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Transition Metal Phosphine Complexes Possessing Phase Transfer Function. Preparation and Reactivities of Palladium Complexes Containing Quaternary Ammonium Groups

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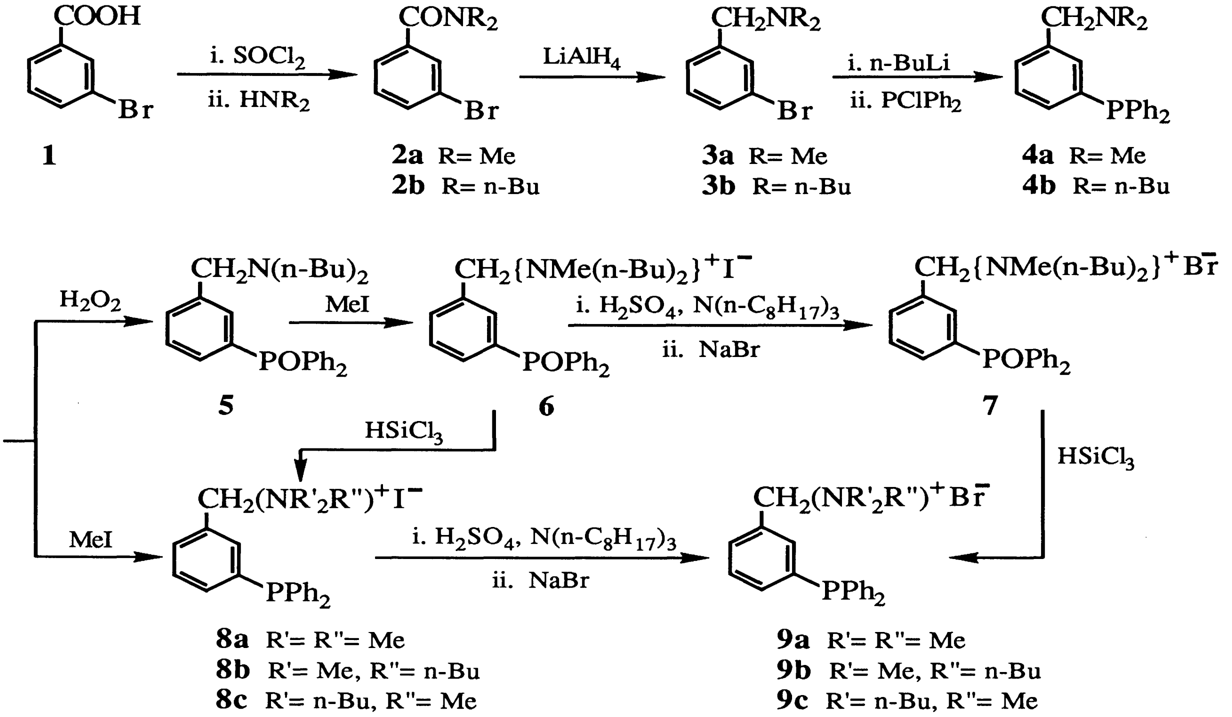
A new type of phosphine ligands (L) bearing quaternary ammonium as a functional group was synthesized. Their palladium complexes, $PdBr_2L_2$, readily underwent halogen exchange with powdered NaI under two-phase conditions, and efficiently catalyzed the fluorocarbonylation of phenyl bromide with powdered KF at atmospheric pressure of CO.

Although the organometallic phase transfer reactions1) involving extraction of metal complex anions by crown ethers or quaternary ammonium salts have been widely studied, transition metal-catalyzed reactions between extracted reagents and organic substrates have been rare. This may be due to a suspicion about the slow reaction owing to the low concentrations of both metal and phase transfer catalysts.2) A fundamental method of improving the reactivity is linking an organic group having phase transfer catalyst function with transition metal catalysts. There have been a few reports3) on the syntheses of phosphine ligands bearing crown ethers and quaternary ammonium groups, but very little is known about the catalysis of their transition metal complexes.4) Here we will report on the synthesis of new triaryl phosphine ligands bearing quaternary ammonium groups and on the catalysis of their palladium complexes under multi-phase conditions.

