Pergamon

Tetrahedron Letters 40 (1999) 4977–4980

TETRAHEDRON
LETTERS

A New Class of Chiral Diphosphines Having Planar Chirality

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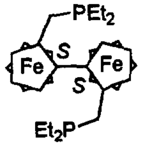
Received 30 March 1999; accepted 10 May 1999

Abstract

Double lithiation of bis(tetra-hydroindenyl)iron followed by phosphorylation using Ph_2PCl affords two different chiral diphosphines having respectively C_1- and C_2-symmetry. Following antipode separation, the compounds can be used as ligands in Rh-catalyzed hydrogenation (up to 97% *ee*) and hydroboration (up to 84% *ee*) of olefins and in Ir-catalyzed hydrogenation of imines (up to 79% *ee*). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Phosphines; Catalysis; Hydrogenation; Asymmetric reactions; Ferrocenes

In spite of the large number of chiral diphosphines known in the literature [1,2], the search for new types of chiral ligands for use in transition metal catalyzed asymmetric reactions continues [3-20]. For example, various chiral ferrocene-based diphosphines have been described [1,2,13-20], asymmetry arising either from central chirality in the side-chains (Type I), from planar chirality of the substituted ferrocene moiety (Type II), or from the combination of both (Type III). Interestingly, very few examples of Type II have been reported so far [16-20], e.g., (*S*,*S*)-EtTRAP-H (**1**) [20]. We now describe a completely different class of ferrocene-derived diphosphines having only planar chirality (Type II), the first examples being compounds **2** and **3** with C_2- and C_1-symmetry, respectively.[1]



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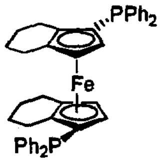
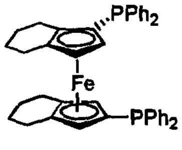


(+)- and (-)-**2**



(+)- and (-)-**3**

Starting point for the preparation of **2** and **3** was bis(tetrahydroindenyl)iron (**4**), which is accessible in quantitative yield by the PtO_2-catalyzed hydrogenation of bis(indenyl)iron [21,22]. Upon treating **4** with two equivalents of preformed *n*-butyllithium/tetramethylethenediamine (TMEDA) at room temperature and then at +60°C (3 h), the red solution was cooled to -40°C and reacted with $ClPPh_2$. The crude product contained a mixture of **2**, **3** and the achiral meso-

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[1] The drawings show one absolute configuration arbitrarily; configurational assignment of (+)- and (-)-**2** and (+)- and (-)-**3** has not been possible so far.

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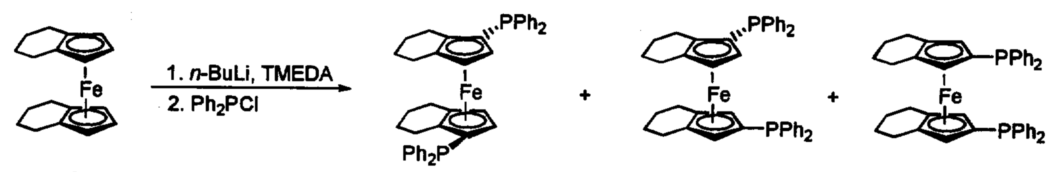
PII: S0040-4039(99)00947-8

diphosphine **5** among other non-identified compounds. This means that double lithiation occurs mainly at the 1,1'-, 1,2'- and 2,2'-positions.



4 **2** **3** **5**

Upon cooling a hexane solution of the crude product to -30°C, a precipitate composed solely of **2** and **3** was obtained in 35% yield. Recrystallization from THF/pentane afforded analytically pure **3** (17% overall yield). Removal of the solvent from the mother liquor and recrystallization from diethyl ether/pentane afforded analytically pure **2** (3% yield). Optimization was not strived for at this stage. Antipode separation of rac-**2** was achieved by chiral HPLC (Chiralcel® OD-H column) and of rac-**3** using the corresponding BH_3 adduct. Typical data for enantiomerically pure (-)-**2** (orange crystals; mp 171°C; ^{31}P NMR (CD_2Cl_2): $\delta = -23.9$ ppm; $[\alpha]^{20}(589\ nm) = -603 \pm 10°$(c 1.02, CD_2Cl_2)) and for (-)-**3** (orange crystals, mp 190°C; ^{31}P NMR (CD_2Cl_2): $\delta = -20.3$ ppm (d, $^1J_{PP'} = 3.8$ Hz, P') and -25.0 ppm (d, $^1J_{PP'} = 3.8$ Hz, P); $[\alpha]^{20}(589\ nm) = -268 \pm 10°$ (c 0.92, CD_2Cl_2)).

