

Synthesis of Arylpalladium(II) Azido Complexes: The Crystal Structure of Pd(C₆H₄-*p*-Me)(N₃)(tmeda) (tmeda=N,N,N',N'-tetramethylethylenediamine)

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There has been an incessant interest on chemistry of transition metal azido complexes for many years due to their analogy with organic azides that undergo various reactions including cycloaddition reactions and nitrene (or imido) compounds formation under thermal or photo irradiated conditions.¹ Among those, the chemistry of late transition metal azido complexes was intensively studied by Beck and his coworkers.² Recently several Ni(II)³⁻⁵, Pd(II)⁶, and Pt(II)^{6,7} azido complexes with chelated or monodentate phosphine and amine ligands have been prepared and studied on effective conversion to the metal nitrido (or imido) species or cluster compounds and on the structural and magnetic properties. Very recently, we have also reported synthesis and some chemical reactions of palladium (II) and platinum (II) azido complexes containing chelated amines and monodentate or chelated tertiary phosphines.⁸ Although extensive studies of late transition metal azide complexes have been established, the chemistry of late transition metal mono azido complexes having alkyl, aryl or halogeno ligand are relatively rare.^{4,7,8a} These complexes, furthermore, might possess a considerable potential utility as a precursor of metal amide complex or organic amines since the use of a suitable reducing agent or thermal conditions would cause the hydrogenation of the coordinated azido group. As an extension of the recent work on the methylpalladium (II) and platinum (II) azido complexes, herein we wish to report the preparation of various azido complexes of arylpalladium (II) containing amine ligand whose aryl group is thermally more stable than alkyl ligand of similar alkylpalladium (II) azido complexes.

Experimental

All the manipulations of air-sensitive compounds were performed under N₂ or argon atmosphere with use of standard Schlenk technique. Solvents were distilled from N-benzophenone. PdPh (I) (tmeda) and PdAr (Me) (tmeda) (Ar=C₆H₅, C₆H₄-*p*-Me, and 1-naphthyl) were prepared by the literature method.^{9,10}

Elemental analyses were carried out by the analytical laboratory at Basic Science Institute of Korea and at Sangji University. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. NMR (¹H, ¹³C{¹H} and ³¹P{¹H}) spectra were obtained on a Varian-300 and Bruker 500 MHz spectrometers. Chemical shifts were referred to an internal Me₄Si and to an external 85% H₃PO₄.

Preparation of PdAr(OCOCF₃)(tmeda)(1: Ar=C₆H₅; 2: Ar=C₆H₄-*p*-Me; 3: Ar=1-naphthyl). To an ethereal solution (80 mL) containing PdPh (Me) (tmeda) (1.15 g, 3.65 mmol) was slowly added CF₃CO₂H (0.416 g, 3.65

mmol). A pale green solid began to precipitate with gas evolution on stirring at room temperature. After stirring for 40 minutes the precipitated solid was filtered and washed with n-hexane (1.44 g, 96%). Recrystallization from THF/n-hexane gave pale green crystals of PdPh (OCOCF₃)(tmeda), **1**. ¹H NMR (500 MHz, CDCl₃, δ): 2.43, 2.55 (s, 12H, N-Me₂), 2.52, 2.68 (m, 4H, N-CH₂), 6.92(t, 1H), 7.01(t, 2H), 7.45(d, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃, δ): 47.70, 51.40 (s, N-Me₂), 57.52, 63.47 (s, N-CH₂), 116.1 (q, CF₃, J(CF)=291 Hz), 123.3, 126.3, 134.2, 148.5 (ipso), 161.3 (q, CCF₃, J(CF)=35 Hz). Anal. Calcd for C₁₄H₂₁N₂O₂F₃Pd: C, 40.74; H, 5.13; N, 6.79. Found: C, 40.34; H, 5.34; N, 6.77.

