Synthesis of a new type of amphilic and water-soluble tertiary phosphine ligands substituted by an ethoxylated phosphonic acid chain and their palladium complexes

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Abstract

The highly water-soluble phosphine ligands $Na_2O_3PCH_2CH_2NH(CH_2CH_2O)_nCH_2CH_2N(CH_2PPh_2)_2$ ($n = 1, 2, 3$) were prepared in 67–80% yields by the modified Mannich reaction using hydroxymethylphosphonium salts as the key materials under mild condition; the palladium(II) complexes of the ligands **3a**–**c** with 2:1 or 4:1 $–PPh_2$ to Pd^{2+} molar ratio were also prepared and characterized, and their catalytic activities were checked by carbonylation reaction of benzylchloride. XPS data showed that the coordination bonds were formed between phosphorous, nitrogen, oxygen and palladium atoms in the palladium complexes **4a**–**c**. Good catalytic activities of the complexes **4a**–**c** were observed in carbonylation reaction of benzylchloride with atmospheric CO.
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1. Introduction

The basic problem of a homogeneous catalytic process is the separation of catalyst from products and the reusability of the catalysts. There are two promising methods for the separation of transition-metal catalyst from the organic phase. One approach involves anchoring the homogeneous catalyst to support on the absorbents such as silica, alumina, active carbon, resins or polymers [1]; another one comprises the use of water-soluble complex catalyst which allows to separate the catalyst from the organic phase containing the reaction materials and products. Although sulfonated phosphines, e.g. 'triphenylphosphine trisulfonate' (TPPTS), are the most common ligands of choice for homogeneous catalysis due to their high solubility in water [2], much effort has been directed toward the synthesis of new type of water-soluble transition-metal complexes by incorporating phosphines with water-soluble groups such as $–CO_2Na$, $–OH$, $–PMe_3{}^+$, $–NMe_3{}^+$ $–PO_3Na_2$ and polyethers [3–8]. We reasoned that a new route for the synthesis of water-soluble phosphine ligands having an ethoxylated aminoethylphosphonic acid side chain would be of particular interest because (i) the starting materials are available and cheaply, the reaction conditions are mild and need no special reagents; (ii) the transition-metal, especially Zr(IV), Ti(IV) and Zn(II), etc. with ligands could form a kind of layered crystal or amorphous metallic phosphate, phosphonate or mixed phosphonate phosphate inorganic polymers [9]; (iii) the procedure of Mannich-type reaction

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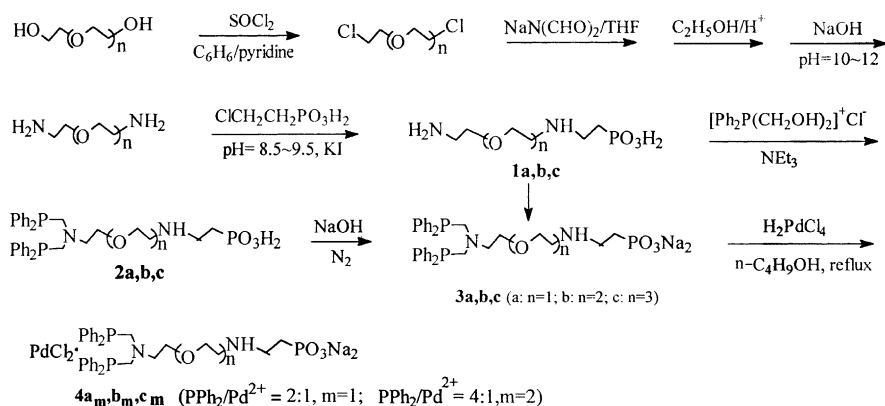
Scheme 1.

with the amines substituted by phosphonic acids and the $[Ph_2P(CH_2OH)_2]^+Cl^-$ is quite simple [10]; (iv) the ethoxylated 2-aminoethyl-phosphonate-modified phosphine ligands have higher solubility than other known phosphonate-modified phosphine ligands such as $Ph_2PCH_2CH_2PO_3H_2$ and o-, p- or m-$Ph_2PC_6H_4$ PO_3H_2 [4,5].

