Journal of Organometallic Chemistry, 214 (1981) 373—380
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

OPTICALLY ACTIVE TRANSITION METAL COMPOUNDS

LXXVI *. CHELATE COMPLEXES OF NORPHOS. DIASTEREOISOMERS WITH OPPOSITE METAL CONFIGURATION EXHIBITING SIMILAR CHIROPTICAL PROPERTIES

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(Received January 5th, 1981)

Summary

The following chelate complexes of the rigid ligand Norphos, a bisphosphine ligand containing the norbornene skeleton, have been prepared: $Cr(CO)_4$(Norphos), $C_5H_5Fe(CO)(Norphos)^+PF_6^-$, and $C_5H_5Mn(NO)(Norphos)^+PF_6^-$. With (—)Norphos the complex $C_5H_5Fe(CO)[(-)Norphos]^+PF_6^-$ forms a pair of diastereomers, differing only in the Fe configuration. The two diastereomers can be separated by fractional crystallization. They have almost the same CD spectra and optical rotation, because the norbornene skeleton in (—)Norphos enforces a rigid λ-conformation for the chelate rings in both isomers. Thus the Fe chromophore makes almost identical contributions to the chiroptical properties of both diastereomers, in contrast to the usual effect of opposite metal configurations in organometallic diastereomers.

Introduction

Norphos belongs to the group of optically active ligands which in the homogeneous hydrogenation of prochiral amino acid precursors with rhodium catalysts give the highest optical inductions [2,3]. However, stable complexes with the ligand Norphos, of interest because of its conformational rigidity and the isomeric possibilities arising from its structure, have not previously been prepared.

a) Conformational rigidity. Several X-ray structure analyses of Diop complexes have been carried out, demonstrating that the ligand Diop can adopt different conformations [4]. In contrast to the seven-membered chelate rings of

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* For part LXXV see ref. 1.

Diop complexes, the ligands Diphos [5], Prophos [6], Chiraphos [7], and Norphos are expected to give rise to five-membered chelate rings. Several X-ray structural analyses of Diphos and Chiraphos complexes show [8—10] that these chelate rings are more or less puckered. This puckering allows the distance between the two phosphorus atoms to vary, enabling the ligand to match different geometrical requirements. In contrast to Diphos, Prophos, and Chiraphos, the new ligand Norphos is not flexible. As a consequence of the rigid norbornene skeleton the two phosphorus atoms of Norphos have a constant distance, which cannot be modified by puckering of the chelate rings but only by angle deformation. Thus it was of interest to investigate the influence of this rigidity upon the ability of Norphos to form monodentate and bidentate complexes with various metal atoms.

b) Isomeric possibilities. The ligands Diop, Diphos, and Chiraphos contain C_2 axes while Prophos and Norphos are unsymmetrical. In Norphos one of the two $P(C_6H_5)_2$ groups is in the *exo* position and the other is in the *endo* position of the norbornene system. Therefore in monodentate complexes with Norphos there should be two isomers. For bidentate Norphos coordination, the possibility of isomers arises in cases where the complex fragment is prochiral. Optically pure Norphos should yield two diastereoisomers which differ only in the configuration at the metal center, whereas with racemic Norphos two diastereoisomeric pairs of enantiomers are to be expected.

Results and discussion

Preparation of $(CO)_4Cr(L\text{-}L')$, L-L' = (±)Norphos, (+)Norphos

From the reaction of $(CO)_4Cr$(norbornadiene-2,5) with equimolar amounts of L-L' = (±)Norphos and (+)Norphos in THF at room temperature the complexes $(CO)_4Cr(L\text{-}L')$, I and II, respectively, are obtained in 85—90% yield. Their properties are similar to those of the corresponding complex $Cr(CO)_4$-(Diphos) [5].

