Optically Active Transition-metal Complexes. Part 79.† Optically Active Organoiron Enantiomers formed by HF Cleavage of the P–N Bond in the Aminophosphine Ligand of Separated Diastereoisomers

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Liquid HF cleaves the P–N bond in $[Fe(\eta\text{-}C_5H_5)(CO)I\{P(C_6H_5)_2\text{-}N(CH_3)CH(CH_3)(C_6H_5)\}]$ (1), without attack at the Fe–I bond, to give quantitatively $[Fe(\eta\text{-}C_5H_5)(CO)I\{P(C_6H_5)_2F\}]$ (2). Using the aminophosphine with (*S*) configuration at the asymmetric carbon atom in the amino-component, (1) forms a pair of diastereoisomers, $(+)_{365}$ and $(-)_{365}$, which only differ in the configuration at iron. The HF cleavage can be used to convert the separated $(+)_{365}$ and $(-)_{365}$ diastereoisomers of (1) into the corresponding enantiomers of (2). Extensive racemisation with respect to the chiral Fe atoms during the HF reaction can be excluded.

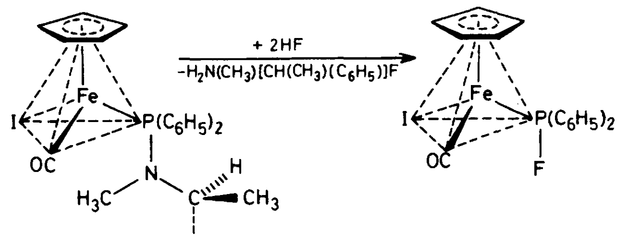
OPTICALLY active organotransition-metal compounds, in which the metal atom is the chiral centre, have been known since 1969,[1] but only a few of them are available as enantiomers.[2] In most cases an optically active resolving agent was introduced into a chiral organometallic compound; the resulting diastereoisomers were separated, but the optically active resolving chirality was not removed.[2,3]

As optically active resolving agents, aminophosphines $(C_6H_5)_2PN(R)CH(CH_3)(C_6H_5)$, with $R = H$, CH_3, C_2H_5, or $CH_2C_6H_5$, containing an asymmetric carbon atom in the amino-component have been used widely.[2-8] Such aminophosphines are easily accessible, optically stable, and they give diastereoisomers which differ in their ^1H n.m.r. spectra. A method for converting diastereoisomeric aminophosphine complexes into enantiomeric complexes would open a new route to optically active organometallic compounds the chirality of which is due to the metal centre alone. In this paper we describe how in the diastereoisomers $(+)_{365}$- and $(-)_{365}$-$[Fe(\eta\text{-}C_5H_5)(CO)I\{P(C_6H_5)_2[N(CH_3)CH(CH_3)(C_6H_5)]\}]$ (1) the amino-group $NCH_3[CH(CH_3)(C_6H_5)]$ of the aminophosphine ligand (*S*)-$P(C_6H_5)_2[N(CH_3)CH(CH_3)(C_6H_5)]$ can be replaced by fluorine, without complete racemisation at the chiral Fe atom.

RESULTS AND DISCUSSION

The green complex (1) [mixture of the diastereoisomers $(+)_{365}$ and $(-)_{365}$] dissolves in liquid HF at 20 °C giving a deep red solution. After removal of HF and chromatography of the residue on silica with toluene–diethyl ether (20 : 1), a brown band is obtained containing compound (2) in 90% yield according to Scheme 1.

The $\nu(C\equiv O)$ band in the i.r. spectrum of (2) at 1 975 cm^{-1} (KBr) is shifted to higher wavenumbers with respect to (1) (1 960 cm^{-1}), because the amino-substituent at phosphorus is replaced by the more electron-attracting fluorine. In the ^1H n.m.r. spectrum of (2) in C_6D_6 the C_5H_5 doublet appears at τ 5.71 [$J(C_5H_5\text{–}P) = 1.4$ Hz], the signals due to the amino-substituent $NCH_3[CH(CH_3)(C_6H_5)]$ being absent. The mass spectrum of (2) shows the molecular ion at *m/e* 480 followed by a fragmentation as expected for a compound of type (2). The mass spectrum and elemental analysis prove that in the reaction of (1) with HF only the P–N bond, not the Fe–I bond, is cleaved.