We have been interested in the syntheses of water-soluble phosphonic acid functionalized phosphine ligands due to the mild synthetic conditions by the modified Mannich reaction using hydroxymethyl phosphonium salts as the key materials. In this paper, we report (i) the synthesis and characterization of three new water-soluble phosphines **3a**–**c**, (ii) the preparation of representative examples of transition-metal complexes, (iii) the use of phosphines **3a**–**c** in the biphasic catalytic carbonylation of benzylchloride. A portion of this work has been previously communicated [11]. The synthesis of the title ligands and their palladium complexes is outlined in Scheme 1.

2. Experimental

2.1. Materials and methods

Tetrahydrofuran (THF), benzene, *tert*-butyl alcohol, triphenylphosphine, 40% chloroethylphosphonic acid solution (CEPA) and $PdCl_2$ were analytic grade. Sodium diformamide was prepared according to the literature reference [12]. 1,5-Diamino-3-oxapentane, 1,8-diamino-3,6-dioxaone and 1,11-dimino-3,6,9-tri-oxaundecane were prepared according to the literature

reference [13]. Bis(hydroxymethyl)diphenylphosphonium chloride was prepared according to the literature [14]. Other solvent were analytic grade. All melting points were measured in an open capillary tube and uncorrected. ^1H NMR and $^{13}C\ \{^1H\}$ NMR spectra were recorded at 298 K in D_2O on AV-300 spectrometer at 300.17 and 75.48 MHz, respectively with $SiMe_4$ (δ, 0.0) as external reference. The $^{31}P\ \{^1H\}$ spectra were recorded at 298 K in D_2O on AV-300 spectrometer at 121.31 MHz with 85% H_3PO_4 (δ, 0.0) as external reference, and their chemical shifts are given in ppm.

Infrared spectra were recorded on Spectrum GX using polystyrene as a standard (KBr pellet). Mass spectra were obtained from KYKY-QP1000A spectrometer using electron impact ionization method. GC analyses were performed on a SP 3400 GAS chromatograph equipped with a flame ionization detector. Elemental analysis were performed on PE 2400 elemental analysis instrument. The binding energy of P_{2p}, N_{1s}, O_{1s} $Pd_{3d_{3/2}}$ and $Pd_{3d_{5/2}}$ in he compound **4a**$_m$–**c**$_m$ was measured on KRTO-SXSAM800 X photoelectron spectrum.

2.2. Synthesis of the ligands and complexes

2.2.1. Synthesis of N-ethylphosphonic acid-1,5-diamino-3-oxapentane (1a), N-ethylphosphonic acid-1,8-diamino-3,6-dioxaone (1b) and N-ethylphosphonic acid-1,11-diamino-3,6,9-tri-oxaundecane (1c): general procedure

An amount of 0.2 mol of CEPA (40% solution), 300 g of ice water, 0.21–0.23 mol of 1,5-diamino-3-

