Rearrangement

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

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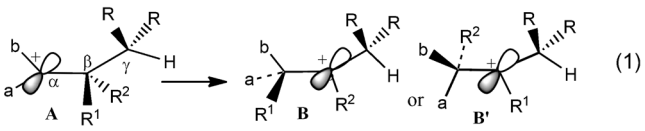
The Wagner–Meerwein rearrangement refers to a 1,2-shift of an alkyl, aryl, and alkenyl group to an adjacent carbocationic center; formation of this carbon–carbon bond has found widespread applications in many Lewis acid or Brønsted acid mediated reactions [Eq. (1)].[1,2] For this well-known reaction, 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.

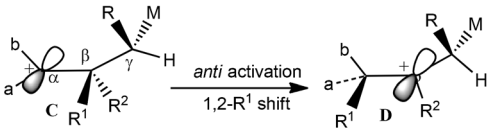
Shown in Scheme 1 is our strategy to illustrate the γ-substituent effect; the key reaction involves a gold-catalyzed oxidative cyclization of 1,4-enyne **3**.[7,8] The initially formed α-oxo gold carbene **E**[9] is expected to have its olefin π electrons parallel to the positive $^+$Au=C p orbital to 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 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′**.

Wagner–Meerwein Migration

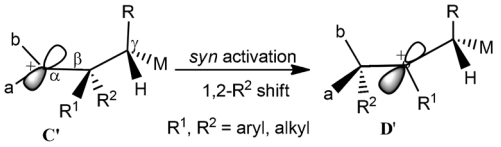


(1)

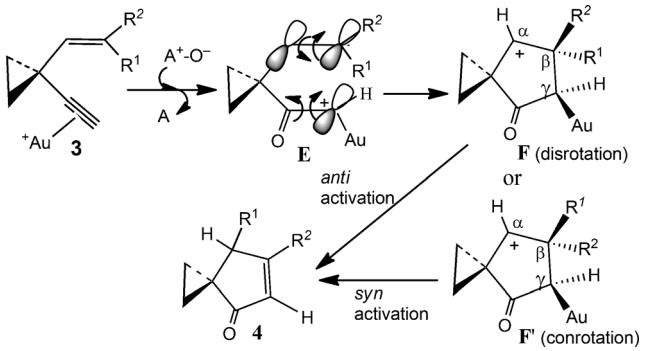
Metal-directing 1,2-migration (this work)



(2)



(3)



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

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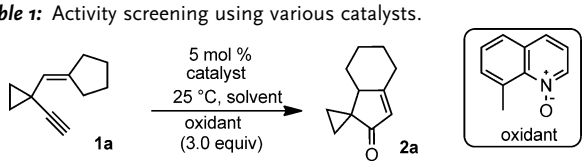
Table 1 shows the oxidative cyclization of 1,4-enyne **1a** by using 8-methylquinoline oxide (3 equiv) as the oxidant in the presence of different catalysts. The feasibility of this reaction

Table 1: Activity screening using various catalysts.



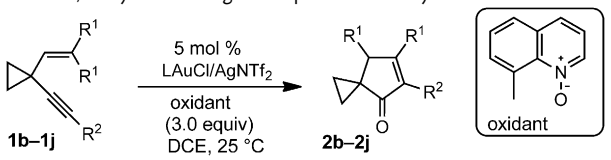
Entry	Catalyst[a]	Solvent	t [h]	Yield [%][b]	
				1a	**2a**
1	$AuCl_3$	DCE	1	–	52
2	$PPh_3AuCl/AgNTf_2$	DCE	2	–	48
3	$LAuCl/AgNTf_2$	DCE	0.5	–	82
4	$IPrAuCl/AgNTf_2$	DCE	1	–	36
5	LAuCl/AgOTf	DCE	0.5	–	71
6	$LAuCl/AgSbF_6$	DCE	0.5	–	66
7	$AgNTf_2$	DCE	24	60	–
8	HOTf	CH_2Cl_2	12	76	–
9	$LAuCl/AgNTf_2$	CH_2Cl_2	1	–	62
10	$LAuCl/AgNTf_2$	CH_3CN	1	–	55

