

Synthesis of a New Type of Amphiphilic and Water - soluble Tertiary Phosphine Ligands Substituted by an Ethoxylated Phosphonic Acid Chain and Their Palladium Complexes

Xiang Kai FU*, Xue Bing MA

College of Chemistry and Chemical Engineering, Southwest-China Normal University,
Chongqing 400715

Abstract: The highly water-soluble phosphine ligands $\text{Na}_2\text{O}_3\text{PCH}_2\text{CH}_2\text{NH}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{PPh}_2)_2$ ($n=1,2,3$) 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 $-\text{CO}_2\text{Na}$, $-\text{OH}$, $-\text{PMe}_3^+$, $-\text{NMe}_3^+$, $-\text{PO}_3\text{Na}_2$ 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 phosphonate-phosphate inorganic polymers⁹; (iii) the procedure of Mannich-type reaction with the amines substituted by phosphonic acids and the $[\text{Ph}_2\text{P}(\text{CH}_2\text{OH})_2]^+\text{Cl}^-$ is quite simple¹⁰; (iv) the ethoxylated 2-aminoethylphosphonate-modified phosphine ligands have higher solubility than other known phosphonate-modified phosphine ligands such as

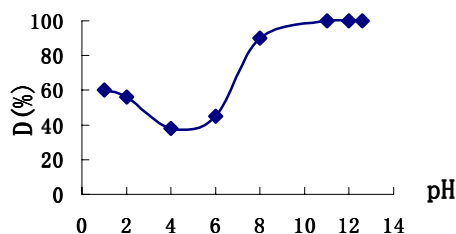
*E-mail: xuebingma@163.net

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 absorption at 2595-2597cm⁻¹ shows the protonation of tertiary phosphines (≡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.

Figure 1 The distribution coefficient (*D*) of **3c** in water phase at different pH



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 spectrogram. *D* is the distribution coefficient of **3a~c** in water phase at specific pH-value.

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

The distribution coefficient *D* for **3c** in water/1,2-dichloroethane system is near 100% at pH 11.0 (**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 H₂PdCl₄ in 2:1 or 4:1 molar ratio in *n*-butanol under N₂ 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 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-c** display ion peak of *m/z* 322 at which demonstrate that one Pd²⁺ ion can complex with two PPh₂ groups.

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

Acknowledgment

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 Hoyer, *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. Hoyer, 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)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