# Combination of sp<sup>2</sup>- and sp<sup>3</sup>-Type Phosphorus Atoms for Gold Chemistry: Preparation, Structure, and Catalytic Activity of Gold Complexes That Bear Ligated 2-Silyl-1,3-diphosphapropenes

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**Abstract:** Kinetically protected 2-silyl-1,3-diphosphapropenes that bear both sp<sup>2</sup>- and sp<sup>3</sup>-type phosphorus atoms were employed in the preparation of gold complexes. The structural properties of the 1,3-diphosphapropene digold(I) complexes were characterized by spectroscopic and crystallographic analyses, which revealed unique aurophilic interactions and conformational

# Introduction

In homogeneous transition-metal catalysis, ligands are important in controlling catalytic properties: accordingly, the design of ligands is crucial for the development of novel catalysts.<sup>[1]</sup> In addition to  $\lambda^3 \sigma^3$ -phosphorus compounds (R<sub>3</sub>P), which have been routinely utilized as transition-metal catalysts, lower-coordinated phosphorus compounds such as kinetically and thermodynamically stabilized phosphaalkenes  $(\lambda^3 \sigma^2$ -phosphorus, -P=C<) are of interest because of their strong  $\pi$ -accepting properties derived from their considerably low-lying LUMO.<sup>[2,3]</sup> Ni-catalyzed olefin polymerization promoted by an  $\eta^3$ -diphosphaallyl ligand was a pioneering application of low-coordinated phosphorus compounds for catalysis,<sup>[4]</sup> and several  $\pi$ -delocalized molecules including low-coordinated phosphorus, such as phosphinine (P-analogue of pyridine) and phosphametallocene, have been utilized for homogeneous catalysis.<sup>[5,6]</sup> Furthermore, Ozawa and Yoshifuji have developed practical transition-metal cat-

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properties of the ligand. The 2-silyl-1,3diphosphapropene-bis(chlorogold) complexes catalyzed cycloisomerization reactions of 1,6-enyne derivatives even in the absence of silver co-catalyst, and

**Keywords:** aurophilicity • cycloisomerization • enynes • gold • phosphaalkenes were able to be recovered after the reaction. The catalytic activity of the digold complexes primarily depended on the sp<sup>2</sup>-type phosphorus atom and the silyl group, and could be tuned by the sp<sup>3</sup>-phosphino group. Additionally, results on the catalytic activity of the digold complex in the presence and absence of silver salts showed considerable differences.

alysts that bear the ligated the 3,4-diphosphinidenecyclobutene moiety to lead to environmentally benign processes.<sup>[7,8]</sup>

A combination of both low-coordinated sp<sup>2</sup>- and normal sp<sup>3</sup>-type phosphorus atoms is a unique design. Such hybridized P2 ligands can display both the strong  $\pi$ -accepting property of sp<sup>2</sup>-type phosphorus atoms and the supplemental characteristics of electronically and sterically tunable sp<sup>3</sup>-phosphino groups. To date, we have studied 1,3-diphosphapropene (-P=C(R)-P<) as a fundamental molecular system that contains both sp<sup>2</sup>- and sp<sup>3</sup>-type phosphorus atoms.<sup>[9,10]</sup> In the course of our research, we have found that a sterically protected 1,3-diphosphapropene that bears a trimethylsilyl group at the 2-position shows high stability and good coordinating ability toward metals, which enables its use in transition-metal catalysis. Additionally, 2-silyl-1,3-diphosphapropene was useful in elucidating the conformational characteristics of the -P=C-P < system.<sup>[11]</sup>

In this paper, we utilize 2-silyl-1,3-diphosphapropenes **1** in gold complexes for the purpose of catalysis. The catalytic activity of gold complexes normally stems from their soft Lewis acidity based on remarkable relativistic effects,<sup>[12]</sup> and effectively activates unsaturated organic moieties to lead to a number of atom-economical molecular transformations.<sup>[13]</sup> Previously we reported that some phosphaalkene gold complexes were effective in catalyzing the cyclization of 1,6-enyne and pent-4-ynoic acids without activation by a silver co-catalyst.<sup>[14]</sup> These findings suggested an advantage of the low-coordinated phosphorus compounds in catalysis. On the

Chem. Asian J. 2011, 6, 3077-3083

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201100310.

