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FULL PAPER

Gold(I) Complexation of the Phosphanoxy-Substituted Phosphaalkenes for the Activation-Free LAuCl Catalysis

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Dedication ((optional))

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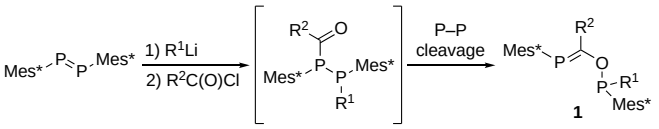
Abstract: The phosphanoxy-substituted phosphaalkene bearing the P=C–O–P skeleton can be prepared from diphosphene Mes*P=PMes* (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$), and the use for catalysis is of interest. In this paper, complexation of the phosphanoxy-substituted phosphaalkenes with gold are investigated, and the catalytic activity of the mono- and bis(chlorogold) complexes are subsequently evaluated. Reaction of the P=C–O–P compound with (tht)AuCl (tht = tetrahydrothiophene) showed dominant coordination on the sp^3 phosphorus, and complete coordination on the sp^2 phosphorus required removal of tetrahydrothiophene. Atoms-In-Molecules (AIM) analysis based on the X-ray structure of the mono(chlorogold) complex indicated pseudo coordinating interaction between the gold centre and the P=C unit. The bis(chlorogold) complexes indicated the conformational isomerism, and catalyzed cycloisomerization/alkoxyclization of 1,6-enyne and for hydration of terminal alkyne without the activation treatment. Even the mono(chlorogold) complexes catalyzed the alkoxycyclization reactions without silver co-catalyst, indicating that the alcohols were effective in activating the AuCl unit.

Introduction

Phosphaalkenes bearing P=C double bond(s) have been utilized as strong π-accepting ligands because of the low-lying LUMO levels comparable with that of carbon monoxide (CO). Although the phosphorus-carbon multiple bonds are normally too reactive to isolate, the kinetic stabilization method using sterically encumbered substituents enables to protect the heavier unsaturated bonds from reactive species.[1,2] So far, many kinds of isolable low-coordinated organophosphorus compounds have been reported,[3,4] and several transition-metal-based Lewis acid catalysts have been developed.[5,6]

We have utilized kinetically stabilized phosphaalkenes for developing homogeneous gold catalysis.[7] Homogeneous gold catalysis featuring the soft π-acidic character has greatly been progressed over the past few decades, and many catalytic molecular transformations have been established.[8,9] In general, the catalytically active gold complexes bearing the ligated phosphines should not contain chloride, because Cl$^-$ ion binds with gold strongly and prevent coordination of the substrates enough to cause the following molecular transformations.[10] However, several phosphaalkene-chlorogold(I) complexes can catalyze molecular transformations without activation using silver co-catalyst.[5a,7,11] It is plausible that the strong π-accepting character of P=C can promote the Lewis acid functionality on the gold centre(s) even in the presence of Cl$^-$ ion. In addition, most of the phosphaalkene-chlorogold(I) catalysts can be recovered after the reactions, which is promising to develop sustainable chemical processes.[12]

The first isolable diphosphene Mes*P=PMes* (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$, supermesityl) is one of the key compounds for recent progress on the chemistry of multiple bonds including heavier main group elements.[13] The “true phosphobenzene” has been utilized as a starting materials for synthesis of low-coordinated phosphorus compounds by cleaving the P=P double bond.[3,4b] Previously, we described a metathesis-type transformation of Mes*P=PMes* by using an organolithium reagent and an acyl chloride affording phosphanoxy-substituted phosphaalkene **1** via the P–P bond cleavage in the acyl-substituted diphosphane intermediates (Scheme 1).[14] The presence of both sp^2 and sp^3 phosphorus atoms in **1** is quite attractive as one of the non-symmetric P2 ligand system. Whereas attempted synthesis of chelate transition-metal complexes bearing **1** has been unsuccessful until now, use of **1** for chemistry of gold complexes has been possible.



Scheme 1. P=P bond cleavage of diphosphene Mes*P=PMes* affording phosphanoxy-substituted phosphaalkene **1**.

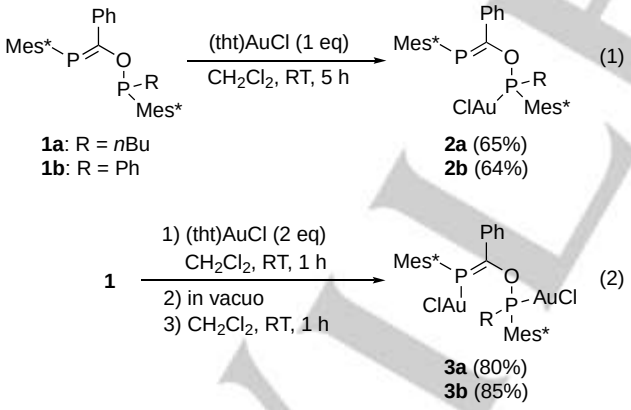
In this paper, we describe preparation and catalytic activity of chlorogold(I) complexes bearing **1**. Although the P=C unit in **1** basically shows inferior coordination ability to AuCl, the sp^2 phosphorus atom is effective to increase catalytic activity of the gold centre even in the presence of chloride ion. In the course of structure determination, the bis(chlorogold) complexes indicated

dynamic conformational changes. Interestingly, weak interaction between the P=C group and the sp^3 phosphanoxy-coordinated gold centre in the mono(chlorogold) complex might be effective to catalyze the cyclization process under the activation-free conditions accompanying alcohols.

