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Coordination Behavior of Sterically Protected Phosphaalkenes on the AuCl Moiety Leading to Catalytic 1,6-Enyne Cycloisomerization

Matthias Freytag,[a] Shigekazu Ito,*[a] and Masaaki Yoshifuji*[a, b]

Abstract: Mes*-substituted 2,3-dimethyl-1,4-diphosphabuta-1,3-diene, 1,2-diphenyl-3,4-diphosphinidenecyclobutene, 2,2-bis(methylsulfanyl)-1-phosphaethene, and 3,3-diphenyl-1,3-diphosphapropenes (Mes* = 2,4,6-tri-*tert*-butylphenyl) were employed as P ligands of gold(I) complexes. The (*E*,*E*)-2,3-dimethyl-1,4-diphosphabuta-1,3-diene functioned as a P2 ligand for digold(I) complex formation with or without intramolecular Au–Au contact, which depends on the conformation of the 1,3-diphosphabuta-1,3-diene. The 1,2-diphenyl-3,4-diphosphinidenecyclobutene, which has a rigid s-*cis* P=C–C=P skeleton, afforded the corresponding digold(I) complexes with a slight distortion of the planar diphosphinidenecyclobutene framework and intramolecular Au–Au contact. In the case of the 2,2-bis(methylsulfanyl)-1-phosphaethene, only the phosphorus atom coordinated to gold, and the sulfur atom showed almost no intra- or intermolecular coordination to gold. On the other hand, the 1,3-diphosphapropenes behaved as nonequivalent P2 ligands to afford the corresponding mono- and digold(I) complexes. Some phosphaalkene–gold(I) complexes showed catalytic activity for 1,6-enyne cycloisomerization without cocatalysts such as silver hexafluoroantimonate.

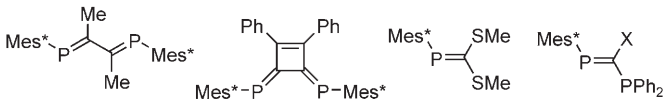
Keywords: cyclization · enynes · gold · metathesis · phosphaalkenes

Introduction

Phosphines are well-utilized compounds for the formation of metal complexes. Although most of them are tervalent phosphorus ligands, phosphorus can form multiple bonds in low coordination states by utilizing steric protection with bulky substituents. Indeed, a number of compounds with phosphorus–carbon double bonds have been synthesized by use of a bulky Mes* (2,4,6-tri-*tert*-butylphenyl) group and have so far been applied for the formation of transition-metal complexes.[1]

Considerable attention has been paid to the chemistry of gold complexes, especially in materials science, medicine, and catalysis in organic synthesis.[2] The properties of gold complexes are influenced by the nature of the ligands and display a number of intriguing characteristics.[2,3] Recently, we reported the preparation and structural determination of a monomeric digold(I) complex with a 1,2-bis(cyclopropyl)-3,4-diphosphinidenecyclobutene derivative, which showed distortion of the rigid diphosphinidenecyclobutene (DPCB) skeleton and effects of cyclopropyl conjugation.[4] Such findings prompted us to investigate phosphaalkene–gold complexes, which have hardly been explored so far.[5]

Herein we employed several kinetically stabilized phosphaalkenes for the preparation of gold complexes. In connection with our recent report,[4] we chose 2,3-dimethyl-1,4-diphosphabuta-1,3-diene **1**,[6] which includes a conformationally flexible P=C–C=P skeleton that displays peculiar properties in molecular dynamics, as well as the DPCB derivative **2**, which has been utilized as a rigid P2 ligand for unique transition-metal catalysts.[7,8] For a compound with a single P=C group, we employed 2,2-bis(methylsulfanyl)-1-



1 **2** **3** **4**

Mes* = 2,4,6-$tBu_3C_6H_2$ X = Me (**a**), Cl (**b**)

[a] Dr. M. Freytag, Dr. S. Ito, Prof. Dr. M. Yoshifuji
Department of Chemistry, Graduate School of Science
Tohoku University
Aoba, Sendai 980-8578 (Japan)
Fax: (+81) 22-795-6562
E-mail: ito@synchem.chem.tohoku.ac.jp

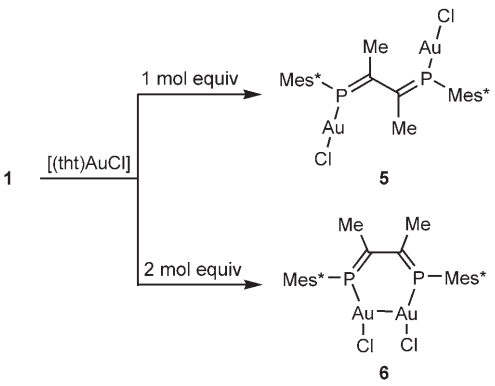
[b] Prof. Dr. M. Yoshifuji
Department of Chemistry
The University of Alabama
Tuscaloosa, Alabama 35487-0336 (USA)
Fax: (+1) 205-348-4704
E-mail: myoshifuji@bama.ua.edu

phosphaethene **3**, in which the methylsulfanyl groups are expected to affect the electronic properties of the P=C moiety to enhance coordination ability.[9] 1,3-Diphosphapropenes **4** include two differently hybridized phosphorus atoms and are anticipated to show unique behavior as P2 ligands.[10] Thus, each compound **1**–**4** has its own character in coordination chemistry. Furthermore, research on the catalytic activity of gold complexes has been remarkably developed in recent years[11] as one of the current interests in the field of organic synthesis, and gold complexes that bear phosphaalkene ligands will stimulate the development of novel synthetic methodologies[12] by utilizing the nature of P=C bonds.[1,7]

Results and Discussion

Gold-Promoted Conformational Changes of the (*E*,*E*)-1,4-Diphosphabuta-1,3-diene

1,4-Diphosphabuta-1,3-diene derivatives are one of the fundamental conjugated systems composed of P=C bonds,[6,9,13] and have been utilized as P2 ligands for several transition-metal complexes.[14] Herein we used (*E*,*E*)-2,3-dimethyl-1,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,4-diphosphabuta-1,3-diene (**1**)[6] by taking the inherently stable planar s-*trans* conformation into consideration.[15] Compound **1** was allowed to react with one molar equivalent of [(tht)AuCl] (tht = tetrahydrothiophene), and the resulting mixture was monitored by ^{31}P NMR spectroscopy. The digold(I) complex **5** and the starting material **1** were observed in a roughly 1:1 ratio (Scheme 1). No monogold(I) complex of **1** appeared to be formed. The products were recrystallized from hexane/dichloromethane, and the single crystals obtained were analyzed by NMR spectroscopy and X-ray crystallography to confirm the structure of **5** (Figure 1 and Table 1). The Au, Cl, and P atoms were refined anisotropically, whereas the carbon atoms were refined isotropically. The molecule takes a planar s-*trans* conformation of C_{2h} symmetry, thus indicating that the conformation of **1** is maintained. Au–Cl and Au–P bond lengths of 2.265(4) and 2.229(4) Å, respectively, were observed for **5**. On the other hand, neither intra- nor intermolecular Au–Au contact was observed, which indicates that the aurophilic interaction[3] seems to be insufficient to change the conformation of **1** and to overcome the steric hindrance around phosphorus. Although the quality of the structure analysis for **5** is not good enough to discuss the metric parameters of the 1,4-diphosphabuta-1,3-diene



Scheme 1. Reaction of 1,4-diphosphabuta-1,3-diene with [(tht)AuCl].

