Synthetic Methods

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Gold-Catalyzed Cyclization/Oxidative [3+2] Cycloadditions of 1,5-Enynes with Nitrosobenzenes without Additional Oxidants**

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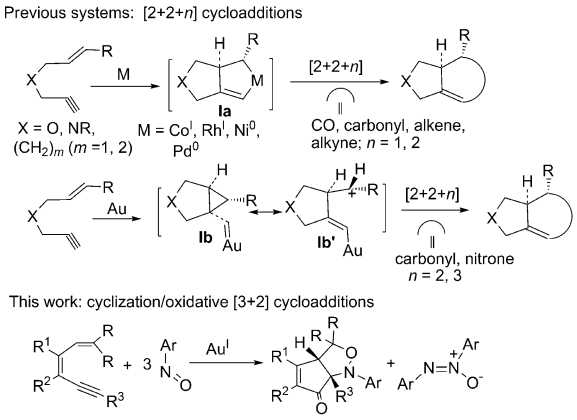
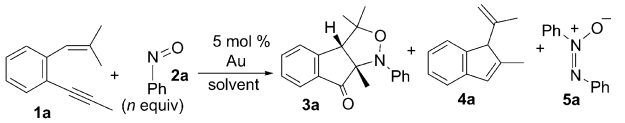
Metal-catalyzed [2+2+*m*] cycloadditions (*m* = 1–3) of 1,*n*-enynes (*n* = 5–7) with small molecules are powerful tools for accessing complicated hetero- and carbocycles.[1,2] These reactions are appealing because their mechanisms can be altered by using different metal complexes. As shown in Scheme 1, low-valent metal species react with these enynes to form metallocycloalkene intermediates (**Ia**) initially,[3] whereas gold(I) catalysts generate the cyclopropyl gold carbene **Ib** which has a resonance structure, that is, the alkenylgold carbocation **Ib′**.[4] We sought a new catalytic [2+2+*m*] cycloaddition of 1,*n*-enynes to generate an additional functionality on the resulting cycloadducts. Although catalytic cycloadditions of nitrosobenzenes have been intensively studied,[5,6] we are aware of no report on the cycloaddition of nitroso species with 1,*n*-enynes (*n* = 5–7).[6] We report herein the gold-catalyzed cyclization/oxidative [3+2] cycloadditions of 1,5-enynes with nitrosobenzenes. Notably, nitrosobenzenes not only provide two-atom building units, but also lead to the alkyne oxidation. Such a reaction pattern is unprecedented in metal-catalyzed cycloadditions of 1,*n*-enynes.



Scheme 1. Metal-catalyzed cycloadditions on 1,*n*-enynes.

This oxidative cycloaddition was realized with the treatment of the 1,5-enyne **1a** (1 equiv) with nitrosobenzene (**2a**; 1.5 equiv) and [P(*t*Bu)$_2$(*o*-biphenyl)AuCl]/AgNTf$_2$ (5 mol%) in 1,2-dichloroethane (DCE; 25 °C, 24 h) to give the oxidative cycloadduct **3a** in 21% yield, together with the cycloisomerization product **4a** in 70% yield (Table 1, entry 1).[7] The yield of **3a** was increased to 41% with [{P(*t*Bu)$_2$(*o*-biphenyl)}-AuCl]/AgSbF$_6$ (5 mol%, entry 2). For the two above-mentioned entries, we also isolated 1,2-diphenyldiazene oxide (**5a**) which was identified upon comparison of its NMR spectra and mass data with those of an authentic sample.[8] The structure of **3a** was confirmed by an X-ray diffraction study to confirm a *cis*-fused ring system with the methyl group and its neighboring hydrogen atom *cis* to each other.[9] Accordingly, three equivalents **2a** are required to achieve the reaction. With an increased loading (4 equiv) of **2a**, the yield of **3a** was significantly increased to 82% (entry 3). Other gold catalysts such as [PPh$_3$AuCl]/AgSbF$_6$ and [IPrAuCl]/AgSbF$_6$ also produced the desired cycloadduct **3a** (entries 4 and 5). [{P(*t*Bu)$_2$(*o*-biphenyl)}AuCl]/AgSbF$_6$ in CH$_2$Cl$_2$ gave **3a** with a yield of up to 85% (entry 6), but afforded **4a** exclusively (87%) with CH$_3$CN as the solvent (entry 7). The yield of **5a** was almost the same as that for **3a** according to the NMR analysis of the crude reaction mixture (entries 3–6).