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other hand, no apparent catalytic activity was observed when 2-methyl-1,3-diphosphapropene was employed in the gold-catalyzed reactions, thus indicating that the relatively strong o-donating sp<sup>3</sup>-phosphino group weakens the Lewis acidity of the gold complex.<sup>[14a]</sup> Here, we report that an appropriate design of the 1,3-diphosphapropene moiety, in which silyl effects<sup>[15]</sup> are utilized, is suitable for a unique type of gold catalysis. Along with catalytic activity, the struc-

Mes <sup>*</sup> SiMe <sub>3</sub> P=C ́PR <sub>2</sub>	
<b>1a</b> : R = Ph <b>1b</b> : R = $p$ -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <b>1c</b> : R = NMe <sub>2</sub> Mes <sup>*</sup> = 2.4.6- <i>t</i> Bu <sub>2</sub> C <sub>6</sub> H <sub>2</sub>	

tural properties of the gold complexes are discussed in terms of conformation. Furthermore, we report novel findings related to the coordination properties of the nonsymmetric P2 ligands on gold atoms.

## **Results and Discussion**

# Structural Characteristics of 2-Silyl-1,3-diphosphapropene Digold(I) Complexes

Compound **1a**, prepared according to our previous report,<sup>[11]</sup> was allowed to react with Au(tht)Cl (tht=tetrahydrothiophene; 2 equiv) to afford the corresponding dinuclear chlorogold(I) complex **2a** in moderate isolated yield (70%; Scheme 1). Interestingly, in the complex formation, we observed considerable changes in the <sup>31</sup>P NMR spectroscopic



Scheme 1. Preparation of digold complex 2a.

resonance peaks. Whereas a mixture of **1a** and Au(tht)Cl (2 equiv) showed two <sup>31</sup>P NMR spectroscopic resonances at  $\delta = 309$  and 41 ppm and a <sup>2</sup>J(P,P) coupling constant of 105 Hz, the recrystallized product showed <sup>31</sup>P NMR spectroscopic shifts ( $\delta = 306$  and 39 ppm) and <sup>2</sup>J(P,P) value (82 Hz) different from those of the reaction mixture. As discussed below, the X-ray structure of **2a** shows that the conformation of the 1,3-diphosphapropene moiety changes to the Cs-like structure from the  $C_1$  form of **1a**.<sup>[11]</sup> As we described in our previous report, 1,3-diphosphapropene displayed two conformations that may be extremely stable even in solution, although the energetic difference between the two conformations is probably small.<sup>[11]</sup> In considering these findings, it is plausible that the intermediary product **2a'** has the same ligand structure as **1a**.

Figure 1 displays the molecular structure of **2a** together with typical metric parameters. The considerable Au–Au contact indicates the aurophilic interaction, and correspondingly the P-Au-Cl angles are distorted from the linear geometry. The Au–Au distance is shorter than that of  $[(E)-Mes^*P=C(Me)PPh_2][AuCl]_2$  (3.084 Å),<sup>[14a]</sup> thus indicating



Figure 1. Molecular structure of 2a (50 % probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–Au2 3.0145(7), Au1–Cl1 2.293(2), Au2–Cl2 2.284(1), P1–Au1 2.251(2), P2–Au2 2.222(2), P1–C1 1.672(5), P2–C1 1.830(7), P1–C2 1.803(7), C1–Si 1.926(6); C1-P1-C2 117.3(3), C1-P1-Au1 129.8(2), C2-P1-Au1 113.0(2), P1-C1-P2 110.3(3), P1-C1-Si 122.0(3), P2-C1-Si 127.5(3), C1-P2-Au2 118.3(2), P1-Au1-Cl1 170.44(5), P1-Au1-Au2 84.60(4), Au2-Au1-Cl1 104.94(4), P2-Au2-Cl2 170.53(5), Au1-Au2-Cl2 104.94(4).

that the silyl substituent might strengthen the aurophilic interaction. Since the bonding energy of the aurophilic interaction is estimated to be 7–8 kcalmol<sup>-1</sup>,<sup>[16]</sup> the conformation of **1a** would be easily influenced. The interatomic distance and angles around the 1,3-diphosphapropene moiety are comparable with those in **1a** except for the conformation around the sp<sup>3</sup>-phosphino group.

Next, we employed a novel 2-silyl-1,3-diphosphapropene derivative **1b**. Aiming to improve the catalytic activity, we employed a bis(4-trifluoromethylphenyl)phosphino group.<sup>[17]</sup> Compound **1b** was prepared from (*E*)- 3,3-dichloro-2-trime-thylsilyl-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene [(*E*)-Mes\*P=C(SiMe<sub>3</sub>)PCl<sub>2</sub>] (see the Supporting Information).<sup>[18]</sup> Similarly to **2a**, digold complex **2b** was obtained as an air-stable crystalline compound. In contrast to **1a**, in the preparation process, no putative conformational rotation that generated the rotational isomer (**2b**') was observed; this result indicates that the substituents on the -P=CP < system might influence the energy difference between the lowest-energy conformers.