Results and Discussion

Preparation and structure of chlorogold complex bearing the ligated P=C–O–P system

According to our previous report,[14] phosphanoxy-substituted phosphaalkenes **1** were prepared from diphosphene Mes*P=PMes*, organolithium reagents, and benzoyl chloride. Reaction of **1** with 1 eq of (tht)AuCl (tht = tetrahydrothiophene) allowed predominant coordination of the gold on the sp^3 phosphorus in the phosphanoxy group, and the corresponding mono(chlorogold) complexes **2** were isolated in moderate yields (Scheme 2, Eq 1). On the other hand, reaction of **1** with 2 eq of (tht)AuCl was sluggish and gave mixtures of bis(chlorogold) complexes **3** together with **2**. This result indicates that, in contrast to most of phosphaalkenes we have investigated so far,[7] coordination ability of the P=C unit in **1** is considerably weak probably due to the presence of the oxo unit, and comparable with that of tetrahydrothiophene. To avoid cumbersome purification processes in the synthesis of **3**, the volatile materials including tetrahydrothiophene were removed from the reaction mixture of **1** and 2 eq of (tht)AuCl, and subsequent addition of the solvent (dichloromethane) was conducted. This procedure was successful, and only bis(chlorogold) complexes **3** were isolated in good yields (Scheme 2, Eq 2). It should be mentioned that de-coordination of AuCl from the sp^2 phosphorus generating gold nanoparticles was somewhat problematic in the preparation and isolation of **3b**.



Scheme 2. Synthesis of chlorogold(I) complexes bearing the phosphanoxy-substituted phosphaalkenes.

Figure 1a shows an ORTEP drawing of **2a** indicating that the P=C moiety directs to the gold centre with the P···Au distance of 3.404 Å. The P2–C1 distance is almost the same as that of **1** (1.701 Å).[14] The structure of **2a** indicates the pseudo chelate interaction, which would relate with the lower coordination ability of **2** (*vide supra*). The Au–Cl distance of 2.296 Å is slightly elongated compared with **3** (*vide infra*), indicating that the P=C unit might be effective to increase the Lewis acidity on the gold centre. The Atoms-in-Molecule (AIM) study[15,16] showed the trajectory from the sp^2 phosphorus atom and the gold centre, indicating both a pseudo σ-donation from the lone pair and a back-donating π-coordination to the P=C unit (Figure 1b).[17] Thus, the presence of P=C–O skeleton in **2a** might increase the Lewis acidity by weakening the Au–Cl interaction. The NBO analysis could not give scalable parameters depicting the small interaction between the gold centre and the sp^2-phosphorus atom.

