

Synthesis, Characterization, and Electrochemical Properties of Azido Palladium and -Platinum(I, II) Complexes with Bis(diphenylphosphino)methane Ligand

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Transition metal azide complexes have been extensively investigated because of their analogy with organic azide which undergoes various reactions including oxidation, carbonylation, 1,3-dipolar cycloaddition, and photochemical irradiation.¹ Earlier work by Beck and his coworkers² demonstrated the oxidation and some carbonylations of nickel, palladium, and platinum(II) azide complexes. Recently, several research groups have also reported the preparation of some nickel azide complexes and their photochemical activation.³⁻⁵ There have been, however, still a limited number of reports on chemical reactivity of late transition metal azide complexes due to their explosive nature on heating and shock sensitivity in the absence of stabilized ligands.

We are interested in preparation and utilization of late transition metal azides as precursors of late transition metal amide complex. For this aim we have undertaken the synthesis of late transition metal azide complexes which may serve as starting materials for preparation of stable late transition metal amide complex. In this work we report preparation and electrochemical behavior of new palladium and platinum azide complexes having bis(diphenylphosphino)methane as supporting ligand.

Experimental

PdCl₂ and K₂PtCl₄ were purchased from Wako Co. in Japan. COD (1.5-cyclooctadiene), tmeda (*N,N,N',N'*-tetramethylethylenediamine), and dppm (bis(diphenylphosphino)methane) were purchased from Aldrich Co. and used without further purification. Pd(tmeda)Cl₂,⁶ Pt(COD)Cl₂,⁷ and M₂(dppm)₂Cl₂ (M=Pd, Pt)^{8,9} were prepared by the literature method.

Elemental analyses were carried out by the analytical laboratory, Tokyo Institute of Technology in Japan. Melting points were taken in a sealed and evacuated capillary tube and were not corrected. UV and IR spectra were recorded on Hitachi U-3200 and Hitachi 270-30 spectrophotometers, respectively. ¹H-NMR spectra were obtained by a varian XL-200 spectrometer. Chemical shifts were referred to an internal Me₄Si. Cyclic voltammetry was conducted with EG & G PARC model 384B analyzer and 303A potentiostat using a conventional three-electrode configuration of a gold-disk working electrode, a platinum-wire auxiliary electrode, and an Ag/AgCl reference electrode. The potentials were calibrated using ferrocene as the external standard.

Preparation of Pd(tmeda)(N₃)₂ (1) and Pt(COD)(N₃)₂

(2). To a stirred THF (200 mL) suspension of Pd(tmeda)Cl₂ (1.56 g, 5.30 mmol) was added methanol (40 mL) solution of NaN₃ (0.76 g, 11.7 mmol) at room temperature. On stirring the yellow suspension turned into a bright orange solution accompanied by precipitation of NaCl. After stirring for 6 h the precipitate removed by filtration. The filtrate was concentrated under vacuum and stored in a freezer at -20°C to give orange solids which were filtered and washed with methanol. Recrystallization from CH₂Cl₂ at -20°C gave orange crystals of 1 (1.20 g, 73%). UV (CH₂Cl₂): λ_{max} 304 (ε 2200), 287 (2400) nm. Anal. Calcd. for C₈H₁₆N₆Pd: C, 23.5; H, 5.3; N, 36.5. Found: C, 23.9; H, 5.1; N, 37.2.

Pt(COD)(N₃)₂ (2) was prepared analogously (55%). Anal. Calcd. for C₈H₁₂N₆Pt: C, 24.8; H, 3.1; N, 21.7. Found: C, 25.0; H, 2.9; N, 21.8.

Preparation of Pd(dppm)(N₃)₂ (3). Dppm (190 mg, 0.50 mmol) was added to a CH₂Cl₂ (15 mL) solution of 1 (150 mg, 0.50 mmol) at room temperature. After stirring for 2 h the resulting yellow solution was reduced to 5 mL under vacuum and added hexane to afford yellow solids of 3, which were recrystallized from CH₂Cl₂/Hexane (3 : 1): 290 mg, 99%. mp. (decomp. 154-157°C). UV (CH₂Cl₂): λ_{max} 324 (ε 19500), 296 (17400) nm. Anal. Calcd. for C₂₅H₂₂N₆Pd: C, 52.2; H, 3.9; N, 14.6. Found: C, 52.4; H, 4.1; N, 14.3.