PdAr (OCOCF₃)(tmeda) (Ar=C₆H₄-*p*-Me and 1-naphthyl) were prepared by a similar procedure as for the complex **1**. Pd(C₆H₄-*p*-Me) (OCOCF₃)(tmeda), **2**: 60%. ¹H NMR (CDCl₃, δ): 2.22 (s, 3H, CH₃), 2.47, 2.60 (s, 12H, N-Me₂), 2.52, 2.69 (m, 4H, N-CH₂), 6.76, 7.22 (d, 2H, aromatic). ¹³C{¹H} NMR (125 MHz, CDCl₃, δ): 20.6 (s, CH₃), 47.78, 51.49 (s, N-Me₂), 57.64, 63.55 (s, N-CH₂), 116.0 (q, CF₃, J(CF)=291 Hz), 127.3, 132.3, 133.9, 143.6 (ipso), 161.5 (q, CCF₃, J(CF)=35 Hz). Anal. Calcd for C₁₅H₂₃N₂O₂F₃Pd: C, 42.22; H, 5.43; N, 6.56. Found: C, 41.87; H, 5.19; N, 6.62. Pd (1-naphthyl) (OCOCF₃)(tmeda), **3**: 92%. ¹H NMR (CDCl₃, δ): 2.00, 2.51, 2.61, 2.64 (s, 12 H, N-Me₂), 2.41-2.64 (m, 4H, N-CH₂), 2.10, 7.35, 7.47, 7.51, 7.63, 9.25 (m, 7H, aromatic). ¹³C{¹H} NMR (CDCl₃, δ): 47.07, 48.33, 50.18, 52.96 (N-Me₂), 57.68, 63.43 (N-CH₂), 115.3 (q, CF₃, J(CF)=290 Hz), 123.1, 124.0, 124.5, 127.6, 131.1, 131.7, 133.4, 138.0, 150.1 (ipso); 161.6 (q, CCF₃, J(CF)=35 Hz). Anal. Calcd for C₁₈H₂₃N₂O₂F₃Pd: C, 46.71; H, 5.01; N, 6.05. Found: C, 46.72; H, 5.00; N, 6.12.

Preparation of PdAr (N₃)(tmeda)(4: Ar=C₆H₅; 5: Ar=C₆H₄-*p*-Me; 6: Ar=1-naphthyl). To a THF solution (40 mL) of PdPh (OCOCF₃)(tmeda) (1.31 g, 0.04 mmol) was added an aqueous THF solution of NaN₃ (0.309 g, 4.75 mmol) by a cannula. After stirring the reaction mixture for 4 h at room temperature the solvent was evaporated to dryness. The pale yellowish residue was then extracted with CH₂Cl₂. The collected yellow extract was reduced to 5 mL under vacuum. Addition of n-hexane (5 mL) caused separation of a yellow solid which was recrystallized from THF/n-hexane. The yield of PdPh (N₃)(tmeda), **4** was 0.941 g (87%). IR (KBr): 2024 cm⁻¹(N₃). ¹H NMR (CDCl₃, 500 MHz, δ): 2.44, 2.55 (s, 12H, N-Me₂), 2.52, 2.66 (m, 4H, N-CH₂), 6.92 (t, 1H), 7.01 (t, 2H), 7.45 (d, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃, δ): 47.78, 50.86 (s, N-Me₂), 57.88, 62.89 (s, N-CH₂), 123.2, 127.2, 133.9, 153.3 (ipso). Anal. Calcd for C₁₂H₂₁N₃Pd: C, 42.17; H, 6.19; N, 20.50. Found: C, 41.96; H, 6.33; N, 20.25.

PdAr (N₃)(tmeda) (Ar=C₆H₄-*p*-Me and 1-naphthyl) were

prepared by a similar procedure as for the complex 4. Pd (C₆H₄-*p*-Me) (N₃) (tmeda), **5**: 83%. IR (KBr): 2032 cm⁻¹ (N₃). ¹H NMR (CDCl₃, δ): 1.66 (s, 3H, CH₃), 2.20, 2.37 (s, 12H, N-Me₂), 2.45, 2.58 (m, 4H, N-CH₂), 6.82, 7.26 (m, 4H, aromatic). ¹³C{¹H} NMR (CDCl₃, δ): 20.8 (CH₃), 47.7, 50.8 (N-Me₂), 57.8, 62.9 (N-CH₂), 128.0, 131.9, 133.6, 148.5 (aromatic). Anal. Calcd for C₁₃H₂₃N₅Pd: C, 43.89; H, 6.52; N, 19.68. Found: C, 43.48; H, 6.33; N, 19.23. Pd (1-naphthyl) (N₃) (tmeda), **6**: 89%. IR (KBr): 2028 cm⁻¹ (N₃). ¹H NMR (CDCl₃, δ): 2.10, 2.52, 2.61, 2.67 (s, 12H, N-Me₂), 2.45-2.79 (m, 4H, N-CH₂), 7.21, 7.39, 7.44, 7.49, 7.56, 7.70, 9.10 (m, 7H, aromatic). ¹³C{¹H} NMR (CDCl₃, δ): 47.1, 48.4, 49.6, 52.0 (N-Me₂), 58.0, 62.8 (N-CH₂), 123.2, 124.4, 124.6, 125.1, 128.1, 130.4, 131.8, 134.1, 138.3, 155.7 (aromatic). Anal. Calcd for C₁₆H₂₃N₅Pd: C, 49.05; H, 5.92; N, 17.87. Found: C, 48.89; H, 5.96; N, 17.74.

