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# Optically active transition metal complexes

# XCVIII *. Synthesis and structure of diastereomers of [(−)-Norphos]Ru(II)($\eta^5$-$C_5H_5$)I

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## Abstract

Two diastereomers of the [(−)-Norphos]Ru(II) complex with $\eta^5$-$C_5H_5$ and iodide as ligands were synthesized by a phosphine-exchange reaction between $(Ph_3P)_2Ru(II)(\eta^5\text{-}C_5H_5)Cl$ and (2*R*,3*R*)-(−)-Norphos, followed by Cl/I displacement. Each of the diastereomers can be separated and their structures and chiroptical properties are discussed on the basis of $^1$H NMR spectroscopy, circular dichroism, and X-ray crystallography.

Norphos has been studied as a potent optically active bidentate phosphine ligand for asymmetric catalytic hydrogenation [1]. Much interest has recently been focussed on $C_2$-symmetrical design of bidentate phosphine ligands [2]. In this sense Norphos can be considered as a pseudo-$C_2$-symmetrical ligand. However, inherent heterotopicity (*exo* and *endo*) of the norbornene skeleton of Norphos should affect the chiral environment of metal complexes and afford diastereometric isomers of the complexes. Pairs of diastereometric complexes containing the (2*R*,3*R*)-(−)-Norphos–M moiety [M = Fe, Cr, and Mn] have been separated and their structures and chiroptical properties reported [3].

Here we report the synthesis of [(−)-Norphos]Ru(II)($\eta^5$-$C_5H_5$)I and the separation of its diastereomers, and discuss the corresponding structures and chiroptical properties.

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* Part XCVII see ref. 3c.

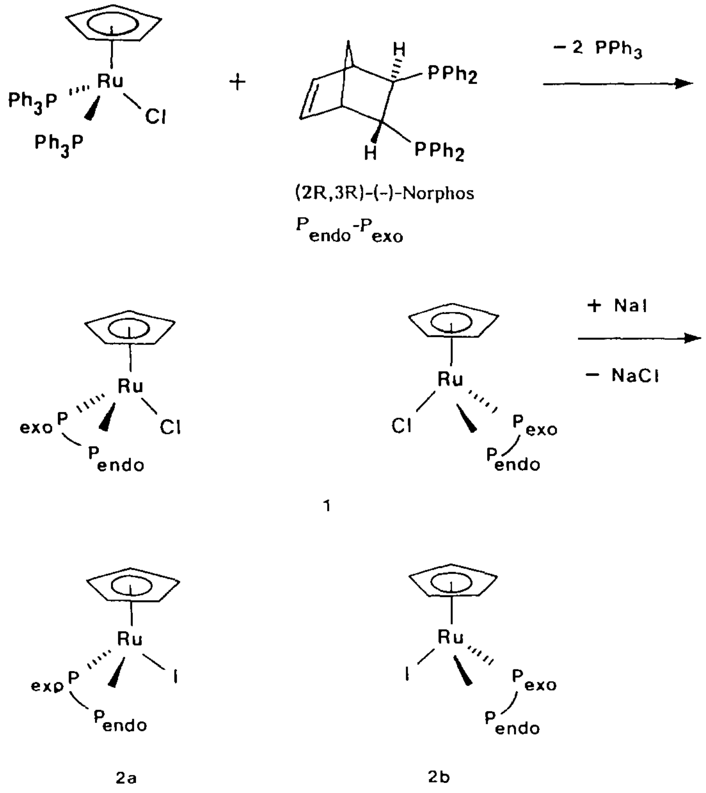
## Results and discussion

The ligand-exchange reaction of $(Ph_3P)_2Ru(\eta^5\text{-}C_5H_5)Cl$ [4] with (2R,3R)-(−)-Norphos in benzene at 70–80 °C for 1 day gave a 1 : 1 mixture of the corresponding diastereomers of $[(-)\text{-Norphos}]Ru(II)(\eta^5\text{-}C_5H_5)Cl$, **1**, in 90% yield. Similar observations have been reported for displacement reactions of half-sandwich ruthenium complexes with other chiral diphosphine ligands [5].

