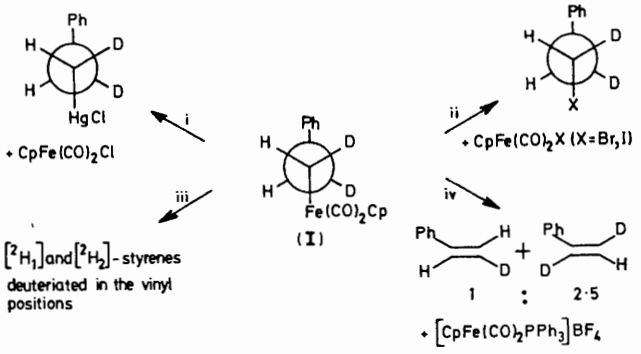
Stereochemistry of Alkyl Transfer and Olefin Elimination Reactions of Transition-metal Phenethyl Complexes

By DAVID SLACK and MICHAEL C. BAIRD*
(*Department of Chemistry, Queen's University, Kingston, Canada*)

Summary Cleavage of the iron–carbon bond of *threo*-PhCHDCHDFe(CO)$_2$Cp (I) by bromine, iodine, and mercuric chloride proceeds with retention of configuration of the alkyl ligand, hydride abstraction from (I) by triphenylmethyl fluoroborate proceeds predominantly by a *trans* elimination reaction, and reaction of (I) with $PdCl_2(NCPh)_2$ gives a phenethylpalladium complex which eliminates deuteriated styrenes with complete loss of stereospecificity.

STEREOCHEMICAL data have recently been offered in support of mechanisms for a variety of reactions of σ-bonded transition-metal alkyl compounds, *i.e.* alkyl transfer[1,2] and migration,[2,3] halogen cleavage,[3–6] and elimination[7] reactions. In order to avoid the inconveniences of using secondary alkyl groups for such studies, Whitesides and his co-workers have demonstrated the advantages of using the Bu^{t}CHDCHD– unit, in particular the compound BuC^{t}HDCHDFe(CO)$_2$Cp (II)[1,3]. Deuterium-decoupled ^{1}H n.m.r. spectroscopy permits discrimination between *threo* and *erythro* diastereoisomers as the latter invariably exhibits larger vicinal H–H coupling constants, and thus information about the stereochemistry of reactions of the alkyl ligand is easily obtained.

In parallel with the work of Whitesides, we have explored the usefulness of the *threo* and *erythro* forms of the 2-phenyl-1,2-dideuterioethyl group as a probe for the stereochemistry of reactions of primary alkyl ligands. In some cases, our results differ considerably from those of Whitesides; the Scheme shows reactions of *threo*-PhCHDCHDFe(CO)$_2$Cp (I) ($^3J_{threo}$ 4·8 Hz, $^3J_{erythro}$ 12·6 Hz).†



Cp = cyclopentadienyl

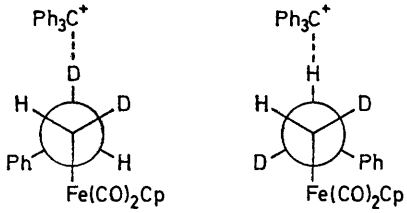
SCHEME

Reagents: i, $HgCl_2$; ii, X_2; iii, $PdCl_2(NCPh)_2$; iv, a, $Ph_3C^+BF_4^-$, b, PPh_3.

Reactions of both (I) and (II) with $HgCl_2$ proceed with retention of configuration, consistent with an S_E2 (cyclic) mechanism.[8] These results contrast with the inversion observed for the similar reaction of a Bu^{t}CHDCHD cobaloxime complex with $HgCl_2$, for which an S_E2 (open)[8] mechanism has been proposed.[2] Although the *threo* and *erythro* isomers of PhCHDCHDHgCl surprisingly exhibit

† Commercially available *cis*-β-methoxy styrene was converted into *erythro*-PhCHDCHDOMe using $RhCl(PPh_3)_3$, [J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), **1966**, 1711] and deuterium gas. Hydroiodic acid cleavage of the ether followed by treatment of the resulting alcohol with tosyl chloride yielded *erythro*-PhCHDCHDOTs, which was converted into (I) with Na[CpFe(CO)$_2$].

identical n.m.r. spectra in $CDCl_3$ solution, their vicinal H–H coupling constants are 6·8 and 9·0 Hz, respectively, in pyridine. The changes are probably a result of partial co-ordination of the solvent to the mercury, thereby for steric reasons increasing the contributions of the *trans*-configurations to the time-averaged n.m.r. spectra of these stereoisomers. Bromination of *threo*-PhCHDCHDHgCl in pyridine at 0 °C proceeds with retention of configuration to give *threo*-PhCHDCHDBr ($^3J_{threo}$ 6·4 Hz, $^3J_{erythro}$ 8·4 Hz); similar results have been observed for secondary alkylmercury compounds,[9] although this appears to be the first such study of a primary alkylmercury compound.



Reactions of (I) and (II) with halogens clearly proceed by different mechanisms, as the former results in retention, the latter in inversion of the alkyl group. Inversion has been noted previously for halogen cleavage reactions of alkylcobaloximes,[5] and retention for similar reactions of alkylmanganese[4] and -palladium[6] compounds, but our results provide the first evidence for different mechanisms for two quite similar compounds of the same metal. Although solvent effects have not been studied in detail, they do not explain the differences, which may lie in steric factors. The Bu^t group is undoubtedly much bulkier than the phenyl group and could more effectively shield the iron from the type of direct attack which an S_E2 (cyclic) mechanism involves.[8]

Treatment of (I) with $Ph_3C^+BF_4^-$ results in β-hydride abstraction to form triphenylmethane and deuteriated styrene complexes of the type $[CpFe(CO)_2(olefin)]BF_4$. Treatment of the latter with triphenylphosphine liberated the styrenes, which were identified by their n.m.r. spectra. The high degree of stereospecificity of the hydride abstraction by the triphenylmethyl carbonium ion is interesting because the major products (85% of the total) are those expected for *trans*-elimination from (II) i.e. from the less stable *gauche* rotamers.

To our knowledge, no other stereochemical data are available for this type of reaction, the mechanism of which is rather controversial at present.[10] Our results are certainly in accord with a direct electrophilic attack on the β-hydrogen (deuterium), while the observed kinetic isotope effect of about 2·5, derived from the ratios of the products, is also consistent with C–H(D) bond-breaking being very important in the rate-determining step.[11]

In direct contrast is the lack of stereospecificity of the olefinic products of the reaction of (I) and $PdCl_2(NCPh)_2$. Alkyl transfer from (I) to the palladium undoubtedly occurs, probably with retention of configuration. Elimination of the styrenes must involve a labile equilibrium between hydridostyrene and 1-phenylethyl complexes, however, as the products $PhCH:CD_2$ and $PhCD:CH_2$ cannot result from *cis* and/or *trans* eliminations directly. Similar scrambling has been observed in the decompositions of *threo*-PhCHDCHDCO$RhCl_2(PPh_3)_2$,[12] *threo*-PhCHDCHD-$IrCl_2CO(PPh_3)_2$,[12] and (*threo*- and *erythro*-2,3-dimethylpentanoyl)pentacarbonylmanganese(I).

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