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Water-soluble metal complexes and catalysts X. BIPHLOPHOS, a novel axially chiral diphosphine ligand: preparation and application in the asymmetric rhodium-catalyzed hydroformylation of styrene☆

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Abstract

A stereospecific synthesis of both enantiomers of the new axially chiral diphosphine ligand 2,2′-bis(diphenylphosphinomethyl)-4,4′,6,6′-tetrachloro-1,1′-biphenyl **5** called BIPHLOPHOS, starting from the readily available pure enantiomers of 4,4′,6,6′-tetrachlorodiphenic acid, was developed. The (−)-enantiomer was then tested in the homogeneous rhodium-catalyzed asymmetric hydroformylation of styrene. The ligand was used to prepare the complex $IrH(CO)(PPh_3)L_2$ ($L_2 = \mathbf{5}$) **6**, the crystal structure of which was determined and compared with the related complex $RhH(CO)(PPh_3)$(BISBI). Additionally, ligand **5** was sulfonated by classical methods to yield a uniform reaction product. This is in sharp contrast to the analogous ligands BISBI and NAPHOS, where sulfonation yields a complicated mixture of products. The sulfonated ligand is excellently water-soluble and shows activities and regioselectivities in the hydroformylation of styrene comparable to the well-investigated ligand BISBI.

Keywords: Rhodium; Hydroformylation; Asymmetric catalysis; Diphosphines; Biphasic catalysis

1. Introduction

Hydroformylation, the largest-volume technical process of organometallic chemistry [1], has a long tradition in our research group [2,3]. Asymmetric hydroformylation of styrene derivatives permits an intriguingly direct access to anti-inflammatory drugs on the basis of 2-aryl-propionic acids, but has still remained a challenging topic in enantioselective catalysis. Not only must the enantioselectivity of the catalyst system be high, but further problems arise from the need for regio- and chemoselectivity, as non-racemic aldehydes or hydrogenation products can be possible by-products [4,5]. Remarkably high enantiomeric inductions with rhodium-based catalyst systems were obtained by Takaya et al. using phosphine–phosphite ligands [6] of the BINAPHOS-type **A** (Scheme 1) or by researchers at DuPont with diphosphite ligands [7]. Chirally modified platinum–tin catalysts have also been known to induce high enantioselectivities [4,5]. However, all these catalysts suffer from the drawback of limited stability in the presence of trace amounts of water. On the other hand, very little is known about water-stable rhodium–phosphine catalysts in asymmetric hydroformylation. Most of the systems tested performed rather poorly, yielding only around 20% *ee* in the hydroformylation of the model substrate styrene [4,5].

Only recently, we described the use of the enantiomerically pure NAPHOS ligand in the mono- and biphasic hydroformylation of styrene, which for the first time permits enantioselectivities of 34% *ee* [8]. In contrast to most diphosphine ligands studied before, the large natural bite angle of NAPHOS permits the

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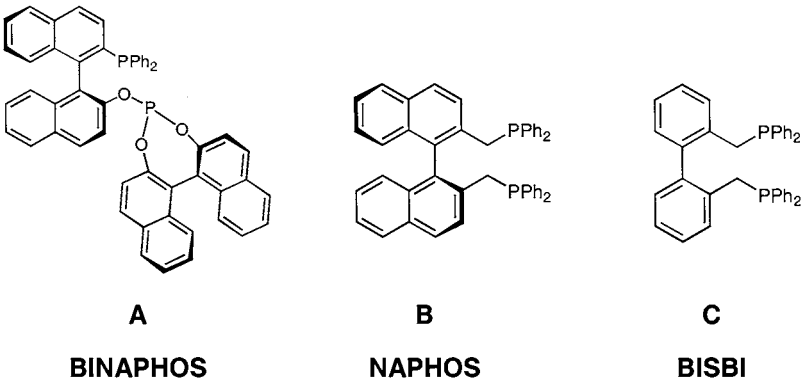


Scheme 1. Biaryl ligands used together with rhodium in hydroformylation reactions.

formation of a nine-membered chelate ring with the rhodium centre. The size of the chelate ring has a strong influence on the coordination mode of the ligand during the catalytic cycle. The recent work of our group concerning the mechanism of rhodium-BINAPHOS catalyzed asymmetric hydroformylation directs utmost attention to the coordination of the diphosphine ligand at the metal centre [9,10]. Therefore, we have continued our studies of chiral large-bite angle diphosphine ligands.

