

# Platinum Group Metals in Phase Transfer Catalysis

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*Phase transfer catalysis is an elegant method for ameliorating the reaction conditions of many organic reactions and improving yields and selectivities. A review is presented of the role and scope of the compounds of the platinum group metals as cocatalysts under phase transfer conditions. The most useful improvements have been found in reactions involving the formation of carbon-carbon bonds such as in carbonylations and vinylations, and in reductions with formate.*

The concept of phase transfer catalysis arose about 30 years ago as a solution to the problem of facilitating reaction between organic substrates immiscible in water and inorganic species insoluble in non-aqueous solvents (1, 2). Since then the field has burgeoned with over 2700 citations in *Chemical Abstracts* as of the end of 1988. Present day commercial usage is estimated to involve 50 to 75 applications and over 50 million pounds per year of products (2, 3). Such an impressive growth has been due to the manifold advantages of phase transfer catalysis:

- improved selectivity
- increased reaction rates
- milder reaction conditions
- reduced energy requirements
- simplified isolation and purification methods
- reduced consumption of organic solvents
- elimination of need for expensive solvents
- allows the use of cheaper raw materials, especially oxidants
- elimination of need for rigorous drying of organic solvents
- very broad scope of action—numerous reaction types possible.

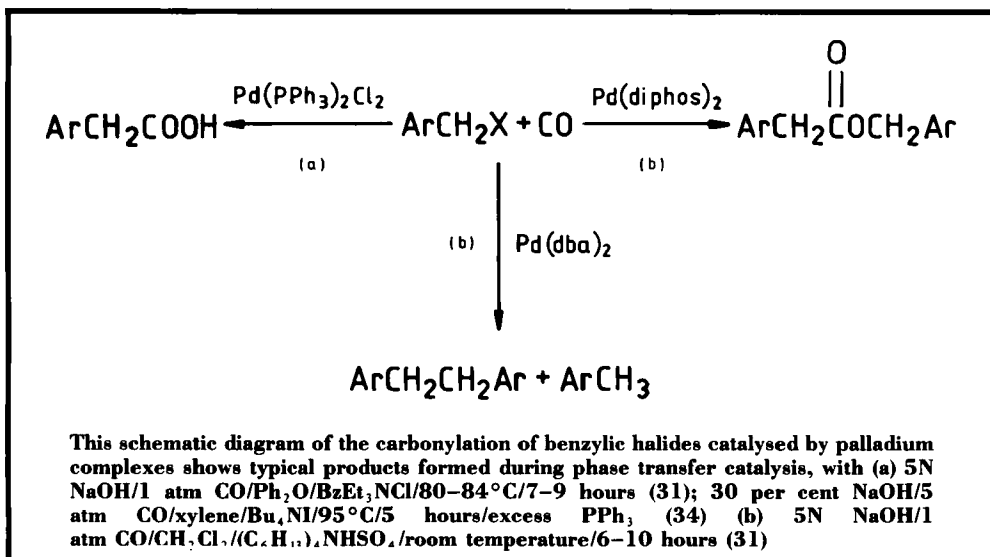
Although general reviews of phase transfer catalysis (2–23) and some reviews of phase transfer catalysis with transition metal compounds (24–29) have been published, it is the purpose of this article to review the role played

by compounds of the platinum group metals as cocatalysts in phase transfer catalysis with emphasis on the scope of the reactions rather than on mechanisms.

## Carbonylation

Carbonylations by palladium are very sensitive to reaction conditions, the product distribution being particularly dependent on the nature of the palladium complex and the organic solvent. This is illustrated in the Figure for the carbonylation of benzylic halides. Carbonylation gives the expected carboxylic acid when either  $\text{Pd}(\text{PPh}_3)_4$  or  $\text{Pd}(\text{diphos})_2$ , where diphos is 1,2-bis(diphenylphosphino)ethane, is used in the absence of a phase transfer catalyst (30); however, when  $\text{Pd}(\text{diphos})_2$  is used in the presence of a phase transfer catalyst (31), the course of the reaction changes dramatically, as shown in the Figure, esters being formed.

