

Rearrangement

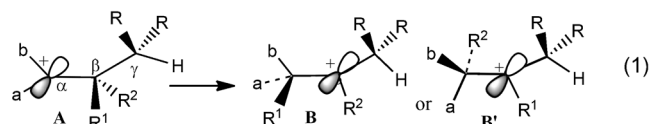
Gold-Catalyzed Oxidative Cyclizations on 1,4-Enynes: Evidence for a γ -Substituent Effect on Wagner–Meerwein Rearrangements**

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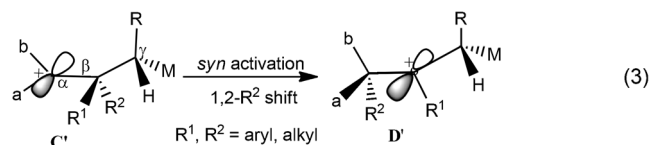
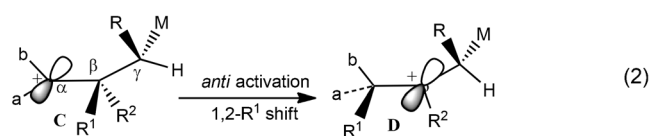
The Wagner–Meerwein rearrangement refers to a 1,2-shift of an alkyl, aryl, and alkenyl group to an adjacent carbocationic center; formation of this carbon–carbon bond has found widespread applications in many Lewis acid or Brønsted acid mediated reactions [Eq. (1)].^[1,2] For this well-known reaction, the 1,2-shift of R^1 versus R^2 is determined primarily by the relative stability of carbocation **B** (or **B'**), as well as the intrinsic properties of the migrating group (Scheme 1).^[1,2] No instance of a γ -substituent to stereospecifically direct a 1,2-shift of the R group in β -position was reported to date; those carbocations bearing a γ -silyl group are no examples either.^[3a] Although the γ -effect on this arrangement was claimed in an early report,^[3b] the 1,2-shift actually occurred within a benzene skeleton comprising the C_β and C_γ carbon atoms. According to carbocation chemistry,^[3–5] we envisage that a metal substituent in the γ -position might facilitate an *anti* activation through hyperconjugation to induce a 1,2- R^1 -shift (**C**→**D**) in an antiperiplanar conformation (**C**) [Eq. (2)].^[3–5] Alternatively, this metal might exert steric interaction to induce a *syn* activation to enable a 1,2- R^2 -shift (**C'**→**D'**) in a synperiplanar conformation **C'** [Eq. (3)].^[3,5] The realization of such an unprecedented effect of a metal in γ -position relies on the availability of suitable carbocations applicable for a study. Herein, we report our experimental and theoretical work to support an *anti*-activation route [Eq. (2)] for $M = Au$ ^[6] (path **C**→**D**) even in a synperiplanar conformation. This work represents an atypical Wagner–Meerwein rearrangement, because the intrinsic properties of the migrating group (R^1 , R^2) are no longer decisive.

Shown in Scheme 1 is our strategy to illustrate the γ -substituent effect; the key reaction involves a gold-catalyzed oxidative cyclization of 1,4-enyne **3**.^[7,8] The initially formed α -oxo gold carbene **E**^[9] is expected to have its olefin π electrons parallel to the positive $^+Au=C$ orbital to achieve a through-space interaction. We envisage that this spatial arrangement will undergo a facile alkene/carbene coupling^[10] to give 2-oxocyclopent-1-yl cation **F** or **F'**, through either a disrotation or