One of the outstanding properties of our BINAS ligand (the sulfonated ligand NAPHOS **B**) is the opportunity of hydroformylation in *biphasic systems* with a water-based catalyst phase, as the ligand can be made completely water-soluble by sulfonation of the aromatic backbone. However, a complicated mixture of sulfonation products is formed due to the multifunctionality of the polyaromatic molecule towards sulfonating reagents [11]. We now present a new chiral diphosphine ligand with a large natural bite angle, which can be selectively sulfonated to a water-soluble product.

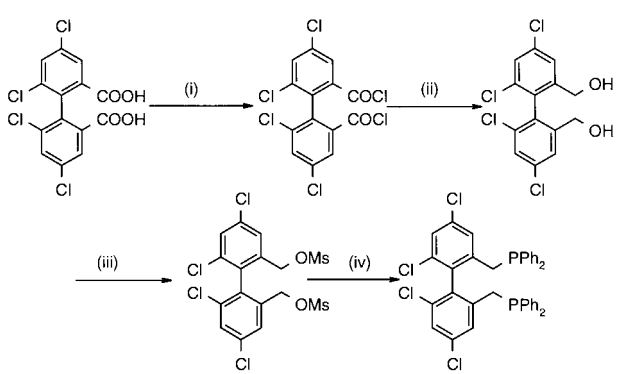
2. Results and discussion

2,2′-Bis(diphenylphosphinomethyl-)1,1′-biphenyl, called BISBI **C** [12], was originally described by researchers at the Kodak company as an efficient ligand for the rhodium-catalyzed hydroformylation of α-olefins with a high selectivity for straight-chain aldehydes. It is the biphenyl homologue of the aforementioned ligand NAPHOS. In contrast to NAPHOS, its axial chirality is not stable at room temperature, and substituents in the 6,6′-positions are required if the enantiomers are to be separated. Although the preparation of 2,2′,6,6′-tetrasubstituted 1,1′-biphenyls is well established, no chiral BISBI-analogous diphosphine ligand has been described up to now.

2.1. Stereospecific ligand synthesis

Starting with 4,4′,6,6′-tetrachlorodiphenic acid, which was easily synthesized and separated into its enantiomers according to well-established literature methods, we developed a classical stereospecific synthetic route to both enantiomers of the optically pure ligand 2,2′-bis(diphenylphosphinomethyl)-4,4′,6,6′-tetrachloro-1,1′-biphenyl (Scheme 2). As the (−)-enantiomer of 4,4′,6,6′-tetrachlorodiphenic acid is obtained more easily using the cheap and non-toxic chiral auxiliary dehydroabietylamine, we describe here the synthesis of the chiral ligand derived from that precursor. The other enantiomer can be prepared with comparable ease from (+)-4,4′,6,6′-tetrachlorodiphenic acid, the isolation of which involves brucine as chiral auxiliary. Because of the toxicity of the latter we limited ourselves to demonstrating the feasibility of the ligand synthesis from the (+)-precursor and continued our investigations with the other enantiomer of the ligand.

(−)-4,4′,6,6′-Tetrachlorodiphenic acid was quantitatively converted to the acid chloride by refluxing it in excess $SOCl_2$ for 2 h. The acid chloride was reduced



Scheme 2. Reagents and conditions: (i) $SOCl_2$, reflux, 2 h; (ii) $Li[AlH_4]$, Et_2O, −78°C, 12 h; (iii) MsCl, NEt_3, CH_2Cl_2, −30°C, 1 h; (iv) $K[PPh_2]$, THF, −78°C, 12 h. Abbreviations: Ph = C_6H_5, Ms = SO_2CH_3.