The synthetic route is outlined in Scheme 1. *m*-Bromobenzoic acid (**1**) as a starting material was readily converted into **3a** and **3b** (68% and 67% yields from **1**, respectively) in three steps. Treatments of **3a** and **3b** with n-BuLi at -78 °C generated the corresponding lithiated dialkylbenzylamines, which reacted with diphenylchlorophosphine to afford **4a** and **4b** (76%, 175-180 °C/100 Pa and 71%, 200-205 °C/100 Pa, respectively) as colorless viscous oils. Quaternizations of the dimethylamino group of **4a** with MeI and n-BuI in toluene successively proceeded to give precipitates of **8a** and **8b**, which were recrystallized from CH_3CN (**8a**; 91%, colorless crystals, mp 181 °C, and **8b**; 74%, colorless crystals, mp 175 °C). Unfortunately, the alkylation of **4b** with MeI exclusively occurred at the phosphorus atom. Therefore, the protection of **4b** was carried out by treatment with H_2O_2, and the resultant phosphine oxide (**5**) was converted to **6** in 95% yield based on **4b**. Reduction of **6** with $HSiCl_3$ afforded **8c** as colorless crystals in 70% yield (mp 136 °C).

Since quaternary ammonium iodides are not good phase transfer catalysts because of far

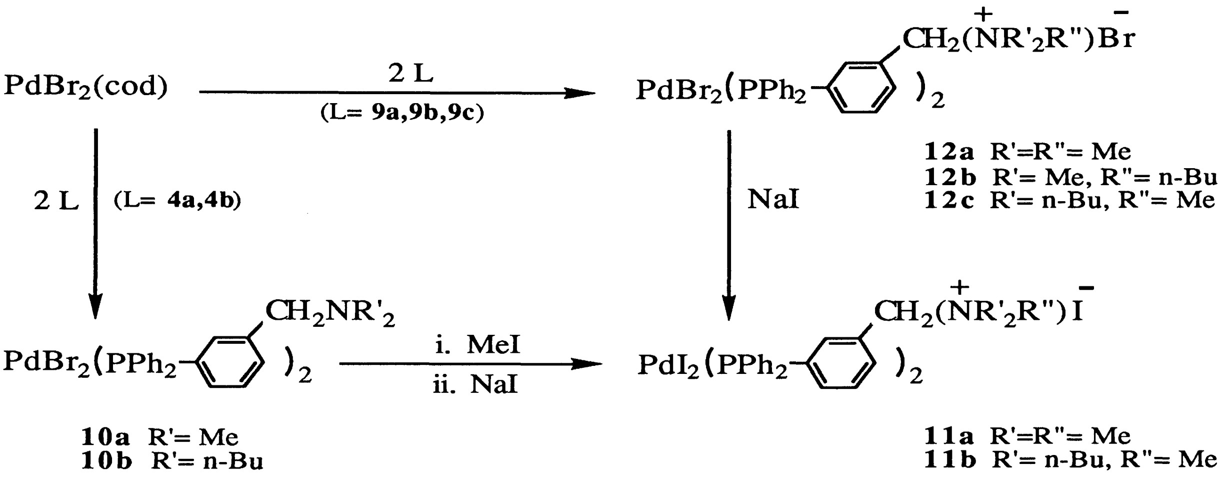


Scheme 1. Synthesis of triarylphosphines bearing quaternary ammonium groups.

stronger affinity of iodide for the ammonium cations in organic media than many other anions,$^{5)}$ the conversion from the iodides **8a**-**8c** to the bromides was attempted. The simple halogen exchange method by shaking CH_2Cl_2 solutions of **8a**-**8c** with a large excess of aqueous NaBr solution, however, was unsuccessful due to the extremely unfavorable bromide-iodide extraction equilibrium. The anion exchange was accomplished by an ion pair extraction method,$^{6)}$ namely, treatments of **8a**-**8c** with trioctylamine and H_2SO_4 under toluene/water two-phase conditions to give the corresponding bisulfates, which were transformed into the bromides **9a**, **9b**, and **9c** by treatment with NaBr (**9a**; mp 210 °C, 72% yield after recrystallization from CH_2Cl_2, **9b**; mp 150 °C, 81%, and **9c**; mp 140 °C, 91%). An analogous halogen exchange of **6** gave **7** (94%), which could also be reduced to **9c** in 90% yield. As the free phosphines were air-unstable in solution, the latter method for preparing **9c** is more convenient than the former.

Their palladium complexes were prepared as follows (Scheme 2). Treatments of $PdBr_2$(cod) (cod=1,5-cyclooctadiene) with **4a** and **4b** in CH_2Cl_2 gave **10a** and **10b** in 87% and 89% yields, respectively. Quaternization of these aminophosphine complexes with MeI in CH_3CN gave brown solids composed of Pd:I:Br=1:3:1. These solids were recrystallized from an aqueous methanol solution containing a large excess of NaI to afford iodide complexes (**11a**; mp 190 °C and **11b**; mp 195 °C) in 60% and 74% yields, respectively. Analogous treatments with NaBr did not give pure bromide complexes, which were prepared from $PdBr_2$(cod) and the ammonium bromides (**9a**-**9c**) in good yields (**12a**; mp 210 °C, 81%, **12b**; mp 180 °C, 76%, and **12c**; mp 195 °C, 74%).