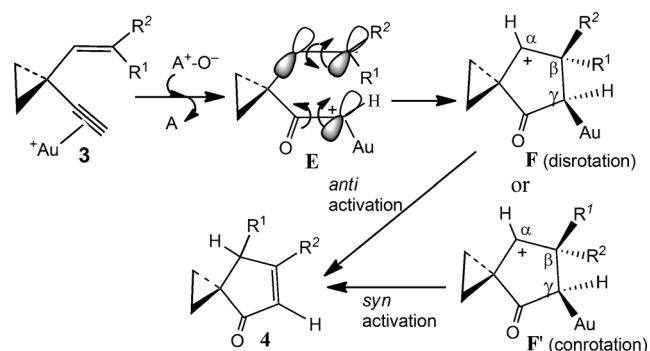
Wagner–Meerwein Migration



Metal-directing 1,2-migration (this work)



conrotation route. We employ these special 1,4-enynes, because their bridged cyclopropanes can stabilize carbocation **F** or **F'** with a “bisected” conformation,^[11] in which the ketone group hinders the expansion of the cyclopropane ring.^[12] A cyclopropyl group greatly enhances the electrophilicity of an alkyne in the presence of a gold catalyst.^[12] Our experimental results disclose that only the *cis*-substituent R^1 at the alkene is transferable to give the observed cyclopentanone **F** selectively. Notably, this stereospecificity of the migration is unaffected when varying the R^1 and R^2 groups to methyl, alkyl, and aryl groups, thereby truly reflecting this significant γ -effect. The object of this work is to clarify if an *anti* or *syn* activation occurs in carbocations with a gold substituent in the γ -position, as in carbocations **F** or **F'**.


Scheme 1. Strategy to study the γ -substituent effect.

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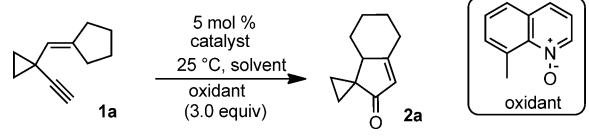
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Table 1 shows the oxidative cyclization of 1,4-enyne **1a** by using 8-methylquinoline oxide (3 equiv) as the oxidant in the presence of different catalysts. The feasibility of this reaction

Table 1: Activity screening using various catalysts.



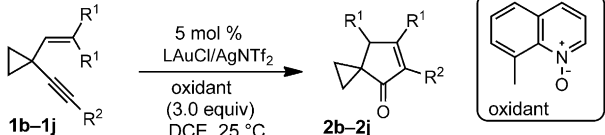
Entry	Catalyst ^[a]	Solvent	t [h]	Yield [%] ^[b] 1a	2a
1	AuCl ₃	DCE	1	—	52
2	PPh ₃ AuCl/AgNTf ₂	DCE	2	—	48
3	LAuCl/AgNTf ₂	DCE	0.5	—	82
4	IPrAuCl/AgNTf ₂	DCE	1	—	36
5	LAuCl/AgOTf	DCE	0.5	—	71
6	LAuCl/AgSbF ₆	DCE	0.5	—	66
7	AgNTf ₂	DCE	24	60	—
8	HOTf	CH ₂ Cl ₂	12	76	—
9	LAuCl/AgNTf ₂	CH ₂ Cl ₂	1	—	62
10	LAuCl/AgNTf ₂	CH ₃ CN	1	—	55

[a] [Substrate] = 0.027 M, L = P(*t*Bu)₂(*o*-biphenyl). IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene. [b] Product yields are reported after purification from a silica gel column.

is reflected by AuCl₃ (5 mol%) in dichloroethane (DCE, 25 °C), which gave the desired oxidative cyclization product **2a** in 52 % yield (Table 1, entry 1); this process involves a ring expansion of a cyclopentylidene moiety while retaining a cyclopropane ring. We tested further the reaction with cationic gold catalysts; P(*t*Bu)₂(*o*-biphenyl)AuNTf₂ gave compound **2a** in 82 % yield, better than PPh₃AuNTf₂ (48 %) and IPrAuNTf₂ (36 %) (Table 1, entries 2–4). Other counter anions, such as in LAuOTf and LAuSbF₆ [L = P(*t*Bu)₂(*o*-biphenyl)], gave decreased yields with 71 % and 66 %, respectively (Table 1, entries 5–6). AgNTf₂ and HOTf alone failed to give the desired product **2a** under similar conditions (Table 1, entries 7–8). For LAuNTf₂, the reactions proceeded less efficiently in dichloromethane and CH₃CN, giving cyclopentenone **2a** in 62 % and 55 % yield, respectively (Table 1, entries 9–10).

