Preparation and Structure of
trans-Bis(phenylethynyl)bis(triethylphosphine)palladium(II)

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The chemistry of metalalkynyl compounds is developing at a rapid pace.[1] The alkynyl ligand is known as a good σ- and π-donor, but as a poor π-acceptor. Alkynylpalladium(II) complexes are prepared by the reaction of an alkynyl anion or a covalent main group alkynyl with a palladium(II) precursor, or by oxidative addition of a terminal alkyne or a chloroalkyne to a palladium(0) precursor.[2] Alkynylpalladium(II) complexes are generally stabilized by phosphine (L) and complexes of the type [PdX(C≡CR)L$_2$] and [Pd(C≡CR)$_2$L$_2$] are usually *trans*.

Alkynyl complexes of the type [Pd(C≡CR)$_2$(PEt$_3$)$_2$] (R= Ph, *p*-O$_2$NC$_6$H$_4$) were first prepared by reaction of [PdBr$_2$(PEt$_3$)$_2$] with the corresponding alkynyl Grignard reagents in diethyl ether.[3] In a similar way, *trans*-[Pd(C≡CCF$_3$)$_2$(PEt$_3$)$_2$] was also prepared.[4] Crystal structures of *trans*-[Ni(C≡CR)$_2$(PEt$_3$)$_2$] and *trans*-[Pt(C≡CR)$_2$(PEt$_3$)$_2$] were reported.[5,6] When *cis*-PdCl$_2$(PEt$_3$)$_2$ reacted with phenylacetylene (PhC≡CH) in the presence of triethylamine (NEt$_3$) in an attempt to prepare *cis*-Pd(C≡CPh)$_2$(PEt$_3$)$_2$, the *trans* derivative formed as a white solid. We report here preparation and structure of *trans*-bis(phenylethynyl)bis(triethylphosphine) palladium(II), *trans*-Pd(C≡CPh)$_2$(PEt$_3$)$_2$.

Experimental Section

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under an argon atmosphere. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for *ca.* 24 h and washed with distilled water and acetone before use. Glassware was either flame-dried or oven-dried. Hydrocarbon solvents were stirred over concentrated H$_2$SO$_4$ for *ca.* 48 h, neutralized with K$_2$CO$_3$, stirred over sodium metal, and distilled by vacuum transfer. Benzene, diethyl ether, and tetrahydrofuran (THF) were stirred over sodium metal and distilled by vacuum transfer. NMR solvents (C$_6$D$_6$ and CDCl$_3$) were degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. PdCl$_2$, phenylacetylene (or ethynylbenzene, PhCCH) were purchased from Fluka company. Triethylamine (NEt$_3$) and triethylphosphine (PEt$_3$) were purchased from Aldrich company. *cis*-PdCl$_2$(PEt$_3$)$_2$ (1) was prepared by the literature method.[7,8]

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsi-

lane. ^{31}P-NMR spectra were also recorded with a Bruker AMX 500 MHz spectrometer with reference to 85% H$_3$PO$_4$. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. Elemental analyses were performed by the Korea Basic Science Center.

Preparation of *trans*-Pd(PEt$_3$)$_2$(CCPh)$_2$ (2). At room temperature, phenylacetylene (0.18 mL, 1.77 mmol) was added to 15 mL of ethanol containing 1 (0.124 g, 0.30 mmol) and triethylamine (0.12 mL, 0.88 mmol). White precipitates gradually formed in 10 h. The resultant precipitates were filtered, washed with a minimum amount of methanol, and dried under vacuum to give a white solid of *trans*-Pd(CCPh)$_2$(PEt$_3$)$_2$, 2 (0.126 g, 0.23 mmol, 77%). This product conveniently recrystallized from benzenehexane.

^{1}H NMR (C$_6$D$_6$): δ 7.593 7.000 (10H, *Ph*), 1.899 (12H, m, PC*H$_2$*CH$_3$), 1.117 (18H, m, PCH$_2$*CH$_3$*). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 131.493 129.975 (*Ph*), 112.180 (t, Pd*C*C), 111.780 (s, Pd*CC*), 18.067 (t, P*C*H$_2$CH$_3$), 9.110 (t, PCH$_2$*C*H$_3$). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 19.723 (s). Anal. Calcd for C$_{28}$H$_{40}$P$_2$Pd: C, 61.71; H, 7.40. Found: C, 61.40; H, 7.26. mp (decom.): 117 119 °C. IR (KBr): 2962, 2930, 2873 2099 (CC), 1593, 1483, 1453, 1408, 1034, 761, 728, 695 cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 31 reflections in the range 15.0° < 2θ < 25.0°. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with psi-scan data. All calculations were carried out with use of the Siemens SHELXTL programs.[9]

