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Stereochemistry and Mechanisms of Mercury(II) Chloride Cleavage of *threo*-1,2-Dideuteriophenethyl Compounds of Iron, Manganese, and Tungsten

D. DONG, D. A. SLACK, and M. C. BAIRD*

Mercury(II) chloride cleaves the alkyl ligands from *threo*-PhCHDCHDFe(CO)$_2$(η^5-C$_5$H$_5$) and *trans*-(*threo*-PhCHDCHD)W(CO)$_2$(PEt$_3$)(η^5-C$_5$H$_5$) with retention of configuration, while that from *cis*-(*threo*-PhCHDCHD)Mn(CO)$_4$PEt$_3$ is cleaved with inversion of configuration, to give phenethylmercury(II) chloride. The first two reactions are believed to proceed via S$_E$(oxidative) processes, the last via an S$_E$2(inversion) mechanism. The differences are rationalized in terms of the expected energy gap between the HOMO and the metal–carbon σ-bonding orbital for each compound.

Cleavage of alkyl–, alkenyl–, or aryl–metal σ bonds by mercury(II) to give the corresponding organomercury(II) compounds (eq 1) is a reaction of great generality and even

$$RML_n + HgX_2 \rightarrow XML_n + RHgX \qquad (1)$$

R = alkyl, alkenyl, aryl   L = neutral, anionic ligands

X = halide, acetate, etc.

of environmental importance[1] but one which is surprisingly poorly understood mechanistically when M is a transition metal. Thus although, as Jensen and Rickborn[2] and Matteson[3] have observed, considerable is known about metal-exchange reactions of organometallic compounds of the main-group metals, much less is known about similar reactions or organotransition-metal compounds.[4,5]

A key datum in the elucidation of the mechanism of a reaction such as (1), when the α-carbon atom of R is saturated, is the stereochemistry of the transformation at the α-carbon atom. We have previously demonstrated the advantages of the primary alkyl ligand *threo*-α,β-dideuteriophenethyl (*threo*-PhCHDCHD) in studying the stereochemistry of a variety of olefin elimination,[6,7] alkyl migration,[7,8] halogen cleavage,[9] and sulfination[8] reactions. We now consider the stereochemistry of mercury(II) chloride cleavage reactions of the compounds *threo*-PhCHDCHDFe(CO)$_2$(η^5-C$_5$H$_5$) (I), *cis*-(*threo*-PhCHDCHD)Mn(CO)$_4$PEt$_3$ (II), and *trans*-(*threo*-PhCHDCHD)W(CO)$_2$(PEt$_3$)(η^5-C$_5$H$_5$) (III), all of

which react with mercury(II) chloride, as in (1), to give PhCHDCHDHgCl. When considered in conjunction with pertinent kinetics studies on similar compounds of the types η^5-C$_5$H$_5$Fe(CO)$_2$R,[4,10] RMn(CO)$_5$,[11,12] and η^5-C$_5$H$_5$M(CO)$_3$R (M = Mo, W),[13] the stereochemical data lead to reasonable conclusions concerning the mechanisms of the reactions. Brief mention of some of this work has been made previously.[14,15]
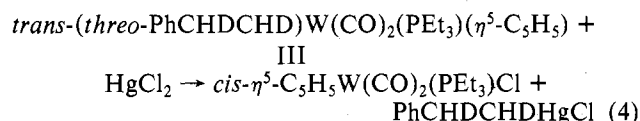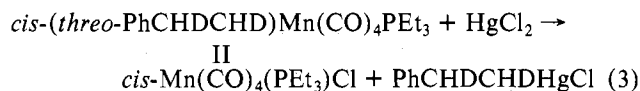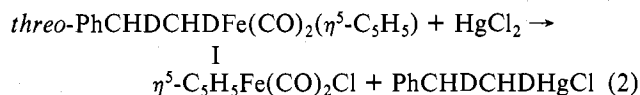
Experimental Section

IR spectra were run on a Perkin-Elmer 180 spectrometer and NMR spectra were taken on a Bruker HX60 spectrometer. Compounds I,[9] II,[8] and III[8] were prepared as described in the literature, by treating *erythro*-PhCHDCHDOTs with the anions [η^5-C$_5$H$_5$Fe(CO)$_2$]$^-$, [Mn(CO)$_4$PEt$_3$]$^-$, and [η^5-C$_5$H$_5$W(CO)$_2$PEt$_3$]$^-$, respectively. All solvents were dried and deoxygenated before use.