An attempt was made to control the stereospecificity of the carbonylation of  $\text{PhCH}(\text{Me})\text{Br}$  using a palladium catalyst formed in situ by the addition of an optically active phosphorus compound to  $\text{Pd}(\text{dba})_2$ , where dba is dibenzylideneacetone. Yields were poor and in only one case was there a significant enantiomeric excess of the product (32). In the absence of any phosphine ligand only the coupled product,  $\text{PhCH}(\text{Me})\text{CH}(\text{Me})\text{Ph}$ , was obtained with  $\text{Pd}(\text{dba})_2$  (33). When  $\text{Pd}(\text{PPh}_3)_4$  was used, a mixture of the acid (36 per cent) and the



ester PhCH(Me)COOCH(Me)Ph (19 per cent) was obtained (30).

The catalyst Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> has been used to selectively carbonylate phenyl halides having more than one halide (24, 34). In each case only one halide was displaced. Thus *p*-dibromobenzene gave *p*-bromobenzoic acid (conversion 90 per cent, selectivity 95 per cent), and 1,3,5-trichlorobenzene gave 3,5-dichlorobenzoic acid (selectivity 97 per cent).

The organic solvent markedly affects the course of reaction in the palladium catalysed carbonylation of vinylic dibromides, RCH=CBr<sub>2</sub>. When R is phenyl coupling occurs in benzene to give PhC≡CC≡CPh in 54 per cent yield, while in *t*-amyl alcohol carbonylation occurs giving PhCH=C(COOH)<sub>2</sub> in 93 per cent yield (35). Coupling does not occur when R is aliphatic. Thus for R=EtCHMe a mixture of the monoacid and diacid is obtained, in benzene giving 64 per cent RCH=CHCOOH and in *t*-amyl alcohol giving 82 per cent RCH=C(COOH)<sub>2</sub>. Vinylic bromides, RCH=CHBr, are carbonylated in good yields to the expected acid using Pd(diphos)<sub>2</sub> or Pd(PPh<sub>3</sub>)<sub>4</sub> (36), although in the latter case the reaction can also proceed without a phase transfer catalyst.

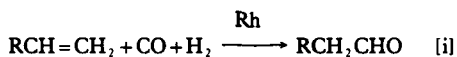
Esters can be prepared via solid-liquid phase

transfer catalysis from organic halides and alcohols (37). Thus Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/1–7 atm CO/NaHCO<sub>3</sub>/ethyl alcohol/Bu<sub>4</sub>Ni was used to facilitate the preparation of ethyl esters from a variety of aliphatic and aryl halides. Yields were 56–95 per cent, but dropped to less than 30 per cent in the absence of a phase transfer catalyst. Phase transfer catalysis with Pd(OAc)<sub>2</sub> provides a modest enhancement in the yields of anhydrides from carbon monoxide, aryl halides, and carboxylic acid salts (38).

The system PdBr<sub>2</sub>/Mn(acac)<sub>2</sub>/NaOH/Bu<sub>4</sub>NBr, where acac is 2,5-pentanedione, was used to synthesise diphenyl carbonate in 60 per cent yield from phenol, carbon monoxide and oxygen (39). Many phase transfer catalysts were examined and the wide range of yields obtained illustrates the necessity of optimising such reactions with respect to the phase transfer catalyst. Under similar conditions, alkyl carbonates can be produced from aliphatic alcohols (40).

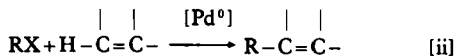
Efforts have been made (41–44) to improve the recovery of rhodium from commercial hydroformylation processes which use rhodium catalysts, Equation [i], by employing phase transfer conditions. Both phase transfer catalysis and rhodium-phosphine complexes with amphiphilic phosphine ligands, such as

Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>N<sup>+</sup>Me<sub>3</sub> (41), (3-HO<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P (42, 44) and Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>COOH (43), were investigated.



