Stereochemistry and Mechanisms of Electrophilic Cleavage Reactions of *cis*-[*threo*-PhCHDCHD)Mn(CO)$_4$PEt$_3$]

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Summary Cleavage reactions of the manganese–carbon bond of *cis*-[(*threo*-PhCHDCHD)Mn(CO)$_4$(PEt$_3$)] (I) by halogens and mercury(II) halides proceed with both retention and inversion of configuration at the α-carbon atom, depending on the reagent used and the solvent conditions; the occurrence of competitive processes involving initial electrophilic attack at both the α-carbon and the metal atoms is inferred.

THE stereochemistry and mechanisms of electrophilic cleavage reactions of transition-metal–alkyl compounds have recently elicited attention.[1,2] In an attempt to rationalize many apparently disparate observations, we have previously suggested that the preferred position of attack of an electrophilic reagent on a metal–alkyl compound may often be the occupied orbital of lowest ionization potential, *i.e.* the HOMO.[1] In the case of d^0 and d^{10} systems, the HOMO would be a filled metal–carbon σ bonding orbital, while for d^1—d^9 systems, inclusive, the HOMO is often a non-bonding orbital of essentially *d* character. With few exceptions, we were able to rationalize a variety of electrophilic cleavage reactions in terms of initial attack on a HOMO.[1]

In an attempt to extend our investigations to other metal systems, we have now studied the halogen and mercury(II) halide cleavage reactions of the compound *cis*-[(*threo*-PhCHDCHD)Mn(CO)$_4$PEt$_3$] (I).† The manganese(I) system is particularly interesting because previous calculations and photoelectron spectral data suggest that, for the parent methyl compound [MeMn(CO)$_5$], the manganese–carbon σ bonding orbital and the manganese non-bonding *d* orbitals are of comparable energy.[3] Thus attack at either carbon or metal may occur.

TABLE. Degree of retention of configuration of the cleavage reaction products

Expt.	Reagent	Solvent	% Retention (±7%)
1	Cl_2	n-C_5H_{12}	17
2	Cl_2	CCl_4	18
3	Cl_2	C_6H_6	13
4	Cl_2	CS_2	12
5	Cl_2	CH_2Cl_2	48
6	Cl_2	MeCN	49
7	Br_2	n-C_5H_{12}	33
8	Br_2	C_6H_6	33
9	Br_2	CH_2Cl_2	42
10	Br_2	Pyridine	61
11	Br_2	MeCN	52
12	I_2	n-C_5H_{12}	68
13	I_2	C_6H_6	70
14	I_2	$CHCl_3$	77
15	I_2	CH_2Cl_2	63
16	$HgCl_2$	CH_2Cl_2	<10
17	$HgBr_2$	CH_2Cl_2	<10

† Compound (I) was prepared by the reaction of *erythro*-PhCHDCHDOSO$_2$C$_6$H$_4$Me-*p* with K[Mn(CO)$_4$PEt$_3$]. The latter was chosen rather than the corresponding pentacarbonylate salt because the tosylate ion has been shown to be a poor leaving group with respect to weakly nucleophilic carbonylate anions (P. L. Bock and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 2826), and because it was anticipated that the phosphine-substituted alkyl compound (I) would be thermally more stable than the corresponding pentacarbonyl compound.

The results of our experiments are in the Table. In all cases, the products of the reactions are *cis*-[$XMn(CO)_4PEt_3$] and either PhCHDCHDX or PhCHDCHDHgX (X = Cl, Br, or I). Chlorination and bromination result in predominant inversion in non-polar solvents, the degree of retention generally increasing as solvent polarity increases. Iodination results in predominant retention, while mercuration results in inversion. The importance of solvent on the stereochemistry of the halogen cleavages seems to decrease in the order $Cl_2 > Br_2 > I_2$, the differences observed for the iodinations not being very significant. In no cases do cleavage reactions of *cis*-[$PhCH_2{}^{13}CH_2Mn(CO)_4PEt_3$] result in scrambling of the methylene carbon atoms.

The results in the Table strongly suggest that the halogenations proceed by two competing pathways. As suggested previously,[1] retention might be expected to result from either a classical S_E2 (retention)[4] process (frontside attack at carbon), or *via* reductive elimination‡ of alkyl halide from an intermediate of the type [$PhCHDCHDMn^{III}X(CO)_4PEt_3$]X (II) (an expected product from attack at the metal). Similarly, inversion may result from either an S_E2 (inversion)[4] process (backside attack at carbon), or by nucleophilic attack by the free halide ion of (II) on the α-carbon atom, with concomitant displacement of the manganese(I) product. As an electron-transfer process to generate (II) should be less likely to occur in non-polar solvents, experiments 1—4 suggest strongly that chlorination here proceeds by an S_E2 (inversion) process, *i.e.* by interaction of the vacant σ^* orbital of the chlorine with the carbon–manganese σ-bonding orbital.[1] However, as it seems unlikely that increasing solvent polarity should tend to make an S_E2 (retention) process more favourable, the increasing degree of retention observed in experiments 5 and 6 seem more consistent with the formation of (II), followed by reductive elimination, as occurs with the compound *threo*-[$PhCHDCHDFe(CO)_2(\eta\text{-}C_5H_5)$].[1] An interesting contrast with the iron compound, however, is the lack of methylene scrambling observed during cleavage of the manganese compound. Possibly reductive elimination from (II) occurs faster than does phenyl migration.

The remaining results in the Table seem to be consistent with this hypothesis of two competing processes. As the halogens increase in size, their σ^* orbitals become more diffuse and overlap with the carbon σ orbital would decrease, making the S_E2(inversion) process less favourable. It also seems likely that solvation problems accompanying formation of (II) would be less serious with the heavier halogens.

The other mechanisms discussed above are possible, but less likely. Steric factors should mitigate against an S_E2-(retention) process becoming more important on going to the heavier halogens, and nucleophilic attack of halide ion on (II) seems most unlikely as such a process should become much more important for the more nucleophilic heavier halide ions. Chain radical processes, which might result in epimerization, should be most important for chlorine in non-polar solvents, in direct contrast to our observations.

The mercuration reactions appear to proceed by an S_E2-(inversion) process, as has been previously reported for alkyl cobaloxime compounds.[5] We believe that direct attack at the metal by the mercury(II) halides is hindered in these cases for steric reasons. The mechanism suggested is consistent with a brief kinetic study of the mercury(II) cleavage of [$MeMn(CO)_5$],[6] but the observed stereochemistry is not as earlier predicted.

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‡ We make no mechanistic implications in using this term.

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