Heteroatom Chemistry
Volume 19, Number 2, 2008

Synthesis and Characterization of Bis(diphenylphosphinomethyl)amino Ligands and Their Ni(II), Pd(II) Complexes: Application to Hydrogenation of Styrene

Mustafa Keleş, Orhan Altan, and Osman Serindağ

Department of Chemistry, Faculty of Science and Literature, University of Çukurova, 01330 Adana, Turkey

Received 30 March 2006; revised 21 March 2007

ABSTRACT: *Transition metal complexes of Ni(II) and Pd(II) with ditertiary bis(diphenylphosphinomethyl)amino ligands, $(Ph_2PCH_2)_2NC(CH_3)_3$ (**1**) and $[(Ph_2PCH_2)Nm\text{-}PhSO_3]Na$ (**2**) (Ph = phenyl), have been synthesized in good yields under nitrogen atmosphere by Schlenk technique. All complexes have been characterized using elemental analyses and spectroscopic techniques such as atomic absorption, FT-IR, and NMR (^1H, ^{31}P). Atomic absorption spectroscopic analysis showed that the reactions of ligands **1** and **2** with $NiCl_2{\cdot}6H_2O$ and $[PdCl_2(COD)]$ occurred in 1:1 molar ratio. The metal complexes $[NiCl_2(Ph_2PCH_2)_2Nm\text{-}PhSO_3Na]$ (**4**) and $[PdCl_2(Ph_2PCH_2)_2Nm\text{-}PhSO_3Na]$ (**6**) were found to be soluble in ethanolic and aqueous solutions, as well as slightly soluble in water. Electrochemical behaviors of complexes were investigated by cyclic voltammetry. Catalytic effects of Pd(II) complexes were tested throughout the hydrogenation of styrene to ethylbenzene.* Heteroatom Chem 19:113–118, 2008; DOI 10.1002/hc.20384

INTRODUCTION

Phosphine ligands and their transition metal complexes have been synthesized because of their various catalytic effects, which introduce in them the most important part of the catalytic systems [1,2]. To recover the catalysts, aqueous biphasic systems have been used since last decade. The catalyst recovery can be solved by biphasic system [3], as one phase contains the dissolved metal complexes and the other products. The importance of water-soluble phosphines is arising day-after-day. Efficient water-soluble ligands can be obtained by linking it to an appropriate hydrophilic group [3,4]. This group may be cationic (e.g., $-[NMe_3]^+$, $-[PMe_3]^+$), anionic (e.g., $-[CO_2]^-$, $-[SO_3]^-$, $-[PO_3]^{2-}$), or nonionic in nature (e.g., $-(OCH_2CH_2)_n$, $-OMe$) [4].

The aim of this study was to synthesize some bis(diphenylphosphinomethyl)amino and sulphonated bis(diphenylphosphinomethyl)amino ligands and their metal complexes of Ni(II) and Pd(II). Although *t*-butyl-substituted aminomethyl phosphine used in this study has been reported previously, the synthetic route was slightly different [5,6]. The compounds have been characterized using various spectroscopic techniques. Electrochemical behaviors of all complexes and catalytic effects of the Pd(II) complexes have also been investigated.

Correspondence to: Osman Serindağ; e-mail: osmanser@cu.edu.tr.

Contract grant sponsor: Research Fund of Çukurova University.
Contract grant number: FBE.2000.YL.40.

EXPERIMENTAL

General

All reactions were carried out under nitrogen atmosphere using conventional Schlenk glassware. Methyl alcohol, ethyl alcohol, dichloromethane, tetrahydrofuran (THF), and diethyl ether were used as solvents, which were dried using established procedures and then immediately distilled under nitrogen atmosphere before use. Tetrabutylammonium perchlorate (TBAP) was purchased from Fluka and $[PdCI_2(COD)]$ complex was prepared as described in literature [7].

