Journal of Organometallic Chemistry, 74 (1974) C17—C20

Preliminary communication

THE USE OF CHIRAL IRON COMPLEXES IN MECHANISTIC STUDIES: THE DECARBONYLATION OF CARBONYL(*PENTAHAPTO*-CYCLOPENTADIENYL)TRIPHENYLPHOSPHINEIRON ACYLS

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(Received April 24th, 1974)

Summary

Photochemical decarbonylation of (+)-(*R*)-$(h^5\text{-}C_5H_5)Fe(CO)(Ph_3P)C(O)Et$ gave (−)-(*S*)-$(h^5\text{-}C_5H_5)Fe(CO)(Ph_3P)Et$ 43% optically pure, thus establishing the stereochemical course of the reaction at the iron center.

There has been considerable attention focused on carbonylation and decarbonylation reactions of transition metal complexes [1]. To date, studies on the photochemical decarbonylation of both dicarbonyl(*pentahapto*-cyclopentadienyl)iron and carbonyl(*pentahapto*-cyclopentadienyl)triphenylphosphineiron acyls, which give the corresponding alkylirons, have provided the following important results about the stereochemistry of these reactions: (i) Alexander has shown [2] that a terminal rather than an acyl CO group is expelled from $(h^5\text{-}C_5H_5)Fe(CO)_2{}^{13}C(O)Me$, (ii) Whitesides et al. [3] showed that *erythro*-3,3-dimethylbutyl-1,2-d_2-carbonyl(*pentahapto*-cyclopentadienyl)triphenylphosphineiron was obtained by photochemical decarbonylation of the corresponding *erythro*-pentanoyl complex which established that there was retention of configuration at the α-carbon atom of the metal alkyl; (iii) Wojcicki [4] in an equally significant series of studies found that the diastereomerically related pairs of enantiomers $(h^5\text{-}C_5H_5)Fe(CO)(Ph_3P)C(O)CH_2CH(Me)Ph$- (*R*,*R*—*S*,*S* and *R*,*S*—*S*,*R*)* and $(h^5\text{-}C_5H_3\text{-}1\text{-}Me\text{-}3\text{-}Ph)Fe(CO)(Ph_3P)C(O)Me$ (*R*,*R*—*S*,*S* and *R*,*S*—*S*,*R*)** on decarbonylation gave the alkyl derivatives with

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*For the purposes of establishing *R* and *S* designations for chiral iron centers of the type $(h^5\text{-}C_5H_5)Fe(CO)(Ph_3P)X$ we are choosing to define the sequence priority as $Ph_3P > h^5\text{-}C_5H_5$ i.e., 1 and 2 unless X is of higher atomic mass than phosphorus e.g. X = I in which case we take $X > Ph_3P > h^5\text{-}C_5H_5$. The essential feature is that these two ligands are always ordered as 1, 2 or 2, 3. To accommodate other situations it is probably better to assign *polyhapto* ligands higher priorities than *monohapto* ones e.g., $h^5\text{-}C_5H_5 > h^2\text{-}C_2H_4 > h^1\text{-}CH_3$. The others are relatively straight forward $h^1\text{-}C(O)OMe > h^1\text{-}CO > h^1\text{-}C(\overset{+}{O}Me)Me > h^1\text{-}C(O)Me > h^1\text{-}C(\overset{+}{N}HMe)Me > h^1\text{-}Et$.

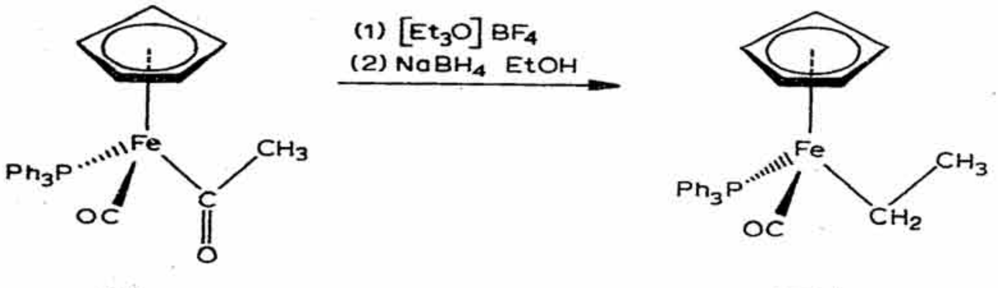
**The rules for establishing the *R* and *S* designations associated with the chirality of π-complexes are those suggested by IUPAC [5].

a high degree of stereospecificity at iron. These last studies could not establish the configurations of the reactants and products.