Whereas the preparation of Rh-complexes by the reaction of **2** and **3** with $Rh(COD)_2BF_4$ posed no problems, these did not crystallize in suitable form for X-ray analyses. However, the octahedral molybdenum complexes rac-**2**/$Mo(CO)_4$ and rac-**3**/$Mo(CO)_4$, prepared in 80% and 61% yield by reacting the corresponding ligands with $Mo(CO)_4$(norbornadiene), were so characterized (Fig. 1, left and center).[2] The results clearly prove the C_2- and C_1-symmetry of the ligands **2** and **3** and also define the chiral environments around the respective metal centers. Upon reacting **3** with $[Ir(COD)(pyr)_2]PF_6$ [23], the complex **3**/$Ir(COD)PF_6$ was obtained in 75% yield, crystals of which were subjected to an X-ray structure analysis (Fig. 1, right).[3]

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[2] X-ray analysis of rac-**2**/$Mo(CO)_4$: $C_{46}H_{40}FeMoO_4P_2$, $M_r = 870.51$ g mol^{-1}, orange-brown prism, crystal size 0.35 × 0.46 × 0.60 mm, monoclinic, $C2/c$ [No. 15], $a = 18.288(2)$, $b = 11.198(1)$, $c = 19.924(1)$ Å, $\beta = 100.00(1)°$, $V = 4018.4(7)$ Å^3, $T = 293$ K, $Z = 4$, $d_{cal} = 1.44$ g cm^{-3}, $\mu = 0.80$ mm^{-1}, Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, ω-2θ-scan, 4585 independent reflections, 3758 with $I > 2\sigma(I)$, $\theta_{max} = 27.5°$, spherical absorption correction (T_{min} 0.7563, T_{max} 0.7581), direct methods, least-squares refinement (on F_o^2, SHELX-97, Sheldrick, G. M., University of Göttingen, 1997), H riding, disorder (70:30) in tetrahydroindenyl group, 244 refined parameters, $R_1 = 0.036$ (obs. data), $wR_2 = 0.098$ (Chebyshev weights), final shift/error 0.001, residual electron density +0.664 eÅ^{-3}. CCDC 116047.
X-ray analysis of rac-**3**/$Mo(CO)_4$: $C_{46}H_{40}FeMoO_4P_2 \cdot CD_2Cl_2$, $M_r = 957.44$ g mol^{-1}, yellow plate, crystal size 0.18 × 0.28 × 0.56 mm, monoclinic, $P2_1/n$ [No. 14], $a = 10.277(1)$, $b = 23.835(1)$, $c = 18.097(1)$ Å, $\beta = 101.75(1)°$, $V = 4340.0(4)$ Å^3, $T = 293$ K, $Z = 4$, $d_{cal} = 1.47$ g cm^{-3}, $\mu = 0.86$ mm^{-1}, data collection as above, 8805 independent reflections, 5003 with $I > 2\sigma(I)$, $\theta_{max} = 26.3°$, analytical absorption correction (T_{min} 0.6644, T_{max} 0.8631), solution and refinement as above, H riding, disorder (50:50) in tetrahydroindenyl groups, 510 refined parameters, $R_1 = 0.062$ (obs. data), $wR_2 = 0.238$ (Chebyshev weights), final shift/error 0.001, residual electron density +1.081 eÅ^{-3}. Atomic coordinates and s.u.'s have been deposited at the Cambridge Crystallographic Data Centre, CCDC 116048.

[3] X-ray analysis of [rac-**3**/Ir(COD)]$^+$[PF_6]$^-$: $[C_{50}H_{52}FeIrP_2]^+[PF_6]^-$, $M_r = 1107.88$ g mol^{-1}, red cube, crystal size 0.38 × 0.40 × 0.40 mm, triclinic, $P\bar{1}$ [No. 2], $a = 10.5989(2)$, $b = 14.4616(3)$, $c = 15.3179(3)$ Å, $\alpha = 86.287(1)$, $\beta = 72.675(1)$, $\gamma = 78.715(1)$ °, $V = 2198.0(1)$ Å^3, $T = 100$ K, $Z = 2$, $d_{cal} = 1.67$ g cm^{-3}, $\mu = 3.53$ mm^{-1}, Siemens SMART CCD diffractometer, $\lambda = 0.71073$ Å, ω-scan, 14880 independent reflections, 13986 with $I > 2\sigma(I)$, $\theta_{max} = 34.13°$, spherical absorption correction (T_{min} 0.1520, T_{max} 0.1843), solution and refinement as above, H riding, 550 refined parameters, $R_1 = 0.045$ (obs. data), $wR_2 = 0.118$ (Chebyshev weights), final shift/error 0.001, residual electron density +4.924 eÅ^{-3} (0.79 Å from Ir). CCDC 116049.

