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PhP–PPh group bound to 1,8-positions of naphthalene: Preparation of *cis* isomer and synthesis of binuclear complex

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ABSTRACT

A thermodynamically less stable cis isomer of 1,2-diphosphacycle was prepared from the corresponding trans isomer. Diphosphine, in which a PhP-PPh bond bridges the 1,8-positions of naphthalene, 1,2diphenyl-1,2-dihydronaphtho[1,8-cd][1,2]diphosphole (1), was first prepared according to a previously reported method, and the trans isomer of 1 was irradiated in tetrahydrofuran with UV-vis light to reach equilibrium with cis-1 in a trans:cis ratio of 1:2. When a similar photochemical conversion was carried out using a saturated hexane solution of trans-1, cis-1 was precipitated in a good yield of 94%. The configuration of cis-1 was confirmed by X-ray analysis. Both cis- and trans-1 diphosphine ligands were used for the preparation of binuclear gold complexes. The crystal structure of $(\mu$ -cis-1)-[AuCl]₂ demonstrated that the two lone pairs of cis-1 are suitably directed for arrangement of the two gold centers in close proximity to each other. The two independent $(\mu$ -cis-1)-[AuCl]₂ molecules in the crystal were found to form a dimer through the multiple intermolecular interaction among the gold centers.

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1. Introduction

Diphosphines (R₂P–PR₂) are useful bridging ligands for syntheses of binuclear complexes, two metal centers of which are coordinated to the respective phosphorus centers of the bridging diphosphines, and are linked in close proximity by a direct P-P bond [1,2]. In practice, however, the distance between the two metal centers varies depending on the torsion angle of the M-P-P-M bond sequence, as shown in Fig. 1. In the synperiplanar conformation shown in Fig. 1a, the two metal centers become closest to each other, and rotation of an R_2PML_n group around the P–P bond makes the metal centers move away from each other, as shown in Fig. 1b. However, the rotation of the R_2PML_n groups is restricted if a P–P bond is a part of a diphosphacycle [2,3]. Diphosphacycles have two configurational isomers, cis and trans, as illustrated in Fig. 1c and d, respectively. The cis isomer is more useful than the trans isomer, because two lone pairs on the diphosphine unit adopt a synperiplanar disposition.

However, of the two 1,2-diphosphacycles shown in Fig. 1c and d, the cis isomer is less stable than the trans isomer due to steric repulsion between the substituents on the two adjacent phosphorus centers. Therefore, although many four-, five-, and six-membered 1,2-diphosphacycles have been reported, most of them are trans isomers [2-4]. A relatively limited number of reports have mentioned the formation of *cis* isomers [5-15], in which bicyclic ring systems are incorporated to avoid repulsion between the substituents on the phosphorus centers [5-14], or a W(CO)₅ fragment is used to reverse the preference for the *trans* isomer [2,15].



Our group has reported 1,2-diphenyl-1,2-dihydronaphtho[1,8cd][1,2]diphosphole (1), in which a P–P bond is connected to a naphthalene group to form a fused five membered diphosphacycle [2]. The cis isomer of 1 has two Ph groups on the same side with respect to the naphthalene plane with two phosphorus lone pairs adopting the synperiplanar disposition, while trans-1 has two Ph groups disposed on mutually opposite sides of the plane. We have previously reported that trans-1 could be isolated in a moderate yield, while cis-1 was difficult to isolate due to low yield

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Fig. 1. (a) Synperiplanar and (b) antiperiplanar conformations of a diphosphinebridged binuclear complex. (c) *cis* and (d) *trans* isomers of diphosphacycle.

and thermodynamic instability from the steric congestion of the two Ph groups. The isolated *trans*-**1** isomer was used for the preparation of a binuclear tungsten complex, (μ -*trans*-**1**)-[W(CO)₅]₂ (*trans*-**2**). The corresponding *cis* complex, (μ -*cis*-**1**)-[W(CO)₅]₂ (*cis*-**2**), which is expected to have a smaller W···W distance, was synthesized starting from *trans*-**1** in accordance with Scheme 1, in which a portion of the *trans*-**1** ligands were isomerized to *cis*-**1** through stepwise reactions [2c]. Although this method gave the binuclear complex with a bridging diphosphacyle in the *cis* configuration, synthesis of the free *cis* ligand is desirable for the preparation of a variety of binuclear complexes.

