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Transition Metal Phosphine Complexes Possessing a Phase Transfer Function. Preparation and Catalytic Reactivity of Palladium Phosphine Complexes Containing Crown Ethers

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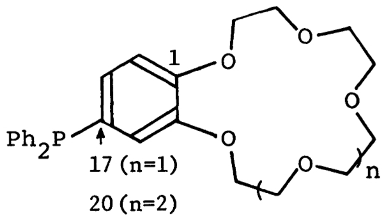
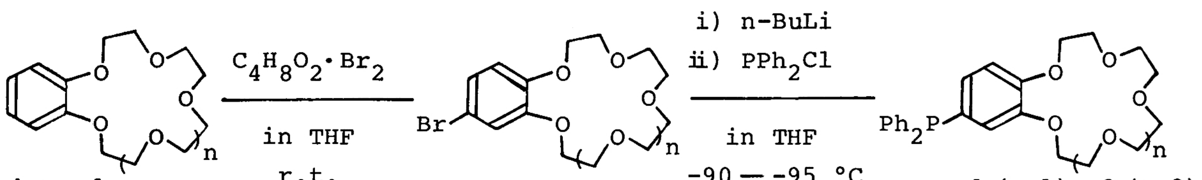
Crown-functionalized triarylphosphines and their palladium complexes were synthesized and characterized. The palladium complexes were found to fulfil the concerted function of the transition metal catalyst and the phase transfer catalyst in the two-phase reduction of 1-chloromethylnaphthalene with formate salts.

The combination of the two features of transition metal complexes and crown ethers in the same molecules constitues a bi-functionalization which not only permits investigations of interactions between ionic compounds insoluble in organic solvents and hydrophobic metal complexes, but also accelerates metal-catalyzed reactions between organic substrates and the ionic compounds. For these purposes, some phosphines having polyether units have recently been synthesized and studied.[1-4] Unfortunately, each of these phosphines has the disadvantage of involving laborious synthetic routes,[1,2] or else chemical instability of the ligating bonds between the phosphine and the polyether moieties,[2,3] so that the applicability, for example to catalytic reactions, seems to be limited.
We previously reported on the catalytic properties of the phosphine complexes having linear polyethers,[4] and will here describe the synthesis and reactivity of palladium complexes whose phosphine ligands have a versatile triary skeleton and crown groups superior to linear polyethers as phase transfer catalyst.



PPh_2(bc-5) (**1**; n=1)
PPh_2(bc-6) (**2**; n=2)

The crowned phosphines, 17-diphenylphosphino-2,5,8,11,14-pentaoxa-bicyclo-[13.4.0]-nonadeca-15,17,19-triene [PPh_2(bc-5); **1**] and 20-diphenylphosphino-2,5,8,11,14,17-hexaoxa-bicyclo[16.4.0]-docosa-18,20,22-triene [PPh_2(bc-6); **2**], were synthesized in short steps as illustrated in Scheme 1. Benzo-[15-crown-5] and benzo-[18-crown-6] were readily brominated with 1.1 equiv. of dioxane-dibromide, and gave 17- and 20-bromo derivatives in 76 and 78% yields, respectively. The brominations were complete within 20 min in THF at room temperature.



Scheme 1.

1 (n=1), **2** (n=2)

The metalation was achieved by halogen-lithium exchange of the bromides with an equivalent of n-BuLi at -90 — -95 °C in THF. Attempts to metalate the bromides with metalic lithium and activated magnesium powder ended in failure.[3)] The crowned phosphines were obtained by immediately treating the lithiated crown solutions with an equivalent of diphenylchlorophosphine at -90 °C and then by allowing the mixtures to reach room temperature over a period of 4 h while stirring. As the lithiated crowns were very sensitive to high temperatures, it was important to keep the temperature below -90 °C during the addition of n-BuLi and PPh_2Cl and to complete these procedures within 30 min. When the reaction was carried out at -78 °C, the yield of **1** was only 30% at most. The purification was achieved by recrystallization from ethanol and provided colorless crystals of **1** [mp 102 °C; MS(m/e) 452(M^+), 408, 364] and **2** [mp 82 °C; MS(m/e) 496(M^+), 452, 408] in 92 and 76% yields, respectively. Though the ^{1}H-NMR spectrum of each compound showed a multiple resonance for three aromatic protons of the benzo-crown group (δ in CD_3COCD_3, 6.8 - 7.0), the ^{13}C-NMR spectra(Table 1) suggested that the diphenylphosphino groups of **1** and **2** were attached to the 17- and 20-positions, respectively. Satisfactory elemental analyses for H and C were obtained for the crowned phosphines.

