Group VIII Metal Complexes as Catalysts for Halogen Exchange Between Alkyl Halides

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Summary Several co-ordinatively unsaturated d^6 and d^8 group VIII metal complexes are efficient catalysts for halogen exchange reactions between a variety of alkyl halides.

Reversible oxidative addition of alkyl halides to the square planar d^8 complexes $[M(CO)(Ph_3P)_2]$ (M = Rh, Ir; X = Cl, Br, I), (equation 1) is well-known.[1] Despite intense interest in the mechanisms[1,2] and catalytic applications[3] of this reaction, catalytic halogen exchange reactions,

$$RX + MX(CO)(Ph_3P)_2 \rightleftharpoons MX_2R(CO)(Ph_3P)_2 \qquad (1)$$

(equation 2) have not been reported. We now report the first examples of alkyl halide exchange reactions, catalysed by co-ordinatively unsaturated group VIII metal complexes. A large number of exchange reactions of this type occur readily and in many instances provide synthetically useful transformations. That catalytic halogen exchange processes have previously been unreported in these systems is surprising since reactions involving oxidative addition of alkyl iodides and alkyl bromides are routinely carried out in chlorinated hydrocarbon solvents.

The exchange of alkyl monohalides with dihalogenoalkanes (equation 3) was used to probe the scope and general applicability of homogeneous catalytic alkyl

$$R^1X^1 + R^2X^2 \xrightleftharpoons{[MX(CO)(Ph_3P)_2]} R^1X^2 + R^2X^1 \qquad (2)$$

$$R^1X^1 + R^2R^3CX^2{}_2 \xrightleftharpoons{\text{metal complex}} R^1X^2 + R^2R^3CX^1X^2 \qquad (3)$$

TABLE Alkyl halide exchange catalysed by group VIII metal complexes[a]

Reactants			Reaction		Products		%
R^1X^1	$R^2R^3CX^2_2$	Catalyst	time/h	Gas	R^1X^2	$R^2R^3CX^1X^2$	Exchange[b]
MeI	CH_2Cl_2	$IrCl(CO)(Ph_3P)_2$	2·0	Ar	MeCl	CH_2ICl	25
MeI	CH_2Cl_2	$RuCl_2(Ph_3P)_3$	2·0	Ar	MeCl	CH_2ICl	96
MeI	CH_2Cl_2	$RhCl(Ph_3P)_3$	2·0	Ar	MeCl	CH_2ICl	96
MeI	CH_2Cl_2	$RhCl(CO)(Ph_3P)_2$	2·0	Ar	MeCl	CH_2ICl	94
MeI	CH_2Cl_2	$RhCl(CO)(Ph_3P)_2$	2·0	CO	MeCl	CH_2ICl	94
MeI	CH_2Br_2	$RhCl(CO)(Ph_3P)_2$	2·0	Ar	MeBr	CH_2IBr	92
MeI	CH_2Br_2	$RhCl(CO)(Ph_3P)_2$	2·0	CO	MeBr	CH_2IBr	93
MeI	$PhCHBr_2$	$RhCl(CO)(Ph_3P)_2$	2·5	CO	MeBr	PhCHIBr	93
$MeCH_2I$	CH_2Cl_2	$RhCl(CO)(Ph_3P)_2$	2·0	CO	$MeCH_2Cl$	CH_2ICl	17
$(Me)_2CHI$	CH_2Cl_2	$RhCl(CO)(Ph_3P)_2$	18·0	CO	—	—	NR
$PhCH_2Br$	CH_2Cl_2	$RhCl(CO)(Ph_3P)_2$	2·0	CO	$PhCH_2Cl$	CH_2BrCl	10
$PhCH_2Br$	CH_2Cl_2	$RhCl(CO)(Ph_3P)_2$	22·5	CO	$PhCH_2Cl$	CH_2BrCl	71
$MeCH_2Br$	CH_2Cl_2	$RhCl(CO)(Ph_3P)_2$	21·0	CO	$MeCH_2Cl$	CH_2BrCl	0·5

[a] A 2×10^{-2}M solution of the metal complex in a mixture of 5·0 ml $R^2R^3CX^2_2$ and 0·5 ml R^1X^1 was stirred at 100 °C under 150 lb in^{-2} of either Ar or CO for the designated time. Product analysis by g.c. [b] % Exchange ± 2% = % yield R^1X^2 = % yield $R^2R^3CX^1X^2$.

halide exchange. The reaction is synthetically useful for the preparation of a variety of mixed halogenoalkanes (Table). Reactions were carried out using 2×10^{-2}M solutions of the metal complex in a mixture of the halogenocarbons ($R^2R^3CX^2_2 : R^1X^1 = 10:1$) at 100 °C under 150 lb in^{-2} of either argon or carbon monoxide. Carbon monoxide was found to be beneficial in stabilizing metal carbonyl complexes. When the reaction was carried out under carbon monoxide pressure clear orange to red solutions were obtained while under argon brown reaction mixtures resulted and at times dark precipitates were noticed. Under CO pressure acyl rhodium complexes must form, but little or no catalytic carbonylation of the alkyl halides occurred under the reaction conditions. Reaction mixtures were analysed by gas chromatography and products were isolated by preparative gas chromatography and identified by comparison of i.r., n.m.r., and mass spectra with authentic samples.

The catalytic reaction most probably occurs *via* a series of oxidative addition and reductive elimination reactions (equations 4 and 5). The factors which control the rates of oxidative addition[1,2] can also affect the efficiency of the catalytic process. For example, the relative rates of alkyl iodide–methylene chloride exchange decrease in the order

$$R^1X^1 + MX^2(CO)(Ph_3P)_2 \rightleftharpoons MX^1X^2(R^1)(CO)(Ph_3P)_2 \rightleftharpoons MX^1(CO)(Ph_3P)_2 + R^1X^2 \quad (4)$$

$$R^2R^3CX^2_2 + MX^1(CO)(Ph_3P)_2 \rightleftharpoons MX^1X^2(R^2R^3CX^2)\text{-}(CO)(Ph_3P)_2 \rightleftharpoons MX^2(CO)(Ph_3P)_2 + R^2R^3CX^1X^2 \quad (5)$$

$MeI > MeCH_2I > (Me)_2CHI$; benzyl bromide undergoes exchange with methylene chloride much faster than does ethyl bromide; and ethyl iodide is more reactive than ethyl bromide.

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