Single crystals of **2b** were obtained from dichloromethane, and Figure 2 displays a drawing of the X-ray structure. In comparison with **2a**, the Au–Au distance is longer, and correspondingly the P-Au-Cl angles are closer to 180°. The elongated Au–Au distance suggests a weaker aurophilic



Figure 2. Molecular structure of **2b** (30 % probability ellipsoids). Hydrogen atoms are omitted for clarity. Fluorine atoms in the CF<sub>3</sub> groups are disordered. Selected bond lengths [Å] and angles [°]: Au1–Au2 3.1589(9), Au1–Cl1 2.283(2), Au2–Cl2 2.274(2), P1–Au1 2.241(2), P2–Au2 2.228(2), P1–C1 1.663(8), P2–C1 1.793(9), P1–C2 1.827(8), C1–Si 1.929(8); C1-P1-C2 117.3(3), C1-P1-Au1 114.0(3), C2-P1-Au1 109.6(3), P1-C1-P2 108.4(5), P1-C1-Si 123.8(5), P2-C1-Si 127.4(5), C1-P2-Au2 125.3(3), P1-Au1-Cl1 175.93(9), P1-Au1-Au2 80.10(6), Au2-Au1-Cl1 103.84(6), P2-Au2-Cl2 174.11(9), Au1-Au2-Cl2 101.31(7).

interaction that results from the electron density around the gold atoms being decreased by the trifluoromethyl groups.<sup>[19]</sup> Other metric parameters of **2b** are similar to those of **2a**.

### **Coordination Properties of 1,3-Diphosphapropene on Gold**

To obtain more information about the unique coordination properties of the nonsymmetric P2 ligand system, we next examined the reaction of **1a** with 1 equiv of Au(tht)Cl. Compound **1a** was mixed with Au(tht)Cl (1 equiv) in chloroform or dichloromethane; after 5 min, **1a** was completely consumed and two adducts, namely, **3a** ( $\delta_P$ =423, 35 ppm; <sup>2</sup>*J*(P,P)=129 Hz) and **4** ( $\delta_P$ =306, 39 ppm; <sup>2</sup>*J*(P,P)= 83 Hz) were observed (Scheme 2). The ratio of **3a** and **4** 



Scheme 2. Two types of coordination modes of 1a toward gold.

reached about 1:1 after 7 h. Judging from our previous findings with mononuclear gold complexes that bear the 1,3-diphosphapropene ligand,<sup>[14a]</sup> the structure of **3a** could be assigned as a mononuclear complex. On the other hand, **4** showed similar <sup>31</sup>P NMR spectroscopic data as **2a**. However, on the basis of the employed materials, the structure of **4** should be different from **2a**. Although attempts to isolate pure **4** were unsuccessful because of compound instability, it is plausible that the structure of **4** includes an eight-membered metallacyclic skeleton, similar to the structure of  $[Ph_2PCH_2PPh_2]_2[AuCl]_2$ .<sup>[20,21]</sup>

In contrast to **1a**, 2-silyl-1,3-diphosphapropene **1c** that bears the P(NMe<sub>2</sub>)<sub>2</sub> group (see the Supporting Information) showed stepwise coordination on gold and afforded an isolable mononuclear gold(I) complex (**3c**), which subsequently furnished digold(I) complex **2c**. In the <sup>31</sup>P NMR spectra, the sp<sup>2</sup> phosphorus of **3c** exhibited a similar chemical shift to that of **3a** together with a comparable  ${}^{2}J(P,P)$  coupling constant.

### Catalytic Activity in the Absence of Silver Co-catalyst

A study of the catalytic properties of the dinuclear complexes **2** was performed using cycloisomerization of 1,6enynes.<sup>[22]</sup> At first, the gold(I) complexes were employed for cycloisomerization of 1,6-enyne **5** in the absence of silver co-catalyst in dichloromethane at room temperature. Whereas no clear catalytic activity was observed for [(*E*)-Mes\*P=C(Me)PPh<sub>2</sub>][AuCl]<sub>2</sub>,<sup>[14a]</sup> dinuclear complexes **2** catalyzed the cycloisomerization without silver co-catalyst (Scheme 3). After 12 h, **2a** and **2b** afforded the correspond-



Scheme 3. Cycloisomerization of 5 catalyzed by 2.