oxapentane, 1,8-diamino-3,6-dioxaone or 1,11-dimino-3,6,9-tri-oxaundecane and 0.3 g KI were mixed and stirred below 15 °C, followed by addition of 10% cold NaOH solution to maintain pH in the range of 9–10 during the whole experimental process. The pH value of the reaction solution was checked every half a day and stirred until the pH value of the solution no longer changed. After about 3/4 volume of water was removed under reduced pressure, hydrochloride acid ($8 \, \text{mol} \, l^{-1}$) was added dropwise to adjust the pH 5–7. The concentrated solution stood in refrigerator for 40 h for crystallization. Then the white solids **1a–c** were filtered, washed with cold water, dried in vacuo and recrystallized in water. **1a**: mp >280 °C. Yield: 36.0 g, 85.0% IR (KBr, ν, cm^{-1}): 3348, 3381 (–NH$_2$), 1263 (P=O), 1154 (P–O), 1067, 954 (PO$_3$H$_2$). ^{1}H NMR (D$_2$O, δ, ppm): δ 1.03 (t, 2H, PCH$_2$), 2.90–2.95 (m, 2H, CH$_2$NH), 3.16–3.22 (m, 2H, NHCH$_2$), 3.38–3.41 (m, 2H, CH$_2$NH$_2$), 3.48–3.54 (m, 4H, CH$_2$OCH$_2$). ^{13}C NMR (D$_2$O, δ, ppm): 9.7 (s, CH$_2$P), 38.6 (s, CH$_2$NH), 48.3 (s, HNC$\underline{H}_2$CH$_2$OCH$_2$C$\underline{H}_2$N) 58.0 (s, CH$_2$OCH$_2$). ^{31}P {^{1}H} NMR (D$_2$O, δ, PPM): 2.0 (s, PO). **1b**: mp >280 °C. Yield: 38.8 g, 75.8%. IR (KBr, ν, cm^{-1}): 3442, 3394 (–NH$_2$), 1235 (P=O), 1147 (P–O), 1074, 944 (PO$_3$H$_2$). ^{1}H NMR (D$_2$O, δ, ppm): 1.03 (s, 2H, PCH$_2$), 2.92–2.95 (t, 2H, CH$_2$NH, ^3J (HH) 5.1 Hz), 3.16–3.19 (t, 2H, HNCH$_2$, ^3J (HH) 5.5 Hz), 3.36–3.40 (t, 2H, CH$_2$NH$_2$, ^3J (HH) 5.1 Hz), 3.49–3.53 (t, 4H, CH$_2$O ^3J (HH) 5.5 Hz), 3.42–3.47 (t, 4H, OC$\underline{H}_2$C$\underline{H}_2$O, ^3J (HH) 10.8 Hz). ^{13}C NMR (D$_2$O, δ, ppm): 10.7 (s, CH$_2$P), 38.0 (s, CH$_2$N), 49.3 (s, NC$\underline{H}_2$CH$_2$) OCH$_2$CH$_2$N) 66.4 (s, CH$_2$O), 67.3 (s, OCH$_2$CH$_2$O). ^{31}P {^{1}H} NMR (D$_2$O, δ, ppm): 3.3 (s, PO). **1c**: mp >280 °C. Yield: 40.4 g, 67.4%. IR (KBr, ν, cm^{-1}): 3447, 3383 (–NH$_2$), 1161 (P–O), 1073, 951 (PO$_3$H$_2$). ^{1}H NMR (D$_2$O, δ, ppm): 1.00 (s, 3H, CH$_2$P), 3.15–3.19 (t, 4H, NC$\underline{H}_2$, ^3J (HH) 5.2 Hz) 3.36–3.38 (t, 2H, CH$_2$NH$_2$, ^3J (HH) 8.0 Hz), 3.42 (m, 12H, CH$_2$O (CH$_2$CH$_2$O)$_2$CH$_2$). ^{13}C NMR (D$_2$O, δ, ppm): 9.2 (s, CH$_2$P), 35.2 (s, CH$_2$N), 58.1 (s, NC$\underline{H}_2$CH$_2$O (CH$_2$CH$_2$O)$_2$CH$_2$C$\underline{H}_2$NH$_2$), 66.4, 66.7, 67.1, 67.3, 67.4, 69.4 (m, CH$_2$O(CH$_2$CH$_2$O)$_2$ CH$_2$). ^{31}P {^{1}H} NMR (D$_2$O, δ, ppm): 3.5 (s, PO).

2.2.2. Synthesis of N′,N′-bis(diphenylphosphino methyl)-N-ethylphosphonic acid-1,5-diamino-3-oxapentane (2a), N′,N′-bis(diphenylphosphinomethyl)-N-ethylphosphonic acid-1,8-diamino-3,6-dioxaone (2b) and N′,N′-bis(diphenylphosphinomethyl)-N-ethylphosphonic acid-1,11-dimino-3,6,9-trioxaun-decan (2c): general procedure

