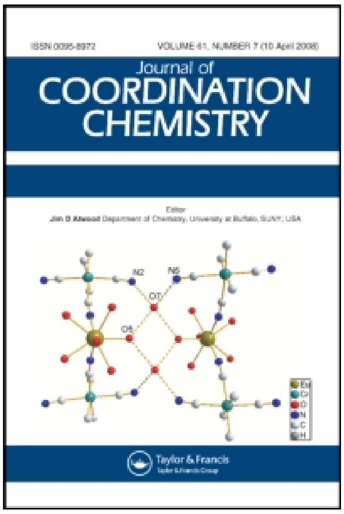

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SYNTHESIS AND CHARACTERIZATION OF HETEROLEPTIC PALLADIUM(II) COMPLEXES CONTAINING DIPHOSPHINE AND DIAMINE LIGANDS

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SYNTHESIS AND CHARACTERIZATION OF HETEROLEPTIC PALLADIUM(II) COMPLEXES CONTAINING DIPHOSPHINE AND DIAMINE LIGANDS

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Heteroleptic palladium(II) complexes containing diphosphine(P^P) and diamine (N^N) ligands, [Pd(P^P)(N^N)]$(ClO_4)_2$ (P^P = *bis*(diphenylphosphino)ethane (dppe), *bis*(diphenylphosphino)propane (dppp), *bis*(diphenylphosphino)butane (dppb), and N^N = ethylenediamine(en), propylenediamine (pn), butylenediamine (bn), 1,2-phenylenediamine (ϕn), 4-methyl-1,2-phenylenediamine (4-Me-ϕn), 4-chloro-1,2-phenylenediamine (4-Cl-ϕn) and 4-nitro-1,2-phenylenediamine (4-NO_2-ϕn)) were synthesized from the complexes [Pd(P^P)Cl_2] and the appropriate diamine (N^N). These mixed-ligand complexes were characterized by spectroscopic measurements (IR, electronic, ^1H and ^{31}P nmr) and electrochemical properties. The ^{31}P nmr of the complexes were considerably different depending on the diphosphine ligands, while the contribution of diamines to the spectra is quite small. The electronic absorption maximum of Pd(II)-dppp which has stronger backbonding in comparison to Pd(II)-dppe or Pd(II)-dppb appeared at lowest energy. Redox potentials and peak currents of the complexes were not much influenced by the various diphosphine and diamine ligands. $[Pd(dppe)(en)]^{2+}$, $[Pd(dppe)(4\text{-}Me\text{-}\phi n)]^{2+}$ and $[Pd(dppp)(en)]^{2+}$ were also prepared by conproportionation reactions from ethylenediamine (or 4-Me-ϕn) and the appropriate diphosphine complexes and could be identified by voltammetry.

Keywords: heteroleptic; palladium; diphosphine; diamine; conproportionation; electrochemistry

INTRODUCTION

Diphosphine-containing D_{4h} complexes are used as homogeneous catalytic agents in organic reactions such as olefin oxidation [1], hydrogenation [2],

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cyclization [3] and carbonylation [4]. Thus heteroleptic d^8-transition metal complexes have been much studies, especially palladium complexes containing diphosphines [5, 6]. However, mixed-ligand dicationic palladium(II) complexes containing a diphosphine and a diamine have scarcely been reported except for species such as $[Pd(dppe)(en)](NO_3)_2$ and $[Pd(dppe)(R,R\text{-dach})](NO_3)_2$ which are well known as antitumor metal complexes [7].

In this study we report the new mixed-ligand palladium $[Pd(P\text{^}P)(N\text{^}N)](ClO_4)_2$ complexes containing diphosphine (P^P) and diamine (N^N) as bidentate ligands, wherein P^P are *bis*(1,2-diphenylphosphino)ethane(dppe), *bis*(1,3-diphenylphosphino)propane (dppp) and *bis*(1,4-diphenylphosphino)butane (dppb), and N^N are 1,2-diaminoethane (en), 1,3-diaminopropane (pn), 1,4-diaminobutane (bn), 1,2-phenylenediamine (ϕn), 4-methyl-1,2-phenylenediamine (4-Me-ϕn), 4-chloro-1,2-phenylenediamine (4-Cl-ϕn) and 4-nitro-1,2-phenylenediamine ($4\text{-}NO_2$-ϕn). We are planning to investigate these complexes as catalysts for olefin oxidation in the future. Spectroscopic and electrochemical properties of these complexes were analyzed. $[Pd(dppe)(en)]^{2+}$, $[Pd(dppe)(4\text{-Me-}\phi n)]^{2+}$ and $[Pd(dppp)(en)]^{2+}$ could also be synthesized using ligand conproportionation and were identified by cyclovoltammetry.

