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# X-Ray Structure Analysis of (–)-$C_5H_5Fe(CO)[(2R,3R)$-Norphos]$PF_6$ and a Set of Measures to Describe Metal/Phosphine Chelate Rings with Respect to Chirality Transfer in Transition Metal Catalysts

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Norphos *2* belongs to the optically-active chelate phosphines which are easily prepared and which give high optical yields in Rh-catalyzed asymmetric hydrogenation of amino acid precursors [1, 2]. In contrast to most of the related optically-active chelate phosphines, *e.g.* the Diphos derivatives Prophos [3] and Chiraphos [4], Norphos is rigid. The distance between the two $P(C_6H_5)_2$ substituents in Norphos cannot be adjusted by a variation of the puckering of the P–C–C–P moiety without distortion of the norbornene system. Nevertheless (–)Norphos forms chelate complexes [5], *e.g.* $C_5H_5Fe(CO)[(-)Norphos]^+PF_6^-$ *1*. We separated the two possible diastereomers due to the two different Fe-configurations and reported on the unusual effect that both diastereoisomers of *1* have almost identical chiroptical properties [5]. The X-ray structure analysis of the less soluble diastereomer of *1* demonstrates the severe distortions of the norbornene skeleton, necessary to match the bonding requirement of the Fe atom in the cyclopentadienyl carbonyl cation.

The optically pure, less soluble diastereomer of $C_5H_5Fe(CO)[(-)Norphos]PF_6$ [5] ($[\alpha]_{436}^{20}$ –1280°, 3 × $10^{-3}$ *M*, $CH_2Cl_2$) was dissolved in $CH_2Cl_2$. After addition of benzene ($CH_2Cl_2$:$C_6H_6$ 5/1) the solution was allowed to crystallize at 5–10 °C. The depositing crystals of $C_5H_5Fe(CO)[(-)Norphos]^+PF_6^-$ contained 1 mol of benzene per mol of complex.

Crystal data: $C_{37}H_{33}OF_6P_3Fe \cdot C_6H_6$, M = 836.54. Triclinic, $a$ = 10.718(3), $b$ = 10.859(4), $c$ = 10.924(4) Å, $\alpha$ = 58.80(3), $\beta$ = 68.19(4), $\gamma$ = 68.90(4)°, $V$ = 987.298 Å$^3$, $Z$ = 1, $D_c$ = 1.407 g/cm$^{-3}$. Space group P1. Mo-Kα radiation, λ = 0.71073 Å.

3786 reflections were collected with a computer-controlled diffractometer in the range $4.0° < 2\theta < 50°$, of which 3285 with $I > 3\sigma(I)$ were used in the refinement. The structure was solved by Patterson and Fourier methods. $R$ = 0.065, $R_w$ = 0.060. Figure 1 shows the structure of the cation $C_5H_5Fe(CO)[(-)Norphos]^+$ and the numbering scheme. Table I gives the atomic parameters.

In *1* the Fe atom is almost in the center of an octahedron, one face of which is formed by the $C_5H_5$ ligand and one face by $P_{exo}$, $P_{endo}$, and C(CO). The P1–Fe–P2 angle is 90.6°; the P1–Fe–C(CO) angle is expanded to 95.4° due to the interactions of the CO ligand with the axial phenyl C1–C6 at P1. On the other hand, the P2–Fe–C(CO) angle is squeezed to 86.5°, a CO interaction with the equatorial phenyl C7–C12 at P2 being absent. The angle between the plane P1–Fe–P2 and the vector Fe–Cp (ring centroid) is 58.02° and the vector Fe–C(CO) 84.1°, respectively.

To form a five-membered chelate ring in *1*, the $P(C_6H_5)_2$ groups of $P_{exo}$ and $P_{endo}$ have to approach each other. In the X-ray structure analysis of *1* a torsional angle P1–C30–C31–P2 of –66.94° demonstrates the severe distortion of the norbornene skele-