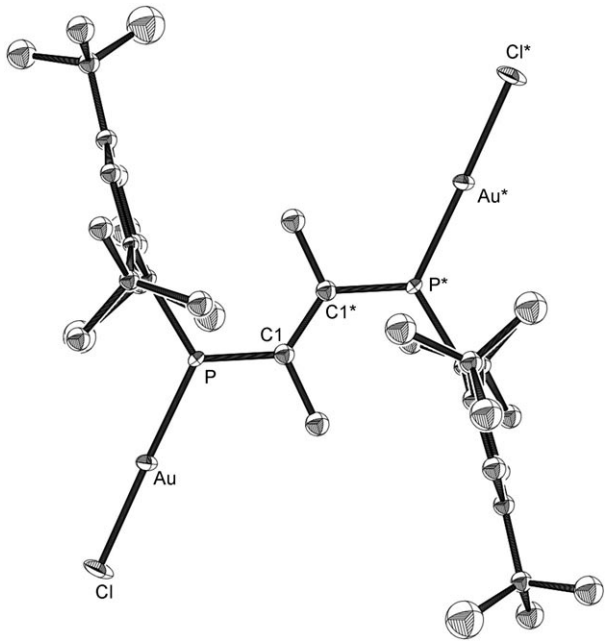


Figure 1. Molecular structure of **5** (ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity.

Abstract in Japanese:

かさ高い Mes*（2,4,6-トリ-t-ブチルフェニル）基で立体保護されたホスファアルケン類を配位子とした金(I)錯体の合成と構造解析および、エンイン環化異性化触媒活性について報告する。P=C–C=P 分子骨格化合物（1,4-ジホスファ-1,3-ブタジエン）を配位子とした二核金(I)錯体の合成において、分子内 Au–Au コンタクトを含む錯体と含まない錯体を選択的に得ることができた。同じく P=C–C=P 構造を含み、分子骨格が堅牢な 3,4-ジホスフィニデンシクロブテン（DPCB）を配位子とした金(I)錯体では、二つの金が分子内 Au–Au コンタクトを伴って配位するので、平面 DPCB 分子骨格の歪みが生じた。P=C–S 構造を含むホスファエテンを配位子とした場合、リンのみに金が配位するのに対して、P=C–P 分子骨格を有する非等価 P2 配位子（1,3-ジホスファプロペン）を用いると、対応する単核および二核金(I)錯体の両方が生成した。今回合成したホスファアルケン–金(I)錯体のいくつかは、強い触媒活性を示すために通常必要な銀塩添加剤なしでも、1,6-エンインの環化異性化反応の触媒として有効であることが分かった。

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Table 1. Crystallographic data for compounds **5**, **6**, **9**, **10**, **13a**, and **14b**.

Compound	**5**	**6**	**9**	**10**	**13a**·0.7CH_2Cl_2	**14b**
Formula	$C_{40}H_{64}Au_2Cl_2P_2$	$C_{40}H_{64}Au_2Cl_2P_2$	$C_{52}H_{68}Au_2Cl_2P_2$	$C_{21}H_{35}AuClPS_2$	$C_{33.4}H_{44.8}Au_2Cl_{4.8}P_2$	$C_{31}H_{39}AuCl_2P_2$
M_r	1071.73	1071.73	1219.90	615.02	1072.38	741.47
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (no. 14)	$Aba2$ (no. 41)	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	10.573(1)	23.169(3)	10.126(2)	15.5470(9)	13.4581(4)	10.2371(3)
b [Å]	8.7368(6)	19.711(3)	33.193(9)	11.3459(7)	9.2613(2)	17.1737(8)
c [Å]	22.901(2)	9.4283(8)	16.273(4)	16.0201(6)	30.3986(9)	10.1212(5)
α [°]	90	90	90	90	90	91.994(1)
β [°]	98.752(3)	90	104.51(2)	117.292(2)	99.0969(6)	116.114(3)
γ [°]	90	90	90	90	90	102.744(3)
V [Å^3]	2090.8(4)	4305.6(8)	5294(2)	2511.3(2)	3741.2(2)	1540.6(1)
Z	2	4	4	4	4	2
T [K]	133	133	203	133	153	133
ρ_{calcd} [mg cm^{-3}]	1.702	1.653	1.530	1.627	1.904	1.598
μ [mm^{-1}]	7.263	7.054	5.747	6.219	8.312	5.087
$2\theta_{max}$ [°]	55	55	51	55	55	55
Observed reflections	15857	13013	9437	20458	30107	11831
Unique reflections	4716	1357	6070	5440	8280	6202
R_{int}	0.073	0.084	0.135	0.030	0.051	0.024
$R1$ ($I>2\sigma(I)$)	0.087	0.052	0.169	0.028	0.051	0.031
R_w (all data)	0.157	0.060	0.309	0.037	0.066	0.042
Parameters	108	132	263	340	367	364
GOF	1.94	1.21	2.26	0.98	1.53	1.26

moiety (the carbon atoms were refined isotropically), which was probably due to unsolved disorder and solvent molecules, the conformation of the P=C–C=P skeleton is obvious.