The metal contents of the complexes were determined using a Hitachi 180-80 Polarized Zeiman atomic absorption spectrometer. Elemental analyses were performed using a LECO CHNS 932 analyzer. FT-IR spectra were recorded as KBr pellets in a 4000–450 cm^{-1} range using a Perkin-Elmer RX1 FT-IR system. ^{1}H and ^{31}P NMR spectra were recorded at 25°C in DMSO-d^6 and $CDCl_3$ using Varian Mercury 200 MHz NMR spectrometer. ^{31}P NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H_3PO_4 as an external standard. The hydrogenated product was analyzed on a Shimadzu GC 14 A gas chromatograph using a 30 m × 0.25 mm ZB-5 column.

A conventional three-electrode electrochemical cell setup using a CHI 660B electrochemical analyzer was used to investigate the electrochemical behaviors of complexes. A platinum electrode was used as the working electrode, an Ag/AgCl electrode was utilized as the reference electrode, and a platinum wire was used as the counter electrode, respectively. Electrochemical tests were conducted in THF, and 0.1 M TBAP was used as the supporting electrolyte.

Synthesis of Bis(diphenylphosphinomethyl)amino Ligands and Metal Complexes

$[(Ph_2PCH_2)_2NC(CH_3)_3]$ (**1**)*:* Phosphonium salt ($[Ph_2P(CH_2OH)_2]CI$) (0.260 g, 0.92 mmol), which was prepared according to literature procedure [8], was dissolved in 2:1 H_2O/MeOH (15 mL). Triethylamine (Et_3N) (0.5 mL, 3.65 mmol) was added to a stirred solution of $[Ph_2P(CH_2OH)_2]CI$, followed by addition of *t*-butylamine (46 μL, 0.46 mmol). The mixture was refluxed for 1 h, and then the product was extracted with CH_2CI_2 and dried over $MgSO_4$. The solvent was removed under vacuum. Yield: 0.173 g (80%). Elemental analysis calculation for $[(Ph_2PCH_2)_2NC(CH_3)_3]$: C, 76.75%; H, 7.04%; N, 2.98%. Found: C, 77.14%; H, 7.15%; N, 3.07%. FT-IR (KBr): ν 3052 (m, Ar-H); 2985 (m, R-H); 1584 (m, C=C (Ph); 1476 (m, C—H); 1094 (m, C—N (*t*-amine)); 742–684 (m, monosubstitued P-Ph_2). ^{1}H NMR ($CDCI_3$, 25°C): δ 7.34–7.18 [m, 20 H, 4 Ph], 3.42 [br, 4 H, 2 (P-CH_2-N)], 1.21 [s, 9H, 2 (N-C-(CH_3)$_3$)] ppm. ^{31}P NMR ($CDCI_3$, 25°C): δ −27.2 [s, *P*Ph_2-CH_2] ppm.

$[(Ph_2PCH_2)_2NPhm\text{-}SO_3Na]$ (**2**)*:* Et_3N (0.8 mL, 5.84 mmol) was added to a stirred solution of $[Ph_2P(CH_2OH)_2]Cl$ (0.5 g, 1.77 mmol) in 2:1 H_2O/MeOH (15 mL) followed by addition of sodium 3-aminobenzenesulfonate (0.175 g, 0.9 mmol) dissolved in CH_2Cl_2, and then the mixture was refluxed for 2 h. The product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was removed under vacuum. Yield: 0.346 g (66%). Elemental analysis calculation for $[(Ph_2PCH_2)_2NPhSO_3Na]$: C, 64.97%; H, 4.74%; N, 2.37%. Found: C, 65.40%; H, 4.57%; N, 2.53%. FT-IR (KBr): ν 3040 (m, Ar-H); 2932 (m, R-H); 1574 (m, C=C (Ph); 1465 (m, C—H); 1126 (m, C-N (*t*-amine)); 1077 (m, S(O)); 810–747-686 (m, mono-and disubstituted Ar-H). ^{1}H NMR ($CDCI_3$, 25°C): δ 7.52–7.32 [m, 20H, 4P-*Ph*], δ 6.90 [m, 4H, N-*Ph*], 3.50 [br, 4H, P-CH_2-N] ppm. ^{31}P NMR ($CDCI_3$, 25°C): δ −26.36 [s, *P*Ph_2-CH_2] ppm.