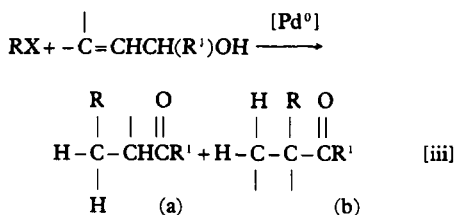
## Vinylation

The Heck vinylation, Equation [ii], of organic halides is an extremely valuable method of synthesising carbon-carbon bonds (45).



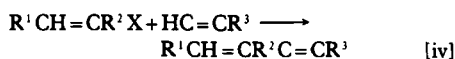
In the absence of phase transfer catalysis these reactions can be slow, and require high temperatures (>100°C) and long reaction times, and the yields are not always good. Phase transfer catalysis has been shown to improve the yields and stereospecificity and to allow the reactions to proceed at room temperature. A series of aromatic iodides, RC<sub>6</sub>H<sub>4</sub>I, was vinylated with CH<sub>2</sub>=CHR<sup>1</sup>, in excellent yields, 80–97 per cent, using the system Pd(OAc)<sub>2</sub>/NaHCO<sub>3</sub>/Bu<sub>4</sub>NCl/DMF, where DMF is *N,N'*-dimethyl formamide, at room temperature (46). The product was exclusively the (*E*) isomer. A similar system, Pd(OAc)<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub>/Bu<sub>4</sub>NCl/DMF was also used to study the vinylation of (*E*)- and (*Z*)-C<sub>4</sub>H<sub>9</sub>CH=CHI (47). Excellent stereospecificities for the (*E,E*) isomer of the product were achieved even when the substrate was the (*Z*) isomer. Various alkynyl iodides have been vinylated at room temperature in 40–60 per cent yield to (*E*)-methylenoates and methylenones using the systems Pd(OAc)<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>/Bu<sub>4</sub>NCl/DMF (48).

Under the same conditions, when allyl alcohols are reacted, Equation [iii] below:



two isomers can be produced (46). Using Pd(OAc)<sub>2</sub>/NaHCO<sub>3</sub>/Bu<sub>4</sub>NCl/DMF, (a) was produced with high selectivity and yield (82–94 per cent). Very recently, it has been shown that high selectivity can be achieved under non phase transfer conditions when the reaction is properly optimised (49).

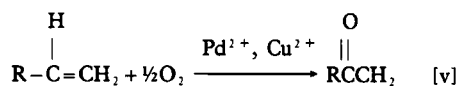
The addition of organic halides to alkynes has also been investigated; thus reaction [iv] shows yields of 24–87 per cent with almost complete stereospecificity using the system Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI/C<sub>6</sub>H<sub>6</sub>/NaOH/BzEt<sub>3</sub>NCl (50).



## Oxidation

### Olefins

Phase transfer catalysts have been used in an attempt to improve the yield of the Wacker reaction, [v].



Although the yields are generally good, only in a few cases is there an improvement compared with the yields obtained without using phase transfer catalysts (some comparisons are given in Table I). The oxidation of styrene was unusual (51) as the product distribution was significantly different under phase transfer conditions (Table I). Wacker type oxidations under phase transfer conditions using rhodium and ruthenium catalysts were inferior to those using palladium (52). However the fact that moderately good yields were obtained with ruthenium is significant, since oxidations with ruthenium generally lead to cleavage of the double bond (53, 54). Examples of cleavage under phase transfer conditions are given in Table II. Again, with a few exceptions, there is usually little improvement in yields compared with non phase transfer conditions (53–55).