X-Ray structure determination. Crystals of **5** suitable for X-ray crystallography were obtained by recrystallization from THF/*n*-hexane mixture and mounted in glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of setting angles of 20 reflections with 20° ≤ 2θ ≤ 30°. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo-Kα radiation (λ=0.71069 Å) and the ω-2θ method. Calculations were carried out by using a program package TEXSAN on a DEC Micro VAXII computer. A full matrix least-squares refinement was carried out by applying anisotropic thermal factors to all the non-hydrogen atoms. Hydrogen atoms were located from calculation by assuming the ideal positions (d(C-H)=0.95 Å) and were included in the structure calculation without further refinement of the parameters. Absorption correction by ψ scan method of the collected data was applied. Crystallographic data and atomic coordinates of the non-hydrogen atoms are listed in Tables 1 and 3. Atomic coordinates of hydrogen atoms and all bond distances and angles are available from the author (Y.-J.K.).

Results and Discussion

In the preceding paper,^{8a} we have shown that alkyl-palladium (II) or platinum (II) trifluoroacetate complexes

Table 1. Crystallographic data for **5**

Formula	C ₁₃ H ₂₃ N ₅ Pd
Formula weight	355.76
Crystal system	trigonal
Space group	R3 (# 148)
a, Å	24.041 (7)
c, Å	15.208 (4)
V, Å ³	7609 (4)
D _{calc} , g cm ⁻³	1.486
μ(MoKα), cm ⁻¹	9.93
F(000)	3472.00
Unique refls (total)	3472
No. observ.	2129
(I>3.00σ(I))	
No. of variables	172
Z	16
2θ _{max}	55.0°
Scan type	ω
Scan rate (°/min)	16.0
R ^a	0.053
Rw ^a	0.062

$$^a R = [\Sigma(F_o - F_c) / \Sigma F_o] \quad R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2]^{1/2} \quad \text{where } w = [\{\sigma(F_o)\}^{-2}]^{-1}$$

Table 2. Selected bond lengths (Å) and angles (°) for **5**

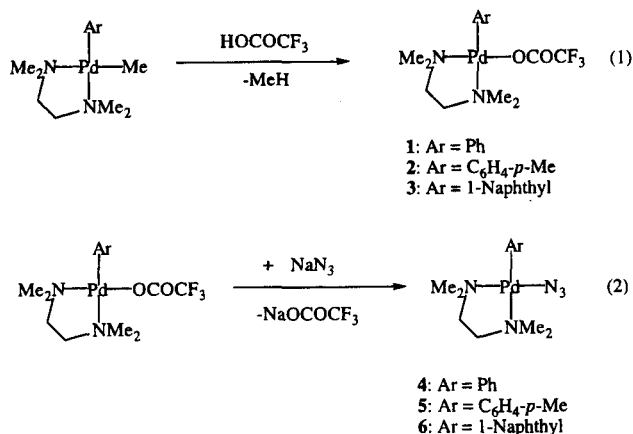
Pd(1)-N(1)	2.017	N(1)-Pd(1)-N(4)	175.4(4)
Pd(1)-N(5)	2.190	N(5)-Pd(1)-C(1)	175.8(5)
Pd(1)-N(4)	2.098	Pd(1)-N(1)-N(2)	126.7(9)
N(1)-N(2)	1.11(1)	N(1)-N(2)-N(3)	174(1)
N(2)-N(3)	1.16(1)	N(4)-Pd(1)-N(5)	86.0(4)
Pd(1)-C(1)	1.95(1)	N(1)-Pd(1)-C(1)	91.9(4)