$[NiCl_2(Ph_2PCH_2)_2NC(CH_3)_3]$(**3**)*:* Ligand **1** (0.103 g, 0.22 mmol) was added to a stirred solution of $NiCl_2{\cdot}6H_2O$ (0.052 g, 0.22 mmol) in ethanol (10 mL). An orange precipitated formed immediately and the mixture was stirred for 30 min. The orange product was filtered, washed with diethyl ether, and finally dried. Yield: 0.122 g (93%). Elemental analysis calculation for $[NiCl_2(Ph_2PCH_2)_2NC(CH_3)_3]$: C, 60.13%; H, 5.51%; N, 2.34%. Found: C, 59.89%; H, 5.80%; N, 2.45%. FT-IR (KBr): ν 3074 (m, Ar-H); 2870 (m, R-H); 1520 (m, C=C (Ph); 1478 (m, C—H); 1020 (m, C-N (*t*-amine)); 725–638 (m, monosubstitued Ar-H). ^{1}H NMR ($CDCI_3$, 25°C): δ 7.70–7.40 [m, 20H, 4Ph], 3.58 [d, 4H, P-CH_2-N], ^{2}J(HP) 3.35 Hz. 1.27 [s, 9H, N-C, –(CH_3)$_3$] ppm. ^{31}P NMR ($CDCI_3$, 25°C): δ 30.4 [br, Ni-*P*Ph_2] ppm.

$[NiCl_2(Ph_2PCH_2)_2N\text{-}m\text{-}PhSO_3Na]$ (**4**)*:* Ligand **2** (0.1 g, 0.169 mmol) was added to a stirred solution of $NiCl_2{\cdot}6H_2O$ (0.05 g, 0.21 mmol) in ethanol (10 mL). An orange precipitate formed immediately and the mixture was stirred for 30 min. The product was washed with diethyl ether and dried. Yield: 0.09 g (74%). Elemental analysis calculation for $[NiCl_2(Ph_2PCH_2)_2NPhSO_3Na]$: C, 53.28%; H, 3.89%; N, 1.94%. Found: C, 53.57%; H, 4.13%; N, 2.05%. FT-IR (KBr): ν 3069 (m, Ar-H); 2915 (m, R-H); 1523 (m, C=C (Ph); 1435 (m, C—H); 1085 (m, C-N (*t*-amine)); 1065 (m, S(O)); 790–675 (m, mono-, and disubstitued Ar-H). ^{1}H NMR ($CDCI_3$, 25°C): δ 7.63–7.38

[m, 20H, 4Ph], 6.8 [m, 4H, N-Ph], 3.61 [d, 4H, P-CH_2-N], ppm. ^2J(HP) 3.28 Hz. ^{31}P NMR ($CDCl_3$, 25°C): δ 26.6 [br, Ni-*P*Ph_2] ppm.

*[$PdCl_2((Ph_2PCH_2)_2NC(CH_3)_3)$] (**5**):* Ligand **1** (0.10 g, 0.213 mmol) was added to a stirred solution of [$PdCl_2$(COD)] (0.08 g, 0.21 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for a further 2 h at room temperature. Addition of diethyl ether gave the yellow solid, which was then filtered and dried. Yield: 0.12 g (88%). Elemental analysis calculation for [$PdCl_2((Ph_2PCH_2)_2NC(CH_3)_3)$]: C, 55.69%; H, 5.10%; N, 2.17%. Found: C, 55.89%; H, 5.40%; N, 2.31%. FT-IR (KBr): ν 3079 (m, Ar-H); 2910 (m, R-H); 1537 (m, C=C (Ph); 1481 (m, C—H); 1027 (m, C-N (*t*-amine)); 718–636 (m, monosubstitued Ar-H). ^{1}H NMR ($CDCl_3$, 25°C): δ 7.77–7.46 [m, 20H, 4Ph], 3.62 [d, 4H, P-CH_2-N], ^2J(HP) 2.12 Hz, 1.23 [s, 9H, N-C-(CH_3)$_3$] ppm. ^{31}P NMR ($CDCl_3$, 25°C): δ 7.4 [br, Pd-*P*Ph_2] ppm.

