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Ligand effect of bulky 2,2-dialkyl-1-phosphaethenes on Au-catalyzed cycloisomerization of 1,6-enynes and lactonization of pent-4-ynoic acids

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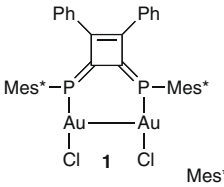
ABSTRACT

2,2-Dimethyl- and 2-benzyl-2-methyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethenes were employed as ligand of mononuclear chlorogold(I) complexes, which catalyzed cycloisomerization of 1,6-enyne affording vinylcyclopentene exclusively in the absence of silver co-catalyst. The reaction mechanisms are discussed based on DFT calculations. In addition to the cycloisomerization, the phosphaalkene–chlorogold(I) complexes catalyzed cyclization of pent-4-ynoic acids providing γ-methylene-γ-lactones under basic conditions.

1. Introduction

Application of phosphaalkene (methylenephosphine) ligands to transition-metal catalysts has been recognized as one of the attractive approaches for organic synthesis [1]. The P=C double bond, which requires suitable stabilization techniques including kinetic protection and thermodynamic perturbation to reduce the inherent instability [2], possesses highly-accepting character due to the low-lying LUMO level [1,3]. In addition, recent studies indicate that σ-donating property of lone pair electrons of phosphorus in the phosphaalkene can be enhanced by substitution effects [4,5]. Recently, a number of unique transition-metal catalysts bearing a DPCB (3,4-diphosphinidenecyclobutene) ligand have been developed especially featuring the π-accepting property of phosphaalkene moiety [1a,b].

In the course of our investigations on low-coordinated organophosphorus compounds in relation to transition-metal catalysis, we found that homogeneous gold catalysts with soft carbophilic Lewis acidity activate carbon–carbon multiple bonds [6]. The highly π-accepting property of phosphaalkene could be effective to raise the Lewis acidity of the gold centers. Furthermore, the σ-donating property of low-coordinated phosphorus would be advantageous for moderate stabilization of putative cationic intermediates [6] in Au-catalyzed transformations. We recently reported [7] that phosphaalkene–chlorogold(I) complexes **1** and **2**, where Mes* stands for 2,4,6-^{t}Bu$_3$C$_6$H$_2$, catalyze cycloisomerization of a 1,6-enyne derivative affording a vinylcyclopentene even in the absence of silver co-catalyst [8]. This finding encouraged us to investigate the detailed properties of phosphaalkene-gold complexes as well as to explore unique organic transformation reactions.



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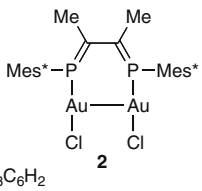

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Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$

To understand fundamental characteristics of phosphaalkene–gold complexes in relation to transition-metal catalysis, phosphaalkene ligands bearing relatively simple substituents are desirable. However, the gold(I) complexes **1** and **2** appeared to involve effects of intramolecular aurophilic interaction [9] due to the presence of two ligating phosphorus atoms in the ligand. These characteristics of **1** and **2** were not sufficient enough to obtain fundamental information to understand much basic effects of phosphaalkene ligand on the gold catalysts.

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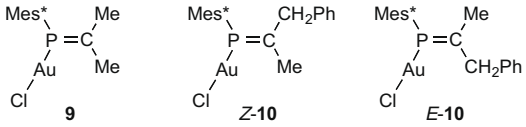
In this paper we studied several mononuclear chlorogold(I) complexes bearing 2,2-dialkyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene ligands in terms of catalytic activity. So far, such plainly substituted phosphaalkenes as those which bear simple alkyl groups have scarcely been studied in relation to coordination chemistry [10]. The simple phosphaalkene-chlorogold(I) complexes showed catalytic activity in cycloisomerization of 1,6-enynes under conditions without silver co-catalyst. Additionally, catalytic activity of the phosphaalkene–gold(I) complexes was examined by use of intramolecular cyclization of pent-4-ynoic acids under basic conditions [11,12].