(1) (2)

SCHEME 1

The HF cleavage of the P–N bond in (1) was also carried out with a sample enriched in the $(-)_{365}$ isomer [$(-)_{365}$: $(+)_{365}$ = 88 : 12]. The product was compound (2) showing $(-)_{365}$ rotation. Similarly, the $(+)_{365}$ isomer of (2) can be obtained starting from the $(+)_{365}$ isomer of (1). These observations demonstrate that the reaction must be stereoselective with respect to the Fe atom.

These results are surprising, because it is well documented that electrophiles E may attack metal centres in organometallic compounds of types (1) and (2).[9,10] If $E = H^+$ adds to the Fe atom in (3) the three-legged piano-stool geometry expands to the four-legged geometry in (4) (Scheme 2). It is known that the metal configuration in pseudotetrahedral complexes like (1)—(3) is optically stable, provided no ligand-dissociation processes occur.[2,11] However, square-pyramidal compounds like (4) are non-rigid and the metal configuration can change by pseudorotation without ligand dissociation.[2,11,12] It has been shown that the barriers to metal-centred inversion in square-pyramidal complexes with a C_5H_5 ligand on top of the pyramid are relatively high if two of the basal co-ordination positions are occupied by a chelate ligand,[2,12] while the barriers are

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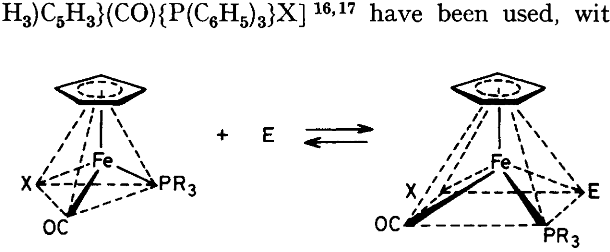
† Part 78, H. Brunner and E. Frauendorfer, submitted for publication.

much lower if the four basal ligands are unidentate,[13] as in the intermediates (4) under discussion.

The stereochemical course of cleavage of iron–alkyl and –halide bonds in organometallic compounds by electrophiles with respect to the metal centre was studied by chiral labelling of the Fe atom. As chiral Fe complexes (3), optically pure $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_5)_3\}X]$ [14] and $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_5)_2[N(CH_3)CH(CH_3)(C_6H_5)]\}X]$ [15] as well as diastereomerically pure $[Fe\{(1,3\text{-}C_6H_5,\text{-}CH_3)C_5H_3\}(CO)\{P(C_6H_5)_3\}X]$ [16,17] have been used, with



(3) (4)

SCHEME 2

X = halide or alkyl, and as electrophiles X_2, HX, HgX_2 (X = halide), or CF_3COOH. The stereochemical outcome with respect to the chiral Fe atom of all these reactions is product formation with varying degrees of retention of configuration and partial racemisation of recovered starting material.[18] Several mechanisms for product formation with predominant retention of configuration can be envisaged, most of them *via* intermediates (4) in which the electrophile E is added to the starting material (3) [19] according to Scheme 2. The partial racemisation of unreacted starting material can best be explained by formation of intermediate (4), the pseudorotation of which can compete with product formation and reversion to (3) + E.

Formation of intermediates (4) by protonation of (1) and (2) in liquid HF and metal-centred rearrangement would lead inevitably to a loss of the optical activity at the Fe atom. As the specific rotations of the enantiomers $(+)_{365}$ and $(-)_{365}$ of (2) were not known, the comparison of the specific rotation of the products of the HF reaction of the $(+)_{365}$ and $(-)_{365}$ isomers of (1) with the optically pure compounds could not be used to determine the stereoselectivity of the conversion of (1) into (2). Also, it proved impossible to separate the ^1H n.m.r. signals of the $(+)_{365}$ and $(-)_{365}$ isomers of (2) by using various optishift reagents. Therefore we have endeavoured to determine the degree of change in configuration at the iron centre during the HF treatment by the following procedure: three samples enriched in the $(-)_{365}$ isomer of (1) $[(-)_{365}: (+)_{365} = 88 : 12]$ were treated for 3.5 h with the same amount of HF at different temperatures; sample A at 20 °C, sample B at −20 °C, and sample C at −60 °C. Then HF was removed from all the samples at the reaction temperatures.