*[$PdCl_2(Ph_2PCH_2)_2Nm$-$PhSO_3Na$] (**6**):* Ligand **2** (0.11 g, 0.176 mmol) was added to a stirred solution of [$PdCl_2$(COD)] (0.06 g, 0.16 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for a further 2 h at room temperature. Addition of diethyl ether gave the yellow solid, which was then filtered off and dried. Yield: 0.10 g (81%). Elemental analysis calculation for [Pd(Ph_2PCH_2)$_2$NPh*m*-SO_3Na]Cl_2: C, 49.97%; H, 3.64%; N, 1.82%. Found: C, 50.6%; H, 3.85%; N, 2.02%. FT-IR (KBr): ν 3078 (m, Ar-H); 2926 (m, R-H); 1538 (m, C=C (Ph); 1433 (m, C—H); 1095 (m, C-N (*t*-amine)); 1013 (m, S(O)); 800–673 (m, mono-, and disubstitued Ar-H). ^{1}H NMR ($CDCl_3$, 25°C): δ 7.83–7.42 [m, 20H, 4Ph], 6.87 [m, 4H, N-Ph] 3.62 [d, 4H, P-CH_2-N] ppm, ^2J(HP) 2.18 Hz. ^{31}P NMR ($CDCl_3$, 25°C): δ 8.12 [br, Ni-*P*Ph_2] ppm.

Hydrogenation of Styrene

Hydrogenation reactions were carried out in a 50-mL stainless steel high-pressure reactor. A mixture of styrene/CH_2Cl_2 (15 mL) in 1:2 ratio and 0.1 mmol of complex **5** or **6** was added as catalyst under nitrogen atmosphere. Afterwards, the reactor was pressurized to 8 bars using hydrogen, and magnetically stirred for 1 h.

RESULTS AND DISCUSSION

Synthesis

Tertiary diphosphine ligands [$(Ph_2PCH_2)_2)_2NC(CH_3)_3$] and [$(Ph_2PCH_2)_2)_2$NPh*m*-$SO_3$Na] were synthesized according to the Mannich reaction by treating phosphonium salt with appropriate primary amine such as *t*-butyl amine or sodium 3-aminobenzenesulfonate (Scheme 1). The transition metal complexes of the bis(diphenylphosphinomethyl)-amino ligands were prepared by using the convenient metal sources as shown in Scheme 1.

The complexes **4** and **6** were found to be soluble in ethanolic and aqueous solutions, as well as slightly soluble in water, whereas **3** and **5** were insoluble in both ethanolic and aqueous solutions.