In an attempt to obtain the digold(I) complex of **1** in better yield, we next examined the reaction of **1** with two molar equivalents of [(tht)AuCl] in dichloromethane. After monitoring the reaction mixture and the workup procedures, we surprisingly isolated a single product that was different from the products obtained by use of one molar equivalent of [(tht)AuCl] (Scheme 1). X-ray crystallography confirmed a digold(I) complex **6** with C_2 symmetry: the P=C–C=P skeleton showed a gauche conformation (Figure 2 and Table 1; the carbon atoms except C1 and C1–Me were refined isotropically). Furthermore, the Au–Au distance was found to be 3.059(1) Å, which confirms the presence of intramolecular Au–Au contact.[3,16] The Au–Cl and Au–P distances of **6**, 2.285(6) and 2.219(4) Å, respectively, are comparable to the corresponding data for **5**. Theoretical calculations suggest that the s-*trans* C_{2h} form is the most stable conformation for the P=C–C=P moiety, and the gauche C_2 form is assigned to a local energy minimum; it is slightly less stable than the C_{2h} form.[15] Apparently, the aurophilic interaction seems to overcome the conformational predominance of the C_{2h} P=C–C=P skeleton in affording **6**. However, **5** did not turn into **6** upon heating. Therefore, it is plausible that the excess amount of [(tht)AuCl] (Scheme 1) may have formed Au_2-type intermediate(s) to afford **6** through a conformational change from C_{2h} to C_2. Indeed, a reaction of **5** with 0.5 molar equivalents of [(tht)AuCl] in dichloromethane gave a 1:1 mixture of **5** and **6** within 0.5 h. Intermolecular aurophilic interaction appears to play a role in the conformation change.

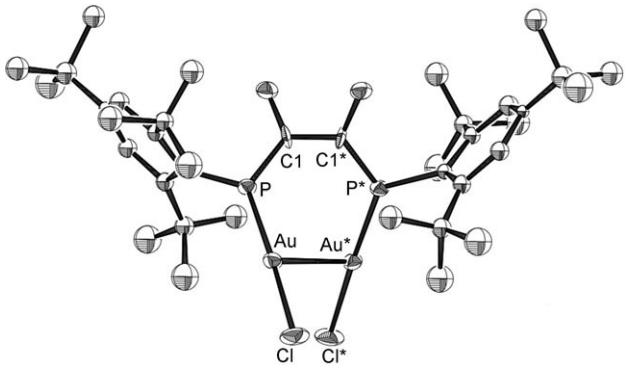
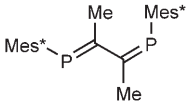


Figure 2. Molecular structure of **6** (ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity. The *p*-*tert*-butyl groups are disordered and one of them is shown.

As described above, both phosphorus atoms of **1** coordinated gold together. On the other hand, the reaction of (*E*,*Z*)-2,3-dimethyl-1,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,4-diphosphabuta-1,3-diene (**7**)[6] with one equivalent of [(tht)AuCl] gave the monogold(I) complex ($\delta_P = 321.9$, 195.7 ppm; $^3J_{P,P} = 194.5$ Hz). The monogold(I) complex and [(tht)AuCl] afforded the corresponding digold(I) complex ($\delta_P = 209.0$, 198.1 ppm; $^3J_{P,P} = 216.1$ Hz). Given the ^{31}P NMR spectroscopic data and the results in Scheme 1, it may be the (*E*)-P=C phosphorus atom in **7** that coordinates gold in the monogold(I) complex. The digold(I) complex of **7** may contain no Au–Au contact due to the nature of the (*E*,*Z*)-1,4-diphosphabuta-1,3-diene skeleton and the steric hindrance. Thus, the coordination properties of the 1,4-diphosphabuta-1,3-diene depend on the configuration. Attempts to purify the gold(I) complexes of **7** were unsuccessful.



7

Preparation of the DPCB–Digold(I) Complex

Although several methods of obtaining the DPCB derivatives have been established,[1,7,8,17] we recently indicated that 2-bromo-3-alkoxy-1-phosphapropenes are good precursors of DPCB derivatives.[18] Compound **2** was synthesized according to Scheme 2 in good yield by utilizing 2-bromo-3-

Scheme 2. Preparation of the DPCB–digold(I) complex.

methoxy-1-phosphapropene **8**;[18a] **2** was then transformed into the digold(I) complex **9**. The structure of **9** was characterized by NMR spectroscopy and X-ray crystallographic analysis (Figure 3 and Table 1). The carbon atoms were re-

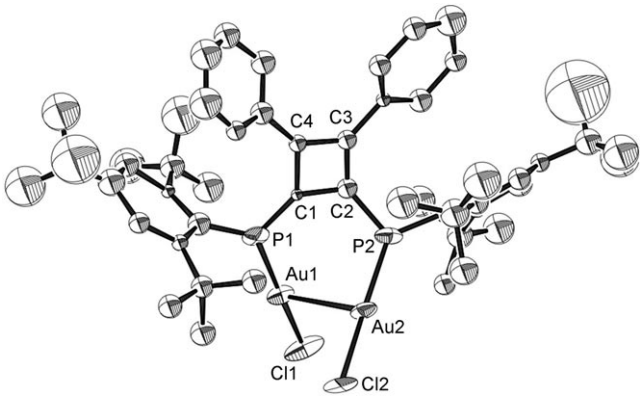
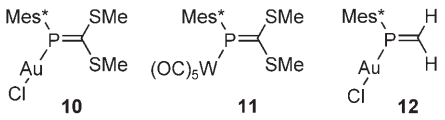


Figure 3. Molecular structure of **9** (ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity.

fined isotropically, whereas the Au, P, and Cl atoms were refined anisotropically. Although the quality of the crystallographic analysis was not good enough for a detailed discussion of the metric parameters, the structure is similar to that of the digold(I) complex from 1,2-bis(cyclopropyl)-3,4-diphosphinidenecyclobutene.[4] The Au1–Au2 distance of 2.995(2) Å implies aurophilic interaction and distortion of the planar DPCB framework upon coordination.

Coordination of the 2,2-Bis(methylsulfanyl)-1-phosphaethene to Gold

The methylsulfanyl group has π-donating ability toward several π-electron systems[19] and can influence the properties of phosphaethenes. Furthermore, the sulfur atom can interact coordinatively with several metals such as gold. Herein we focused on the coordination property of **3**[9] to gold. Compound **3** was allowed to react with [(tht)AuCl], and the corresponding complex **10** was obtained in good yield. The X-ray structure displayed in Figure 4 (see also Table 1)



