ORGANOMETALLICS
Article
Cite This: *Organometallics* XXXX, XXX, XXX−XXX
pubs.acs.org/Organometallics

A Gold(I) Complex with a 1,1′-Binaphthyl-Substituted Diphosphene: Synthesis, Structure, and Catalytic Application to Intramolecular Hydroarylation Reactions

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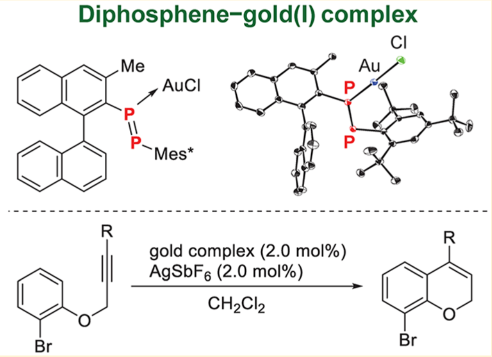
Supporting Information

ABSTRACT: A gold(I) complex with a 1,1′-binaphthyl-substituted diphosphene was synthesized and fully characterized. A phosphorus atom with a less-hindered binaphthyl group coordinates to a gold(I) moiety in an η^1 fashion. Both experiment and theoretical calculations supported the facile rotation around the C(Naph)−P bond in neutral and cationic diphosphene−gold(I) complexes. The newly obtained complex **2** was applied to the intramolecular hydroarylation of aryl propynyl ethers **5**, and 2*H*-chromenes **6** were formed in 83−94% yield. Furthermore, the chiral diphosphene−gold(I) complex (*S*)-**2** was used in the atropselective reaction to furnish **6b**,**c** with up to 9% ee, which is the first example of the use of a diphosphene as a ligand for the transition-metal-catalyzed organic transformation.



INTRODUCTION

Phosphorus chemistry has rapidly advanced in the last two decades due to a plethora of intriguing properties, such as coordination ability to transition metals and their chiral environments.[1] Trivalent organophosphorus compounds, such as phosphine, phosphite, and phosphoramidite, are some of the most intensely investigated compounds as ligands because of their strong coordination ability to transition metals and/or their chiral environments derived from the high inversion barrier. The development of new ligands that exhibit high catalytic activities has posed a continuous challenge in modern organic syntheses.

In contrast to conventional phosphorus(III) compounds with coordination number 3, ligands exploiting low-coordinate phosphorus species, such as phosphaalkenes and phosphinines, are still underdeveloped.[2] These are promising candidates due to the low-lying LUMO level derived from the π^* orbital of the P=C bond. Diphosphinidenecyclobutenes (DPCBs, **A**),[2d,3] PN-bidentate (**B**), or PNP pincer-type (**C**) ligands with phosphaalkenes[4] and phosphinine ligands (**E** and **F**) combined with oxazoline, pyridine, and phosphine to give bidentate-type ligands[2e,3] are utilized in transition-metal-catalyzed organic transformations, including asymmetric reactions[4b,5a,b,6] (Figure 1). As has been illustrated for gold(I) complexes, Ito, Yoshifuji, and co-workers reported the cycloisomerization of 1,6-enynes and the lactonization of pent-4-ynoic acids catalyzed by phosphaalkene−chlorogold(I) complexes with **A** or **D**,[7] and Müller and co-workers indicated that two phosphinine−gold(I) complexes with **G** showed catalytic activity for the cycloisomerization of a 1,6-enyne and a propynyl-tethered benzamide.[8]

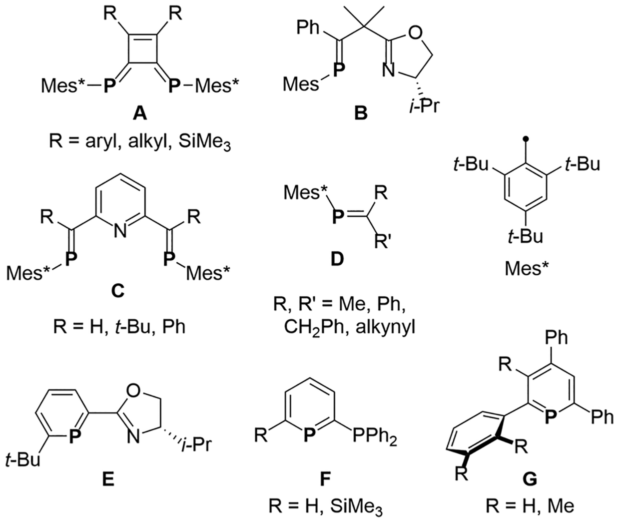


Figure 1. Examples of phosphaalkenes and phosphinines utilized as ligands for catalytic organic transformations.