Compound: **1a–c** (0.075 mol), sodium carbonate (8 g, 0.075 mol) and 30 ml of water were charged in flask, the solution of bis(hydroxymethyl)diphenylphosphonium chloride (42.4 g, 0.15 mol), 60 ml of water and 60 ml of methanol were added dropwise. Then, triethylamine (15.3 g, 0.15 mol) was added to maintain pH 8.5–9.5 and heated at 75 °C for 3–4 h. The white solids **2a–c** can be obtained by acidifying the reaction mixture with 3 mol l^{-1} hydrochloric acid to pH 3–4 in cooling, filtration, recrystallization from aqueous methanol (v/v 1:1) and drying in vacuo. **2a**: mp 142–144 °C. Yield: 37.2 g, 81.2% (found: C, 63.21; H, 6.47, N, 4.61. Calc. for C$_{32}$H$_{39}$N$_2$O$_4$P$_3$: C, 62.92; H, 6.35; N, 4.43%). IR (KBr, ν, cm^{-1}): 1589, 1488, 1478, 1438 (–C$_6$H$_5$), 1419 (P–C$_6$H$_5$), 1309 (P=O), 1121, 1114 (P–O), 1060, 1053 (PO$_3$H$_2$). ^{1}H NMR (D$_2$O, δ, ppm): 7.80–7.63 (m, 20H, C$_6$H$_5$), 5.09 (s, 4H, PCH$_2$N), 3.28–3.24 (m, 10H, CH$_2$NHCH$_2$CH$_2$O-CH$_2$CH$_2$N), 1.52–1.57 (t, 2H, J = 6.7, CH$_2$PO$_3$H$_2$). ^{13}C NMR (D$_2$O, δ, ppm): 9.7 (s, CH$_2$P), 38.6 (s, CH$_2$N), 48.3 (s, NCH$_2$CH$_2$OCH$_2$CH$_2$N), 50.8 (d, C$\underline{H}_2$PPh$_2$, J(PC) = 239.8 Hz), 58.0 (s, CH$_2$OCH$_2$), 111.5 (d, J(PC) 315 Hz), 127.8 (d, J(PC) = 47.7 Hz), 131.1 (d, J(PC) = 34.2 Hz), 133.1 (d, J(PC) = 12.3 Hz) ^{31}P {^{1}H} NMR (D$_2$O, δ, ppm): 1.18 (s, PO$_3$H$_2$), −12.6 (d, PPh$_2$). **2b**: mp 147–148 °C. Yield: 35.5 g, 72.3% (found: C, 62.63; H, 6.65; N, 4.30. Calc. for C$_{34}$H$_{43}$N$_2$O$_5$P$_3$: C, 62.10; H, 6.33; N, 4.06%). IR (KBr, ν, cm^{-1}): 1588, 1488, 1478, 1438 (–C$_6$H$_5$), 1419 (P–C$_6$H$_5$), 1308 (P=O), 1121, 1114 (P–O) 1060, 1058 (PO$_3$H$_2$). ^{1}H NMR (D$_2$O, δ, ppm): 7.98–7.78 (m, 20H, C$_6$H$_5$), 5.24 (s, 4H, PCH$_2$N), 3.26–3.23 (m, 14H, CH$_2$NH(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$N), 1.42–1.38 (t, 2H, J 5.3, CH$_2$PO$_3$H$_2$). ^{31}P {^{1}H} NMR (D$_2$O, δ, ppm): 4.4 (s, PO$_3$H$_2$), −12.5 (s, PPh$_2$). **2c**: mp 156–158 °C. Yield: 35. 3 g, 67.4% (found: C, 62.17; H, 6.76; N, 3.39. Calc. for C$_{36}$H$_{47}$N$_2$O$_6$P$_3$: C, 61.2; H, 6.12; N, 3.21%). IR (KBr, ν, cm^{-1}): 1589, 1488, 1478, 1438 (–C$_6$H$_5$), 1419 (P–C$_6$H$_5$), 1309 (P=O), 1121, 1115 (P–O), 1060, 1053 (PO$_3$H$_2$). ^{1}H NMR (D$_2$O, δ, ppm):