A yellow crystal of **2**, shaped as a block, of approximate dimensions 0.38 × 0.43 × 0.70 mm^3, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h0l* (*l* = 2*n*+1) and 0*k*0 (*k* = 2*n*+1), unambiguously indicated *P*2$_1$/*c* as the space group. The structure was solved by the direct method and refined by full-matrix least-squares calculations of *F*^{2}s, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. The phenyl hydrogen atoms were

Table 1. X-ray data collection and structure refinement for **2**

formula	$C_{28}H_{40}P_2Pd$
fw	544.94
temperature. K	295(2)
crystal system	monoclinic
space group	$P2_1/c$
a, Å	9.164(2)
b, Å	10.945(1)
c, Å	14.813(3)
β, deg	105.36(1)
V, Å^3	1432.7(4)
Z	2
d_{cal}. g cm^{-3}	1.263
μ. mm^{-1}	0.772
T_{min}	0.2853
T_{max}	0.3740
$F(000)$	568
No. of reflections measured	3484
No. of reflections unique	2621
No. of reflections with $I > 2\theta(I)$	2246
No. of parameters refined	166
2θ range (°)	3.5-50.0
scan type	w
scan speed	variable
GOF (goodness-of-fit on F^2)	1.062
Max.. min. in $\Delta\rho$ (eÅ^{-3})	0.450. -0.723
R	0.0323
$wR_2{}^a$	0.0839

$^a wR_2 = \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]^{1/2}$

located and refined with isotropic temperature factors. The other hydrogen atoms were generated in idealized positions and refined using a riding model.

Final atomic positional parameters are shown in Table 2.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^3 \times 10^3$) for **2**

	x	y	z	U (eq)^a
Pd(1)	0	0	0	55(1)
P(1)	-1326(1)	-772(1)	992(1)	67(1)
C(1)	-2033(4)	-2328(3)	692(2)	96(1)
C(2)	-811(6)	-3223(4)	683(3)	113(2)
C(3)	-299(4)	-829(4)	2222(2)	94(1)
C(4)	-1139(6)	-1251(5)	2911(3)	137(2)
C(5)	-3039(6)	106(4)	914(4)	114(2)
C(6)	-2706(7)	1438(5)	1135(4)	158(2)
C(7)	1786(3)	403(3)	1064(2)	64(1)
C(8)	2838(3)	622(2)	1725(2)	65(1)
C(9)	4056(3)	831(2)	2549(2)	63(1)
C(10)	4447(5)	-60(3)	3237(3)	82(1)
C(11)	5637(7)	115(4)	4014(3)	104(1)
C(12)	6429(4)	1185(5)	4129(3)	109(1)
C(13)	6048(4)	2095(4)	3481(3)	99(1)
C(14)	4852(3)	1913(3)	2681(2)	77(1)

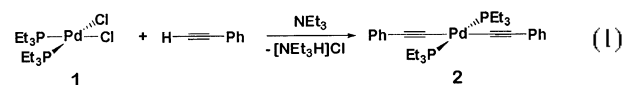^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond distances (Å) and bond angles (°) in **2**

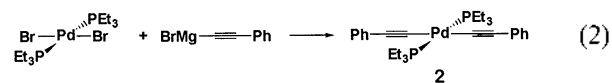|					
Pd1—C7	1.998 (3)	Pd1—P1	2.3009(7)	P1—C3	1.818(3)
P1—C5	1.818(4)	P1—C1	1.834(4)	C7—C8	1.202(4)
C8—C9	1.437(3)				
C7A—Pd1—C7	180.0	C74—Pd1—P1	87.82		
C7—Pd1—P	92.18(8)	C3—P1—C5	106.9(2)		
C3—P1—C1	105.5(2)	C5—P1—C1	103.4(2)		
C8—C7—Pd1	177.7(2)	C7—C8—C9	176.4(3)		

The selected bond distances and bond angles are shown in Table 3.
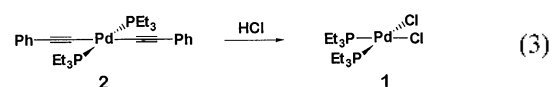
Results and Discussion