Table 3. Atomic coordinates and isotropic temperature factors for **5**

Atom	x	y	z	B _{eq}
Pd(1)	0.22829(4)	0.08401(4)	0.85046(6)	3.95(2)
N(1)	0.1793(5)	0.1317(5)	0.8585(8)	6.9(3)
N(2)	0.2001(5)	0.1847(6)	0.8634(7)	5.1(3)
N(3)	0.2165(5)	0.2386(6)	0.8702(9)	8.3(4)
N(4)	0.2721(5)	0.0275(5)	0.8417(7)	4.9(3)
N(5)	0.1372(4)	-0.0061(4)	0.8353(7)	5.4(3)
C(1)	0.3099(5)	0.1623(5)	0.8725(9)	4.5(3)
C(2)	0.3482(7)	0.2023(6)	0.8061(8)	5.6(4)
C(3)	0.4084(7)	0.2598(7)	0.823(1)	6.7(4)
C(4)	0.4286(6)	0.2768(6)	0.911(1)	7.1(5)
C(5)	0.3885(7)	0.2357(8)	0.9783(10)	6.8(4)
C(6)	0.3309(6)	0.1802(6)	0.9583(8)	5.4(3)
C(7)	0.4914(6)	0.3381(7)	0.934(1)	12.0(6)
C(8)	0.3130(7)	0.0421(7)	0.765(1)	8.4(5)
C(9)	0.3129(9)	0.0333(9)	0.9176(10)	11.6(7)
C(10)	0.2184(8)	-0.0387(8)	0.833(2)	12.7(7)
C(11)	0.1589(9)	-0.555(7)	0.826(2)	14.1(8)
C(12)	0.0949(7)	-0.0190(7)	0.910(1)	9.6(5)
C(13)	0.1039(7)	-0.0066(8)	0.754(1)	9.9(5)

containing chelated amine or phosphine ligand are easily prepared by protonolysis of dialkylpalladium (II) complexes with trifluoroacetic acid and that the trifluoroacetate ligand is readily replaced by azide to give the corresponding palladium (II) or platinum (II) azido complexes. The same synthetic method is applied to obtain various arylpalladium (II) azido complexes. Thus, we initially prepared arylpalladium (II) trifluoroacetate complexes from the protonolysis of arylmethylpalladium (II) complexes Pd(Ar)Me (tmeda) (Ar = phenyl, C₆H₄-*p*-Me, and 1-naphthyl)^{9,10} by trifluoroacetic acid (eq. 1), and then examined metathetical reactions of the trifluoroacetate complexes with sodium azide to give the arylpalladium (II) azido complexes as shown in Eq. (2).

The reactions (2) occur in aqueous THF solution similarly to the already reported metathetical synthesis of metal halides with sodium azide. The complexes 4-6 are isolated in moderate to good yields as yellow crystalline solids,



which are thermally stable in the solid state as well as in solution. The complexes are characterized by IR, NMR (¹H and ¹³C{¹H}) and elemental analyses. IR spectra show a strong absorption band due to asymmetric stretching vibrations ν(N₃) in 2024-2032 cm⁻¹ range. The ¹H NMR spectra of 4-6 show the two NMe₂ groups as two singlets, the two CH₂ groups as a complex AA'BB' pattern, for the tmeda ligand and the aromatic signals as well-separated multiplets. The ¹³C NMR spectra of the complexes also support the presence of the tmeda ligand and the corresponding aromatic group.

In contrast with the reaction (2), several of our attempts to obtain arylpalladium (II) azido complexes PdPh (N₃) (tmeda) from the reaction of PdPh (I) (tmeda) with excess sodium azide caused the formation of PdPh (N₃) (tmeda), 4 in a low yield with (<5%) recovery of starting materials. This result indicates that the trifluoroacetate ligand is more facile than the iodo ligand on the addition of nucleophile. Thus, the above reaction (2) provides a convenient synthetic method for various new arylpalladium (II) azido complexes. Furthermore, the isolated arylpalladium (II) azido complexes containing tmeda ligand are believed as a useful precursor for arylpalladium (II) azido complexes with auxiliary phosphine ligands since the coordinated to Pd (II) complexes tmeda undergoes a facile substitution on addition of monodentate or chelated tertiary phosphines ligand.

Yellow single crystals of 5 suitable for X-ray analysis were obtained from THF/n-hexane solution at -20°C. The

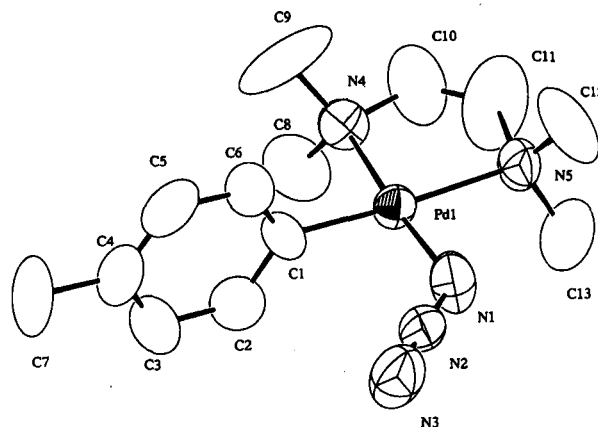


Figure 1. ORTEP drawing of 5 showing the atomic labeling scheme and 50% probability thermal ellipsoids.

