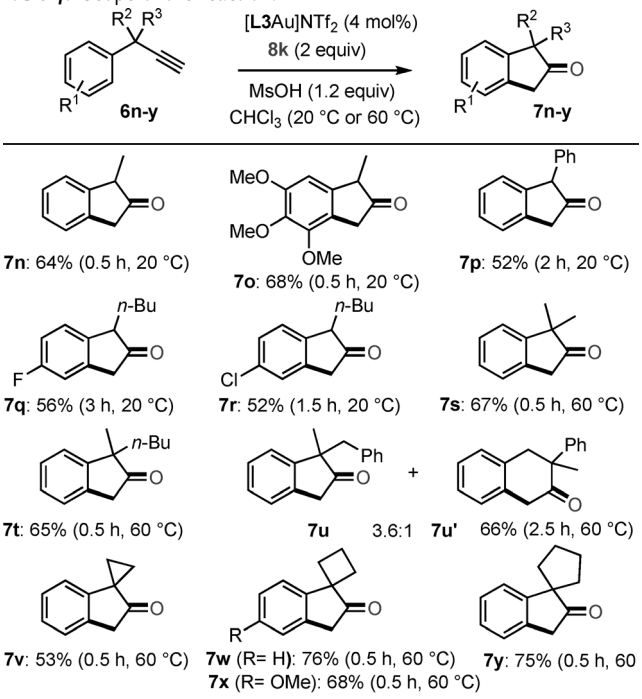
[a] Substrate concentration: 0.2 M. [b] Yield of isolated product. Yield as determined by NMR spectroscopy is given within parentheses.



(compare entries 6–9). Gratifyingly, the indan-2-ones **7n** and **7s** could be thus obtained after only 0.5 hours in 64 (at 20°C) and 67% yield (at 60°C), respectively.[19] Again, the phosphonite-based [**L3**Au]NTf_2 catalyst gave better results than

the simple phosphite-based [**L1**Au]NTf_2 catalyst (compare entries 4 and 5 with 9 and 10). These modified experimental conditions were next applied to an array of diversely substituted propynyl arenes (**6n–y**; Table 4). Moderate to good yields (52–76%) of the corresponding indan-2-ones **7n–y** were obtained with the same functional group tolerance previously observed.

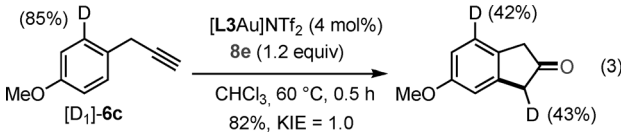
Table 4: Scope of the reaction.[a]

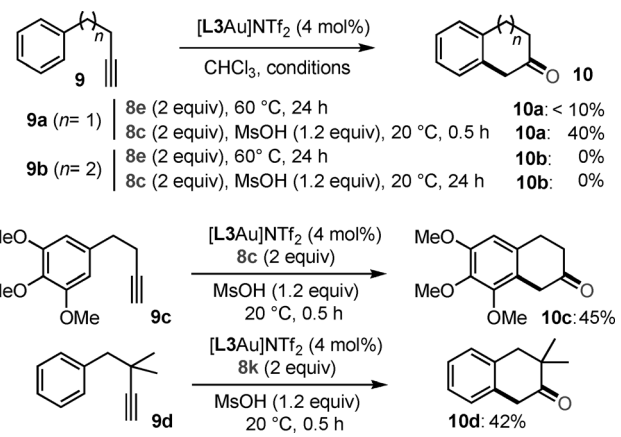


[a] Substrate concentration: 0.2 M. Yields of isolated products. Reaction time and temperature giveint within parentheses.

The formation of the isomeric β-tetralone **7u′** as a by-product in the oxidative cyclization of **6u** encouraged us to attempt an extension of this chemistry to butynyl and pentynyl derivatives (Scheme 3). With **9b** possessing a 3-carbone linker between the alkyne functionality and the phenyl group, no cyclized product could be obtained whatever the experimental conditions used. However, the use of [**L3**Au]NTf_2 as the catalyst in the presence of **8c** or **8k** and methanesulfonic acid allowed the moderately efficient formation of the β-tetralones **10a**, **10c**, and **10d**.[20]