2. Results and discussion

2.1. Preparation of Au complexes

In this study we first chose a simple methyl group for a substituent in the 2-position of the 2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene moiety, because methyl is considered to be suitable to understand fundamental effects of alkyl group on the phosphaalkene–gold catalysts. Additionally, benzyl group was also employed to evaluate effects of the aromatic ring expecting enhancement in the catalytic activity [13]. 2,2-Dimethyl-1-phosphaethene **6** [10] was synthesized from **4** [4,14] which was prepared from 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene **3** [15]. Similarly, 2-benzyl-2-methyl-1-phosphaethenes *Z*/*E*-**7** were synthesized from 2-bromo-1-phosphapropenes **4** and **5** [16], respectively (Scheme 1). In ^{31}P NMR spectrum, *Z*/*E*-**7** as well as **6** showed a chemical shift in a higher-field compared to that for 2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene **8** (δ_P 288.6) [17], indicating electron-donating effect of the alkyl groups.

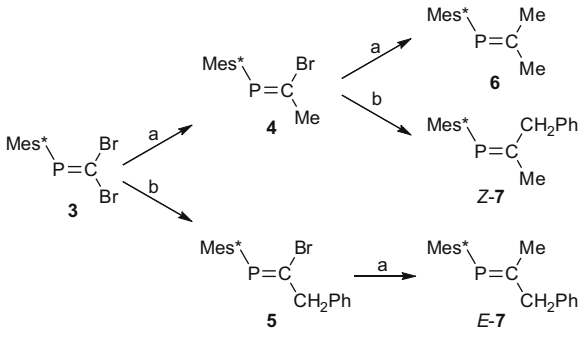
Compounds **6** and *Z*/*E*-**7** were allowed to react with Au(tht)Cl (tht = tetrahydrothiophene) to afford the corresponding mononuclear chlorogold(I) complexes **9** and *Z*/*E*-**10**, respectively, as air and room-temperature stable colorless solid. Although all attempts to recrystallize either complex **9** or **10** resulted in affording amorphous solid, which was not suitable to X-ray crystallography, structures of **9** and **10** were reasonably characterized by spectroscopic measurements. Coordination of gold causes higher-field ^{31}P NMR shift. In ^{1}H NMR spectrum, coordination of gold causes remarkable increase in the $^3J_{PH}$ constants between phosphorus and the CH_2R (R = H, Ph) group. On the other hand, the phenyl group of *E*-**10** showed almost the same chemical shift as that of the corresponding ligand *E*-**7**, indicating almost no significant π-interaction to the gold atom. As for the phenyl group of *Z*-**10**, considerably higher-field shift compared with *Z*-**7** was observed in ^{1}H NMR spectrum due to diatropic ring-current effect of the Mes* ring. Thus, the gold center of **10** does not seem to be influenced by the benzyl group. It is worth mentioning that the presence of alkyl groups is effective to the stability of **9** and **10**, because the chlorogold(I) complexes bearing **8** is not stable enough to allow isolation.



2.2. Au-catalyzed cyclizations

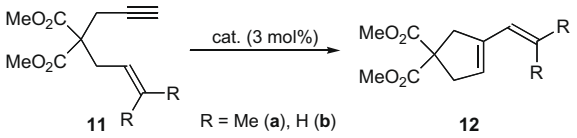
We next examined catalytic activity of **9** and **10** in the cycloisomerization of 1,6-enyne derivatives **11** [8]. Similar to **1** and **2** [7], **9** and **10** catalyzed sluggish but exclusive conversion of **11a** to vinylcyclopentenes **12a** [8] at ambient temperature in the absence of silver co-catalyst under open-air conditions (Table 1, Entry 1–3). On the other hand, use of distilled dichloromethane (dried from phosphorus pentoxide) inhibited the reaction from **11a** to **12a**, suggesting that the cycloisomerization of **11a** catalyzed by **9** or **10** presumably requires the presence of water as an activator of the gold center [18a,b]. In the case of **11b**, **9** and **10** did not accelerate cycloisomerization at an ambient temperature. Therefore, we examined reaction of **11b** in the presence of **9** or **10** at higher temperature (70 °C in 1,2-dichloroethane) and observed an *exo-dig* process to the corresponding vinylcyclopentene **12b** in moderate yields (Table 1, Entry 4–6). Interestingly, no isomer **13** was formed under these conditions, while the reaction conditions with AuCl- or $AlCl_3$-catalyst showed non-specificity [18c]. Furthermore, formation of **12b** exhibits a sharp contrast to the previous finding by Echavarren et al. that the combination of $Au(PPh_3)Cl/AgSbF_6$ gave a cyclohexene derivative **14b** from **11b** mainly via the 6-*endo-dig* mechanism [8]. On the other hand, in the reaction of **11b**, we could not characterize any side products except for a small amount of the remaining starting material [19]. Both **9** and **10** showed almost the same catalytic activity, indicating that benzyl and methyl groups are practically identical in the employed ligands (**6** and **7**). Comparison of the yield of **12b** by catalyst *Z*-**10** with that of *E*-**10** suggests that steric hindrance may influence the catalytic activity.