We tested this oxidative reaction on additional 1,4-enynes **1b–1j** to examine the substrate scope; the reactions were performed with LAuNTf₂ (5 mol %) and 8-methylquinoline oxide (3 equiv) in DCE (25 °C). As shown in Table 2, entries 1–3, the reactions are extensible to internal alkyne substrates **1b–1d** bearing electron-deficient phenyl substituents (R² = 4-XC₆H₄, X = F, CN, and NO₂); the resulting cyclopentenone products **2b–2d** were obtained in 83–91 % yield. The molecular structure of compound **2d** was characterized by X-ray diffraction.^[13] We also prepared 1,4-enyne **1e** bearing a cyclohexylidene moiety; its Au-catalyzed reaction gave the desired cyclopentenone **2e** including a fused seven-membered ring (Table 2, entry 4). Such oxidative ring expansions were also operable for internal alkynes **1f** (R² = Me), **1g** (R² = Ph), and **1h** (R² = 4-MeCOC₆H₄) to give expected products **2f–2h** in (72–78 %) yield (Table 2, entries 5–7). The reaction is further extensible to the synthesis of eight-

Table 2: 1,4-Enynes bearing two equivalent alkenyl substituents.^[a]



Entry	2 (yield [%]) ^[b]	t [h]	Entry	2 (yield [%]) ^[b]	t [h]
1	2b (83)	6.5	6	2g (72)	12
2	2c (89)	7	7	2h (78)	0.5
3	2d (91)	7	8	2i (71)	1
4	2e (78)	0.5	9	2j (86)	3
5	2f (75)	2.5			

[a] [substrate] = 0.027 M, L = P(*t*Bu)₂(*o*-biphenyl). [b] Product yields are reported after purification from a silica gel column.

membered carbocycle **2i** (71 % yield) by using cycloheptylidene derivative **1i**. We tested the reaction on a propylidene substrate **1j** that afforded the vicinal dimethyl cyclopentenone **2j** in 86 % yield.

We prepared both *E*- and *Z*-configured 1,4-enynes **3a–f** to assess the migration ability of the alkenyl *cis*- and *trans*-substituents (Table 3). With *E*-configured olefins, the reactions proceeded more rapidly than with their corresponding *Z*-isomers, because the former easily attain conformation **E** (see Scheme 1, size: R² > R¹). For 1,4-enyne **E-3a**, we observed a 1,2-methyl migration for its resulting product **4a** (Table 3, entry 1), but for its *Z*-isomer **Z-3a**, a 1,2-phenyl shift occurred to deliver a distinct regioisomer **4a'** (entry 2). These observations reveal that the *cis*-position is the preferable migration site. As shown in Table 3, entries 3–6, the 1,2-shifts of the *cis*-substituents are again observed for 1,4-enynes **E-3b**, **E-3c**, **Z-3b**, and **Z-3c** bearing different electron-rich or

Table 3: Oxidative cyclization of 1,4-enynes in *E*- and *Z*-forms.^[a]

Entry	3	4 (yield [%]) ^[b]	t [h]	Entry	3	4 (yield [%]) ^[b]	t [h]
1		 4a (78)	0.5	10		 4e' (71)	5
2		 4a' (81)	2	11		 4f (71)	7
3		 4b (72)	0.5	12		 4f' (73)	10
4		 4c (79)	0.5				
	Ar = 4-ClC ₆ H ₄						
	Ar = 4-MeOC ₆ H ₄						
5		 4b' (77)	2.5	13		 4g (76)	0.5
6		 4c' (83)	1.5				
	Ar = 4-MeOC ₆ H ₄						
7		 4d (62)	1	14		 4g' (43) + 4g (34)	1.5
	Ar = 4-OMeC ₆ H ₄						
8		 4d' (68)	4	15		 4h (67)	8
9		 4e (79)	1	16		 4h' (64)	15

[a] [Substrate] = 0.027 M, 5 mol %, LAuNTf₂ L = P(*t*Bu)₂(*o*-biphenyl); oxidant (3 equiv), DCE, 25 °C.