ing cyclized product 6 in good yield. Thus, the introduction of a silyl substituent at the 2-position was effective in improving the catalytic activity of 1,3-diphosphapropene gold complexes, because the  $R_3Si$  moiety could serve as a  $\pi$ -withdrawing group.<sup>[15]</sup> Relative to 2a and 2b, the electron-withdrawing substituent on the sp<sup>3</sup>-phosphino group slightly improved the catalytic activity.<sup>[17]</sup> Interestingly, the gold complexes 2 were recovered after the reaction and could be reused.<sup>[23]</sup> On the other hand, digold complex 2c showed low catalytic activity, probably due to a mesomeric effect of the nitrogen lone pairs putatively reducing the electrophilic character. Mononuclear complex 3c showed no catalytic activity, thereby indicating the importance of the P=C moiety in these reactions. The trimethylsilyl group was the optimal silyl substituent for obtaining catalytically active 2-silyl-1,3diphosphapropene digold complexes.<sup>[24]</sup>

The observed catalytic activity of **2** in the absence of silver co-catalyst is principally based on the low-lying LUMO of the P=C moiety,<sup>[2,14]</sup> which strengthens the soft electrophilic character of the gold centers and additionally is

# **FULL PAPERS**

assisted by silyl effects<sup>[11,15]</sup> and the aurophilic interaction.<sup>[12]</sup> A key finding related to the catalytic mechanism is that 2 was recovered after the reaction (vide supra). This finding might indicate that the structure of 2 was not largely per-

turbed in the cycloisomerization reaction. Therefore, it is plausible that the nature of the  $\pi$ -accepting property of the P= C structure caused a formal increase in the oxidation number of the gold center(s), thereby activating the acetylene part of 5 without a large structural change of the digold complex. This hypothesis may be consistent with the finding that increasing the steric encumbrance Furthermore, 2a and 2b could be employed for cycloisomerization of 1,6-enyne that bears the NTs (Ts=tosyl) moiety (10) under AgX-free conditions, although the conversion was moderate (Scheme 5). In contrast to the case of



Scheme 5. Cycloisomerizations of 10 catalyzed by 2.

around the P=C group of the 1,3-diphosphapropene remarkably lowered the reaction rate.<sup>[24]</sup> In theoretical studies, attempts to characterize the hypothesized reaction intermediates are in progress.

Next, we examined cycloisomerization of the less reactive substrate 7 in the presence of a catalytic amount of 2a or 2b. Although yields of the cycloisomerized product 8 were low at room temperature (5% (2a) and 8% (2b)), the reaction accelerated upon heating (Scheme 4). On the other



Scheme 4. Cycloisomerizations of 7 catalyzed by 2.

hand, the coordination on the sp<sup>2</sup> phosphorus was lost when the reaction was carried out at over 80 and 70 °C for **2a** and **2b**, respectively; the higher temperature lowered the yield of the cycloisomerized product on account of the generation of noncatalytic mononuclear species **3a** and **3b** ( $\delta_P$ =434, 34 ppm, <sup>2</sup>*J*(P,P)=130 Hz). The decomposition from **2b** to **3b** at the lower temperature indicates the effect of the CF<sub>3</sub> group, which lessened the  $\sigma$ -donating property of the sp<sup>2</sup> phosphorus, as predicted by the lower-field <sup>31</sup>P chemical shift of the sp<sup>2</sup>-phosphorus nucleus. Whereas an ordinary cationic Au catalyst such as Ph<sub>3</sub>PAuSbF<sub>6</sub> (prepared from Ph<sub>3</sub>PAuCl and AgSbF<sub>6</sub>) predominantly afforded the *endodig* product,<sup>[22]</sup> the amount of **9** was small in the reactions catalyzed by **2**. Although the reaction mechanism has yet to



Ph<sub>3</sub>PAuSbF<sub>6</sub>,<sup>[22]</sup> **2a** and **2b** afforded four products **11–14**. Complex **2a** afforded the *exo-dig* cyclization product **11** as the major product, whereas **2b** strongly promoted the *endo-dig* pathway to product **12**. Both **2a** and **2b** afforded the alternative *endo-dig* product **13**. Additionally, small amounts of the ene reaction product **14** were also produced. Generally, in Au catalysis, such an ene reaction process is rarely observed,<sup>[22b]</sup> and thus these results suggest the usefulness of the employed ligands in exploration for novel Au-catalyzed

transformations. The lower conversion using **2b** might be a consequence of its instability at higher temperatures and competitive coordination of the nitrogen on the gold centers preventing activation of the acetylene moiety.