Phase transfer catalysis in the Wacker reaction with cyclodextrins is notable, as the olefin is transferred to the aqueous phase where oxidation takes place; on the other hand

quaternary ammonium salts transfer the olefin to the organic phase. Internal olefins are not oxidised using quaternary ammonium salts (56), but are oxidised using  $\beta$ -cyclodextrin (51). Thus *cis*- and *trans*-MeCH=CHMe are oxidised to 2-butanone in 76 per cent and 70 per cent yields, respectively. The yield of methyl ketone from straight chain olefins peaks when the carbon chain of the substrate is nine carbon atoms long (57).

No doubt this is related to the hole size of the cyclodextrin. Internal olefins are also oxidised using PEG-400 (58), where PEG is polyethyleneglycol, although a significant amount of double bond migration also occurs. Yields decrease when either shorter, PEG-200, or longer, PEG-1000, chain lengths are used.

### Aromatic Hydrocarbons

In most cases subjecting aromatic compounds to oxidative phase transfer conditions results in oxidation of an aliphatic side chain. Methylbenzenes were oxidised with RuCl<sub>3</sub>/NaOCl/Bu<sub>4</sub>NBr/CH<sub>2</sub>ClCH<sub>2</sub>Cl and the products depended on the electronic properties of the non methyl substituent (68). When the substituent was H or electron withdrawing, for example, NO<sub>2</sub>, halide or NO, the methyl group was oxidised to a carboxyl group in yields of 93-98 per cent. Electron donating groups resulted in ring chlorination.

The system RuCl<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/DDAB, where DDAB is (C<sub>10</sub>H<sub>22</sub>)<sub>2</sub>Me<sub>2</sub>NBr, was used to oxidise the side chains of aromatic rings (69) in good yields, but the selectivity was usually not very good. Tetralin was oxidised to  $\alpha$ -tetralone with this system in 65 per cent yield (69), and with RuO<sub>2</sub>/NaIO<sub>4</sub>/C<sub>6</sub>H<sub>6</sub>/Adogen-464 in 74 per cent yield (70). Ring cleavage occurred, resulting in a mixture of phthalic acid and 3-methyl-phthalic acid, when 1-methylnaphthalene was oxidised with RuO<sub>2</sub>/NaIO<sub>4</sub>/C<sub>6</sub>H<sub>6</sub>/Adogen-464 (70).

### Alcohols

There are many methods available for the platinum group metals catalysed oxidation of alcohols (53, 54). Indeed, when properly op-

timised, some of these reactions have given results equal to those employing phase transfer conditions. Thus although high yields have been obtained under phase transfer conditions using RuO<sub>2</sub>/NaIO<sub>4</sub> (71) or RuCl<sub>3</sub>/NaBrO<sub>3</sub> (72), the same oxidations can be carried out in the absence of a phase transfer catalyst in equally high yield when the reaction conditions are finely tuned. For example, oxidations with RuO<sub>2</sub>/NaBrO<sub>3</sub> have been performed in the absence of phase transfer catalysts in nearly quantitative yields (73), and the addition of acetonitrile to the conventional RuO<sub>2</sub>/NaIO<sub>4</sub>/CCl<sub>4</sub> system dramatically improves yields in many cases (55).

Phase transfer catalysis provides a definite benefit in the case of oxidations with Ru/H<sub>2</sub>O<sub>2</sub>. No oxidation of alcohols takes place in the absence of a phase transfer catalyst; instead ruthenium metal precipitates and the hydrogen peroxide is catalytically decomposed to oxygen (74).

When a phase transfer catalyst is added, yields of 60-100 per cent are obtained, primary alcohols being converted into aldehydes and secondary alcohols into ketones.

Some oxidations involving transfer between a solid and a liquid phase are greatly enhanced by phase transfer catalysis. Thus the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively, takes place in high yields with the phase transfer systems Pd(OAc)<sub>2</sub>/NaHCO<sub>3</sub>/PhI/Bu<sub>4</sub>NCl/DMF (75) or RuCl<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>/CCl<sub>4</sub>/DDAB (76).