Preparation of Pt(dppm)(N₃)₂ (4). Dppm (360 mg, 0.94 mmol) was added to a CH₂Cl₂ (20 mL) solution 2 (360 mg, 0.94 mmol). Stirring the mixture for 2 h caused precipitation of 4 as a white solid, which was filtered, washed with ether, and dried *in vacuo*: 480 mg, 77%. mp. (decomp. 215-217°C). UV (CH₂Cl₂): λ_{max} 261 (ε 29300) nm. Anal. Calcd. for C₂₅H₂₂N₆Pt: C, 45.3; H, 3.3; N, 12.7. Found: C, 45.5; H, 3.3; N, 12.4.

Preparation of Pd₂(dppm)₂(N₃)₂ (5) and Pt₂(dppm)₂(N₃)₂ (6). To a stirred CH₂Cl₂ (20 mL) solution of Pd₂(dppm)₂Cl₂ (410 mg, 0.39 mmol) was added methanol (10 mL) solution of NaN₃ (80 mg, 1.2 mmol) under argon. During stirring the initial red solution turned a reddish-orange solution. After stirring for 5 h the solution was concentrated under reduced pressure and stored in a freezer to afford reddish-orange crystals of 5, which were recrystallized from CH₂Cl₂. The crystalline solids were completely dried under vacuum to avoid solvent coordination: 250 mg, 60%. mp. (decomp. 201-202°C). UV (CH₂Cl₂): λ_{max} 429 (ε 18700), 292 (23000) nm. Anal. Calcd. for C₅₀H₄₄N₆Pd₂: C, 56.4; H, 4.2; N, 7.9. Found: C, 56.5; H, 4.1; N, 7.5. Complex 5 was already prepared in a methanol solvated form, Pd₂(dppm)₂(N₃)₂·1/2 CH₃OH.⁹

Complex 6 was similarly obtained as yellow crystalline solids (72%). UV (CH₂Cl₂): λ_{max} 324 (ε 13300) nm. Anal. Calcd. for C₅₀H₄₄N₆Pt₂: C, 48.3; H, 3.6; N, 6.8. Found: C, 48.3; H, 3.6; N, 6.4.

Results and Discussion

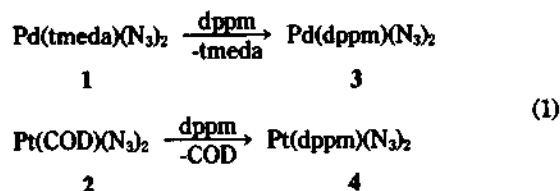
We initially attempted to make M(dppm)(N₃)₂ (M=Pd, Pt) by treatment of M(dppm)Cl₂ (M=Pd, Pt) with excess amounts of NaN₃ in CH₂Cl₂ or DMF but the complexes were obtained in poor yields probably due to the very low solubility of metal complexes in those solvents. Thus, we decided to try the following ligand substitution reaction as an alternate route. Reaction of Pd(tmeda)Cl₂ with two equivalents of NaN₃

Table 1. IR and ¹H-NMR Data

Compound	IR ^a ν(N ₃)	¹ H-NMR ^b	
		-CH ₂ -	-C ₆ H ₅
Pd(tmeda)(N ₃) ₂ (1)	2050	2.7(s) ^c	
Pt(COD)(N ₃) ₂ (2)	2052	1.9-2.9(m) ^d	
Pd(dppm)(N ₃) ₂ (3)	2036	4.2(t) J(HP)=10.8	7.4-7.6(m), 7.6-7.9(m)
Pt(dppm)(N ₃) ₂ (4)	2044	4.4(t) J(HP)=10.9	7.4-7.7(m), 7.7-7.9(m)
Pd ₂ (dppm) ₂ (N ₃) ₂ (5)	2014	4.1(bq) J(HP)=4	7.2-7.5(br)
Pt ₂ (dppm) ₂ (N ₃) ₂ (6)	2024	4.3(q) J(HP)=4 J(PtH)=561	7.4-7.7(m)

^aKBr disk. ^b200 MHz in CDCl₃ at room temperature. Chemical shifts values are in ppm relative to an internal standard SiMe₄ and coupling constants are in Hz. ^cCH₂ hydrogen peaks are overlapped. ^dVinyllic CH hydrogen peaks are observed at 4.9-5.8 ppm (m). Abbreviations: s, singlet; t, triplet; m, multiplet; q, quintet; bq, broad quintet; br, broad.