Table 1: Tests over various gold catalysts.



Entry[a]	Au	*n*	Solvent	*t* [h]	Yield [%][b] 3a	4a	5a
1	[LAuCl]/AgNTf$_2$	1.5	DCE	24	21	70	18
2	[LAuCl]/AgSbF$_6$	1.5	DCE	14	41	53	35
3	[LAuCl]/AgSbF$_6$	4.0	DCE	4	82	6	57 (75)[c]
4	[PPh$_3$AuCl]/AgSbF$_6$	4.0	DCE	4	77	8	(76)[c]
5	[IPrAuCl]/AgSbF$_6$	4.0	DCE	5	72	16	(73)[c]
6	[LAuCl]/AgSbF$_6$	4.0	CH$_2$Cl$_2$	3	85	6	(82)[c]
7	[LAuCl]/AgSbF$_6$	4.0	CH$_3$CN	24	–	87	–

[a] [**1a**] = 0.3 M, 25 °C. [b] Yield of product isolated from silica gel column. [c] Yield determined by NMR spectroscopy. L = P(*t*Bu)$_2$(*o*-biphenyl), IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene), Tf = trifluoromethanesulfonyl.

The oxidative cycloadditions of **2a** (4 equiv) with various 1,5-enynes (**1b**–**1i**) bearing a variety of alkynyl and phenyl substituents (R, X, and Y) is shown (Table 2). The reactions

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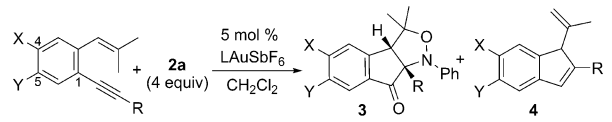
Table 2: Oxidative [3+2] cycloadditions using various enynes.



Entry[a]	Enyne	*t* [h]	Yield [%][b]	
	X = *Y* = *H*			
1	R = *n*Bu (**1b**)	10	73 (**3b**)	6 (**4b**)
2	R = *i*Pr (**1c**)	7	77 (**3c**)	5 (**4c**)
3	R = cyclopropyl (**1d**)	8	77 (**3d**)	11 (**4d**)
4	R = Ph (**1e**)	36	81 (**3e**)	10 (**4e**)
	R = *Me*			
5	X = Cl, Y = H (**1f**)	3	80 (**3f**)	9 (**4f**)
6	X = H, Y = Cl (**1g**)	5	83 (**3g**)	9 (**4g**)
7	X = OMe, Y = H (**1h**)	5	– (**3h**)	80 (**4h**)
8	X = H, Y = OMe (**1i**)	4	78 (**3i**)	8 (**4i**)

[a] [**1**] = 0.30 M, L = P(*t*Bu)$_2$(*o*-biphenyl). [b] Yield of product isolated from silica gel column.

were run with [{P(*t*Bu)$_2$(*o*-biphenyl)}AuCl]/AgSbF$_6$ (5 mol%) in CH_2Cl_2 (25 °C, 0.3 M). We made no attempts to isolate **5a** for these reactions. Various internal alkynes (**1b–e**) were used in this reaction to give the desired compounds **3b–e** together with the indene derivatives **4b–e** in small quantities (entries 1–4). The reactions are sensitive to the substituents on the phenyl ring (**1f–i**); we obtained the desired cycloadducts **3f**,**g** and **3i** (entries 5, 6, and 8) in satisfactory yields, whereas **1h** gave only the cycloisomerization product **4h** in 80% yield (entry 7). This substituent effect provides insight into the mechanism of the reaction.[10]