7.97–7.76 (m, 20H, C_6H_5), 5.23 (s, 4H, PCH_2N), 3.28–3.25 (m, 18H, $CH_2NH(CH_2CH_2O)_3CH_2CH_2N$), 1.39–1.36 (t, 2H, J 4.0, $CH_2PO_3H_2$). ^{13}C NMR (D_2O, δ, ppm): 10.5 (s, CH_2P), 38.9 (s, CH_2N), 46.6 (s, N$\underline{CH_2}CH_2OCH_2\underline{CH_2}$N), 50.8 (d, $\underline{CH_2}PPh_2$, J(PC) = 239.1 Hz), 62.0 (s, CH_2OCH_2), 111.5 (d, J(PC) = 315.3 Hz), 127.6 (t, J(PC) = 42.9 Hz), 131.1 (t, J(PC) = 34.2 Hz), 133.1 (t, J(PC) = 27.9 Hz) ^{31}P {^1H} NMR (D_2O, δ, ppm): 4.7 (s, PO_3H_2), −12.2 (s, PPh_2).

2.2.3. Synthesis of disodium salts of N′,N′-bis(diphenylphosphinomethyl)-N-ethylphosphonate-1,5-diamino-3-oxapentane (3a), N′,N′-bis(diphenylphosphinomethyl)-N-ethylphosphonate-1,8-diamino-3,6-dioxaone (3b) and N′,N′-bis(diphenylphino methyl)-N-ethylphosohonate-1,11-dimino-3,6,9-tri-oxaundecane (3c): general procedure

Compound: **2a–c** (0.1 mol) was dissolved in methanol. Aqueous sodium hydroxide solution (50%, w/v) was added dropwise under N_2 protection, After 30 min, the residue was cooled in refrigerator, allowed to crystallize overnight, filtered and dried in vacuo at 50 °C to give **3a–c** as white solids in 82–90% yield.

Compound: **3a**, IR (KBr, ν, cm^{-1}): 3308 (–NH–), 1561, 1543, 1451 (–C_6H_5), 1009 (PO_3^{2-}). ^{31}P {^1H} NMR (D_2O, δ, ppm): 5.2 (s, PO), −12.6 (d, PPh_2); **3b**: IR (KBr, ν, cm^{-1}): 3132 (–NH–), 1556, 1543, 1452 (–C_6H_5), 1013 (PO_3^{2-}). ^{31}P {^1H} NMR (D_2O, δ, ppm): 4.4 (s, PO), −12.5 (d, PPh_2); **3c**: IR (KBr, ν, cm^{-1}): 3130 (–NH–), 1556, 1545, 1438 (–C_6H_5), 1026 (PO_3^{2-}). ^{31}P {^1H} NMR (D_2O, δ, ppm): 37.5 (s, PO), 3.2 (s, PO_3^{2-}), −12.2 (d, PPh_2).

2.2.4. Synthesis of the palladium(II) complexes: general procedure

$PdCl_2$ (0.177 g, 1 mmol) was dissolved in concentrated hydrochloric acid, and then distilled off the excessive hydrochloric acid to get brown red H_2PdCl_4. An amount of 60 ml of *n*-butanol and ligands **3a–c** (2 or 1 mmol) were added. The mixture was allowed to reflux for 4 h under N_2, evaporated to 30 ml of *n*-butanol under reduced pressure, cooled, and allowed to stand overnight in refrigerator. The solids were filtered, washed with *n*-butanol and dried under reduced pressure to give the products **4a_m–c_m** as solids in

70–78% yield. ^{31}P {^1H} NMR (D_2O, δ, ppm): **4a_1**: 44.5; **4a_2**: 42.6; **4b_1**: 44.2; **4b_2**: 40.3; **4c_1**: 28.1; **4c_2**: 28.0.

2.2.5. General procedure for catalytic carbonylation reaction of benzylchloride

A 150-ml three-neck round-bottom flask was charged with $PdCl_2$ (9 mg, 0.005 mmol) which dissolved in several drops of concentrated hydrochloric acid and evaporated, 20 ml of water, **3a–c**, and a stir bar, pressurized with N_2, heated at 55 °C for 0.5 h, and cooled to room temperature. Then the flask was added 15 ml of 1,2-dichloroethane, evacuated, flushed with CO several times, pressurized with 0.1 MPa CO, placed in an oil bath and heated at 55 °C for 0.5 h, and followed by adding benzylchloride (0.63 g, 5 mmol). Half an hour later, NaOH solution (1.25 mol l^{-1}, 4.0 ml) was added slowly during the whole carbonylation reaction process for 22 h at 55–58 °C. The reaction mixture was then allowed to cool to room temperature, acidified with 3 mol l^{-1} HCl to pH 1–2. The product phenylacetic acid in the substratum was separated by separatory funnel and collected. The aqueous phase in the upper layer was extracted with 1,2-dichloroethane (10 ml × 2) and all the organic phase was combined. The component analysis in combined organic phase was carried out on gas chromatograph, and the content of **3a–c** and palladium complexes in aqueous phase was measured by ultraviolet spectroscopy.