Mercuration reactions were carried out by treating each phenethylmetal compound with a slightly more than equimolar amount of HgCl$_2$ in acetone (I) or methylene chloride (II, III). The courses of the reactions could be followed by observing the disappearance of the carbonyl stretching bands of I,[9] II,[8] and III[8] and the appearance of the carbonyl stretching bands of the products η^5-C$_5$H$_5$Fe(CO)$_2$Cl, *cis*-Mn(CO)$_4$(PEt$_3$)Cl, and *trans*-η^5-C$_5$H$_5$W(CO)$_2$(PEt$_3$)Cl, respectively. In all cases, the reactions appeared to proceed very cleanly, with no formation of metal–mercury compounds, as has been observed in some cases.[4] After completion of the reactions, the organomercury products were obtained by removing the solvent under reduced pressure, extracting the solids with petroleum ether, and then recrystallizing the residues from methylene chloride–petroleum ether. Phenethylmercuric chloride is a white, crystalline compound, mp 168–169 °C (lit.[16] 165.5–166 °C).
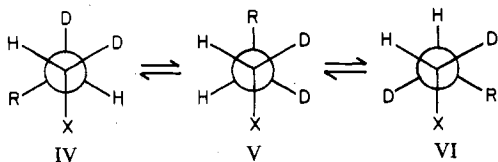
Results and Discussion

As indicated by the infrared spectra of the reaction solutions and the generally high yields of phenethylmercuric chloride (60–80%), the reactions proceeded as in eq 2–4.

threo-PhCHDCHDFe(CO)$_2$(η^5-C$_5$H$_5$) + HgCl$_2$ →
$$\text{I}$$
$$\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{Cl} + \text{PhCHDCHDHgCl} \quad (2)$$

cis-(*threo*-PhCHDCHD)Mn(CO)$_4$PEt$_3$ + HgCl$_2$ →
$$\text{II}$$
$$\textit{cis}\text{-Mn(CO)}_4\text{(PEt}_3\text{)Cl} + \text{PhCHDCHDHgCl} \quad (3)$$

trans-(*threo*-PhCHDCHD)W(CO)$_2$(PEt$_3$)(η^5-C$_5$H$_5$) +
$$\text{III}$$
$$\text{HgCl}_2 \rightarrow \textit{cis}\text{-}\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2\text{(PEt}_3\text{)Cl} +$$
$$\text{PhCHDCHDHgCl} \quad (4)$$

The deuterium-decoupled ^{1}H NMR spectra of the deuterated phenethylmercury chloride products in CDCl$_3$ were all identical and, indeed, were identical with the spectrum of an epimeric sample of PhCHDCHDHgCl (δ(*CHD*Ph) = 2.94, δ(*CHD*Hg) = 2.22, $^3J_{HH}$ = 7.4 Hz). In dry pyridine, however, the resonances of the threo and erythro diastereomers (δ(*CHD*) = 2.93, δ(*CHD*Hg) = 2.13) are readily distinguished because of their different vicinal hydrogen coupling constants, 6.8 and 9.0 Hz, respectively.

Possible reasons for the solvent effects merit discussion. The observed NMR parameters of a compound of the type RCHDCHDX are weighted averages of the three, rapidly interconverting, staggered conformations IV–VI,[7,17,18] illustrated here for one enantiomer of the threo diastereomer.


As steric factors appear to be very important in deciding the relative stabilities of the trans and gauche configurations,[17] V is generally favored, and its NMR parameters contribute the most to the observed NMR spectra.

Although the steric requirements of the –HgCl moiety have been a subject of some controversy,[19] the diastereomers *threo*- and *erythro*-Me$_3$CCHDCHDHgCl exhibit quite different vicinal hydrogen coupling constants (comparable with those of the corresponding diastereomers of Me$_3$CCHDCHDCl and Me$_3$CCHDCHDBr).[17] As the resonances of the threo and erythro isomers of PhCHDCHDCl and PhCHDCHDBr are readily distinguishable,[9] the coincidence of the spectra of the two isomers of PhCHDCHDHgCl in CDCl$_3$ is presumably not solely a result of steric factors.