## Reduction

### Reductions with Hydrogen

Rhodium complexes with amphiphilic phosphine ligands have been used to reduce unsaturated organic compounds with hydrogen (77, 78). Benzene derivatives were reduced to cyclohexane derivatives under mild conditions using the system [Rh(1,5-hexadiene)Cl]<sub>2</sub>/1-2 atm H<sub>2</sub>/CH<sub>2</sub>ClCH<sub>2</sub>Cl/H<sub>2</sub>O/Aliquat-336/room temperature (79), or RhCl<sub>3</sub>/2 atm H<sub>2</sub>/CH<sub>2</sub>ClCH<sub>2</sub>Cl/H<sub>2</sub>O/Aliquat-336/room temperature (80).

The latter system was also employed in

**Table I**  
**Oxidation of Some Olefins to Methyl Ketones with Oxygen\***  
**A Comparison with non Phase Transfer Conditions**

Substrate	Products	Conditions	Yield, per cent	Reference
1-dodecene	2-dodecanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /DMF	87	59
1-dodecene	2-dodecanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /CTAB/ <i>n</i> -C <sub>10</sub> H <sub>22</sub> / <i>n</i> -C <sub>5</sub> F <sub>12</sub> <sup>b</sup>	98	60
1-dodecene	2-dodecanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /CTAB	62	56
1-decene	2-decanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /DMF	73	61
1-decene	2-decanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /CTAB	73	56
1-decene	2-decanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /α-CD	76	57
1-decene	2-decanone	RhCl <sub>3</sub> /CuCl <sub>2</sub> /CTAB	44	52
1-decene	2-decanone	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> /CTAB	64	52
1-decene	2-decanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /PEG-400 <sup>c</sup>	60	58
1-butene	2-butanone	PdCl <sub>2</sub> /PMV <sup>b</sup>	14	62
1-butene	2-butanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /CTAB <sup>d</sup>	65	56
1-butene	2-butanone	PdCl <sub>2</sub> /CuCl <sub>2</sub> /PEG-400 <sup>c</sup>	71	58
1-butene	2-butanone	PdCl <sub>2</sub> /PMV/CTAB/C <sub>10</sub> H <sub>22</sub> <sup>t</sup>	85	62
styrene	PhCH <sub>2</sub> CHO	PdCl <sub>2</sub> /CuCl <sub>2</sub> /CH <sub>3</sub> CN	44	63
styrene	PhCOCH <sub>3</sub>	PdCl <sub>2</sub> /CuCl <sub>2</sub> /β-CD	80	51
	PhCHO		10	
	PhCH <sub>2</sub> CHO		10	

\*1 atm O<sub>2</sub>, unless otherwise noted  
 CTAB = cetyltrimethylammonium bromide  
 PMV = phospho-6-molybdo-6-vanadic acid

