chromatographed on silica gel eluting with CH_2Cl_2 to afford 70 mg (87%) of crystalline hexamethoxy[1$_6$]OCP **5**.

Mp 238-240 ℃; IR (KBr) 3030, 2940, 1610, 1515, 1450, 1280, 1240, 1210, 1100 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 7.05-7.00 (m, 6H, Ar*H*), 6.79-6.75 (m, 6H, Ar*H*), 6.63 (s, 6H, Ar*H*), 3.80 (s, 18H, OCH_3), 3.67 (s, 12H, $ArCH_2$); ^{13}C NMR ($CDCl_3$ 50.29 MHz) δ 147.54, 138.50, 130.40, 128.33, 126.13, 114.02, 55.90, 35.59; EIMS m/z 720 (M^+), 687, 476, 355, 239, HRMS (EI) calcd for $C_{48}H_{48}O_6$ 720.3450, found 720.3431.

5,6,19,20,33,34-Hexahydroxyheptacyclo[36.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}.0^{31,36}] dotetr-aconta-1(38),3(8),4,6,10(15),11,13,17(22),18,20,24(29),25,27,31(36),32,34,39,41-octadecaene. Hexahydroxy-[1$_6$]OCP (6). To a solution of hexamethoxy[1$_6$]OCP (**5**) (50 mg, 69.4 μmol) in CH_2Cl_2 (5 mL) was added BBr_3 (0.21 g 840 μmol) at 0 ℃ under nitrogen. The mixture was stirred at rt for 5 h. The reaction mixture was quenched with water, extracted with EtOAc, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was triturated with *n*-hexane to give 42 mg (96%) of crystalline hexahydroxy-[1$_6$]OCP **6**.

Mp >230 ℃ dec; IR (KBr) 3648-3000, 2912, 1600, 1507, 1437, 1283, 1177, 1132, 870, 736 cm^{-1}; ^1H NMR (acetone-d_6, 200 MHz) δ 7.60 (s, 6H, O*H*), 7.15-6.95 (m, 6H, Ar*H*), 6.40 (s, 6H, Ar*H*), 3.64 (s, 12H, $ArCH_2$); ^{13}C NMR (acetone-d_6 50.29 MHz) δ 144.10, 140.02, 130.51, 126.96, 117.49, 35.81; FABMS m/z 606 (M^-).

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A Facile Preparation, Structure, and Some Reactions of *trans*-PdPhI(PMe$_3$)$_2$

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Aryl halides are converted into amides or esters on treatment with carbon monoxide and amine (or alcohol and amine) in the presence of palladium catalysts.[1] Throughout these catalytic reactions arylpalladium halide complexes, PdAr(X)L$_2$ (X=Cl, Br, I and L=tertiary phosphine) are believed as a key intermediate. Furthermore, these complexes are considered as indispensable starting materials or intermediates for the mechanistic study of Pd-catalyzed organic synthesis such as Heck arylation or Stille's C-C coupling reaction.[2] Arylpalladium iodide complexes, PdAr(I)L$_2$ are more widely used than the corresponding chloride and bromide complexes in related studies of Pd-catalyzed synthetic organic reactions.

The arylpalladium halide complexes are usually formed through oxidative addition of aryl halide to Pd(O) species.[3] *Trans*-PdPhI(PMe$_3$)$_2$ is isolated from the reaction of PhI with Pd(PMe$_3$)$_4$[4]. Oxidative addition of PhI to Pd(PPh$_3$)$_4$, followed by ligand diplacement reaction by PMe$_3$ might produce the same complex also. On the other hand, reaction of PhI with *trans*-PdEt$_2$(PMe$_3$)$_2$ also gives *trans*-PdPhI(PMe$_3$)$_2$.[1] However, these reactions have a limitation because of air-sensitivity or thermal lability of both Pd(0) and Pd(II) complexes as a starting material.

In this work we have easily prepared *trans*-PdPhI(PMe$_3$)$_2$ and related complexes, *trans*-PdPhIL$_2$ (L=PMePh$_2$ and L$_2$ =Ph$_2$PCH$_2$PPh$_2$) in high yield at room temperature from the ligand exchange reaction of PdPhI(tmeda) (tmeda=*N,N,N',N'*-tetramethylethlenediamine) with equimolar amounts of phosphine ligands. We here report preparation and structure of *trans*-PdPhI(PMe$_3$)$_2$ and its reactions with isocyanides.