The same chromatographic work-up for samples A and B gave (2) as product with optical activity α (0.3 mg cm^{-3}, toluene, 20 °C, 365 nm) −1 000° (for A) and −1 420° (for B), showing that the reaction at lower temperatures is more stereoselective with respect to the Fe atom. Whereas P–N bond cleavage was quantitative after 3.5 h of HF treatment for samples A and B, unreacted starting material could be recovered from sample C after reaction at −60 °C. Chromatographic separation with toluene gave a ratio of (2) : (1) = 3 : 1. As was to be expected, compound (2) of sample C showed an even higher optical activity, α (20 °C, 365 nm) = −1 730°, than compound (2) of samples A and B. On the other hand, according to the ^1H n.m.r. analysis, the diastereoisomer ratio $(-)_{365} : (+)_{365}$ for (1) in the recovered starting material of sample C was decreased to 64 : 36, indicating a partial epimerisation at the Fe atom during treatment with HF. Thus, by HF treatment of (1), it will not be possible to obtain optically pure (2) by lowering the reaction temperature further because the P–N cleavage reaction becomes too slow and partial epimerisation of the starting material (1) cannot be avoided even under these mild conditions.

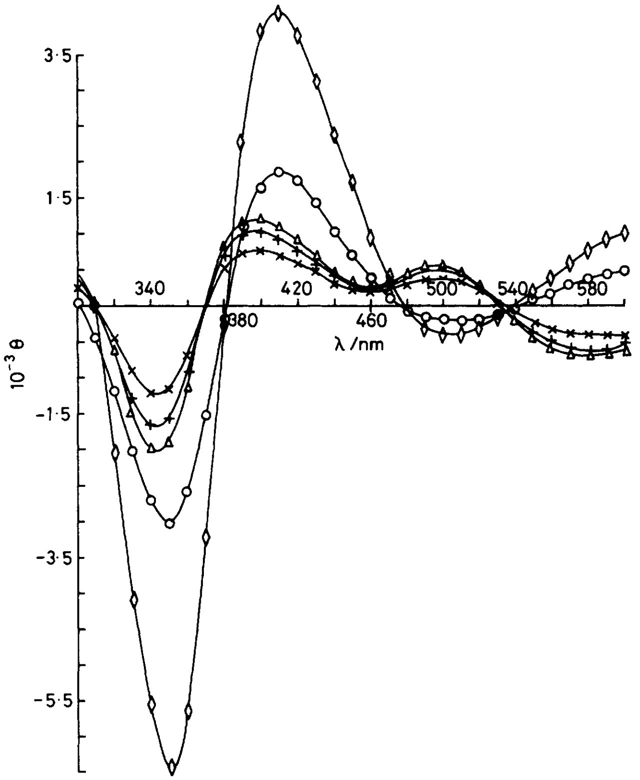


FIGURE C.d. spectra of $[Fe(\eta\text{-}C_5H_5)(CO)I\{P(C_6H_5)_2[N(CH_3)CH(CH_3)(C_6H_5)]\}]$ (1) and $[Fe(\eta\text{-}C_5H_5)(CO)I\{P(C_6H_5)_2F\}]$ (2) in toluene solution (3×10^{-4} mol dm^{-3}) on a Jasco J40A. Curves: (◇), starting material (1) used for HF treatment $[(-)_{365}: (+)_{365} = 88 : 12]$; (○), recovered starting material (1) from sample C (−60 °C) $[(-)_{365} : (+)_{365} = 64 : 36]$; (△), compound (2) from sample C (−60 °C); (+), compound (2) from sample B (−20 °C); and (×), compound (2) from sample A (20 °C). θ represents molecular ellipticity

It is also apparent from the circular dichroism (c.d.) spectra in the Figure that the formation of compound (2) becomes more stereoselective as the reaction temperature is lowered and that the recovered unreacted starting material has lost some of its optical purity. From the intensity of the c.d. spectra of compound (2), formed at −60 °C, it can be estimated that it consists of an enantiomer mixture of roughly $(-)_{365} : (+)_{365} = 3 : 1$.

