SUPPLEMENTARY INFORMATION

Structural characterisation of Cu-complexes of chiral ferrocenyl diphosphine ligands

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General. Chiral ligands **JosiPhos, rev-JosiPhos, TaniaPhos**. CuBr·SMe₂ was purchased from Aldrich or Acros, and used without further purification. tBuOMe was purchased as anhydrous grade, stored on 4 Å MS and used without further purification. Solvents used were either technical grade (pentane) or distilled from the indicated drying agents (dichloromethane: P₂O₅). CD₂Cl₂ and CDCl₃ were used for NMR. ¹H NMR, ¹³C{¹H} NMR, and ³¹P{¹H} NMR spectra were obtained with Varian VXR600, 500, 400 spectrometers equipped with a 5 mm z-gradient broadband probe. ¹H NMR, ³¹P NMR and ¹³C NMR spectra were obtained at 499.9 MHz and 202.2 MHz respectively. ¹H, ³¹P and ¹³C chemical shifts (δ) were measured relative to the residual solvent peak (CD₂Cl₂ δ = 5.30 ppm for hydrogen atoms, δ = 53.5 ppm for carbon atoms, CDCl₃, δ = 7.26 ppm for hydrogen atoms, δ = 77.0 ppm for carbon atoms). ³¹P chemical shifts are referenced to the standard PPh₃ (-9 ppm). Exact mass spectra were recorded on a LTQ Orbitrap XL (ESI+) or on a DART Xevo G2 QTof.

**Procedure for preparing CuBr complex of enantiopure ligand**¹

A solution of corresponding enantiopure ligand (0.006 mmol) and CuBr·SMe₂ (0.006 mmol) in tBuOMe or DCM (1.3 ml) in a Schlenk tube was stirred at rt for 1 h. The solvent was removed under vacuum and the resulting orange crude residue was washed with cold pentane to afford enantiopure CuBr-complex as an orange powder.

**Procedure for preparing CuBr complex of racemic ligand**¹

To a solution of corresponding (+) ligand (0.006 mmol) and (-) ligand (0.006 mmol) in DCM or tBuOMe (2.6 ml) was added, CuBr·SMe₂ (0.012 mmol). The resulting solution was stirred at rt for 1 h. The precipitate formed within that period. The reaction mixture was filtered and the resulting orange crude residue was washed with cold pentane to afford CuBr-complex of racemic ligand as an orange powder.

1. **X-ray diffraction data with crystal packing characteristics**

X-ray crystal structure determinations

Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (\( = 0.71073 \) Å) at a temperature of 150(2) K. Software packages used for intensity integration were Eval15\(^2\) (10304, 10292) and Saint\(^3\) (10297). Absorption correction and scaling was performed based on multiple measured reflections with SADABS and TWINABS.\(^4\) The structures were solved by Direct Methods using the programs SHELXS-9710. Least-squares refinement was performed with SHELXL-97\(^4\) against \( F^2 \) of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.\(^5\)

Rac-CuBr- rev-JosiPhos: CCDC 908802 (10304a), rac-CuBr- JosiPhos: CCDC 908803 (10292a), rac-CuBr-TaniaPhos: CCDC 908804 (10297a) and enant. CuBr-TaniaPhos: CCDC 909403 (CP 928) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

\[ \text{rac-CuBr- rev-JosiPhos (10304a): } C_{72}H_{88}Br_{2}Cu_{2}Fe_{2}P_{4}, \text{ Fw = 1475.90, yellow needle, 0.23 x 0.07 x 0.05 mm}^3, \text{ monoclinic, } C2/c (\text{no. 15}), \alpha = 25.5740(13), b = 13.1576(5), c = 21.5042(7) \text{ Å, } \beta = 118.745(2) \text{ °, } V = 6344.3(4) \text{ Å}^3, Z = 4, D_x = 1.545 \text{ g/cm}^3, = 2.51 \text{ mm}^{-1}. \]

53920 Reflections were measured up to a resolution of \( (\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ Å}^{-1} \). 7293 Reflections were unique (\( R_{\text{int}} = 0.062 \)), of which 5387 were observed \([I>2\sigma(I)]\). 371 Parameters were refined with no restraints. R1/wR2 \([I > 2\sigma(I)]: 0.0333 / 0.0672 \). R1/wR2 \([\text{all refl.}]: 0.0596 / 0.0751 \). S = 1.018. Residual electron density between -0.35 and 0.48 e/Å\(^3\).