Experimental

All manipulations of air-sensitive compounds were performed under N_2 or argon atmosphere with use of standard Schlenk technique. Solvents were distilled from Na-benzophenone. PdCl$_2$, PMe$_3$, PMePh$_2$, Ph$_2$PCH$_2$PPh$_2$, isocyanides (*tert*-butyl, clclohexyl, 2,6-dimethylphenyl), and tmeda were commercial grade reagents and used without further purification. PdPhI(tmeda) was prepared by the literature method.[5]

Elemental analyses were carried out by Korea Basic Science Center, Seoul. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectra were obtained by a Bruker 300 and 500 MHz spectrometers. ^1H and ^{13}C NMR spectra were referred to solvent

peaks: δ_H 7.26 (residual $CHCl_3$) and δ_C 77.0 for $CDCl_3$ and ^{31}P NMR spectra were referred to an external 85% H_3PO_4, respectively.

Preparation of *trans*-PdPhI(PMe_3)$_2$, (1). To a stirred THF (20 mL) solution containing PhPhI(tmeda) (0.52 g, 1.21 mmol) at room temperature was slowly added PMe_3 (2.66 mL, 1.0 M in toluene) by a syringe. After stirring for 2 h, the reddish orange solution was evaporated to give a crude solid of **1**, (0.54 g) which was washed with ether (2 mL×2) and then recrystallized from THF/hexane (1 : 1) (0.48 g, 86 %).

Trans-PdPhI(PPh_2Me)$_2$, (**2**) and PdPhI($Ph_2PCH_2PPh_2$), (**3**) were obtained analogously in 95% and 86% yields, respectively. Complexes **1** and **2** were characterized by ^1H, and $^{31}P\{^1H\}$ spectra and compared with the literature data.[4a,b] **3**: ^1H NMR (500 MHz, $CDCl_3$, δ): 4.49 (bs, 2H, -CH_2-), 6.50 (t, 2H, aromatic), 6.60 (t, 1H, aromatic), 6.70 (d, 2H, aromatic), 7.25-7.41 (m, 20H, aromatic). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$, δ): 38.9 (bs, P-CH_2-), 123.9, 128.6, 128.8, 130.0, 131.3, 133.4, 135.6 (s, aromatic). ^{31}P NMR (200 MHz, $CDCl_3$, δ): 11.2(s). Anal. Calcd for $C_{31}H_{27}P_2IPd$: C, 53.59; H, 3.92. Found: C, 53.36; H, 4.01.

Reactions of 1 with *tert*-Butyl Isocyanide, Cyclohexyl Isocyanide, and 2,6-Dimethylphenyl Isocyanide. To a stirred THF (4 mL) solution containing *trans*-PdPhI(PMe_3)$_2$ (0.168 g, 0.36 mmol) at room temperature was added *tert*-butyl isocyanide (33 mg, 0.40 mmol). The initial colorless solution turned to yellow. After stirring for 2 h, the solvent was removed to give a yellow solid. Recrystallization of the solid from THF/hexane (1 : 1) gave yellow crystals of *trans*-Pd[C(Ph)=N(C$(CH_3)_3$]I(PMe_3)$_2$, (**4**) in 94% yields (0.184 g). IR (KBr): 1600 cm^{-1} (C=N). ^1H NMR (500 MHz, $CDCl_3$, δ): 1.37 (t, 18H, J=3.5 Hz, P$(CH_3)_3$), 1.55 (s, 9H, C$(CH_3)_3$), 7.28 (m, 3H, aromatic), 8.19 (broad, 2H, aromatic). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$, δ): 16.3 (t, J=14 Hz, P$(CH_3)_3$), 31.7 (s, C($\underline{C}H_3)_3$), 57.8 (s, $\underline{C}(CH_3)_3$), 127.8, 128.8, 130.3, 144.9 (t, J=10 Hz, ipso, aromatic), 178.0 (t, J=4 Hz, $\underline{C}$(Ph)=N-). ^{31}P NMR (200 MHz, $CDCl_3$, δ): −22.3 (s). Anal. Calcd for $C_{17}H_{32}NP_2IPd$: C, 37.43; H, 5.91; N, 2.57. Found: C, 37.36; H, 5.87; N, 2.18.