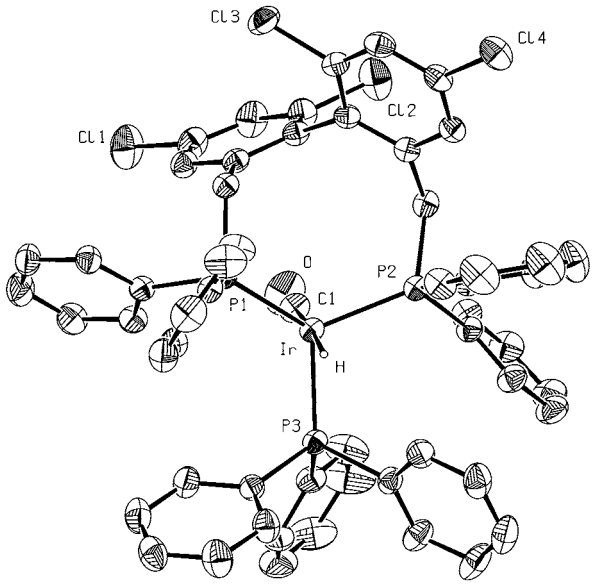


Fig. 1. PLATON plot and numbering scheme of the crystal structure of $IrH(CO)(TPP)L_2$ **6**. All hydrogens except for the hydride have been omitted for clarity. Important dimensions include; bond lengths (Å): Ir–P(1) 2.2772(7), Ir–P(2) 2.2965(7), Ir–P(3) 2.3058(7), Ir–C(1) 1.903(3), Ir–H 1.57(4); bond angles (°): P(1)–Ir–P(2) 124.23(2), P(1)–Ir–P(3) 121.52(2), P(2)–Ir–P(3) 110.17(2), C1–Ir–H 174.9(15).

to 4,4′,6,6′-tetrachloro-2,2′-bibenzylic alcohol with Li-$[AlH_4]$ in diethyl ether in excellent yield. Then, its hydroxo functionalities were converted to leaving groups by mesyl chloride in CH_2Cl_2 using triethylamine as a base, which yielded considerably better results than the reaction with tosyl chloride in pyridine [13]. The reaction of the diol with HBr or PBr_3 was also studied, but did not prove better than introducing the mesyl group. The dimesylate was subsequently reacted with a 0.5 M stock solution of potassium diphenylphosphide in THF at low temperature (-78°C) to give the desired diphosphine in moderate yield. Recrystallisation from ethanol gave a colorless, analytically pure powder.

2.2. Synthesis and structure of an iridium–BIPHLOPHOS complex

The complex $IrH(CO)(TPP)L_2$ **6** ($TPP = P(C_6H_5)_3$, $L_2 =$ **5**) was synthesized as a stable model substance for the catalytically active rhodium hydrido dicarbonyl complex. When equimolar amounts of $IrH(CO)(TPP)_3$ and **5** were stirred in CH_2Cl_2 overnight, a complete exchange of two TPP ligands with **5** occurred. After washing with methanol, the pure complex **6** could be isolated as a yellow solid. Crystallisation from CH_2Cl_2/pentane yielded crystals suitable for X-ray analysis (Fig. 1). The ligand spans two equatorial positions in the trigonal bipyramidal complex. The third equatorial position is taken by triphenylphosphine, whereas the two apical positions are taken by a hydrido and a CO ligand. The bite angle of the chelating ligand **6** in this complex is 124.2°, which is very similar to the bite angle of 124.8° Casey observed in the analogous model complex $RhH(CO)(TPP)L_2$ ($L_2 =$ BISBI) [14] (Table 1). Thus, the chloro substituents in the 6,6′-positions of the biphenyl backbone do not seem to hinder the flexibility of the ligand and hence influence the coordination behavior of the ligand with respect to BISBI.

The crystal structure is in full agreement with the NMR spectra obtained from **6** in C_6D_6. The ^{1}H-NMR spectrum shows a doublet of triplets at -11.1 ppm (dt, J(H–P3) 16.1 Hz, J(H–P1/P2) 24.2 Hz) caused by the coupling of the hydride ligand to the three coordinated phosphorus atoms. The ^{31}P-NMR spectrum reveals a complicated ABX coupling pattern of the diastereotopic chelating phosphorus atoms with the triphenylphosphine.

2.3. Sulfonation of (±)-5

Sulfonation of NAPHOS yields complicated mixtures of water-soluble sulfonated phosphine ligands, which—depending on the reaction conditions—consist of regioisomers of several products with a variable degree of sulfonation, ranging from two to eight [8,15]. On the contrary, sulfonation of the ligand **5** yields a highly water-soluble, uniform product.