Table 3 shows our results on additional 1,5-enynes (**1j–p**). For the substrates **1j–l** bearing various trisubstituted alkenes including cyclopentylidene, cyclohexylidene, and 3-pentylidene groups (entries 1–3), the corresponding products **3j–l** were obtained in reasonable yields (72–82%). We also prepared the trisubstituted alkene **1m** with both *E* and *Z* configurations (entries 4 and 5), and their gold-catalyzed reactions resulted in the same cycloadduct **3m** with the methyl group *cis* to the neighboring hydrogen atom. Notably, this *cis*-configured product is 0.75 kcal mol^{-1} higher in energy than the *trans*-configured isomer.[11] Similarly, both *trans*- and *cis*-styrene derivatives of **1n** (entries 6 and 7) gave the same cycloadduct **3n**, wherein the two adjacent hydrogen atoms are *cis* configured according to the ^{1}H NMR NOE spectra (see the Supporting Information). To our delight, the reactions also proceeded with the nonbenzoid substrates **1o** and **1p** (entries 8 and 9), thus delivering the products **3o** and **3p**, respectively.

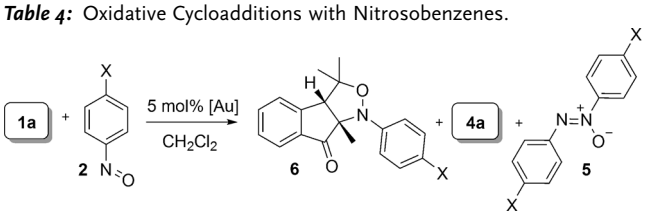
Table 4 shows the reactions using different nitrosobenzenes (**2b–f**). The cycloadducts **6b–f** and 1,2-diphenyldiazene oxides **5b–f** were obtained in nearly the same proportions. The reactions worked efficiently not only for the electron-deficient nitrosobenzenes **2b–d** (entries 1–3), but also for the electron-rich analogues **2e**,**f** (entries 4 and 5). The reaction time of 4–8 hours for the nitroso species **2e**,**f** is attributed to their ability to coordinate to the gold catalyst. In all cases **4a** was produced in small proportions (0–11%).

Table 3: Oxidative cycloadditions on 1,5-enynes.

Entry[a]	Enyne	*t* [h]	Yield [%][b]	
1	**1j** (*n* = 1)	11	77 (**3j**)	9 (**4j**)
2	**1k** (*n* = 2)	2.5	72 (**3k**)	11 (**4k**)
3	**1l**	5.5	82 (**3l**)	8 (**4l**)[c]
4	(*E*)-**1m** (R^1 = Ph, R^2 = Me)	14	75 (**3m**)	10 (**4m**)
5	(*Z*)-**1m** (R^1 = Me, R^2 = Ph)	15	77 (**3m**)	9 (**4m**)
6	(*E*)-**1n** (R^1 = 4-MeOC$_6$H$_4$, R^2 = H)	24	63 (**3n**)	–
7	(*Z*)-**1n** (R^1 = H, R^2 = 4-MeOC$_6$H$_4$)	20	67 (**3n**)	–
8	**1o** (R = Me)	14	85 (**3o**)	–
9	**1p** (R = *n*Bu)	15	82 (**3p**)	–

[a] [**1**] = 0.3 M, 5 mol% [{P(*t*Bu)$_2$(*o*-biphenyl)}Au]SbF$_6$, CH_2Cl_2, **2a** (4 equiv), 25 °C. [b] Yield of product isolated from silica gel column. [c] *E*/*Z* = 2.5.

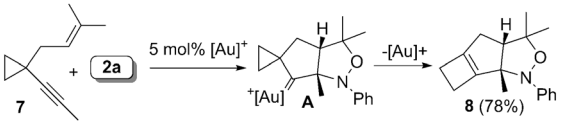
Table 4: Oxidative Cycloadditions with Nitrosobenzenes.