The Cl/I displacement reaction of **1** (130 mg) with NaI (50 equiv.) was carried out under reflux in methanol (ca. 0.006 *M*, small amounts of precipitates formed) for 3 days. The reaction gave the diastereomers **2a** and **2b** in an 18 : 82 ratio, on the basis of $^1H$ NMR of the olefin protons of the corresponding iodo ruthenium complex, in 91% combined yield. The products were further purified by recrystallization from benezene–hexane at room temperature in the dark.

At room temperature, the exchange reaction with **1** (95 mg) and NaI (70 equiv.) in methanol (0.007 *M*) for 3 days gave an orange precipitate (57% yield), which was collected and exhibited a diastereomer ratio of **2a** : **2b** = 78 : 22. From the solution a 33% yield of **2a** : **2b** = 46 : 54 was obtained.

When a mixture of **2a** : **2b** = 62 : 38 was treated at ca. 60 °C for one day with NaI (5 equiv.) in methanol (0.004 *M*, completely homogeneous during the reaction, no precipitation) a 17 : 83 ratio of **2a** : **2b** in 90% yield was obtained. We therefore consider **2b** to be the thermodynamically more stable isomer.



Scheme 1

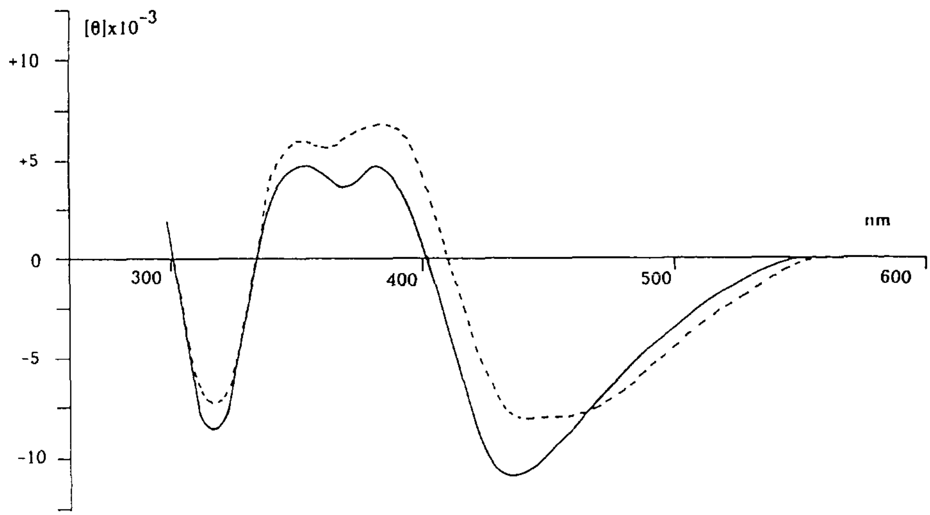


Fig. 1. CD-spectra of **2a** (**2a** : **2b** = 85 : 15, — — —) and **2b** (———) (1.2×10$^{-3}$ mol/l, $CH_2Cl_2$).

Pure **2b** was obtained from the 18 : 82 mixture of **2a** : **2b**, and **2a** was enriched from **2a** : **2b** = 78 : 22 to 85 : 15, both by two recrystallizations from benzene–hexane at room temperature in the dark, to give orange-red prisms (recovery ca. 30%).

Thus we obtained the enriched isomers. In the solid state the complexes are stable in air. In solution, they are stable in methanol, but not in dichloromethane and chloroform.