Reaction of cyclohexyl isocyanide with **1** was similarly carried out to give the complex, Pd[C(Ph)=N(C_6H_{11})]I(PMe_3)$_2$, (**5**) in 88% yield. IR (KBr): 1596 cm^{-1} (C=N). ^1H NMR (500 MHz, $CDCl_3$, δ): 1.29 (m, 4H, -CH_2), 1.38 (t, 18H, J=3.4 Hz, P$(CH_3)_3$), 1.64 (m, 4H, -CH_2), 1.82 (m, 2H, -CH_2), 4.04 (m, 1H, CH), 7.28 (m, 3H, aromatic), 8.08 (m, 2H, aromatic). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$, δ): 16.6 (t, J=15 Hz, P$(CH_3)_3$, 24.5 (s, CH_2), 25.9 (s, CH_2), 33.9 (s, CH_2), 67.2 (s, CH), 127.9, 128.9, 129.5, 143.7 (t, J=7.0 Hz, ipso, aromatic), 177 (t, J=4.0 Hz, $\underline{C}$(Ph)=N-). ^{31}P NMR (200 MHz, $CDCl_3$, δ): −20.7 (s). Anal. Calcd for $C_{19}H_{34}NP_2IPd$: C, 39.91; H, 5.99; N, 2.45. Found: C, 39.90; H, 6.03; N, 2.32.

Pd[C(Ph)=N(2,6-$Me_2C_6H_3$)]I(PMe_3)$_2$, (**6**) was analogously obtained in 95% yield. IR (KBr): 1562 cm^{-1} (C=N). ^1H NMR (500 MHz, $CDCl_3$, δ): 1.23 (t, 18H, J=3.4 Hz, P$(CH_3)_3$), 2.49 (s, 3H, CH_3), 6.94 (t, 1H, aromatic), 7.07 (d, 2H, aromatic), 7.39 (m, 3H, aromatic), 8.27 (d, 2H, aromatic). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$, δ): 16.7 (t, J=15 Hz, P$(CH_3)_3$), 20.7 (s, CH_3), 128.0, 128.6, 129.2, 129.4, 130.0, 146.0, 147.3 (s, aromatic), 189.4 (t, J=3.0 Hz, $\underline{C}$=N-), ^{31}P NMR (200 MHz, $CDCl_3$, δ): −21.8 (s). Anal. Calcd for $C_{21}H_{32}NP_2IPd$: C, 42.48; H, 5.43; N, 23.58. Found: C, 42.36; H, 5.71; N, 23.51.

Table 1. Crystallographic Data and Results of Refinements of **1**

formula	$C_{12}H_{23}P_2IPd$
fw	462.54
temperature, K	293
wavelength (Å)	0.71073
crystal system	monoclinic
space group	$P2_1/a$
a, Å	11.493(4)
b, Å	11.191(3)
c, Å	14.199(4)
β, deg	108.55(3)
V, Å^3	1731.4(9)
Z	4
$d_{calc,g\ cm^{-3}}$	1.774
μ, cm^{-1}	30.18
F(000)	896
no. of reflns collected	2703
no. of reflns used, I>2 σ(I)	2552
no. of params	146
scan range	3<2θ<47
scan type	ω-2θ
Max. in Δρ (e A^{3-})	0.701
GOF on F^2	1.161
R	0.0315
wR_2[a]	0.0794

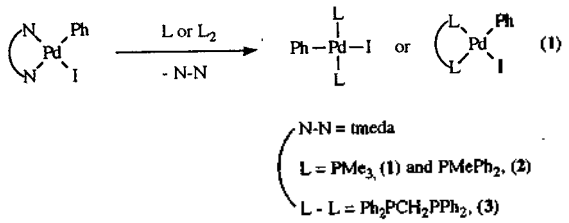
[a] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

X-ray Structure Determination. All X-ray data were collected with use of a Mac Science 4-circle diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with 20<2θ<30°. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. Decay corrections were made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out on the personal computer with use of the SHELXS-86 and SHELXL-93 programs.[7]

A pale yellow crystal of **1**, shaped as block, of approximate dimensions 0.2×0.3×0.3 mm, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h00(h=2n+1)$, $0k0$ $(k=2n+1)$, $h01(h=2n+1)$, unambiguously indicated $P2_1/a$ as a space group. The structure was solved by the heavy atom methods. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model. Final atomic positional parameters for non-hydrogen atoms, anisotropic thermal parameters, full bond distances and angles, and tables of observed and calculated structure factors are available as supplementary materials.

Results and Discussion

It is well known that nitrogen donor or olefin ligand coordinated to the late transition metal complex is coordinatively labile and can be readily displaced by strongly basic mono- or diphosphine.[8] So, we tried to find an easy and high-yield synthesis of arylpalladium(II) iodide complex using the palladium complex having nitrogen donor or olefin ligand as the precursor. Recently van Koten and his coworkers[5a] showed the ligand exchange reaction using PdPhI(tmeda), which is moderately air-stable in the solid state as in solution and can be easily treated, by triphenylphosphine. Thus, we also applied to afford the arylpalladium(II) iodide complexes from the displacement of PdPhI(tmeda) by mono and chelated phosphines (PMe_3, $PMePh_2$, and $Ph_2PCH_2PPh_2$) in a stochiometric ratio as shown in Eq. (1).