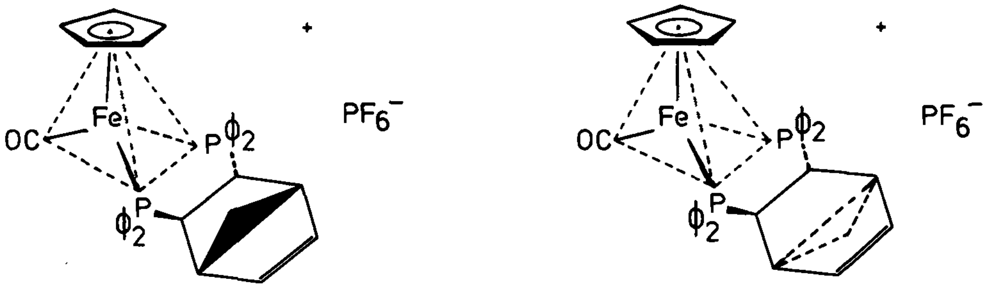
The IR spectra of compounds I and II in hexane solution show the $\nu(C{\equiv}O)$ pattern (2005m, 1923m, 1902s, 1898s) typical for $Cr(CO)_4(L\text{-}L')$ complexes as well as the characteristic Norphos bands. The mass spectrum of I exhibits a low intensity molecular ion. The fragmentation begins with the loss of 2 CO groups, the fragment $(Norphos)Cr(CO)_3^+$ being absent. This effect, found for many complexes of the type $(L\text{-}L)M(CO)_4$ in which (L-L) is a phenyl-containing ligand, has been attributed to the formation of π-arene complexes [11—14]. The fragmentation pattern of I and the chiroptical properties of II are detailed in the Experimental section.

Thus, the rigid ligand Norphos is capable of forming chelate complexes similar to those of flexible ligands like Diphos, a conclusion corroborated by the following examples.

Preparation of $C_5H_5Fe(CO)(L\text{-}L')^+PF_6^-$, L-L' = (±)Norphos, (—)Norphos

In the reaction of $C_5H_5Fe(CO)_2I$ with equimolar amounts of L-L' = (±)Norphos, (—)Norphos in boiling benzene, similar to the preparation of the corresponding Diphos complex [15], the compounds $C_5H_5Fe(CO)(L\text{-}L')^+I^-$ are formed in 80—86% yield. By precipitation with NH_4PF_6 the iodides were converted into the hexafluorophosphates $C_5H_5Fe(CO)(L\text{-}L')^+PF_6^-$, III and IV.

SCHEME 1



IV

The IR spectra of the complexes III and IV contain a strong $\nu(C\equiv O)$ band at 1975 cm^{-1} (KBr), indicating that Norphos is a better donor than Diphos ($C_5H_5Fe(CO)(Diphos)^+PF_6^-$: $\nu(C\equiv O)$ 1990 cm^{-1}, KBr).

In the ^1H NMR spectra of $C_5H_5Fe(CO)(Norphos)^+PF_6^-$, III and IV, the two phosphorus atoms couple with the C_5H_5 protons, giving rise to a 1 : 2 : 1 triplet for each isomer. Thus, the two diastereomeric pairs of enantiomers of III and the two diastereomers of IV exhibit two C_5H_5 triplets. In acetone-d_6 these two triplets (5.05 and 5.01 τ; $J(P{-}C_5H_5)$ 1.6 Hz) form a five-line-pattern, from which the mole fractions of the diastereomers can easily be obtained. In the reaction of $C_5H_5Fe(CO)_2I$ with Norphos followed by PF_6^- precipitation the diastereomers differing only in the Fe configuration are present in approximately equal amounts. Thus almost no optical induction is observed in the formation of the asymmetric centre at the Fe atom.