Diphosphene having a P=P double bond in the molecule is also a promising candidate due to its significantly low-lying P=P π^* orbital,[9,10] which should enhance the π-accepting character of the transition metal. A variety of diphosphene transition-metal complexes featuring η^1- or η^2-type coordination modes have been explored,[9a,e,11] even before the isolation of the first example of diphosphene, Mes*P=PMes* (Mes* =

Received: October 9, 2019

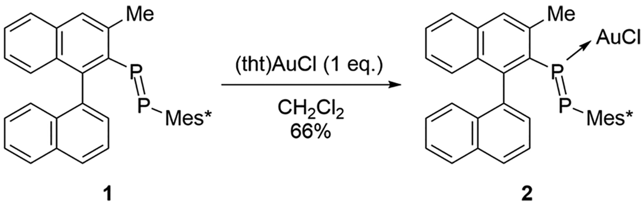
DOI: 10.1021/acs.organomet.9b00665

2,4,6-tri-*tert*-butylphenyl).[12] In 2009, Protasiewicz and co-workers reported the first isolation of the gold(I) complexes of Mes*P═PMes*, where one or both lone pairs on the phosphorus atoms coordinate to the gold atoms in an η^1 fashion.[13] However, to the best of our knowledge, a diphosphene complex has never been used as a ligand for catalytic organic transformations.[14] We recently reported the synthesis and optical properties of the first chiral diphosphene **1** with a 1,1′-binaphthyl group.[15] We wish to report herein the complexation of **1** with a gold(I) atom and the application of the obtained diphosphene−gold(I) complex **2** to the intramolecular hydroarylation of aryl propynyl ethers.

■ RESULTS AND DISCUSSION

We applied a similar method to that reported by Protasiewicz and co-workers for the synthesis of the gold(I) complex of **1**.[13] Treatment of binaphthyl-substituted diphosphene **1** with 1 equiv of (tht)AuCl (tht = tetrahydrothiophene) in CH_2Cl_2 resulted in the formation of the diphosphene−gold(I) complex **2** in 66% yield as yellow crystals (Scheme 1). The ^{31}P NMR signals of **2** were observed upfield (δ_P 405.9 and 315.7) relative to those of **1** (δ_P 451.5 and 525.7).[15] The coupling constant of $^1J_{PP}$ = 535 Hz indicated an η^1 coordination with retention of the double-bond character of the P═P bond after complexation (cf. **1**, $^1J_{PP}$ = 570 Hz; Mes*(ClAu)P═PMes* (**3a**),[13] δ_P 338.8 and 386.0, $^1J_{PP}$ = 538 Hz).[16]

Scheme 1. Synthesis of Binaphthyl-Substituted Diphosphene−Gold(I) Complex 2



The X-ray crystallographic analysis of **2** revealed that the phosphorus atom with a binaphthyl group coordinates to a gold(I) moiety (Figure 2), probably due to the relatively lesser steric hindrance of the binaphthyl group in comparison to the bulky Mes* group. The P2 atom and benzene ring A of the naphthyl group at the 1-position take the syn configuration as in **1**.[15] Theoretical calculations revealed that the syn isomer is slightly more stable than the anti isomer, but the energy difference is less than 1 kcal mol^{-1} depending on the applied functionals (Table S2). The intermolecular π−π interaction between naphthyl plane with a methyl group was observed in the crystal packing (Figure S20), while no intermolecular Au−Au contact was observed. The P═P bond length of **2** (2.0266(9) Å) is slightly shorter than that of **1** (2.0323(6) Å)[15] but is longer than those of diphosphene−gold(I) complexes **3a** (1.975(5) Å) and **3b** (2.003(4) Å) (Figure 3).[13] In addition, the P−Au and Au−Cl bond lengths of **2** (2.2107(7) and 2.2753(7) Å, respectively) are both also longer than those of **3a** (2.180(4) and 2.222(4) Å, respectively) and **3b** (2.201(2) and 2.250(2) Å, respectively). The reason for the difference between **2** and **3** is unclear at present, although both compounds have aryl groups on the phosphorus atoms. The geometry around gold is almost linear with a P1−Au−Cl angle of 177.53(2)°. The Au−C22 distance of 3.59 Å implies a weak gold−aryl interaction in **2**.