In this paper, we report a practical method for the synthesis of *cis*-**1**, in which free *trans*-**1** is converted to *cis*-**1** by irradiation with UV–vis light. Photochemical *trans*-to-*cis* conversion is well known for unsaturated compounds having C=C and N=N bonds [16–19], while little is known regarding that for the P–P single bond of a diphosphacycle. The only example is that reported by Regitz et al. [11]. Although they reported the isomerization of 1,2-dihydro-1,2-diphosphete (**3**), *cis*-**3** was not separated from a 1:1 mixture with *trans*-**3**. Here we report the isolation of *cis*-**1**, and its properties as a bridging ligand.

2. Results and discussion

2.1. Preparation of cis-1

A crude mixture of *trans*- and *cis*-**1** was prepared in a moderate yield by the reaction of 1,8-dilithionaphthalene with PCl₂Ph



Scheme 1.

according to our previously reported method [2]. A ${}^{31}P{}^{1}H{}$ nuclear magnetic resonance (NMR) spectrum of this mixture showed two singlets at -9 and -19 ppm in an intensity ratio of 10:1, which were assigned to trans-1 and cis-1, respectively. The minor cis isomer was separated by chromatography using an Al₂O₃ column. Although the total vield of *cis*-**1** was only 1–2%. the molecular structure of *cis*-**1** was confirmed by X-ray analysis, as shown in Fig. 2, in which both Ph groups on the phosphorus centers are on the same side with respect to the naphthalene plane. Selected bond distances and angles of *cis*-1 are listed in Table 1. The P–P bond length of *cis*-1 is 2.2710 (7) Å, which is slightly greater than that of trans-1 (2.2240 (6) Å) reported previously [2c]. A greater electrostatic repulsion between lone pairs of cis-1 in the synperiplanar conformation might be responsible for the longer P–P bond. In the ¹H NMR spectrum of *cis*-1, three signals assigned to the naphthalene group were observed at 7.59, 7.72, and 7.93 ppm, which are close to those of trans-1 (7.63, 7.84, and 7.97 ppm, respectively) [2]. In contrast, signals assigned to Ph groups of cis-1 appeared at 6.59, 6.80, and 6.95 ppm, which are at a substantially lower chemical shift than those of trans-1 at 7.10-7.15 ppm [2]. The two Ph groups in cis-1 adopt a parallel arrangement, as shown in Fig. 2, which is responsible for the shielded protons compared to those of trans-1.

2.2. Photochemical isomerization

The *cis* isomer of **1** could be directly obtained from a reaction mixture, although the yield was very low. A more practical method is desirable for preparation of binuclear complexes using *cis*-**1** as a bridging group. Therefore, because *trans*-**1** was obtained in a moderate yield, a *trans*-to-*cis* conversion was attempted. Firstly, the thermal transformation of *trans*-**1** to *cis*-**1** was conducted by heating a solution of pure *trans*-**1** in toluene. The ³¹P{¹H}</sup> NMR spectrum of the solution showed that only a trace amount (~ 1%) of *cis*-**1** was formed, which indicates the much higher thermodynamic stability of *trans*-**1**. The thermodynamic preference was also confirmed by an almost complete conversion of isolated *cis*-**1** to *trans*-**1** at 80 °C within 3 h.

On the other hand, irradiation of *trans*-1 with UV—vis light proved successful. When a solution of *trans*-1 in tetrahydrofuran (THF) was irradiated for 1 h with UV—vis light using a medium pressure mercury lamp, a substantial amount of *trans*-1 was found to be converted to *cis*-1 to reach an equilibrium with a *trans*:*cis* ratio of 1:2. In addition, it was found that a similar photochemical reaction using hexane as the solvent gave *cis*-1 as a precipitate, while all of the remaining *trans*-1 stayed in solution. This is probably because *cis*-1 has a larger dipole moment than *trans*-1, and



Fig. 2. Molecular structure of *cis*-1. Ellipsoids are shown at 50%. Hydrogen atoms are omitted for clarity.

Table 1

Selected bond lengths and angles for *cis*-1, $(\mu$ -*cis*-1)-[AuCl]₂ (*cis*-4), and $(\mu$ -*trans*-1)-[AuCl]₂ (*trans*-4).