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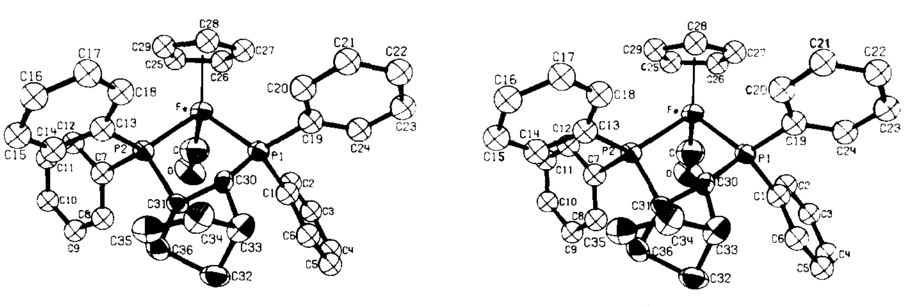

Fig. I. Stereoscopic view of the cation $C_5H_5Fe(CO)[(-)Norphos]^+$. *Selected bond lengths and bond angles:* Fe–C 1.858(20), Fe–P1 2.231(5), Fe–P2 2.237(4), C–O 1.095(19), average Fe–C(Cp) 2.143(15), average P–C(phenyl) 1.828(15), average P–F 1.567(14), Fe–Cp ring centroid 1.794 Å; Fe–C–O 177.8°, P1–Fe–C 95.4(6), P2–Fe–C 86.5(6), P1–Fe–P2 90.6(2)°. *Bond lengths of the non-phenyl Norphos part:* P1–C30 1.832, P2–C31 1.840, C30–C31 1.553, C30–C33 1.619, C31–C36 1.576, C33–C32 1.565, C36–C32 1.620, C33–C34 1.534, C36–C35 1.533, C34–C35 1.355 Å.

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TABLE. I. Atomic Parameters of the Non-hydrogen Atoms in the Cation $C_5H_5Fe(CO)[(-)Norphos]^+$.

| | | X | Y | Z |
|---|---|---|---|---|
| 1 | Fe | −0.4328 | −0.4328 | −0.4328 |
| 2 | P1 | −0.5624 | −0.3339 | −0.2787 |
| 3 | P2 | −0.2533 | −0.5065 | −0.3355 |
| 4 | C | −0.3599 | −0.2681 | −0.5755 |
| 5 | O | −0.3153 | −0.1730 | −0.6624 |
| 6 | C30 | −0.4566 | −0.4196 | −0.1448 |
| 7 | C31 | −0.3094 | −0.3947 | −0.2356 |
| 8 | C32 | −0.3645 | −0.2982 | −0.0684 |
| 9 | C33 | −0.4731 | −0.3941 | −0.0056 |
| 10 | C34 | −0.3956 | −0.5460 | 0.0881 |
| 11 | C35 | −0.2599 | −0.5596 | 0.0215 |
| 12 | C36 | −0.2419 | −0.4152 | −0.1185 |
| 13 | C1 | −0.6015 | −0.1334 | −0.3557 |
| 14 | C2 | −0.6134 | −0.0485 | −0.5015 |
| 15 | C3 | −0.6463 | 0.1048 | −0.5606 |
| 16 | C4 | −0.6673 | 0.1732 | −0.4739 |
| 17 | C5 | −0.6554 | 0.0882 | −0.3282 |
| 18 | C6 | −0.6226 | −0.0651 | −0.2690 |
| 19 | C7 | −0.0952 | −0.4550 | −0.4711 |
| 20 | C8 | −0.0485 | −0.3388 | −0.4935 |
| 21 | C9 | 0.0681 | −0.2962 | −0.6037 |
| 22 | C10 | 0.1380 | −0.3698 | −0.6914 |
| 23 | C11 | 0.0912 | −0.4859 | −0.6690 |
| 24 | C12 | −0.0254 | −0.5285 | −0.5588 |
| 25 | C13 | −0.1922 | −0.6957 | −0.2070 |
| 26 | C14 | −0.0568 | −0.7420 | −0.1924 |
| 27 | C15 | −0.0140 | −0.8814 | −0.0844 |
| 28 | C16 | −0.1065 | −0.9744 | 0.0091 |
| 29 | C17 | −0.2418 | −0.9281 | −0.0053 |
| 30 | C18 | −0.2847 | −0.7887 | −0.1134 |
| 31 | C19 | −0.7290 | −0.3816 | −0.1643 |
| 32 | C20 | −0.7345 | −0.5281 | −0.0645 |
| 33 | C21 | −0.8599 | −0.5652 | 0.0278 |
| 34 | C22 | −0.9797 | −0.4558 | 0.0202 |
| 35 | C23 | −0.9742 | −0.3093 | −0.0797 |
| 36 | C24 | −0.8488 | −0.2722 | −0.1719 |
| 37 | C25 | −0.3912 | −0.5103 | −0.5918 |
| 38 | C26 | −0.5253 | −0.4200 | −0.5842 |
| 39 | C27 | −0.6045 | −0.4859 | −0.4386 |
| 40 | C28 | −0.5193 | −0.6169 | −0.3562 |
| 41 | C29 | −0.3874 | −0.6320 | −0.4509 |