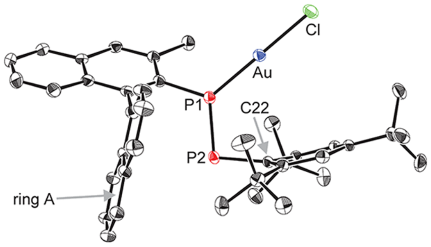


Figure 2. Molecular structure of **2**.

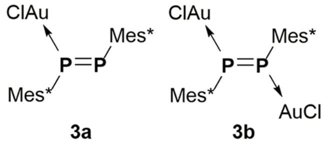
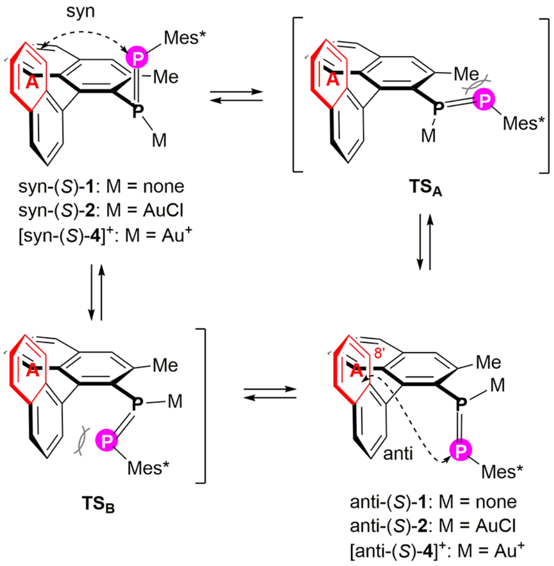


Figure 3. Diphosphene−gold(I) complexes **3**.

In our previous report, we showed the facile rotation around the C(Naph)−P bond of **1** at room temperature.[15] The transition energy was estimated to be lower than 5 kcal mol^{-1} in both rotations in the vicinity of the methyl group at the 3-position of the naphthyl group (**TS$_A$**) and the naphthyl group (**TS$_B$**) (Scheme 2). To reveal the effect for the C(Naph)−P bond rotation in the gold complex (syn−anti isomerization), the energy barriers of (*S*)-**2** and the cationic gold complex [(*S*)-**4**]$^+$ without chloride were investigated by theoretical calculations at the B3LYP functional with the basis set of LanL2DZ (for Au) and 6-31G(d) (for the other atoms) level in conjunction with the PCM model (CH_2Cl_2).[17] With reference to the previous report, the syn configuration indicates that the P atom with a Mes* group and benzene ring A in the naphthyl group at the 1-position have the same orientation, whereas the anti configuration indicates an inverse orientation (Scheme 2). The calculated energies of **TS$_A$**-(*S*)-**2**, **TS$_B$**-(*S*)-**2**, [**TS$_A$**-(*S*)-**4**]$^+$, and [**TS$_B$**-(*S*)-**4**]$^+$ are 8.7, 9.2, 5.3,

Scheme 2. Interconversion between Syn and Anti Isomers of 1, 2, and [4]$^+$



and 7.2 kcal mol^{-1}, respectively, and the energies slightly increase in the order of **1**, [**4**]$^+$, and **2**. It should be noted that the anti isomer is slightly more stable (~1 kcal mol^{-1}) than the syn isomer in [(*S*)-**4**]$^+$, in contrast to (*S*)-**2**, which is likely due to the effective gold−aryl (Naph) interaction (the distance between gold and the carbon atom at the 8′-position is 3.05 Å).

This conformational change was experimentally investigated by a VT-NMR study. When a CD_2Cl_2 solution of **2** was cooled from 20 to −90 °C, one of the doublet signals in the lower field region (δ 406.5) became broad, while the other (δ 315.1) still remained as a doublet in the ^{31}P NMR spectrum (Figure 4).

