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 by a new and simple route under mild conditions in good yield; the palladium (II) complexes of the ligands **3a~c** with 2:1 or 4:1 -PPh₂ to Pd²⁺ molar ratio were also prepared and characterized.

Keywords: Water-soluble, diphenylphosphinomethyl, phosphine ligands, palladium complexes, synthesis.

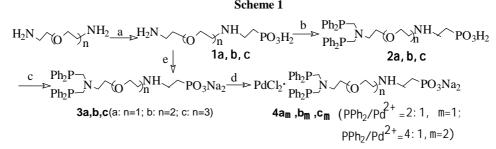
The basic problem of a homogeneous catalytic process is the separation of catalyst from products and the reusability of the catalysts. There are two promising methods for the separation of transition-metal catalyst from the organic phase. One approach involves anchoring the homogeneous catalyst to support on the absorbents such as silica, alumina, active carbon, resins or polymers¹, 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 ligand of choice for homogeneous catalysis due to their high solubility in water², 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 -CO₂Na , -OH , -PMe₃⁺, $-NMe_3^+$ -PO₃Na₂ and polyethers³⁻⁸. We reasoned that a new route for 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 cheap, the reaction conditions are mild and need no special reagents; (ii) the transition metal, especially Zr(IV), Ti(IV) and Zn(II) et al., with ligands could form a kind of layered crystal or amorphous metallic phosphate, phosphonate or mixed phosphonatephosphate inorganic polymers⁹; (iii) the procedure of Mannich-type reaction with the amines substituted by phosphonic acids and the $[Ph_2P(CH_2OH)_2]^+Cl^-$ is quite simple¹⁰; (iv) the ethoxylated 2-aminoethylphosphonate-modified phosphine ligands have higher solubility than other known phosphonate-modified phosphine ligands such as

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Xiang Kai FU et al.

 $Ph_2PCH_2CH_2PO_3H_2$ and o, p or $m-Ph_2PC_6H_4PO_3H_2^{4-5}$.

The synthesis of the title ligands is outlined in **Scheme 1**. A homologous series of the water-soluble ditertiary phosphines $Na_2O_3PCH_2CH_2NH(CH_2CH_2O)_nCH_2CH_2N(CH_2Ph_2)_2$ (n=1,2, 3) has been prepared in good yield. Our approach combines the introduction of the $-N-CH_2-PPh_2$ moiety and the formation of the ethoxylated 2-aminoethylphosphonic acid disodium salts with polar substituting group.



Reagents and conditions: a, 40% CICH₂CH₂PO₃H₂ solution, NaOH, pH=8.5-9.5, 5-20°C,7d. b, $[Ph_2P(CH_2OH)_2]^+CI^-$, H₂O, NEt₃ 75°C; acidified by 3 mol•L⁻¹ hydrogen chloride solution. c, NaOH/ H₂O, N₂ protection. d, H₂PdCl₄, *n*-butanol, reflux, 4-5 h, N₂ protection. e, $[Ph_2P(CH_2OH)_2]^+CI^-$, H₂O, NEt₃ 75°C; pH was adjusted to 12~13 with NaOH.

Exeperimental

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. After the reaction mixture was cooled to room temperature, 6 mol•L⁻¹ sodium hydroxide solution was added to adjust pH to 12~13 under N₂ protection. The white solid was allowed to stand overnight in refrigerator, filtered, washed with 1:1 (v/v) ethanol/water and dried *in vacuo* to give **3a~c** as white solids in 82-90% yield. The white solids **2a~c** also 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*.

PdCl₂ (0.177 g, 1 mmol) was dissolved in concentrated hydrochloric acid, and then distilled off the excessive hydrochloric acid to get brown red H₂PdCl₂. 60 mL of *n*-butanol and ligands **3a~c** (2 mmol, or 1 mmol) were added. The mixture was allowed to reflux for 4 h under N₂, evaporated to 30 mL of *n*-butanol under reduced pressure, cooled, and allowed to stand overnight in refrigerator. The solid was filtered, washed with *n*-butanol and dried under reduced pressure to give the products **4a_m~c_m** as solids in 70-78% yield.

Results and Discussion

Compound 1a~c have been prepared in 75-90% yields by reacting equimolar amounts of

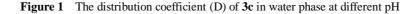
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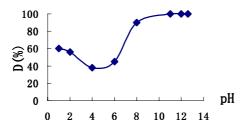
Synthesis of a New Type of Amphilic and Water-soluble Tertiary 841 Phosphine Ligands

2-chloro- ethylphosphonic acid (40% aqueous solution) with ethoxylated diamine in a dilute alkaline solution below 20°C for seven days¹¹. Then the medium was adjusted to pH=7, followed by evaporating most of the water, cooled to give the phosphonic acids white solid **1a~c**. The compound **1a** in D₂O solution showed only single resonance in the ³¹P NMR spectrum for phosphonic acid at δ 3.98.

Phosphines **2a~c** possess water- soluble property to some extent even in acidic conditions. Their structures were characterised by IR, ¹H NMR, ³¹P NMR, MS spectroscopies and elemental analysis. The IR absorbtion at 2595-2597cm⁻¹ shows the protonation of tertiary phosphines ($\equiv P^+$ -H) at low pH values, which may hinder the formation of corresponding transition-metal complexes.

Usually, oxidation of phosphine is the main side reaction in the step c, and the content of diphenylphosphine oxide in the reaction mixture can be detected by ³¹P NMR spectra. Its chemical shift is found at δ 37.39. For avoiding the oxidation of phosphine, the reactions were carried out under N₂ atmosphere at 5-10°C in aqueous methanol. In this case, even after storage for several months, no oxidation product could be detected.