The purpose of this communication is to establish unambiguously the stereochemical course of the photochemical decarbonylation of the carbonyl *pentahapto*-cyclopentadienyltriphenylphosphineiron acyls at the iron centers. The results of our study do not depend upon the knowledge of the absolute configuration of the chiral complexes used. We have assigned the absolute stereochemistries of the species described below on the basis of a comparison of their circular dichroism (CD) spectra* to that of (+)-(*R*)[(h^5-C_5H_5)Fe(CO)-(Ph_3P){C((*S*)NHCH(Me)Ph)Me}]BF_4 [6] whose absolute configuration has been determined by X-ray crystallography [7].

The starting acyls (+)-(*R*)-(h^5-C_5H_5)Fe(CO)(Ph_3P)C(O)Me (I) ($[\alpha]^{27}_{436}$ −1550°, lit. [8b] −1550°) and (+)-(*R*)-(h^5-C_5H_5)Fe(CO)(Ph_3P)C(O)Et (II) ($[\alpha]^{27}_{436}$ −800°) were obtained, in ca. 26% yield, using a modification of Brunner's [8b] procedure for the synthesis of I. The complex I was converted into (+)-(*R*)-(h^5-C_5H_5)Fe(CO)(Ph_3P)Et (IIIa) ($[\alpha]^{27}_{436}$ −256°) by the known [6] reaction sequences (Scheme 1) which leaves the iron center untouched**. The intermediate salt [(+)-(*R*)-(h^5-C_5H_5)Fe(CO)(Ph_3P){C(OEt)Me}]BF_4 (IV) ($[\alpha]^{27}_{436}$ −1150°) has a CD spectrum of the same sense as those for both II and IIIa.

SCHEME 1



(I)

(IIIa)

The propanoyl II was photolysed in degassed THF solutions (λ 3600 Å) to give (−)-(*S*)-(h^5-C_5H_5)Fe(CO)(Ph_3P)Et (IIIb) ($[\alpha]^{27}_{436}$ +110°; 43% optically pure). The stereochemical change is shown in Scheme 2.

The complexes IIIa and IIIb are clearly enantiomeric as can be seen from their CD spectra (Fig. 1). The complex IIIb was separated by chromatography [Al_2O_3 (3% H_2O) benzene]. In a similar series of experiments I gave, after brief irradiation and chromatographic separation [Al_2O_3 (3% H_2O) benzene/pentane 1/4 v/v], optically active (−)-(*S*)-(h^5-C_5H_5)Fe(CO)(Ph_3P)Me (V)

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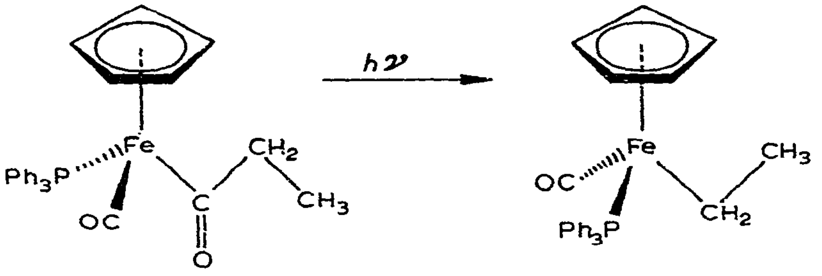
*The CD spectra of a variety of resolved (h^5-C_5H_5)Fe(CO)(Ph_3P)X complexes are very similar, in the range 300-500 nm and are thought to depend only on the absolute configuration at the iron center [8]. Additional support for this approach can be found in the following. The expected *trans*-(1*R*,-2*R*)-1-phenylcyclopropane was obtained in a cyclopropanation [9] reaction using (+)-(*R*)-(h^5-C_5H_5)Fe(CO)(Ph_3P)CH_2O-(−)-menthyl, assigned in this manner. Both of the diastereomers (+)-(*R*)-(h^5-C_5H_5)Fe(CO)(Ph_3P)-(1*S* and 1*R*)CH(OEt)Me have similar CD spectra [10].