Fig. 1 shows a proposed mechanism of the present cycloisomerization reaction, where **11** gives **12** being catalyzed by low-coordinated phosphaalkene–ligated gold. In this catalytic cycle, π-coordination of an alkyne moiety to gold initiates the reaction to form **B**, and the resulting intermediate **C** appears to give **D** through a homoallyl cation rearrangement leading to the formation of the



Scheme 1. Preparation of phosphaalkenes. *Reagents and conditions*: (a) i: ^{n}BuLi, THF, ii: MeI, −78 °C and (b) i: ^{n}BuLi, THF, ii: $PhCH_2Br$, −78 °C.

Table 1
Cycloisomerization of **11** affording **12**.



Entry	R	Cat.	Solvent	Temp. (°C)	Time (h)	Yield (%)
1	Me	**9**	CH_2Cl_2	20	24	Quant. [a]
2	Me	*E*-**10**	CH_2Cl_2	20	24	Quant.[a]
3	Me	*Z*-**10**	CH_2Cl_2	20	24	Quant.[a]
4	H	**9**	$ClCH_2CH_2Cl$	70	4	76
5	H	*E*-**10**	$ClCH_2CH_2Cl$	70	4	63
6	H	*Z*-**10**	$ClCH_2CH_2Cl$	70	4	72

[a] Determined by ^{1}H NMR.

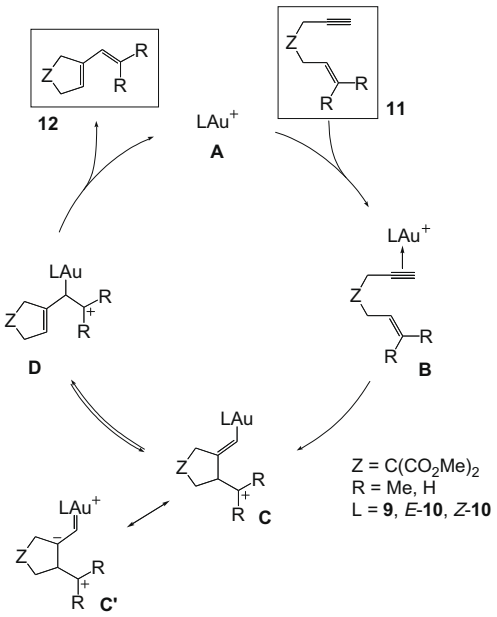
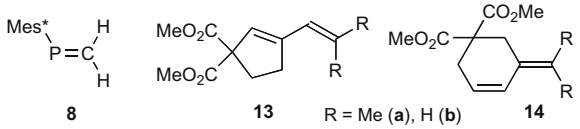


Fig. 1. Proposed reaction mechanism of cycloisomerization assisted by low coordinated phosphaalkene–Au catalyst. Counter anions (Cl^-) are omitted.

product with elimination of gold catalyst **A**, which corresponds to the single cleavage procedure as discussed in the previous reports [6c,8]. We have to point out that the homoallyl cation rearrangement of **C** or **C′** (one of the resonance forms) may include the contribution of a cyclopropylcarbene **C″** (a constitutional isomer of **C**) as described previously (Fig. 2), [6c,8,20]. However, in taking a number of findings of gold-catalyzed cyclization of enyne derivatives into account, cyclopropyl carbenoids such as **C″** should be judged as an imaginary formula, whereas cationic intermediates should be predominant in the reaction course [6k].