			Cis- 1	Cis- 4		Trans- 4
				Molecule 1	Molecule 2 ^a	
Selected bond length (Å)						
P2	P1		2.2710(7)	2.2331 (18)	2.2294 (18)	2.208 (3)
Au1	P1			2.2259 (14)	2.2254 (15)	2.209 (2)
Au2	P2			2.2309 (14)	2.2275 (13)	2.213 (2)
P1	C1		1.8291 (18)	1.818 (5)	1.814 (5)	1.797 (9)
P2	C8		1.8320 (18)	1.806 (5)	1.806 (6)	1.808 (9)
P1	C11		1.8323 (17)	1.803 (6)	1.822 (6)	1.796 (9)
P2	C17		1.8259 (18)	1.812 (6)	1.789 (5)	1.794 (9)
Au1	Cl1			2.2869 (13)	2.2903 (14)	2.274 (2)
Au2	Cl2			2.2938 (13)	2.2852 (13)	2.269 (2)
Selected bond angles (deg)						
P1	Au1	Cl1		174.03 (5)	175.19 (5)	176.26 (9)
P2	Au2	Cl2		167.58 (5)	168.41 (5)	175.40 (9)
Au1	P1	P2		114.04 (7)	112.95 (7)	114.94 (12)
Au2	P2	P1		115.65 (7)	115.31 (7)	111.23 (11)
C1	P1	P2	92.99 (6)	93.01 (17)	92.22 (17)	93.6 (3)
C8	P2	P1	93.02 (6)	93.83 (17)	93.25 (17)	94.5 (3)
C11	P1	P2	102.54 (6)	109.80 (18)	106.75 (17)	105.0 (3)
C17	P2	P1	104.12 (6)	113.79 (17)	112.73 (18)	104.0 (3)
C11	P1	C1	104.05 (8)	105.7 (2)	104.0 (3)	108.8 (4)
C8	P2	C17	104.22 (8)	107.0 (2)	107.4 (3)	105.5 (4)

^a For atom labels of molecule 2, Au1, Au2, Cl1, Cl2, P1, P2, C1, C8, C11, and C17 should be read as Au3, Au4, Cl3, Cl4, P3, P4, C23, C30, C33, and C39, respectively.

thus its solubility in the non-polar solvent is significantly lower than that of *trans*-**1**. Eventually, as shown in Scheme 2, a practical amount (94%) of *cis*-**1** was obtained by irradiation of a hexane solution saturated with *trans*-**1** for 6 h, and more *cis*-**1** could be obtained if the irradiation was repeated after concentration of the recovered *trans*-**1** solution.

2.3. Synthesis of metal complexes

In the previous method shown in Scheme 1, a binuclear tungsten complex bridged with *cis*-1 was prepared starting from $[W(trans-1)(CO)_5]$. Now the same binuclear complex $(\mu$ -*cis*-1)- $[W(CO)_5]_2$ (*cis*-2) can be obtained in a good yield through a direct reaction of *cis*-1 with a slight excess of $[W(CO)_5(thf)]$. However, as reported previously, a shorter W...W distance of 5.1661 (3) Å in *cis*-2 than that of 5.8317 (2) Å in the *trans* analog *trans*-2 was observed, but the difference was only 0.6652 (2) Å, which was smaller than expected [2c]. The reason for the small difference must be steric congestion between the bulky $[W(CO)_5]$ fragments in *cis*-2.

To remove such steric factor, an AuCl fragment was selected as a small metal fragment. In addition, gold(I) complexes have attracting recent interest because of the "aurophilicity" which plays an important role to form molecular assemblies of gold(I) complexes in a solid state [20]. The present *cis* diphosphine ligand, *cis*-1, is expected to form a binuclear gold complex with the two gold centers in close proximity. Therefore, it is of interest whether the two gold centers form an intramolecular Au–Au bond or an assembly of the binuclear gold complexes by cooperative intermolecular Au–Au interactions.



Scheme 2.

The binuclear gold complexes were prepared by reaction of *cis*or *trans*-**1** with two equivalents of AuCl(tht) (tht = tetrahydrothiophene). The reactions proceeded smoothly to give the binuclear complexes (μ -*cis*-**1** and μ -*trans*-**1**)-[AuCl]₂ (**4**), *cis*- and *trans*-**4**, respectively. The ³¹P{¹H} NMR spectra of *cis*- and *trans*-**4** showed a sharp singlet at 24.2 and 33.0 ppm, respectively, which are at lower field by about 40 ppm than those of the corresponding free ligands. In ¹H and ¹³C{¹H} NMR spectra, signals assigned to naphthalene groups of *cis*- and *trans*-**4** indicated spectral patterns consistent with their *C*_s and *C*₂ symmetry, respectively.