3. Results and discussion

3.1. Synthesis and characterization

Compound **1a–c** have been prepared in 67–85% yields by reacting equimolar amounts of 2-chloro-ethylphosphonic acid (40% aqueous solution) with ethoxylated diamine in a dilute alkaline solution below 15 °C for 7 days. They are all white crystals with high melting point (>260 °C), and can be obtained by direct work-up and recrystallization from water. In this step, 2-chloroethylphosphonic acid is easily decomposed above 15 °C, so the temperature is a essential factor which needed to controlled. The compounds **1a–c** in D_2O solution showed only single resonance in the ^{31}P NMR spectra for phosphonic acid

Table 1

Entry	DCl + D$_2$O (ppm)	D$_2$O (ppm)	NaOD + D$_2$O (ppm)
1a	6.0	2.0	1.6
1b	5.9	3.3	0.6
1c	6.2	3.5	1.6

at $\delta = 2.0$, 3.3, or 3.5, respectively, which demonstrated that the pure products had been obtained and no polysubstitution products exist. It can be also verified by the IR data of symmetrical and asymmetrical stretch vibration of –NH$_2$ at 3448–3381 cm^{-1}. The compounds **1a**–**c** contains two dissociable protons which are involved in the dissociation of the –PO$_3$H$^-$ and –NH$_3$$^+$ groups, all the species can be traced and measured by the determination of the dissociation constants [14]. The pK_1 and pK_2 characteristic of the dissociation of –PO$_3$H$_2$ in **1a**–**c** is 6.85, 6.83, 6.82 and 10.53, 10.51, 10.48, respectively. So, H$_2$NCH$_2$CH$_2$(OCH$_2$CH$_2$)$_n$NHCH$_2$CH$_2$PO$_3$H$^-$ (pH 6.82–10.48), H$_3$N$^+$CH$_2$CH$_2$(OCH$_2$CH$_2$)$_n$NHCH$_2$-CH$_2$PO$_3$H$^-$ (pH $\leq$ 6.82) and H$_2$NCH$_2$CH$_2$(OCH$_2$-CH$_2$)$_n$NHCH$_2$CH$_2$PO$_3$$^{2-}$ (pH $\geq$ 10.48) species dominantly formed in the studied range of pH 4–13 for the systems, which is verified by corresponding chemical shifts in ^{31}P NMR spectrum for phosphonic acid (–PO$_3$H$_2$) in different pH medium showed in Table 1.

^{31}P NMR spectrum for phosphonic acid (–PO$_3$H$_2$) in different pH medium.

Usually, oxidation of phosphine is the main side reaction in the preparation of compounds **2a**–**c** and **3a**–**c**, and the content of diphenylphosphine oxide in the reaction mixture can be detected by ^{31}P NMR spectra. Its chemical shift is found at $\delta = 37.4$. For avoiding the oxidation of phosphine, the reactions were carried out under N$_2$ atmosphere at 5–10 °C in aqueous methanol. In this case, even after storage for several months, no oxidation product could be detected. Compounds **2a**–**c** and **3a**–**c** contain two groups in the ^{31}P NMR spectra corresponding to the phosphine and phosphonate moieties, respectively. After the diphenylphosphinomethyl groups were introduced into the compounds **1a**–**c** by reaction of bis(hydroxymethyl)diphenylphosphonium chloride with –NH$_2$ groups, then the IR data of symmetrical and asymmetrical stretch vibration of –NH$_2$ at 3448–3381 cm^{-1} were not observed. All compounds **2a**–**c** contain several intense in the 1121–900 cm^{-1}