ton compared to a torsional angle of ±120° between *endo*-$P(C_6H_5)_2$ and *exo*-$P(C_6H_5)_2$ in ideal norbornene geometry. The twisting of the $P_{endo}$ and $P_{exo}$ substituents accompanying the chelate ring formation continues in the entire norbornene skeleton, demonstrated by a torsional angle C33–C30–C31–C36 of 19.31°, although the torsional angle C33–C34–C35–C36 of the double bond at the other side of the norbornene system is only 0.96°. During catalysis Norphos probably is bonded in a bidentate way [6]. Due to the angle strain resulting from chelate complex formation more than comparable chelate ligands Norphos should tend to chelate ring opening relieving this distortion.

The puckering of five-membered chelate rings MPCCP has also been observed for other 1,2-bis(diphenyl)phosphine complexes, even when the C–C bond is not part of another cyclic system [6, 7]. It is also present in complexes of 1,2-diamino ethane derivatives, *e.g.* $(-)_{589}\{tris[(+)\text{-}1,2\text{-diaminocyclohexane}]Co\}Cl_3\cdot 5H_2O$ [8] in which the torsional angle NCCN of the chelate ring is 59.3° compared to 66.9° in the PCCP system of *1*. The deviation of C30 and C31 from the plane P1–Fe–P2 is evident from Fig. 1, C30 being on the side of the Cp and C31 on the side of the CO ligand. The torsional angles P2–Fe–P1–C30 and P1–Fe–P2–C31 are −14.8° and −16.0°. These angles (and also the torsional angle P1–C30–C31–P2 of −66.9°) are much larger [6] than the corresponding angles in complexes of non-cyclic chelate phosphines [7–9] as a consequence of the presence of the norbornene system. It is generally accepted that the transfer of chirality in the catalyst from the asymmetric centers of the ligand backbone to the substrate occurs via the 4 phenyl groups [9]. The arrangement of the 4 phenyl rings relative to the 2 phosphorus atoms is a direct consequence of the geometry of the five-membered MPCCP ring. It is best described in terms of 2 parameters: axial or equatorial character and proximity, discussed in subsequent paragraphs.

As C31 is below the P1–Fe–P2 plane the bond P2–C7 to phenyl C7–C12 is forced into a pseudo-equatorial position (torsional angle P1–Fe–P2–C7 −129.5°) and the bond P2–C13 to phenyl C13–C18 into a pseudo-axial position (torsional angle P1–Fe–P2–C13 103.4°). The corresponding torsional angles on the P1 side are −127.1° for P2–Fe–P1–C19 to the equatorial phenyl C19–C24 and 106.2° for P2–Fe–P1–C1 to the axial phenyl C1–C6. Thus, the differences in the torsional angles of equatorial and axial phenyls with the P1–Fe–P2 system (20–25°) are much larger for Norphos complexes [6] than for related compounds.

As a new parameter to describe how far the phenyl rings reach over to other metal coordination sites the torsional angle M–P–P–$C_{ipso}$ is proposed, which we shall refer to as the proximity parameter. In this measure the two torsional angles in *1* for the axial phenyls are on the P1-side Fe–P2–P1–C1 −99.7° and on the P2 side Fe–P1–P2–C13 −108.4°. The corresponding torsional angles for the equatorial phenyls are on the P1 side Fe–P2–P1–C19 89.1° and P2 side Fe–P1–P2–C7 79.9°. These proximity parameters, usually close to 90°, measure how far the cylinders (defined by the rotation of the phenyls) are oriented towards or away from the other coordination sites at a metal atom.