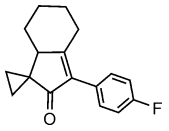
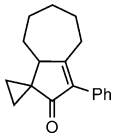
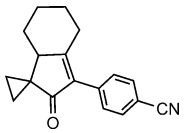
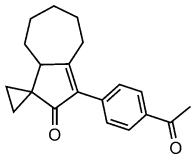
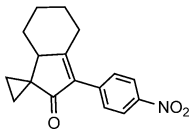
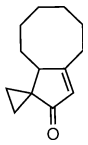
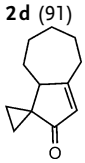
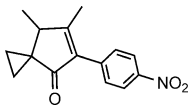
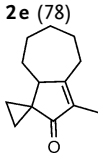
[a] [Substrate] = 0.027 M, L = P(*t*Bu)$_2$(*o*-biphenyl). IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene. [b] Product yields are reported after purification from a silica gel column.

is reflected by $AuCl_3$ (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)$AuNTf_2$ gave compound **2a** in 82% yield, better than PPh_3AuNTf_2 (48%) and $IPrAuNTf_2$ (36%) (Table 1, entries 2–4). Other counter anions, such as in LAuOTf and $LAuSbF_6$ [L = P(*t*Bu)$_2$(*o*-biphenyl)], gave decreased yields with 71% and 66%, respectively (Table 1, entries 5–6). $AgNTf_2$ and HOTf alone failed to give the desired product **2a** under similar conditions (Table 1, entries 7–8). For $LAuNTf_2$, the reactions proceeded less efficiently in dichloromethane and CH_3CN, 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 $LAuNTf_2$ (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 (R^2 = 4-XC_6H_4, X = F, CN, and NO_2); 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** (R^2 = Me), **1g** (R^2 = Ph), and **1h** (R^2 = 4-$MeCOC_6H_4$) 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-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.

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

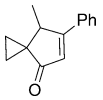
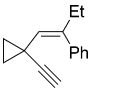
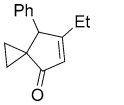
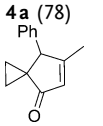
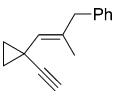
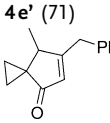
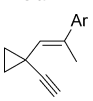
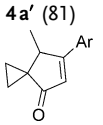
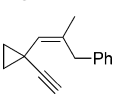
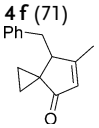
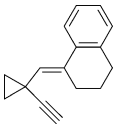
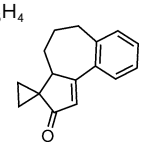
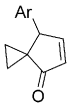
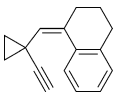
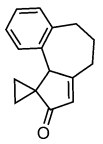
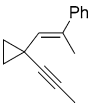
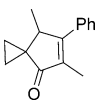
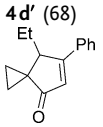
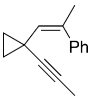
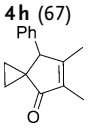


Entry	**2** (yield [%])[b]	t [h]	Entry	**2** (yield [%])[b]	t [h]
1	 **2b** (83)	6.5	6	 **2g** (72)	12
2	 **2c** (89)	7	7	 **2h** (78)	0.5
3	 **2d** (91)	7	8	 **2i** (71)	1
4	 **2e** (78)	0.5	9	 **2j** (86)	3
5	 **2f** (75)	2.5			

[a] [substrate] = 0.027 M, L = P(*t*Bu)$_2$(*o*-biphenyl). [b] Product yields are reported after purification from a silica gel column.

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: $R^2 > R^1$). 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	***E*-3a**[a] 	**4a** (78) 	0.5	10	***Z*-3e** 	**4e'** (71) 	5
2	***Z*-3a** 	**4a′** (81) 	2	11	***E*-3f** 	**4f** (71) 	7
3	***E*-3b** Ar = 4-ClC_6H_4	**4b** (72)	0.5	12	***Z*-3f**	**4f'** (73)	10
4	***Z*-3c** Ar = 4-$MeOC_6H$ 	**4c** (79) 	0.5				
5	***Z*-3b** Ar = 4-ClC_6H_4	**4b′** (77)	2.5	13	***E*-3g** Ar = 4-$MeOC_6H_4$	**4g** (76)	0.5
6	***Z*-3c** Ar = 4-$MeOC_6H_4$ 	**4c′** (83) 	1.5				
7	***E*-3d** 	**4d** (62) 	1	14	***Z*-3g** Ar = 4-$OMeC_6H_4$ 	**4g′** (43) + **4g** (34) 	1.5
8	***Z*-3d** 	**4d′** (68) 	4	15	***E*-3h** 	**4h** (67) 	8
9	***E*-3e**	**4e** (79)	1	16	***Z*-3h**	**4h′** (64)	15