[b] Product yields are reported after purification by using a silica gel column.

electron-deficient benzenes, giving cyclopentenone derivatives **4b** and **4c** (72% and 79%) through a 1,2-methyl migration and their regioisomers **4b'** and **4c'** (77% and 83%) through a 1,2-phenyl shift. We tested the ring expansions on substrates **E-3d** and **Z-3d**, which conformed to the same migration pattern to give desired products **4d** and **4d'** selectively. Such a site selectivity works well with *E*- and *Z*-configured olefins **3e** bearing ethyl and phenyl groups; their corresponding products **4e** and **4e'** were obtained in satisfactory yields (79–71%, Table 3, entries 9,10). This stereospecificity of the migration is applicable to 1,4-enynes **E-3f** and **Z-3f** bearing two distinct methyl and benzyl groups, delivering desired products **4f** and **4f'** in 71% and 73% yields,

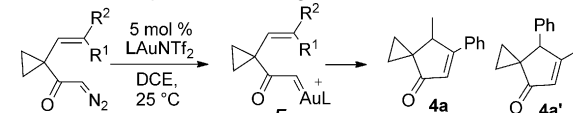
respectively (Table 3, entries 11,12). The oxidative cyclization of disubstituted olefin **E-3g** is compatible with our expectation to give only species **4g** in 76% yield (Table 3, entry 13), whereas its *Z*-isomer **Z-3g** gave a mixture of cyclopentenone species **4g** (34%) and **4g'** (43%), which were separable by using silica column chromatography (entry 14). We believe that a portion of species **4g** in entry 14 was produced from an intrinsic deprotonation in the proposed intermediate **F** (or **F'**; Scheme 1, R² = H). This stereoselective migration pattern also occurs with internal alkyne substrates **E-3h** and **Z-3h**, producing desired products **4h** and **4h'**, respectively. The fact that only *cis*-substituents are transferable for various aryl, methyl, and alkyl substituents strongly indicates the pronounced γ -effect of Au to direct a 1,2-shift with stereospecificity.

Table 4 depicts our control experiments to confirm the intermediacy of oxo gold carbenes **E**. We prepared diazo-containing *E*-configured olefin **E-5**, and its treatment with gold catalyst (5 mol %) gave only cyclopentenone **4a** in 64% yield with a methyl migration (Table 4, entry 1). For its *Z*-isomer **Z-5**, we obtained the other regioisomer **4a'** in 68% yield with a 1,2-phenyl migration (Table 4, entry 2); compound **4a'** represents the product from a typical Wagner–Meerwein rearrangement. Again, only *cis*-substituents are found to migrate. Entries 3–6 (Table 4) illustrate the ligand effects of gold catalysts on the Wagner–Meerwein rearrangement. A large electron-

deficient phosphite ligand as in AuP(OPh)₃NTf₂ (5 mol %) gave the Wagner–Meerwein product **4a'** as the major species (44%) when using *E*-configured olefin **E-5** (entry 3); this phosphite ligand gave **4a'** exclusively with *Z*-configured olefin **Z-5** (entry 4). In contrast, the small ligand in Au(PMe₃)NTf₂ gave the methyl migration product **4a** (45%) preferably with **E-5** (entry 5). Accordingly, the γ -effect is more prominent for an electron-rich phosphine ligand according to the observed trend: P(*t*Bu)₂(*o*-biphenyl) > PMe₃ > P(OPh)₃.

We tested also the migratory cyclizations of diazo species **Z-5** or **E-5** with other metal carbene intermediates (Table 5). [Rh₂(OAc)₄] (0.05 mol %) also showed a 1,2-shift of the

Table 4: Control experiments and ligand effects.