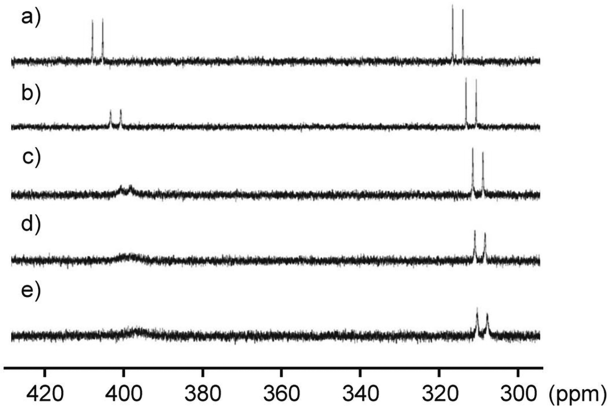
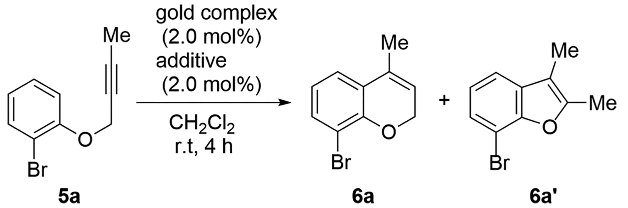


Figure 4. Temperature dependence of $^{31}P\{^1H\}$ NMR spectra (202.5 MHz) of **2** in CD_2Cl_2. (a) 20 °C; (b) −40 °C; (c) −70 °C; (d) −80 °C; (e) −90 °C.

Table 1. Intramolecular Hydroarylation of 5a: Screening for Reaction Conditions



entry	catalyst	additive	yield (%) of **6a**[a]	yield (%) of **6a′**[a]
1	**2**	$AgSbF_6$	94 (89)	6 (4)
2[b]	**2**	$AgSbF_6$	89 (83)	6 (5)
3[c]	**2**	$AgSbF_6$	62	4
4[d]	**2**	$AgSbF_6$	16	1
5[e]	**2**	$AgSbF_6$	71	2
6	none	$AgSbF_6$	0	0
7	**1**	$AgSbF_6$	0	0
8	**2**	$AgNTf_2$	95	3
9	**2**	AgOTf	22	trace
10	**2**	$AgBF_4$	16	3
11	**2**	$NaBAr^F_4$[f]	78	15
12	(tht)AuCl	$AgSbF_6$	81	8
13	$(Ph_3P)AuCl$	$AgSbF_6$	86	5
14	**3a**	$AgSbF_6$	85	8

[a] Yields were determined by ^{1}H NMR spectroscopic analysis using 1,1,2,2-tetrachloroethane as the internal standard. Isolated yields are shown in parentheses. [b] At 40 °C. [c] $AgSbF_6$ was initially treated with gold complex **2** before adding the substrate. [d] 1 mol % of $AgSbF_6$. [e] 4 mol % of $AgSbF_6$. [f] $NaBAr^F_4$ = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

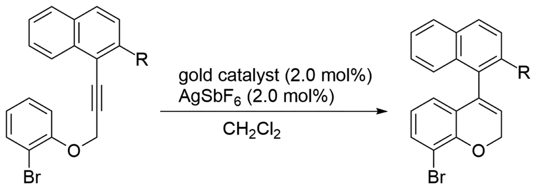
Since the former signal (δ 406.5) was assignable to the phosphorus atoms with a Mes* group on the basis of the GIAO calculations of **2** (Table S3), the observed coalescence should be due to the C(Naph)−P bond rotation described above (Scheme 2).[18] The activation energy ($\Delta G^{\ddagger}_{198}$) should be roughly estimated as 8.2 kcal mol^{-1} by using the coalescence temperature (198 K) and the J_{PP} coupling constant (528 Hz).[19] The experimental value of $\Delta G^{\ddagger}$ (~8 kcal mol^{-1}) is in good agreement with the calculated value (~9 kcal mol^{-1}). To our regret, the precise determination of syn/anti ratio was unsuccessful because the signals did not apparently split into two signals under the applied conditions.