\[ \text{rac-CuBr-JosiPhos (10292a): } C_{36}H_{44}BrCuFeP_{2}, \text{ Fw = 737.95, orange block, 0.53 x 0.29 x 0.21 mm}^3, \text{ triclinic, } \text{P}_{\text{1}} (\text{no. 2}), \alpha = 10.2840(5), b = 12.7983(6), c = 13.8363(6) \text{ Å, } \alpha = 66.466(3), \beta = 72.416(2), \gamma = 84.314(2) \text{ °, } V = 1591.15(13) \text{ Å}^3, Z = 2, D_x = 1.540 \text{ g/cm}^3, \mu = 2.51 \text{ mm}^{-1}. \]

The crystal consisted of several fragments and the intensity integration was performed with three orientation matrices. 32999 Reflections were measured up to a resolution of \( (\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ Å}^{-1} \). 7312 Reflections were unique (\( R_{\text{int}} = 0.022 \)), of which 6596 were observed \([I>2\sigma(I)]\). 373 Parameters were refined with no restraints. R1/wR2 \([I > 2\sigma(I)]: 0.0230 / 0.0577 \). R1/wR2 \([\text{all refl.}]: 0.0271 / 0.0590 \). S = 1.061. Residual electron density between -0.45 and 0.39 e/Å\(^3\).

**rac-CuBr-TaniaPhos (l0297a):** C_{43}H_{39}BrCuFeP \cdot CH_2Cl_2, \text{ Fw} = 915.92, \text{ yellow needle, 0.32 x 0.12 x 0.07 mm}^3, \text{ monoclinic, P2}_1/c \text{ (no. 14), } a = 12.7006(17), b = 15.406(2), c = 22.137(3) \, \AA, \beta = 114.090(3) \degree, V = 3954.3(9) \, \AA^3, Z = 4, D_x = 1.539 \, \text{g/cm}^3, \mu = 2.16 \, \text{mm}^{-1}. 43034 \text{ Reflections were measured up to a resolution of (sin } \theta/\lambda_{\text{max}} = 0.65 \, \text{Å}^{-1}. 9044 \text{ Reflections were unique (R_{int} = 0.074), of which 5658 were observed [I>2\sigma(I)]. 471 Parameters were refined with no restraints. R1/wR2 [I > 2\sigma(I)]: 0.0476 / 0.1052. R1/wR2 [all refl.]: 0.1021 / 0.1239. S = 1.010. Residual electron density between -0.85 and 0.77 e/Å³.}

**Enant.-CuBr-TaniaPhos (cp928):** C_{43}H_{39}BrCuFeNP_2, M_r = 831.03, \text{ orthorhombic, P2}_12_12_1, a = 11.268(3), b = 16.852(4), c = 18.885(4) \, \AA, V = 3586.0(15) \, \AA^3, Z = 4, D_x = 1.539 \, \text{g/cm}^3, F(000) = 1696, \mu = 22.34 \, \text{cm}^{-1}, \lambda(\text{MoK} \alpha) = 0.71073 \, \text{Å}, T = 100(1) \, \text{K}, 28199 \text{ reflections measured, GooF = 0.948, } wR(F^2) = 0.1548 \text{ for 7340 unique reflections and 445 parameters and } R(F) = 0.0623 \text{ for 4153 reflections obeying } F_o \geq 4.0 \sigma(F_o) \text{ criterion of observability. The asymmetric unit consists of one molecule of the title compound.}

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<th>Space group</th>
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<td>C2/c (no. 15)</td>
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</tbody>
</table>

*a monohydrate; *b disordered structure; CH_2Cl_2 solvate.

Figure 1a. Molecular structure of rac-CuBr- rev-JosiPhos (10304a) in the crystal (50% probability level). Hydrogen atoms are omitted for clarity. Symmetry operation i: 1-x, 1-y, 1-z. Crystals were obtained from gel in CH$_2$Cl$_2$. Crystallization of racemic copper bromide complex was achieved using the antisolvent crystallization technique.\textsuperscript{7}

Figure 1b. Molecular structure of *enant*-CuBr- *rev*-JosiPhos (CP960\textsuperscript{2} as well as Q1610) in the crystal (50% probability level). C-H hydrogen atoms are omitted for clarity. Symmetry operation i: -x, y, 0.5-z.
Figure 2. Molecular structure of rac-CuBr-JosiPhos (I0292a) in the crystal (50% probability level). Only one enantiomer of the racemic crystal structure is shown. Hydrogen atoms are omitted for clarity. Crystals were obtained from a mixture of t-BuOMe and CH$_2$Cl$_2$. 
Figure 3a. Molecular structure of rac-CuBr-TaniaPhos (10297a) in the crystal (50% probability level). Only one enantiomer of the racemic crystal structure is shown. Hydrogen atoms and CH$_2$Cl$_2$ solvent molecule are omitted for clarity. Crystals were obtained from a mixture of t-BuOMe/CH$_2$Cl$_2$. 
Figure 3b. Molecular structure of enantiopure-CuBr-TaniaPhos (cp928) in the crystal (50% probability level). Each asymmetric unit contains one formula unit (molecule) with no atom setting at special position. The orthorhombic unit cell contains four discrete units of the title compound separated by normal van der Waals distances. (Fig. 2). The chiral center of C23 showed the $R$-configuration. A short Cu-H23 distance of 2.263 Å is observed; the angle over H23 is 140.7° (Cu-H23-C23). Crystals were obtained from a mixture of $t$-BuOMe/CH$_2$Cl$_2$. 
2. CuBr- rev-JosiPhos complex