EXPERIMENTAL

Materials and Instruments

$Ph_2P(CH_2)_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, $Ph_2P(CH_2)_4PPh_2$, $NH_2(CH_2)_2NH_2$, $NH_2(CH_2)_3NH_2$, $NH_2(CH_2)_4NH_2$, 1,2-phenylenediamine, 4-methyl-1,2-phenylenediamine, 4-chloro-1,2-phenylenediamine, 4-nitro-1,2-phenylenediamine and $PdCl_2$ were purchased from Aldrich and Fluka. The solvents CH_3OH, CH_2Cl_2, and C_6H_6 were refluxed over calcium hydride under nitrogen, and checked for purity by GC just before use. Infrared spectra were measured in KBr pellets from 4000 ~ 600 cm^{-1} using a Perkin Elmer 1430 FT-IR spectrophotometer, and ^1H and ^{31}P nmr spectra were measured on a Bruker ARX 300 MHz instrument in CD_3CN. Chemical shifts for the complexes were measured relative to external standards TMS and 85% H_3PO_4. Elemental analyses were performed using a Perkin Elmer 240 analyzer, and electronic spectra were measured on a Shimadzu UV-256 spectrophotometer in CH_2Cl_2.

Synthesis of the New Complexes

The neutral complexes, $[PdCl_2(dppe)]$, $[PdCl_2(dppp)]$ and $[PdCl_2(dppb)]$ used as a starting materials [8-10] for synthesis of $[Pd(P\text{^}P)(N\text{^}N)](ClO_4)_2$ complexes and the homoleptic complexes, and $[Pd(dppe)_2](NO_3)_2$ and $[Pd(dppp)_2](NO_3)_2$ [11, 12] used in the ligand conproportionation reactions were prepared by modifying procedures described in the references.

Bis(diphenylphosphino)ethanediaminepalladium(II) perchlorate, $[Pd(dppe)(N^\wedge N)](ClO_4)_2$ (1)

$[Pd(dppe)(en)](ClO_4)_2$ (**1A**), $[Pd(dppe)(pn)](ClO_4)_2$ (**1B**), $[Pd(dppe)(bn)](ClO_4)_2$ (**1C**), $[Pd\text{-}(dppe)(4\text{-}Me\text{-}\phi n)](ClO_4)_2$ (**1D**), $[Pd(dppe)(\phi n)](ClO_4)_2$ (**1E**), $[Pd(dppe)(4\text{-}Cl\text{-}\phi n)](ClO_4)_2$ (**1F**) and $[Pd(dppe)(4\text{-}NO_2\text{-}\phi n)](ClO_4)_2$ (**1G**) were synthesized from a clear yellow solution of $[PdCl_2(dppe)]$ and appropriate diamine (N^N) according to the following typical procedure. $PdCl_2(dppe)$(0.5 mmol) was suspended in $CH_2Cl_2\text{-}CH_3OH$ (1:1), and then a benzene solution (15 cm^3) of $AgClO_4$ (1 mmol) was added. The resulting solution was stirred for 3 h at room temperature. After filtering off the AgCl precipitated, the corresponding diamine (N^N: 0.5 mmol) was added and the mixture stirred for another hour at room temperature. The solvent was removed under reduced pressure and concentrated to about 5 cm^3. Addition of diethylether to the solution gave a white precipitate. The precipitate was filtered, washed several times with ether, recrystallized from $CH_3CN\text{-}(C_2H_5)_2O$ and dried *in vacuo* for 12 h. **1A**. Yield: 60%. *Anal.* calcd.: C, 44.03; H, 4.22; N, 3.67%. Found: C, 44.27; H, 4.42; N, 3.53%. **1B**. Yield: 40%. *Anal.* calcd.: C, 44.78; H, 4.41; N, 3.60%. Found: C, 45.04; H, 4.73; N, 3.96%. **1C**. Yield: 35%. *Anal.* calcd.: C, 45.50; H, 4.58; N, 3.54%. Found: C, 45.19; H, 4.51; N, 3.53%. **1D**. Yield: 55%. *Anal.* calcd.: C, 48.06; H, 4.16; N, 3.40%. Found: C, 48.52; H, 4.57; N, 3.86%. **1E**. Yield: 60%. *Anal.* calcd.: C, 47.41; H, 3.98; N, 3.46%. Found: C, 46.94; H, 4.08; N, 3.24%. **1F**. Yield: 45%. *Anal.* calcd.: C, 45.50; H, 3.70; N, 3.32%. Found: C, 45.19; H, 3.87; N, 3.41%. **1G**. Yield: 30%. *Anal.* calcd.: C, 44.91; H, 3.65; N, 4.91%. Found: C, 43.58; H, 3.58; N, 4.74%.

Bis(diphenylphosphino)propanediaminepalladium(II) perchlorate, $[Pd(dppp)(N^\wedge N)](ClO_4)_2$ (2)