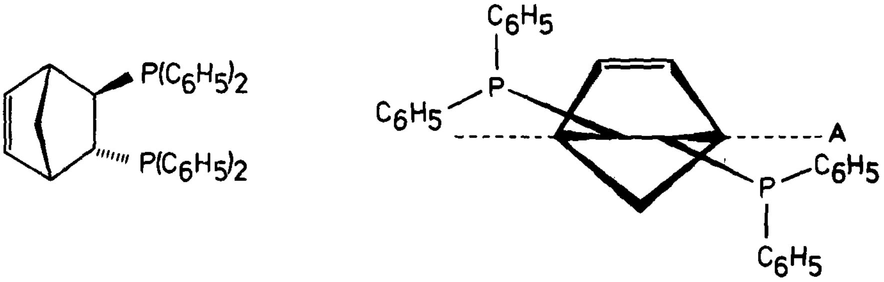
A 1 g quantity IVa, IVb was recrystallized seven times from 7 ml CH_2Cl_2/14 ml toluene at −25° C. Surprisingly, there was no isomer separation or even enrichment. Therefore, 400 mg of the mixture IVa, IVb was dissolved in 4 ml CH_2Cl_2 and the same quantity of benzene was added. After stirring for 30 minutes at room temperature the less soluble fraction separated as a yellow powder. Repetition of this separation procedure five times gave the optically pure less soluble isomer, showing the high field triplet in the NMR, as a crystalline solid.

The mother liquor from the first crystallization step contains the more soluble diastereomer, showing the low field triplet in the NMR in an enrichment of 75 : 25.

Stereochemistry and chiroptical properties

(−)Norphos has the geometry and the absolute configuration [3] indicated in Scheme 2. In the right hand drawing the molecule is viewed from the side of the double bond and the norbornene roof, opposite to the side of the $P(C_6H_5)_2$ groups. Line A represents the plane containing the two bridgehead carbons of the norbornene skeleton and the two carbon atoms to which the $P(C_6H_5)_2$ groups are bonded.

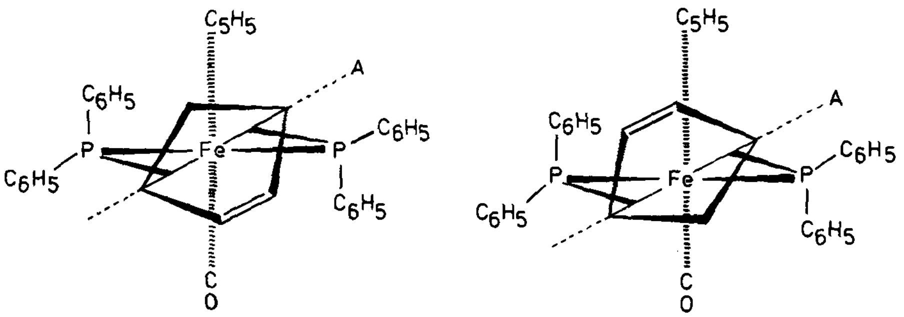
SCHEME 2



If both the *exo*-$P(C_6H_5)_2$ and *endo*-$P(C_6H_5)_2$ groups of (—)Norphos, together with a C_5H_5 ring and a CO ligand are attached to a Fe atom to give the cation $C_5H_5Fe(CO)[(-)Norphos]^+$, two isomers IVa and IVb, are possible. The midpoint of the C_5H_5 ring, the CO ligand, P_{exo} and P_{endo} define a tetrahedron with four different substituents which give rise to two opposite configurations at the Fe atom, and thus a pair of diastereomers, IVa and IVb, differing only in the Fe configuration.