region of the IR spectra which have been assigned to the phosphonic acid group. But in the sodium salts **3a**–**c** phosphonate group only show a broad and intense infrared adsorption at 1026–1009 cm^{-1}. The palladium complexes **4a**–**c** are all colored crystals with high melting point (>250 °C), and can be easily obtained by direct work-up from *n*-butanol. Due to the complexing of –PPh$_2$ groups with palladium atoms, each compound has a ^{31}P chemical shift of 28.0–44.5 ppm, and a strong absorption of P–Pd bond in the IR spectrum at 562 cm^{-1}, both characteristic of coordination between –PPh$_2$ groups with palladium atoms.

3.2. *The distribution coefficient (D) of **3a**–**c** in water*

The distribution of **3a**–**c** in organic/aqueous system is pH dependent, which can be measured as follows: 10 mg **3a**–**c** were added 5 ml of HCl or NaOH water solution with accurate pH values and 5 ml of cyclohexane or 1,2-dichloroethane. After intensive oscillating and demixing, the content of **3a**–**c** in organic and aqueous layers were quantitatively determined by ultraviolet spectrograph. D is the distribution coefficient of **3a**–**c** in water phase at specific pH value:

$$D = \frac{C(\text{H}_2\text{O})}{[C(\text{H}_2\text{O}) + C(\text{org})]} \times 100\%$$

The distribution coefficient D for **3c** in water/1,2-dichloroethane system is near 100% at pH 11.0 (Fig. 1), but that of **3a** and **3b** is only 97% and 92% respectively, which can be concluded that due to **3c** possesses more ethoxy groups, it is easier to be extracted into the
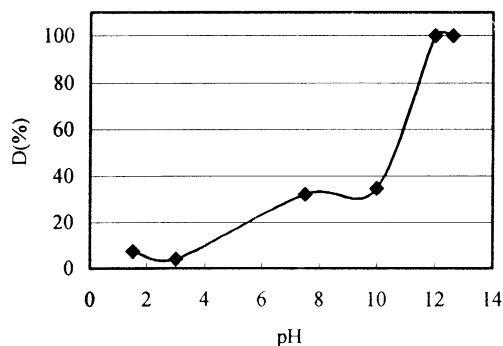

Fig. 1. The distribution coefficient D for **3c** in water/1,2-dichloroethane system.

aqueous phase than the other ligands **3a** and **3b**. Furthermore, it is noted that compounds **2a–c** are more soluble in water to some extent below pH 3, which are attributed to the protonation of –NH– groups to amine salts $-NH_2^+-$. From Fig. 1, it is concluded that the distribution coefficient D for **3c** in water/1,2-dichloroethane system coincided with the species of $(Ph_2PCH_2)_2NCH_2CH_2(OCH_2CH_2)_3NHCH_2CH_2$ PO_3H_2 in different pH medium which can be traced and measured by the pK_1 5.20 and pK_2 9.08 characteristic of the dissociation of $-PO_3H_2$, and the different species showed a distinct variation in aqueous solubility. $(Ph_2PCH_2)_2NCH_2CH_2(OCH_2CH_2)_3NHCH_2$ $CH_2PO_3Na_2$ has the highest solubility, $(Ph_2PCH_2)_2$-$NCH_2CH_2(OCH_2CH_2)_3NHCH_2CH_2PO_3HNa$ has the intermediate solubility, and $(Ph_2PCH_2)_2NH^+CH_2$-$CH_2(OCH_2CH_2)_3NHCH_2CH_2PO_3H^-$ has the lowest solubility.