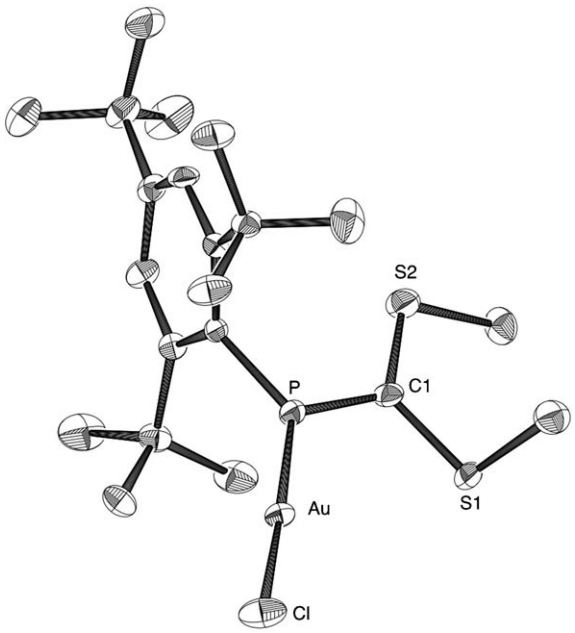


Figure 4. Molecular structure of **10** (ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au–Cl 2.278(1), Au–P 2.225(1), S1–C1 1.758(4), S2–C1 1.746(4), P–C1 1.682(4), P–C_{Mes*} 1.825(4), Cl–Au–P 176.12(4), Au–P–C1 121.2(1), Au–P–C_{Mes*} 131.9(1), C1–P–C_{Mes*} 106.7(2), S1–C1–S2 124.1(2), S1–C1–P 114.9(2), S2–C1–P 121.0(2).

shows that the sulfur atom has almost no obvious coordination bonding with gold (intramolecular S1···Au 3.61 Å; intermolecular S1···Au 3.45 Å). Nevertheless, the elongated S1–C1 distance (1.758(4) Å) compared to the S2–C1 distance (1.746(4) Å) and the corresponding data for **11** (1.747(6) and 1.738(6) Å, respectively)[9] may indicate some interaction between the S1 and the gold atoms. Such weak S···Au interaction has been described.[20] The methylsulfanyl group may contribute to stabilizing the structure, whereas **12** (δ_P = 239.0 ppm), which does not contain this group, gradually decomposed during purification.

Coordination of 1,3-Diphosphapropenes to Gold

We developed 1,3-diphosphapropene derivatives composed of both sp^2 and sp^3 phosphorus atoms as an example of P2 ligands with a low-coordinated phosphorus atom,[10,21] and herein we utilized them for complex formation with gold. (*E*)-2-Methyl-3,3-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene (**4a**)[10a] was mixed with [(tht)AuCl] in di-

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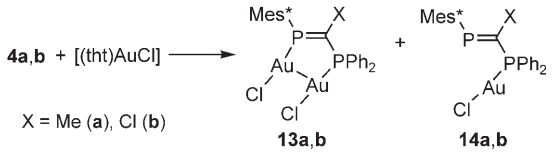
chloromethane and, after concentration and recrystallization, the corresponding digold(I) complex **13a** was obtained in good yield (Scheme 3). Even if 1 equivalent of [(tht)AuCl] was allowed to react with **4a**, no monogold(I)



Scheme 3. Reaction of 1,3-diphosphapropenes with [(tht)AuCl].

complex **14a** was observed in the reaction mixture, and **13a** was isolated in 18% yield together with recovery of the starting material. The X-ray structure of **13a** (Figure 5 and Table 1) shows that the metric parameters around P1, P2,

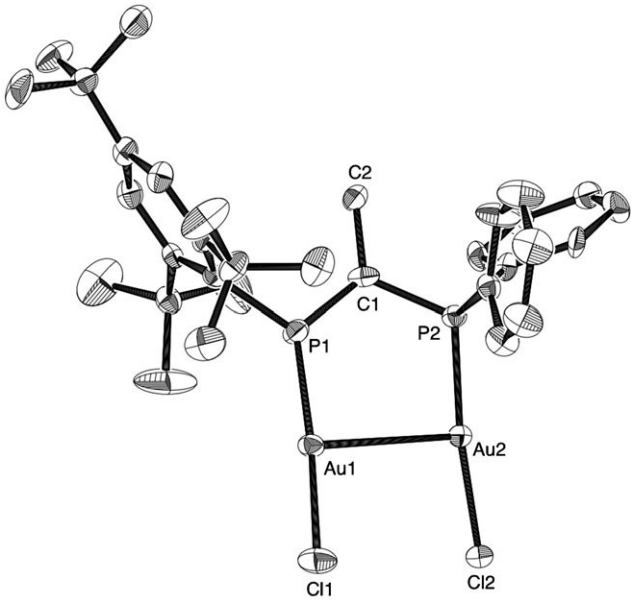


Figure 5. Molecular structure of **13a** (ellipsoids at 50% probability). Hydrogen atoms and the solvent molecules (dichloromethane) are omitted for clarity. Selected bond lengths (Å) and angles (°): Au1–Au2 3.0843(5), Au1–Cl1 2.278(2), Au1–P1 2.226(2), Au2–Cl2 2.295(2), Au2–P2 2.230(2), P1–C1 1.678(9), P1–C_{Mes*} 1.821(9), P2–C1 1.821(10), P2–C_{Ph} 1.818(10), P2–C_{Ph} 1.826(9), C1–C2 1.50(1), Au2–Au1–Cl1 99.87(7), Au2–Au1–P1 85.57(6), Cl1–Au1–P1 174.41(10), Au1–Au2–Cl2 99.58(6), Au1–Au2–P2 87.29(6), Cl2–Au2–P2 173.12(9), Au1–P1–C1 124.1(3), Au1–P1–C_{Mes*} 126.8(3), C1–P1–C_{Mes*} 107.9(4), Au2–P2–C1 115.8(3), Au2–P2–C_{Ph} 113.3(3), Au2–P2–C_{Ph} 112.0(3), C1–P2–C_{Ph} 103.1(4), C1–P2–C_{Ph} 105.5(4), C_{Ph}–P2–C_{Ph} 106.2(4), P1–C1–P2 115.7(5), P1–C1–C2 124.5(7), P2–C1–C2 119.4(7).

and C1 are comparable to those of **4b**.[21a] The P–Au and Au–Cl bond lengths are in the usual range, and the Au–Au contact is in the range of those of the reference substances.[16] The metallacycle itself has an envelope conformation: Au1, P1, C1, and P2 are coplanar (mean deviation: 0.0003(8) Å), whereas Au2 is located 0.964(4) Å outside the plane. This distortion is confirmed by the Cl1–Au1–Au2–Cl2 torsion angle of 25.57(10)°.

The lower coordination ability of **4b**[10b] was observed in its coordination to gold. Compound **4b** was allowed to react with [(tht)AuCl], and after workup a mixture of the digold(I) complex **13b** and the monogold(I) complex **14b** was obtained in a 2:3 ratio (Scheme 3). Crystallization of the mixture afforded colorless prisms and pale-yellow plates. One of the colorless prisms was analyzed by X-ray crystallography to reveal the molecular structure of **14b** (Figure 6 and Table 1). Attempts to separate **13b** and **14b** by chromatographic methods were unsuccessful. X-ray structure analysis of **13b** was not successful owing to the insufficient quality of the crystals for X-ray diffraction.

