Cationic Complexes of Transition Metals as a New Type of Phase-transfer Catalyst

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Cationic complexes of the type $[ML_2Cl_2]^+Cl^-$ (M = Rh, Ir, Fe; L = 2,2′-bipyridyl or 1,10-phenanthroline) were found to act as phase-transfer catalysts that can be used as bifunctional catalysts in consecutive reactions of metal-complex and phase-transfer catalysis.

Among the various types of phase-transfer catalysts the greatest recognition has been won by onium compounds, mainly tetra-alkyl-ammonium and -phosphonium salts.[1] As a rule, effective phase-transfer catalysts must contain a relatively lipophilic cation (of Bu_4N^+ type) and a relatively hydrophilic anion (generally HSO_4^-, F^-, Cl^-, Br^-). We assumed that other similar ionic compounds and in particular cationic complexes of transition metals with lipophilic ligands may also be used as catalysts for two-phase reactions. To support this assumption several phase-transfer reactions were carried out in the presence of $[Rh(bipy)_2Cl_2]^+Cl^-$ (**1**), $[Rh(phen)_2Cl_2]^+Cl^-$ (**2**), $[Ir(phen)_2Cl_2]^+Cl^-$ (**3**), and $[Fe(phen)_2Cl_2]^+Cl^-$ (**4**) cationic complexes.†

$[Rh(bipy)_2Cl_2]^+Cl^-$ (**1**)
$[Ir(phen)_2Cl_2]^+Cl^-$ (**3**)
$[Rh(phen)_2Cl_2]^+Cl^-$ (**2**)
$[Fe(phen)_2Cl_2]^+Cl^-$ (**4**)

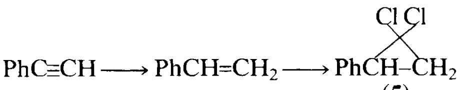
A typical phase-transfer reaction is, for example, the exchange of halogen in alkylhalides for a thiocyanate anion [reaction (1)], which in a liquid–liquid two-phase system is effectively catalysed by tetra-alkylammonium salts and in the absence of catalyst is very slow to proceed.[3] 1-Chlorobutane in the presence of complexes (**1**)—(**3**) was found to react with potassium thiocyanate [molar ratio Bu^nCl : KSCN (5% aq. solution) : catalyst = 1 : 2 : 0.05; 100 °C, 4 h] to afford n-butylthiocyanate in 82, 90, and 100% yields, respectively (g.l.c.). Thus, cationic complexes (**1**)—(**3**) facilitate nucleophilic substitution of chlorine to thiocyanate anion in a two-phase system, although the rate of reaction (1) in the presence of (**1**)—(**3**) is lower than in the case of usual phase-transfer catalysts.[3]

However, the possibility of phase-transfer demonstrated for cationic complexes makes them essentially different and confers certain advantages as compared with the routinely used catalysts. The principal advantage lies in their bifunctionality, because in the presence of transition metal complexes, including cationic ones, various reactions of homogeneous metal-complex catalysis (hydrogenation, hydrogen transfer, hydrosilylation, oxidation, *etc.*) are carried out.[4] Hence, it becomes possible to accomplish at least two different types of reactions (homogeneous metal-complex and phase-transfer catalysis) using the same catalyst.

One of the typical processes in metal-complex catalysis is homogeneous hydrogenation,[4] and among phase-transfer reactions the transformations of unsaturated substrates reacting with chloroform under dichlorocarbene generation conditions.[5,6]

To test the bifunctional nature of cationic transition metal complexes two pairs of reactions were carried out in the presence of iridium complex (**3**): (A) homogeneous hydrogenation of phenylacetylene to styrene followed by $:CCl_2$ addition under phase-transfer conditions, and (B) homogeneous hydrogenation of cinnamaldehyde to hydrocinnamaldehyde with subsequent transformation of the latter into the alcohol (**6**) as a result of trichloromethyl anion addition in a two-phase $CHCl_3$–50% aq. NaOH system.

$$Bu^nCl + KSCN \longrightarrow Bu^nSCN + KCl \qquad (1)$$



$$PhC{\equiv}CH \longrightarrow PhCH{=}CH_2 \longrightarrow PhCH{-}CH_2 \ (CCl_2) \qquad (A)$$

(**5**)

$$PhCH{=}CHCHO \longrightarrow PhCH_2CH_2CHO \longrightarrow Ph\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H(OH)\overset{4}{C}Cl_3 \qquad (B)$$

(**6**)

Phenylacetylene (1% chloroform solution) in the presence of complex (**3**) (1 mol.%) at 60 °C, and 1.01 MPa H_2 (1 atm = 0.101 MPa) was completely converted during 2 h and afforded styrene as the main product (~10% of ethylbenzene was also formed). The addition of 50% aq. NaOH to the reaction mixture followed by stirring for 12 h at 40 °C led to 1,1-dichloro-2-phenylcyclopropane (**5**) in 80% yield at 85% styrene conversion. The addition of $:CCl_2$ to styrene was also carried out in the presence of complex (**4**). In conditions similar to those described above, compound (**5**) was formed in 40% yield (styrene conversion 45%).

Using complex (**3**) (1 mol %) the hydrogenation of cinnamaldehyde (1% chloroform solution, 60 °C, 1.01 MPa H_2, 35 h) was also performed. In these conditions a mixture of hydrocinnamaldehyde (~80%), hydrocinnamyl alcohol (~15%), and cinnamyl alcohol (1—2%) was obtained. Dropwise addition of 50% aq. NaOH to the reaction mixture followed by stirring at 0 °C for 4 h afforded compound (**6**)‡ in 75% yield. Small amounts of hydrocinnamyl alcohol and hydrocinnamic acid were also formed in the parallel Cannizzaro reaction.[6]

After carrying out the studied pairs of reactions and isolation of products by vacuum-distillation the catalysts were recovered after recrystallization from ethanol–2-methoxyethanol (1 : 1). The control experiments show that the activity of regenerated catalysts in the hydrogenation and studied phase-transfer reactions is completely retained.

Thus, cationic complexes of rhodium, iridium, and iron with lipophilic ligands were found to act as catalysts in two-phase nucleophilic substitution, dichlorocyclopropanation, and nucleophilic addition reactions. They can be also used as bifunctional catalysts in consecutive reactions of metal-complex and phase-transfer catalysis.

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† Complexes (**1**)—(**4**) were prepared by the reaction of corresponding metal trichlorides with 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) in ethanol–2-methoxyethanol (1 : 1) as described in ref. 2.

‡ The new compound (**6**) is a viscous yellowish oil, b.p. 116 °C/0.1 mm Hg; ^{13}C n.m.r. (22.63 MHz, $CDCl_3$), δ: 31.86, 32.90 (C-1, C-2), 82.03 (C-3), 104.13 (C-4), 126.23, 128.44, 140.72 (ring carbons); ^1H n.m.r. (90 MHz, $CDCl_3$, $SiMe_4$), δ: 1.8—3.2 (m, 5H, $-CH_2CH_2-$, $-OH$), 3.98 (dd, 1H, J_1 10, J_2 2 Hz, $-CH_2CH-OH$), 7.22 (m, 5H, Ph); mass (70 eV), m/z: 251.9918 (M^+, for ^{35}Cl, $C_{10}H_{11}OCl_3$), 117.0707 ($C_9H_9^+$); calc.: 251.9875; 117.0707.