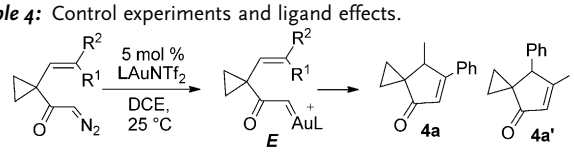
[a] [Substrate] = 0.027 M, 5 mol%, LAuNTf$_2$ L = P(*t*Bu)$_2$(*o*-biphenyl); oxidant (3 equiv), DCE, 25 °C.
[b] Product yields are reported after purification by using a silica gel column.

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, $R^2 = H$). 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)$_3$NTf$_2$ (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(PMe$_3$)NTf$_2$ 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) > PMe_3 > P(OPh)$_3$.

We tested also the migratory cyclizations of diazo species ***Z*-5** or ***E*-5** with other metal carbene intermediates (Table 5). [Rh$_2$(OAc)$_4$] (0.05 mol%) also showed a 1,2-shift of the

Table 4: Control experiments and ligand effects.

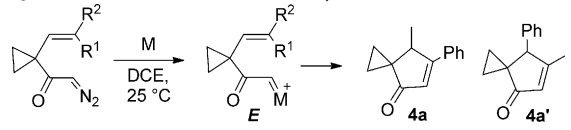


R^1 = Me, R^2 = Ph (***E*-5**)
R^1 = Ph, R^2 = Me (***Z*-5**)

Entry	Diazo[a]	Ligand(L)	*t* [h]	Yield [%][b]	
				4a	**4a′**
1	***E*-5**	P(*t*Bu)$_2$(*o*-biphenyl)	0.5	64	–
2	***Z*-5**	P(*t*Bu)$_2$(*o*-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 = Me, R^2 = Ph (***E*-5**)
R^1 = Ph, R^2 = Me (***Z*-5**)

Entry	Diazo[a]	M (mol%)	*t* [h]	Yield [%][b]	
				4a	**4a′**
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**	$LAgSbF_6$ (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 $AgSbF_6$ (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 = SbF_6, NTf_2) 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)$_2$PhAu 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

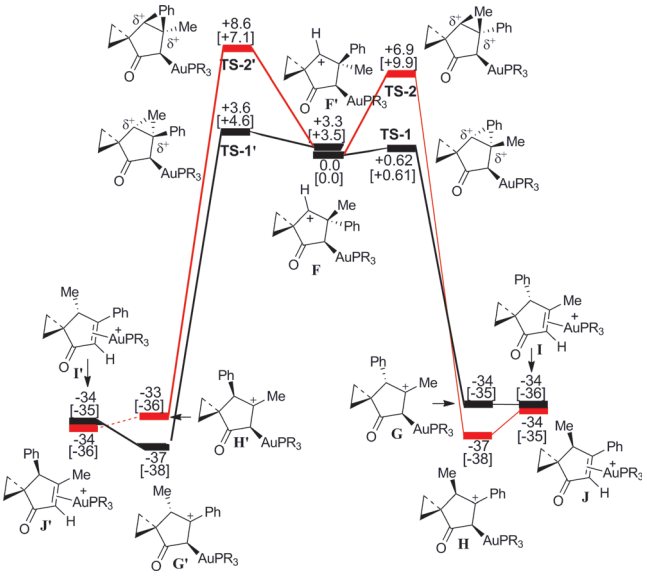
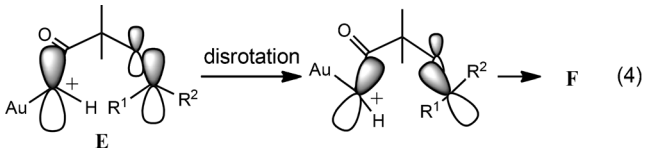


Figure 1. Energy profiles for four possible 1,2-migrations. The black line corresponds to the observed path. DFT calculations were performed by using the B3LYP/LAN2DZ method in the gaseous phase (values in []), and the Onsager method was used to consider solvent effects in dichloromethane (values without brackets). Energies are given in kcal mol^{-1}. PR_3 = P(*t*Bu)$_2$Ph.