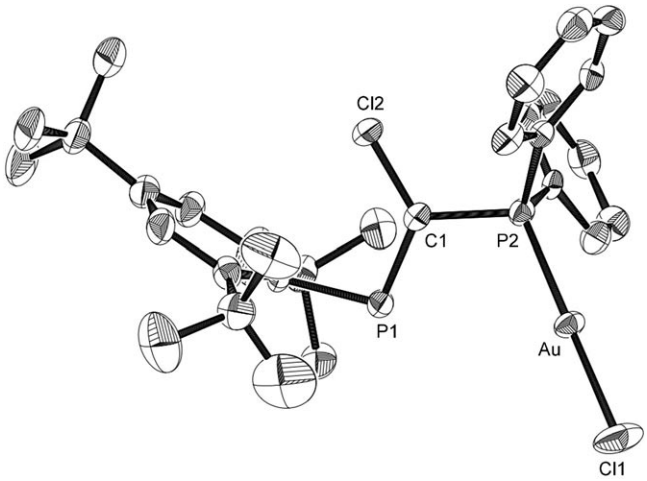
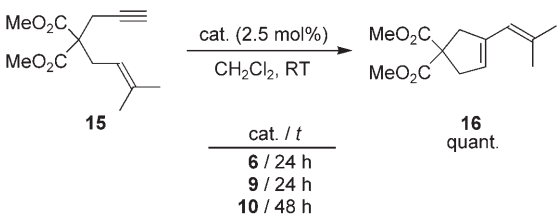


Figure 6. Molecular structure of **14b** (ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au–Cl1 2.283(1), Au–P2 2.229(1), C1–Cl2 1.735(4), P1–C1 1.689(4), P1–C_{Mes*} 1.844(4), P2–C1 1.819(4), P2–C_{Ph} 1.805(4), P2–C_{Ph} 1.813(4), Cl1–Au1–P1 179.14(4), Au–P2–C1 110.2(1), Au–P2–C_{Ph} 113.8(1), Au–P2–C_{Ph} 113.8(1), Cl2–C1–P1 126.3(3), Cl2–C1–P2 117.0(2), C1–P1–C_{Mes*} 101.1(2), C1–P2–C_{Ph} 105.5(2), C_{Ph}–P2–C_{Ph} 103.9(2), C_{Ph}–P2–C_{Ph} 108.9(2), P1–C1–P2 116.2(2).

1,6-Enyne Cycloisomerization Reactions Catalyzed by Gold(I) Complexes

In an attempt to utilize the gold(I) complexes obtained in organic synthesis,[11,12] we did a preliminary examination of a metathesis-like 1,6-enyne cycloisomerization of **15** in dichloromethane at room temperature to afford the vinylcyclopentene **16**[11,22] (Scheme 4). Normally, such gold-catalyzed reactions need a silver cocatalyst to generate reactive



Scheme 4. Au-catalyzed 1,6-enyne cycloisomerization reactions.

Au intermediates. On the contrary, complexes **6**, **9**, and **10** catalyzed the cycloisomerization without silver cocatalyst, although the reaction was slow. Complexes **5** and **13a** showed almost no catalytic activity. These findings indicate that the presence of the P=C group, aurophilic Au–Au contact, and a sulfur-containing group may be important in developing relatively active gold catalysts. The energetically low-lying lowest unoccupied molecular orbital (LUMO) of the phosphorus–carbon double bond would effectively raise the Lewis acidity of the gold complex to activate the acetylene moiety.[1,9] The aurophilic Au–Au contact[3] may facilitate the catalysis.[23] The sulfur atom may weaken the Au–Cl bond by electron-donating effects to generate the $[L-Au]^+$ (L = P ligand) species, whereas the PPh_2 moiety may retard any reactive coordination sites.[24,25] Interestingly, the complexes recovered from the cycloisomerization after workup were catalytically active for reuse.

Conclusions

Gold(I) complexes that bear phosphaalkene ligands were prepared, and the effects of substituents on coordination properties were examined. The 1,4-diphosphabuta-1,3-diene **1** afforded the corresponding digold(I) complexes in different conformations selectively, as did the open-chain complex **5** and the six-membered metallacycle **6**, and no interconversion between **5** and **6** was observed. The DPCB **2** takes two gold atoms to form the six-membered metallacycle **9** by distorting the planar DPCB skeleton. Although the methylsulfanyl group in **3** showed no obvious coordination to gold(I), the structure of **7** indicates weak S···Au interactions. The 2-methyl-1,3-diphosphapropene **4a** afforded only the digold(I) complex **13a**, whereas the lower coordination ability of the 2-chloro-1,3-diphosphapropene **4b** led to a mixture of mono- and digold(I) complexes **13b** and **14b**. The catalytic activity of **6**, **9**, and **10** in the cycloisomerization of 1,6-enynes indicated the usefulness of phosphaalkene ligands and suggested a design for novel gold catalysts. We continue to investigate phosphaalkene–gold complexes from the viewpoint of organic synthesis as well as the exploration of novel functional materials.

Experimental Section

General

All manipulations with organolithium reagents were carried out under an argon atmosphere by means of standard Schlenk techniques, and the solvents employed were dried by appropriate methods. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE400 spectrometer in $CDCl_3$ at 298 K with internal Me_4Si (^1H, ^{13}C) or external H_3PO_4 (^{31}P) standard. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. ESI MS spectra were recorded on a Bruker APEX3 spectrometer. GC–MS (ESI) spectra were recorded on an Agilent 5973N system. Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Tohoku University. Reactions that involved gold were conducted in the dark to avoid decomposition of any gold products and intermediates, but no precautions were taken to exclude air. Compounds **1**,[6] **3**,[9] **4a**,[10a] and **4b**[10b] were prepared according to our previous reports.

Syntheses

2: *tert*-Butyllithium (0.82 mmol, 1.6 M solution in pentane) was added to a solution of **8**[18a] (200 mg, 0.41 mmol) in THF (15 mL) at −78 °C. The mixture was stirred for 15 min, then treated with 1,2-dibromoethane (0.20 mmol) and allowed to warm to room temperature. The solvent and volatile materials were removed in vacuo, and the residue was extracted with hexane. Silica-gel column chromatography (hexane) of the hexane extracts afforded **2** (130 mg, 84 %).