### Effects of Silver Salts on the Catalytic Activity

In addition to the silver-salt-free conditions, we attempted to evaluate effects of silver co-catalyst so as to explore the novel catalytic aspects of the digold complexes. By using **2a**, we examined cycloisomerization of **7** and **10**, which displayed low reactivity in the silver-salt-free conditions.

Scheme 6 displays the cycloisomerization of 7 in the presence of 2a and silver salt (2 equiv relative to 2a). Addition of silver tetrafluoroborate and hexafluorophosphate for activation of 2a led to almost complete consumption of the starting material and provided the cycloisomerized products 8 and 9 in moderate to good yield in shorter reaction times. In contrast to the ordinary sp<sup>3</sup>-phosphine gold complexes such as Ph<sub>3</sub>PAuSbF<sub>6</sub><sup>[22]</sup> the *exo-dig* and *endo-dig* products were obtained in about a 1:1 ratio, thus indicating the effects of the sterically encumbered sp<sup>2</sup>-type phosphorus moiety.<sup>[25]</sup> On the other hand, a combination of 2a and AgSbF<sub>6</sub> afforded a small amount of 8 and a mixture of unidentified products, although all the starting material was consumed. Therefore, the sp<sup>2</sup>-type phosphorus might induce catalytic activity that is too high and in turn cause undesirable decomposition of the starting envne substrate.

Next, we examined cycloisomerization of 10 in the presence of 2a and silver salt (2 equiv relative to 2a) and ob-



Scheme 6. Cycloisomerizations of 7 in the presence of 2a and silver salt.

served nearly quantitative transformation to the cycloisomerized products (Scheme 7). Similarly to a previous report, the *endo-dig* product **12** was predominantly obtained when



Scheme 7. Cycloisomerizations of **10** in the presence of **2a** and silver salt. [a] Determined by NMR spectroscopy; [b] reaction time: 24 h.

AgBF<sub>4</sub>, AgPF<sub>6</sub>, or AgSbF<sub>6</sub> was employed as co-catalyst. Thus, the combination of **2a** and silver co-catalyst showed catalytic activity toward **10** similar to that of typical phosphine gold complexes. On the other hand, slow formation of the ene-type product **14**, which was predominantly formed when AgOTs was used as co-catalyst, indicated the generation of an intriguing Au catalytic species under the reaction conditions.<sup>[26]</sup>

## Conclusions

Sterically protected 2-trimethylsilyl-1,3-diphosphapropenes 1 can be utilized as a nonsymmetric P2 ligand system for unique digold(I) complexes 2. The molecular structures of 2 were determined and discussed in terms of conformational characteristics and aurophilic interactions. The dinuclear gold complexes 2 catalyzed cycloisomerization reactions of 1,6-enyne derivatives without silver co-catalysts, thus indicating that this catalyst design is appropriate for the nonsymmetric P2 ligand system. These findings are expected to be useful in the exploration for novel gold catalysts that enable more efficient molecular transformation with high se-

# CHEMISTRY

lectivity. In this work, we have obtained some preliminary findings on the substituent effects, and furthermore, we are continuing to study appropriate designs for more efficient gold catalysts that bear ligated 1,3diphosphapropenes by examining various substituents.

# **Experimental Section**

 $^{1}$ H,  $^{13}$ C, and  $^{31}$ P NMR spectra were recorded with a Bruker AV300M spectrometer with Me<sub>4</sub>Si ( $^{1}$ H,  $^{13}$ C) and H<sub>3</sub>PO<sub>4</sub> ( $^{31}$ P) as internal and external standards. Mass spectra were recorded with JEOL JMS-T100CS and JMS-700 spectrometers. X-ray diffraction data were collected with

Rigaku RAXIS-Rapid and Bruker APEXII CCD diffractometers, and structural refinement was carried out with the SHELX-97 programs.<sup>[27]</sup> Preparation of **1b** and **1c** is described in the Supporting Information.