The X-ray structures of these complexes are presented in Figs. 3 and 4, respectively, in which the AuCl fragment coordinates to each phosphorus donor atom to form the expected binuclear complexes. Two independent molecules were found in the crystal of cis-4. Selected bond distances and angles of the two cis-4 and trans-4 molecules are given in Table 1. A mean Au-P bond distance of the two cis-4 molecules is 2.2274 (14) Å, which is slightly greater than that of trans-4, 2.211 (2) Å, but both distances are in a range for a usual Au-P bond distance. P-P bond distances of the two cis-4 molecules are 2.2331 (18) and 2.2294 (18) Å, which are significantly reduced by 0.0379 and 0.0416 Å, respectively, from that of free cis-1 (2.2710 (7) Å). In contrast, for *trans*-**4**, a reduction of the P–P bond distance upon the coordination of free *trans*-**1** to the two Au centers becomes much smaller. The P–P bond distance of trans-4 (2.208 (3) Å) is smaller by 0.016 Å than that of free trans-1 (2.2243 (6) Å). The greater reduction of the P–P bond in *cis*-4 is mainly due to removal of the lone pair–lone pair repulsion present in free *cis*-1 which has longer P–P bond than free *trans*-1. *vide supra*.

Mean P–Au–Cl angles of *cis*-**4** and *trans*-**4** are 171.30 (5)° and 175.83 (9)°, respectively, indicating that the former deviates from a linear structure probably due to the Au···Au interaction present only in the former, *vide infra*. In *cis*-**4**, a pair of the P–Au–Cl units for each independent molecule adopts the synperiplanar arrangement with Au–P–P–Au torsion angles of 11.6 (1) and 18.3 (1)° to form a "U" shape structure. The intramolecular Au···Au distances of two



Fig. 3. Structures of two independent *cis*-**4** molecules in the crystal. Ellipsoids are shown at 50%. Hydrogen atoms are omitted for clarity. Broken lines indicate Au–Au interactions, and their distances are 3.1960 (4) Å (Au1–Au3), 3.1934 (4) Å (Au2–Au4), 3.6121(4) Å (Au1–Au4), and 3.4608 (4) Å (Au2–Au3).



Fig. 4. Molecular structure of *trans*-4. Ellipsoids are shown at 50%. Hydrogen atoms are omitted for clarity.

cis-**4** are 4.1260 (4) Å for Au1···Au2 and 4.1007 (3) Å for Au3···Au4, indicating absence of the intramolecular Au···Au interaction. These values are substantially smaller than the corresponding value of 5.2390 (7) Å in *trans*-**4**, and are significantly less than the W···W distance of 5.1661 (3) Å in *cis*-**2**, as expected. Reduction of M–P distances in the gold complexes compared to the tungsten complexes also contributes to the shorter M···M distances, but a dominant factor is considered to be the reduction in the steric bulkiness of the metal fragments in the gold complex [21].

It is noteworthy that the two independent *cis*-**4** molecules in the crystal form a dimeric assembly, as shown in Fig. 3, where the two "U" shape parts of the *cis*-**4** molecules are interlocked each other. One *cis*-**4** molecule interacts with the other through multiple Au–Au interactions represented by broken lines in Fig. 3. The intermolecular Au–Au distances are 3.1960 (4) Å (Au1–Au3), 3.1934 (4) Å (Au2–Au4), 3.6121 (4) Å (Au1–Au4), and 3.4608 (4) Å (Au2–Au3). The two former distances are in a common range for typical Au–Au interactions [20]. On the other hand, no intermolecular Au–Au interaction was found in the crystal structure of *trans*-**4**. The contrasting results suggest that the two Au centers in close proximity in *cis*-**4** work simultaneously to form the dimer through the multiple Au–Au interactions [22], while such cooperative interaction is not possible for the two remote Au centers in *trans*-**4**, resulting in the discrete molecule in a solid state.

3. Conclusions

The thermodynamically less stable *cis* isomer of a diphosphacycle, *cis*-**1**, was prepared by a practical method, in which the corresponding *trans* isomer, *trans*-**1**, was photochemically converted to *cis*-**1** in good yield (94%). The two lone pairs of *cis*-**1** are suitably directed to coordinate the two AuCl fragments in close proximity, which facilitates the formation of a dimer with their "U" shape parts interlocked by the multiple intermolecular interaction among the gold centers.

The reaction mechanism for the photochemical conversion will be the subject of future research, and syntheses of a variety of binuclear complexes with *cis*-**1** are currently underway.

4. Experimental section

4.1. General remarks

All reactions were carried out under a dry nitrogen atmosphere using Schlenk tube techniques. All solvents were distilled and dried using sodium (for hexane and toluene), sodium/benzophenone (for ether and THF), or P₂O₅ (for CH₂Cl₂). The purified solvents were stored under nitrogen. 1,8-Dilithionaphthalene and AuCl(tht) were prepared according to methods in the literature [23,24]. Al₂O₃ (standardized, Merck) and other reagents were used as received.