The phase transfer capability of **1** was evaluated by the extractability for picrate salts from a solid phase into a toluene solution. The experiments were carried out with vigorous stirring of a toluene suspension(30 ml) containing anhydrous powdered picrates(3 mmol) and **1** (100 μmol/dm^3) at 20 °C for 24 h, and the extractability was calculated from UV absorbance of the supernatants.[4a)] The values for Li and Na salts were 48 and 73 μmol/dm^3, respectively. Since those of benzo-[15-crown-5] were 53 and 76 μmol/dm^3 respectively, the phase transfer capability of the crowned phosphines was estimated to be equal to that of the benzocrowns.

The palladium complexes, trans-$PdCl_2L_2$ (**3**; L=**1** and **4**; L=**2**), could readily be

Table 1. ^{13}C-NMR Spectral Data for the Crowned Phosphines and Their Complexes

Compound	δ (Hz ; J_{cp} for **1** and **2**, $J_v = J_{cp} + J_{cp'}$ for **3** and **4**) a)					
	1-C	15-C	16-C	17-C	18-C	19-C
1	151.3(s)	150.2(7.5)	120.2(21.6)	129.1(9.8)	128.4(21.6)	114.6(9.7)
3	151.1(s)	148.1(13.7)	121.7(15.7)	121.7(52.8)	129.1(11.7)	112.5(11.7)
	1-C	18-C	19-C	20-C	21-C	22-C
2	151.2(s)	150.1(7.8)	120.2(21.5)	129.1(9.8)	128.4(19.6)	114.7(7.8)
4	150.6(s)	147.7(13.7)	120.6(15.8)	120.1(51.0)	128.4(11.7)	112.3(11.7)

a) **1** and **2** in CD_3COCD_3, **3** and **4** in $CDCl_3$, at 27 °C, J_v; virtual coupling constant.

prepared by treatment of $PdCl_2(NCPh)_2$ with the crowned phosphines in benzene at 80 °C for 5 min. On addition of methanol the reaction mixtures gave analytically pure orange crystals of 3 [dec p 195 °C; IR(nujol) ν_{PdCl} 355 cm^{-1}] and 4 [dec p 170 °C; IR(nujol) ν_{PdCl} 356 cm^{-1}] in 92 and 81% yields, respectively. The ^1H-NMR spectra showed three aromatic proton signals with coupling to two virtually coupled phosphorous atoms [3 ; δ in $CDCl_3$ 6.82(dt, J=8.3, J_v=2.6 Hz, 19-H), 7.17 (ddt, J=8.3, J_v=10.2 Hz, 18-H), 7.45(dt, J_v=11.7 Hz, 16-H) and 4 ; δ in $CDCl_3$ 6.81(dt, J=8.3, J_v=2.5 Hz, 22-H), 7.17(ddt, J=2.0, J_v=9.0 Hz, 21-H), 7.53(dt, J_v= 11.7 Hz, 19-H)], and confirmed the substitution position of the diphenylphosphino group. The appearance of virtual coupling indicates that the complexes have a trans-configuration. Though the palladium complexes could easily be recrystallized from CH_2Cl_2 and methanol, crystals of $PdCl_2L_2\cdot\frac{1}{2}CH_2Cl_2$ were formed.

$$\underset{(\mathrm{CHCl_3\text{-}soln.})}{\text{trans-}\mathrm{PdCl_2L_2}} \quad + \quad \underset{(\mathrm{solid})}{\mathrm{NaBr}} \quad \xrightarrow[\substack{\text{fast (L=}\mathbf{1}\text{)} \\ \text{slow (L=}\mathrm{PPh_3}\text{)}}]{40\ ^\circ\mathrm{C}} \quad \text{trans-}\mathrm{PdBr_2L_2}$$