Concerning the formation of **C**, it is worth mentioning that the computational study has found structure **E** (Fig. 2) as one of the optimized structures in a model reaction of 7-methyloct-6-en-1-yne assisted by gold(I) metal with $HP=CH_2$ ligand on the B3LYP/6-31G* (C,H,P) /LanL2DZ (Au) level [21], whereas **C′** could also be considered as has been discussed elsewhere [6k,8]. On the other hand, computational calculation on the reaction of hept-1-en-6-yne turned out that **F** (Fig. 3) is an optimized structure, which will lead to the formation of the product of **14** type, suggesting steric encumbrance of the ligands as well as shorter P(sp^2)–Au distances than the regular P(sp^3)–Au might play a key role in the present regioselectivity in these kinetically controlled pathways [8,18b]. Other mechanisms might be considered because the proposed mechanism described in Fig. 1 includes generation of less preferable primary carbocation intermediates in the case of **11b**. Indeed, an alternative reaction mechanism via **G** (Au···CMe_2 3.855 Å), which is energetically less stable by 3.3 kcal/mol than **E**, might not be excluded leading to the formation of bicyclo[3.2.0]hept-5-ene [8b] after reductive elimination in the cycloisomerization, although no experimental evidence to support this mechanism has been obtained so far [12].



As a related subject of cycloisomerization of 1,6-enynes, we examined cyclization of pent-4-ynoic acids affording γ-methylene-γ-lactones. Whereas Utimoto and coworkers reported cyclization of **15** affording **16** by use of palladium(II) catalyst in the presence of triethylamine [11a], **9** catalyzed the *exo-dig* cyclization of **15** in the presence of pyridine at room temperature under open-air conditions to give the corresponding γ-methylene-γ-lactone **16** in a good yield (Scheme 2). Thus, pyridine, though potentially a ligand to transition metals, did not influence the gold catalyst

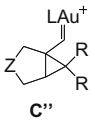
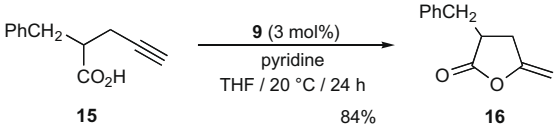


Fig. 2. An alternative contribution for **C** (or **C′**).



Scheme 2. Cyclization of 2-benzylpent-4-ynoic acid **15**.

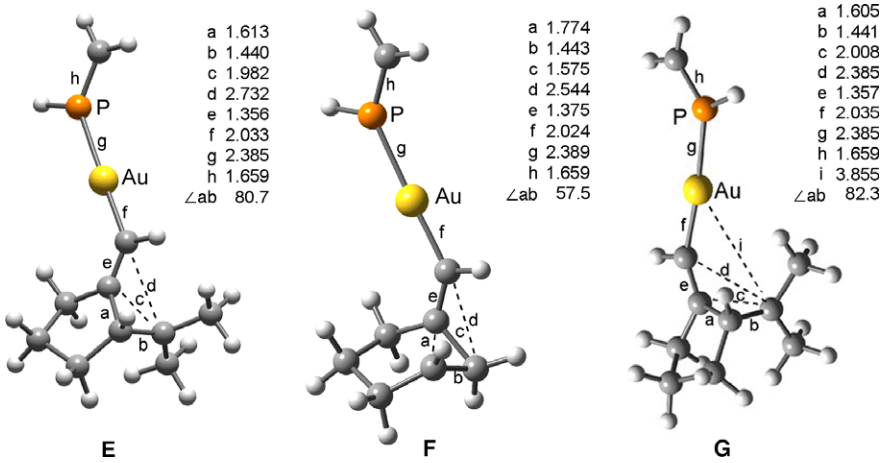
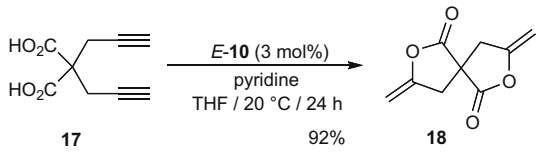


Fig. 3. Optimized structures related to the cycloisomerization reaction (**E**–**G**) at B3LYP/6-31G* (C, H, P)/LanL2DZ (Au) level. Selected geometrical parameters (length: Å; angle: °) are shown. Dihedral angles (Au–C–C–CH_2) for **E**, **F**, and **G** are −165.5°, −9.8°, and 169.5°, respectively.



Scheme 3. Cyclization of 2,2-di(prop-2-ynyl)malonic acid **17**.

but plausibly activated the carboxylic acid moiety. In the reaction of **15** with **9** and triethylamine, however, an unidentified product was obtained although the starting material was consumed. Thus, catalyst **9** requires moderately basic conditions for the cyclization compared with the palladium(II) catalysis. In addition to **9**, *E*-**10** catalyzed cyclization of **17** to the corresponding spiro product **18** in good yield (Scheme 3) [11b,c].