5: [(tht)AuCl][26] (0.059 mmol) was added to a solution of **1** (36 mg, 0.059 mmol) in dichloromethane (6 mL), and the mixture was stirred for 2 h. The volatile parts were removed in vacuo, and the residue was dissolved in dichloromethane (1 mL), which was layered under pentane (5 mL). The crystals formed at the interface were filtered and washed with hexane to afford **5** as yellow crystals (10 mg, 16 %). M.p.: 203–205 °C (decomp.); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (s, 4H, arom), 1.65 (s, 36H, *o*-*t*Bu), 1.57 (s, 6H, Me), 1.37 ppm (s, 18H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 177.7$ (dd, $^1J_{P,C} = 10.0$ Hz, $^2J_{P,C} = 1.9$ Hz, P=C), 155.9 (d, $^2J_{P,C} = 2.3$ Hz, *o*-Mes*), 152.7 (s, *p*-Mes*), 131.8 (d, $^1J_{P,C} = 11.6$ Hz, *ipso*-Mes*), 122.9 (s, *m*-Mes*), 39.0 (s, *o*-CMe_3), 35.6 (s, *p*-CMe_3), 33.8 (pt, $(^4J_{P,C} + {}^7J_{P,C})/2 = 2.0$ Hz, *o*-C*Me*$_3$), 31.6 (s, *p*-C*Me*$_3$), 21.9 ppm (s, P=C*Me*); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 200.5$ ppm; MS (ESI): *m*/*z* calcd for $C_{40}H_{64}Au_2Cl_2P_2 + Na$: 1093.3084; found: 1093.3093.

6: A solution of **1** (27 mg, 0.044 mmol) and [(tht)AuCl] (0.088 mmol) in dichloromethane (5 mL) was stirred for 1.5 h, then the volatile parts were evaporated in vacuo. The residue was dissolved in dichloromethane (1 mL) and layered under pentane (5 mL). The crystals formed at the interface were filtered off and washed with hexane to afford **6** as yellow-orange crystals (22 mg, 47 %). M.p.: 223–224 °C (decomp.); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.57$ (s, 4H, arom), 1.72 (s, 36H, *o*-*t*Bu), 1.36 ppm (s, 18H, *p*-*t*Bu) (Me signals were overlapped by the *o*-*t*Bu signal); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 171.0$ (dd, $^1J_{P,C} = 36.4$ Hz, $^2J_{P,C} = 32.6$ Hz, P=C), 157.0 (pt, $(^2J_{P,C} + {}^5J_{P,C})/2 = 2.3$ Hz, *o*-Mes*), 155.0 (s, *p*-Mes*), 124.2 (pt, $(^1J_{P,C} + {}^4J_{P,C})/2 = 11.8$ Hz, *ipso*-Mes*), 123.9 (pt, $(^3J_{P,C} + {}^6J_{P,C})/2 = 4.4$ Hz, *m*-Mes*), 39.4 (s, *o*-CMe_3), 35.8 (s, *p*-CMe_3), 34.4 (s, *o*-C*Me*$_3$), 31.5 (s, *p*-C*Me*$_3$), 23.0 ppm (pt, $(^2J_{P,C} + {}^3J_{P,C})/2 = 3.0$ Hz, P=C*Me*); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 186.6$ ppm; MS (ESI): *m*/*z* calcd for $C_{40}H_{64}Au_2Cl_2P_2 + Na$: 1093.3084; found: 1093.3090.

9: A solution of **2** (130 mg, 0.172 mmol) and [(tht)AuCl] (0.327 mmol) in dichloromethane (10 mL) was stirred for 2 h, then the volatile parts were evaporated in vacuo. The residue was dissolved in dichloromethane (1 mL) and layered under pentane (5 mL). The crystals formed at the interface were filtered off and washed with hexane to afford **9** as yellow-orange crystals (170 mg, 81 %). M.p.: 275–277 °C (decomp.); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$ (s, 4H, arom), 7.11 (t, $^3J_{H,H} = 7.5$ Hz, 2H, *p*-Ph), 6.86 (t, $^3J_{H,H} = 7.5$ Hz, 4H, *m*-Ph), 6.69 (d, $^3J_{H,H} = 7.5$ Hz, 4H, *o*-Ph), 1.72 (s, 36H, *o*-*t*Bu), 1.36 ppm (s, 18H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 167.3$ (dd, $^1J_{P,C} = 36.4$ Hz, $^2J_{P,C} = 32.6$ Hz, P=C), 157.3 (s, *o*-Mes*), 155.9 (dd, $^2J_{P,C} = 12.9$ Hz, $^3J_{P,C} = 11.6$ Hz, C=C), 155.0 (s, *p*-Mes*), 130.1 (s, *ipso*-Ph), 129.1 (s, *p*-Ph), 128.6 (s, *m*-Ph), 128.1 (s, *o*-Ph), 124.0 (pt, $(^3J_{P,C} + {}^6J_{P,C})/2 = 4.9$ Hz, *m*-Mes*), 121.9 (pt, $(^1J_{P,C} + {}^4J_{P,C})/2 = 14.0$ Hz, *ipso*-Mes*), 39.7 (s, *o*-CMe_3), 35.8 (s, *p*-CMe_3), 35.0 (s, *o*-C*Me*$_3$), 31.7 ppm (s, *p*-C*Me*$_3$); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 134.7$ ppm; MS (ESI): *m*/*z* calcd for $C_{52}H_{70}Au_2Cl_2P_2 + Na$: 1241.3397; found: 1241.3393.

10: A solution of **3** (55 mg, 0.14 mmol) and [(tht)AuCl] (46 mg, 0.14 mmol) in dichloromethane (8 mL) was stirred for 1 h, then the volatile parts were evaporated in vacuo. Compound **10** was recrystallized from a solution of dichloromethane (1.5 mL) and hexane (20 mL) at −10 °C. The crystals formed at the interface were filtered off and washed with hexane to afford **10** as pale-green crystals (71 mg, 82 %). M.p.: 156–159 °C; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.53$ (d, $^4J_{P,H} = 3.8$ Hz, 2H, arom), 2.49 (d, $^4J_{P,H} = 2.7$ Hz, 3H, SMe), 2.30 (d, $^4J_{P,H} = 2.4$ Hz, 3H, SMe), 1.63 (s, 18H, *o*-*t*Bu), 1.36 ppm (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 174.5$ (d, $^1J_{P,C} = 65.7$ Hz, P=C), 156.3 (s, *p*-Mes*), 154.9 (d, $^2J_{P,C} = 2.5$ Hz, *o*-Mes*), 124.9 (d, $^1J_{P,C} = 21.4$ Hz, *ipso*-Mes*), 123.8 (d,

$^3J_{P,C}$=9.0 Hz, *m*-Mes*), 39.2 (s, *o*-*C*Me$_3$), 35.8 (s, *p*-*C*Me$_3$), 34.1 (d, $^4J_{P,C}$= 2.1 Hz, *o*-C*Me*$_3$), 31.5 (s, *p*-C*Me*$_3$), 20.0 (d, $^3J_{P,C}$=14.4 Hz, SMe), 18.5 ppm (d, $^3J_{P,C}$=1.9 Hz, SMe); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=183.0 ppm; MS (ESI): *m*/*z* calcd for $C_{21}H_{35}AuClS_2P$+Na: 637.1164; found: 637.1161.