The above reactions easily proceed to give phenylpalladium(II) iodide complexes in high yields at room temperature. These reactions provide a convenient synthetic utility for the known and new arylpalladium halide complexes.

Pale yellow crystals of **1** suitable for X-ray analysis are obtained from ether solution. An ORTEP drawing of **1** shown in Figure 1, together with the selected bond lengths and bond angles exhibits a typical square -planar coordination containing one phenyl, two PMe_3 ligands, and one iodide ligand around palladium center. The equatorial plane, defined by Pd, P1, P2, I, and C1, is essentially planar with the average displacement of 0.016 Å from this plane. The phenyl ring and the equatorial plane are mutually orthogonal.

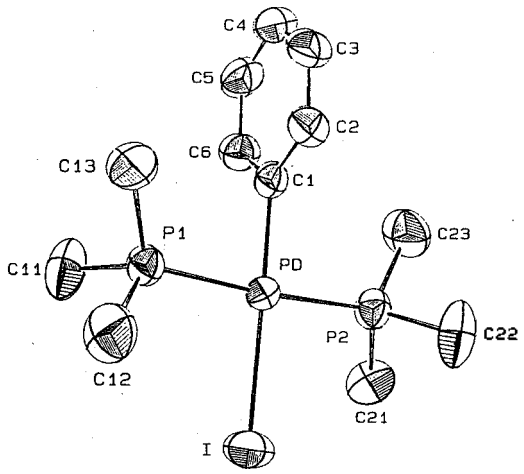
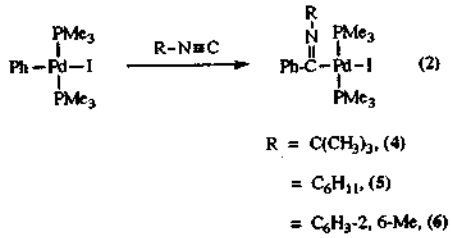


Figure 1. ORTEP drawing of the molecular structure of **1** with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and bond angles (deg) for one of the molecules of 1: Pd-I, 2.695(9); Pd-C(1), 2.012(6); Pd-P(2), 2.315(2); Pd-P(1), 2.320 (2); C(1)-Pd-I, 178.1(14); P(2)-Pd-P(1), 175.6(5); C(1)-Pd-P(1), 86.8 (14); C(1)-Pd-P(2), 88.7(14); P(2)-Pd-I, 91.3; P(1)-Pd-I, 93.1; C(6)-C(1)-Pd, 120.5; C(2)-C(1)-Pd, 122.1(4); C(6)-C(1)-C(2), 117.4(5).

Reactions of **1** with an equal amount of *tert*-butyl, cyclohexyl, and 2,6-dimethylphenyl isocyanides, which are isoelectronic with CO, causes insertion of isocyanides into palladium-carbon bond as shown in Eq. (2). The isolated complexes are characterized by IR, NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectroscopy, and elemental analyses.



IR spectra of **4-5** show the C=N stretch frequencies at *ca.* 1600 cm^{-1}, which is normal value corresponding to the known imino complexes,[9] but complex **6** displays decrease of the wave number by about 30 cm^{-1} probably due to aromatic π-cojugation. $^{13}C\{^1H\}$ NMR spectra of the complexes show the carbon peak of the C=N fragments at *ca.* δ 180-190 ppm, as a triplet with a J=3-4 Hz coupled with two phosphous atoms of PMe_3 ligand. All spectroscopic data support the structure of $PdI\{C(Ph)=NR\}(PMe_3)_2$.

It has been reported that isocyanides insert into palladium-carbon bond and the insertion reaction depends on the steric hindrance of both isocyanides and phosphine ligands.[10] The above reactions using the palladium complex having strongly basic and compact trimethylphosphine ligand exhibit clean and quantitative isocyanides insertion into palladium-carbon bond at room temperature in spite of steric hindrance of *tert*-butyl, 2,6-dimethyl isocyanide. On the basis of spectroscopic data other side products such as dimer, $[\mu\text{-}I\text{-}(PMe_3)(C(Ph)=NR)Pd]_2$ or ionic intermediate, *trans*-$[Pd(PMe_3)_2(CNR')(Ph)]I$ are not observed in the reaction mixture.

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Supplementary Material Available. Tables of atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinate and isotropic displacement parameters (4 pages); table of observed and calculated structure factors (6 pages) are available from the one of authors (S.-W. L.).

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