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 ($\Delta H^{\neq}_{(sol)}$ = +0.62 kcal mol^{-1}) much smaller than that of a methyl shift ($\Delta H^{\neq}_{(sol)}$ = +6.9 kcal mol^{-1}). On its diastereomer **F′**, we obtained a small barrier for a methyl migration ($\Delta H^{\neq}_{(sol)}$ = +3.6 kcal mol^{-1}), but a large activation energy for a phenyl shift ($\Delta H^{\neq}_{(sol)}$ = +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 PMe_3Au^+, 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.



E

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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[1] a) G. Wagner, *J. Russ. Chem. Soc.* **1899**, *31*, 690; b) H. Meerwein, *Justus Liebigs Ann. Chem.* **1914**, *405*, 129 – 175.

[2] Reviews: a) J. R. Hanson in *Comprehensive Organic Synthesis*, *Vol. 3* (Eds.: B. M. Trost, I. Fleming, G. Pattenden), Pergamon, Oxford, **1991**, chap. 3.1, pp. 705 – 719; b) B. Ricknorn in *Comprehensive Organic Synthesis*, *Vol. 3* (Eds.: B. M. Trost, I. Fleming, G. Pattenden), Pergamon, Oxford, **1991**, chap. 3.2 – 3.3, pp. 721 – 776.

[3] Suginome and co-workers studied a 1,2-γ-silyl shift activated by a γ-silyl group;[3a] the *syn* and *anti* activations relied on the configurations of two silyl groups. In other words, there is no stereospecificity induced by the γ-silyl group. This example is a typical Wagner–Meerwein rearrangement, because both diastereomeric carbocations show the same 1,2-silyl shift; a) M. Suginome, A. Takama, Y. Ito, *J. Am. Chem. Soc.* **1998**, *120*, 1930 – 1931; b) S. M. Starling, S. C. Vonwiller, J. N. H. Reek, *J. Org. Chem.* **1998**, *63*, 2262 – 2272.

[4] For selected example, see: a) P. F. Hudrlik, A. M. Hudrlik, G. Nage-ndrappa, T. Yimenu, E. Zellers, E. Chin, *J. Am. Chem. Soc.* **1980**, *102*, 6894 – 6896; b) K. Miura, T. Hondo, H. Saito, H. Ito, A. Hosomi, *J. Org. Chem.* **1997**, *62*, 8292 – 8293; c) T. Ooi, T. Kiba, K. Maruoka, *Chem. Lett.* **1997**, 519 – 520; d) K. Tanino, N. Yoshitani, F. Moriyama, I. Kuwa-jima, *J. Org. Chem.* **1997**, *62*, 4206 – 4207; e) A. S. K. Hashmi, W. Yang, F. Rominger, *Angew. Chem.* **2011**, *123*, 5882 – 5885; *Angew. Chem. Int. Ed.* **2011**, *50*, 5762 – 5765; f) A. S. K. Hashmi, W. Yang, F. Rominger, *Adv Synth. Catal.* **2012**, *354*, 1273 – 1279; g) A. S. K. Hashmi, W. Yang, F. Rominger, *Chem. Eur. J.* **2012**, *18*, 6576 – 6580.

[5] T. Uyehara, J. Yamada, T. Kato, *Tetrahedron Lett.* **1985**, *26*, 5069 – 5072.

[6] Reviews on 1,2-alkyl migration catalyzed by gold catalysts: a) B. Crone, S. F. Kirsch, *Chem. Eur. J.* **2008**, *14*, 3514 – 3522; b) A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360 – 5369; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232 – 5241; c) A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Aldrichimica Acta* **2010**, *43*, 37 – 46.

[7] For gold-catalyzed oxidative cyclization of 1,5-enyne, see D. Vasu, H.-H. Hung, S. Bhunia, S. A. Gawade, A. Das, R.-S. Liu, *Angew. Chem.* **2011**, *123*, 7043 – 7046; *Angew. Chem. Int. Ed.* **2011**, *50*, 6911 – 6914. The reported reactions herein are unrelated to Wagner – Meerwein rearrangements.

[8] For gold-catalyzed reactions on 1,4-enynes, see selected examples: a) X. Shi, D. J. Gorin, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 5802 – 5803; b) D. Vasu, A. Das, R.-S. Liu, *Chem. Commun.* **2010**, *46*, 4115 – 4117; c) N. Marion, S. Diez-Gonzalez, P. Fremont, A. R. Noble, S. P. Nolan, *Angew. Chem.* **2006**, *118*, 3729 – 3732; *Angew. Chem. Int. Ed.* **2006**, *45*, 3647 – 3650; d) T. T. Haug, T. Harschneck, A. Duschek, C.-U. Lee, J. T. Binder, H. Menz, S. F. Kirsch, *J. Organomet. Chem.* **2009**, *694*, 510 – 514.

