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TRANSITION METAL PHOSPHINE COMPLEXES POSSESSING A PHASE TRANSFER FUNCTION. PREPARATION AND PROPERTIES OF POLYETHER-SUBSTITUTED PHOSPHINES AND THEIR PALLADIUM COMPLEXES

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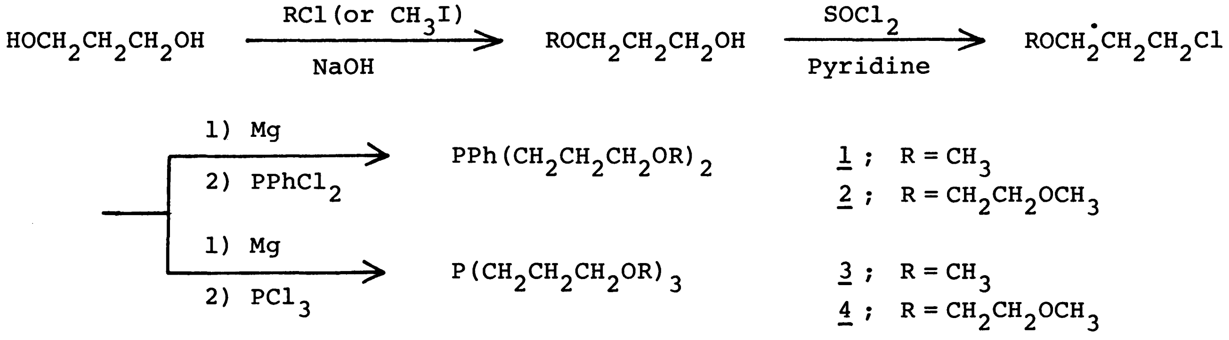
For the purpose of endowing transition metal phosphine complexes with a phase transfer function, tertiary phosphines modified by polyether chains were prepared, and their properties were examined. The palladium complexes of these phosphines were very efficient as catalysts for the reduction of bromobenzene with sodium hydride under a liquid-solid two-phase condition.

Although aryl and vinyl halides are quite inert in classical polar reactions, substitutions of these halides with various nucleophiles can readily be achieved with the catalysis of palladium phosphine complexes.1) This catalytic reaction suffers at least one serious disadvantage. That is to say, some of the widely-used nucleophilic agents are insoluble in organic solvents, while the phosphine complexes are lipophilic. The analogous troubles are also encountered in other catalytic reactions. However, there have been few studies aiming at removing this defect.2) The only known approach is the concurrent use of phase transfer catalysts with metal complexes.3) We have therefore been studying the improvement of the metal complex catalysts by including phosphines containing polyether chains. Herein we describe the palladium complexes which function both as a phase transfer and a metal catalyst in a liquid-solid two-phase system.

The tertiary phosphines containing polyether chains were synthesized by the following routes.



$$HOCH_2CH_2CH_2OH \xrightarrow[NaOH]{RCl(or\ CH_3I)} ROCH_2CH_2CH_2OH \xrightarrow[Pyridine]{SOCl_2} ROCH_2CH_2CH_2Cl$$

$$\xrightarrow[2)\ PPhCl_2]{1)\ Mg} PPh(CH_2CH_2CH_2OR)_2 \qquad \underline{1};\ R = CH_3 \quad \underline{2};\ R = CH_2CH_2OCH_3$$

$$\xrightarrow[2)\ PCl_3]{1)\ Mg} P(CH_2CH_2CH_2OR)_3 \qquad \underline{3};\ R = CH_3 \quad \underline{4};\ R = CH_2CH_2OCH_3$$

$$CH_2{=}CHCOCH_3 \xrightarrow[2)\ NaBH_4]{1)\ ROH\ ,\ ROLi} ROCH_2CH_2CH(OH)CH_3 \xrightarrow[Pyridine]{SOCl_2} ROCH_2CH_2CHClCH_3$$

$$\xrightarrow[2)\ PCl_3]{1)\ Mg} P[CH(CH_3)CH_2CH_2OR]_3$$

5 ; $R = CH_3$
6 ; $R = CH_2CH_2OCH_3$
7 ; $R = CH_2CH_2OCH_2CH_2OCH_3$

All these phosphines were isolated as colorless viscous liquids by distillation.[4)] The ^{1}H-NMR and IR spectra of these phosphines were in agreement with the expected structures. The ^{31}P-NMR of compounds 1, 2, 3, and 4 showed the corresponding single signals, while phosphines 5, 6, and 7 having the branched methyl groups gave two peaks in the relative intensities of about 1 : 3. Since their chemical shifts are consistent with the values predicted by the empirical equation,[5)] the two signals appear to be due to the diastereomers.