Because of the inherent conformational rigidity of the norbornene skeleton of Norphos, λ-conformation of the phosphine-chelate rings is enforced upon both diastereoisomers, resulting in the same *exo–endo* pattern of the four phenyl rings. Therefore, similar chiroptical properties were expected for **2a** and **2b**. This is corroborated by the almost identical CD curves of **2a** and **2b** (Fig. 1); for this measurement, two pure crystals (ca. 6 mg) of **2b** were selected from the enriched crystals after their purity was checked by $^1$H NMR. This exceptional effect has been reported for the corresponding diastereomers of [Norphos]Fe(Cp)$CO^+PF_6^-$ [3] and [Prophos]Ru(Cp)Cl [5], and attributed to the pseudo-$C_2$-symmetrical stereochemistry of Norphos and Prophos. In general, however, chirality at a metal atom makes major contributions to chiroptical values, leading to almost mirror-image curves in the visible range of the CD-spectra for diastereomers with differing configurations at the metal chromophore [6], for example, Ru [7], Fe [8], Mn [9], and Co [10].

An X-ray diffraction study of the diastereomers also shows the same stereochemical environment around the ruthenium atom (Fig. 2). A crystal of **2b** including **2a** was selected from the enriched sample obtained by recrystallization of a 7 : 93 mixture of **2a** and **2b** from benzene–hexane. Elemental analysis of the crystals was consistent with the formulation $C_{36}H_{33}IP_2Ru$, M.W. 755.58. Disorder of ca. 30% indicates that the crystal of **2b** contained the isomer **2a** (as indicated by dotted lines in Fig. 2). The previously used priority sequence of ligands [3,6,8], $I > C_5H_5 > P_{endo} > P_{exo}$, shows that the Ru atom has the *R* configuration in **2b** and the *S* configuration in **2a**.

The two phenyl rings (C(11)–C(16) and C(41)–C(46)) are oriented nearly parallel to the cyclopentadienyl ring, whereas the other two (C(21)–C(26) and C(31)–C(36))

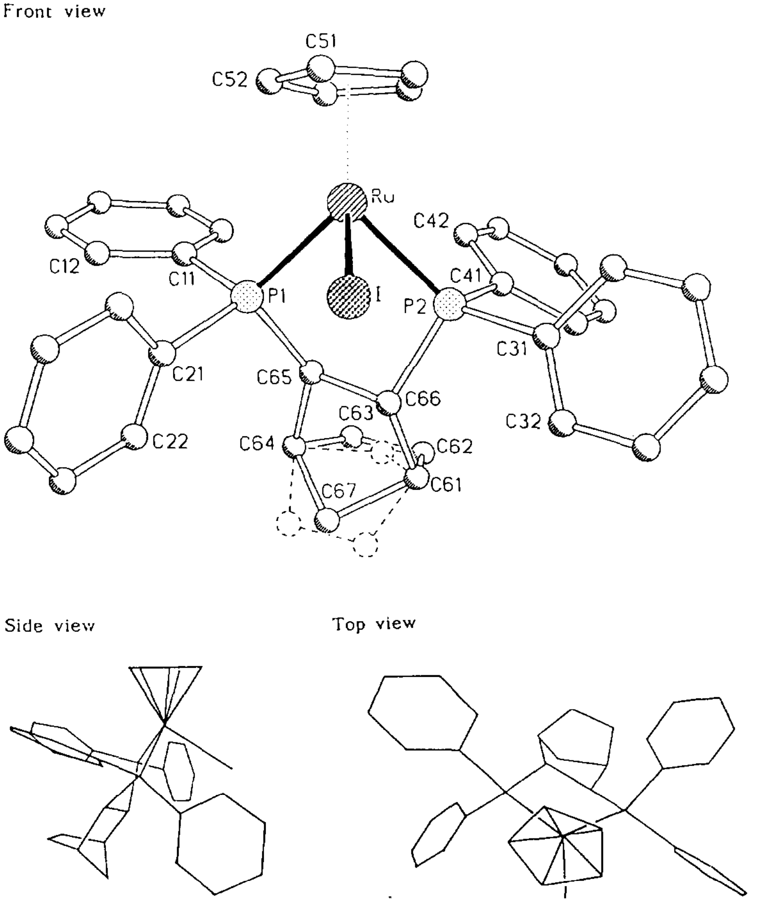


Fig. 2. Top: The molecular structure of **2b** in the crystal. The minor disorder component **2a** is indicated by broken lines. Below: two alternative views of **2b** (see text). Selected bond lengths (Å) and angles (deg): Ru–I 2.739(2), Ru–P(1) 2.305(2), Ru–P(2) 2.310(2), Ru–C 2.175(5)–2.227(7), P(1)–Ru–P(2) 86.1(1), P(1)–Ru–I 93.0(1), P(2)–Ru–I 85.8(1), Ru–P(1)–C(65) 105.0(2), Ru–P(2)–C(66) 105.6(2).