Compounds (1) and (2), which must have the same configuration at iron, show c.d. bands at 350 and at 400 nm having the same signs; but the c.d. bands at 500 and 580 nm are clearly different. It seems that the bands of (2) are shifted to shorter wavelength compared to (1), especially as far as the longer wavelength region is concerned. This shift is small for the band at 340 nm but is more pronounced for that at 400 nm. Then, the minimum in the spectrum of (2) at 460 nm would correspond to the negative c.d. band of (1) at 500 nm and the band of (2) at 500 nm would be equivalent to the band of (1) at 600 nm. For a correlation between c.d. spectra and configuration at iron in $[Fe(\eta\text{-}C_5H_5)(CO)(PR_3)X]$ compounds the two c.d. maxima of opposite sign at 300—350 and 350—400 nm have been proposed to be diagnostic.[20] Based on this correlation the absolute configuration (*S*) at the Fe atom must be assigned to the $(-)_{365}$ isomers of (1)[21] and (2) (as shown in Scheme 1), given that the priority sequence of ligands is $I > C_5H_5 > P(C_6H_5)_2X > CO$ and that the specification of configuration is carried out as described recently.[22-24]

Cleavage of P–N bonds by gaseous or liquid HCl in complexes similar to (1) has been studied.[25-27] However, this method cannot be used to convert separated organometallic diastereoisomers into enantiomers, because it could be shown that the reaction of $(+)\text{-}[Mo(\eta\text{-}C_5H_5)(CO)(NO)\{P(C_6H_5)_2[N(CH_3)CH(CH_3)(C_6H_5)]\}]$ with liquid HCl gave only racemic products.[28] As demonstrated in this study for the $(+)_{365}$ and $(-)_{365}$ isomers of (1), P–N bond cleavage with liquid HF is at present the best method for enantiomer formation from resolved diastereoisomers containing aminophosphine ligands.

EXPERIMENTAL

All operations were carried out in an inert atmosphere of nitrogen. Anhydrous HF was manipulated *in vacuo*.

Cleavage by HF *of the* P–N *Bond in* $[Fe(\eta\text{-}C_5H_5)(CO)I\{P(C_6H_5)_2[N(CH_3)CH(CH_3)(C_6H_5)]\}]$ (1).—Compound (1) (320 mg, 0.54 mmol) (mixture of diastereoisomers) was dissolved in liquid HF (1 g) at 20 °C. After 3.5 h the HF was evaporated at room temperature. To remove traces of HF the sample was pumped at 10^{-5} mmHg (*ca.* 13.6 × 9.8 Pa) pressure for about 5 h. Then, the sample was dissolved in the minimum quantity of toluene and the solution was chromatographed on silica with toluene–diethyl ether (20 : 1) as the eluant. A brown band developed which contained 230 mg, corresponding to a yield of 90%, of $[Fe(\eta\text{-}C_5H_5)(CO)I\{P(C_6H_5)_2F\}]$ (2) (Found: C, 45.6; H, 3.10; N, 0.05. Calc. for $C_{18}H_{15}FFeIOP$: C, 45.05; H, 3.15; N, 0%).

All the other experiments differed from that described only in using optically active starting material (1), $(-)_{365}$ or $(+)_{365}$, and different reaction temperatures with HF (including for removal of HF). The only differences observed were the formation of a small amount of an insoluble yellow product in the HF reactions at 20 °C which was absent in the low-temperature HF reactions and the non-quantitative conversion of (1) into (2) at −60 °C.

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the BASF AG, and the Dynamit Nobel AG for support of this work.

[2/145 *Received*, 25th *January*, 1982]

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