$[Pd(dppp)(en)](ClO_4)_2$ (**2A**), $[Pd(dppp)(pn)](ClO_4)_2$ (**2B**), $[Pd(dppp)(bn)](ClO_4)_2$ (**2C**), $[Pd(dppp)(4\text{-}Me\text{-}\phi n)](ClO_4)_2$ (**2D**), $[Pd(dppp)(\phi n)](ClO_4)_2$ (**2E**), $[Pd(dppp)(4\text{-}Cl\text{-}\phi n)](ClO_4)_2$ (**2F**) and $[Pd(dppp)(4\text{-}NO_2\text{-}\phi n)](ClO_4)_2$ (**2G**) were synthesized from the reaction of $[Pd\text{-}Cl_2(dppp)]$ and diamine (N^N) using the same procedure as for $[Pd(dppe)(N^\wedge N)](ClO_4)_2$ except for use of higher temperature. The precipitates obtained gave satisfactory analyses. **2A**. Yield: 80%. *Anal.* calcd.: C, 44.78; H, 4.41; N, 3.60%. Found: C, 45.01; H, 4.40; N, 3.55%. **2B**. Yield: 78%. *Anal.* calcd.: C, 45.50; H, 4.75; N, 3.54%. Found: C, 45.90; H, 4.54; N, 3.63%. **2C**. Yield: 80%. *Anal.* calcd.: C, 46.20; H, 4.75; N, 3.48%. Found: C, 46.52; H, 4.71; N, 3.60%. **2D**. Yield: 65%. *Anal.* calcd.: C, 48.69; H, 4.33; N, 3.34%. Found: C, 48.55; H, 4.52; N, 3.01%. **2E**. Yield: 70%. *Anal.* calcd.: C, 48.06; H, 4.16; N, 3.40%. Found: C, 48.38; H, 4.38; N, 3.18%. **2F**. Yield: 67%. *Anal.* calcd.: C, 46.15; H, 3.88; N, 3.26%. Found: C, 45.97; H, 4.26; N, 3.64%. **2G**. Yield: 50%. *Anal.* calcd.: C, 45.57; H, 3.83; N, 4.83%. Found: C, 45.57; H, 4.14; N, 4.46%.

Bis(diphenylphosphino)butanediaminepalladium(II) perchlorate, [Pd(dppb)(N^N)]$(ClO_4)_2$ (3)

[Pd(dppb)(en)]$(ClO_4)_2$ (**3A**), [Pd(dppb)(pn)]$(ClO_4)_2$ (**3B**), [Pd(dppb)(bn)]$(ClO_4)_2$ (**3C**), [Pd-(dppb)(4-Me-ϕn)]$(ClO_4)_2$ (**3D**), [Pd(dppb)(ϕn)]$(ClO_4)_2$ (**3E**) and [Pd(dppb)(4-Cl-ϕn)]$(ClO_4)_2$ (**3F**) were synthesized from the reaction of [$PdCl_2$(dppb)] with the corresponding diamine (en, pn, bn, 4-Me-ϕn, ϕn, 4-Cl-ϕn, and 4-NO_2-ϕn) according the procedures used for [Pd(dppe)(N^N)]$(ClO_4)_2$ and [Pd(dppp)(N^N)]$(ClO_4)_2$. The yields were very low. **3A**. Yield: 25%. *Anal.* calcd.: C, 45.50; H, 4.58; N, 3.54%. Found: C, 45.72; H, 4.40; N, 3.5%. **3B**. Yield: 23%. *Anal.* calcd.: C, 46.20; H, 4.75; N, 3.48%. Found: C, 46.60; H, 4.73; N, 3.54%. **3C**. Yield: 23%. *Anal.* calcd.: C, 46.87; H, 4.92; N, 3.42%. Found: C, 47.10; H, 5.12; N, 3.50%. **3D**. Yield: 50%. *Anal.* calcd.: C, 49.29; H, 4.49; N, 3.29%. Found: C, 49.18; H, 4.50; N, 3.31%. **3E**. Yield: 65%. *Anal.* calcd.: C, 48.69; H, 4.33; N, 3.34%. Found: C, 49.07; H, 4.53; N, 3.68%. **3F**. Yield: 47%. *Anal.* calcd.: C, 46.79; H, 4.05; N, 3.21%. Found: C, 47.39; H, 4.32; N, 3.18%.

The synthesis were performed under nitrogen using conventional Schlenk techniques, although the white solid products were found to be air stable.

Electrochemical Properties of Complexes

Voltammetric measurements were carried out using an EG & G PAR 175 universal programmer equipped with PAR RE0091 X-Y recorder. The working and counter electrodes were glassy carbon and platinum wire, respectively. All potentials were measured and reported *vs* SCE as reference electrode, which was separated from the bulk solution by a fritted glass junction. Tetrabutylammoninumborate (TBAB) as supporting electrolyte was used for all electrochemical experiments. These were conducted with TBAB at 0.1 mol dm^{-3} and $[Pd(P^\wedge P)_2]^{2+}$ and $[Pd(P^\wedge P)(N^\wedge N)]^{2+}$ at 8×10^{-4} mol dm^{-3}. Ligand conproportionation reactions were observed in solutions containing ethylenediamine (or 4-Me-ϕn) and $[Pd(dppe)_2]^{2+}$ (or $[Pd(dppp)_2]^{2+}$) using cyclovoltammetry.