CDCl₃

rev-Josiphos CuBr enantiopure complex $^1$H-NMR -CD$_2$Cl$_2$
rev-Josiphos CuBr enantiopure complex $^{31}$P-NMR -CD$_2$CP

PPh$_3$
rev-Josiphos CuBr enantiopure complex $^{13}$C-NMR -CD$_2$CP
ESI-MS of CuBr- rev-JosiPhos enantiopure complex in t-BuOMe
ESI-MS of CuBr- rev-JosiPhos enantiopure complex in CH$_2$Cl$_2$
DART-MS of CuBr-rev-JosiPhos enantiopure complex in CH$_2$Cl$_2$

FRA-REV-JOSIPHOS--E-DCM  m/z 2000  T 500C
FRA-REV-JOSIPHOS--E-DCM 254 (4.311) Cm (250:261)  TOF MS ES+

1.04e5
ESI-MS of CuBr-L1 racemic complex in CH$_2$Cl$_2$
3. CuBr- JosiPhos complex

Josiphos- CuBr enantiopure complex

\[ \text{H-NMR -} CD^2 CF \]
Josiphos-CuBr enantiopure complex $^{13}$C-NMR CD$_2$ CF
ESI-MS of CuBr- JosiPhos enantiopure complex in t-BuOMe
ESI-MS of CuBr- JosiPhos enantiopure complex in CH$_2$Cl$_2$
DART-MS of CuBr-JosiPhos enantiopure complex in CH$_2$Cl$_2$

FRA-JOSIPHOS-E-DCM-500C-m/z 2000
FRA-JOSIPHOS-E-DCM-500C-2 180 (3.060) Cm (178:189)

TOF MS ES+
2.86e5
DART-MS of CuBr- JosiPhos enantiopure complex solid sample

FRA-JOSIPHOS-E-SOLID-500C-m/z 2000
FRA-JOSIPHOS-E-SOLID-500C 134 (2.282) Cm (93:199)

TOF MS ES+
5.18e6

1.6 min to 3.40 min
Josiphos CuBr racemic complex
$^1$H-NMR -CD$_2$ CF
Josiphos CuBr racemic complex $^{31}$P-NMR -CD$_2$CF$_3$
Josiphos-CuBr racemic complex \(^{13}\)C-NMR CD\(^2\)CF\(_3\)
Josiphos-CuBr racemic complex  $^{13}$C-NMR CD$_2$C$_6$
ESI-MS of CuBr-JosiPhos racemic complex in CH$_2$Cl$_2$
DART-MS of CuBr- JosiPhos racemic complex in CH₂Cl₂

JOSIPHOS--R-DCM  m/z 2000  T 500C
JOSIPHOS--R-DCM 178 (3.026) Cm (174:181)

TOF MS ES+

3.58e5

m/z

0 200 400 600 800 1000 1200 1400 1600 1800

%
DART-MS of CuBr-JosiPhos racemic solid sample

FRA-JOSIPHOS-SOLID-R-22-01-2012
FRA-JOSIPHOS-SOLID-R-22-01-2012 175 (2.976) Cm (149:180)

TOF MS ES+
4.44e5
4. CuBr- TaniaPhos complex

Taniaphos- CuBr enantiopure complex  CD₂Cl₂ ¹H-NMR
enantiopure TaniaPhos-CuBr-L3  d-DCM, P-NMR, 400MHz
ESI-MS CuBr- TaniaPhos enantiopure complex in t-BuOMe
ESI-MS CuBr- TaniaPhos enantiopure complex in CH$_2$Cl$_2$
Taniaphos-CuBr racemic complex  CDCl$_3$ $^1$H-NMR

DCM

SMe$_2$

HFO

TMS
Taniaphos-CuBr racemic complex  CDCl$_2$ $^{31}$P-NMR

PPI3
ESI-MS CuBr- TaniaPhos racemic complex in CH$_2$Cl$_2$
DART-MS CuBr TaniaPhos racemic complex in CH$_2$Cl$_2$