[9] Generation of α-carbonyl gold carbenoids through the oxidation of alkynes with pyridine-based oxides; see reference [7] and selected examples: a) J. Xiao, X. Li, *Angew. Chem.* **2011**, *123*, 7364 – 7375; *Angew. Chem. Int. Ed.* **2011**, *50*, 7226 – 7236; b) L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258 – 3259; c) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550 – 8551; d) L. Ye, W. He, L. Zhang, *Angew. Chem.* **2011**, *123*, 3294 – 3297; *Angew. Chem. Int. Ed.* **2011**, *50*, 3236 – 3239; e) W. He, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8482 – 8485; f) A. Mukherjee, R. B. Dateer, R. Chaudhari, S. Bhunia, S. N. Karad, R.-S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 15372 – 15375; g) P. W. Davies, A. Cremonesi, N. Martin, *Chem. Commun.* **2011**, *47*, 379 – 381; h) E. L. Noey, Y. Luo, L. Zhang, K. N. Houk, *J. Am. Chem. Soc.* **2012**, *134*, 1078 – 1084.

[10] For related Au^I- and Ag^I-catalyzed alkene/carbene couplings, see ref. [7] and a) G.-Y. Lin, C.-W. Li, S.-H. Hung, R.-S. Liu, *Org. Lett.* **2008**, *10*, 5059 – 5062; b) A. S. K. Hashmi, M. Burhle, R. Salathe, J. W. Bats, *Adv. Synth. Catal.* **2008**, *350*, 2059 – 2064. Notably, there is no stereospecificity of a migration reported herein.

[11] This bisected conformation allows an efficient interaction of cyclopropyl σ bonding electrons with their adjacent empty p orbital. See reviews: a) G. A. Olah, V. Reddy, G. K. S. Prakash, *Chemistry of the Cyclopropyl Group*, Part 2 (Eds.: Z. Rappoport), Wiley, Chichester, UK, **1995**, pp. 813 – 859; b) G. A. Olah, V. Reddy, G. K. S. Prakash, *Chem. Rev.* **1992**, *92*, 69 – 95.

[12] Cyclopropyl alkynes were often used in gold-catalyzed reactions because of their higher reactivity compared to normal alkynes. See: a) A. Fürstner, C. Aïssa, *J. Am. Chem. Soc.* **2006**, *128*, 6306 – 6307; b) M. Shi, L.-P. Liu, J. Tang, *J. Am. Chem. Soc.* **2006**, *128*, 7430 – 7431; c) C.-W. Li, K. Pati, G.-Y. Lin, S. M. Abu Sohel, H.-H. Hung, R.-S. Liu, *Angew. Chem.* **2010**, *122*, 10087 – 10090; *Angew. Chem. Int. Ed.* **2010**, *49*, 9891 – 9894; d) H. H. Liao, R.-S. Liu, *Chem. Commun.* **2011**, *47*, 1339 – 1341; e) C.-Y. Yang, M.-S. Lin, H.-H. Liao, R.-S. Liu, *Chem. Eur. J.* **2010**, *16*, 2696 – 2699; f) D. J. Gorin, D. G. Watson, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 3736 – 3737; g) S. Ye, Z.-X. Yu, *Org. Lett.* **2010**, *12*, 804 – 807.

[13] CCDC 916773 (**2d**) 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.

[14] All computations were done using the Gaussian 03 package: M. J. Frisch, et al. Gaussian 03, revision C. 02: Gaussian, Inc., Pittsburgh, PA, **2003**.
[15] The B3LYP method, see: a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789; d) The B97D method. see: S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787 – 1799; e) The LANL2DZ basis sets, see: P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270 – 284.
[16] The Onsager model, see: a) M. W. Wong, M. J. Frisch, K. B. Wbierg, *J. Am. Chem. Soc.* **1991**, *113*, 4776 – 4782; b) J. G. Kirkwood, *J. Chem. Phys.* **1934**, *2*, 351 – 361; c) L. Onsager, *J. Am. Chem. Soc.* **1936**, *58*, 1486 – 1493.
[17] The PCM method, see: a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117 – 129; b) M. Cossi, V. Barone, R. Canni, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327 – 335; c) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995 – 2001.