gives Pd(tmeda)(N₃)₂ (1) as orange crystalline solids. Treatment of complex 1 by bis(diphenylphosphino)methane ligand results in quantitative formation of Pd(dppm)(N₃)₂ (3) as yellow solids. Also, Pt(dppm)(N₃)₂ (4) is readily obtained in 77% yield from the reaction of Pt(COD)(N₃)₂ (2) with dppm ligand (Eq. 1)



These results indicate that the nitrogen donor or olefin ligand coordinated to Pd(II) or Pt(II) azide complexes is coordinatively labile and can be displaced by a better σ-donating ligand such as dppm ligand similarly to the corresponding transition metal alkyl complexes.⁶ On the other hand, readily soluble dinuclear complexes M₂(dppm)₂Cl₂ (M = Pd, Pt) in CH₂Cl₂ at room temperature reacted with ca. 3 equivalents of NaN₃ to give Pd₂(dppm)₂(N₃)₂ (5) in 60% and Pt₂(dppm)₂(N₃)₂ (6) in 72% yield, respectively (Eq. 2).



Complexes 1-6 are thermally and air stable in the solution and solid state. During melting point measurement complexes 1 and 2 without phosphine ligand show the explosive nature in the capillary tube. Both the mononuclear and dinuclear platinum complexes show poorer solubility in organic solvents than the palladium complexes. All complexes were characterized by IR and ¹H-NMR spectroscopy as well as elemental analyses. The infrared spectra show a characteristic sharp band in the region 2014-2052 cm⁻¹ which can be assigned to the azide asymmetric stretch. It is well known that the asymmetric stretch bands are always found near 2000 cm⁻¹.² Table 1 summarizes IR and ¹H-NMR data. The asymmetric

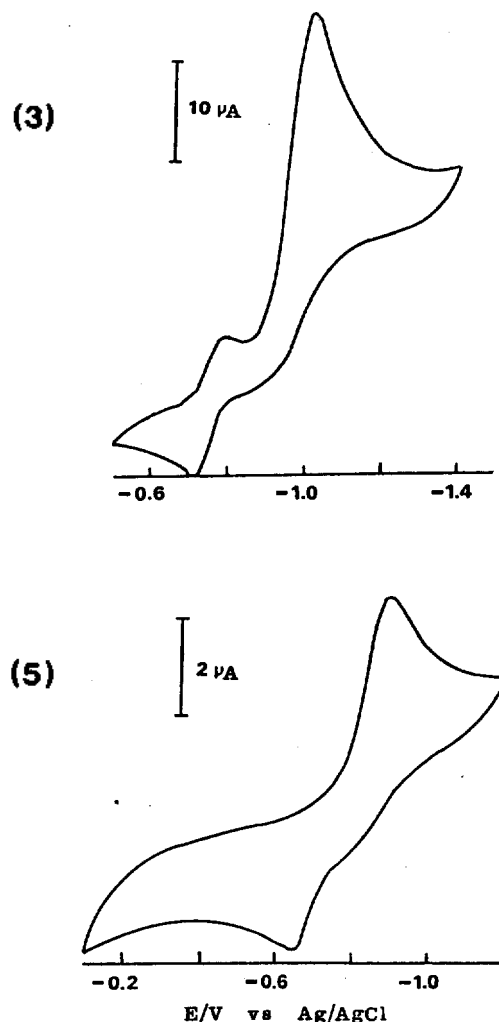


Figure 1. Cyclic voltammograms for palladium azide complexes Pd(dppm)(N₃)₂ (3) and Pd₂(dppm)₂(N₃)₂ (5) with gold-disk electrode in 0.1 M TBAP/CH₃CN and a scan rate of 100 mV/s.

ν(N₃) bands of dinuclear M(I) (M = Pd, Pt) azide complexes are relatively lower than those of mononuclear M(II) (M = Pd, Pt) azide complexes probably due to weak *trans* influence¹⁰ of palladium or platinum *trans* to azido group of the former. ¹H-NMR spectra of the complexes with dppm ligand show signals due to methylene protons of dppm ligand as a typical triplet or broad quintet and multiplets due to the phenyl group.