RESULTS AND DISCUSSION

The syntheses can be summarized as follows

$$K_2PdCl_4 + P\text{^}P \xrightarrow[\text{HCl }(H_2O)]{n\text{-PrOH}} PdCl_2(P\text{^}P) + 2KCl \qquad (1)$$

$$PdCl_2(P\text{^}P) + 2AgClO_4 \rightarrow CH_2Cl_2{+}CH_3OH(1{:}1)\ [Pd(P\text{^}P)(HOMe)_2](ClO_4)_2 + 2AgCl \qquad (2)$$

$$[Pd(P\text{^}P)(HOMe)_2](ClO_4)_2 + N\text{^}N \rightarrow [Pd(P\text{^}P)(N\text{^}N)](ClO_4)_2 \qquad (3)$$

$PdCl_2(P\text{^}P)$ complexes were prepared by adding diphosphine (P^P) to a suspension of K_2PdCl_4 in *n*-propanol. Conventionally, $PdCl_2(P\text{^}P)$ complexes have been synthesized by reaction of anhydrous palladium(II) chloride or dichlorocyclooctadienepalladium(II) complexes with diphosphine ligands. However, the synthetic route described in (*1*) [10a] gave good yields (approximately 90 ~ 94%) by comparison with the two other methods mentioned above. The mixed-ligand complexes $[Pd(P\text{^}P)(N\text{^}N)](ClO_4)_2$ were obtained by adding the appropriate amount of diamine to a solution of $PdCl_2(P\text{^}P)$ and two equivalents of $AgClO_4$. All new complexes were characterized by IR, ^1H nmr, ^{31}P nmr, electronic spectra, redox potentials and elemental analysis. The results of the new palladium(II) complexes were already described in experimental part, and IR, electronic spectra, ^1H nmr, ^{31}P nmr and electrochemical data are collected in Tables I to VI, respectively.

IR and Electronic Spectra

As shown in Table I, IR spectra of all the new complexes showed a very strong and relatively broad absorption at about 1,095 cm^{-1} and a medium intensity band at 623 cm^{-1} assignable to the perchlorate ion. [13] These results show that the synthesized complexes are cationic species. Other absorption bands at 3000 ~ 3200, 1600 and 1437 cm^{-1} are assignable to N-H and P-Ph stretching vibrations, respectively, reflecting that amine and phosphine ligands are contained in the complexes, although formation of these mixed-ligand complexes might more clearly be identified by ^1H and ^{31}P nmr spectra.

Square planar d^8 metal complexes in which the ligands have π-orbital give three *d-d* transition bands ($A_{1g} \rightarrow A_{2g}$, $A_{1g} \rightarrow B_{1g}$ and $A_{1g} \rightarrow E_g$) and three charge transfer bands ($A_{1g} \rightarrow B_{1u}$, $A_{1g} \rightarrow A_{1u}$ and $A_{1g} \rightarrow E_{1a}$) [14]. The *d-d* transitions generally appear in the range 600 ~ 400nm [15]. The spectra of the new complexes as reported in Table II showed the three absorption bands between

TABLE I IR data (cm^{-1}) for heteroleptic dicationic palladium(II) complexes [Pd(P^P)(N^N)](ClO$_4$)$_2$

Complex	$\nu(ClO_4^{-1})$	$\nu(P\text{-}\phi)$	$\nu(NH_2)$
1a	1088(s,br) 623(m)	1437(m)	3284(m,br) 3243(m,br) 1588(m,br)
1b	1088(s,br) 623(m)	1437(m)	3284(m,br) 3243(m,br) 1588(m,br)
1c	1090(s,br) 623(m)	1437(m)	3283(m,br) 3266(m,br) 1607(m,br)
1d	1096(s,br) 623(m)	1437(m)	3223(m,br) 1574(m,br)
1e	1099(s,br) 621(m)	1437(m)	3217(m,br) 1572(m,br)
1f	1101(s,br) 621(m)	1437(m)	3200(m,br) 1566(m,br)
1g	1101(s,br) 623(m)	1437(m)	3185(m,br) 1564(m,br)
2a	1090(s,br) 623(m)	1437(m)	3285(m,br) 3235(m,br) 1586(m,br)
2b	1090(s,br) 623(m)	1437(m)	3316(m,br) 3246(m,br) 1588(m,br)
2c	1099(s,br) 623(m)	1437(m)	3326(m,br) 3256(m,br) 1586(m,br)
2d	1099(s,br) 623(m)	1437(m)	3262(m,br) 1559(m,br)
2e	1090(s,br) 621(m)	1437(m)	3257(m,br) 1559(m,br)
2f	1086(s,br) 621(m)	1437(m)	3237(m,br) 1551(m,br)
2g	1099(s,br) 623(m)	1437(m)	3200(m,br) 1528(m,br)
3a	1098(s,br) 623(m)	1437(m)	3316(m,br) 3239(m,br) 1588(m,br)
3b	1088(s,br) 623(m)	1437(m)	3316(m,br) 3239(m,br) 1598(m,br)
3c	1092(s,br) 625(m)	1437(m)	3316(m,br) 3254(m,br) 1609(m,br)
3d	1103(s,br) 621(m)	1437(m)	3212(m,br) 1569(m,br)
3e	1096(s,br) 623(m)	1437(m)	3291(m,br) 3202(m,br) 1568(m,br)
3f	1098(s,br) 623(m)	1437(m)	3295(m,br) 3191(m,br) 1564(m,br)

TABLE II Electronic spectra features of the dicationic palladium(II) complexes [Pd-(P^P)(N^N)]$(ClO_4)_2$ in CH_2Cl_2.

Complex	λ_{max}, *nm* (ϵ, M^{-1} cm^{-1})		
1d			464(615)
1f	545(1220)	508(820)	
1g	541(90)	503(84)	
2d	546(71)	509(90)	
2e	542(5)	502(4)	
2f	547(226)	506(167)	
2g	543(22)	502(22)	
3d			484(148)
3e	542(240)	501(190)	468(169)
3f	547(990)	505(1220)	485(1260)

TABLE III ^1H nmr data (ppm) for [Pd(P^P)(N^N)] $(ClO_4)_2$ containing aliphatic diamines in CD_3CN.