3. Conclusion

Mononuclear chlorogold(I) complexes ligated with 2,2-dialkyl-1-phosphaethene ligand (**9**, **10**) catalyzed regioselective cycloisomerization of 1,6-enynes **11** affording vinylcyclopentenes **12** exclusively via activation of the C≡CH moiety without silver co-catalyst. DFT calculation of the model compounds indicated the inherent electronic properties of the P=C structure for effective generation of cationic intermediates. Additionally, we have succeeded in catalytic cyclization of pent-4-ynoic acids to γ-methylene-γ-lactones by use of **9** or **10** in the presence of pyridine. Thus, we confirmed that the phosphaalkene ligand is effective to promote catalytic activity of the chlorogold(I) complexes. On the other hand, computational studies based on the conventional mechanisms of cycloisomerization of 1,6-enyne would require more detailed analysis to elucidate ligand effect of phosphaalkenes on gold catalysis. Studies on detailed mechanism of the catalytic activity and application to organic synthesis for various functional molecules are underway.

4. Experimental

All manipulations were carried out under an argon atmosphere by the standard Schlenk technique. All solvents employed were dried by appropriate methods. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker Avance 400 spectrometer with Me_4Si (^{1}H, ^{13}C) and H_3PO_4 (^{31}P) as internal and external standards. Mass spectra were recorded with a Bruker APEX3 spectrometer. Compounds **3** [15], **4** [14], **5** [16], **11a** [23], **11b** [24], **15** [25], and **17** [26] were prepared according to the literature methods.

4.1. Compound *6*

To a solution of **4** (1.00 g, 260 mmol) in THF (40 mL) was added butyllithium (2.64 mmol, 1.4 M in hexane solution, 1 M = 1 mol dm^{-3}) at −78 °C and stirred for 5 min. Iodomethane (3.9 mmol) was added to the mixture at −78 °C and gradually allowed to warm to room temperature. The volatile materials were removed in vacuo and the residue was purified by column chromatography (SiO_2, hexane) to afford 290 mg of **6** (29% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23 (d, $^{3}J_{PH}$ = 13.6 Hz, 3H, Me), 1.34 (s, 9H, *p*-^{t}Bu), 1.60 (s, 18H, *o*-^{t}Bu), 2.12 (d, $^{3}J_{PH}$ = 24.8 Hz, 3H, Me), 7.39 (d, $^{4}J_{PH}$ = 1.2 Hz, 2H, Mes*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 243.4 [10].

4.2. Compound *Z*-*7*

To a solution of **4** (400 mg, 1.04 mmol) in THF (15 mL) was added butyllithium (1.05 mmol) at −78 °C and stirred for 5 min. Benzyl bromide (1.56 mmol) was added to the mixture at −78 °C and gradually allowed to warm to room temperature. The volatile materials were removed in vacuo and the residue was purified by column chromatography (SiO_2, hexane) to afford 120 mg of *Z*-**7** (29% yield): Colorless solid, m.p. 83–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.34 (s, 9H, *p*-^{t}Bu), 1.50 (s, 18H, *o*-^{t}Bu), 2.04 (d, $^{3}J_{PH}$ = 25.2 Hz, 3H, Me), 2.84 (d, $^{3}J_{PH}$ = 11.6 Hz, 2H, CH_2), 6.75–6.81 (m, 2H, Ph), 7.08–7.17 (m, 3H, Ph), 7.41 (d, $^{4}J_{PH}$ = 1.2 Hz, 2H, Mes*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 226.4; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 25.3 (d, $^{2}J_{PC}$ = 46.8 Hz, Me), 31.4 (s, *p*-C*Me*$_3$), 33.1 (d, $^{4}J_{PC}$ = 7.3 Hz, *o*-C*Me*$_3$), 35.0 (s, *p*-C*Me*$_3$), 38.0 (s, *o*-C*Me*$_3$), 44.5 (d, $^{2}J_{PC}$ = 16.2 Hz, CH_2), 121.4 (s, *m*-Mes*), 125.9 (s, *p*-Ph), 127.9 (s, *m*-Ph), 129.6 (s, *o*-Ph), 137.4 (d, $^{1}J_{PC}$ = 58.8 Hz, *ipso*-Mes*), 138.7 (d, $^{3}J_{PC}$ = 6.7 Hz, *ipso*-Ph), 149.6 (s, *p*-Mes*), 154.0 (s, *o*-Mes*), 182.0 (d, $^{1}J_{PC}$ = 42.5 Hz, P=C); ESI-MS calcd for $C_{27}H_{39}P$+Na, 417.2682, found: *m*/*z* 417.2681; Anal. Calc. for $C_{27}H_{39}P$: C, 82.19; H, 9.96. Found: C, 82.20; H, 9.77%.