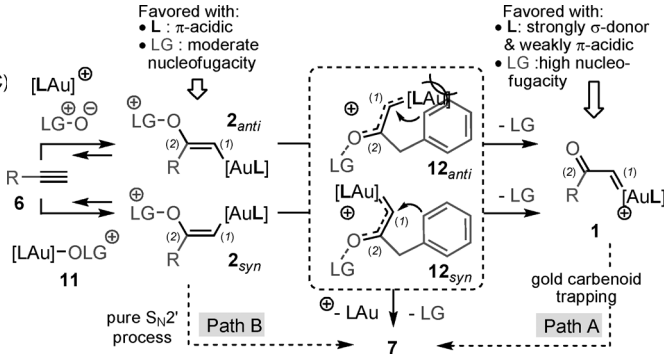
To gain further insight into the mechanism of this oxidative cyclization, an additional experiment was performed . The *ortho*-monodeuterated substrate [D_1]-**6c** was subjected to the optimal catalytic conditions using [**L3**Au]NTf_2 and **8e** to determine a possible kinetic isotope effect (KIE) [Eq. (3)].





Scheme 3. Extension to the formation of β-tetralones. Ms = methanesulfonyl.

The normal value of 1.0 for the KIE suggests that the oxidative cyclization proceeds more likely by a Friedel–Crafts-type electrophilic aromatic substitution. Such a mechanism is also supported by the observation that the transformation is favored when electron-rich aromatic substrates are employed (Tables 2 and 4). On the basis of our experimental observations, different mechanistic proposals are given in Scheme 4. The reaction is inititated by the nucleophilic addition of the oxidant (LG^+-O^-) on the alkyne **6** (Scheme 4). This attack could be *anti* (**6**→$\mathbf{2}_{anti}$) as generally proposed[1] or *syn* (**6**→$\mathbf{2}_{syn}$) with the participation of the preformed LAu-O-LG^+ species **11**,[21] as recently proposed by Hashmi et al.[1c] The exact nature of the intermediate in the cyclization process, and more precisely the involvement of an α-oxo gold carbenoid of type **1** generated from $\mathbf{2}_{anti}$ or $\mathbf{2}_{syn}$ by fragmentation, is however less certain.



Scheme 4. Possible reactive intermediates in the oxidative process.

The observation that gold complexes bearing π-acidic ligands such as phosphites were more reactive catalysts than those possessing an *i*Pr ligand[22] does not argue in favor of the intermediacy of such a species.[23] The formation of indan-2-ones is also unlikely to proceed directly via $\mathbf{2}_{anti}$ or $\mathbf{2}_{syn}$ by a pure S_N2' process with an unfavorable 5-*endo-trig* cyclization of the aromatic nucleus onto the vinyloxypyridinium

moiety.[23] From a general point of view, the pure α-oxo gold carbenoid intermediate **1** and the β-gold vinyloxypyridium intermediate **2** (*syn* or *anti*) can be seen as two limiting forms in gold-catalyzed oxidative processes. Their possible involvement should depend on a series of parameters including the electronic nature of the ligand (**L**) and the nucleofugacity of the leaving group (LG), which should play an important role. A push-pull system with a strongly σ-donating and weakly π-acidic ligand in combination with a highly electron-deficient leaving group could favor the formation of the gold carbenoid **1**. Conversely, the formation of **1** should be disfavored by the association of a π-acidic ligand (as π donation from the gold atom to C1 would be curtailed) with a leaving group of moderate nucleofugacity.[22] Alternatively to what has been generally proposed,[1] and to take into account the effect of the ligand/gold fragment in the limiting form **2**, we propose that the reactive intermediate is better pictured as **12**. This structure resembles a reactive form of **2**, midway between **1** and **2**, in which a relative π donation from gold would participate in the elongation of the O-LG bond with an overall decrease in electron density at position C1 and a decrease of the C1-C2 bond order. In this respect, $\mathbf{12}_{syn}$ appears to be a more likely reactive intermediate for the cyclization since it does not possess the same disfavorable steric interactions which can be found in $\mathbf{12}_{anti}$. By comparison with $\mathbf{2}_{syn}$, $\mathbf{12}_{syn}$ would favor an electrostatic attraction between the electrophilic C1 center and the aromatic nucleus, thus lowering the energy of the transition state leading to the "anti-Baldwin" formation of the indan-2-one products.