Direct sulfonation of the racemic ligand was performed as previously described [11], using fuming sulfuric acid with a content of free SO_3 of 30%. Reversed-phase HPLC experiments showed that a single product had formed, accompanied only by small amounts (about 6%) of the phosphine oxide of the sulfonated species. Comparison of its retention time under the conditions used with authentic samples of other two- to eightfold sulfonated ligands of the TPP-, BISBI- and NAPHOS type allowed the conclusion that the product bears two sulfonato groups. As the tetrachlorobiphenyl backbone of the ligand is stable against electrophilic substitution by sulfonato groups (the starting material 4,4′,6,6′-tetrachlorodiphenic acid is recrystallized from concentrated sulfuric acid at 150°C), the substitution must take place at the phenyl rings of the diphenylphosphino moieties. Assuming a uniform distribution of the sulfonato groups over the phenyl rings,

Table 1
Comparison of bond angles of $IrH(CO)(TPP)L_2$ ($L_2 =$ **5**) and $RhH(CO)(TPP)L_2$ ($L_2 =$ BISBI) (P1, P2, P3 numbered as in Fig. 1)

Bond angles (°)			
$IrH(CO)(TPP)L_2$ ($L_2 =$ **5**)		$RhH(CO)(TPP)L_2$ ($L_2 =$ BISBI)	
P(1)–Ir–P(2)	124.23(2)	P(1)–Rh–P(2)	124.8(1)
P(1)–Ir–P(3)	110.17(2)	P(2)–Rh–P(3)	122.6(1)
P(2)–Ir–P(3)	121.52(2)	P(1)–Rh–P(3)	108.0(1)

Table 2
Rhodium-catalyzed hydroformylation of styrene[a]

Ligand	Solvent	Temperature (°C)	% Converted[b]	Regioselectivity i/n[c]	% *ee*
BISBI	Toluene	40	56	4.7	–
(±)-**5**	Toluene	40	52	4.4	–
Sulfonated BISBI	Toluene/water	40	21	4.8	–
Sulfonated (±)-**5**	Toluene/water	40	16	4.6	–
(−)-**5**	Toluene	40	49	4.5	15
(−)-**5**	Toluene	80	68	4.2	–

[a] Standard conditions: substrate/Rh ratio: 300/1; ligand/Rh ratio: 2/1; pressure: 50 bar (1:1 mixture of H_2 and CO); reaction time: 16 h.
[b] Determined by GC.
[c] i/n = branched/linear.

the two phosphorus atoms should become stereogenic centres due to their three different substituents, resulting in the formation of eight stereoisomers because of the chirality of the backbone. However, neither HPLC nor NMR analysis, as we used them, were capable of separating the different diastereomers.

2.4. Catalytic performance

The described ligands were tested and compared to the BISBI ligand in homogeneous and bisphasic (water/organic) rhodium-catalyzed hydroformylation of styrene. BISBI and sulfonated BISBI were compared to the racemic diphosphine **5** and the sulfonated racemic ligand **5** with respect to their activity and i/n-selectivity. Subsequently, (−)-**5** was tested in the homogeneous hydroformylation of styrene (Table 2).

The comparison with BISBI showed high similarity in all cases. Both activity and selectivity for the favored product hydratropaldehyde compare very well. Only the activity of sulfonated **5** is somewhat lower than that of sulfonated BISBI. When the nonracemic diphosphine (−)-**5** was used at temperatures up to 40°C, an enantiomeric excess of 15% of (*S*)-hydratropaldehyde could be observed, whereas only racemic product was detected, when the reaction was conducted at 80°C. This compares to 34% *ee* obtained with enantiopure NAPHOS under very similar conditions [8]. So the asymmetry of the binaphthyl backbone in NAPHOS seems to have a more pronounced effect on the optical induction than that of the substituted biphenyl backbone. This can reasonably be attributed to its higher steric constraint.

3. Conclusion

As compared to the racemic ligand BISBI, the coordination behaviour of the new ligand BIPHLOPHOS remains basically unaffected by the *ortho* substituents in the biphenyl backbone. However, the optical induction of this ligand in the asymmetric hydroformylation of styrene is inferior to the known diphosphine ligand NAPHOS, its binaphthyl analogue. In contrast to NAPHOS, the described ligand shows complete selectivity to a twofold sulfonated product in sulfonation with fuming sulfuric acid, thus simplifying the analysis of the product properties enormously. Further work on the new atropisomeric diphosphine ligand is underway.