4.3. Compound *E*-*7*

To a solution of **5** (300 mg, 0.65 mmol) in THF (15 mL) was added butyllithium (0.66 mmol) at −78 °C and stirred for 5 min. Iodomethane (0.97 mmol) was added to the reaction mixture at −78 °C and gradually allowed to warm to room temperature. The volatile materials were removed in vacuo and the residue was purified by column chromatography (SiO_2, hexane) to afford 221 mg of *E*-**7** (86% yield): Colorless solid, m.p. 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.11 (d, $^{3}J_{PH}$ = 14.0 Hz, 3H, Me), 1.31 (s, 9H, *p*-^{t}Bu), 1.46 (s, 18H, *o*-^{t}Bu), 3.73 (d, $^{3}J_{PH}$ = 21.2 Hz, 2H, CH_2), 7.17–7.28 (m, 5H, Ph), 7.37 (brs, 2H, Mes*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 228.3; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 23.0 (d, $^{2}J_{PC}$ = 16.6 Hz, CH_2), 31.3 (s, *p*-C*Me*$_3$), 32.4 (d, $^{4}J_{PC}$ = 7.3 Hz, *o*-C*Me*$_3$), 34.9 (s, *p*-C*Me*$_3$), 38.0 (s, *o*-C*Me*$_3$), 47.5 (d, $^{2}J_{PC}$ = 43.6 Hz, Me), 121.4 (s, *m*-Mes*), 126.2 (s, *p*-Ph), 128.1 (s, *m*-Ph), 129.1 (s, *o*-Ph), 137.7 (d, $^{1}J_{PC}$ = 58.5 Hz, *ipso*-Mes*), 139.3 (d, $^{3}J_{PC}$ = 13.7 Hz, *ipso*-Ph), 149.6 (s, *p*-Mes*), 153.7 (d, $^{2}J_{PC}$ = 1.3 Hz, *o*-Mes*), 182.9 (d, $^{1}J_{PC}$ = 40.7 Hz, P=C); ESI-MS calcd for $C_{27}H_{39}P$+Na, 417.2682, found: *m*/*z* 417.2681; Anal. Calc. for $C_{27}H_{39}P{\cdot}0.1H_2O$: C, 81.81; H 9.97. Found: C, 81.71; H, 10.06%.

4.4. Compound *9*

A mixture of **6** (120 mg, 0.38 mmol) and Au(tht)Cl (0.22 mmol) in dichloromethane (10 mL) was stirred for 12 h at room temperature. The volatile materials were removed in vacuo and the residue was washed with hexane to afford 92 mg of **9** (76% yield): Colorless powder, m.p. 158–160 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.34 (s, 9H, *p*-^{t}Bu), 1.38 (d, $^{3}J_{PH}$ = 32.4 Hz, 3H, Me), 1.60 (s, 18H, *o*-^{t}Bu), 2.28 (d, $^{3}J_{PH}$ = 36.4 Hz, 3H, Me), 7.53 (d, $^{4}J_{PH}$ = 3.6 Hz, 2H, Mes*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 178.3; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 24.9 (d, $^{2}J_{PC}$ = 7.2 Hz, Me), 26.6 (d, $^{2}J_{PC}$ = 20.2 Hz, Me), 31.0 (s, *p*-C*Me*$_3$), 33.5 (d, $^{4}J_{PC}$ = 1.4 Hz, *o*-C*Me*$_3$), 35.2 (s, *p*-C*Me*$_3$), 38.6 (s, *o*-C*Me*$_3$), 123.0 (d, $^{3}J_{PC}$ = 9.5 Hz, *m*-Mes*), 124.2 (d, $^{1}J_{PC}$ = 33.1 Hz, *ipso*-Mes*), 153.9 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Mes*), 155.9 (d, $^{2}J_{PC}$ = 1.3 Hz, *o*-Mes*), 175.5 (d, $^{1}J_{PC}$ = 74.8 Hz, P=C); ESI-MS calcd for $C_{21}H_{35}AuClP$+Na, 573.1723, found: *m*/*z* 573.1721; Anal. Calc. for $C_{21}H_{35}AuClP$: C, 45.78; H, 6.40. Found: C, 45.64; H, 6.17%.