Like other diastereomers, IVa and IVb can be separated on the basis of their different solubilities. However, with respect to their chiroptical properties the diastereomers IVa and IVb are unique. Normally two diastereoisomers, differing only in the metal configuration, give almost mirror image CD and ORD spectra, because the electronic transitions in the visible region and the near ultra violet are dominated by the metal chromophore, the chiral centers in the ligands making only minor contributions to the chiroptical properties [16—18]. Thus, the two diastereomers IVa and IVb, differing only in the Fe configuration, were expected to give nearly mirror image CD and ORD spectra. Surprisingly, IVa and IVb have almost identical CD spectra (Fig. 1) and optical rotations (Experimental section). This can be explained as follows. Coordination of (—)Norphos to a $C_5H_5(CO)Fe$ unit has only two possibilities (Scheme 3). If the Fe atom is toward the back and C_5H_5 is up, then *exo*-P can be on the left and *endo*-P on the right (IVa) or vice versa (IVb). Consequently IVa has the

SCHEME 3



IV

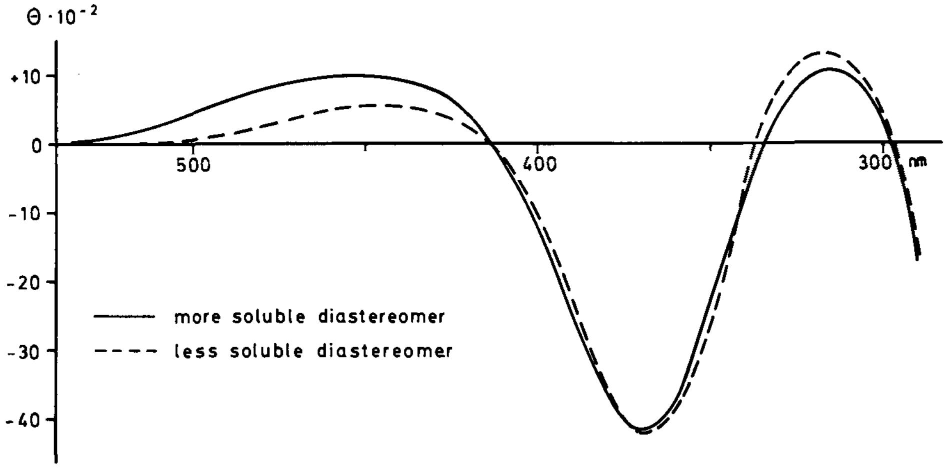


Fig. 1. CD spectra of $C_5H_5Fe(CO)[(-)Norphos]^+PF_6^-$ IV [less soluble diastereomer (optically pure) and more soluble diastereomer (isomer ratio 75 : 25)]; 2×10^{-3} mol/l in CH_2Cl_2, Jasco J 40 A.

CH_2 group of the norbornene skeleton up towards C_5H_5 and the double bond down towards CO, and in IVb the other way round. In both cases the puckering of the chelate ring FeP—A—P is the same. Both in IVa and in IVb the two lines P_{exo}—P_{endo} and A define a left-handed helix and consequently a rigid λ-conformation for the five-membered chelate ring. In addition to the same chelate ring conformation the two bonds from each phosphorus atom to the phenyl rings also have the same orientation in both IVa and IVb (Scheme 3). Thus, the metal chromophores in the two isomers are very similar, although the metal configurations are opposite. Therefore, the Fe chromophores in IVa and IVb make nearly identical contributions to the chiroptical properties, in contrast to the usual effects of opposite metal configurations in organometallic diastereomers.

Preparation of $C_5H_5Mn(NO)(L\text{-}L')^+PF_6^-$, L-L' = (±)Norphos, (—)Norphos

The complexes $C_5H_5Mn(NO)(L\text{-}L')^+PF_6^-$ are prepared by reaction of $C_5H_5Mn(CO)_2(NO)^+PF_6^-$ with (±)Norphos and (—)Norphos, respectively, in boiling acetone [19—21]. The red disubstitution products are very similar to the corresponding Diphos complexe in both physical and chemical properties [19]. As in $C_5H_5Mn(NO)(Diphos)^+PF_6^-$, the $\nu(N{\equiv}O)$ frequency in $C_5H_5Mn(NO)$-$[(\pm)Norphos]^+PF_6^-$, V, and in $C_5H_5Mn(NO)[(-)Norphos]^+PF_6^-$, VI, appears at 1745 cm^{-1} (KBr).