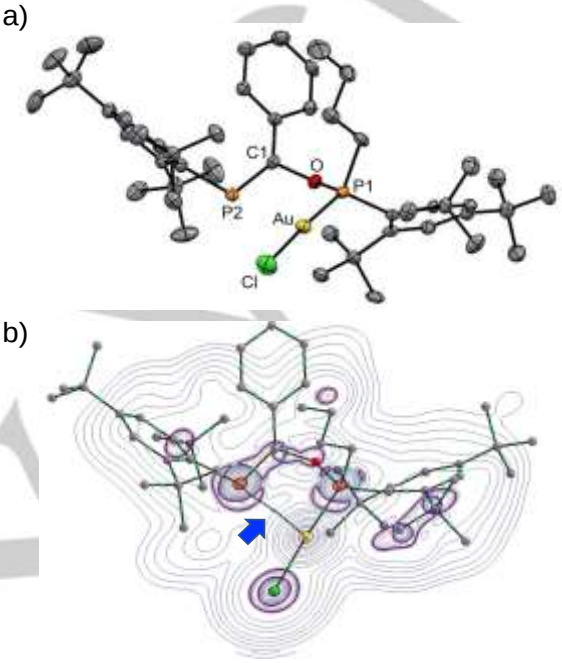


Figure 1. a) An ORTEP drawing of **2a** of 50% probability level. Hydrogen atoms are omitted for clarity. One of the *o*-CMe_3 groups in the P1-connected Mes* unit is disordered, and the atoms of the predominant occupancy factor (0.68) are shown. Bond lengths (Å) and angles (°): Au–Cl 2.296(3), P1–Au 2.232(2), O–P1 1.633(5), O–C1 1.431(8), C1–P2 1.698(8), P1–Au–Cl 176.5(1), P1–O–C1 123.5(4). b) A 2D contour plot of the Laplacian distribution $\nabla^2\rho(r)$ in **2a** in the plane of P1, P2, and Au. The bond critical points (BCPs) are colored light green. The AIM analysis was conducted based on the single point calculation at the ωB97XD/SDD(Au), 6-31+G(d). At the BCP between the sp^2 phosphorus atom and the gold centre (blue arrow), $\rho(r)$ and $\nabla^2\rho(r)$ of 0.0144 e $Bohr^{-3}$ and +0.0332 e $Bohr^{-5}$ are characterized, respectively.

Although the solution quality was not acceptable due to the lack of X-ray diffraction data enough to determine the metric parameters completely, the X-ray structure of **3a** (R = *n*Bu) revealed two conformers without obvious Au–Au contact, and intramolecular Au···Au distances of 5.563 and 5.663 Å were observed in the crystalline state (Figure 2). The P=C–O–P skeleton in **1** is comparable with dppe [1,4-bis(diphenylphosphino)ethane] that provides bis(chlorogold) complex avoiding the intramolecular aurophilic interaction.[18]

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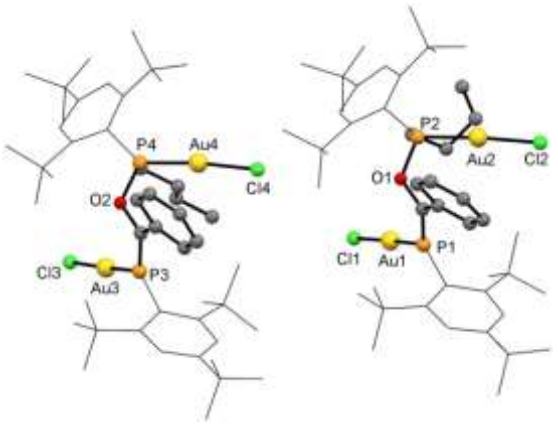


Figure 2. A drawing of the qualitatively determined structures of **3a** in the crystalline state. Hydrogen atoms are omitted for clarity. Bond lengths around the gold centres (Å): P1–Au 2.226(4), P2–Au2 2.238(3), Au1–Cl1 2.264(6), Au2–Cl2 2.285(3), P3–Au3 2.230(4), P4–Au4 2.234(3), Au3–Cl3 2.270(6), Au4–Cl4 2.278(3).

In the NMR analyses of **3b** (R = Ph), the broadened ^{31}P NMR (121 MHz) signals were observed around δ 140 and 180 at 300 K (Figure 3a), which is in sharp contrast with **3a** (δ_P 138.7, 154.0; $^3J_{PP}$ = 40.4 Hz). The ^{31}P NMR spectrum of **3b** might correlate with the rapid interconversion between at least two conformers. Neither separation nor sharpening of the ^{31}P NMR signals was observed between 183–323 K. Preliminary DFT calculations for **3b** as well as the X-ray structure of **3a** indicated that the aurophilic interaction[19] might not be advantageous. Therefore, we speculated that the presence of four aromatic rings in **3b** might produce the propeller-type conformations (Figure 3b). In the ^{1}H VT-NMR analyses (400 MHz, THF-d_8), the aromatic protons showed coalesce around 243 K, and the protons of the Ph-C=P unit became non-equivalent below 213 K ($\Delta\nu$ ~ 360 Hz, see Supporting Information). According to the Gutowky-Holm's formula,[20] activation energy ($\Delta G^{\ddagger}$) of 11 kcal/mol was roughly estimated.

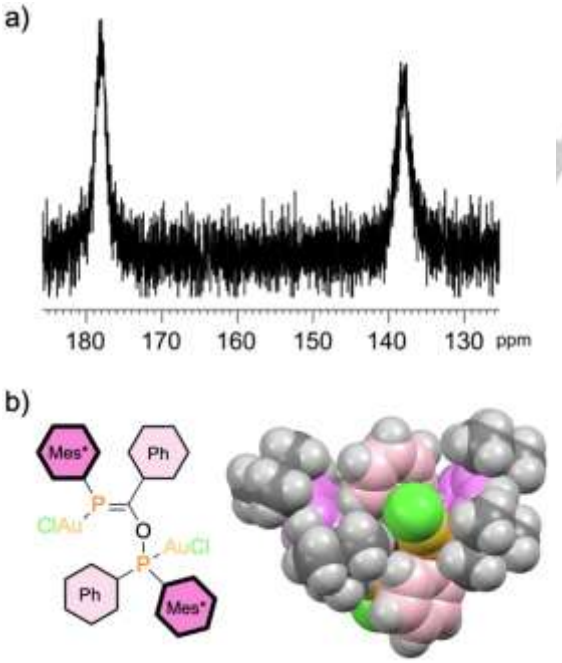
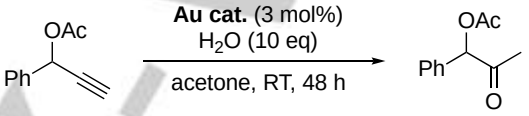


Figure 3. a) A ^{31}P{^{1}H} NMR spectrum of **3b** (121 MHz, 300K, C_6D_6). b) A space-filling drawing of the DFT-simulated structure of **3b** at the ωB97XD/SDD(Au), 6-31G(d) level.