NMR spectra were recorded on a Jeol LA-300 spectrometer. ¹H and ¹³C NMR chemical shifts were reported relative to Me₄Si and were determined by reference to the residual solvent peaks. ³¹P NMR chemical shifts were reported relative to H₃PO₄ (85%) used as an external reference. Elemental analyses were performed with a Perkin–Elmer CHNS 2400II elemental analyzer. Photolysis was carried out using Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The emission lines used and their relative intensities (in parenthesis) were: 577.0 (69), 546.1 (82), 435.8 (69), 404.7 (42), 365.0 (100), 334.1 (7), 312.6 (38), and 302.2 (9) nm.

4.2. Synthesis of 1,2-diphenyl-1,2-dihydronaphtho[1,8-cd][1,2] diphosphole (1) (trans- and cis-1)

Diphosphine **1** was synthesized by modification of a previously reported method [2]. A Schlenk tube charged with ⁿBuLi (28 mL, 46 mmol, 1.65 mol/L hexane solution) and ether (30 mL) was cooled to -30 °C. 1-Bromonaphthalene (5.3 mL, 38 mmol) was slowly added to the Schlenk tube and the mixture was stirred for 1.5 h. After the product was settled as a white precipitate, the supernatant was removed. The precipitate was washed 4 times with hexane (50 mL aliquots) at -20 °C, and then ^{*n*}BuLi (30 mL, 49 mmol, 1.65 mol/L hexane solution) and tetramethylethylenediamine (8.2 mL, 54 mmol) were added. The mixture was kept at 75 °C until the evolution of gas ceased (\sim 3 h). During heating, the mixture became homogeneous, followed by formation of a yellow precipitate. The yellow product was settled and the supernatant was removed. After the precipitate was washed 4 times with hexane (50 mL aliquots), hexane (100 mL) was added. The mixture was cooled to -30 °C and PhPCl₂ (5.7 mL, 42 mmol) was added dropwise to the mixture, which was then stirred for 2 h during which the mixture was warmed to room temperature, ensuring that the temperature did not rise above 20 °C. The supernatant containing diphosphine 1 was separated, and 1 was further extracted from the residue using toluene (50 mL aliquots) 4 times. The supernatant and extracts were combined, and the solvents were removed under reduced pressure. The crude product was loaded into an Al₂O₃ column (30 mm i.d. \times 300 mm). Trans-1 was eluted with CH₂Cl₂/ hexane = 1/1 and *cis*-1 followed. Since the latter band overlapped with the tail of the former, pure *cis*-1 was obtained from the tail of the latter band. Removal of solvents in vacuo gave trans-1 (2.51 g, 19%) and cis-1 (0.24 g 1.9%). Although trans-1 was fully characterized in the previous report [2], NMR data were given below for comparison.

Data for *trans*-**1**. ¹H NMR (300.5 MHz, CD₂Cl₂): δ 7.10–7.20 (m, 10H, Ph), 7.63 (t, *J*_{HH} = 7.0 Hz, 2H, 3,6-Naph), 7.84 (m, 2H, 2,7-Naph), 7.97 (d, *J*_{HH} = 8.1 Hz, 2H, 4,5-Naph). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂): δ 127.8 (t, *J*_{PC} = 3.7 Hz, 3,6-Naph), 128.5 (s, 4,5-Naph), 128.8 (t, *J*_{PC} = 2.8 Hz, *m*-Ph), 128.9 (s, *p*-Ph), 132.4 (t, *J*_{PC} = 12.4 Hz, o-Ph), 132.6 (t, *J*_{PC} = 12.4 Hz, 2,7-Naph), 134.1 (s, Naph), 138.9 (t, *J*_{PC} = 5.0 Hz, *ipso*-Ph), 142.1 (t, *J*_{PC} = 14.0 Hz, *ipso*-Naph), 142.3 (s, Naph). ³¹P{¹H} NMR (121.7 MHz, CD₂Cl₂): δ -8.6 (s).

Data for *cis*-**1**. ¹H NMR (300.5 MHz, CD₂Cl₂): δ 6.57–6.61 (m, 4H, o-Ph), 6.80 (t, *J*_{HH} = 7.5 Hz, 4H, *m*-Ph), 6.95 (t, *J*_{HH} = 7.3 Hz, 2H, *p*-Ph), 7.59 (t, *J*_{HH} = 7.5 Hz, 2H, 3,6-Naph), 7.70–7.75 (m, 2H, 2,7-Naph), 7.93 (d, *J*_{HH} = 8.3 Hz, 2H, 4,5-Naph). ¹³C{¹H} NMR (75.6 MHz, CD₂Cl₂): δ 127.7 (t, *J*_{PC} = 2.3 Hz, 3,6-Naph), 128.1 (t, *J*_{PC} = 3.0 Hz, *m*-Ph), 128.2 (s, 4,5-Naph), 128.3 (s, *p*-Ph), 131.8 (t, *J*_{PC} = 11.6 Hz, 2,7-Naph), 133.1 (t, *J*_{PC} = 10.9 Hz, *o*-Ph), 134.3 (s,

