The chemistry of metalalkynyl compounds is developing at a rapid pace. 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 alkynyl or a cheloralkyne to a palladium(0) precursor. Alkynylpalladium(II) complexes are generally stabilized by phosphine (L) and complexes of the type [PdX(C\text{R})_2L_2] are usually trans.

Alkynyl complexes of the type [Pd(C≡CR)₂(PEt₃)] (R=Ph, p-O₂NC₆H₄) were first prepared by reaction of [PdBr₂(PEt₃)] with the corresponding alkynyl Grignard reagents in diethyl ether. In a similar way, trans-[Pd(C≡CCF₃)₂(PEt₃)] was also prepared. Crystal structures of trans-[Ni(C≡CR)₂(PEt₃)] and trans-[Pt(C≡CR)₂(PEt₃)] were reported. When cis-PdCl₂(PEt₃) reacted with phenylacetylene (PhC≡C) in the presence of triethylamine (NEt₃) in an attempt to prepare cis-Pd(C≡CPh)₂(PEt₃), 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(PEt₃).

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 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 H₂SO₄ for 48 h, and dried under vacuum to give a white solid of trans-Pd(C≡CPh)₂(PEt₃).

Preparation of trans-Pd(PEt₃)₂(CCCPh)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(C≡CCPh)₂(PEt₃)₂ (0.126 g, 0.23 mmol, 77%). This product conveniently recrystallized from benzenehexane.

1H NMR (CD₂Cl₂): δ 7.5937.000 (10H, Ph), 1.899 (12H, m, PCH₂CH₃), 1.117 (18H, m, PCH₂C₆H₅). 13C{¹H}-NMR (CD₂Cl₂): 117.11 (18H, m, PCH₂CH₃). 31P{¹H}-NMR (CD₂Cl₂): δ 19.723 (s). Anal. Calcd for C₃₈H₃₈P₄: C, 59.57; P, 40.43. Found: C, 59.43; P, 40.20. MP (decomp.): 170ºC. 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.

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

**Results and Discussion**

**Preparation.** When cis-PdCl₂(PEt₃)₂ is treated with phenylacetylene (PhC≡CH) in the presence of triethylamine (NEt₃), trans-Pd(PhC≡CH)₂(PEt₃)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-PdCl₂(PhC≡CH)₂(PEt₃)₂. The change in relative orientation of phosphate ligands (PEt₃) 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 PdR₂L₂ that lose one of the phosphine ligands before reductive elimination. ¹⁰

\[
\begin{align*}
\text{Br}_2\text{PdBr}_2 + \text{Br}_2\text{MgBr} \rightarrow &\text{PdBr}_2\text{MgBr} \\
&\text{PdCl}_2\text{MgCl} + \text{PdCl}_2\text{MgCl} \\
&\text{PdCl}_2\text{MgCl} + \text{PhC≡CH} \rightarrow \text{PdCl}_2\text{Ph} + \text{MgCl}_2
\end{align*}
\]

As mentioned earlier, compound 2 was originally prepared by the reaction of trans-PdBr₂(PEt₃)₂ with PhC≡CMgBr in diethyl ether (eq. 2). In addition, this compound was reported with data of elemental analysis and dipole moment, but without spectroscopic data such as NMR and IR spectra.

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

**Compound 2** has been treated with unsaturated organic compounds such as ethylene (H₂C=CH₂), carbon monoxide (CO), dimethyl acetylenedicarboxylate (CH₂O₂CC≡CCO₂CH₃), 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 C₆H₅I, Ph₂PBF₄, and CH₃SO₃CF₃ nor with a carbon...
nucleophile \( \text{H}_2\text{C} = \text{CHCH}_3\text{MgBr} \). However, 2 reacts with excess \( \text{CH}_3\text{I} \) (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 \(^{31}\text{P}\) 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 \( \text{CH}_2\text{Cl}_2 \) 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 (PEt\(_3\)) ligands and two trans phenylethynyl (-C\( \equiv \)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 \( \text{Å} \). In addition, the C8 and C8A atoms are also coplanar with the equatorial plane with the atomic placement of 0.001 \( \text{Å} \). In addition, the C8A and C8 atoms appear to be involved in a weak hydrogen bond of the type C-H-O (C-H = 1.02(4) \( \text{Å} \)), which is expected for \( \text{sp}^2\)-hybrid carbons. The C=C bond distance of the organic fragment -C=C-C(sp\(^2\), aromatic) has been reported to be in the range of 1.30-1.33 \( \text{Å} \), which is somewhat shorter than that of C7-C8 (1.29(2) \( \text{Å} \)). In fact, it is known that the metalalkynyl C=C bonds are slightly elongated (ca. 0.01 \( \text{Å} \)) relative to free organic alkenes.\(^{1}\) This type of bond lengthening is usually explained by resonance structures, as shown below. In other words, \( \text{M} \rightarrow \text{C} = \text{C} \rightarrow \text{C} = \text{C} \rightarrow \text{R} \)

In Table 4 are summarized metrical bonding parameters 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 \( \text{Å} \) for Ni, 1.31 \( \text{Å} \) Pd, and 1.28 \( \text{Å} \) 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-CC8 and H14-CC8 are 2.60(4) \( \text{Å} \) and 2.62(3) \( \text{Å} \), respectively, which are considerably shorter than the sum of van der Waals radii of H (1.2 \( \text{Å} \)) and C (1.7 \( \text{Å} \)) atoms. In addition, the contact of C8C10 and that of C8-C14 are 2.449(5) \( \text{Å} \) and 2.454(4) \( \text{Å} \), which are also much shorter than the sum (3.4 \( \text{Å} \)) 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)\(^\circ\) and 12(2)\(^\circ\). 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 \( \text{C-H} \cdots \text{C=C} \), although the angles of C10-H10-CC8 and C14-H14-CC8 are relatively small (69(2)\(^\circ\), 70(2)\(^\circ\)).

In summary, we have prepared trans-Pd(CCPh)\(_2\)(PEt\(_3\))\(_2\) (2) from cis-PdCl\(_2\)(PEt\(_3\))\(_2\) and determined the molecular structure of 2 by X-ray diffraction. The change in relative orientation of phosphine ligands (PEt\(_3\)) 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 \( \text{C-H} \cdots \text{C=C} \).

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References