Table 1. ^{31}P-NMR Spectral Data for L and trans-$PdCl_2L_2$ (L = Phosphine) [a)]

Phosphine	1	2	3	4	5 [c)]	6 [c)]	7 [c)]
Shift (δ) [b)]	-26.0	-25.8	-32.1	-32.0	10.6 (73) 7.2 (27)	10.3 (78) 6.7 (22)	10.9 (78) 7.4 (22)
Complex	8 [d)]	9 [d)]	10	11	12	13	14
Shift (δ) [b)]	10.8 (b)	11.5 (b)	11.6	11.2	38.8	39.0	38.8

a) The spectra were recorded in C_6D_6 at 25°C and 40.25 MHz. b) δ taken positively downfield from 85% H_3PO_4 as external reference. c) The intensity ratios (%) are given in parentheses. d) b : broad peak.

The phase transfer capability of these phosphines was evaluated by the extractability for a solid phase of sodium picrate into toluene. The experiment was carried out by vigorously stirring a toluene suspension (30 ml) containing anhydrous powdered sodium picrate (3 mmol) and phosphine (1.0×10^{-4} mol dm^{-3}) at 20°C for 24 h, and the extractability shown in Table 2 was caluculated from UV absorbance of the supernatant at 345 nm based on the ε_{max} (12800) of sodium picrate in toluene in the presence of hexaglyme (1.0×10^{-3} mol dm^{-3}). A prolonged stirring (for 6 days) had no further effect on the absorbance. The extractability increased with an increase in the number of oxygen atoms on the phosphine molecule, and conspicuously so on addition of the phosphines containing more than four oxygen atoms. This is attributed to the enhancement of solubilization per one oxygen atom. This fact indicates that these phosphines possess crown-like functions. Although the ratios of extracted picrate to phosphines 1 - 6 were lower than 1, the ratio for 7 was 1.65. Hence the 1:2 host-guest complexation may be possible for 7. Hexaglyme, which contains seven oxygen atoms and is a typical noncyclic extractant, was inferior to 7 in the extractability, but superior in the extractability per one oxygen atom. Therefore, the phase transfer capability of these phosphines is estimated to be

Table 2. Extractability for Sodium Picrate from Solid Phase into Toluene

Phosphine	1	2	3	4	5	6	7	Hexaglyme
Extractability (μ mol dm^{-3})	0.8	7.8	1.3	20	10	48	165	142
Extractability/Number of Oxygen	0.4	2.0	0.4	3.3	3.3	8.0	18	20

roughly equal to that of glymes.[6] It is interesting to note that 6 was a more effective "host" than 4. This fact may be ascribed to the enhancement of lipophilicity owing to the branched methyl groups, because the methyl groups may sterically decrease the chelate effect.

The palladium complexes, trans-$PdCl_2L_2$, were prepared by the reaction of $PdCl_2(NCPh)_2$ with the phosphines (L) in benzene. The chromatography of reaction

$$PdCl_2(NCPh)_2 \; + \; 2\,L \longrightarrow \text{trans-}PdCl_2L_2$$

8 ; L=1 9 ; L=2 10 ; L=3
11 ; L=4 12 ; L=5 13 ; L=6
14 ; L=7

products on silica gel columns gave yellow oils, except for 8, which was obtained as yellow crystals and decomposed at 108°C. Satisfactory elemental analyses for H, C, and Cl were obtained for all the complexes. Each complex exhibited a single IR absorption band due to ν_{Pd-Cl} in the 345-350 cm^{-1} region, suggesting the trans configuration. This is also supported by the ^{31}P-NMR.[7]