Naph), 135.3 (t, J_{PC} = 19.5 Hz, *ipso*-Ph), 140.9 (t, J_{PC} = 14.4 Hz, *ipso*-Naph), 141.8 (t, J_{PC} = 4.4 Hz, Naph). ³¹P{¹H} NMR (121.7 MHz, CD₂Cl₂): δ –19.4 (s). Anal. Calcd for C₂₂H₁₆P₂: C, 77.19; H, 4.71. Found: C, 77.04; H, 4.57.

4.3. Photochemical synthesis of cis-1

Trans-**1** (770 mg, 2.25 mmol) was dissolved in hexane (60 mL) at 60 °C and the hexane solution was irradiated with a mercury arc lamp for 6 h at 0 °C to give *cis*-**1** as a white precipitate. The product was separated and washed with hexane, then dried *in vacuo* to give a white powder of *cis*-**1** (726 mg, 94%).

4.4. Synthesis of (μ-cis-1)-[W(CO)₅]₂ (cis-2)

A solution of W(CO)₆ (68 mg, 0.19 mmol) in THF was irradiated with a mercury arc lamp for 6 h and then *cis*-1 (24 mg, 0.07 mmol) was added. After stirring the solution overnight, the mixture was found to contain a monotungsten complex [W(*cis*-1)(CO)₅] as well as the ditungsten complex *cis*-2 in a 1:1 ratio. To complete the reaction, THF was removed *in vacuo* and the residue was redissolved in CH₂Cl₂ (5 mL) and stirred for 2 days. After the solvent was removed *in vacuo*, the products were extracted with ether. The extracts were loaded into an Al₂O₃ column and eluted with CH₂Cl₂. A band containing *cis*-2 was collected, and dried *in vacuo*. The residue was washed with hexane and dried again to give a white powder of *cis*-2 (52 mg, 75%). The spectroscopic data were identical to those reported previously [2].

4.5. Synthesis of (μ-cis-1)-[AuCl]₂ (cis-4)

A Schlenk tube was charged with *cis*-**1** (19 mg, 0.056 mmol), AuCl(tht) (36 mg, 0.11 mmol), and CH₂Cl₂. The mixture was stirred for 2 h, after which the solvent was removed. The *cis*-**4** obtained was washed 5 times with ether (5 mL aliquots), and dried *in vacuo*. Yield: 44 mg (97%). ¹H NMR (300.5 MHz, CDCl₃): δ 7.05 (t, *J*_{HH} and *J*_{PH} = 7.6 Hz, 4H, Ph), 7.20–7.32 (m, 6H, Ph), 7.80 (t, *J*_{HH} = 7.5 Hz, 2H, 3,6-Naph), 7.97 (dd, *J*_{HH} or *J*_{PH} = 6.3 Hz, *J*_{HH} or *J*_{PH} = 12.7 Hz, 2H, 2,7-Naph), 8.20 (d, *J*_{HH} = 8.1 Hz, 2H, 4,5-Naph). ¹³C{¹H} NMR (75.6 MHz, CDCl₃): δ 128.3 (t, *J*_{PC} = 6.5 Hz, 3,6-Naph), 128.6 (t, *J*_{PC} = 5.6 Hz, *m*-Ph), 131.7 (s, 4,5-Naph), 132.3 (s, *p*-Ph), 133.5 (t, *J*_{PC} = 8.4 Hz, 2,7-Naph), 135.1 (t, *J*_{PC} = 8.7 Hz, *o*-Ph). ³¹P{¹H} NMR (121.7 MHz, CD₂Cl₂): δ 24.7 (s). Anal. Calcd for C₂₂H₁₆Au₂Cl₂P₂: C, 32.74; H, 2.00. Found: C, 32.53; H, 1.94.