Complex	*P^P*		*N^N*	
	phenyl	*-CH$_2$-*	*-NH$_2$-*	*-CH$_2$-*
1a	7.77	2.84	3.87	2.99
		2.72		
1b	7.78	2.89	3.36	2.92
		2.77		1.95
1c	7.80	2.95	3.47	2.40
		2.80		1.77
2a	7.62	2.86	3.30	2.84
		2.17		
2b	7.65	2.84	3.25	2.74
		2.15		1.84
2c	7.69	2.94	3.09	2.14
		2.14		1.81
3a	7.69	2.90	3.35	2.72
		2.02		
3b	7.74	2.74	2.98	2.68
		1.95		1.82
3c	7.79	2.82	3.05	2.02
		1.85		1.67

464 and 547 nm. Values of molar absorptivities (10 ~ 1000 M^{-1} cm^{-1}) are indicative of *d-d* transitions. The first (540 ~ 548 nm) and second peaks (501 ~ 509 nm) are probably due to $A_{1g} \rightarrow A_{2g}$ and $A_{1g} \rightarrow B_{1g}$, respectively. The other peaks (464 ~ 486 nm) are assignable to $A_{1g} \rightarrow E_g$. The difference can be explained by considering Pd → phosphorus backbonding. The *d-d* transition of

TABLE IV ^1H nmr data (ppm) for $[Pd(P^\wedge P)(N^\wedge N)](ClO_4)_2$ containing aromatic diamines in CD_3CN.

Complex	*P^P*		*N^N*		
	Phenyl	*-CH$_2$-*	*Phenyl*	*-NH$_2$-*	*-CH$_3$-*
1d	7.83	2.83	7.12	5.43	2.29
	7.64	2.75	7.10		
			7.03		
1e	7.80	2.84	7.27	5.52	
	7.64	2.76	7.25		
1f	7.82	2.85	7.25	5.44	
	7.66	2.77	7.23		
			7.18		
1g	7.79	2.93	6.80	4.70	
	7.65	2.84	6.77		
2d	7.66	2.82	7.02	4.92	2.26
	7.52	2.16	7.02		
			6.84		
2e	7.66	2.85	7.22	4.50	
	7.50	2.16	7.06		
2f	7.64	2.82	7.03	4.86	
	7.50	2.14	7.00		
			6.97		
2g	7.66	2.82	6.80	4.58	
	7.50	2.15	6.77		
3d	7.72	2.71	7.03	4.89	2.24
	7.62	2.18	6.93		
			6.83		
3e	7.72	2.72	7.22	4.94	
	7.62	2.15	7.05		
3f	7.71	2.72	7.23	4.89	
	7.60	2.13	7.07		
			7.03		

Pd(II)-dppp system, having stronger π-backbonding than Pd(II)-dppe (or Pd(II)-dppb), would appear at lower energy.

^{1}H and ^{31}P nmr Spectra

The basic ^1H nmr features for the complexes are listed in Tables III and IV. ^1H nmr spectra for each complex were very similar. For example, the spectrum of **1a** showed a multiplet due to phenyl groups at 7.77 ppm, a singlet due to amide protons at 3.87 ppm, a singlet due to ethylene protons of diamine at 2.99 ppm and medium peaks due to the ethylene protons of the diphosphine at 2.84 and 2.72 ppm. Similar patterns were observed for **2A** and **3A**. However, the chemical shift of amine protons of Pd(II)-dppp or -dppb systems appear at higher field than

TABLE V ^{31}P nmr data[a] for the dicationic palladium(II) complexes $[Pd(P^\wedge P)(N^\wedge N)](ClO_4)_2$ in CD_3CN.

Complex	*^{31}P (ppm)*	*$\Delta\delta_p$ (ppm)*	*Complex*	*^{31}P (ppm)*	*$\Delta\delta_p$ (ppm)*
1a	64.35	0.00	**2d**	8.30	0.12
1b	66.13	1.78	**2e**	8.18	0.00
1c	66.99	2.64	**2f**	8.52	0.34
1d	65.64	3.78	**2g**	12.04	3.86
1e	61.86	0.00	**3a**	26.69	0.00
1f	62.70	0.84	**3b**	30.85	4.16
1g	75.03	3.17	**3c**	30.39	4.70
2a	7.95	0.00	**3d**	27.68	3.08
2b	11.45	3.50	**3e**	24.60	0.00
2c	10.24	2.19	**3f**	29.26	4.66

[a] At 121.5 MHz; chemical shifts are in ppm relative to external 80% H_3PO_4.

TABLE VI Redox Potentials (V *vs* SCE) of the dicationic Pd(II) complexes $[Pd(P^\wedge P)(N^\wedge N)]^{2+}$.