Catalytic activity of bis(chlorogold) complexes bearing the ligated P=C–O–P system

As we have demonstrated so far, phosphaalkene-chlorogold(I) complexes can catalyze several molecular transformations by activating the terminal alkyne units without silver co-catalyst.[7a-f] Bis(chlorogold) complexes **3** can also be used for several catalytic reactions without Ag salt. Tables 1 and 2 display hydration of 2-propynyl acetate and cycloisomerization of 1,6-enyene catalyzed by **3**, respectively. Both **3a** and **3b** showed comparable catalytic activity with the mononuclear chlorogold complex bearing Mes*P=CPh$_2$.[7a] Complexes **3** showed no decomposition in the hydration and cycloisomerization reactions.

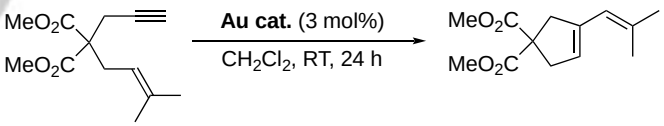
Table 1. Gold-catalyzed hydration of 2-propynyl acetate.



Au cat.	Yield (%)[a]	Recovery (%)[b]
3a	69	31
3b	60	40

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

Table 2. Gold-catalyzed cycloisomerization of 1,6-enyne.



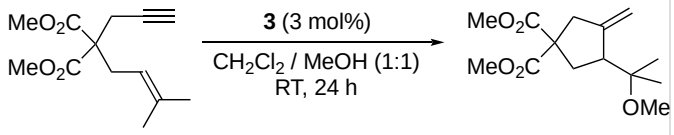
Au cat.	Yield (%)[a]	Recovery (%)[b]
3a	95	0
3b	93	7

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

Table 3 summarizes alkoxycyclization of 1,6-enyne catalyzed by **3**. Whereas **3a** showed a moderate catalytic activity, **3b** gave the methylenecyclopentene product in an excellent yield. However, both **3a** and **3b** showed de-coordination of AuCl from the P=C unit in the catalytic process, and the mononuclear complexes **2** were obtained after the alkoxycyclization reaction. Although the detailed mechanism has been unclear, the sensitive P(sp^2)-Au bond to alcohol might correlate with the lower coordination ability of the sp^2 phosphorus in **1**. Considerable amount of the de-coordination product **2b** after the catalytic reaction using **3b**

correlated with the instability observed during the preparation process.

Table 3. Gold-catalyzed alkoxycyclization of 1,6-enyne.

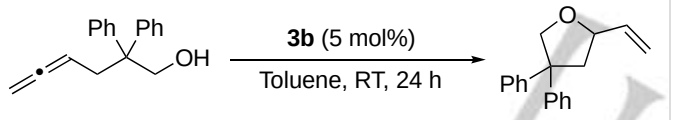


3	Yield (%)[a]	Recovery of 1,6-enyne (%)[a]	Recovery of 3 (%)[b]	Yield of 2 (%)[b]
3a	73	23	84	16
3b	97	3	67	33

[a] Determined by ^{1}H NMR. [b] Determined by ^{31}P NMR.

The superior catalytic activity of **3b** for the allkoxycyclization prompted to examine other catalytic reaction including hydroalkoxylation. As shown in Table 4, 2,2-diphenylhexa-4,5-dien-1-ol was converted into the corresponding 2-vinyltetrahydrofuran in a low yield (Entry 1). Use of $AgSbF_6$ as a co-catalyst improved the yield up to 91% (Entry 2).

Table 4. Gold-catalyzed intramolecular hydroalkoxylation of allenyl alcohol.



