Catalysis of Halogen Exchange Between Alkyl Halides

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Summary The catalytic effect of transition-metal–phosphine complexes on the exchange of halide between alkyl halides is shown to be due to the quaternisation of the labile phosphine ligands; the true catalyst is demonstrated to be the halide ion.

THE exchange of halide groups between simple alkyl halides was described many years ago by Calingaert *et al.*[1] who utilised an aluminium halide as catalyst. Recently, a variety of transition-metal complexes have been reported[2] to act as catalysts for halogen exchange between activated alkyl halides. The suggested mechanism was that of oxidative addition of the alkyl halide to the transition-metal complex followed by halide exchange on the metal and reductive elimination of the alkyl halide. We now present evidence that the true catalyst in these reactions involving transition-metal–phosphine complexes is a halide ion generated by the quaternisation of labile phosphines by the alkyl halide.

TABLE. Relative reactivities of catalysts for halide exchange between MeI and CH_2Cl_2[a]

Catalyst	Concentration/ mol l^{-1}	Relative reactivity
$[Bu_4N]I$	4×10^{-2}	10·0
$[Bu_4N]I$	2×10^{-2}	5·0
$[Bu_4N]I$	1×10^{-2}	2·5
$[MePh_3P]Br$	2×10^{-2}	5·0
$[Rh(Ph_3P)_3Cl]$	2×10^{-2}	7·3
$[Rh(Ph_3P)_2Cl]_2$	2×10^{-2}	2·3
$[Rh(Ph_3P)_2(CO)Cl]$	2×10^{-2}	3·5
$[Ir(Ph_3P)_2(CO)Cl]$	2×10^{-2}	1·2
$[Ir(acac)(CO)_2]$	2×10^{-2}	<0·1
$[Ir(COD)Cl]_2$	2×10^{-2}	<0·1
$[Ph_4As][Ir(CO)_2I_2]$	2×10^{-2}	<0·1
$[Zn(Ph_3P)_2Br_2]$	2×10^{-2}	7·0
Ph_3P	2×10^{-2}	5·0

[a] A solution of the catalyst in a mixture of 5·0 ml CH_2Cl_2 and 0·5 ml MeI was heated in a sealed evacuated glass tube at 100 °C for 2 h. The products were analysed by n.m.r. spectroscopy.

Thus, quaternary ammonium or phosphonium halide salts or phosphines are capable of catalysing the exchange reaction in the absence of transition metals (see Table). The rate is first order in halide ion. Conductivity measurements on solutions following reaction showed that the solutions involving the metal–phosphine complexes had become conducting indicating quaternisation of the phosphines.† Experiments with $[Ir(acac)(CO)_2]$, $[Ir(COD)Cl]$, and $[Ph_4As][Ir(CO)_2I_2]$ are particularly relevant since Ir^I complexes oxidatively add MeI rapidly[3] even at room temperature but do not catalyse the exchange reaction to an appreciable extent. These iridium complexes do not contain quaternisable ligands.

By contrast, although oxidative additions of Zn^{II} are unknown, $Zn(Ph_3P)_2Br_2$ acts as a 'catalyst' since the phosphines are labile and can be quaternised.

The variations in rate with metal–phosphine complexes used reflect on the relative lability of the metal–ligand bonding.

The relationship observed[2] between the rate of reaction and the structure of the alkyl halide follows the order found for the relative rate of attack of iodide ion on alkyl chlorides[4] and also the relative rate of quaternisation of phosphines.

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† The product from the reaction involving $[Rh(Ph_3P)_3Cl]$ as the catalyst was isolated and shown to contain the $[MePh_3P]^+$ cation.

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