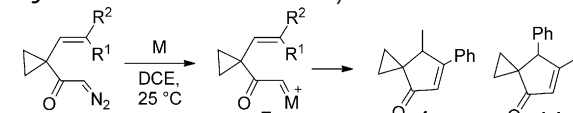


$R^1 = \text{Me}, R^2 = \text{Ph}$ (**E-5**)
 $R^1 = \text{Ph}, R^2 = \text{Me}$ (**Z-5**)

Entry	Diazo ^[a]	Ligand(L)	<i>t</i> [h]	Yield [%] ^[b]	
				4 a	4 a'
1	E-5	P(<i>t</i> Bu) ₂ (<i>o</i> -biphenyl)	0.5	64	—
2	Z-5	P(<i>t</i> Bu) ₂ (<i>o</i> -biphenyl)	1.0	—	68
3	E-5	P(OPh) ₃	0.5	29	44
4	Z-5	P(OPh) ₃	2	—	80
5	E-5	PMe ₃	0.5	45	27
6	Z-5	PMe ₃	2	—	78

[a] [substrate] = 0.027 M. [b] Product yields are reported after purification by using a silica gel column.

Table 5: Reaction with other metal catalysts.



$R^1 = \text{Me}, R^2 = \text{Ph}$ (**E-5**)
 $R^1 = \text{Ph}, R^2 = \text{Me}$ (**Z-5**)

Entry	Diazo ^[a]	M (mol %)	<i>t</i> [h]	Yield [%] ^[b]	
				4 a	4 a'
1	E-5	[Rh ₂ (OAc) ₄] (0.05)	0.5	56	—
2	Z-5	[Rh ₂ (OAc) ₄] (0.05)	0.5	—	65
3	E-5	Cu(OTf) ₂ (1)	2.5	—	77
4	Z-5	Cu(OTf) ₂ (1)	3.0	—	79
5	E-5	AgSbF ₆ (5)	1.0	—	68
6	Z-5	AgSbF ₆ (5)	2.0	—	71
7	E-5	LAGbF ₆ (5)	8.0	16	60
8	E-5	LAGNTf ₂ (5)	12.0	21	47

[a] [Substrate] = 0.027 M. L = P(*t*Bu)₂(*o*-biphenyl). [b] Product yields are reported after purification by using a silica gel column.

alkenyl *cis*-substituent to give cyclopentenone derivatives **4a** and **4a'**, respectively, from **E-5** and **Z-5** diazo species (Table 5, entries 1–2). Notably, the use of both Cu(OTf)₂ (1 mol %) and AgSbF₆ (5 mol %) resulted in a typical Wagner–Meerwein rearrangement to give species **4a'** (68–79%), when using either **E-5** or **Z-5** olefins species (Table 5, entries 3–6). But electron-rich phosphine-containing silver catalysts, LAgX (X = SbF₆, NTf₂) gave the methyl migration product **E-5** in 16% and 21% yields respectively (Table 5, entries 7–8).

The control experiments confirm the intermediacy of α -oxo gold carbenes **E** in our working mechanism (Scheme 1), but we are still uncertain about the role of two possible carbocations **F** and **F'** to produce the resulting cyclopentenones **4**. We sought information from density functional theory on the 1,2-shifts of two possible carbocations **F** and **F'**,^[14,15] these calculations were performed using the B3LYP/LANL2DZ and B97D/LANL2DZ methods, with AuL = P(*t*Bu)₂PhAu in the gaseous phase. We also used the Onsager model^[16] and the PCM^[17] (polarized continuum model) to

consider the solvent effects (in dichloroethane); the results are provided in Figure 1 and Figure S1 in the Supporting Information, respectively; the computational results on the two solvent models gives well agreeable conclusions. Figure 1