**We have assumed that the optical purity of IIIa is 100%. The stereoselectivity of the decarbonylation based on this assumption compares quite favorably to that found by NMR techniques [4].



(II) (IIIb)

SCHEME 2

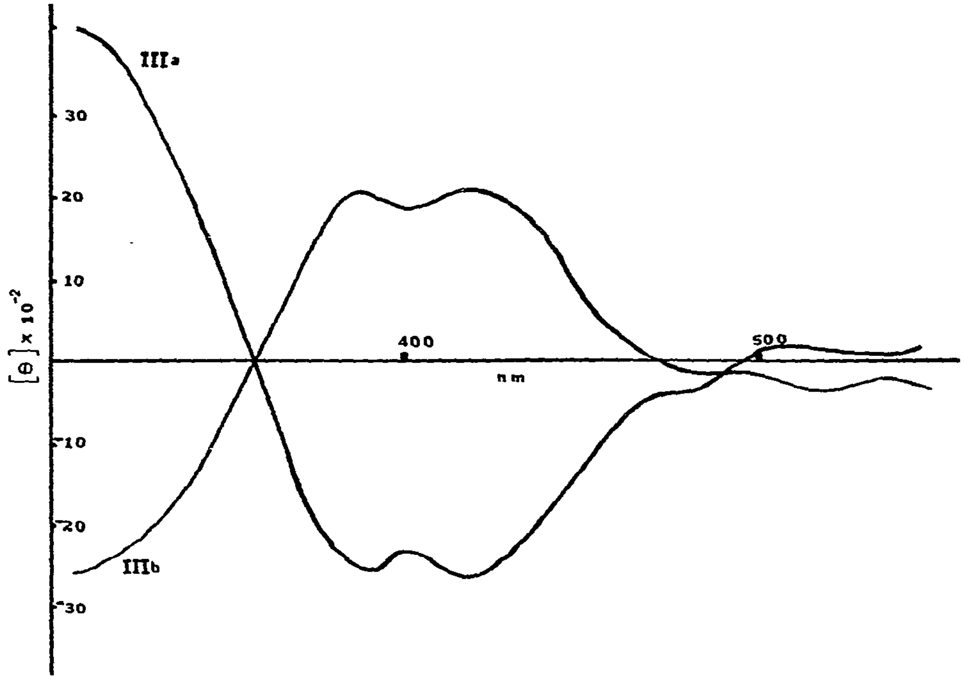


Fig. 1. The CD spectra of IIIa and IIIb in benzene.

([α]$^{27}_{436}$ +140°). However, in this case, unlike IIIb, the extent of racemization cannot be determined. Irradiation of V or extended radiation of I leads to racemic V. To prevent this secondary photochemical racemization and photochemical decomposition* the conditions chosen for the photolysis are fairly crucial.

These results show that there is a high degree of stereoselectivity which

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*The optimum conditions for the photolysis were found by monitoring the reactions (using UV-vis. spectra in the range 300-650 nm) as a function of time. After periods greater than 20 minutes the formation of product, which absorbs more strongly than reactant at 3600 Å, was no longer linear with time. By choosing 10 min irradiation time (c 0.02 g/25 ml) sufficient product (ca. 5% conversion) could be obtained. In a typical run 50 × 3 ml sealed samples were irradiated and the combined products separated from the starting acyls which were recovered optically pure.

results in largely an inversion of configuration at iron (in a topological sense, *R* to *S*) in going from II to IIIb and in going from I to V. However, we would like to emphasize that this does not imply that there is a Walden-like inversion taking place. Rather, the simplest mechanism which is consistent with our results is that the ethyl (or methyl) group migrates into the site vacated by the leaving CO group.

Acknowledgments

We thank the National Science Foundation for financial support (A.D. grant GP−3733X) and the Ford Foundation (N.M. a Doctoral Fellowship). In addition, we would like to thank Professors M.S. Wrighton, G.M. Whitesides and A. Wojcicki for helpful discussions and for communicating their results to us prior to publication.

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