13a: [(tht)AuCl] (0.86 mmol) was added to a solution of **4a** (210 mg, 0.43 mmol) in dichloromethane (15 mL), and the mixture was stirred for 2 h. The volatile parts were removed in vacuo, and the residue was dissolved in dichloromethane (1.5 mL), which was layered under pentane (8 mL). The crystals formed at the interface were filtered and washed with hexane to afford **13a** as pale-brown crystals (305 mg, 74%). The reaction and recrystallization procedures were carried out in the dark. The reaction of **4a** with [(tht)AuCl] (1 equiv) afforded **13a** in 18% yield. M.p.: 217–219 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.70–7.51 (m, 12H, arom), 1.59 (s, 18H, *o*-*t*Bu), 1.35 (dd, $^3J_{P,H}$=32.2 Hz, $^3J_{P,H}$=11.8 Hz, 3H, Me), 1.32 ppm (s, 9H, *p*-*t*Bu); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ=156.1 (dd, $^1J_{P,C}$=59.2 Hz, $^2J_{P,C}$=20.6 Hz, P=*C*), 155.8 (d, $^2J_{P,C}$=2.3 Hz, *o*-Mes*), 155.6 (d, $^2J_{P,C}$=2.3 Hz, *p*-Mes*), 134.0 (d, $^2J_{P,C}$=14.1 Hz, *o*-Ph), 133.0 (d, $^4J_{P,C}$=2.5 Hz, *m*-Mes*), 130.1 (d, $^4J_{P,C}$=12.0 Hz, *p*-Ph), 127.2 (dd, $^1J_{P,C}$= 59.9 Hz, $^3J_{P,C}$=13.4 Hz, *ipso*-Ph), 124.4 (d, $^3J_{P,C}$=9.0 Hz, *m*-Ph), 123.8 (pt, ($^1J_{P,C}$+$^3J_{P,C}$)/2=17.3 Hz, *ipso*-Mes*), 39.3 (s, *o*-*C*Me$_3$), 35.8 (s, *p*-*C*Me$_3$), 34.6 (s, *o*-C*Me*$_3$), 31.4 (s, *p*-C*Me*$_3$), 21.7 ppm (d, $^4J_{P,C}$=9.5 Hz, P=C*Me*); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ=260.0 (d, $^2J_{P,P}$=142.5 Hz, P=C), 39.0 ppm (d, $^2J_{P,P}$=142.5 Hz, PPh_2); MS (ESI): *m*/*z* calcd for $C_{32}H_{42}Au_2Cl_2P_2$+Na: 975.1362; found: 975.1367.

13b and **14b**: A solution of **4b** (100 mg, 0.20 mmol) and [(tht)AuCl] (0.37 mmol) in dichloromethane (8 mL) was stirred for 1 h. The volatile parts were removed in vacuo, and the residue was dissolved in dichloromethane (1.5 mL), which was layered under pentane (5 mL). The colorless crystals of [(tht)AuCl] formed at the interface were separated, and the procedure was repeated. Within 3 days, pale-yellow crystals of **13b** and colorless crystals of **14b** suitable for X-ray analysis were formed. The crystals were filtered and washed with hexane to afford a mixture of **13b** and **14b** (2:3, 84 mg). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): **13b**: δ=267.5 (d, $^2J_{P,P}$=146.4 Hz, P=C), 41.0 ppm (d, $^2J_{P,P}$=146.4 Hz, PPh_2); **14b**: δ=335.4 (d, $^2J_{P,P}$=218.3 Hz, P=C), 42.4 ppm (d, $^2J_{P,P}$=218.3 Hz, PPh_2); elemental analysis: calcd (%) for $C_{31}H_{39}ClP_2$·1.4AuCl: C 46.34, H 4.89, Cl 10.56; found: C 46.04, H 4.90, Cl 10.01.

1,6-Enyne cycloisomerization: A solution of **15**[27] (0.42 mmol) and **6**, **9**, or **10** (0.011 mmol, 2.5 mol%) in dichloromethane (5 mL) was stirred at room temperature. The reaction mixture was monitored by GC–MS to confirm consumption of **15** and to observe **16**[28] solely. **16**: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.74 (s, 1H, =CH), 5.40 (s, 1H, =CH), 3.75 (s, 6H, CO_2Me), 3.21 (s, 2H, CH_2), 3.05 (s, 2H, CH_2), 1.83 (s, 3H, =CMe), 1.79 ppm (s, 3H, =CMe); MS (EI): *m*/*z*=238 $[M]^+$.

X-ray Crystallography

X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ= 0.71070 Å). The data are listed in Table 1. The structures were solved by direct methods (SIR92)[29] and expanded by using Fourier techniques (DIRDIF94).[30] A symmetry-related absorption correction was applied with the program ABSCOR.[31] Structure solution, refinement, and graphical representation were carried out with the teXsan package.[32] CCDC-605322 (**5**), -605323 (**6**), -607194 (**9**), -607193 (**10**), -601467 (**13a**·0.7CH_2Cl_2), and -601466 (**14b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre at www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**; b) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**.

[2] a) *Gold: Progress in Chemistry, Biochemistry, and Technology* (Ed.: H. Schmidbaur), Wiley, Chichester, **1999**; b) *The Chemistry of Organic Derivatives of Gold and Silver (Chemistry of Functional Groups)* (Eds.: S. Patai, Z. Lappoport), Wiley, Chichester, **1999**; c) M. Tamura, H. Fujihara, *J. Am. Chem. Soc.* **2003**, *125*, 15742.

[3] P. Pyykkö, *Angew. Chem.* **2004**, *116*, 4512; *Angew. Chem. Int. Ed.* **2004**, *43*, 4412.

[4] S. Ito, M. Freytag, M. Yoshifuji, *Dalton Trans.* **2006**, 710.

[5] a) A decanuclear gold(I) cluster cation that bears ligated phosphaalkenes: L. Weber, U. Lassahn, H.-G. Stammler, B. Neumann, K. Karaghiosoff, *Eur. J. Inorg. Chem.* **2002**, 3272; b) gold nanoparticles that bear phosphinines: A. Moores, F. Goettmann, C. Sanchez, P. Le Floch, *Chem. Commun.* **2004**, 2842.