Entry	Nitroso compound[a]	*t* [h]	Yield [%][b] 6	4a	5
1	X = NO_2 (**2b**)	0.5	71 (**6b**)	11	67 (**5b**)
2	X = Cl (**2c**)	1	77 (**6c**)	6	71 (**5c**)
3	X = Br (**2d**)	0.5	79 (**6d**)	5	75 (**5d**)
4	X = *t*Bu (**2e**)	4	80 (**6e**)	7	76 (**5e**)
5	X = OMe (**2f**)	8	91 (**6f**)	–	84 (**5f**)

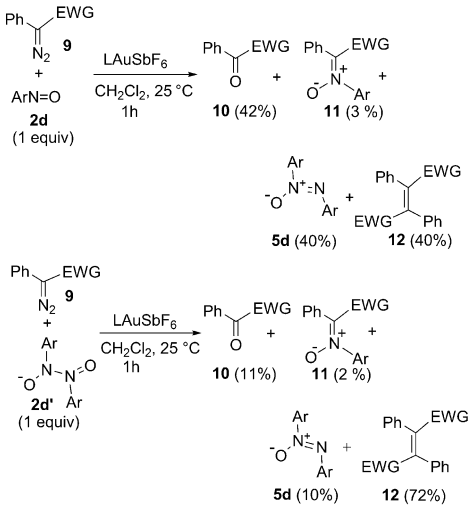
[a] [**1a**] = 0.3 M, nitroso (4 equiv), [{P(*t*Bu)$_2$(*o*-biphenyl)}Au]SbF$_6$, CH_2Cl_2, 25 °C. [b] Yield of product isolated from silica gel column.

Equation (1) shows relevant data to support the intermediacy of the gold carbenes **A**. We prepared the acyclic 1,5-enyne **7** which reacted with **2a** (4 equiv) and the gold catalyst (5 mol%) to deliver the tricyclic species **8** in 78% yield. Formation of this compound arose from a 1,2-cyclopropane migration to the neighboring gold carbene center in species **A**. Equation (1) represents the first formal [2+2+1] cycloaddition for the enyne/nitroso functionalities.



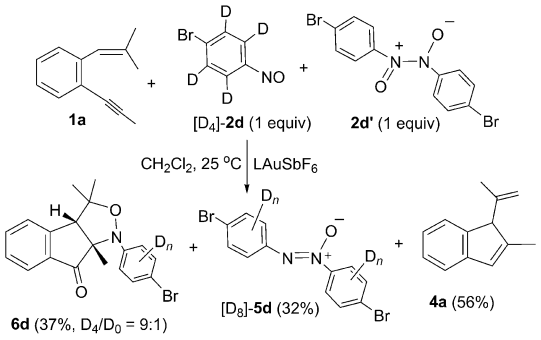
(1)

The nitrosobenzenes **2a–e** are in equilibrium with a dimeric species in solution.[12] Their respective reactivities toward the oxidation of gold carbenes should be addressed. We tested the gold-catalyzed oxidation of the diazocarbonyl species **9** with a nitroso species to compete with its catalytic diazo decomposition to the olefin **12** (Scheme 2). The treatment of this diazo species with [{P(*t*Bu)$_2$(*o*-biphenyl)}AuCl]/AgSbF$_6$ (5 mol%) and monomeric the nitroso species **2d** (1 equiv) gave the dicarbonyl compound **10** and 1,2-diphenyldiazene oxide **5d** in 42 and 40% yield, respectively. With **2d′** (1 equiv),[13] the desired **10** and **11** were obtained in 11 and 2% yields, respectively, together with the tetrasubstituted olefin **12** in large 72%. Accordingly, we postulate that **2d′** is a poor oxygen donor and the resulting **10** and **11** presumably arose from the slow release of the monomeric form **2d**.