Subsequently, we investigated the catalytic activity of the newly obtained diphosphene−gold(I) complex **2**.[20] We decided to perform the intramolecular hydroarylation of 2-bromophenyl butynyl ether **5a** as the substrate in the presence of 2 mol % of gold complex and an additive.[21] The reaction provided 6-endo cyclized product **6a** as the major product together with a small amount of isomeric benzofuran **6a′**.[21a] Initial screening for solvent (CH_2Cl_2, 89%; THF, 0%; toluene, 36%; acetonitrile, 52%) at 40 °C with $AgSbF_6$ as the additive demonstrated that CH_2Cl_2 was the best solvent. The reaction at room temperature gave a slightly improved yield (Table 1, entry 1 vs entry 2). It is worth mentioning that the order of addition of the reagents markedly affected the yield of product **6a**.[22] When $AgSbF_6$ was added to the mixture of **5a** and gold(I) complex **2** in CH_2Cl_2, the reaction proceeded smoothly to give **6a** in 94% yield (entry 1). On the other hand, the yield of **6a** was drastically decreased to 62% when **5a** was added to a solution containing the cationic gold complex $[(\mathbf{1})Au]^+[SbF_6]^-$, which would be generated by the initial mixing of **2** and $AgSbF_6$ in CH_2Cl_2 for 2 min at room temperature (entry 3).[23] We believe that one of the reasons for the difference might be the low stability of $[(\mathbf{1})Au]^+[SbF_6]^-$ without an alkyne. Furthermore, the use of 0.5 or 2 equiv of silver (relative to gold) led to low yields (entries 4 and 5). No reaction occurred in the absence of the gold complex **2** (entry 6) or in the combination with diphosphene **1** and $AgSbF_6$ (entry 7). These results indicate the following. (1) The generation of the cationic gold complex is necessary, but an excess amount of silver salt precludes the catalytic activity. (2) The cationic silver complex itself would not work as the catalytically active species in this reaction. (3) $[(Ag)Mes^*P{=}P(BNp^{Me})(AuCl)]^+$ (BNp^{Me} = 3-methyl-[1,1′-binaphthalene]-2-yl), a diphosphene with the additional η^1 coordination of a silver cation onto another phosphorus atom, could be considered,[24] but it would also be unlikely as the catalytically active species. (4) $[(\mathbf{1})Au]^+[SbF_6]^-$ could be the catalytically active species, but the heteronuclear species of Au and Ag should also be considered. In fact, an electrospray ionization mass spectroscopy (ESI-MS) analysis of a mixture of **2** and $AgSbF_6$ in CH_2Cl_2/MeCN indicated the existence of $[(\mathbf{1})Au]^+$ and $[(\mathbf{1})AuCl + Ag]^+$, showing signals at *m*/*z* 771.2 and 913.1, respectively (Figure S17). To our regret, attempts to isolate and characterize the cationic diphosphene−gold(I) complex were unsuccessful.

The additives were also surveyed in screening experiments (Table 1).[25] An additive was added last at room temperature in the following experiments. The use of $AgSbF_6$ or $AgNTf_2$ afforded **6a** in excellent yield in comparison to other silver salts, such as AgOTf and $AgBF_4$ (entries 1 and 8−10). $NaBAr^F_4$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) was also applicable as an additive, although the yield was slightly lower (entry 11). This result indicates that [(**1**)Au]$^+$ promoted this transformation and that silver also assisted the improvement of the activity in gold catalysis.[22a] The catalytic activity of **2** was slightly higher than those of (tht)AuCl, (Ph_3P)AuCl, and **3a** (entries 12−14).

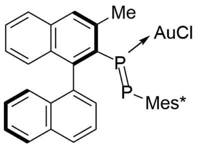
The successful hydroarylation described above and the previous isolation of chiral diphosphene **1**[15] encouraged us to examine the enantioselective reaction. Among the possible candidates,[20a,b] atropselective intramolecular hydroarylation of **5b**,**c** was carried out (Table 2),[26] where a 2-methoxy-1-naphthyl (**b**) or a 2-methyl-1-naphthyl (**c**) group was attached to the alkyne instead of a methyl group as in **5a**. The reactions of **5b**,**c** resulted in the formation of cyclized products **6b**,**c** in high yields, albeit with low ee values (1% ee for **6b** and 9% ee for **6c**, entries 1 and 2).[27] The use of gold complex (*R*)-**7** with a MeO-MOP ligand (MeO-MOP = 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl)[28] also resulted in low ee values (5−6% ee, entries 3 and 4). Thus, the monodentate ligand of the binaphthyl backbone with both diphosphene and phosphine does not seem to be suitable for achieving high enantioselectivity for this reaction. On the other hand, it is intriguing that the ee value of **6c** (9% ee) was higher than that of **6b** (1% ee) in (*S*)-**2**, whereas the ee values of **6b**,**c** were comparable in (*R*)-**7** (5−6% ee). The C(Naph)−P bond rotation in (*S*)-**2** in solution (vide supra) may contribute to the change of the chiral environment (i.e., syn/anti ratio) depending on the substrate.