Stabilization of the gauche conformation could occur, however, if a bonding interaction between the arene ring of the phenethyl group and the mercury is possible. Space-filling molecular models suggest that very close contact between one edge of the arene ring and the mercury could indeed occur, and while such arene complexes have never been isolated, arene complexes of mercury(II) halides are known.[20,21] Although the equilibrium constant for a reaction such as (5) would be

PhCHDCHDHgCl + nC$_5$H$_5$N ⇌
$$\text{PhCHDCHDHgCl(C}_5\text{H}_5\text{N)}_n \quad n = 1, 2 \quad (5)$$
$$\text{VII}$$
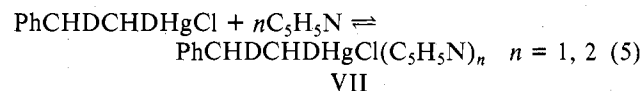
expected to be very small,[24,25] labile three- or four-coordinate species such as VII would probably be formed to some extent when PhCHDCHDHgCl is dissolved in pyridine. The result would be not only disruption of the arene–mercury coordination but also an increase in the average (on the NMR time

scale) steric requirements of the mercury. Both effects would result in stabilization of the trans relative to the gauche conformation, readily explaining the ^{1}H NMR results in pyridine. Similar observations and interpretations have been made previously[26] for the ^{1}H NMR spectra of substituted 3-arylpropylmercury halides in pyridine and in nondonor solvents.

On the basis of the assignments in pyridine, reactions 2 and 4 proceeded cleanly (>90%) with retention of configuration while reaction 3 proceeded with inversion. Verification of the assignments was made by cleaving the presumed *threo*-PhCHDCHDHgCl, prepared as in (2), with bromine in pyridine. Similar cleavage reactions of secondary alkylmercury compounds proceed with retention of configuration[2] and, as expected, *threo*-PhCHDCHDBr was obtained here.

The observation of retention of configuration in (2) is consistent with the work of Whitesides on the mercuration of the very similar *threo*-Me$_3$CCHDCHDFe(CO)$_2$(η^5-C$_5$H$_5$).[18] A detailed kinetics study of the mercuration reactions of a wide variety of compounds of the type η^5-C$_5$H$_5$Fe(CO)$_2$R^4 has shown that while the course and the mechanism of such reactions are strongly dependent on the nature of R, primary alkyl compounds are generally cleaved as in (2), phenethyl being quite typical in this regard. The kinetics data were interpreted[4] in terms of a reversible oxidation of η^5-C$_5$H$_5$Fe(CO)$_2$R to give an intermediate, VIII, containing an iron–mercury bond (6), a mechanism which we will hereafter refer to as an example of an S$_E$(oxidative) process.[27]

$$\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{R} + 2\text{HgCl}_2 \rightleftharpoons$$
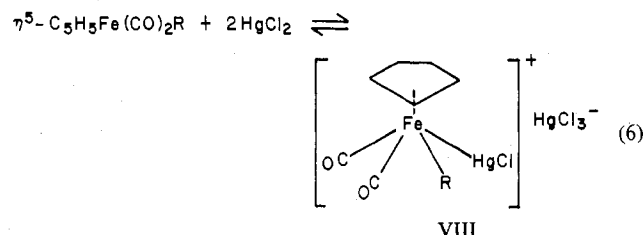
$$\text{VIII}$$

Formation of VIII was postulated to be reversible because it had been found[28] that mercuration of resolved compounds of the type η^5-C$_5$H$_5$Fe*(CO)(PPh$_3$)R with a deficiency of mercuric halide yields unreacted starting material which is partially racemized. The stereochemical data reported here are then consistent with reductive elimination, with retention of configuration at the α-carbon atom of R, as postulated by Wojcicki.[4,29]


$$\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{Cl} + \text{HgCl}_2 \quad (7)$$
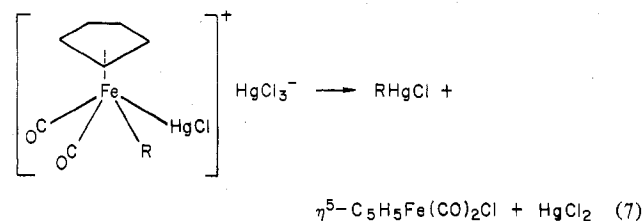
As net retention at the metal is also observed for similar mercuration reactions of the compounds η^5-C$_5$H$_5$Fe(CO)(PPh$_3$)R,[30] presumably chloride ion coordinates to the generated [η^5-C$_5$H$_5$Fe(CO)(PPh$_3$)]$^+$, a 16-electron species, before complete racemization can occur. Interestingly, as shown by Flood[31] using η^5-C$_5$H$_5$Fe(CO)$_2$CD$_2$CH$_2$Ph, methylene scrambling does not occur during mercuric halide cleavage of the phenethyl compound, as it does during halogen cleavage reactions.[9,31] The reasons for the difference are not clear, as the same type of oxidized species is believed to occur in both cases. It may be that, while a species such as [η^5-C$_5$H$_5$Fe-(CO)$_2$(CH$_2$CH$_2$Ph)X]$^+$ is sufficiently long-lived that scrambling can occur, a species such as [η^5-C$_5$H$_5$Fe(CO)$_2$-(CH$_2$CH$_2$Ph)(HgCl)]$^+$ eliminates the alkylmercury chloride