Preparation. When cis-PdCl$_2$(PEt$_3$)$_2$ is treated with phenylacetylene (PhC≡CH) in the presence of triethylamine (NEt$_3$), $trans$-Pd(C≡CPh)$_2$(PEt$_3$)$_2$ is formed as a yellow solid (eq. 1). In this reaction, triethylamine acts as a base to remove HCl liberating from the reaction mixture. In fact, we tried this reaction to prepare the cis derivative, cis-Pd(C≡CPh)$_2$(PEt$_3$)$_2$. The change in relative orientation of phosphine ligands (PEt$_3$) from cis to $trans$ during the reaction suggests that the reaction might have proceeded with a prior dissociation of phosphine. This type of reactivity has frequently been observed for Pd(II) complexes of the type PdR$_2$L$_2$ that lose one of the phosphine ligands before reductive elimination.[10]

$$Et_3P-\underset{Et_3P}{\overset{Cl}{Pd}}-Cl + H-\!\!\equiv\!\!-Ph \xrightarrow[-[NEt_3H]Cl]{NEt_3} Ph-\!\!\equiv\!\!-\underset{Et_3P}{\overset{PEt_3}{Pd}}-\!\!\equiv\!\!-Ph \qquad (1)$$

As mentioned earlier, compound **2** was originally prepared by the reaction of $trans$-PdBr$_2$(PEt$_3$)$_2$ with PhC≡CMgBr in diethyl ether (eq. 2).[3] In addition, this compound was reported with data of elemental analysis and dipole moment, but without spectroscopic data such as NMR and IR spectra.

$$Br-\underset{Et_3P}{\overset{PEt_3}{Pd}}-Br + BrMg-\!\!\equiv\!\!-Ph \longrightarrow Ph-\!\!\equiv\!\!-\underset{Et_3P}{\overset{PEt_3}{Pd}}-\!\!\equiv\!\!-Ph \qquad (2)$$

On treatment with excessive HCl in diethyl ether, compound **2** is transformed back to the starting material **1** (eq. 3).

$$Ph-\!\!\equiv\!\!-\underset{Et_3P}{\overset{PEt_3}{Pd}}-\!\!\equiv\!\!-Ph \xrightarrow{HCl} Et_3P-\underset{Et_3P}{\overset{Cl}{Pd}}-Cl \qquad (3)$$

Compound **2** has been treated with unsaturated organic compounds such as ethylene (H$_2$C–CH$_2$), carbon monoxide (C≡O), dimethyl acetylenedicarboxylate (CH$_3$O$_2$CC≡CCO$_2$CH$_3$), and acetylene (HC≡CH) to check whether or not insertion reaction into the PdC bond occurs, but no sign of reaction has been observed.

Compound **2** reacts neither with carbon electrophiles such as C$_6$H$_5$I, Ph$_2$I$^+$BF$_4^-$, and CH$_3$OSO$_2$CF$_3$ nor with a carbon
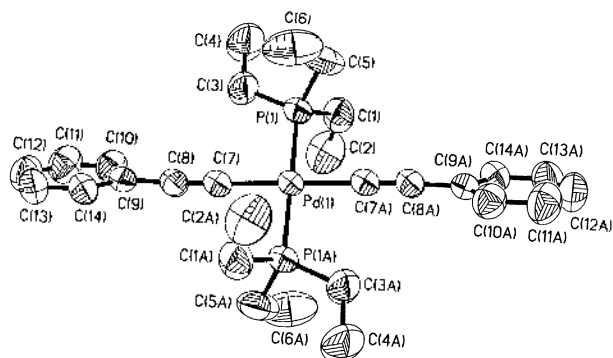
Figure 1. *ORTEP* drawing[23] of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Symmetry-equivalent atoms (denoted by the letter A) are generated by the center of inversion.

nucleophile $H_2C = CHCH_2MgBr$. However, **2** reacts with excess CH_3I (20 fold) in THF at room temperature to give a mixture of three components, of which **2** is the most abundant (70%). The reaction has been monitored by ^{31}P NMR spectroscopy that exhibits three peaks corresponding to **2** and the other two species. The attempt to separate the reaction mixture has not been successful. We have also carried out this reaction under other conditions such as refluxing toluene and CH_2Cl_2 at room temperature, but no reaction has occurred.