4.5. Compound *Z*-*10*

A mixture of *Z*-**7** (83 mg, 0.21 mmol) and Au(tht)Cl (0.20 mmol) in dichloromethane (5 mL) was stirred for 12 h at room temperature. The volatile materials were removed in vacuo and the residue was washed with hexane to afford 110 mg of *Z*-**10** (86% yield): Colorless powder, m.p. 158–160 °C (decomp); ^{1}H NMR (400 MHz,

$CDCl_3$) δ = 1.35 (s, 9H, *p*-^{t}Bu), 1.61 (s, 18H, *o*-^{t}Bu), 2.23 (d, $^3J_{PH}$ = 37.6 Hz, 3H, Me), 2.86 (d, $^3J_{PH}$ = 24.8 Hz, 2H, CH_2), 6.74–6.77 (m, 2H, Ph), 7.18–7.20 (m, 3H, Ph), 7.56 (d, $^4J_{PH}$ = 4.0 Hz, 2H, Mes*); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 180.4; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 24.9 (d, $^2J_{PC}$ = 21.5 Hz, Me), 31.0 (s, *p*-C*Me*$_3$), 34.1 (d, $^4J_{PC}$ = 1.4 Hz, *o*-C*Me*$_3$), 35.2 (s, *p*-CMe_3), 38.9 (s, *o*-CMe_3), 43.1 (d, $^2J_{PC}$ = 7.1 Hz, CH_2), 123.1 (d, $^3J_{PC}$ = 16.2 Hz, *m*-Mes*), 123.8 (d, $^1J_{PC}$ = 6.4 Hz, *ipso*-Mes*), 126.9 (s, *p*-Ph), 128.4 (s, *m*-Ph), 129.2 (s, *o*-Ph), 136.1 (d, $^3J_{PC}$ = 14.7 Hz, *ipso*-Ph), 154.1 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes*), 156.6 (s, *o*-Mes*), 175.6 (d, $^1J_{PC}$ = 73.2 Hz, P=C); ESI-MS calcd for $C_{27}H_{39}AuClP$+Na, 649.2036, found: *m*/*z* 649.2034; Anal. Calc. for $C_{21}H_{39}AuClP{\cdot}0.3H_2O$: C, 51.28; H, 6.31. Found: C, 51.20; H, 6.25%.

4.6. Compound E-**10**

A mixture of *E*-**7** (77 mg, 0.20 mmol) and Au(tht)Cl (0.19 mmol) in dichloromethane (5 mL) was stirred for 12 h at room temperature. The volatile materials were removed in vacuo and the residue was washed with hexane to afford 86 mg of *E*-**10** (72% yield): Colorless powder, m.p. 156–159 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.25 (d, $^3J_{PH}$ = 28.8 Hz, 3H, Me), 1.31 (s, 9H, *p*-^{t}Bu), 1.54 (s, 18H, *o*-^{t}Bu), 3.98 (d, $^3J_{PH}$ = 31.6 Hz, 2H, CH_2), 7.22–7.32 (m, 5H, Ph), 7.50 (d, $^4J_{PH}$ = 3.6 Hz, 2H, Mes*); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 180.2; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 22.1 (d, $^2J_{PC}$ = 6.8 Hz, Me), 31.0 (s, *p*-C*Me*$_3$), 33.6 (d, $^4J_{PC}$ = 1.3 Hz, *o*-C*Me*$_3$), 35.2 (s, *p*-CMe_3), 38.7 (s, *o*-CMe_3), 46.2 (d, $^2J_{PC}$ = 19.6 Hz, CH_2), 123.4 (d, $^3J_{PC}$ = 9.4 Hz, *m*-Mes*), 123.8 (d, $^1J_{PC}$ = 31.6 Hz, *ipso*-Mes*), 127.5 (s, *p*-Ph), 128.5 (s, *m*-Ph), 128.9 (s, *o*-Ph), 136.2 (d, $^3J_{PC}$ = 18.5 Hz, *ipso*-Ph), 154.0 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Mes*), 156.2 (d, $^2J_{PC}$ = 2.0 Hz, *o*-Mes*), 175.5 (d, $^1J_{PC}$ = 72.3 Hz, P=C); ESI-MS calcd for $C_{27}H_{39}AuClP$+Na, 649.2036, found: *m*/*z* 649.2036; Anal. Calc. for $C_{21}H_{39}AuClP$: C, 51.72; H, 6.27. Found: C, 51.71; H, 6.02%.

