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SUPPLEMENTARY INFORMATION

Structural characterisation of Cu-complexes of chiral ferrocenyl diphosphine ligands

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CuBr-JosiPhos

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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 ligand¹

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 ligand¹

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

¹ Caprioli, F.; Madduri, A.V. R.; Minnaard, A. J.; Harutyunyan, S. R. *Chem Comm.* **2013**, 5450.

X-ray crystal structure determinations

Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 150(2) K. Software packages used for intensity integration were Eval15² (**10304**, **10292**) and Saint³ (**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-97⁴ 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.

rac-CuBr- rev-JosiPhos (10304a): $C_{72}H_{88}Br_2Cu_2Fe_2P_4$, Fw = 1475.90, yellow needle, $0.23 \times 0.07 \times 0.05 \text{ mm}^3$, monoclinic, C2/c (no. 15), $a = 25.5740(13)$, $b = 13.1576(5)$, $c = 21.5042(7) \text{ \AA}$, $\beta = 118.745(2)^\circ$, $V = 6344.3(4) \text{ \AA}^3$, $Z = 4$, $D_x = 1.545 \text{ g/cm}^3$, $\mu = 2.51 \text{ mm}^{-1}$. 53920 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65 \text{ \AA}^{-1}$. 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. $R1/wR2$ [all refl.]: 0.0596 / 0.0751. $S = 1.018$. Residual electron density between -0.35 and $0.48 \text{ e/\AA}^3$.

rac-CuBr-JosiPhos (10292a): $C_{36}H_{44}BrCuFeP_2$, Fw = 737.95, orange block, $0.53 \times 0.29 \times 0.21 \text{ mm}^3$, triclinic, $P\bar{1}$ (no. 2), $a = 10.2840(5)$, $b = 12.7983(6)$, $c = 13.8363(6) \text{ \AA}$, $\alpha = 66.466(3)$, $\beta = 72.416(2)$, $\gamma = 84.314(2)^\circ$, $V = 1591.15(13) \text{ \AA}^3$, $Z = 2$, $D_x = 1.540 \text{ g/cm}^3$, $\mu = 2.51 \text{ mm}^{-1}$. 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 $(\sin \theta/\lambda)_{\max} = 0.65 \text{ \AA}^{-1}$. 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. $R1/wR2$ [all refl.]: 0.0271 / 0.0590. $S = 1.061$. Residual electron density between -0.45 and $0.39 \text{ e/\AA}^3$.

² Schreurs, A. M. M.; Xian, X.; Kroon-Batenburg, L.M.J. *J. Appl. Cryst.* **2010**, 43, 70.

³ Bruker (2001), SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.

⁴ Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112.

⁵ Spek, A.L. *Acta Cryst.* **2009**, D65, 148.

***rac*-CuBr-TaniaPhos (I0297a):** C₄₃H₃₉BrCuFeP · CH₂Cl₂, Fw = 915.92, yellow needle, 0.32 x 0.12 x 0.07 mm³, monoclinic, P2₁/c (no. 14), a = 12.7006(17), b = 15.406(2), c = 22.137(3) Å, β = 114.090(3) °, V = 3954.3(9) Å³, Z = 4, D_x = 1.539 g/cm³, = 2.16 mm⁻¹. 43034 Reflections were measured up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. 9044 Reflections were unique (R_{int} = 0.074), of which 5658 were observed [I > 2σ(I)]. 471 Parameters were refined with no restraints. R1/wR2 [I > 2σ(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):** C₄₃H₃₉BrCuFeNP₂, M_r = 831.03, orthorhombic, P2₁2₁2₁, a = 11.268(3), b = 16.852(4), c = 18.885(4) Å, V = 3586.0(15) Å³, Z = 4, D_x = 1.539 gcm⁻³, F(000) = 1696, μ = 22.34 cm⁻¹, λ(MoKα) = 0.71073 Å, T = 100(1) K, 28199 reflections measured, GooF = 0.948, wR(F²) = 0.1548 for 7340 unique reflections and 445 parameters and R(F) = 0.0623 for 4153 reflections obeying F_o ≥ 4.0 σ(F_o) criterion of observability. The asymmetric unit consists of one molecule of the title compound.

Entry	CuBr-Ligand	CCDC number		Space group	D _x [g/cm ³]	K.P.I. ⁶
1	<i>rac</i> -CuBr- revJosiPhos	CCDC 908802	I0304a	C2/c (no. 15)	1.545	69.8%
2	<i>enant</i> -CuBr- revJosiPhos	CCDC 610500	CP960 ^a	C222 ₁ (no. 20)	1.475	67.0%
3	<i>enant</i> -CuBr- revJosiPhos	CCDC 909405	Q1610 ^a	C222 ₁ (no. 20)	1.417	^{-b}
4	<i>rac</i> -CuBr- JosiPhos	CCDC 908803	I0292a	P $\overline{1}$ (no. 2)	1.540	69.7%
5	<i>enant</i> -CuBr- JosiPhos	CCDC 261573	CP963	P2 ₁ (no. 4)	1.529	69.3%
6	<i>rac</i> -CuBr- TaniaPhos	CCDC 908804	I0297a ²	P2 ₁ /c (no. 14)	1.539	68.0%
7	<i>enant</i> -CuBr- TaniaPhos	CCDC 909403	CP928	P2 ₁ 2 ₁ 2 ₁ (no. 19)	1.539	68.5%

^a monohydrate; ^b disordered structure ; ^c CH₂Cl₂ solvate.