Complex	$M(II) \xrightarrow[(E_p)_{red}]{2e^-} M(O)$	*Complex*	$M(II) \xrightarrow[(E_p)_{red}]{2e^-} M(O)$
1a	−1.12V	**2d**	−0.90V
1b	−1.11V	**2e**	−0.88V
1c	−1.11V	**2f**	−0.88V
1e	−0.90V	**2g**	−0.90V
1f	−0.90V	**3a**	−1.09V
1g	−0.95V	**3b**	−1.10V
2a	−1.13V	**3d**	−0.93V
2b	−1.12V	**3e**	−0.92V
2c	−1.13V	**3f**	−0.91V

Peak potential recorded with a glassy-carbon electrode in acetonitrile solution containing $[Pd(P^\wedge P)(N^\wedge N)]^{2+}$ and TEAP (0.01M); scan rate 0.1 Vs^{-1}.

Pd(II)-dppe (Table III). The difference could be explained by considering the bite angle of the diphosphine (∠ P-Pd-P: 85.8° for $[PdCl_2(dppe)]$ 90.6° for $[PdCl_2(dppp)]$, 91° for $[PdCl_2(dppb)]$) [16] affecting electron density on the amine groups. ^1H nmr spectra of complexes containing aromatic diamines also showed the same pattern. However, there was a difference of chemical shift between **1A** and **1E**. The diamine protons appear at 3.87 ppm for the aliphatic and at 5.52 ppm for the aromatic diamine. The difference is believed to be due to the electron withdrawing nature of the phenyl group in the latter case.

As shown in Table V, ^{31}P nmr spectra of the complexes displayed only a singlet, indicating that all have similar structures. ^{31}P nmr shifts of $[Pd(P^\wedge P)(N^\wedge N)]^{2+}$ are considerably different depending on the diphosphine ligands but the contribution of diamines to the chemical shift is quite small.

The ^{31}P nmr shift of dppp complexes appear at higher field than those of dppe or dppb; the shift increased in the order dppp (8 ~ 12 ppm) < dppb (27 ~ 30 ppm) < dppe (64 ~ 75 ppm) and thus **2** containing dppp showed the smallest chemical shift regardless of diamine ligands. The angles $\angle$P-M-P are 85° for $[Pd(NCS)\text{-}(dppe)(SCN)]$, 85.8° for $PdCl_2(dppe)$, 89° for $[Pd(NCS)_2(dppp)]$ and 90.6° for $PdCl_2(dppp)$ [16, 17]. From these data, dppp is quantitatively predicted to have the smallest ring strain, and to form π back bonding most conveniently with Pd(II). Even so, the ligand chemical shift (or i.r. parameters) can not be used to clearly resolve the σ and π controversy [18, 19]. The effect of diamine on ^{31}P shift was not large, but clearly appeared. The differences ($\Delta\delta_p = \delta_{p(N^\wedge N)} - \delta_{p(en)}$) between the chemical shift ($\delta_{p(N^\wedge N)}$) of $[Pd(P^\wedge P)(N^\wedge N)](ClO_4)_2$ and that of $[Pd(P^\wedge P)(en)](ClO_4)_2$ as reference are listed in Table V. ^{31}P nmr spectra of **1** shifted generally to the low field with the chelate ring number of diamine. Such a change of chemical shift could be attributable to ring strain effects of the diamine affecting in form the Lewis acidity of diphosphine backbonding with Pd. These observation indicate that the structures of palladium(II) complexes are all square planar irrespective of diphosphine or diamine.

Electrochemical Behaviour of the Complexes

Redox potential is often used to evaluate the electronic nature of M-L bonds. [21] In general, the reduction potential for a given metal complex shifts to a more positive values due to decreased electron density at the metal center if the ligand is a good π acceptor or weak σ donor. However, it has not been clarified that the potential is a measure of the integrated electron density around metal [19]. Cyclic voltammograms of **1A**, **2A** and **3A** are illustrated in Figure 1, from which it is apparent that these complexes have a two electron, irreversible wave corresponding to (*4*). The separations of peak potentials were equal to about 100 mV.

$$[Pd(P^\wedge P)(N^\wedge N)]^{2+} + 2e \rightarrow [Pd(P^\wedge P)(N^\wedge N)] \qquad (4)$$

Reduction potentials of $[Pd(P^\wedge P)(N^\wedge N)]^{2+}$ appear in the range −0.878 ~ −0.947 V for aromatic diamines and −1.09 ~ −1.13 V for aliphatic diamines.. The aromatic diamine decreases electrons at the metal when compared to aliphatic diamines. However, in general the peak potentials and the anodic-cathodic currents were almost unaffected by the diphosphines and diamines. These results infer that diffusion coefficients of $[Pd(P^\wedge P)(N^\wedge N)]^{2+}$ do not differ appreciably.