Table 3. Catalytic Reduction of Bromobenzene with Sodium Hydride in a Liquid-Solid Two-Phase System [a]

Catalyst	Yield of Benzene (%) [b]
trans-$PdCl_2[P(n\text{-}Bu)_3]_2$	10
trans-$PdCl_2[P(n\text{-}Bu)_3]_2$ - Hexaglyme [c]	10
trans-$PdCl_2[PPh(CH_2CH_2CH_2OCH_2CH_2OCH_3)_2]_2$	12
trans-$PdCl_2[P(CH_2CH_2CH_2OCH_3)_3]_2$	15
trans-$PdCl_2[P(CH_2CH_2CH_2OCH_2CH_2OCH_3)_3]_2$ [d]	70
trans-$PdCl_2[P(CH_2CH_2CH_2OCH_2CH_2OCH_3)_3]_2$	64
trans-$PdCl_2[P(CH_2CH_2CH_2OCH_2CH_2OCH_3)_3]_2$ [e]	15
$P(CH_2CH_2CH_2OCH_2CH_2OCH_3)_3$ [f]	8
trans-$PdCl_2[P(c\text{-}C_6H_{11})_3]_2$	13
trans-$PdCl_2[P(c\text{-}C_6H_{11})_3]_2$ - 18-Crown-6 [c),g]	23
trans-$PdCl_2\{P[CH(CH_3)CH_2CH_2OCH_3]_3\}_2$	15
trans-$PdCl_2\{P[CH(CH_3)CH_2CH_2OCH_2CH_2OCH_3]_3\}_2$	93
trans-$PdCl_2\{P[CH(CH_3)CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3]_3\}_2$ [g]	93
$P[CH(CH_3)CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3]_3$ [f]	10

a) A mixture of PhBr (5 mmol), NaH (15 mmol), trans-$PdCl_2L_2$ (0.1 mmol), and L (0.2 mmol) in toluene (5 ml) was stirred at 130°C for 20 h. b) The yields were determined by GC. c) Each phase transfer catalyst (0.4 mmol) was added. d) L (4) was not used. e) L (0.5 mol) was added. f) 4 or 7 (0.4 mmol) was used as catalyst. g) For 8 h.

The Reduction of aryl bromides with sodium hydride is not achieved even on refluxing in dioxane.8) In the presence of palladium phosphine complexes, the aryl bromides are readily reduced to arenes with sodium methoxide9) or sodium formate10), though a highly polar solvent such as DMF or ethanol is required. However, the palladium-catalyzed reduction using sodium hydride are not known because sodium hydride is insoluble in organic solvents. Therefore we chose this reduction system as a model reaction to study the catalysis of the palladium complexes possessing phase transfer capabilities. The reduction of bromobenzene was carried out using trans-$PdCl_2L_2$ and 2L as the catalyst, and the results are shown in Table 3. As expected, no significant reaction occurred in the presence of palladium complexes such as $PdCl_2[P(n\text{-}Bu)_3]_2$ and $PdCl_2[P(c\text{-}C_6H_{11})_3]_2$ having no polyether chains. Similarly the reduction was hardly catalyzed by polyethers such as 7 and hexaglyme alone. On the other hand, the palladium complexes of polyether-substituted phosphines were very efficient. The catalytic activity was enhanced with an increasing number of oxygen atoms on the phosphine, and correlated well with the extractability of the ligand for sodium picrate. Using 14 as the catalyst, a 93% yield of benzene was realized within only 8 h. A small amount of biphenyl (5% yield) was also found. In the absence of the excess phosphine, the complex catalyst was gradually reduced to metallic palladium during the reaction, while the reduction rate was somewhat fast. On the contrary, the use of a large excess of phosphine resulted in a decrease in the catalytic efficiency. Interestingly, the reaction catalyzed by $PdCl_2[P(n\text{-}Bu)_3]_2$ or $PdCl_2[P(c\text{-}C_6H_{11})_3]_2$ was little improved by the addition of a phase transfer catalyst like hexaglyme or 18-crown-6 in spite of their high extractabilities.6) Consequently, we conclude that the need to endow the transition metal complexes with a phase transfer function is the most important means for the effective fulfillment of catalysis in such two-phase systems.

References

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