too quickly to allow scrambling to occur. Precedents for this hypothesis are scarce, but we note, for instance, that reductive elimination of alkanes from di- and trialkylmetal compounds is generally much more facile than is reductive elimination of alkyl halides.[32] Although too little is known of mechanisms of reductive elimination reactions[33] to predict how the postulated intermediates might behave, it does seem that simultaneous coordination of two "one electron donor" ligands[34] of low electronegativity (R·, ClHg·, H·) often results in complexes which are thermodynamically unstable.

The mechanistic implications of the stereochemistry of the mercury(II) chloride cleavage of III (retention) are less clear. Although much less is known of the chemistry of compounds of the type η^5-C$_5$H$_5$M(CO)$_2$(L)R (M = Mo, W; L = tertiary phosphine; R = alkyl, aryl) than is the case with the iron system discussed above, the course of the mercuration reaction (4) corresponds well with the chemistry of similar compounds, as reported in the literature.[35] Compound III was chosen for study as a representative of the group 6 metals for a number of reasons. The less nucleophilic, unsubstituted carbonylate anions [η^5-C$_5$H$_5$M(CO)$_3$]$^-$ (M = Mo, W) were found not to displace tosylate from *erythro*-PhCHDCHDOTs,[9] and the phosphine-substituted phenethyl compounds were expected to be more robust thermally than the unsubstituted analogues, as is often the case.[36] The tungsten compound, III, has been investigated in preference to the molybdenum analogue because preliminary studies of halogenation reactions of the former yielded products which were much better defined (see below).

The only kinetics study to date of mercuration reactions of compounds of the type η^5-C$_5$H$_5$M(CO)$_3$R (M = Mo, W; R = pyridinomethyl)[13] was complicated by the fact that the course of the reaction seemed to vary as the concentration of reagents was changed. The study was carried out on aqueous solutions, however, and the data may not be at all comparable to the other studies. In fact, η^5-C$_5$H$_5$M(CO)$_3$Me (M = Mo, W) do not react with mercury(II) halides in nonaqueous solvents.[35,37] Although the kinetics data were interpreted in terms of a classical S$_E$2 attack, it is interesting to note that they also suggested a bimolecular reaction between mercury(II) and the organometallic substrate to form a rather ill-defined complex. Thus an S$_E$(oxidative) process (eq 8) may

$$RHgCl + \eta^5\text{-}C_5H_5W(CO)_2(PEt_3)Cl \quad (8)$$
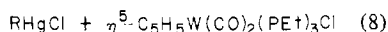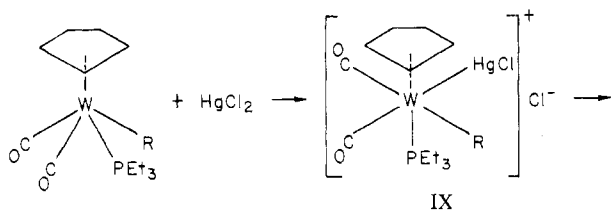
also occur, as postulated above for the iron system. Indeed, for reasons outlined below, we believe that an oxidative mechanism may well warrant increased consideration in future mechanistic studies on this type of compound.

Intermediates such as IX are not entirely without precedent, as compounds of the type η^5-C$_5$H$_5$M(CO)$_2$X$_3$[38] have been reported and, indeed, halogenation of III gives an unstable compound which appears to be either [η^5-C$_5$H$_5$W(CO)$_2$-(PEt$_3$)(CHDCHDPh)I]I or η^5-C$_5$H$_5$W(CO)(PEt$_3$)-(CHDCHDPh)I$_2$.[39] Reductive elimination of phenethylmercury chloride from IX would be analogous to the similar reaction postulated above in (7), thus explaining the observed retention of configuration.