4.6. Synthesis of $(\mu$ -trans-1)-[AuCl]₂ (trans-4)

The *trans* analog was prepared in a manner similar to that previously described, but starting from *trans*-**1** (18 mg, 0.053 mmol) and AuCl (THT) (42 mg, 0.13 mmol). Yield: 41 mg (96%). ¹H NMR (300.5 MHz, CDCl₃): δ 7.25–7.50 (m, 8H, Ph), 7.60 (t, *J*_{HH} = 7.1 Hz, 2H, *p*-Ph), 7.91 (t, *J*_{HH} = 7.7 Hz, 2H, 3,6-Naph), 8.07 (dd, *J*_{HH} or *J*_{PH} = 6.9 Hz, *J*_{HH} or *J*_{PHP} = 12.9 Hz, 2H, 2,7-Naph), 8.32 (d, *J*_{HH} = 8.4 Hz, 2H, 4,5-Naph), 1³C{¹H} NMR (75.6 MHz, CDCl₃): δ 128.7 (t, *J*_{PC} = 6.5 Hz, 3,6-Naph), 130.2 (t, *J*_{PC} = 5.6 Hz, *m*-Ph), 132.5 (s, 4,5-Naph), 133.8 (t, *J*_{PC} = 10.3 Hz, o-Ph), 133.9 (s, *p*-Ph), 134.6 (t, *J*_{PC} = 8.1 Hz, 2,7-Naph). ³¹P {¹H} NMR (121.7 MHz, CD₂Cl₂): δ 34.0 (s). Anal. Calcd for C₂₂H₁₆Au₂Cl₂P₂: C, 32.74; H, 2.00. Found: C, 32.73; H, 1.93.

4.7. X-ray crystallography

Crystals for X-ray diffraction analysis were grown by slow diffusion of pentane vapor into a THF solution of *cis*-1, hexane vapor into a CH_2Cl_2 solution of *cis*-4, and ether vapor into a THF solution of *trans*-4. Measurements were conducted using a Mac Science

Table 2

	Cis- 1	Cis- 4	Trans- 4
Formula	C ₂₂ H ₁₆ P ₂	C47H38Au4Cl10P4	$C_{22}H_{16}Au_2Cl_2P_2$
a/Å	8.7940 (2)	17.9392 (16)	14.6492 (8)
b/Å	10.1680 (2)	14.4197 (13)	7.9741 (4)
c/Å	11.2210 (3)	20.3615 (18)	19.6241 (10)
α/deg	64.086 (1)	90.0	90.0
β/deg	77.000(1)	91.855 (1)	110.5853 (12)
γ/deg	68.044 (2)	90.0	90.0
V/Å ³	834.73 (3)	5264.3 (8)	2146.00 (19)
Ζ	2	4	4
Formula weight	342.29	1869.02	807.12
Space group	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
Temp/°C	-73	-173	-100
λ/Å	0.71069	0.71073	0.71075
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.362	2.358	2.498
μ (Mo K α)/mm ⁻¹	0.259	11.776	14.061
$R_1 (I > 2\sigma(I))$	0.0356	0.0325	0.0439
wR ₂ ^a	0.0952	0.0865	0.0876

a $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2};$ $w = 1/[\sigma^2(F_0^2) + (ap)^2 + bp];$ $p = (F_0^2 + 2F_c^2)/3.$ a and b values for cis-1, cis-4, and trans-4 are 0.0459 and 0.7421, 0.0550 and 0.0, and 0.0117 and 37.7773, respectively.

DIP2030 imaging-plate-based diffractometer at 200 K for *cis*-1, a Bruker APEX-II Ultra CCD-based diffractometer at 100 K for *cis*-4, and a Rigaku SCX mini CCD-based diffractometer at 173 K for *trans*-4. The structures were solved by the direct method and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located at ideal positions and refined isotropically. All calculations were performed using the SHELXL-97 crystallographic software package [25]. A summary of data collection and structure refinement details is provided in Table 2.

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Appendix. Supplementary material

CCDC 826280, 826281, and 826282 contain the supplementary crystallographic data *cis*-1, *trans*-4, and *cis*-4, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

 For recent examples, see (a) J. Fornies, C. Fortuno, S. Ibanez, A. Martin, Inorg. Chem. 47 (2008) 5978–5987;

(b) Y. Miyake, Y. Nomaguchi, M. Yuki, Y. Nishibayashi, Organometallics 26 (2007) 3611–3613;

(c) P. Barbaro, M. Di Vaira, M. Peruzzini, S.S. Costantini, P. Stoppioni, Chem. Eur. J. 13 (2007) 6682–6690;

(d) C. Compain, F. Mathey, Z. Anorg. Allg. Chem. 632 (2006) 421-424;

(e) J. Fornies, C. Fortuno, S. Ibanez, A. Martin, A.C. Tsipis, C.A. Tsipis, Angew. Chem. Int. Ed. 44 (2005) 2407–2410;

(f) A.J.M. Caffyn, M.J. Mays, J. Organomet. Chem. 690 (2005) 2209–2219;
(g) C. Fave, M. Hissler, T. Karpati, J. Rault-Berthelot, V. Deborde, L. Toupet, L. Nyulaszi, R. Reau, J. Am. Chem. Soc. 126 (2004) 6058–6063.