face the iodine atom (see side and top views in Fig. 2). The configuration of the phenyl rings is considerably different from those previously found in $C_2$-symmetrical edge–face systems for $C_2$-chiral bisphosphine ligands [3]. It is noteworthy that the shapes of the coordinating ligands indicate that the four phenyl rings can flexibly change their configuration and are not fixed in the pseudo $C_2$-symmetry of Norphos.

Characteristic differences in the $^1$H chemical shifts (Table 1) between **2a** and **2b** are well explained by their structure. The olefin protons of **2a** appear at $\delta$ 5.00 and 5.87 ppm, whereas those of **2b** at $\delta$ 5.57 and 6.42 ppm. Compared to the olefin protons of free Norphos (6.05 and 6.26 ppm) [11], the two signals of **2a** are shifted to higher field by 0.4–1.0 ppm. This phenomenon is attributed to an anisotropic effect by the two phenyl rings C(21)–C(26) and C(31)–C(36). In contrast, for **2b**, one olefin proton is shifted to higher field by 0.37 and the other is shifted to lower field by 0.16 ppm. The methylene protons of both isomers behave in the opposite manner, while the protons of the cyclopentadienyl ring of both isomers exhibit the

Table 1

$^1$H NMR spectroscopic data for **1**, **2a**, and **2b** in $CDCl_3$ (TMS)

| Complex | Chemical shift (δ, ppm) and assignment | |
|---|---|---|
| **1** | 0.39 (d, $J = 8.4$ Hz, 1 H) | 1.16 (d, $J = 8.4$ Hz, 1 H) |
| | 1.48 (d, $J = 7.7$ Hz, 1 H) | 1.63 (d, $J = 7.4$ Hz, 1 H) |
| | 2.60–2.85 (m, 2 H) | 2.90–3.15 (m, 3 H) |
| | 3.36 (m, 1 H) | |
| | 4.30 (s, 5 H, $C_5H_5$) | 4.39 (s, 5 H, $C_5H_5$) |
| | 5.04 (m, 1 H, C=C*H*) | 5.19 (m, 1 H, C=C*H*) |
| | 5.88 (m, 1 H, C=C*H*) | |
| | 7.25–7.70 (m, 18 H, $C_6H_5$) | |
| | 8.03 (m, 2 H, $C_6H_5$) | 8.08 (m, 2 H, $C_6H_5$) |
| **2a** | 1.62 (d, $J = 8.4$ Hz, 1 H, $CH_2$) | |
| | 1.83 (d, $J = 8.4$ Hz, 1 H, $CH_2$) | |
| | 2.58 (m, 1 H, P-C*H*) | |
| | 2.90 (broad s, 1 H, C*H*) | |
| | 3.21 (broad s, 1 H, C*H*) | |
| | 3.57 (m, 1 H, P-C*H*) | |
| | 4.40 (s, 5 H, $C_5H_5$) | |
| | 5.00 (dd, $J = 3.3$ and 5.5 Hz, 1 H, C=C*H*) | |
| | 5.87 (dd, $J = 3.3$ and 5.5 Hz, 1 H, C=C*H*) | |
| | 7.22–7.60 (m, 18 H, $C_6H_5$) | |
| | 8.08 (m, 2 H, $C_6H_5$) | |
| **2b** | 0.36 (d, $J = 8.2$ Hz, 1 H, $CH_2$) | |
| | 1.56 (d, $J = 8.2$ Hz, 1 H, $CH_2$) | |
| | 2.80 (broad s, 1 H, C*H*) | |
| | 3.00 (broad s, 1 H, C*H*) | |
| | 3.05–3.18 (m, 2 H, P-C*H*) | |
| | 4.40 (s, 5 H, $C_5H_5$) | |
| | 5.57 (dd, $J = 2.7$ and 5.4 Hz, 1 H, C=C*H*) | |
| | 6.42 (dd, $J = 2.7$ and 5.4 Hz, 1 H, C=C*H*) | |
| | 7.22–7.54 (m, 18 H, $C_6H_5$) | |
| | 8.08 (m, 2 H, $C_6H_5$) | |

same chemical shift. Differences are also found around the norbornene skeletons. These observations are consistent with results of the X-ray diffraction study.