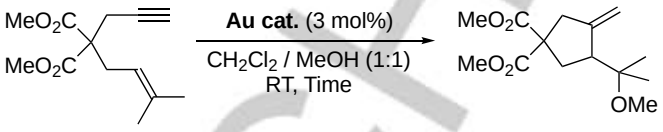
Entry	Additive	Yield (%)[a]	Recovery (%)[a]
1	-	11	89
2	$AgSbF_6$ (10 mol%)	91	9

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

Mono(chlorogold) complexes (2) for the activation-free gold catalysis

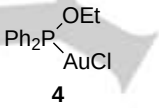
In addition to bis(chlorogold) complexes **3**, catalytic reactions using the mononuclear complexes **2** were also examined. The hydration and the cycloisomerization reactions did not occur in the presence of **2**. On the other hand, alkoxycyclization of 1,6-enyne was catalyzed in the presence of **2** (Table 5). Both **2a** and **2b** provided small amounts of the cyclization product after 24 h (Entry 1, 2). Elongation of the reaction time was effective to improve the yield up to 62% with **2a** (Entry 3) and, to our delight, 95% with **2b** (Entry 4). No decomposition of **2** was observed after the catalytic processes. Warming at 40 °C was effective to accelerate the reaction (Entry 5, 6). The methoxydiphenylphosphine-chlorogold(I) complex **4**[21] showed no catalytic activity, indicating that the presence of the P=C unit in **2** is responsible to the gold-catalyzed the alkoxycyclization under the activation-free condition (Entry 7). The intramolecular hydroalkoxylation of allenyl alcohol was not facilitated by **2b** even in the presence of $AgSbF_6$ (see Supporting Information).

Table 5. Alkoxycyclization of 1,6-enyne catalyzed by mononuclear complexes **2**.



Entry	Au cat.	Time (d)	Yield (%)[a]	Recovery of 1,6-enyne (%)[a]
1	**2a**	1	19	81
2	**2b**	1	15	85
3	**2a**	6	62	38
4	**2b**	6	95	<5
5	**2b**[b]	1	25	75
6	**2b**[b]	3	80	20
7	**4**	1	0	>99

[a] Determined by ^{1}H NMR. [b] Reaction was carried out at 40 °C.



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As discussed above, the presence of P=C–O skeleton in **2a** might increase the Lewis acidity by interacting over the gold centre. Also, possible H-bond interaction between the chloride in **2** and methanol might be advantageous to the activation-free catalytic alkoxycyclization. Although the detailed analysis should be conducted, Figure 4 suggests a plausible interaction that increase the Lewis-acid character on the gold centre in **2**.[22,23] In the alkoxycyclization reaction with **3**, methanol might facilitate de-coordination of AuCl from the sp^2 phosphorus atom (see Table 3). The ^{31}P NMR titration study showed that the amount of methanol affected the ^{31}P chemical shifts and the spin-spin coupling parameters, although the deviation was considerably small (see Supporting Information).

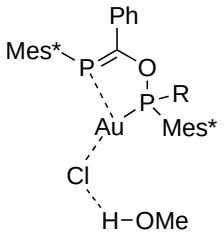
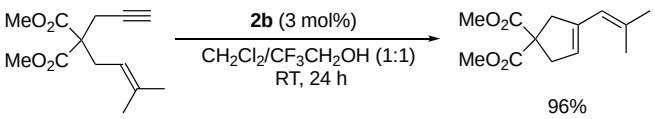


Figure 4. Plausible interaction between **2** and methanol increasing the Lewis acidity of the gold centre.

To explore the effects of alcohol on the catalytic activity of the mono(chlorogold) complex in more detail, reaction of 1,6-enyne

in the presence of other alcohols was investigated. Whereas *t*BuOH deactivated the catalytic functionality of **2b**, use of 2,2,2-trifluoroethan-1-ol (CF_3CH_2OH) was quite effective to promote the cycloisomerization process (Scheme 3). Although the low nucleophilicity of CF_3CH_2OH was useless for the alkoxylation process, the increased Lewis acid character by the perfluorinated ethanol was suitable to activate the alkyne unit leading to the vinylcyclopentene product.



Scheme 3. Cycloisomerization of 1,6-enyne promoted by **2b** in the presence of 2,2,2-trifluroethan-1-ol.

Conclusion

In conclusion, we described utility of the phosphaoxy-substituted phosphaalkenes for the activation-free gold catalysis. The mononuclear structure of **2** accompanied weak interaction between the P=C unit and the gold centre, which might increase the Lewis acidity. Bis(chlorogold) complexes **3** did not contain the aurophilic interaction, and showed the conformational isomerism probably due to the presence of four aryl substituents. Bis(chlorogold) complexes **3** containing the P(sp^2)–Au bond catalyzed cyclioisomerization/alkoxycyclization of 1,6-enyne and hydration of 2-propynyl acetate without the activation treatment. Interestingly, even mono(chlorogold) complexes **2** showed catalytic activity in the alkoxycyclization, indicating the additional effects of alcohol for increase of the Lewis acidity. The findings of this study suggest novel design for the sustainable gold catalysis as well as for elucidation of catalytic mechanisms promoted by the phosphaalkene unit.