The distribution of $3a \sim c$ in organic / aqueous system is pH dependent, which can be measured as follows: 10 mg $3a \sim c$ 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 $3a \sim c$ in organic and aqueous layers were quantitatively determined by ultraviolet spectrogram. *D* is the distribution coefficient of $3a \sim c$ in water phase at specific pH-value.

$D = \{C(H_2O)/[C(H_2O) + C(org)]\} \times 100\%$

The distribution coefficient *D* for **3c** in water/1,2-dichloroethane system is near 100% at pH 11.0 (**Figure 1**), but that of **3a**, **b** 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 aqueous phase than the other ligands **3a**, **b**. Furthermore, it is noted that compounds **2a~c** are more soluble in water to some extent below pH 4 than they are at pH 4~6 respectively, which are attributed to the protonation of -NH- groups to amine salts.

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}

Xiang Kai FU et al.

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 *eV* and 0.3-0.5 *eV*, which indicate that coordination bonds are formed among phosphorous, nitrogen and palladium atoms in the complexes. The MS spectra of palladium complexes $4a \sim c$ display ion peak of m/z 322 at which demonstrate that one Pd^{2+} ion can complex with two PPh₂ groups.

To summarize, we have prepared and characterised a new, highly water-soluble ethoxylated 2-aminoethylphosphonate-modified phosphine ligands and their palladium complexes. The catalytic properties of the palladium complexes of $4a \sim c$ in carbonylation, hydroformylation and hydrogenation reactions in biphasic system (water / organic phase) are currently under investigation.

Achnowledgment

Financial support from Chongqing Scientific Committee is gratefully acknowledged.

References and Notes

- 1. W. Henderson, G. M. Olsen and L. S. Bonnington, J. Chem. Soc., Chem. Commun, 1994, 1863.
- 2. E.G. Kuntz, Chemtech, 1987, 15, 570.
- 3. D. C. Mudalige, G. L Rempel, J. Mol. Catal. A: Chemical, 1997, 116, 309.
- 4. T. L. Schull, J. C. Fettinger, D. A. Knight., Inorg. Chem., 1996, 35, 6717.
- 5. J. W. Ellis, K. N. Harrison, P. A. T Hoye, *Inorg. Chem.*, **1992**, *31*, 3026.
- 6. T. Okano, Y. Moriyama, H. Konishi, Chem. Lett., 1986, 1463.
- 7. T. Malmstrom, C. Andersson, Chem. Commun., 1996, 1135.
- 8. B. Mohr, D. M. Lynn, R. H. Grubbs, Organometallics, 1996, 15, 4317.
- 9. A. Clearfield, Comments Inorg. Chem., 1990, 10, 89.
- 10. J. Fawcett, P. A. T. Hoye, R. D. W. Kemmitt, J. Chem.Soc. Dalton Trans., 1993, 2563.
- 11. X.K. Fu, C.B. Gong, X.B. Ma, Synth. Commn., 1998, 28 (14), 2659.
- 12. **2a**: mp 142-144°C; IR (KBr, ν /cm⁻¹): 1589, 1488, 1478, 1438 (-C₆H₅), 1419 (P-C₆H₅), 1309, 1121, 1114 (P=O), 1060, 1053 (PO₃H₂), 997 (P-O). ¹H NMR (D₂O, δ ppm, J_{H2}): 7.80–7.63 (m, 20H, C₆H₅), 5.09 (s, 4H, PCH₂N), 3.28-3.24 (m, 10H, CH₂NHCH₂CH₂OCH₂CH₂N), 1.52-1.57 (t, 2H, J 6.7, CH₂PO₃H₂). ³¹P {¹H} NMR (CDCl₃, δ ppm): 1.18 (s, PO₃H₂), -57.0 (d, PPh₂). **2b**: mp 147-148°C; IR (KBr, ν /cm⁻¹): 1588, 1488, 1478, 1438 (-C₆H₅), 1419 (P-C₆H₅), 1308, 1121, 1114 (P=O), 1060, 1058 (PO₃H₂), 997 (P-O).. ¹H NMR (D₂O, δ ppm, J_{H2}): 7.98–7.78 (m, 20H, C₆H₅), 5.24 (s, 4H, PCH₂N), 3.26-3.23 (m, 14H, CH₂NH(CH₂CH₂O)₂CH₂CH₂N), 1.42-1.38 (t, 2H, J 5.3, CH₂PO₃H₂). ³¹P {¹H} NMR (CDCl₃, δ ppm): 4.4 (s, PO₃H₂), -12.5 (s, PPh₂). **2c**: mp 156-158°C; IR (KBr, ν /cm⁻¹): 1589, 1488, 1478, 1438 (-C₆H₅), 1419 (P-C₆H₅), 1309, 1121, 1115 (P=O), 1060, 1053 (PO₃H₂), 997 (P-O). ¹H NMR (D₂O, δ ppm, J_{H2}): 7.97–7.76 (m, 20H, C₆H₅), 5.23 (s, 4H, PCH₂N), 3.28-3.25 (m, 18H, CH₂NH(CH₂CH₂O)₃CH₂CH₂O)₃CH₂CH₂N), 1.39-1.36 (t, 2H, J 4.0, CH₂PO₃H₂). ³¹P {¹H} NMR (CDCl₃, δ ppm): 4.7 (s, PO₃H₂), -12.2 (s, PPh₂).

Received 3 December, 2001