## Experimental

*General remarks.* All manipulations were performed under nitrogen. Benzene was distilled from sodium benzophenone ketyl and dichloromethane was distilled from phosphorus pentoxide. $^1$H NMR spectra were recorded on a Bruker WM 250 spectrometer. Optical rotation measurements were determined in dichloromethane in cells of 1 cm path length by use of a Perkin–Elmer 241 polarimeter. CD spectra were measured in dichloromethane on a JASCO J-40A apparatus, in cells of 0.1 cm path length. Elemental analyses were performed by the Microanalytical Laboratory, University of Regensburg. $(Ph_3P)_2Ru(II)(\eta^5\text{-}C_5H_5)Cl$ was prepared as described previously (refs. 4 and 5).

### *Preparation of [( − )-Norphos]Ru(II)($\eta^5$-$C_5H_5$)Cl,* **1**

A solution of $(Ph_3P)_2Ru(\eta^5\text{-}C_5H_5)Cl$ (145 mg, 0.20 mmol) and (−)-Norphos (102 mg, 0.22 mmol) in benzene (20 ml) was stirred at 70–80 °C for 1 day under nitrogen. The reaction mixture was then concentrated and the residue was purified by column chromatography (silica gel, Merck 7734, 5 g; eluants: first 50 ml of $CH_2Cl_2$ then $CH_2Cl_2/Et_2O$ 1 : 1). The progress of the reaction was monitored by tlc, Merck 5554. $R_f = 0.7$ for the starting complex and 0.5 for the product ($CH_2Cl_2$/hexane/$Et_2O$ 7 : 2 : 1 as the eluent). The yellow band was collected. Removal of the solvent gave **1** as an orange solid (120–130 mg, > 90% yield). Mp. 131–135 °C (dec); Anal. of **1**: Found: C, 65.83; H, 5.01. $C_{36}H_{33}ClP_2Ru$ calcd.: C, 65.11; H, 5.03%.

### *Preparation and separation of [( − )-Norphos]Ru(II)($\eta^5$-$C_5H_5$)I,* ***2a** and **2b***

A solution of the ruthenium chloride complex **1** (130 mg, 0.195 mmol) and NaI (1.5 g, 10 mmol) in 30 ml of methanol was heated at 50–60 °C for 3 days. The mixture was then concentrated to ca. 3 ml under reduced pressure. Then 100 ml of dichloromethane was added, the solution was washed with 3 × 10 ml of water, and dried over anhydrous sodium sulfate. After filtration and concentration, the residue was purified by column chromatography (silica gel, Merck 7734, 5 g, $CH_2Cl_2/Et_2O$ 1 : 1). The orange band was collected (tlc, Merck 5554, $R_f = 0.7$ for **2**, $CH_2Cl_2$/hexane/$Et_2O$ 7 : 2 : 1). Removal of the solvents gave a mixture of **2a** and **2b** (18 : 82, 135 mg, 91%). The mixture was recrystallized twice from benzene–hexane at room temperature in the dark to give orange-red prisms of pure **2b** in 30% yield. Mp. 260–263 °C; Anal. of **2**: Found: C, 57.37; H, 4.53. $C_{36}H_{33}IP_2Ru$ calcd.: C, 57.23; H, 4.40%. Optical rotation ($c = 0.09$, $CH_2Cl_2$): $[\alpha]^{21}_{589}$ −449 °, $[\alpha]^{21}_{578}$ −492 °, $[\alpha]^{21}_{546}$ −646 °, $[\alpha]^{21}_{436}$ −196 °. CD spectrum ($1.21 \times 10^{-3}$ mol/l, $CH_2Cl_2$); $[\theta]^{21}_{\lambda}$ values of maxima, minima and nodes (λ, nm); −10940 (435), 0 (401), +4550 (380), +3720 (365), +4969 (350), 0 (334), −8680 (316), 0 (302).