Experimental Section

All experiments were carried out under inert atmosphere (nitrogen or argon) unless otherwise noted. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were measured on a Bruker AVANCE 300 spectrometer or a JEOL JNM-ECZ400S (400 MHz) spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from $CHCl_3$ as an internal standard (δ = 7.26) in $CDCl_3$, C_6H_6 as an internal standard (δ = 7.16) in C_6D_6. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ = 77.16) in $CDCl_3$, C_6D_6 as an internal standard (δ = 128.4). Chemical shifts of ^{31}P NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard (δ = 0). Mass spectra were measured on a JEOL JMS-T100LC spectrometer. X-ray diffraction data were measured on a Rigaku RAXIS-RAPID diffractometer. The structures were solved by a direct method (SHELXL-2014).[24] The X-ray structure solution and refinement were carried out using the Yadokari-XG software.[25] Density Functional Theory (DFT) calculations were carried out using Gaussian 09 (B.01) package.[26]

Preparation of **2a**: A mixture of **1a** (71.5 mg, 0.10 mmol) and (tht)AuCl (32.1 mg, 0.10 mmol) in dichloromethane (1 mL) was stirred for 5 h at the room temperature. After the volatile materials are removed *in vacuo*, the resultant residue was washed with hexane (5 ml) to afford **2a** as a pink solid (61.1 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (t, 3H, *J* = 6.7 Hz), 0.85–1.20 (m, 5H), 1.33 (s, 18H), 1.46 (s, 18H), 1.50 (s, 18H), 2.30–2.50 (m, 1H), 6.22 (d, 2H, *J* = 7.9 Hz), 6.77 (pt, 2H, *J* = 7.8 Hz), 6.95 (t, 1H, *J* = 7.1 Hz), 7.31–7.35 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.1, 23.4 (d, *J* = 15.9 Hz), 25.9, 31.0, 31.4, 32.9 (d, *J* = 6.7 Hz), 33.0 (d, *J* = 6.8 Hz), 34.6, 35.0, 37.1 (d, *J* = 33.3 Hz), 40.0–41.0, 122.5 (d, *J* = 8.4 Hz), 124.7 (d, *J* = 1.8 Hz), 126.8 (d, *J* = 6.3 Hz), 127.2 (d, *J* = 2.0 Hz), 128.0 (d, *J* = 3.4 Hz), 131.0 (dd, *J* = 61.7 Hz, *J* = 3.8 Hz), 138.7 (d, *J* = 3.3 Hz), 138.9 (d, *J* = 3.5 Hz), 151.3, 151.9 (d, *J* = 3.3 Hz), 155.3 (d, *J* = 2.1 Hz), 155.7 (d, *J* = 1.5 Hz), 187.9 (dd, *J* = 44.0 Hz, *J* = 8.8 Hz); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 123.9 (d, *J* = 93.0 Hz), 198.7 (d, *J* = 93.0 Hz); HRMS (APCI) calcd for $C_{47}H_{72}AuClNaOP_2$ $[M+Na]^+$ 969.4310, found 969.4312.

X-ray crystallographic data of **2a**: $C_{47}H_{72}ClOP_2Au$, M_W = 947.40, crystal dimensions = 0.230 x 0.200 x 0.080 mm^3, orthorhombic, *P*na2$_1$ (#33), *a* = 20.3117(4), *b* = 22.7508(8), *c* = 10.2382(7) Å, *V* = 4731.1(4) Å^3, *Z* = 4, *T* = 123 K, λ = 0.71075 Å, ρ_{calc} = 1.330 g m^{-3}, $\mu_{MoK\alpha}$ = 3.265 mm^{-1}, F_{000} = 1952, –26≤*h*≤26, –29≤*k*≤28, –12≤*l*≤13, 45194 total reflections (2θ_{max} = 54.97°), 10327 unique (R_{int} = 0.0369), *R* = 0.0383 (σ>2σ(*I*)), 0.0441 (all data), w*R*2 = 0.1146 (σ>2σ(*I*)), 0.1201 (all data), *S* = 0.952 (482 parameters). CCDC-2025940.

Preparation of **2b**: A mixture of **1b** (73.5 mg, 0.10 mmol) and (tht)AuCl (32.1 mg, 0.10 mmol) in dichloromethane (1 mL) was stirred for 5 h at the room temperature. After the volatile materials are removed *in vacuo*, the resultant residue was washed with hexane (5 ml) to afford **2b** as a white solid (62.2 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (s, 9H), 1.02 (s, 9H), 1.26 (s, 9H), 1.36 (s, 9H), 1.40 (s, 9H), 1.62 (s, 9H), 6.05–6.09 (m, 2H), 6.65–6.71 (m., 2H), 6.88 (t, 1H, *J* = 2.9 Hz), 7.05–7.08 (m, 2H), 7.20–7.30 (m, 3H), 7.32–7.41 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 31.1, 31.4, 32.2 (d, *J* = 6.0 Hz), 32.9 (d, *J* = 6.7 Hz), 33.6 (d, *J* = 2.9 Hz), 33.9, 34.7, 34.9, 37.2, 38.1, 39.8, 41.4, 123.1 (d, *J* = 11.2 Hz), 123.7 (d, *J* = 7.7 Hz), 126.3 (d, *J* = 4.2 Hz), 126.7 (d, *J* = 1.7 Hz), 126.8 (d, *J* = 6.3 Hz), 127.5 (d, *J* = 3.1 Hz), 127.9–128.3, 131.0 (dd, *J* = 62.3 Hz, *J* = 5.9 Hz), 132.5 (d, *J* = 2.1 Hz), 137.2 (d, *J* = 60.6 Hz), 138.9 (dd, *J* = 17.3 Hz, *J* = 4.5 Hz), 151.1, 152.1 (d, *J* = 2.6 Hz), 154.6, 156.0 (d, *J* = 3.7 Hz), 158.9 (d, *J* = 8.0 Hz), 160.7 (d, *J* = 3.8 Hz), 186.9 (d, *J* = 13.7 Hz); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 107.6 (d, *J* = 124.4 Hz), 188.9 (d, *J* = 124.4 Hz); HRMS (APCI) calcd for $C_{49}H_{68}AuClNaOP_2$ $[M+Na]^+$ 989.3997, found 989.3976.

