

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

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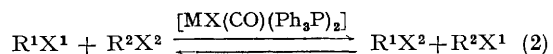
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Summary Several co-ordinatively unsaturated d^6 and d^8 group VIII metal complexes are efficient catalysts for halogen exchange reactions between a variety of alkyl halides.

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 applications³ of this reaction, catalytic halogen exchange reactions,



(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

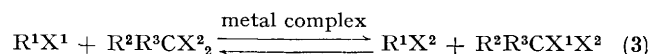


TABLE Alkyl halide exchange catalysed by group VIII metal complexes^a

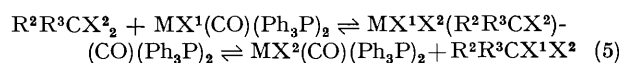
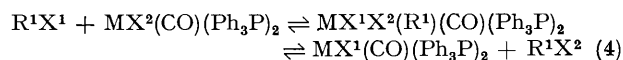
Reactants		Catalyst	Reaction time/h	Gas	Products		% Exchange ^b
R ¹ X ¹	R ² R ³ CX ₂ ²				R ¹ X ²	R ² R ³ CX ¹ X ²	
MeI	CH ₂ Cl ₂	IrCl(CO)(Ph ₃ P) ₂	2.0	Ar	MeCl	CH ₂ ICl	25
MeI	CH ₂ Cl ₂	RuCl ₂ (Ph ₃ P) ₃	2.0	Ar	MeCl	CH ₂ ICl	96
MeI	CH ₂ Cl ₂	RhCl(Ph ₃ P) ₃	2.0	Ar	MeCl	CH ₂ ICl	96
MeI	CH ₂ Cl ₂	RhCl(CO)(Ph ₃ P) ₂	2.0	Ar	MeCl	CH ₂ ICl	94
MeI	CH ₂ Cl ₂	RhCl(CO)(Ph ₃ P) ₂	2.0	CO	MeCl	CH ₂ ICl	94
MeI	CH ₂ Br ₂	RhCl(CO)(Ph ₃ P) ₂	2.0	Ar	MeBr	CH ₂ IBr	92
MeI	CH ₂ Br ₂	RhCl(CO)(Ph ₃ P) ₂	2.0	CO	MeBr	CH ₂ IBr	93
MeI	PhCHBr ₂	RhCl(CO)(Ph ₃ P) ₂	2.5	CO	MeBr	PhCHIBr	93
MeCH ₂ I	CH ₂ Cl ₂	RhCl(CO)(Ph ₃ P) ₂	2.0	CO	MeCH ₂ Cl	CH ₂ ICl	17
(Me) ₂ CHI	CH ₂ Cl ₂	RhCl(CO)(Ph ₃ P) ₂	18.0	CO	—	—	NR
PhCH ₂ Br	CH ₂ Cl ₂	RhCl(CO)(Ph ₃ P) ₂	2.0	CO	PhCH ₂ Cl	CH ₂ BrCl	10
PhCH ₂ Br	CH ₂ Cl ₂	RhCl(CO)(Ph ₃ P) ₂	22.5	CO	PhCH ₂ Cl	CH ₂ BrCl	71
MeCH ₂ Br	CH ₂ Cl ₂	RhCl(CO)(Ph ₃ P) ₂	21.0	CO	MeCH ₂ Cl	CH ₂ BrCl	0.5

^a A 2×10^{-2} M solution of the metal complex in a mixture of 5.0 ml R²R³CX₂² and 0.5 ml R¹X¹ 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 $\pm 2\%$ = % yield R¹X² = % yield R²R³CX¹X².

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 halogeno-carbons (R²R³CX₂²:R¹X¹ = 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



MeI > MeCH₂I > (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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¹ R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2797.

² P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511; J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136; I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 1969, 2604; A. J. Deeming and B. L. Shaw, *ibid.*, 1969, 1562; R. J. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5519; F. R. Jensen and B. Knickel, *ibid.*, 1971, **93**, 6339; J. S. Bradley, D. E. Connor, D. Dolphin, J. Labinger, and J. A. Osborn, *ibid.*, 1972, **94**, 4043; J. K. Stille and M. T. Regan, *ibid.*, 1974, **96**, 1508.

³ For recent reviews see, C. W. Bird, 'Transition Metal Intermediates in Organic Chemistry,' Academic Press, New York, 1967, ch. 7; G. N. Schrauzer, 'Transition Metals in Homogeneous Catalysis,' Marcel Dekker, New York, 1971, pp. 196-201.