To a solution of **1** (95 mg, 0.143 mmol) in 10 ml of methanol was added a solution of NaI (1.5 g, 10 mmol) in 10 ml of methanol. The mixture was kept for 3 days in the dark at room temperature. The orange-red solid that precipitated was collected to give a mixture of **2a** and **2b** (78 : 22, 61 mg, 57%). After the work-up as described above, 36 mg (33%) of the mixture **2a** : **2b** = 46 : 54 was obtained from the solution.

The mixture **2a** : **2b** = 78 : 22 was recrystallized twice from benzene–hexane at room temperature in the dark to give orange-red prisms, in 30% yield, of the mixture **2a** : **2b** = 85 : 15; Mp. 264–265 °C; Anal. Found: C, 57.30; H, 4.67. $C_{36}H_{33}IP_2Ru$ calcd.: C, 57.23; H, 4.40%. Optical rotation (**2a** : **2b** = 85 : 15, $c = 0.09$, $CH_2Cl_2$): $[\alpha]^{21}_{589}$ −446 °, $[\alpha]^{21}_{578}$ −501°, $[\alpha]^{21}_{546}$ −664 °, $[\alpha]^{21}_{436}$ −250 °. CD spectrum (85 : 15, $1.22 \times 10^{-3}$ mol/l, $CH_2Cl_2$); $[\theta]^{21}_{\lambda}$ values of maxima, minima and nodes (λ, nm); −7850 (440), 0 (410), +7020 (385), +5780 (360), +6200 (350), 0 (334), −7020 (315), 0 (300).

### *Crystal structure determination of* ***2b***

*Crystal data*: $C_{36}H_{33}IP_2Ru$, $M_r = 755.6$. Orthorhombic, $P2_12_12_1$, $a = 12.627(5)$, $b = 15.697(5)$, $c = 16.010(5)$ Å, $U = 3173$ Å$^3$, $Z = 4$, $D_x = 1.58$ Mg m$^{-3}$, $\lambda$(Mo-$K_\alpha$) = 0.71069 Å, $\mu = 1.6$ mm$^{-1}$, $F(000) = 1504$, $T = 291$ K.

*Data collection and reduction*: A crystal of dimensions 0.45 × 0.2 × 0.2 mm was mounted in a glass capillary. 7424 intensities were measured by use of a Siemens *R*3 four-circle diffractometer using monochromated Mo-$K_\alpha$ radiation ($2\theta_{max}$ 50°, $\pm h + k + l$). An absorption correction based on $\psi$-scans was applied, with transmission factors of 0.86–0.94. Merging equivalents gave 5553 unique reflections ($R_{int}$ 0.021),