4.7. Cycloisomerization of **11**

A solution of **11** (0.30 mmol) and **9** or *Z*/*E*-**10** (9.0 μmol) in dichloromethane or 1,2-dichloroethane (9 mL) was stirred at room temperature for 24 h (for **11a**) or heated at 70 °C for 4 h (for **11b**). The solvent was removed in vacuo and the residue was treated by column chromatography (SiO_2, hexane/EtOAc 5:1). **12a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.76 (s, 3H, Me), 1.81 (s, 3H, Me), 3.03 (2H, brs, CH_2), 3.18 (brs, 2H, CH_2), 3.73 (s, 6H, CO_2Me), 5.37 (brs, 1H, CH), 5.72 (brs, 1H, CH) [7,8]. **12b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.10 (brs, 2H, CH_2), 3.13 (brs, 2H, CH_2), 3.75 (s, 6H, CO_2Me), 5.09 (d, $^3J_{HH}$ = 17.6 Hz, 1H, CH), 5.10 (d, $^3J_{HH}$ = 10.4 Hz, 1H, CH), 5.58 (brs, 1H, CH), 6.47 (dd, $^3J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 10.4 Hz, 1H, CH) [27].

4.8. Cyclization of **15**

A solution of **15** (56 mg, 0.30 mmol), **9** (9.0 μmol), and pyridine (0.30 mmol) in THF (9 mL) was stirred for 24 h. The volatile materials were removed in vacuo and the residue was treated with column chromatography (SiO_2, hexane/EtOAc 5:1) to afford 48 mg of **16** (86% yield). **16**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.60 (ddt, $^3J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 14.0 Hz, 1H, CH), 2.77–2.87 (m, 2H, CH_2), 3.04–3.27 (m, 1H, CH_2), 3.25 (dd, $^3J_{HH}$ = 14.0 Hz, $^4J_{HH}$ = 4.2 Hz, 1H, CH_2), 4.26 (dd, $^4J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 4.2 Hz, 1H, C = CH_2), 4.70 (dd, $^4J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 4.2 Hz, 1H, C = CH_2), 7.18–7.34 (m, 5H, Ph) [11].

4.9. Cyclization of **17**

A solution of **17** (18.0 mg, 0.10 mmol), *E*-**10** (3.0 μmol), and pyridine (0.10 mmol) in THF (3 mL) was stirred for 24 h. The volatile materials were removed in vacuo and the residue was treated with column chromatography (SiO_2, hexane/EtOAc 5:1) to afford 16.5 mg of **18** (92% yield). **18**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.93–2.91 (m, 1H, CH_2), 2.97–2.96 (m, 1H, CH_2), 3.46–3.45 (m, 1H, CH_2), 3.50–3.49 (m, 1H, CH_2), 4.51–4.50 (m, 1H, C=CH_2), 4.94–4.92 (m, 1H, C=CH_2) [11].

4.10. DFT calculations

All computational optimizations for **E**–**G** were performed with the GAUSSIAN 03 package [21] using 6-31G* (for C, H, P) and LanL2DZ (for Au) basis sets and a B3LYP functional. Initial structures for the DFT procedures were obtained from ab initio calculations at the HF/6-31G*/LanL2DZ level.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.040.

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(b) ^{31}P NMR monitoring of a solution of *E*-**10** in wet chloroform indicated that the chlorogold(I) complex was affected by water (δ_P 135);
(c) Reaction of **11a** in the presence of AuCl (3 mol%) in dichloromethane at room temperature for 24 h afforded **12a** (86%) together with **13a** (4%) and **14a** (9%). Reaction of **11a** in the presence of $AuCl_3$ under similar conditions afforded **12a** (43%), **13a** (7%), and **14a** (48%). For compound **13a**, see [27]; for compound **14a**, see [28].
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