#### Preparation of 2 a

solution of  $1 a^{[11]}$ (875 mg, Α 1.60 mmol) and Au(tht)Cl (2.88 mmol) in dichloromethane (60 mL) was stirred at room temperature. The volatile materials were removed in vacuo, and the residue was recrystallized from dichloromethane and hexane to afford 2 (1.20 g, 74% yield) as yellowbrown crystals. 1H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = -0.27$  (s, 9H; SiMe<sub>3</sub>), 1.33 (s, 9H; p-tBu), 1.71 (s, 18H; o-tBu), 7.52–7.63 ppm (m, 12H; arom); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta =$ 

1.7 (d,  ${}^{4}J(P,C) = 2.3 \text{ Hz}$ ; SiMe<sub>3</sub>), 30.9 (s; *p*-CMe<sub>3</sub>), 35.3 (s; *p*-CMe<sub>3</sub>), 35.8 (s; *o*-CMe<sub>3</sub>), 39.6 (s; *o*-CMe<sub>3</sub>), 124.5 (d,  ${}^{3}J(P,C) = 9.1 \text{ Hz}$ ; *m*-Mes\*), 126.6 (pt,  ${}^{1}J(P,C) + {}^{3}J(P,C) = 17.3 \text{ Hz}$ ; *ipso*-Mes\*), 129.0 (dd,  ${}^{1}J(P,C) = 58.9 \text{ Hz}$ ,  ${}^{3}J(P,C) = 13.6 \text{ Hz}$ ; *ipso*-Ph), 129.5 (d,  ${}^{3}J(P,C) = 12.3 \text{ Hz}$ ; *m*-Ph), 132.7 (d,  ${}^{4}J(P,C) = 2.3 \text{ Hz}$ ; *p*-Ph), 135.2 (d,  ${}^{2}J(P,C) = 14.8 \text{ Hz}$ ; *o*-Ph), 153.3 (dd,  ${}^{1}J(P,C) = 22.6 \text{ Hz}$ ,  ${}^{1}J(P,C) = 6.8 \text{ Hz}$ ; P=C), 154.6 (d,  ${}^{2}J(P,C) = 4.0 \text{ Hz}$ ; *o*-Mes\*), 155.7 ppm (d,  ${}^{4}J(P,C) = 2.0 \text{ Hz}$ ; *p*-Mes\*);  ${}^{29}\text{Si}[{}^{1}\text{H}\}$  NMR (60 MHz, CDCl<sub>3</sub>):  $\delta = 38.8 \text{ ppm}$  (d,  ${}^{2}J(P,C) = 82.6 \text{ Hz}$ ; PPh<sub>2</sub>), 305.7 (d,  ${}^{2}J(P,P) = 82.6 \text{ Hz}$ ; P=C); APCI-MS: *m*/*z*: calcd for C<sub>34</sub>H<sub>49</sub>Au<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub>Si [*M*+H]\*: 1011.1787; found: 1011.1753.

#### Preparation of 2 b

Similarly to **1a**, **2b** was obtained from **1b** and Au(tht)Cl (2 equiv) in 74% isolated yield as brown crystals. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = -0.28$  (s, 9H; SiMe<sub>3</sub>), 1.33 (s, 9H; *p*-*t*Bu), 1.72 (s, 18H; *o*-*t*Bu), 7.62 (brs, 2H; arom), 7.84–7.97 ppm (m, 8H; arom); <sup>13</sup>C[<sup>1</sup>H] NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 1.8$  (dd, <sup>3</sup>*J*(P,C) = 3.8, 2.3 Hz; SiMe<sub>3</sub>), 30.9 (s; *p*-CMe<sub>3</sub>), 35.4 (s; *p*-CMe<sub>3</sub>), 35.9 (s; *o*-CMe<sub>3</sub>), 39.7 (s; *o*-CMe<sub>3</sub>), 121.3 (brs; *m*-Mes\*), 124.6 (d, <sup>3</sup>*J*(P,C) = 9.2 Hz; *m*-C<sub>6</sub>H<sub>4</sub>), 125.9 (dd, <sup>1</sup>*J*(P,C) = 20.3 Hz, <sup>3</sup>*J*(P,C) = 14.3 Hz; *ipso*-Mes\*), 126.0–126.8 (m; CF<sub>3</sub>), 133.1 (dd, <sup>1</sup>*J*(P,C) = 56.3 Hz, <sup>3</sup>*J*(P,C) = 14.3 Hz; *ipso*-C<sub>6</sub>H<sub>4</sub>), 134.8 (dq, <sup>4</sup>*J*(P,C) = 3.0 Hz, <sup>2</sup>*J*(F,C) = 33.0 Hz; *p*-C<sub>6</sub>H<sub>4</sub>), 135.4 (d, <sup>4</sup>*J*(P,C) = 15.8 Hz; *o*-C<sub>6</sub>H<sub>4</sub>), 149.7 (dd, <sup>1</sup>*J*-(P,C) = 21.0 Hz, <sup>1</sup>*J*(P,C) = 7.5 Hz; *p*=C), 154.8 (d, <sup>2</sup>*J*(P,C) = 4.5 Hz; *o*-Mes\*), 156.3 ppm (d, <sup>4</sup>*J*(P,C) = 2.3 Hz; *p*-Mes\*); <sup>31</sup>P[<sup>1</sup>H] NMR (121 MHz, CDCl<sub>3</sub>):  $\delta = 38.3$  (d, <sup>2</sup>*J*(P,P) = 96.0 Hz; P=C); APCI-MS: *m*/*z*: calcd for C<sub>36</sub>H<sub>47</sub>Au<sub>2</sub>Cl<sub>2</sub>F<sub>6</sub>P<sub>2</sub>Si [*M*+H]<sup>+</sup>: 1147.1535; found: 1147.1541.