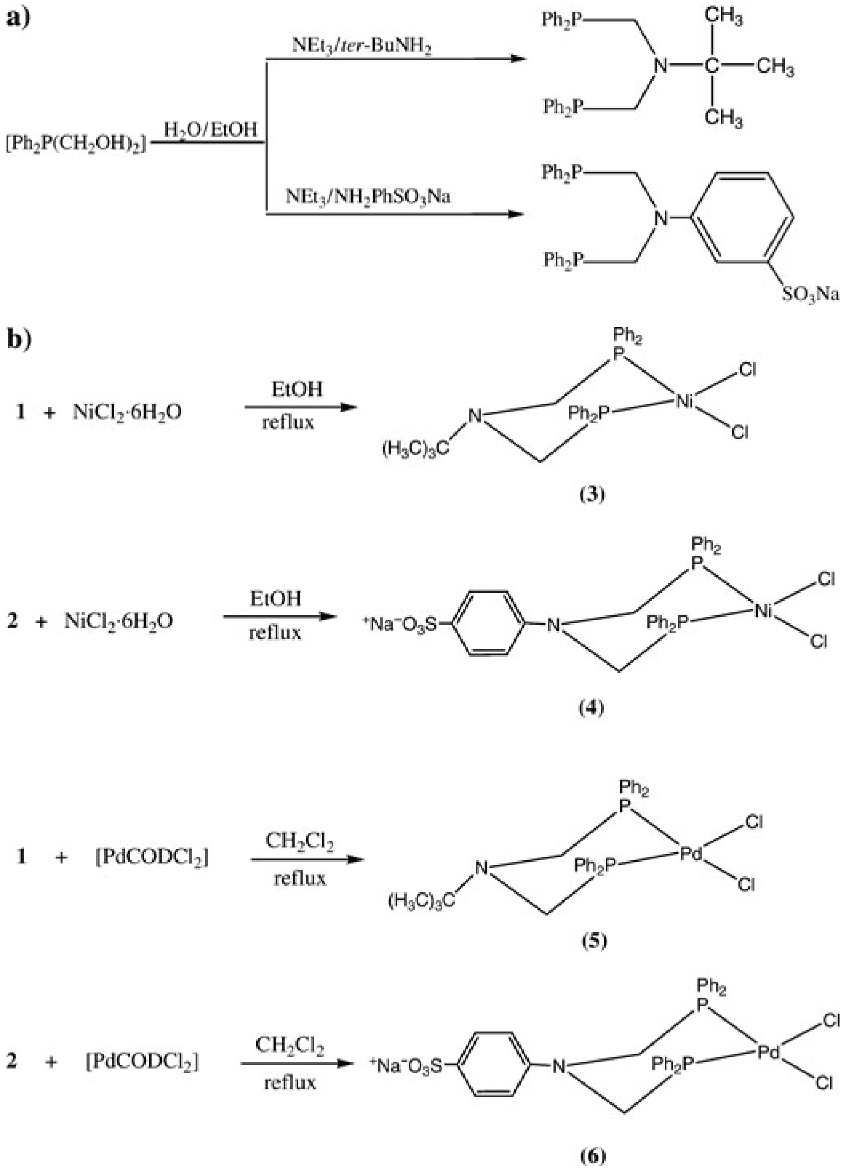
Characterization

Bis(diphenylphosphinomethyl)amino ligands and their metal complexes have been characterized using ^{1}H NMR, ^{31}P NMR, and FT-IR spectroscopic techniques, elemental analyses, and cyclic voltammetry technique.

Assignment of ^{1}H NMR spectra of ligands and metal complexes showed that the chemical shift value (δ) of the aromatic protons of the phenyl ring occurs in a range around 6.9–7.83 ppm. The peaks for P-CH_2-N protons of ligands and their Ni(II) and Pd(II) complexes were observed around 3.42–3.62 ppm, which are in agreement with the values reported in literature [9,10]. The two-bond phosphorus-hydrogen coupling constant values ^2J(HP) occur in the range of 2.12–3.35 Hz and are in agreement with the reported values [11–14]. As expected, the proton signals for N-C-CH_3 appeared around 1.25 ppm. Assignment of ^{1}H NMR spectra showed no remarkable differences between the free phosphine ligands and the metal complexes.

^{31}P NMR spectra of the complexes showed more shielded signals than the bis(diphenylphosphinomethyl)amino ligands, as shown in Table 1. The coordination shift values of the complexes (Δ), defined by $\Delta = \delta$ (complex) $- \delta$ (free ligand), vary depending on the metal centers and the ligand itself (Table 1). The values of Δ have been correlated with many metal phosphine complexes [9–15]. On the basis of ^{31}P NMR data for the geometry of metal complexes, it has been proposed that these complexes possess square planar geometry, as in those of reported studies [9,13].

Phosphines and their metal complexes were further characterized by FT-IR spectra. *t*-Amine bands of the ligand **1** and metal complexes **3** and **5** were found in the relatively lower energy region than for ligand **2** and its metal complexes on FT-IR spectra. C—H stretching bands of phenyl rings on phosphorus have been found around 3040–3078 cm^{-1}. In addition, the peaks around 747–636 cm^{-1} are assigned to monosubstituted phenyl rings on phosphorus (P-Ph), whereas the peaks in the range of 810–790 cm^{-1}



SCHEME 1 Synthesis of (a) bis(diphenylphosphinomethyl)amino ligands and (b) their Ni(II) and Pd(II) complexes.

are assigned to disubstituted phenyl rings of N-C_6H_4-SO_3 moiety of ligand **2** and its metal complexes **4** and **6**.