The two diastereoisomers of $C_5H_5Mn(NO)[(-)Norphos]^+PF_6^-$, VIa and VIb, which differ only in the configuration at the metal atom, can be separated as follows: 750 mg of the diastereoisomer mixture are dissolved in 3 ml CH_2Cl_2 and then treated with 6 ml benzene. After stirring for several minutes at room temperature the solution becomes turbid. After one hour the supernatant solution containing the more soluble diastereoisomer is separated from the precipitate. This procedure is repeated with the residue. After five cycles the less soluble diastereoisomer is obtained from a nearly colorless solution indicating that the isomer separation is complete.

As was observed for the Fe compounds IVa and IVb, the chiroptical properties of the two diastereoisomers VIa and VIb, differing only in the Mn configuration, are very similar. This is not surprising in view of the fact that the Fe(CO) complexes IV are isoelectronic and analogous to the corresponding Mn(NO) complexes VI [22].

Experimental section

All the experiments were carried out with dry solvents under nitrogen.

Preparation of $Cr(CO)_4$[(+)Norphos], II

A solution of 0.26 g (1 mmol) $Cr(CO)_4$(norbornadiene-2,5) and 0.47 g (1 mmol) (+)Norphos in 7 ml THF is stirred for 20 hours at room temperature. The solvent is evaporated and the residue chromatographed on SiO_2. With petroleum ether/benzene (1/2) the complex $Cr(CO)_4$[(+)Norphos] can be eluted as a greenish-yellow zone. Crystallization from THF/petroleum ether at —25° C results in a yellow powder. Yield 580 mg (92%). M.p. 226° C. (Found: C, 66.45; H, 4.98; mol. wt. mass spectr. 626. $C_{35}H_{28}CrO_4P_2$ calcd.: C, 67.09; H, 4.50%; mol. wt. 626.5).

Mass spectrum of $Cr(CO)_4$[(±)Norphos], I. m/e values (rel. int. with respect to ^{52}Cr): $Cr(CO)_4$(Norphos)$^+$ 626 (6), $Cr(CO)_2$(Norphos)$^+$ 570 (3); Cr(CO)(Norphos)$^+$ 542 (3); Cr(Norphos)$^+$ 514 (74); Norphos$^+$ 464 (2), $CrC_2H_2[P(C_6H_5)_2]_2^+$ 448 (40), $Cr[P(C_6H_5)_2]_2^+$ 422 (20), $C_2H_2[P(C_6H_5)_2]_2^+$ 396 (11), $C_7H_8P(C_6H_5)_2^+$ 277 (63), $CrP(C_6H_5)_2^+$ 237 (19), $P(C_6H_5)_2^+$ 185 (21), Cr^+ 52 (100).

Optical rotations of $Cr(CO)_4$[(+)Norphos], II. $[\alpha]_{578}^{25}$ +395°, $[\alpha]_{546}^{25}$ +355°, $[\alpha]_{436}^{25}$ +515° (benzene, 3×10^{-3} mol/l).

CD spectrum of $Cr(CO)_4$[(+)Norphos] II. $[\theta]_{\lambda}^{25}$ values of maxima, minima and nodes $[\frac{\text{grad} \cdot \text{l}}{\text{Mol} \cdot \text{cm}}]$, benzene, 3×10^{-3} mol/l: $\lambda = 390$ nm, $\theta = -1.5 \times 10^3$; $\lambda = 370$ nm, $\theta = 0$; $\lambda = 355$ nm, $\theta = +3 \times 10^3$ (sh); $\lambda = 325$ nm, $\theta = +1.2 \times 10^4$, $\lambda = 300$, $\theta = 0$.

Preparation of $C_5H_5Fe(CO)$[(—)Norphos]$^+PF_6^-$, IV

A solution of 608 mg (2 mmol) $C_5H_5Fe(CO)_2I$ and 925 mg (2 mmol) (—)Norphos in 30 ml benzene is refluxed for 15 hours. After cooling to room temperature the precipitate is filtered off and washed several times with 5 ml benzene. For purification the residue is dissolved in CH_2Cl_2 and precipitated with benzene. Yield is $C_5H_5Fe(CO)$[(—)Norphos]$^+I^-$, 1.20 g (86%).