4. Experimental

All reactions were carried out using standard Schlenk technique in an oxygen-free nitrogen atmosphere. Solvents were dried with standard methods and distilled under nitrogen. IR spectra were recorded on a Perkin–Elmer 1600 series FT-IR spectrometer, the ^{1}H-, ^{13}C- and ^{31}P-NMR spectra on a Jeol JNM GX 400 or a Bruker AMX 400 instrument. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. The purity of the sulfonated ligand was checked by reversed-phase HPLC on a C18-modified silica column with UV detection and elution in gradient mode (H_2O–MeOH). The number of sulfonato-groups in the product was determined by comparison with authentic samples of two- to eightfold sulfonated derivatives of triphenylphosphane, BISBI and NAPHOS with respect to their retention times. Enantiomeric excesses of the aldehydes were measured on a Chrompack CP 9000 gas chromatograph (50 m Lipodex A column, carrier gas: Helium, split injector, flame ionisation detector) after reduction to the corresponding alcohols. Their absolute configuration was determined by comparison with an authentic sample of (*R*)-(+)-2-phenylpropanol. Hydroformylation experiments were performed in a Parr 300 ml stainless-steel autoclave, using dried and degassed styrene and a 1:1 mixture of hydrogen and carbon monoxide. Elemental analyses were carried out in the microanalytical laboratory of our institute.

4.1. Resolution of (±)-4,4′,6,6′-tetrachlorodiphenic acid **1**

(±)-**1** was prepared and separated into its enantiomers according to the procedure of Atkinson et al. [16] [17]. A boiling solution 22.6 g (79.2 mmol) of (+)-dehydroabietylamine (Merck–Schuchardt, 95%) in 360 ml of 95% ethanol was rapidly added to a boiling solution of 30 g (79.2 mmol) of (±)-**1** in ethanol. The mixture was boiled for an additional 10 min and then cooled to room temperature in a covered Erlenmeyer flask, whereupon a large amount of colorless needles precipitated. This was collected on a Büchner funnel and thoroughly washed with ethanol and dried in vacuo to yield 10.6 g (15.9 mmol, 70.6%) of the dehydroabietylamine salt of (−)-**1**. $[\alpha]_D^{25} = 38.6°$ (c 0.7, methanol). Anal. Found: H, 5.64; C, 61.08; N, 2.06; $C_{34}H_{37}Cl_4NO_4$ Calc.: H, 5.60; C, 61.36; N, 2.10%. All mother liquors and washings were collected and evaporated for the isolation of (+)-**1** via the brucine salt as described in the literature.

Free (−)-**1** was prepared from its dehydroabietylamine salt by slowly adding Na_2CO_3 to 150 ml of an aqueous suspension of the salt (20 g, 30.0 mmol), covered by a layer of 150 ml diethyl ether, until the pH of the aqueous phase reached the value of 10. After separation of the layers, the aqueous phase was extracted with three 50 ml portions of ether and subsequently stirred at 60°C until the smell of ether had disappeared. Then, it was acidified with the calculated amount of 1 N HCl until it reached pH 2. The colorless precipitate was washed with water and dried to yield 9.5 g (25 mmol, 83%) of (−)-**1**. $[\alpha]_D^{25} = -141.4°$ (c 1.3, $CHCl_3$). M.p. 250–253°C. ^{1}H-NMR (d_6-dmso): 7.96 ppm (d, 3,3′-H, 2H, $J = 2.1$ Hz); 7.93 ppm (d, 5,5′-H, 2H, $J = 2.1$ Hz). ^{13}C-NMR (d_6-dmso): 165.0, 136.5, 134.6, 133.5, 133.3, 132.0, 128.7 ppm. IR (KBr, cm^{-1}): 3500–500 (st, COOH); 1706 (st, C=O). Anal. Found: H, 1.89; C, 44.15; O, 16.98; $C_{14}H_6Cl_4O_4$. Calc.: H, 1.6; C, 44.46; O, 16.93%.

4.2. (+)-4,4′,6,6′-tetrachlorodiphenic acid chloride **2**

A total of 9.5 g of (−)-**1** was dissolved in 75 ml of $SOCl_2$ and refluxed for 2 h. After evaporation of $SOCl_2$ in vacuo, the remaining off-white oil was dissolved in diethyl ether. When the ether was pumped off, the product remained as a slightly yellow powder (10.0 g, 23.9 mmol, 96%) $[\alpha]_D^{25} = 21.5°$ (c 0.233, $CHCl_3$). IR (KBr, cm^{-1}): 3076 (w, aryl-H); 1758 (st, C=O). ^{1}H-NMR ($CDCl_3$): 8.16 ppm (d, 3,3′-H, 2H, $J = 1.8$ Hz); 7.71 ppm (d, 5,5′-H, 2H, $J = 1.8$ Hz). ^{13}C-NMR ($CDCl_3$): 165.5, 135.7, 135.5, 135.4, 135.1, 134.8, 131.9 ppm.