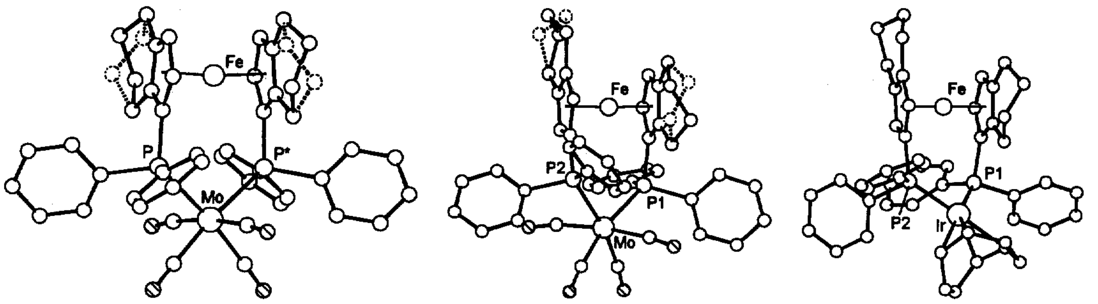
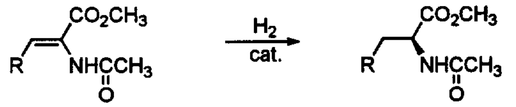


Figure 1 Crystal structures of rac-2/Mo(CO)$_4$ (left, P-Mo-P* 99.31(3)°, torsion angle P-Cp--Cp'-P* 22(1)°, where Cp is the centroid of Cp ring), rac-3/Mo(CO)$_4$ (center, P1-Mo-P2 98.19(6)°, tors. P1-Cp--Cp'-P2 42(1)°) and [rac-3/Ir(COD)]$^+$ cation (right, P1-Ir-P2 95.33(3)°, tors. P1-Cp--Cp'-P2 32(1)°).

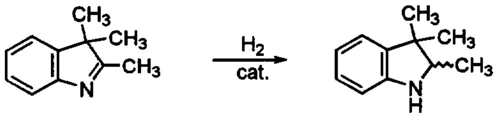
In order to test the new ligands in catalysis, they were treated with Rh(COD)$_2$BF$_4$ and the respective Rh-complexes used *in situ* as catalysts (0.1 mol-%) in the hydrogenation of olefins **6a-b** (22°C/1 bar H$_2$/24 h in CH$_2$Cl$_2$). In most cases > 95% conversion was achieved under these conditions, with the exception of the hydrogenation of **6b** using catalyst (-)-**3**/RhBF$_4$ (only 40% conversion which results in a switch in absolute configuration of product **7b**). The results show that the C_2-symmetric ligand **2** is much more stereoselective than the C_1-symmetric analog **3**:



6 a R = H
b R = Ph

7 a using (-)-2/RhBF$_4$: 96% *ee* (*R*); (-)-3/RhBF$_4$: 64% *ee* (*R*)
b using (-)-2/RhBF$_4$: 97% *ee* (*R*); (-)-3/RhBF$_4$: 41% *ee* (*S*)

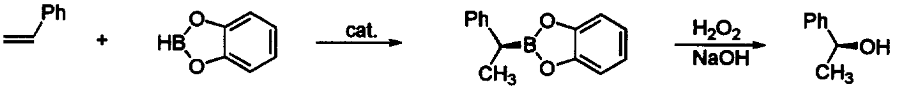
The superiority of **2** relative to **3** was also observed in the hydrogenation of imine **8**, mediated by the catalysts (1 mol-%) prepared by treating the ligands with [Ir(COD)Cl]$_2$, conversion to **9** being 86-95% (22°C/65 bar H$_2$/18 h in CH$_2$Cl$_2$). The absolute configuration of **9** has not been determined to date [23].



8 **9**

(-)-2/IrCl: 79% *ee* (+)-enantiomer
(-)-3/IrCl: 17% *ee* (-)-enantiomer
(+)-3/IrPF$_6$: 21% *ee* (+)-enantiomer

Finally, the Rh-catalysts (0.75 mol-%) used in the hydrogenation of olefins **6** were also tested in the Rh-catalyzed hydroboration of styrene (**10**), with formation of *S*-2-phenylethanol (**13**) following oxidative workup. Surprisingly, in this case the C_1-symmetric ligand (-)-**3** turned out to be superior. Thus, in toluene at -50°C (12 h), *ee*-values of 52% and 77% were observed upon using ligands (-)-**2** and (-)-**3**, respectively, regioselectivity in favor of the branched products being > 99%. In 1,2-dimethoxyethane as solvent (-60°C/12 h), ligand (-)-**3** led to an *ee*-value of 84% in favor of *S*-**13**. Other ligands have been used with varying degrees success [24-27].



10 **11** **12** **13** (90%)

In summary, the first members of a new class of chiral ferrocene-based diphosphines have been prepared, characterized and tested as ligands in various asymmetric catalytic reactions. Studies are currently under way to establish the factors which determine the direction and extent of asymmetric induction.

Acknowledgement

Eckart W. Beuttenmüller thanks the Fonds der Chemischen Industrie for a Kekulé doctoral stipend and Mireia Pastó is grateful to the Spanish Programa Nacional de Becas de Formación Personal Investigador en el Extranjero (Subprograma de Perfeccionamiento de Doctores y Tecnólogos) for a postdoctoral stipend.

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