In conclusion, we have developed a new access to variously substituted indan-2-ones involving a gold(I)-catalyzed oxidative cyclization of propynyl arenes. During this study, a new class of biarylphosphonite gold(I) complexes was prepared and shown to be superior catalysts possessing the ideal electronic and steric properties for performing rapid and efficient oxidative transformations. Further mechanistic studies and extensions of this oxidative cyclization are currently underway.

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Keywords: cyclization · gold · homogeneous catalysis · oxidation · synthetic methods

[1] For a minireview, see: J. Xiao, X. Li, *Angew. Chem.* **2011**, *123*, 7364 – 7375; *Angew. Chem. Int. Ed.* **2011**, *50*, 7226 – 7236. For selected examples, see: a) Y. Luo, K. Ji, Y.-X. Li, L. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 17412; b) Y. Wang, K. Ji, S. Lan, L. Zhang, *Angew. Chem.* **2012**, *124*, 1951; *Angew. Chem. Int. Ed.* **2012**, *51*, 1915; c) A. S. K. Hashmi, T. Wang, S. Shi, M. Rudolph, *J. Org. Chem.* **2012**, *77*, 7761; d) S. Bhunia, S. Ghorpade, D. B. Huple, R.-S. Liu, *Angew. Chem.* **2012**, *124*, 2993; *Angew. Chem. Int. Ed.* **2012**, *51*, 2939; e) M. Xu, T.-T. Ren, C.-Y. Li, *Org. Lett.* **2012**, *14*, 4902; f) R. B. Dateer, K. Pati, R.-S. Liu, *Chem. Commun.* **2012**, *48*, 7200; g) M. Murai, S. Kitabata, K. Okamoto, K. Ohe, *Chem. Commun.* **2012**, *48*, 7622; h) W. Yuan, X. Dong, Y. Wei, M. Shi, *Chem. Eur. J.* **2012**, *18*, 10501; i) W. He, L. Xie, Y. Xu, J. Xiang, L. Zhang, *Org. Biomol. Chem.* **2012**, *10*, 3168; j) D. Qian, J. Zhang, *Chem. Commun.* **2012**, *48*, 7082; k) L. Ye, W. He, L. Zhang, *Angew. Chem.* **2011**, *123*, 3294; *Angew. Chem. Int. Ed.* **2011**, *50*, 3236; l) W. He, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8482; m) D. Vasu, H.-H. Hung, S. Bhunia, S. A. Gawade, A. Das, R.-S. Liu, *Angew. Chem.* **2011**, *123*, 7043; *Angew. Chem. Int. Ed.* **2011**, *50*, 6911; n) D. Qian, J. Zhang, *Chem. Commun.* **2011**, *47*, 11152; o) P. W. Davies, A. Cremonesi, N. Martin, *Chem. Commun.* **2011**, *47*, 379; p) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550; q) L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258.

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[7] See the Supporting Information for more details.

[8] The reduced initial rates could be due to the greater steric bulk of **8d**,**e**, and would kinetically disfavor their nucleophilic addition to the gold-activated alkyne (Scheme 1b).

[9] [**L1**Au]NTf_2 has been screened as a catalyst in several studies; see Ref. [1i,b,l]. For a recent study in which phosphite ligands were crucial for good success, see: A. S. K. Hashmi, T. Häffner, W. Yang, S. Pankajakshan, S. Schäfer, L. Schultes, F. Rominger, W. Frey, *Chem. Eur. J.* **2012**, *18*, 10480.

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[14] Calculated using Samb*V*ca with the standard parameters. See Ref. [10].

[15] The difference in reactivity between [**L2**Au]NTf_2 and [**L3**Au]NTf_2 is hard to explain given their structural similarities.

[16] This result tends to prove that the possible coordination of the pyridine oxide with the gold(I) catalyst has only little influence on the reaction.

[17] M. Salim, A. Capretta, *Tetrahedron* **2000**, *56*, 8063.

[18] A lower yield was obtained under the standard reaction conditions (ca. 40%).

[19] Lower yields were obtained with other acids ($HNTf_2$, TFA).

[20] A higher flexibility and/or a disfavored cyclization transition state might explain the lower yields.

[21] In line with the results reported by Hashmi et al. (Ref. [1c]), NMR experiments showed a very favorable coordination of [**L3**Au]NTf_2 with **8e**. See the Supporting Information for more details.

[22] Contrary to NHC ligands, the π-acidic character of phosphites and phosphonites should disfavor extrusion of the pyridine, as the π-donation from gold to the vinyloxypyridinium system should be limited. See: D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482.

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