The observation of inversion of configuration during the mercuration of II (mercury(II) bromide gave similar results) is quite inconsistent with an S$_E$(oxidative) process and suggests rather a classical S$_E$2 inversion mechanism, involving a bi-

molecular, backside attack by the electrophilic reagent on the α-carbon atom. Experiments conducted using *cis*-PhCH$_2$*CH$_2$Mn(CO)$_4$PEt$_3$, labeled at the α-carbon atom to the extent of 5% with carbon-13, gave PhCH$_2$*CH$_2$HgCl ($\delta(\alpha$-CH$_2$) = 35.2, $\delta(\beta$-CH$_2$) = 34.6 from Me$_4$Si) in which no methylene scrambling had occurred. Again relevant kinetics studies reported in the literature are consistent with a bimolecular process[11,12] although, as with the tungsten system, relatively little is known of the chemistry of such alkylmanganese compounds with electrophilic reagents. Halogen cleavage reactions of II appear to proceed by competing S$_E$2(inversion) and S$_E$(oxidative) processes,[15] and while it is not obvious why mercury(II) chloride would prefer only the former, we note that other octahedral d^6 complexes behave similarly. Thus while mercuration reactions of alkylcobaloximes appear to proceed entirely via a bimolecular, S$_E$2-(inversion) process,[40-42] halogen cleavage reactions proceed via an S$_E$(oxidative) process.[42-49]

We have recently[9] considered the different possible reaction pathways for electrophilic cleavage reactions of alkylmetal compounds from the points of view of both the metal electron configuration and the symmetries and relative energies of the (potentially) interacting orbitals. In the cases of d^0 and d^{10} metal systems, where the highest occupied molecular orbital (HOMO) of the metal compounds is predominantly of metal–carbon σ-bonding character, concerted reactions involving direct electrophilic attack at carbon by molecular species should be governed by orbital symmetry considerations. In contrast, in those cases of d^1–d^9 systems where the metal–carbon σ-bonding orbital exhibits a significantly higher ionization potential than do filled, essentially nonbonding metal d orbitals, attack at the latter, i.e., oxidative processes, may occur. In the case of the aforementioned iron system, photoelectron data for η^5-C$_5$H$_5$Fe(CO)$_2$Me show that the iron–carbon σ-bonding orbital lies some 33 kcal/mol below the HOMO, a filled d orbital.[50] Consistent with this large difference, halogenation and mercuration reactions *appear* to proceed solely via S$_E$(oxidative) processes.[4,9,30,51]

Extending the argument, we note that the tungsten compound, III, not only adds iodine to form a tungsten(IV) species but may also undergo mercuration via an S$_E$(oxidative) process. In the case of η^5-C$_5$H$_5$W(CO)$_3$Me, photoelectron spectra indicate an energy separation between the carbon–tungsten σ-bonding orbital and the HOMO of some 38 kcal/mol,[52] suggesting an even greater proclivity for S$_E$(oxidative) processes than that exhibited by the iron system.

In contrast, halogenation and mercuration reactions of II proceed by both (presumably) concerted attack at the manganese–carbon σ-bonding orbital and S$_E$(oxidative) processes. As we have pointed out previously,[15] however, photoelectron data for MeMn(CO)$_5$ suggest an energy separation between the manganese–carbon σ-bonding orbital and the HOMO of only about 18 kcal/mol.[53,54] Although this is still a very large energy difference, the combination of steric and electronic effects brought about by substitution of carbon monoxide by triethylphosphine and methyl by phenethyl may enable competitive attack at both types of orbitals of II to occur.

Although photoelectron spectroscopy data for alkylcobaloximes do not appear to be available, the electronic spectrum of a very similar type of compound, [MeCo^{III}([14]aneN$_4$)-(H$_2$O)]$^{2+}$,[55] has been interpreted in terms of the cobalt–methyl bonding orbital being the HOMO. Thus it seems quite possible that, for the alkylcobaloximes, the cobalt–carbon σ-bonding orbital and the nonbonding d orbitals are of comparable energy.

threo-1,2-Dideuteriophenethylmetal Compounds

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research, the latter for a graduate scholarship to D.A.S.

Registry No. I, 55102-02-8; II, 67347-86-8; III, 67423-85-2; HgCl₂, 7487-94-7; *threo*-PhCHDCHDHgCl, 55057-79-9; *erythro*-PhCHDCHDHgCl, 55057-78-8.

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