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| Ru | 4719.7(3) | 4890.0(2) | 7770.6(2) | 40(1) |
| I | 5149.8(2) | 3358.0(2) | 8515.8(2) | 45(1) |
| P(1) | 3443(1) | 4312(1) | 6911(1) | 45(1) |
| P(2) | 5923(1) | 4476(1) | 6762(1) | 41(1) |
| C(11) | 2369(4) | 5010(3) | 6539(3) | 52(2) |
| C(12) | 1321(5) | 4840(4) | 6706(4) | 87(3) |
| C(13) | 523(5) | 5352(5) | 6394(5) | 107(3) |
| C(14) | 757(5) | 6038(4) | 5909(4) | 73(2) |
| C(15) | 1767(5) | 6196(4) | 5708(4) | 75(2) |
| C(16) | 2575(5) | 5691(4) | 6019(5) | 82(3) |
| C(21) | 2707(4) | 3379(3) | 7276(4) | 56(2) |
| C(22) | 2406(5) | 2729(4) | 6772(5) | 78(3) |
| C(23) | 1862(6) | 2027(5) | 7116(7) | 103(4) |
| C(24) | 1640(6) | 1998(5) | 7929(7) | 108(4) |
| C(25) | 1905(5) | 2660(5) | 8435(5) | 88(3) |
| C(26) | 2457(4) | 3343(4) | 8116(4) | 75(2) |
| C(31) | 7163(4) | 3984(3) | 7095(3) | 47(2) |
| C(32) | 7437(5) | 3154(4) | 6921(4) | 65(2) |
| C(33) | 8397(6) | 2821(5) | 7188(5) | 81(3) |
| C(34) | 9088(5) | 3325(5) | 7633(5) | 87(3) |
| C(35) | 8829(5) | 4153(4) | 7818(4) | 72(2) |
| C(36) | 7873(4) | 4477(4) | 7558(4) | 62(2) |
| C(41) | 6405(4) | 5255(3) | 6001(3) | 45(2) |
| C(42) | 5816(4) | 5974(3) | 5808(3) | 49(2) |
| C(43) | 6140(5) | 6519(3) | 5187(4) | 61(2) |
| C(44) | 7076(5) | 6379(3) | 4765(4) | 68(2) |
| C(45) | 7674(5) | 5680(4) | 4952(4) | 65(2) |
| C(46) | 7352(4) | 5119(4) | 5561(3) | 59(2) |
| C(51) | 4475(7) | 5499(4) | 9012(4) | 91(3) |
| C(52) | 3692(5) | 5781(4) | 8450(5) | 81(3) |
| C(53) | 4180(5) | 6205(3) | 7794(4) | 65(2) |
| C(54) | 5253(5) | 6206(3) | 7936(4) | 62(2) |
| C(55) | 5471(5) | 5763(3) | 8673(4) | 69(2) |
| C(61) | 5544(5) | 3311(4) | 5240(4) | 71(2) |
| C(62) | 5448(11) | 3945(7) | 4584(7) | 78(4) |
| C(63) | 4426(10) | 4128(7) | 4480(7) | 79(4) |
| C(64) | 3833(5) | 3645(4) | 5073(4) | 66(2) |
| C(65) | 4133(4) | 4077(3) | 5927(3) | 48(2) |
| C(66) | 5231(4) | 3676(3) | 6121(3) | 48(1) |
| C(67) | 4458(9) | 2798(7) | 5125(7) | 69(3) |
| C(62′) | 5009(17) | 2555(12) | 5134(12) | 65(6) |
| C(63′) | 3968(19) | 2720(14) | 5130(14) | 69(7) |
| C(67′) | 4895(20) | 3946(11) | 4534(11) | 46(5) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

of which 4712 with $F > 4\sigma(F)$ were used for all calculations (program system: Siemens XS/XLS). The orientation matrix was refined from diffractometer angles of 50 reflections in the $2\theta$ range 20–23°.

*Structure solution and refinement.* The structure was solved by the heavy-atom method. Early in the refinement it became clear that the crystal consisted of a mixture of **2b** and **2a**, and a disorder model was therefore necessary for the atoms C(62), C(63) and C(67). The minor component, corresponding to **2a**, is present to the extent of 31% (from refined site-occupation factors) and is indicated in Fig. 2 by broken lines; the dimensions of the disordered moieties should clearly be interpreted with caution. The absolute configuration was determined by an $\eta$-refinement; $\eta$ refined to $-1.02(6)$, whereupon the structure was inverted for the final cycles. Refinement proceeded to $R$ 0.027, $WR$ 0.029 for 359 parameters (non-H atoms anisotropic except for the minor disorder component, H atoms included using a riding model). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$; $S = 1.1$, max. $\Delta/\sigma = 0.002$, max. $\Delta\rho = 0.65$ e Å$^{-3}$.

Final atomic coordinates are presented in Table 2. Full details of the structure determination (complete bond lengths and angles, H atom coordinates, thermal parameters, structure factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2. Copies may be obtained on request by quoting the full literature citation and the reference number CSD-54948.

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