We have attempted to isolate platinum amide complex from the reduction of platinum azide complex by reducing agent. Treatment of Pt(dppm)(N₃)₂ with excess amounts of LiAlH₄ in THF at room temperature results in reddish brown solids. Although the IR spectrum of this product shows absorption peak due to NH₂ band at 3440, 3420 cm⁻¹ which might suggest the formation of platinum amide complex such as Pt(dppm)(NH₂)₂, but its analytical data are inconsistent with the proposed structure presumably because of dinuclear complex, Pd₂(μ-NH₂)(dppm)₂ formation in part derived from the fact that monomeric amide complexes with lone electron pair on nitrogen have a strong tendency to form dimers.¹¹ We could not separate the mononuclear platinum amide com-

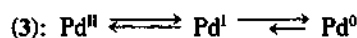
Table 2. Electrochemical Data^a

Compound	Solvent	Wave 1 ^b		$E_{1/2}$	Wave 2
		E_{pa}/V	E_{pc}/V		E_{pc}
Pd(dppm)(N ₃) ₂	CH ₃ CN	-0.85	-0.76	-0.81	-1.08
	DMF	-0.83	-0.64	-0.74	-1.09
Pd(dppm)Cl ₂	CH ₃ CN	-0.86	-0.76	-0.81	-1.12
	DMF	-0.86	-0.65	-0.76	-1.16
Pd ₂ (dppm) ₂ (N ₃) ₂	CH ₃ CN	-0.90	-0.64	-0.77	
	DMF	-1.14	-0.53	-0.84	
Pd ₂ (dppm) ₂ Cl ₂	CH ₃ CN	-0.90	-0.69	-0.80	
	DMF	-1.12	-0.52	-0.82	

^aPotentials referred to an Ag/AgCl electrode at a scan rate of 100 mV s⁻¹ and with 0.1 M TBAP as supporting electrolyte; $E_{1/2}$ for $Fc^+/Fc = +0.48$ V. ^b E_{pc} and E_{pa} are the peak potentials of the reduction and oxidation waves, respectively.

plex from the reaction mixture. Dppm bridged dinuclear type of complexes having halogen ligand are previously well studied.^{9b} However, comparable studies including electrochemical property between mononuclear and dinuclear complexes are scarce to our knowledge.

Electrochemistry. We have examined the electrochemical behavior of 3-6 complexes having dppm ligand. Cyclic voltammogram of mononuclear Pd(II) complex, Pd(dppm)(N₃)₂ (3) exhibits a reversible one electron reduction ($E_{1/2} = -0.81$ V) and an irreversible one-electron reduction ($E_{1/2} = -1.08$ V) in CH₃CN (see Figure 1). As can be seen in Figure 1, relative high intensity of complex 3 by irreversible one-electron reduction can be attributed to Pd^I/Pd⁰ reduction accompanied by partial dissociation of azide ligands to give palladium black. In DMF solvent we also observe similar redox features. The potentials corresponding to the features are summarized in Table 2. On the other hand, dinuclear Pd(II) complex, Pd₂(dppm)₂(N₃)₂ (5) shows a reversible one electron reduction ($E_{1/2} = -0.77$ V) in CH₃CN. In case of Pd(dppm)Cl₂ and Pd₂(dppm)₂Cl₂ under the same conditions we have also observed similar electrochemical behavior. This observation supports that the azido ligand in the palladium and platinum azide complexes has character as pseudohalide.^{1b} On the basis of the electrochemical behavior of mononuclear and dinuclear palladium azide complexes we suggest the following process.



In contrast with the above palladium (I, II) azide complexes platinum (I, II) azide complexes display no redox features within various solvent limits which support higher stability than palladium azide complexes. In the present work we described the preparation and some properties of palladium and platinum azide complexes and to the best of our knowledge the comparison between M(I) and M(II) (M = Pd, Pt) azide complexes was unnoted.

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Ruthenium-catalyzed Partial Oxidation of Alcohols by Paraformaldehyde

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Transition metal-catalyzed oxidations of alcohols have recently attracted considerable interest and various metal compounds and oxidant systems have been reported.¹ Ruthenium complex combined with several oxidants is also effective for the oxidation of alcohols.^{2,3} Recently, Bäckvall reported that RuCl₂(PPh₃)₃ exhibited a remarkable activity in hydrogen transfer from propan-2-ol to several ketones at reflux condition.⁴

In this Note, we wish to report that primary aliphatic and benzylic alcohols are readily oxidized to the corresponding aldehydes by paraformaldehyde in the presence of a catalytic amount of RuCl₂(PPh₃)₃.