Elemental analyses of ligands and AAS for metal contents give the basic formulas of the complexes. AAS results also indicate that these complexes have a 1:1 metal to ligand ratio.

Electrochemical Behavior of Complexes

The electrochemical behavior of complexes (**3–6**) was studied by using cyclic voltammetry technique. The cyclic voltammograms of complexes are shown in Fig. 1 and their corresponding data are given in Table 2.

Cyclic voltammograms show that Ni(II)/Ni(0) and Pd(II)/Pd(0) redox potentials are shifted to a more negative value depending on the existence of

TABLE 1 ^{31}P NMR Data for Ligands and Metal Complexes[a]

Ligands and Complexes	δ_P *(ppm)*	$\Delta\delta$ *(ppm)*
1	−27.20 [s, *P*Ph$_2$-CH$_2$]	–
2	−26.36 [s, PPh$_2$-CH$_2$]	–
3	30.40 [s, Ni-PPh$_2$]	57.60
4	26.60 [s, Ni-PPh$_2$]	52.96
5	7.40 [s, Pd-*P*Ph$_2$]	34.60
6	8.12 [s, Pd-*P*Ph$_2$]	34.48

[a] ^{31}P Chemical shift, $\Delta = \delta$ (complex) $-$ δ (free ligand).

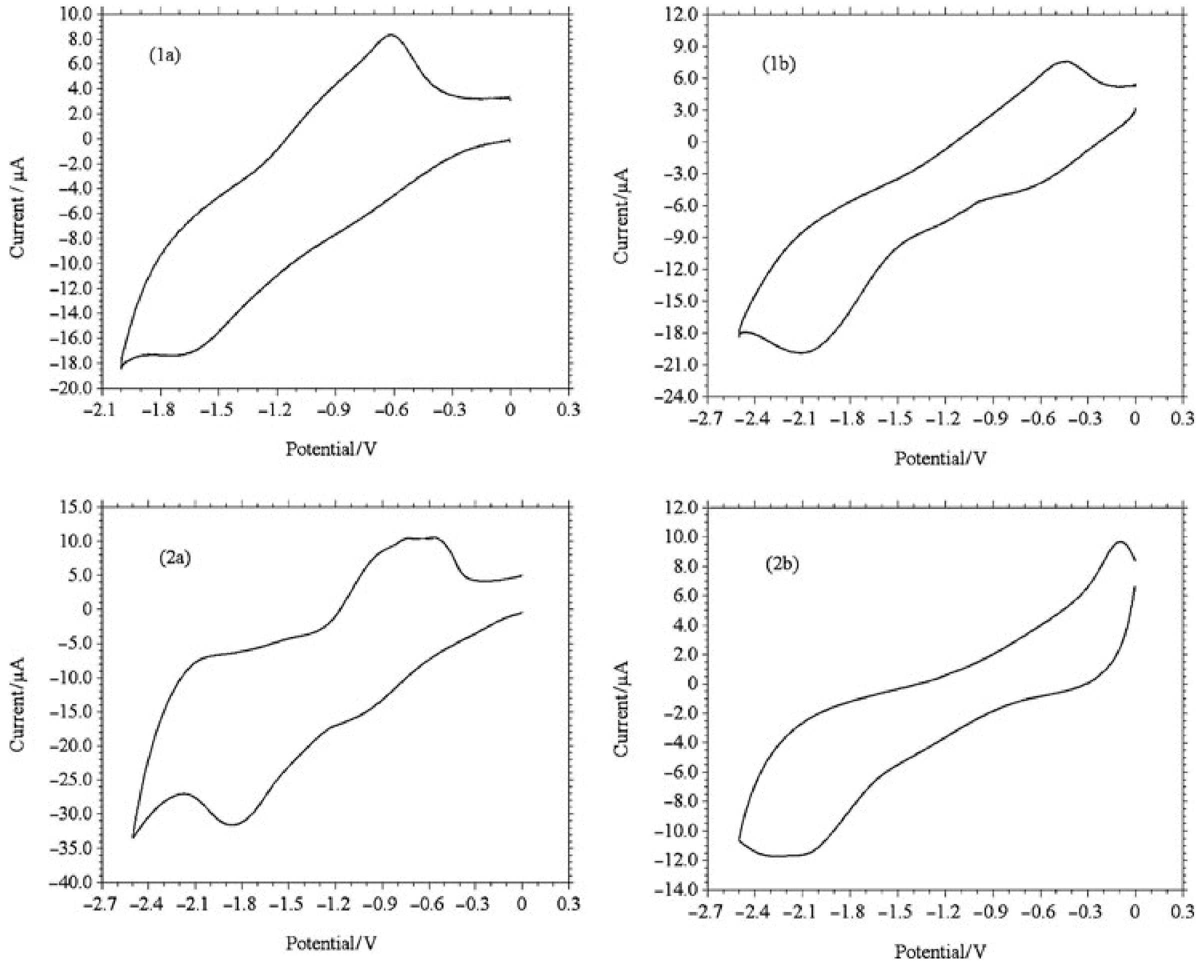


FIGURE 1 Cyclic voltammograms for complexes **3–6** (scan rate = 300 mVs^{-1}).

phosphine ligand as an electron-rich component. The magnitude of potentials of these complexes affects the π-acidity strength and influences the electrochemical behavior of the complexes.

As can be seen from Fig. 1, the cyclic voltammograms of the complexes have different peaks, which relate to different ligands. In each voltammogram, one irreversible reduction peak is observed. A large potential difference between reduction and oxidation peaks indicates that the redox process is quite non-Nernstian. The complexes of π-acceptor ligands such as phosphines may undergo two-electron reduction with the stabilization of Ni^0 and Pd^0 [16]. Peak