Preparation of **3a**: A mixture of **1a** (71.5 mg, 0.10 mmol) and (tht)AuCl (64.1 mg, 0.20 mmol) in dichloromethane (1 mL) was stirred for 1 hour at the room temperature. After the volatile materials are removed under the reduced pressure, the resultant residue was dissolved in dichloromethane (1 mL) under nitrogen atmosphere. The mixture was stirred for 1 h at the room temperature, and the volatile materials were removed under the reduced pressure. The resultant residue was washed with hexane (5 ml) to afford **3a** as a pink solid (98.2 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85–0.91 (m, 1H), 1.03 (t, 3H, *J* = 7.3 Hz), 1.31 (s, 18H), 1.37 (s, 9H), 1.54 (s, 9H), 1.68 (s, 9H), 1.83 (s, 9H), 1.83–2.00 (m, 2H), 2.10–2.30 (m, 1H), 2.73–2.85 (m, 1H), 3.55–3.69 (m, 1H),5.79–5.83 (m, 2H), 6.67 (pt, 2H, *J* = 7.2 Hz), 6.99–7.06 (m, 1H), 7.29–7.31 (m, 2H), 7.53–7.58 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.1, 23.8 (d, *J* = 21.1 Hz), 31.1, 32.3 (d, *J* = 5.6 Hz), 33.9, 34.2, 34.3 (d, *J* = 1.7 Hz), 34.7, 35.4, 38.2 (d, *J* = 25.6 Hz), 38.9 (d, *J* = 2.0 Hz), 39.0 (d, *J* = 2.1 Hz), 40.5 (d, *J* = 3.9 Hz), 118.7 (d, *J* = 32.3 Hz), 123.1 (d, *J* = 10.1 Hz), 123.9 (d, *J* = 7.7 Hz), 124.5 (d, *J* = 36.3 Hz), 125.3 (d, *J* = 9.5 Hz), 125.9 (d, *J* = 9.3 Hz), 127.1 (d, *J* = 10.1 Hz), 128.0 (d, *J* = 3.7 Hz), 130.7 (d, *J* = 5.8 Hz), 136.1 (d, *J* = 4.4 Hz), 153.1 (d, *J* = 4.5 Hz), 155.6 (d, *J* = 3.0 Hz), 157.4, 158.2 (d, *J* = 3.3 Hz), 158.6, 159.6 (d, *J* = 18.3 Hz), 183.5 (dd, *J* = 103.2 Hz, *J* = 6.1 Hz); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 138.7 (d, *J* = 40.4 Hz), 154.0 (d, *J* = 40.4 Hz); HRMS (APCI) calcd for $C_{47}H_{72}Au_2Cl_2NaOP_2$ $[M+Na]^+$ 1201.3664, found 1201.3654.

X-ray crystallographic data of **3a**: $C_{47}H_{72}Cl_2OP_2Au2$ M_W = 1179.81, crystal dimensions = 0.160 x 0.160 x 0.080 mm^3, triclinic, *P*-1 (#2), *a* = 15.9562(5), *b* = 18.3089(6), *c* = 20.0597(8) Å, α = 116.9745(9), β = 98.5272(10), γ = 101.1501(5) °, *V* = 4934.0(3) Å^3, *Z* = 4, *T* = 143 K, λ = 0.71075 Å, ρ_{calc} = 1.588 g m^{-3}, $\mu_{MoK\alpha}$ = 6.145 mm^{-1}, F_{000} = 2336, –20≤*h*≤20, –23≤*k*≤23, –26≤*l*≤25, 79631 total reflections (2θ_{max} = 54.97°), 22476 unique (R_{int} =

0.0634), *R* = 0.0583 (σ>2σ(*I*)), 0.1073 (all data), w*R*2 = 0.1477 (σ>2σ(*I*)), 0.2350 (all data), *S* = 1.436 (898 parameters). See Supporting Information.