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A solution of **1c** ( $\approx$ 1.5 mmol, see the Supporting Information) and Au-(tht)Cl (1.5 mmol) in dichloromethane (45 mL) was stirred at room temperature. The volatile materials were removed in vacuo, and the residue was washed with hexane to afford **3c** (1.05 g, 98% yield) as a yellow solid. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -0.10 (s, 9H; SiMe<sub>3</sub>), 1.35 (s, 9H; *p*-*t*Bu), 1.52 (s, 18H; *o*-*t*Bu), 2.91 (d, <sup>3</sup>*J*(P,H) = 12.0 Hz, 6H; NMe<sub>2</sub>), 7.41 ppm (d, <sup>4</sup>*J*(P,H) = 2.0 Hz, 2H; Mes\*); <sup>13</sup>C[<sup>1</sup>H] NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 1.5 (d, <sup>3</sup>*J*(P,C) = 2.3 Hz; SiMe<sub>3</sub>), 30.9 (s; *p*-*CMe<sub>3</sub>), 34.0* (d, <sup>2</sup>*J*(P,C) = 8.3 Hz; NMe<sub>2</sub>), 122.2 (s; *m*-Mes\*), 138.0 (dd, <sup>1</sup>*J*(P,C) = 74.3 Hz, <sup>3</sup>*J*(P,C) = 26.3 Hz; *ipso*-Mes\*), 151.5 (s; *o*-Mes\*), 153.7 (d, <sup>2</sup>*J*(P,C) = 2.) Hz; *p*=(C); <sup>31</sup>P[<sup>1</sup>H] NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 104.3 (d, <sup>2</sup>*J*(P,P) = 127.6 Hz; P-(NMe<sub>2</sub>)<sub>2</sub>), 409.8 ppm (d, <sup>2</sup>*J*(P,P) = 127.6 Hz; P=C). MS measurements did not afford the [*M*]<sup>+</sup> peak due to instability of the ionization conditions.

#### Preparation of 2 c

A solution of **3c** (571 mg, 0.80 mmol) and Au(tht)Cl (0.80 mmol) in dichloromethane (35 mL) was stirred at room temperature for 2 h. The volatile materials were removed in vacuo, and the residual solid was recrystallized from dichloromethane/hexane to afford **2c** (550 mg, 73% yield) as pale-brown crystals. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -0.07$  (s, 9H; SiMe<sub>3</sub>), 1.36 (s, 9H; *p*-*t*Bu), 1.75 (s, 18H; *o*-*t*Bu), 2.92 (d, <sup>3</sup>*J*(P,H) = 12.0 Hz, 6H; NMe<sub>2</sub>), 7.62 ppm (d, <sup>4</sup>*J*(P,H) = 2.0 Hz, 2H; Mes\*); <sup>13</sup>C[<sup>1</sup>H] NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -1.3$  (s; SiMe<sub>3</sub>), 30.8 (s; *p*-CMe<sub>3</sub>), 34.5 (dd, <sup>2</sup>*J*(P,C) = 8.3 Hz; NMe<sub>2</sub>), 35.2 (s; *o*-CMe<sub>3</sub>), 39.5 (s; *p*-CMe<sub>3</sub>), 155.5 (s; *p*-Mes\*), 162.7 ppm (pt, <sup>(1</sup>*J*(P,C)+<sup>1</sup>*J*(P,C))/2 = 24.0 Hz; P=C); <sup>31</sup>P[<sup>1</sup>H] NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 111.5$  (d, <sup>2</sup>*J*(P,C) = 114.2 Hz; P=C)(Me<sub>2</sub>)<sub>2</sub>), 303.1 ppm (d, <sup>2</sup>*J*(P,C) = 114.2 Hz; F=C); APCI-MS: *m*/z: calcd for C<sub>26</sub>H<sub>50</sub>Au<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Si [*M*]<sup>+</sup>: 944.1927; found: 944.1932.