potentials for metal complexes show that the nature of the R group on the bis(diphenylphosphinomethyl)amino ligands plays an important role in the potentials of the cathodic processes. Cyclic voltammograms of the complexes **4** and **6**, which possess aromatic groups, are reduced at a more cathodic potential than those for complexes **3** and **5**. These results are in agreement with the expected stronger electron-donor character of the sulphanilic group [17].

TABLE 2 Cyclic Voltammetric Data for Complexes [Ni(L)Cl$_2$] and [Pd(L)Cl$_2$]

Complexes	*E$_{pc}$ (V)*	*E$_{pa}$ (V)*	*E$_{1/2}$ (V)*
3	−1.68	−0.61	−1.15
4	−2.11	−0.43	−1.27
5	−1.86	−0.63	−1.25
6	−1.98	−0.20	−1.09

Catalytic Behavior

The catalytic activity of the palladium complexes **5** and **6** was tested on the hydrogenation of styrene under the same conditions of pressure and temperature. Compound **5** exhibited a better catalytic activity for the hydrogenation of styrene than compound **6** under the studied conditions. On the other hand, both complexes exhibit a good performance throughout the hydrogenation of styrene to

TABLE 3 Hydrogenation of Palladium Complexes **5** and **6** in 5 mM CH_2Cl_2 Solution (Styrene/Catalyst = 430:1; $P = 8$ bar)

Complexes	*T (°C)*	*Time (h)*	*Conversion (%)^a*	*TOF^b(h^{-1})*
5	40	1	100	430
6	40	1	97.6	420

[a] Determined by GC analysis.

[b] $\mathrm{TOF} = \left(\frac{\text{mol substrate}}{\text{mol catalyst}}\right) \times \text{time}$.

ethylbenzene (Table 3). It can be concluded that these catalysts show high performance as well as behave as "phosphine dendrimer-stabilized palladium nanoparticles" [18], and show higher performance than that reported for some Ru(II) phosphine complexes [19,20].