[6] S. Ito, S. Kimura, M. Yoshifuji, *Chem. Lett.* **2002**, 708.

[7] a) F. Ozawa, M. Yoshifuji, *C. R. Chim.* **2004**, *7*, 747; b) M. Yoshifuji, *J. Synth. Org. Chem. Jpn.* **2003**, *61*, 1116.

[8] R. Appel, V. Winkhaus, F. Knoch, *Chem. Ber.* **1987**, *120*, 243.

[9] S. Ito, S. Kimura, M. Yoshifuji, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 405.

[10] a) H. Liang, K. Nishide, S. Ito, M. Yoshifuji, *Tetrahedron Lett.* **2003**, *44*, 8297; b) S. Ito, M. Yoshifuji, *Chem. Commun.* **2001**, 1208.

[11] a) S. Ma, S. Yu, Z. Gu, *Angew. Chem.* **2006**, *118*, 206; *Angew. Chem. Int. Ed.* **2006**, *45*, 200; b) A. S. K. Hashmi, *Angew. Chem.* **2005**, *117*, 7150; *Angew. Chem. Int. Ed.* **2005**, *44*, 6990; c) A. Hoffmann-Röder, N. Krause, *Org. Biomol. Chem.* **2005**, *3*, 387; d) A. M. Echavarren, C. Nevado, *Chem. Soc. Rev.* **2004**, *33*, 431; e) A. S. K. Hashmi, M. C. Blanco, E. Kurpejpvic, W. Frey, J. B. Bats, *Adv. Synth. Catal.* **2006**, *348*, 709.

[12] B. M. Trost, *Angew. Chem.* **1995**, *107*, 285; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259.

[13] a) S. Ito, M. Yoshifuji, *Chem. Lett.* **2000**, 1390; b) S. Ito, M. Yoshifuji, *Chem. Lett.* **1998**, 651; c) S. Ito, K. Toyota, M. Yoshifuji, *Chem. Lett.* **1995**, 747; d) R. Appel, J. Hünerbein, N. Siabalis, *Angew. Chem.* **1987**, *99*, 810; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 779.

[14] a) R. Appel, B. Niemann, W. Schuhn, M. Nieger, *J. Organomet. Chem.* **1988**, *347*, 299; b) A. Ionkin, W. Marshall, *Chem. Commun.* **2003**, 710.

[15] S. M. Bachrach, M. Liu, *J. Am. Chem. Soc.* **1991**, *113*, 7929.

[16] P. G. Jones, *Gold Bull.* **1981**, *14*, 102.

[17] a) K. Toyota, K. Abe, K. Horikawa, M. Yoshifuji, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1377; b) A. Nakamura, S. Kawasaki, K. Toyota, M. Yoshifuji, *Chem. Lett.* **2004**, 1570; c) M. Yoshifuji, K. Toyota, M. Murayama, H. Yoshimura, A. Okamoto, K. Hirotsu, S. Nagase, *Chem. Lett.* **1990**, 2195; d) G. Märkl, P. Kreitmeier, H. Nöth, K. Polborn, *Angew. Chem.* **1990**, *102*, 958; *Angew. Chem. Int. Ed. Engl.* **1990** *29*, 927.

[18] a) S. Ito, S. Sekiguchi, M. Yoshifuji, *J. Org. Chem.* **2004**, *69*, 4181; b) S. Ito, S. Sekiguchi, M. Freytag, M. Yoshifuji, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1142.

[19] F. Bernardi, A. Mangini, N. D. Epiotis, J. R. Larson, S. Shaik, *J. Am. Chem. Soc.* **1977**, *99*, 7645.

[20] a) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, M. Rodríguez-Castillo, *Dalton Trans.* **2006**, 3672; b) B.-C. Tzeng, Y.-C. Huang, W.-M. Wu, C.-Y. Lee, G.-H. Lee, S.-M. Peng, *Cryst. Growth Des.* **2004**, *4*, 63.

[21] a) H. Liang, S. Ito, M. Yoshifuji, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1177; b) S. Ito, K. Nishide, M. Yoshifuji, *Organometallics* **2006**, *25*, 1424; c) S. Ito, H. Liang, M. Yoshifuji, *J. Organomet. Chem.* **2005**, *690*, 2531; d) S. Ito, H. Liang, M. Yoshifuji, *Chem. Commun.* **2003**, 398; e) H. Liang, S. Ito, M. Yoshifuji, *Org. Biomol. Chem.* **2003**, *1*, 3054; f) H. Liang, S. Ito, M. Yoshifuji, *Org. Lett.* **2004**, *6*, 425; g) K.

Nishide, H. Liang, S. Ito, M. Yoshifuji, *J. Organomet. Chem.* **2005**, *690*, 4809.
[22] a) C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 2456; *Angew. Chem. Int. Ed.* **2004**, *43*, 2402; b) C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677; c) C. Nieto-Oberhuber, S. López, M. P. Muñoz, E. Jiménez-Núñez, E. Buñuel, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1694; d) S. T. Diver, A. J. Giessert, *Chem. Rev.* **2004**, *104*, 1317; e) G. C. Lloyd-Jones, *Org. Biomol. Chem.* **2003**, *1*, 215; f) C. Aubert, O. Buisine, M. Malacria, *Chem. Rev.* **2002**, *102*, 813; g) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654; h) A. Fürstner, P. Hannen, *Chem. Commun.* **2004**, 2546; i) F. Gagosz, *Org. Lett.* **2005**, *7*, 4129; j) N. Mézailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005**, *7*, 4133.
[23] D. J. Gorin, N. R. Davis, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 11260.
[24] $[(Ph_2PCH_2PPh_2)Au_2Cl_2]$ showed almost no catalytic activity for the cycloisomerization in spite of the presence of intramolecular Au–Au contact: P. Lange, A. Schier, H. Schmidbaur, *Z. Naturforsch.* **1997**, *52*, 769.
[25] Complex **5a** catalyzed the cycloisomerization from **15** to **16** almost quantitatively in the presence of $Ag[SbF_6]$.
[26] R. Uson, A. Laguna, M. Laguna, *Inorg. Synth.* **1989**, *26*, 85.
[27] R. Mook, Jr., P. M. Sher, *Org. Synth.* **1993**, *8*, 381; R. Mook, Jr., P. M. Sher, *Org. Synth.* **1988**, *66*, 75.
[28] T. R. Hoye, J. A. Suriano, *Organometallics* **1992**, *11*, 2044.
[29] A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[30] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, The DIRDIF94 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen (The Netherlands), **1994**.
[31] T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo (Japan), **1995**.
[32] Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands (USA), **1985** and **1999**.

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