Having specified the phenyl positions with respect to axial/equatorial and proximity character the only way left for a phenyl ring to respond to a given chirality in the ligand backbone is by rotation around the P–$C_{ipso}$ bond. Phenyl orientations have been called face-exposed or edge-exposed, depending on whether they present their faces or edges towards the neighboring coordination positons at the metal basal plane [9]. As a new, unambiguous measure for defining face/edge exposure the torsional angle M–P–$C_{ipso}$–$C_{ortho}$ is suggested, wherein $C_{ortho}$ is the *ortho*-carbon atom nearest to the metal atom. In this gauge, face- and edge-exposed phenyls adopt torsional angles of around ±30, ±60°, depending on whether they occupy axial/equatorial positions and to which end of the chelate ligand they are bonded. In the present case of *1* the phenyls C19–C24 (Fe–P1–C19–C20 59.8°) and C13–C18 (Fe–P2–C13–C18 –28.9°) are face-exposed, whereas the phenyls C1–C6 (Fe–P1–C1–C2 31.3°) and C7–C12 (Fe–P2–C7–C12 –72.5°) are edge-exposed.

Most of the chelating diphosphine ligands used in asymmetric catalysis have $C_2$ symmetry. Therefore the equatorial, face-exposed phenyl rings on the two phosphorus atoms are on different sides of the P–Rh–P plane [9]. In Norphos there is no $C_2$ axis and in the iron complex *1* the areas above and below the P1–Fe–P2 plane are different because of the presence of the cyclopentadienyl ligand and the carbonyl group, respectively. So, in this case the two phenyls on the $C_5H_5$ side are face-exposed and the two others edge-exposed.

The planes of the two phenyls C1–C6 and C19–C24 at P1 and those of the two phenyls C7–C12 and C13–C18 at P2 form angles of 103.9° and 76.7°, respectively. So, as usual the two phenyls of each $P(C_6H_5)_2$ group are almost perpendicular to each other [9].

Figure 1 shows that the *ortho*-hydrogen at C20 of the equatorial phenyl C19–C24 at P1 is located between the *endo* hydrogen at C30 and the Fe atom. The axial phenyl C1–C6 on the same P1 avoids contact with the *exo*-hydrogen at C31 by a perpendicular arrangement to phenyl C19–C24. On the other hand the *ortho*-hydrogen at C8 of the equatorial phenyl C7–C12 at P2 is not located between the *exo*-hydrogen at C31 and the Fe atom but on the other side of the hydrogen at C31. The reason could be a positive interaction of the phenyl C13–C18, perpendicular to C7–C12, with the double bond in the norbornene skeleton. This only seems possible in the observed arrangement of phenyls at P2.

Phenyl orientation has been defined with regard to axial/equatorial character and to face/edge exposure on the basis of angles between planes [9], a concept with an inherent ambiguity [10]. In contrast to angles between planes, torsional angles are well defined, non-ambiguous and easy to visualize [11]. Therefore we propose the following steps to adequately describe metal/phosphine chelate rings, including the arrangement of the phenyl rings in the $P(C_6H_5)_2$ groups, exemplified for *1*:

(1) the P1–Fe–P2 angle (90.6°), the two Fe–P bond lengths (2.23 and 2.38 Å), and the three torsional angles P1–Fe–P2–C31 (–16.0°), P2–Fe–P1–C30 (–14.8°), and P1–C30–C31–P2 (–66.9°) define size and puckering of the chelate ring;

(2) the four torsional angles P1–Fe–P2–C13 (103.4°), P2–Fe–P1–C1 (106.2°), and P1–Fe–P2–C7 (–129.5°), P2–Fe–P1–C19 (–127.1°) define the axial/equatorial character of the P-phenyls;

(3) the four torsional angles Fe–P2–P1–C1 (–99.7°), Fe–P2–P1–C19 (89.1°), Fe–P1–P2–C7 (79.9°), and Fe–P1–P2–C13 (–108.4°) define the proximity of the P-phenyls to other metal coordination sites;

(4) the four torsional angles Fe–P1–C1–C2 (31.3°), Fe–P1–C19–C20 (59.8°), Fe–P2–C7–C12 (–72.5°), and Fe–P2–C13–C18 (–28.9°) define the face/edge exposure of the P-phenyls.

For the preparation of *1* (–)Norphos was used, the absolute configuration of which is known to be (2*R*,3*R*) [2, 6]. From the present X-ray determination the absolute configuration at the Fe atom, shown correctly in Fig. 1 is (*S*), provided the priority sequence of ligands is $C_5H_5 > P_{endo} > P_{exo} > CO$ [12].

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