<sup>a</sup>400 psi O<sub>2</sub>  
 CD = cyclodextrin

<sup>c</sup>200 psi O<sub>2</sub>

<sup>d</sup>180 psi O<sub>2</sub>

**Table II**  
**Oxidative Cleavage of Olefins**

Substrate	Products	Conditions	Yield, per cent	Reference
1-octene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COOH	RuO <sub>2</sub> /H <sub>5</sub> IO <sub>6</sub> /hexane/(C <sub>12</sub> H <sub>26</sub> ) <sub>3</sub> N	93	64
<i>cis</i> -4-octene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	RuO <sub>2</sub> /NaOCl/NaOH/CH <sub>2</sub> Cl <sub>2</sub> /Bu <sub>4</sub> NBr	84	65
1-pentadecene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH	RuO <sub>2</sub> /NaOCl/NaOH/CH <sub>2</sub> Cl <sub>2</sub> /Bu <sub>4</sub> NBr	100	65
styrene	PhCHO	RuCl <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /CH <sub>2</sub> ClCH <sub>2</sub> Cl/DDAB	64	66
	PhCOOH		6	
	styrene oxide		4	
styrene	PhCHO	PdCl <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> /CH <sub>2</sub> ClCH <sub>2</sub> Cl/DDAB	12	66
	PhCOOH		14	
	PhCOCH <sub>3</sub>		56	
styrene	PhCHO	[(bpy) <sub>2</sub> (py)RuO] <sup>2+</sup> /NaOCl/ CH <sub>2</sub> Cl <sub>2</sub> /BDTC	47	67
	styrene oxide		13	
<i>trans</i> -stilbene	PhCHO	[(bpy) <sub>2</sub> (py)RuO] <sup>2+</sup> /NaOCl/ CH <sub>2</sub> Cl <sub>2</sub> /BDTC	42	67
	styrene oxide		7	
<i>cis</i> -stilbene	PhCHO	[(bpy) <sub>2</sub> (py)RuO] <sup>2+</sup> /NaOCl/ CH <sub>2</sub> Cl <sub>2</sub> /BDTC	35	67

BDTC = BzMe<sub>2</sub>(C<sub>14</sub>H<sub>26</sub>)NCl

reducing acetylenes to olefins, and therefore is the phase transfer analog of the Lindlar catalyst (81) (palladium poisoned with lead supported on calcium carbonate). Like the Lindlar catalyst, which gives mainly *cis* products, the phase transfer conditions could be adjusted to give mainly the *cis* isomers, although the selectivity is not as high as that usually achieved with the Lindlar catalyst.

Under these conditions hydrogenolysis of halides tends to occur; thus 59 per cent of the fluorine in fluorobenzene and all the chlorine in chlorobenzene are removed (80).

The system  $\text{RhCl}_3/\text{I atm H}_2/\text{CH}_2\text{ClCH}_2\text{Cl}/\text{H}_2\text{O}/\text{Aliquat-336}$  has also been used to reduce  $\alpha,\beta$  unsaturated esters, ketones, and carboxylic acids at the carbon-carbon double bond with yields of 87–96 per cent (82).

Imines have been reduced to the corresponding amine in the three phase system  $[\text{Rh}(\text{PPh}_3)_2(\text{1,5-cyclooctadiene})]\text{PF}_6/\text{I atm H}_2/\text{ether}/\text{H}_2\text{O}/\text{Triton X-100}/\text{solid imine}/\text{room temperature}$  (83). The choice of solvent was critical; no reaction occurred in PEG/water or toluene/water.

### Reductions with Formate

Formate has been used to reduce a variety of organic substrates under phase transfer conditions. For example,  $\text{PhCH}=\text{CHOPh}$  was reduced to  $\text{PhCH}_2\text{CH}_2\text{COPh}$  by  $\text{NaOOCH}$  with  $\text{RuCl}_2(\text{PPh}_3)_3/o\text{-C}_6\text{H}_4\text{Cl}_2/\text{H}_2\text{O}/(\text{C}_6\text{H}_{13})_4\text{NHSO}_4$  at  $109^\circ\text{C}$  in 99 per cent yield (84).

Other  $\alpha,\beta$  unsaturated carbonyl compounds were also reduced successfully at the carbon-carbon double bond. The best phase transfer catalyst was  $(\text{C}_6\text{H}_{13})_4\text{NHSO}_4$ , which gave quantitative reduction in minutes; others required hours.

Saturated aldehydes and ketones are reduced to alcohols at  $90^\circ\text{C}$  using Aliquat-336 (85). The best catalyst for aldehyde reduction was found to be  $\text{RuCl}_2(\text{PPh}_3)_3$ , while a 1:10 mixture of  $\text{RhCl}(\text{PPh}_3)_3$  and triphenylphosphine was the best for ketones. Nitrobenzenes could not be reduced with formate under phase transfer conditions (85).