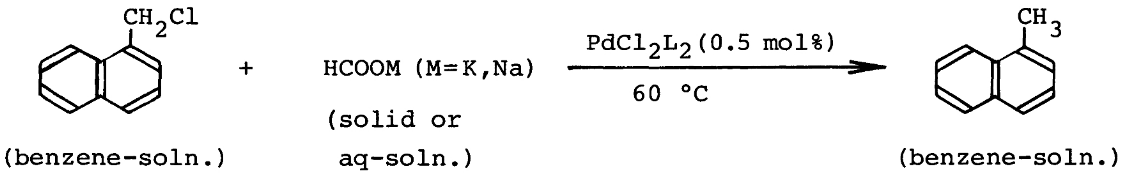
The crowned complex, 3, readily underwent a halogen exchange reaction with 50 equiv of powdered NaBr in $CHCl_3$, and quantitatively yielded the dibromo complex, trans-$PdBr_2L_2$ (L=1), at 40 °C for 1 h. On the other hand, the exchange reaction of $PdCl_2(PPh_3)_2$ was slow, and the yield of the dibromo complex after 10 h was estimated to be only 30% on the basis of the UV spectra. These results indicate that the bromin anion extracted by the crown moiety is able to approach the palladium center notwithstanding tight pairing with the sodium cation.

Table 2. Two-phase Reduction of 1-Chloromethylnaphthalene in Benzene with Solid and Aqueous Formate Salts [a]

Catalyst system	Reductant	Yield/% of 1-methylnaphthalene	
		Solid formate	Aqueous formate
$PdCl_2(PPh_3)_2$	NaOOCH	1	
$PdCl_2[PPh_2(bc\text{-}5)]_2$ (3)	NaOOCH	2	
$PdCl_2[PPh_2(bc\text{-}5)]_2$ (3)	KOOCH	39	
$PdCl_2(PPh_3)_2$	KOOCH	17	18
$PdCl_2(PPh_3)_2$ + 2 bc-6 [b]	KOOCH	27	40
$PdCl_2[PPh_2(dmp)]_2$ [c] + 2 bc-6 [b]	KOOCH	31	
$PdCl_2[PPh_2(bc\text{-}6)]_2$ (4)	KOOCH	86 (98) [d]	63

a) A mixture of catalyst(0.025 mmol), $C_{11}H_9Cl$(5 mmol), and reductant(10 mmol of powdered formate or 4 ml of aqueous formate solution(5 mol/dm^3)) in benzene(10 ml) was vigorously stirred at 60 °C for 3 h or 16 h, respectively. b) Benzo-[18-crown-6](0.05 mmol) was used as an additive. c) dmp = 3,4-dimethoxyphenyl. d) For 4 h.

As a model catalytic reaction, we studied the reduction of 1-chloromethylnaphthalene in benzene with a solid or aqueous solution of formate salts. As a matter of course, $PdCl_2(PPh_3)_2$ had no significant catalytic activity under either the solid-liquid or the aqueous-organic two-phase conditions, and the product yields were lower than the corresponding yields in the reductions with 3. Though the systems using potassium formate were more effective than those using sodium salt, this may be ascribed to the fundamental higher reactivity of potassium salt. The 18-crown-6 skeleton has high affinity to potassium cation. Therefore the activity of 4 was especially high. It is interesting that the mixed system of $PdCl_2(PPh_3)_2$ and twice moles of benzo-[18-crown-6] was not so active as 4 in spite of equivalency in extractability between 2 and benzo-[18-crown-6]. This difference in reactivity is unlikely to be explained only by electronic and steric effects of the phosphine ligands, because the mixed system of $PdCl_2[PPh_2(dmp)]_2$ was almost equal to that of $PdCl_2(PPh_3)_2$ in reactivity. Therefore it is reasonable to understand this result to arise from the difference between intermolecular and intramolecular reactions of activated substrate on palladium with extracted formate. Namely, the intermolecular reaction in the mixed system is slow as a result of low concentrations of both species, whereas the intramolecular reaction in the system of the crowned complexes is not affected by the concentration. In conclusion, it has been demonstrated that the crowned phosphine complexes fulfil the concerted catalyst function in the two-phase reaction. We are extending our studies to other two-phase reactions and shall report these results in due course.



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