⁶ Kitajgorodskij Packing Index, see Kitajgorodskij, A.I.: *Molecular Crystals and Molecules*, New-York, Academic Press (1973).

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 CH₂Cl₂. Crystallization of racemic copper bromide complex was achieved using the antisolvent crystallization technique.⁷

⁷ Choquesillo-Lazarte, D.; García-Ruiz, J. M. *J. Appl. Cryst.* **2011**, 44, 172.

Figure 1b. Molecular structure of *enant*-CuBr- **rev-JosiPhos** (CP960² 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 (**10292a**) 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 CH₂Cl₂.

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 CH₂Cl₂ solvent molecule are omitted for clarity. Crystals were obtained from a mixture of *t*-BuOMe/CH₂Cl₂.

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/CH₂Cl₂.

2. CuBr- rev-JosiPhos complex

rev-Josiphos CuBr enantiopure complex ^{13}C -NMR - CD_2Cl_2

ESI-MS of CuBr- rev-JosiPhos enantiopure complex in *t*-BuOMe

Acq. File: 120216Francesca-TBME.wiff
Sample Comment:
Acq. Date: Thursday, February 16, 2012

Acq. Time: 13:48
Sample Name: 1-Rev-JosiPhos-E in TBME

Method Name: N/A

Sample Name: 1-Rev-JosiPhos-E in TBME

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

ESI-MS of CuBr- rev-JosiPhos enantiopure complex in CH₂Cl₂

DART-MS of CuBr-rev-JosiPhos enantiopure complex in CH₂Cl₂

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 CH₂Cl₂

Acq. File: 120214Franceska.wiff
Sample Comment: in DCM
Acq. Date: Tuesday, February 14, 2012

Acq. Time: 10:34
Sample Name: 4-REV-JosiPhos R

Method Name: N/A

Sample Name: 4-REV-JosiPhos R

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

NO₂HO
H21.01 HSWM

3. CuBr- JosiPhos complex

Josiphos-CuBr enantiopure complex ^{13}C -NMR CD_2Cl_2

ESI-MS of CuBr- JosiPhos enantiopure complex in *t*-BuOMe

Acq. File: 120216Francesca-TBME.wiff
Sample Comment:
Acq. Date: Thursday, February 16, 2012

Acq. Time: 14:10
Sample Name: 2-JosiPhos-E in TBME

Method Name: N/A

Sample Name: 2-JosiPhos-E in TBME

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

ESI-MS of CuBr- JosiPhos enantiopure complex in CH₂Cl₂

Acq. File: 120214Franceska.wiff
Sample Comment: in DCM
Acq. Date: Tuesday, February 14, 2012

Acq. Time: 09:22
Sample Name: 1-JosiPhos E

WASH
WITH
CH₃CN

Method Name: N/A

Sample Name: 1-JosiPhos E

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

DART-MS of CuBr- JosiPhos enantiopure complex in CH₂Cl₂

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

Josiphos-CuBr racemic complex ^{13}C -NMR CD_2Cl_2

ESI-MS of CuBr- JosiPhos racemic complex in CH₂Cl₂

Acq. File: 120214Francesca.wiff
Sample Comment: in DCM
Acq. Date: Tuesday, February 14, 2012

Acq. Time: 09:54
Sample Name: 2-JosiPhos R

WASH
CH₃CN

Method Name: N/A

Sample Name: 2-JosiPhos R

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

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

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

ESI-MS CuBr- TaniaPhos enantiopure complex in *t*-BuOMe

Acq. File: 120216Francesca-TBME.wiff
Sample Comment:
Acq. Date: Thursday, February 16, 2012

Acq. Time: 14:22
Sample Name: 3-TaniaPhos-E in TBME

Method Name: N/A

Sample Name: 3-TaniaPhos-E in TBME

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

ESI-MS CuBr- TaniaPhos enantiopure complex in CH₂Cl₂

Acq. File: 120214Franceska.wiff
Sample Comment: in DCM
Acq. Date: Tuesday, February 14, 2012

Acq. Time: 11:49
Sample Name: 9-TaniaPhos E

Method Name: N/A

Sample Name: 9-TaniaPhos E

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

ESI-MS CuBr- TaniaPhos racemic complex in CH₂Cl₂

Acq. File: 120214Franceska.wiff
Sample Comment: in DCM
Acq. Date: Tuesday, February 14, 2012

Acq. Time: 12:01
Sample Name: 10-TaniaPhos R

WASH
WITH CH₃OH

Method Name: N/A

Sample Name: 10-TaniaPhos R

Scan Mode: Profile

Project: Monsters

Batch Name: ManualTune.bat

Dwell: 0.4 ms

DART-MS CuBr TaniaPhos racemic complex in CH₂Cl₂

FRA-TANIAPHOS-R-DCM m/z 2000 T 500C

FRA-TANIAPHOS-R-DCM 153 (2.604) Cm (148:171)

TOF MS ES+
1.00e6