Aryl bromides underwent hydrogenolysis using  $\text{PdCl}_2(\text{PPh}_3)_2/\text{PPh}_3$  and  $(\text{C}_6\text{H}_{13})_4\text{NHSO}_4$  (86, 87). This proved to be a useful technique for preparing monodeuterated aromatic compounds on substituting  $\text{D}_2\text{O}$  for  $\text{H}_2\text{O}$  (87). Hydrogenolysis of 1-(chloromethyl)naphthalene was achieved using a palladium catalyst in which a phosphine functionalised with a crown ether was bound to the palladium (88). A mixture of  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  and benzo-[18-crown-6] was far less effective than the functionalised palladium complex.

### Miscellaneous Reductions

Aniline derivatives are prepared in excellent yields, 84–100 per cent, from the corresponding nitrobenzenes by reduction with carbon monoxide at 1 atmosphere pressure, at room temperature, using  $\text{Ru}_3(\text{CO})_{12}/\text{NaOH}/\text{C}_6\text{H}_6/\text{MeO}(\text{CH}_2)_2\text{OH}/\text{BzEt}_3\text{NCl}$  (89). The method gives good selectivity. No hydrogenolysis occurs in the reduction of *p*-chloronitrobenzene to *p*-chloroaniline (100 per cent yield), and no reduction of the aldehyde group occurs in the reduction of *p*-nitrobenzaldehyde to *p*-aminobenzaldehyde (100 per cent yield). Similar results are obtained with the mixed catalyst  $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{Co}_2(\text{CO})_8$ , where COD is 1,5-cyclooctadiene, (90). Unhindered nitrobenzenes are reduced successfully at room temperature and 1 atmosphere pressure with syngas (1:1 carbon monoxide:hydrogen) using  $\text{RuCl}_2(\text{PPh}_3)_3/\text{C}_6\text{H}_5\text{CH}_3/5\text{M NaOH}/\text{BzEt}_3\text{NCl}$  (91). Reduction is much less facile when either carbon monoxide or hydrogen is used alone. Olefin, halide, and carbonyl functional groups are not reduced under the same conditions.

The reduction of phenyl bromide in yields of up to 93 per cent was achieved with sodium hydride, under solid-liquid conditions, using a palladium phosphine catalyst in which the phosphine was functionalised with an aliphatic polyether (92). The optimum yield was critically dependent on the chain length of the polyether, and little reduction occurred without a phase transfer catalyst or even with a mixture

of a phase transfer catalyst and a palladium catalyst.

Benzylic alcohols were dehydrogenated to ketones in fair to good yields using  $[\text{Rh}(\text{CO})_2\text{Cl}]_2/8\text{M NaOH}/\text{C}_6\text{H}_6/\text{BzEt}_3\text{NCl}$  (93). Secondary alcohols gave ketones, while the primary alcohol 2-naphthalenemethanol gave 2-naphthaldehyde.

## Conclusions

The most useful application of phase transfer catalysis with platinum group metal complexes appears to be the formation of carbon-carbon bonds, particularly in carbonylations and vinylations. Indeed, the scope of vinylation reactions has recently been extended to include the allylation of alkyl iodides with allylsilanes using  $\text{Pd}(\text{OAc})_2$  (94) and the allylation of acrylate esters with arylsulphonyl chlorides (95). The only industrial process employing a platinum group metal catalyst under phase

transfer conditions is the hydroformylation of propylene to butanal by Ruhr Chemie using a rhodium compound with the ligand  $(3\text{-HO}_3\text{SC}_6\text{H}_4)_3\text{P}$ . The separation of the rhodium complex from the products is simplified as a result of the water solubility of the rhodium complex.

While there are a few instances of phase transfer catalysed oxidations in which the use of platinum group metal complexes have proven advantageous, in general there are many facile methods of oxidation using platinum group metal catalysts which do not require phase transfer conditions.

Similarly, reductions with hydrogen and platinum group metals complexes under phase transfer catalysis conditions are not generally used, since there is a wide variety of supported platinum group metal catalysts which are readily accessible to perform such reductions conveniently (96).

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