[2] (a) T. Mizuta, T. Nakazono, K. Miyoshi, Angew. Chem. Int. Ed. 41 (2002) 3897;
 (b) T. Mizuta, T. Nakazono, K. Miyoshi, Angew. Chem. Int. Ed. 42 (2003) 712;
 (c) T. Mizuta, S. Kunikata, K. Miyoshi, J. Organomet. Chem. 689 (2004) 2624–2632.

- [3] F. Mathey (Ed.), Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a new Domain, Pergamon, Amsterdam, 2001.
- [4] For recent examples, see (a) M. Scheer, C. Kuntz, M. Stubenhofer, M. Zabel, A.Y. Timoshkin, Angew. Chem. Int. Ed. 49 (2010) 188–192;
 - (b) D. Panichakul, F. Mathey, Organometallics 28 (2009) 5705-5708;
 - (c) M. Bode, J. Daniels, R. Streubel, Organometallics 28 (2009) 4636–4638; (d) N.H.T. Huy, T.V. Gryaznova, L. Ricard, F. Mathey, Organometallics 24 (2005) 2930–2934;
 - (e) N.H.T. Huy, P. Chaigne, I. Dechamps, L. Ricard, F. Mathey, Heteroatom Chem. 16 (2005) 44-48.
- [5] D. Tofan, C.C. Cummins, Angew. Chem. Int. Ed. 49 (2010) 7516–7518.
- [6] A.S. Ionkin, W.J. Marshall, B.M. Fish, Dalton Trans. (2009) 10574–10580.
- [7] N.A. Piro, C.C. Cummins, Inorg. Chem. 46 (2007) 7387-7393.
- [8] C. Jones, C. Schulten, A. Stasch, Dalton Trans. (2007) 1929-1933.
- [9] N.A. Piro, J.S. Figueroa, J.T. McKellar, C.C. Cummins, Science 313 (2006) 1276–1279.
- [10] R.W. Alder, C. Ganter, M. Gil, R. Gleiter, C.J. Harris, S.E. Harris, H. Lange, A.G. Orpen, P.N. Taylor, J. Chem. Soc., Perkin Trans. 1 (1998) 1643–1656.
- [11] T.W. Mackewitz, C. Peters, U. Bergstraesser, S. Leininger, M. Regitz, J. Org. Chem. 62 (1997) 7605–7613.
- [12] R.W. Alder, D.D. Ellis, J.K. Hogg, A. Martin, A.G. Orpen, P.N. Taylor, Chem. Commun. (1996) 537–538.
- [13] R.W. Alder, C. Ganter, C.J. Harris, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1992) 1170–1172.

- [14] X. Li, D. Lei, M.Y. Chiang, P.P. Gaspar, J. Am. Chem. Soc. 114 (1992) 8526–8531.
 [15] N. Maigrot, L. Ricard, C. Charrier, P. Le Goff, F. Mathey, Bull. Soc. Chim. Fr. 129 (1992) 76–78.
- [16] M. Irie, Chem. Rev. 100 (2000) 1685–1716.
- [17] N. Tamai, H. Miyasaka, Chem. Rev. 100 (2000) 1875-1890.
- [18] C. Dugave, L. Demange, Chem. Rev. 103 (2003) 2475-2532.
- [19] H. Nishihara, Coord. Chem. Rev. 249 (2005) 1468–1475.
- [20] H. Schmidbaur, A. Schier, Chem. Soc. Rev. 37 (2008) 1931–1951 and references therein.
- [21] The reviewer pointed out a possibility that a formation of a dimer in the crystal of *cis*-4 (vide infra) contributes to the reduction of the intramolecular Au···Au distances. However, a mean bond angle of the P–P–Au sequence of *cis*-4 (114.49(7)°) is almost comparable to, to be precise, slightly greater than that of *trans*-4 (113.18(12)°) which is considered to be a P–P–Au bond angle with no intermolecular Au···Au interaction, suggesting that the contribution from the dimer formation is limited.
- [22] The dimer formed in a solid state probably dissociates into monomers in solution, because ¹H and ¹³C NMR spectra are consistent with a monomer having the C_s symmetry.
- [23] L. Brandsma, H.D. Verkruijsse, Preparative Polar Organometallic Chemistry, vol. 1, Springer-Verlag, Berlin, 1987, 195–197.
- [24] R. Usón, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.
- [25] G.M. Scheldrick, SHELX-97: Programs for Crystal Structure Analysis. University of Göttingen, Germany, 1997.