molecular structure of 5 with the atomic numbering scheme is shown in Figure 1. Selected bond distances and angles are given in Table 2. The molecule has a slightly distorted square planar coordination around the palladium center with a tmeda ligand and mutually cis-positioned 4-methylphenyl and azido ligands. The plane of the 4-methylphenyl group is oriented almost perpendicular to the coordination plane. The Pd(1)-N(1) (azido) bond distance of the complex is 2.017 (9) Å which is almost similar to those found in [(C₆H₅CH₂)₃P]₂Pd(N₃)₂ (2.045 (6) Å)¹¹ and Pd₂(N₃)₂²⁻ (2.004 (5) Å)¹², but is slightly shorter than that of *trans*-PdMe (N₃) (PMe₃)₂ (2.132 (9) Å).^{8a} The longer Pd-N5 bond (2.190 (9) Å) *trans* to the 4-methylphenyl group than Pd-N4 bond (2.098 (9) Å) is also similar to that of PdPh(tmeda)⁹, indicating a larger *trans* influence of the aryl group than the iodo ligand. The bond angles of Pd-N(1)-N(2) (126.7 (9)°) and N(1)-N(2)-N(3) (174 (1)°) belong to the reasonable range of the bond angle (119-129°) and (164-175°) of already reported palladium azido complexes. However, the N(1)-N(2) (1.11 (1) Å) distance is relatively shorter than the N(2)-N(3) (1.16 (1) Å) which is in contrast with other coordinated Pd (II) azides except one example of [(C₆H₅CH₂)₃P]₂Pd(N₃)₂.¹¹

In summary we have obtained new arylpalladium(II) azido complexes from the reaction of arylpalladium (II) trifluoroacetate complexes with NaN₃, in which the trifluoroacetate ligand replaces readily with the weak nucleophile. The complexes obtained in the present study are expected to serve as precursor of various aryl organopalladium complexes.

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 10. PdAr (Me) (tmeda) (Ar=1-naphthyl) was prepared similarly to the procedure for PdAr (Me) (tmeda) (Ar=Ph, C₆H₄-p-Me) in reference 9. Pd(1-naphthyl) (Me) (tmeda), 54%. ¹H NMR (CDCl₃, δ): 0.08 (s, 3H, Pd-CH₃), 2.01, 2.41, 2.60, 2.66 (s, 12H, N-Me₂), 2.40-2.74 (m, 4H, N-CH₂), 7.27, 7.43, 7.76, 8.94 (m, 7H, aromatic). ¹³C{¹H} NMR (CDCl₃, δ): -9.95 (Pd-CH₃), 47.50, 48.00, 48.69, 49.60 (N-Me₂), 59.24, 60.12 (N-CH₂), 120.6, 122.4, 123.6, 124.6, 127.6, 133.4, 133.8, 136.4, 140.8, 168.1 (ipso).
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Photochemical Reaction of Carbon Monoxide in Aqueous Methanol Containing Ammonia

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As industrial society has been developed, fossil fuels such as coal, oil, and natural gas have been increasingly used as energy source. During the combustion of fossil fuels, obnoxious gases such as nitrogen oxides, sulfur oxides and carbon oxides are produced. These gases are the main source of air pollution. Especially, carbon monoxide is very toxic compound and oxidized in the atmosphere to give carbon dioxide which causes green house effect or ozone depletion. On the other hand, it is industrially important compound because it could be used as a raw material for chemical syntheses. Earlier investigation showed that carbon monoxide reacts with hydrogen atom to give CHO radical¹ and Marz *et al.* proved the presence of this radical by ESR spectroscopy.² Arai *et al.*^{3,4} and Getoff *et al.*⁵⁻¹⁰ have studied the radiation induced reduction of CO in gas phase and in liquid phase, respectively. A problem for the reaction is, however, to use the special γ -ray device requiring various safety equipments. To circumvent this difficulty, we have employed photochemical method using UV light at 184.9

nm and reported the result along with the reaction mechanism for the chemical reaction of aqueous carbon monoxide.¹¹ We also reported that the reactivity of CHO radical formed in the reduction is higher in aqueous state than in hydrated state,¹² and that the carbonylation can be also occurred in the presence of other substances.^{13,14} Ammonia generated from decomposition of a large amount of garbage, causes also a serious environmental pollution. Very recently, we have described the photochemical decomposition of aqueous ammonia.¹⁵ It was found from the study that hydrazine was produced by the dimerization of $\dot{N}H_2$ radicals. In particular, the presence of ammonia during the irradiation of aqueous organic solution could lead to the formation of amine compounds.

In the present study, methanol was selected as a model substance for an organic solvent and we have investigated the possibility of carbonylation and amination, and proposed the reaction mechanisms for the photochemical transformation of carbon monoxide in aqueous methanol.