3.3. XPS analysis of palladium complexes

Phosphines **3a–c** reacted with H_2PdCl_4 in 2:1 or 4:1 molar ratio in *n*-butanol under N_2 for 4–5 h to form complexes **4a–c**. XPS data show that the binding energy of P_{2p}, N_{1s} and O_{1s} in the complexes **4c$_1$** with 2:1 molar ratio increased 0.3, 1.5, 0.8 eV, respectively, **4c$_2$** with 4:1 molar ratio increased 0.2, 1.3 and 0.2 eV, and that of $Pd_{3d3/2}$ and $Pd_{3d5/2}$ decreased 0.2–0.3 and 0.3–0.5 eV, which indicate that coordination bonds are formed among phosphorous, nitrogen, oxygen and palladium atoms in the complexes. The MS spectra of palladium complexes **4a–c** display ion
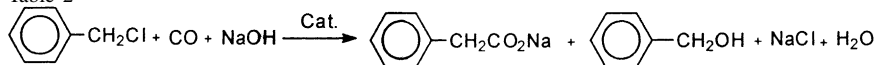
peak of *m/z* 322 at which demonstrate that one Pd^{2+} ion can complex with two PPh_2 groups.

3.4. Catalytic carbonylation reaction

Under phase-transfer conditions in the presence of a base (e.g. sodium hydroxide), $PdCl_2$, triphenylphosphine, and tetrabutylammonium iodide, the carbonylation of benzylchloride can be achieved to give phenylacetic acid in high yield [15]. This catalytic system is ideally suited to assess the performance of hydrophilic phosphonate functionalized phosphine ligands such as **3a–c**. ^{31}P NMR analysis of the solution containing palladium chloride and **3a** which heated at 55 °C for 0.5 h indicated several new resonances including a singlet 42.6 ppm which assigned to the new palladium species. A singlet at 37.5 ppm was also observed and has been assigned to the oxide of **3a**. After the flask was pressurized with carbon monoxide and heated at 55 °C for 0.5 h, the immediate color change from yellow to reddish-brown, presumably resulting from the reduction of palladium(II) complexes to a zerovalent palladium phosphine complexes [16]. The mixture was heated for 22 h at 55 °C, then the organic phase was separated, and the yield of phenylacetic acid and the side products in different reaction conditions gathered in Table 2 was measured on gas chromatograph. Ultraviolet spectroscopy showed that the content of ligands **3a–c** and their palladium complexes in water was recovered in 85–92%.

The biphasic catalytic carbonylation of benzylchloride catalyzed by the palladium complexes of **3a–c**.

Table 2

$$\langle\bigcirc\rangle\text{—CH}_2\text{Cl} + \text{CO} + \text{NaOH} \xrightarrow{\text{Cat.}} \langle\bigcirc\rangle\text{—CH}_2\text{CO}_2\text{Na} + \langle\bigcirc\rangle\text{—CH}_2\text{OH} + \text{NaCl} + \text{H}_2\text{O}$$

Entry	Ligand	Molar ratio of to Pd^{2+} charged ($-PPh_2/Pd^{2+}$)	Conversion (%)	The content of phenylcarbinol (%)	The yield of phenylacetic acid (%[a]), based on the peak areas of benzylchloride
1	**3a**	8:1	100	93.8 (5.48 min)	6.2 (8.75 min[b])
2	**3a**	16:1	100	83.9 (5.52 min)	16.1 (8.72 min)
3	**3a**	32:1	79.6	6.7 (5.81 min)	72.9 (8.72 min)
4	**3a**	64:1	76	5.2 (5.81)	70.8 (8.78 min)
5	**3b**	32:1	82.2	7.7 (5.81 min)	74.5 (8.72 min)
6	**3c**	32:1	82.3	6.2 (5.81 min)	76.1 (8.72 min)

Experimental conditions: 0.1 MPa CO, 55–58 °C, 22 h. Measurement conditions of gas chromatograph: col 100 °C (0.03 min) → 280 °C (10 min), 20 °C/min; INJ 250 °C OV-17; Aux 320 °C FID.

[a] Based on the peak areas of benzylchloride in GC spectra.

[b] The retention time.

In summary, we have reported the synthesis of new highly water-soluble phosphonate-functionalized phosphines and representative palladium(II) complexes. XPS data clearly indicated that coordination bonds are formed among phosphorous, nitrogen, oxygen and palladium atoms in the complexes **4a–c**. We expect that the phosphonated phosphine ligands **3a–c** in combination with transitional metals such as Pd, Rh and Pt will be one of new and important types of catalysts for the biphasic catalytic hydrogenation, carbonylation and hydrofomylation of olefinic hydrocarbon and chlorhydrocarbons.

Acknowledgements

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