CONCLUSIONS

1. Different bidentate tertiary complexes of Ni(II) and Pd(II) metals with bis(diphenylphosphinomethyl)amino ligands have been synthesized and characterized using spectroscopic methods.
2. From ^{31}P NMR spectra, it can be concluded that coordination of bis(diphenylphosphinomethyl)-amino ligand to metal center gives shielded chemical shift value compared with the free ligand.
3. The solubility tests showed that complexes **4** and **6** are soluble in ethanol and water and are also slightly soluble in water, whereas complexes **3** and **5** are insoluble in both ethanol and water.
4. The peak potentials obtained from the cyclic voltammograms show that phosphine complexes of Ni(II) and Pd(II) reduced to Ni(0) and Pd(0), respectively.
5. The results of gas chromatography analysis exhibited that the metal complexes showed high catalytic activities in hydrogenation reaction of styrene to give ethylbenzene.

ACKNOWLEDGMENTS

The authors thank to Research Found of Çukurova University for financial support to this project and to Dr. Gulfeza Kardaş and Dr. Arif Hesenov for CV and GC analyses, respectively.

REFERENCES

[1] Costa, M.; Pelagatti, P.; Pelizzi, C.; Rogolino, D. J Mol Cat A: Chem 2002, 178, 21–26.

[2] Shin, S.; RajanBabu, T. V. Org Lett 1999, 1(8), 1229–1232.

[3] Hanson, B. E.; Coord Chem Rev 1999, 185–186, 795–807.

[4] Brauer, D. J.; Hingst, M.; Kottsieper, K. W.; Liek, C.; Nickel, T.; Tepper, M.; Stelzer, O.; Sheldrick, W. J Organomet Chem 2002, 64514–64526.

[5] Davies, D. L.; Neild, J.; Prouse, L. J. S.; Russell, D. R. Polyhedron 1993, 12(17), 2121.

[6] Davies, D. L. F.; Healey, I.; Howarth, J.; Russell, D. R. J Organomet Chem 1989, 376, C31.

[7] Drew, D.; Doyle, J. R. Inorg Synth 1990, 28, 346.

[8] Fawcett, P. A.; Hoye, P. A. T.; Kemmitt, R. D. W.; Law, D. J.; Russell, J. Chem Soc Dalton Trans 1993, 2563.

[9] Fawcett, J.; Kemmit, R. D. W.; Russell, D. R.; Serindag, O. J Organomet Chem 1995, 486, 171–176.

[10] Serindağ, O.; Kemmitt, R. D. W.; Fawcett, J.; Russell, D. R. Trans Met Chem 1999, 24, 486–491.

[11] LaPointe, A. M. J Comb Chem 1999, 1, 101–104.

[12] Kuznetsov, R. M.; Baluera, A. S.; Serova, T. M.; Nikonov, G. V. Russ J Gen Chem 71(6), 958–961.

[13] Serindağ, O.; Kemmitt, R. D. W.; Fawcett, J.; Russell, D. R. Trans Met Chem 1995, 20, 548–551.

[14] Appleton, G. T.; Hall, J. R.; Harris, A. D.; Kimlin, A. H.; McMahon, J. I. Aust J Chem 1984, 37, 1883–1840.

[15] Garrou, P. E. Chem Rev 1981, 81, 229–250.

[16] Gilbert, J. G.; Addison, A. W.; Butcher, R. J. Inorg Chim Acta 2000, 308, 22–30.

[17] Almeida, F. M. T.; Carvalho, M. F. N. N.; Galvão, A. M.; Čermák, J.; Blechta, V.; Pombeiro, A. J. L.; Shaw, B. L. Inorg Chim Acta 2001, 313, 77.

[18] Wu, L.; Li, B. L; Huang, Y. Y.; Zhou, H. F.; He, Y. M.; Fan, Q. H. Org Lett 2006, 8(16), 3605–3608.

[19] Moldes, I.; Encarnación, E.; Ros, J.; Alvarez-Larena, A.; Piniella, J. F. J Organomet Chem 1998, 566, 165–174.

[20] Wang, Y.; Wu, X.; Cheng, F.; Jin, Z.; J Mol Cat A: Chem 2003, 195, 133–137.