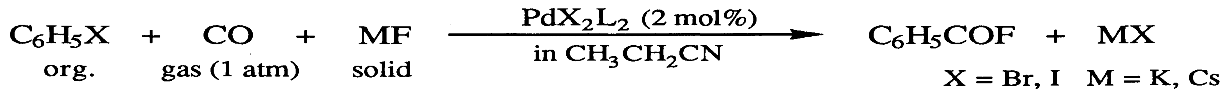
The bromide complex (**12c**) readily underwent halogen exchange with powdered NaI under



Scheme 2. Preparation of palladium phosphine complexes.

$CHCl_3$/solid two phase conditions, and formed the iodide complex (**11b**) quantitatively at 5 °C in 0.5 h on the basis of UV analysis. On the other hand, an analogous reaction of $PdBr_2(PPh_3)_2$ was quite slow, and it took about 3 h to complete the halogen exchange. These results indicate that the quaternary ammonium group in the palladium complex is able to function satisfactorily as a phase transfer catalyst.

The practical value of the palladium complexes was evaluated in the fluorocarbonylation of phenyl iodide with CO and CsF under solid/liquid two-phase conditions. While palladium phosphine complexes were reported to catalyze the fluorocarbonylation,7) the catalytic activity of $PdI_2(PPh_3)_2$ was poor under the two-phase conditions at 70 °C (Table 1). The yield of benzoyl fluoride was somewhat improved by the addition of a considerable amount of tetrabutyl ammonium bromide. As contrasted with these catalyst systems, **11a** and **11b** showed high catalytic activities by themselves. In the fluorocarbonylation using phenyl bromide and KF, which were less reactive than phenyl iodide and CsF, **12a**-**12c** were also proved to be more effective than $PdBr_2(PPh_3)_2$. The catalytic activity (**12c**>**12b**>**12a**) was clearly correlated with the extractability which depends on the length of the alkyl chains of the ammonium groups. It is noteworthy that the catalytic activity of the ammonium phosphine complexes was higher than that of the mixed system of $PdX_2(PPh_3)_2$



$$\underset{\text{org.}}{C_6H_5X} + \underset{\text{gas (1 atm)}}{CO} + \underset{\text{solid}}{MF} \xrightarrow[\text{in } CH_3CH_2CN]{PdX_2L_2\text{ (2 mol\%)}} C_6H_5COF + MX \quad X = Br, I \quad M = K, Cs$$

and NBu_4Br. The catalyses of the ammonium phosphine complexes and of the mixed catalyst system probably involve intra- and inter-molecular reactions between an activated substrate on palladium and an extracted fluoride anion with the ammonium cation, respectively. The rate of the inter-molecular reaction is dependent on the concentrations of the reacting substances, whereas that of the intra-molecular reaction is not. In this reaction, the concentrations of both metal and phase transfer catalysts are low. Therefore, the high efficiency of the ammonium phosphine complexes is ascribable to the intramolecular reaction. In conclusion, it has been demonstrated that the attachment of ammonium groups to the palladium catalyst is effective in enhancing the efficiency of the metal catalyst in the multi-phase reaction.

Table 1. Fluorocarbonylation of phenyl iodide and bromide with CO and MF

Catalyst	Additive	Substrate	MF	Temp/°C	Time/h	Yield of PhCOF/%[a]
$PdI_2(PPh_3)_2$		PhI	CsF	70	8	29
$PdI_2(PPh_3)_2$	$N(n\text{-}Bu)_4Br$[b]	PhI	CsF	70	8	45
11a		PhI	CsF	70	8	60
11b		PhI	CsF	70	8	86
$PdBr_2(PPh_3)_2$		PhBr	KF	80	20	19
$PdBr_2(PPh_3)_2$	$N(n\text{-}Bu)_4Br$[b]	PhBr	KF	80	20	27
12a		PhBr	KF	80	20	34
12b		PhBr	KF	80	20	43
12c		PhBr	KF	80 (100)	20	50 (95[c])

The reaction was carried out by vigorously stirring a mixture of PhX (5 mmol), powdered CsF or spray-dried KF (10 mmol), PdX_2L_2 (0.1 mmol), and L (0.1 mmol) in EtCN (5 ml) under CO (1 atm). a) Determined by GC. b) $N(n\text{-}Bu)_4Br$ (1.0 mmol) was used. c) CO (2 atm).

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