Scheme 2. Oxidation of gold carbenes by mono- or dimeric nitroso species. EWG = CO_2Et, Ar = 4-BrC_6H_4

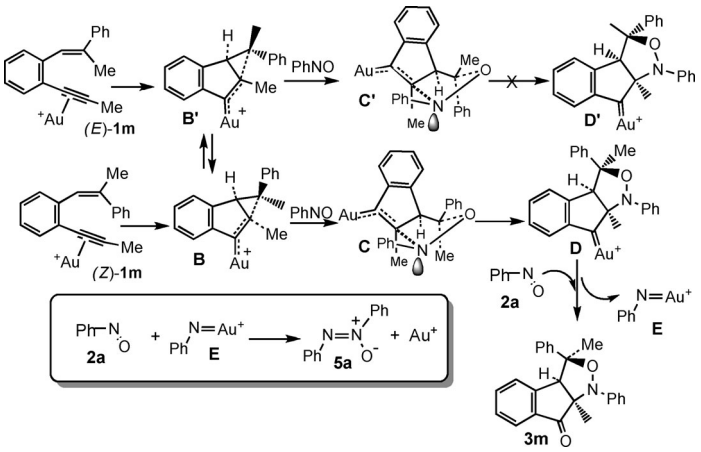
In a separate experiment, the treatment of **1a** with [D_4]-**2d** (1 equiv), **2d′** (1 equiv), and [{P(*t*Bu)$_2$(*o*-biphenyl)}-Au]SbF$_6$ (5 mol%) in CH_2Cl_2 (25°C) gave the desired [D_4]-**6d** as a major component (D_4/D_0 = 9:1; Scheme 3). ^{1}H NMR analysis of **5d**, using $CDCl_3$ as an internal standard, indicated



Scheme 3. Deuterium-labeling experiment.

a very small proton content (< 10%). The ^{13}C NMR spectrum resembled that of the fully deuterated sample [D_8]-**5d** (see the Supporting Information). Its FAB mass spectra showed primarily the signal for [D_8]-**5d**. Again, this deuterium-labeling experiment confirms that the monomeric form **2d** is actually the oxygen source for **6d**.

A plausible mechanism (Scheme 4) to account for the stereoselectivity of **3m** from either (*E*)-**1m** or (*Z*)-**1m** is shown. For (*Z*)-**1m**, the initially formed cyclopropyl carbene **B** has a an alkenylgold carbocation resonance structure, which enables a [3+2] cycloaddition with nitrosobenzene to form the cyclic transition-state **C** by either a concerted or stepwise process.[13] This process is feasible because the alkenyl phenyl group lies at the less hindered equatorial position. This cycloaddition generates the gold carbene **D** with the observed stereochemistry. For (*E*)-**1m**, the nitroso cycloaddition might encounter difficulty because the corresponding cyclic transition-state **C′** has the phenyl group at the axial position. This proposed stereochemistry is analogous to that for the Sn(OTf)$_2$-catalyzed [3+2] cycloaddition of substituted cyclopropane derivatives with aldehydes.[14,15] We postulate an equilibrium between **B** and **B′** because of their significant alkenylgold carbocation resonance structures.



Scheme 4. A plausible mechanism for gold-catalyzed oxidative cycloaddition.

According to our control experiments (Schemes 2 and 3), the subsequent oxidations of the resulting gold-carbenes **D** rely on the monomeric nitroso species **2a.**[16,17] This process is expected to generate **3m** and the gold nitrenes **E** simultaneously. We hypothesize that this nitrene species reacts further with nitrosobenzene to regenerate the gold catalyst and **5a**. Notably, **2a** is inactive toward the oxidation of species **B** (or **B′**), which is not a pure gold carbene because of their additional resonance structures.