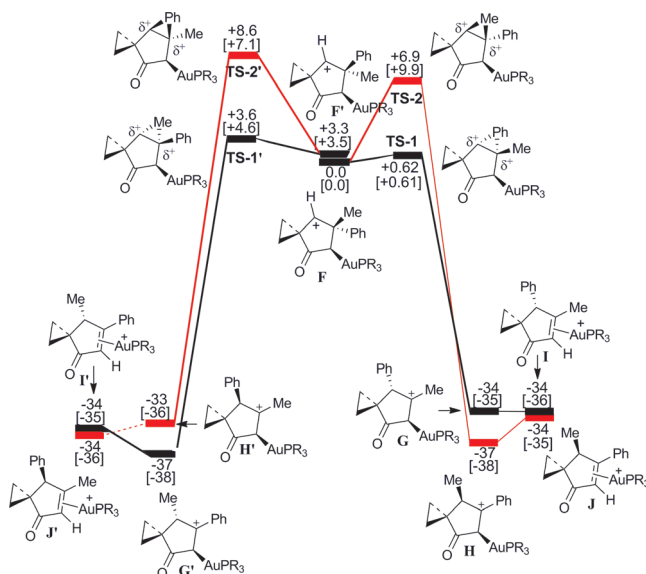
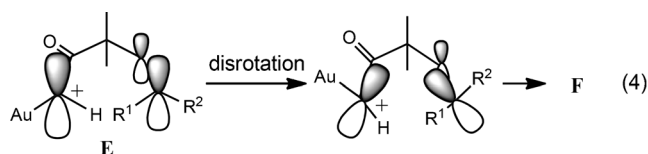


Figure 1. Energy profiles for four possible 1,2-migrations. The black line corresponds to the observed path. DFT calculations were performed by using the B3LYP/LANL2DZ method in the gaseous phase (values in []), and the Onsager method was used to consider solvent effects in dichloromethane (values without brackets). Energies are given in kcal mol^{−1}. PR₃ = P(*t*Bu)₂Ph.

presents the results of calculations to assess four possible 1,2-shifts on the two carbocations. For carbocation **F**, a 1,2-phenyl shift has a barrier ($\Delta H^{\ddagger}_{\text{sol}} = +0.62$ kcal mol^{−1}) much smaller than that of a methyl shift ($\Delta H^{\ddagger}_{\text{sol}} = +6.9$ kcal mol^{−1}). On its diastereomer **F'**, we obtained a small barrier for a methyl migration ($\Delta H^{\ddagger}_{\text{sol}} = +3.6$ kcal mol^{−1}), but a large activation energy for a phenyl shift ($\Delta H^{\ddagger}_{\text{sol}} = +8.6$ kcal mol^{−1}). These differences (> 5.0 kcal mol^{−1}) are significant to distinguish the *syn* and *anti* activation. These results clearly suggest that a gold substituent in the γ -position in the two cationic intermediates activates a 1,2-shift of the β -*anti* substituent through hyperconjugation. As a large amount of enthalpic energy (> 30 kcal mol^{−1}) is released for these transpositions, these 1,2-migrations should be irreversible. Accordingly, the migrations with smaller barriers, that is, **F** → **TS-1** → **G** and **F'** → **TS-1'** → **G'** will become the dominant pathways. The geometries of carbocations **H**, **G** and **H'**, **G'** resemble those of π -alkene complexes **I**, **J** and **I'**, **J'**, because their energy levels are very close to each other.

We rule out the intermediacy of **F'** in Scheme 1, because its corresponding *syn*-activation (**F'** → **4**) is inconsistent with our computational results. Our control experiments in Table 4 also support an *anti*-activation route, because the stereospecificity of the migration is more prominent when a small electron-rich ligand, as in PMe₃Au⁺, is used than when a large electron-deficient ligand, as in P(OPh)₃Au⁺, is used; ligand

size is not a decisive factor. The postulated route **E**→**F** is easily comprehensible, because this disrotation route allows an efficient overlap between two interacting p orbitals in the early stage of rotation [Eq. (4)], whereas the conrotation fails to give an overlap until the late stage of rotation.



To date, there is no example of the Wagner–Meerwein rearrangement where a metal substituent in the γ -position can direct a 1,2-shift of the neighboring group with stereospecificity. To demonstrate this γ -effect, we sought the solution from the gold-catalyzed cyclization of 1,4-enynes **1**; in this cyclization only the *cis*-alkenyl substituent is transferable. Our control experiments suggest the intermediacy of α -carbonyl gold carbenes **E'**. We performed theoretical calculations to demonstrate a preferable *anti* activation for two possible carbocations **F** and **F'**. Both experimental and theoretical work disclose that a gold substituent in the γ -position can direct a 1,2-shift of the *anti*- β -substituent regardless of its intrinsic properties. This discovery provides insight into a new aspect of the Wagner–Meerwein rearrangement.

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