Preparation of **3b**: A mixture of **1a** (73.5 mg, 0.10 mmol) and (tht)AuCl (64.1 mg, 0.20 mmol) in dichloromethane (1 mL) was stirred for 1 h at the room temperature. After the volatile materials are removed under the reduced pressure, the resultant residue was dissolved in dichloromethane (1 mL) under nitrogen atmosphere. The mixture was stirred for 1 h at the room temperature, and the volatile materials were removed under the reduced pressure. The resultant residue was washed with hexane (5 ml) to afford **3b** as a pink solid (102.1 mg, 85%). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 31.0, 31.0, 33.8 (d, *J* = 3.5 Hz), 34.3, 34.5, 34.8, 35.1, 38.9 (d, *J* = 1.4 Hz), 39.9, 41.3, 122.8 (d, *J* = 10.4 Hz), 123.5, 124.8, 126.5–128.5, 129.4, 133.3, 135.0 (dd, *J* = 54.8 Hz, *J* = 0.7 Hz), 135.4–136.5, 153.1 (d, *J* = 3.0 Hz), 154.6 (d, *J* = 2.8 Hz), 157.5 (d, *J* = 1.4 Hz), 158.1, 159.3–159.7, 161.4, 190.6 (d, *J* = 47.3 Hz); HRMS (APCI) calcd for $C_{49}H_{68}Au_2Cl_2NaOP_2$ $[M+Na]^+$ 1221.3351, found 1221.3307.

Hydration of propargyl acetate[27]: To a corresponding chlorogold complex (3 mol%), a solution of propargyl acetate (17.4 mg, 0.10 mmol) in acetone (1 mL) and H_2O (1.0 mmol) was added at the room temperature. After stirred for 48 hours, the reaction mixture was directly loaded on a silica gel (SiO_2) column and eluted with hexane/ethyl acetate 6:1 to give 2-oxo-1-phenylpropyl acetate as a colorless oil.

Cycloisomerization of 1,6-enyne[28]: To a corresponding chlorogold complex (3 mol%), a solution of 1,6-enyne (25.3 mg, 0.10 mmol) in dichloromethane (1 mL) was added at the room temperature. After stirred for 24 h, the reaction mixture was directly loaded on a silica gel column and eluted with hexane/ethyl acetate 6:1 to give the cycloisomerization product as a colorless oil.

Alkoxycyclization of 1,6-enyne[28]: To a corresponding chlorogold complex (3 mol%), a solution of 1,6-enyne (25.3 mg, 0.10 mmol) in dichloromethane (0.5 mL) and methanol (0.5 mL) was added at the room temperature. After stirred for 24 h, the reaction mixture was directly loaded on a silica gel column and eluted with hexane/ethyl acetate 6:1 to give the product as a colorless oil.

Intramolecular hydroalkoxylation of allenyl alcohol[29]: A mixture of **3b** (5 mol%) and additive in toluene (0.4 mL) was stirred for 10 min at room temperature. To the mixture in toluene was added 2,2-diphenylhexa-4,5-dien-1-ol (25.3 mg, 0.10 mmol) in toluene (0.6 mL) at room temperature. After stirring for 24 h, the reaction mixture was directly loaded on a short silica gel column and eluted with hexane/ethyl acetate to give the 2-vinyltetrahydrofuran as a colorless oil.

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Keywords: phosphaalkenes • gold catalysis • conformational isomerism • electron density distribution • coordination chemistry

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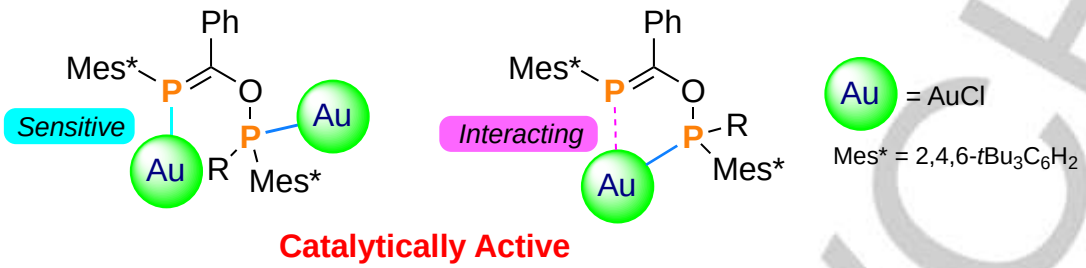

Catalytically Active

The phosphanoxy-substituted phosphaalkens are employed for developing the chemistry of LAuCl complexes. The bis(chlorogold) complexes indicated the conformational isomerism, and the relatively sensitive P(sp^2)–Au bonding was effective for the activation-free gold catalysis. Even the mono(chlorogold) complexes including the Au···P=C pseudo coordination interaction enabled the activation-free reactions including alcohols.

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