1A, **1D** and **2A** attempted to be synthesized from the reaction of the homoleptic complexes $[Pd(dppe)_2]^{2+}$ (or $[Pd(dppp)_2]^{2+}$) with en (or 4-Me-ϕn) as in (*5*) and (*6*).

$$[Pd(P^\wedge P)_2]^{2+} + en \rightarrow [Pd(P^\wedge P)(en)]^{2+} + P^\wedge P \qquad (5)$$

$$[Pd(P^\wedge P)_2]^{2+} + 4\text{-Me-}\phi n \rightarrow [Pd(P^\wedge P)(4\text{-Me-}\phi n)]^{2+} + P^\wedge P \qquad (6)$$

$[Pd(dppe)_2]^{2+}$ in acetonitrile exhibits cyclic voltammetric behaviour characterized by a two electron, one step, reversible reduction wave as shown in Figure 2a [22]. The addition of equimolar amounts of en to $[Pd(dppe)_2]^{2+}$ solutions resulted in a significant change of voltammetric trace leading to the pattern in Figure 2b, which was identical to that (Figure 1a) displayed by a solution of **1A** independently prepared, except for the waves I-II. These waves are identical to the pattern of Figure 2a exhibited by the solution of $[Pd(dppe)_2]^{2+}$. This indicates that the homoleptic complex $[Pd(dppe)_2]^{2+}$ might be regenerated at a scan rate of

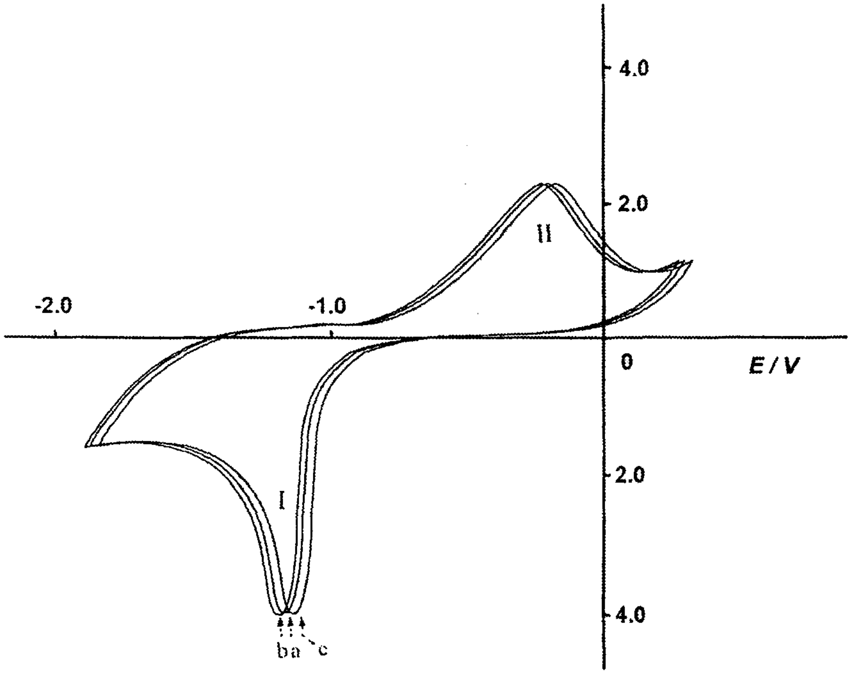

FIGURE 1 Voltammograms recorded with a glassy-carbon electrode for 0.1 mol dm^{-3} $[NBu_4][BF_4]$-acetonitrile solutions containing $[Pd(dppe)(en)]^{2+}$ (a), $[Pd(dppp)(en)]^{2+}$ (b) and $[Pd(dppb)(en)]^{2+}$ (c) complexes (8.0×10^{-4} mol dm^{-3}), respectively. at a scan rate of 0.1 Vs^{-1}.

0.1 Vs^{-1}. Cyclic voltammetric behaviour of $[Pd(dppp)_2]^{2+}$ in acetonitrile prior to and after the addition of en are illustrated in Figure 3. The redox wave after the addition of en (Figure 3b) is identical to that observed for independently prepared **2A** (Figure 1b). Here we conclude that the addition of en to $[Pd(dppe)_2]^{2+}$ or $[Pd(dppp)_2]^{2+}$ leads to the formation of **1A** (or **2A**). However, no chemical reaction following the electroreduction of **2A** could be found. These ligand conproportionations were relatively slow, requiring about 10 h to go to