1.2 g (1.7 mmol) $C_5H_5Fe(CO)$[(—)Norphos]$^+I^-$ are dissolved in 10 ml CH_3OH. A solution of 300 mg (1.8 mmol) NH_4PF_6 in 20 ml water is added. Yellow $C_5H_5Fe(CO)$[(—)Norphos]$^+PF_6^-$ separates out immediately. It is filtered off, washed several times with water, then with ether, and dried in high vacuum. Yield of $C_5H_5Fe(CO)$[(—)Norphos]$^+PF_6^-$ 1.23 g (97%). The compound crystallizes from CH_2Cl_2/toluene (1/1) at —25° C as yellow, cubic crystals. (Found: C, 58.76; H, 4.40. $C_{37}H_{33}F_6FeOP_3$ calcd.: C, 58.75; H, 4.40%). M.p. of the optically pure less soluble diastereomer of $C_5H_5Fe(CO)$[(—)Norphos]$^+PF_6^-$ 250—252° C (dec.).

Optical rotations of $C_5H_5Fe(CO)[(-)Norphos]^+PF_6^-$, *IV*. Less soluble diastereomer: $[\alpha]^{17}_{578}$ −200°, $[\alpha]^{17}_{546}$ −195°, $[\alpha]^{17}_{436}$ −1280° (CH_2Cl_2, 3 × 10^{-3} mol/l).

More soluble diastereomer: $[\alpha]^{17}_{578}$ −190°, $[\alpha]^{17}_{546}$ −210°, $[\alpha]^{17}_{437}$ −870° (CH_2Cl_2, 3 × 10^{-3} mol/l).

Preparation of $C_5H_5Mn(NO)[(-)Norphos]^+PF_6^-$, *VI*

A solution of 525 mg (1.5 mmol) $C_5H_5Mn(CO)_2(NO)^+PF_6^-$ and 815 mg (1.76 mmol) (−)Norphos in 10 ml acetone is refluxed for 15 hours. After evaporation of the solvent the residue is dissolved in CH_2Cl_2 and precipitated with petroleum ether. The compound crystallizes from CH_2Cl_2/toluene/ether (1/1/2). $C_5H_5Mn(NO)[(-)Norphos]^+PF_6^-$ forms reddish-brown crystals, soluble in CH_2Cl_2, THF, acetone, and acetonitrile. Yield 1.10 g (98%). (Found: C, 56.02; H, 4.47. $C_{36}H_{33}MnF_6NOP_3$ calcd.: C, 57.08; H, 4.39%). M.p. of the optically pure less soluble diastereomer of $C_5H_5Mn(NO)[(-)Norphos]^+PF_6^-$ 222°C.

Optical rotations of $C_5H_5Mn(NO)[(-)Norphos]^+PF_6^-$, *VI*. Less soluble diastereomer: $[\alpha]^{17}_{546}$ −205°, $[\alpha]^{17}_{436}$ −845°, $[\alpha]^{17}_{365}$ −950° (CH_2Cl_2, 3 × 10^{-3} mol/l).

More soluble diastereomer: $[\alpha]^{17}_{546}$ −210°, $[\alpha]^{17}_{436}$ −725°, $[\alpha]^{17}_{365}$ −905° (CH_2Cl_2, 3 × 10^{-3} mol/l).

Acknowledgements

A.F.M. Mokhlesur Rahman thanks the Bangladesh Council of Scientific and Industrial Research Laboratories, Dacca, for study leave and the DAAD, Bonn, for a scholarship. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the BASF AG for financial support and M. Muschiol for the preparation of (±)Norphos, (+)Norphos and (−)Norphos.

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