4.3. (+)-4,4′,6,6′-Tetrachloro-2,2′-bibenzylic alcohol **3**

A total of 10.0 g (24 mmol) was dissolved in diethyl ether and cooled to −78°C. A suspension of 1.21 g (31.9 mmol) of $LiAlH_4$ in diethyl ether was added in portions. Then, the mixture was allowed to warm to room temperature and was stirred over night. After hydrolysis with water and 10% H_2SO_4, the aqueous phase was extracted with three portions of ether and the combined organic phases washed with a saturated brine solution and dried over $MgSO_4$. After evaporation of the solvent the product remained as a colorless foam (7.95 g, 22.6 mmol, 94%). $[\alpha]_D^{25} = 47.3°$ (c 0.165, $CHCl_3$). IR (KBr, cm^{-1}): 3295 (br, O–H); 2966 (w, aliph. C–H); 1015 (m, C–O). ^{1}H-NMR ($CDCl_3$): 7.47 ppm (s, arom. H, 4H); 4.22 ppm (dd, CH_2, 4H); 2.58 ppm (br, OH, 2H).

4.4. (+)-4,4′,6,6′-Tetrachloro-2,2′-bis(methanesulfonatomethyl)-1,1′-biphenyl **4**

A total of 7.95 g (22.6 mmol) of **3** was dissolved in 150 ml of CH_2Cl_2. After 5.5 g (54.3 mmol) of triethyl amine had been added, the mixture was cooled to −40°C and a solution of 5.7 g (49.6 mmol) of methanesulfonic acid chloride was added from a dropping funnel. Stirring was continued at −30°C for 1 h, before the reaction mixture was washed with 250 ml of cold 1 N HCl, three 100 ml portions of cold water and 100 ml of saturated brine solution. The organic phase was dried over $MgSO_4$ at −30°C before the solvent was evaporated at room temperature. The resulting colorless oil crystallized after standing in the fridge overnight (10.6 g, 20.9 mmol, 92%). $[\alpha]_D^{25} = 36.2°$ (c 0.77, $CHCl_3$). $[\alpha]_D^{25} = 65.4°$ (c 0.673, $_{C6}H_6$). $m/z = 352, 333, 317, 297, 282, 267, 246, 233, 207$. ^{1}H-NMR ($CDCl_3$): 7.57 ppm (d, 3,3′-H, 2 H, $J = 1.8$ Hz); 7.54 ppm (d, 5,5′-H, 2H, $J = 1.8$ Hz); 4.77 ppm (dd, CH_2, 4H) 2.89 ppm (s, CH_3, 6H). ^{13}C-NMR ($CDCl_3$): 136.0, 135.0, 131.9, 130.3, 128.1, 125.9, 67.4, 37.9 ppm.

4.5. (−)-4,4′,6,6′-Tetrachloro-2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl **5**

A total of 10.6 g (20.9 mmol) of the mesylate **4** was dissolved in 150 ml of THF and cooled to −78°C. An 83 ml volume of a 0.5 M solution of $KPPh_2$ in THF was slowly added from a dropping funnel. After stirring for 1 h at −78°C, the mixture was allowed to warm to room temperature overnight. A 1 ml volume of degassed water was added and the solvent removed in vacuo, whereupon the residue was washed thoroughly with toluene. The toluene washings were gathered and the solvent removed. Chromatography on silica (pentane/toluene) yielded a colorless oil, which gave a colorless powder after crystallisation from degassed acetone (4.7 g, 6.82 mmol, 32.7%). $[\alpha]_D^{25} = -18.4°$ (c 0.33, CH_2Cl_2). m/z: 654, 618, 503, 468, 431, 308, 183. ^{1}H-NMR (C_6D_6): 7.3–6.8 ppm (m, aryl-C–H, 24H); 3.20 ppm (dd, CH_2, 4H). ^{13}C-NMR (C_6D_6): 141.1–125.6 ppm, 35.32 ppm (dd, CH_2). ^{31}P-NMR (C_6D_6): −13.3 ppm (s).