Before this work, transition-metal catalyzed cycloadditions of 1,*n*-enynes ($n = 5$–7) were strictly restricted to the [2+2+*m*] cycloaddition ($m = 1$–3) modes. In this work, we achieved a cyclization/oxidative [3+2] cycloaddition of 1,5-enynes and nitrosobenzene with high stereocontrol. These oxidative cycloadditions are applicable a variety of 1,5-enynes and nitrosobenzenes. According to our control experiments, monomeric nitrosobenzenes not only react with the cyclopropyl gold-carbene intermediates, but also lead to the oxidation of the key gold carbene intermediates.[18] This novel enyne oxidative cycloaddition highlights the use of gold catalysis.

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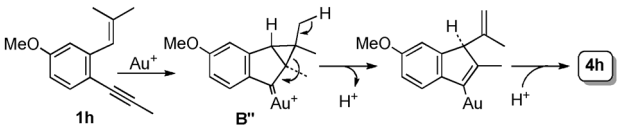
[9] CCDC 908146 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] For the 1,5-enyne **1h** (Table 2, entry 7), the methoxy substituent stabilizes the resonance structure of the cyclopropyl gold carbene **B″** which tends to lose one proton to give the cycloisomerization product **4h**.



[11] The energy differences between **3m** and its diastereomer was calculated using the B3LYP/6-311++G** level of theory. ^{1}H NOE spectra of compounds **3m** and **3n** are provided in the Supporting Information.

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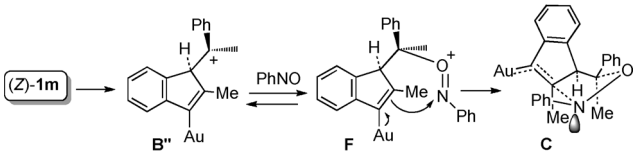
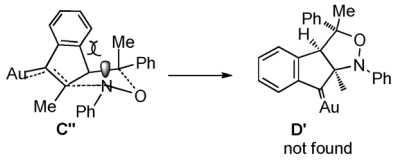
[13] We do not exclude the possibility that cyclic the transition-state **C** is derived from the benzylic cation **B″** through a prior coordination of the nitroso species to its cationic center to form

F. A subsequent addition of the alkenylgold bond of **F** to the coordinated nitrosobenzene also forms **C**. This process rationalizes well the nonstereospecificity of the cycloaddition.

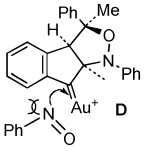


[14] a) P. D. Pohlhaus, S. D. Sanders, A. T. Parsons, W. Li, J. S. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 8642–8650; b) P. D. Pohlhaus, J. S. Johnson, *J. Org. Chem.* **2005**, *70*, 1057–1059; c) M. J. Campbell, J. S. Johnson, A. T. Parsons, P. D. Pohlhaus, S. D. Sanders, *J. Org. Chem.* **2010**, *75*, 6317–6325; d) P. D. Pohlhaus, J. S. Johnson, *J. Am. Chem. Soc.* **2005**, *127*, 16014–16015; e) M. J. Campbell, J. S. Johnson, *J. Am. Chem. Soc.* **2009**, *131*, 10370–10371.

[15] An alternative cyclic transition state **C″** is unlikely to occur because the axial methyl group exerts steric interaction with the bulky indene ring.



[16] Nitrosobenzene was reported to undergo a nitrogen attack on the less hindered gold carbenes (see Ref. [6b]), but this process is likely impeded by steric hindrance for **D** in our system. Attack of the oxygen atom of nitrosobenzene on the gold carbene is also documented in a nonoxidation process (see Ref. [6a]).



[17] We preclude the possibility that water and oxygen are the oxygen sources for the oxidation of **D** since we failed to obtain positive evidence using either H_2O^{18} or O_2^{18}.

[18] We have performed additional experiments using a mixture of **2d′** (*m* equiv) and m**2d** (*n* equiv), thus amounting to three ArNO molecules ($2m+n=3$). Oxidative cycloadduct **6d** was obtained in decreased yields with increasing proportions of **2d′** ($m=1.5, n=0$; $m=1, n=1$; $m=0, n=3$). See Table S1 in the Supporting Information.