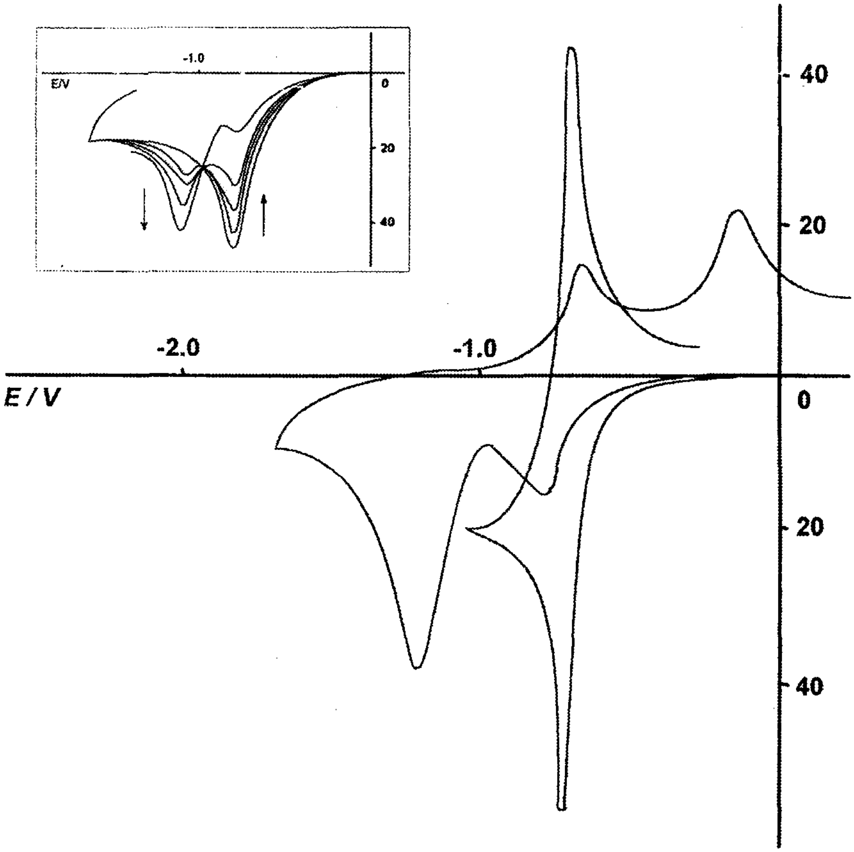

FIGURE 2 Cyclic voltammograms recorded with a glassy-carbon electrode for 0.1 mol dm^{-3} $[NBu_4][ClO_4]$-acetonitrile solutions containing (a) $[Pd(dppe)_2]^{2+}$ (8.0×10^{-4} mol dm^{-3}) and (b) $[Pd(dppe)_2]^{2+}$ (8.0×10^{-4} mol dm^{-3}) after addition of equimolar ethylenediamine and equilibration, at a scan rate of 0.1 Vs^{-1}; (a) $[Pd(dppe)_2]^{2+} + 2e^- \rightarrow [Pd(dppe)_2]$: two electron, one step; (b) $[Pd(dppe)(en)]^{2+} + 2e^- \rightarrow [Pd(dppe)(en)]$: two electron, one step. Inset are typical CV changes with respect to time in solutions containing $[Pd(dppe)_2]^{2+}$ and ethylenediamine.

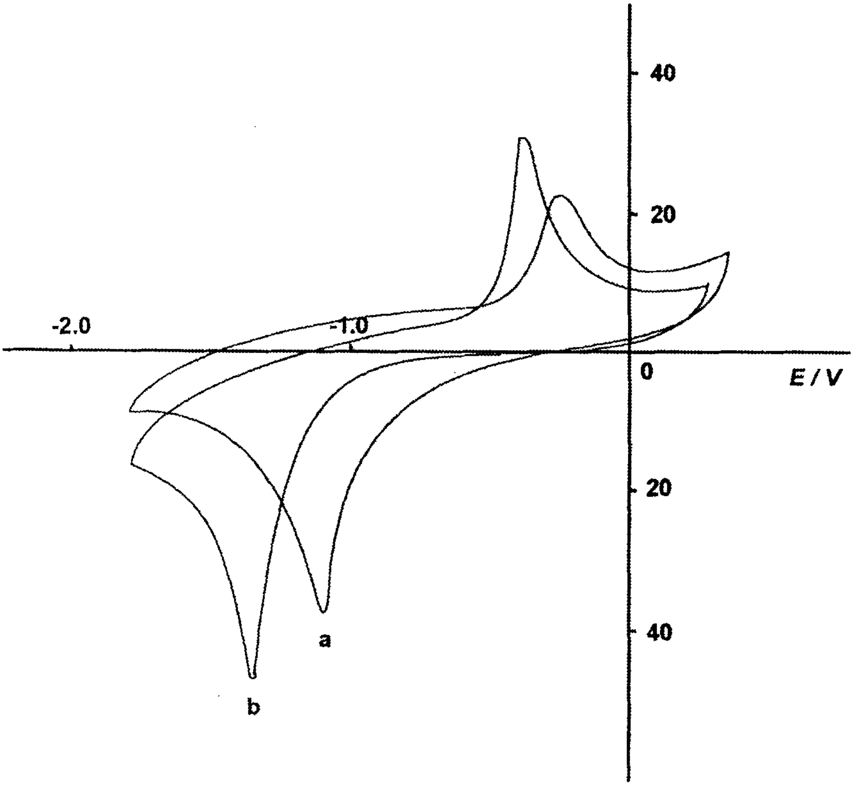

FIGURE 3 Cyclic voltammograms recorded with a glassy-carbon electrode for 0.1 mol dm^{-3} $[NBu_4][ClO_4]$-acetonitrile solutions containing (a) $[Pd(dppp)_2]^{2+}$ (8.0×10^{-4} mol dm^{-3}) and (b) $[Pd(dppp)_2]^{2+}$ (8.0×10^{-4} mol dm^{-3}) after addition of equimolar propylenediamine and equilibration, at a scan rate of 0.1 Vs^{-1}; (a) $[Pd(dppp)_2]^{2+} + 2e^- \rightarrow [Pd(dppp)_2]$: two electron, one step; (b) $[Pd(dppp)(en)]^{2+} + 2e^- \rightarrow [Pd(dppp)(en)]$: two electron, one step.

completion. The heteroleptic complexes $[Pd(P^\wedge P)(en)]^{2+}$ obtained from the homoleptic complexes $[Pd(P^\wedge P)]^{2+}$ were stable even in solutions containing large amounts of en, *i.e.*, no chemical reaction of $[Pd(P^\wedge P)(en)]^{2+}$ was observed.

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