Table 2. Atropselective Intramolecular Hydroarylation of 5b,c

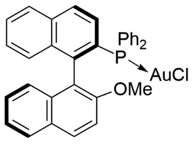


5b (R = OMe)
5c (R = Me)

6b (R = OMe)
6c (R = Me)



(*S*)-(+)-**2**



(*R*)-(+)-**7**

entry	substrate	catalyst	yield (%) of **6**	ee (%)
1[a]	**5b**	(*S*)-**2**	83	1
2[b]	**5c**	(*S*)-**2**	86	9
3[a]	**5b**	(*R*)-**7**	76	5
4[b]	**5c**	(*R*)-**7**	72	6

[a] At −10 °C for 12 h. [b] At 0 °C for 4 h.

■ CONCLUSION

We synthesized gold complex **2** with a binaphthyl-substituted diphosphene and revealed its molecular structure. The phosphorus atom with a less-hindered binaphthyl group coordinates to a gold(I) moiety in an η^1 fashion. Both experiment and theoretical calculations supported the facile rotation around the C(Naph)−P bond in both neutral complex **2** and cationic complex [**4**]$^+$ in solution. Furthermore, investigation of the catalytic activity of **2** in gold(I)-catalyzed intramolecular hydroarylation showed that a diphosphene ligand worked similarly to a phosphine ligand such as PPh_3. The use of the chiral diphosphene−gold(I) complex (*S*)-**2** promoted the atropselective reaction with ee values as high as 9%. These results denote substantial progress in the chemistry of low-coordinate phosphorus compounds including diphosphenes. Our group is actively pursuing further investigations of coordination to other transition metals and asymmetric organic transformation and the development of new diphosphenes with high catalytic activity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00665.

Experimental procedures, characterization data, crystallographic details, and computational results (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1958207 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Scientific Research (B; #18H01983 to K.K.) and (C; #18K05090 to A.T.), and a Grant-in-Aid for Scientific Research on Innovative Areas “Precisely Designed Catalysts with Customized Scaffolding” (#JP18H04269 to K.K.) from JSPS (Japan). A.T. also thanks the Sumitomo Foundation (180777) and the Takasago International Corporation for research fellowship. The authors thank Professor Ikuko Miyahara (Osaka City University) for assistance in X-ray crystallographic analysis. All theoretical calculations were carried out at the Research Center for Computational Science (Japan).

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(17) We did not consider the axial isomerization of the binaphthyl moiety (*R*−*S* isomerization), since the racemization energy of **1** estimated to be 37.7 kcal mol^{-1} is high enough to keep its chirality below room temperature (see ref 15).

(18) In the ^{1}H NMR spectra of **2** in a CDCl$_3$ solution at room temperature, *o-tert*-butyl signals of a Mes* group were observed at 0.79 and 1.29 ppm as two independent signals (Figure S1), which was in contrast to **1** showing only a broad singlet signal at 1.04 ppm. Thus, the rotation around the C(Mes*)−P bond should be restricted by the introduction of the AuCl moiety.

(19) The determination of the $\Delta G^{\ddagger}$ value essentially requires the resonance frequencies of the separated signals. According to the GIAO calculation, the difference in the ^{31}P chemical shift of the P2 atom (with a Mes* group) in the *syn*-(*S*)-**2** and *anti*-(*S*)-**2** isomers was ca. 25 ppm (5.0×10^3 Hz under these conditions) (Table S3). When this value was used as the $\Delta \nu$ value for the estimation, the $\Delta G^{\ddagger}$ value was calculated to be 7.6 kcal mol^{-1}. See also the Supporting Information.

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DOI: 10.1021/acs.organomet.9b00665