4.6. Synthesis of Ir(H)(CO)(PPh_3) 6

A total of 60 mg (0.087 mmol) of **5** and 88 mg of $Ir(H)(CO)(PPh_3)_3$ was weighed into a Schlenck tube, dissolved in 5 ml of CH_2Cl_2 and stirred overnight. Then, the solvent was pumped off and the yellow foamy residue washed three times with methanol (Yield: 78 mg, 0.067 mmol, 76%). Crystals suitable for X-ray crystallography were obtained from CH_2Cl_2/pentane. ^{1}H-NMR (C_6D_6): 7.8–6.8 ppm (m, phenyl- and biaryl-H, 24H); 4.31–3.51 ppm (m, CH_2, 4H); −11.1 ppm (dt, J(H–P3) 16.1 Hz, J(H–P1/P2) 24.2 Hz). ^{31}P-NMR (C_6D_6): (PPh_3: P3; **5**: P1 and P2): 8.842 ppm (dd, J(P3–P2): 124.1 Hz, J(P3–P1): 109.0 Hz), 6.575–2.854 ppm (m, J(P1–P2): 137.7 Hz). IR (KBr, cm^{-1}): 2068 (m); 1928 (vs). Anal. Found: H, 3.84; C, 58.55; O, 1.32; $C_{57}H_{44}Cl_4IrOP_3$. Calc.: H, 3.79; C, 58.46; O, 1.37%.

4.7. Crystal data for Ir(H)(CO)(PPh_3) 6

$C_{57}H_{44}Cl_4IrOP_3$, $M = 1171.8$, triclinic, $P\bar{1}$, $a = 11.2628(1)$ Å, $b = 15.0054(2)$ Å, $c = 17.5377(2)$ Å, $\alpha = 74.1530(7)°$, $\beta = 73.1160(6)°$, $\gamma = 70.2764(7)$, $V = 2618.87(5)$ Å^3, $Z = 2$, $\rho_{calc} = 1.486$ g cm^{-3}, $F(000) = 1168$, μ(Mo–K$_\alpha$) = 2.88 mm^{-1}, $\lambda = 0.71073$ Å, $T = 193(2)$ K. The 26 520 reflections measured on a Nonius Kappa CCD area detector diffractometer [18] yielded 12 299 unique data ($2\theta_{max} = 61.08°$, $R_{int} = 0.047$). Preliminary positions of heavy atoms were found by direct methods [19], while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least square refinement [20]. The hydrogen atoms were placed in calculated positions. They were included in the structure factor calculation but not refined. A highly disordered solvent molecule was dealt with by the Calc Squeeze option, implemented in the program Platon [21], leaving a void of 172 Å^3 ($x = 0.0$; $y = 0.5$; $z = 0.5$). The final refinement on F^2 converged at $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2]\}^{1/2} = 0.0757$ on all data, conventional $R_1 = 0.0277$ on F values of 11 903 reflections having $F_o^2 > 2\sigma(F_o^2)$, GoF = 1.077 for all F^2 values and 599 refined parameters. Largest difference peak and hole (e Å^{-3}): 1.24, −2.77.

4.8. Sulfonation of (±)-4,4′,6,6′-tetrachloro-2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl 5

A total of 600 mg (0.88 mmol) of **5** was dissolved in 20 ml of degassed concentrated H_2SO_4 and stirred for 48 h at room temperature. Then 20 ml of fuming sulfuric acid (65% SO_3) was added and the mixture stirred overnight. The mixture was poured onto 100g of degassed ice, resulting in a clear, slightly yellow solution, which was neutralized with 25% degassed NaOH. All water was removed at the rotary evaporator. Then, the residue was stirred with 30 ml of degassed methanol and washed several times with the same solvent. When the solvent was evaporated, a slightly yellow, glassy solid remained. Yield: 660 mg (0.74 mmol, 84%) ^{1}H-NMR (D_2O): 7.6–6.7 ppm (m, phenyl- and biaryl-H, 22H); 3.23–3.05 ppm (m, CH_2, 4H). ^{31}P-NMR (D_2O): −10.69 ppm (s); 22.3 ppm (s, trace amounts of phosphine oxide). HPLC: P(V)/P(III) = 5.7%, retention time comparable to BISBI with two sulfonato groups.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC No. 113563. Copies of the data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: teched@chemcrys.cam.ac.uk).

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