#### X-ray Crystallographic Data of 2

Compound 2a: Diffractometer: Bruker APEXII CCD:  $C_{34}H_{48}Au_2Cl_2P_2Si \cdot CH_2Cl_2$ ; yellow prisms (CH<sub>2</sub>Cl<sub>2</sub>),  $M_r = 1096.51$ ; crystal dimensions  $0.09 \times 0.08 \times 0.07 \text{ mm}^3$ , triclinic, space group  $\overline{P}1$  (no. 2); a =11.504(3), b = 11.557(3), c = 17.021(4) Å; a = 79.155(2),  $\beta = 75.779(2)$ ,  $\gamma = 11.504(3)$ 64.213(2)°; V=1966.5(7) Å<sup>3</sup>; Z=2;  $\lambda=0.71073$  Å; T=93 K;  $\rho_{calcd}=$ 1.852 g cm<sup>-3</sup>;  $\mu$ (Mo<sub>K $\alpha$ </sub>)=7.859 mm<sup>-1</sup>;  $F_{000}$ =1060; 11496 total reflections  $(2\theta_{\text{max}} = 54.96^{\circ}); \text{ index } \text{ranges} = -14 \le h \le 14, -14 \le k \le 10, -22 \le l \le 22;$ 8661 unique reflections ( $R_{int} = 0.021$ ); R1 = 0.0314 ( $I > 2\sigma(I)$ ); 0.0408 (all data);  $wR2 = 0.0708 (I > 2\sigma(I))$ ; 0.0747 (all data); S = 1.024 (409 parameters). Compound 2b: Diffractometer: Rigaku RAXIS-Rapid detector;  $C_{36}H_{46}Au_2Cl_2F_6P_2Si$ ; reddish yellow prisms (CH<sub>2</sub>Cl<sub>2</sub>),  $M_r = 1147.59$ ; crystal dimensions  $0.18 \times 0.08 \times 0.05 \text{ mm}^3$ ; monoclinic, space group  $P2_1/a$  (no. 14); a = 13.5083(6), b = 16.7758(8), c = 19.6676(10) Å;  $\beta = 102.0761(14)^{\circ}; V = 100.0761(14)^{\circ}$ 4358.3(4) Å<sup>3</sup>; Z=4;  $\lambda$ =0.71075 Å; T=123 K;  $\rho_{calcd}$ =1.749 g cm<sup>-3</sup>;  $\mu$ - $(Mo_{Ka}) = 6.997 \text{ mm}^{-1}$ ;  $F_{000} = 2208$ ; 36539 total reflections  $(2\theta_{max} = 54.96^{\circ})$ ; index ranges =  $-17 \le h \le 17$ ,  $-21 \le k \le 21$ ,  $-25 \le l \le 25$ ; 9950 unique reflections  $(R_{int}=0.084)$ ; R1=0.0579  $(I>2\sigma(I))$ ; 0.0881 (all data); wR2= $0.1505 (I > 2\sigma(I)); 0.1763 (all data); S = 1.044 (583 parameters).$ 

CCDC 819182 (**2a**) and CCDC 819183 (**2b**) contain 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.

### General Procedure for the Cycloisomerization of 1,6-Enynes

Compounds 5,<sup>[28]</sup> 7,<sup>[29]</sup> and 10<sup>[30]</sup> (0.20 mmol) were allowed to react with a gold complex (3 or 5 mol%) in dichloromethane or 1,2-dichloroethane (2 mL). The solvent was evaporated and the residue was extracted with hexane. The organic layer was purified by silica-gel column chromatography (hexane/AcOEt). Products 6,<sup>[14,22]</sup> 8,<sup>[14b,31]</sup> 9,<sup>[32]</sup> 11,<sup>[33]</sup> 12,<sup>[22b]</sup> 13,<sup>[34]</sup> and 14<sup>[30]</sup> were characterized by <sup>1</sup>H NMR spectroscopic data. Silver co-catalyst was employed for reactions described in Scheme 6 and Scheme 7.

# Acknowledgements

This work was supported in part by Grants-in-Aid for Scientific Research (nos. 20750098 and 22350058) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and Nissan Chemicals Co. Ltd. The authors thank Prof. Hiroharu Suzuki and Dr. Masataka Oishi of Tokyo Institute of Technology, and Dr. Kenji Yoza of Bruker AXS, for supports of X-ray crystallographic analyses.

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Received: March 29, 2011 Published online: August 10, 2011