Structure. The molecular structures of **2** with the atomic numbering scheme is shown in Figure 1. The Pd metal in compound **2** lies on a crystallographic center of symmetry, and that is why this compound has the Z value of 2 instead of 4. Compound **2** has two *trans* triethylphosphine (PEt₃) ligands and two *trans* phenylethynyl (-C≡CPh) ligands. The coordination sphere of Pd can be described as a square plane. The equatorial plane, defined by P1, P1A, C7, C7A, and Pd1, is essentially planar with the average atomic displacement of 0.001 Å. In addition, the C8 and C8A atoms are also coplanar with the equatorial plane with the atomic displacement of 0.003 Å. With respect to the equatorial plane, the phenyl ring (C9-C14) has a dihedral angle of 44.6(1)°.

The PdP bond distance of 2.3009(7) Å belongs to the typical range (2.294-2.336 Å) for 4-coordinate, square planar Pd(II)-PMe₃ complexes.[11] The Pd1-C7-C8 and C7-C8-C9 bond angles are nearly close to 180°, which is expected for *sp*-hybrid carbons. The C≡C bond distance of the organic fragment -C≡C-C(*sp²*, aromatic) has been reported to be in the range of 1.181-1.195 Å,[12] which is somewhat shorter than that of C7-C8 (1.202(4)) Å. In fact, it is known that the metalalkynyl C≡C bonds are slightly elongated (*ca.* 0.01 Å) relative to free organic alkynes.[1] This type of bond lengthening is usually explained by resonance structures, as shown below. In other words, M → C≡CR π-backbonding makes the M-C bond shorter and the C≡C bond longer.

M̄–C≡C–R   ⟶   M⁺ C· C=R̄

In Table 4 are summarized metrical bonding parameters

Complex	M-C	C≡C	C-Ph	M-C≡C	C≡C-Ph	reference
trans-Ni(PEt₃)₂(C≡CPh)₂						
	1.88(1)	1.22(1)	1.46(2)	177(1)	177(1)	5
trans-Pd(PEt₃)₂(C≡CPh)₂						
	1.998(3)	1.202(4)	1.437(3)	177.7(2)		this work
trans-Pt(PEt₃)₂(C≡CPh)₂						
	1.98(1)	1.21(1)	1.43(1)	177.8(9)	176(1)	6

that are important in characterizing the M-C≡C-Ph fragment in related compounds. Table 4 shows that, except for M-C bond distances, the bonding parameters are equivalent within experimental error. The difference in M-C bond distances probably arises from the difference in covalent radii of the group 8 metals (1.26 Å for Ni, 1.31 Å Pd, and 1.28 Å for Pt).[13]

Recently, the hydrogen bond in organometallic compounds has been the focus of research. It is now accepted that most kinds of C-H groups can act as hydrogen-bond donors.[14-19] It has been reported that the C≡C bond may accept hydrogen bonds from polarized C-H bonds.[20,21] In addition, it is worth noting that the acceptor potential of a C≡C bond bonded to a metal exceeds that in the free state.[22] In compound **2**, the distances of H10···C8 and H14···C8 are 2.60(4) Å and 2.62(3) Å, respectively, which are considerably shorter than the sum of van der Waals radii of H (1.2 Å) and C (1.7 Å) atoms. In addition, the contact of C8···C10 and that of C8···C14 are 2.449(5) Å and 2.454(4) Å, which are also much shorter than the sum (3.4 Å) of van der Waals radii of C atoms. Moreover, the fragments of H10-C10-C9-C8 and H14-C14-C9-C8 are roughly planar with torsion angles of 4(2)° and 12(2)°. On the basis the bonding parameters described above, the ortho hydrogens (H10, H14) of the phenyl ring in **2** appear to be involved in a weak hydrogen bond of the type C-H···C≡C, although the angles of C10-H10···C8 and C14···C8 are relatively small (69(2)°, 70(2)°).
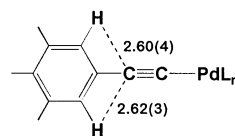
In summary, we have prepared *trans*-Pd(CCPh)₂(PEt₃)₂ (**2**) from *cis*-PdCl₂(PEt₃)₂ and determined the molecular structure of **2** by X-ray diffraction. The change in relative orientation of phosphine ligands (PEt₃) from *cis* to *trans* during the reaction suggests that the reaction proceeds with a prior dissociation of phosphine. The crystal structure shows that the ortho hydrogens of the phenyl ring in **2** appear to be involved in a weak hydrogen bond of the type C-H···C≡C.

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