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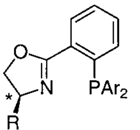
[12] Interestingly, the spectroscopic data of diaminodiols **24**–**27** reveal the complexation with one molecule of either Et_3N or Et_3P, depending on the protocol used for their preparation (10% Pd/C, Et_3N or Et_3P/H_2O).

A New Class of Modular Phosphinite–Oxazoline Ligands: Ir-Catalyzed Enantioselective Hydrogenation of Alkenes[**]

Jörg Blankenstein and Andreas Pfaltz[*]

Phosphinooxazolines **1** (phox ligands) have been successfully applied in many different enantioselective metal-catalyzed processes.[1] We have recently found that iridium–phox complexes are efficient catalysts for the enantioselective hydrogenation of unfunctionalized alkenes,[2] a class of substrates that gives unsatisfactory results with other catalysts.[3] The best enantioselectivities (up to 99% *ee*) have been observed for 1-alkyl-1,2-diaryl-substituted alkenes, while other alkenes such as monoaryl-1,2-dimethyl-substituted alkenes are converted with only moderate enantiomeric excesses. Here we report a new class of ligands, the phosphinite–oxazolines **2**, which induce high enantioselectivity with a much broader range of alkenes and, thus, significantly enhance the scope of Ir-catalyzed hydrogenation.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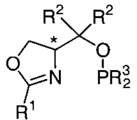
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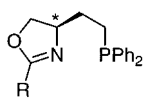
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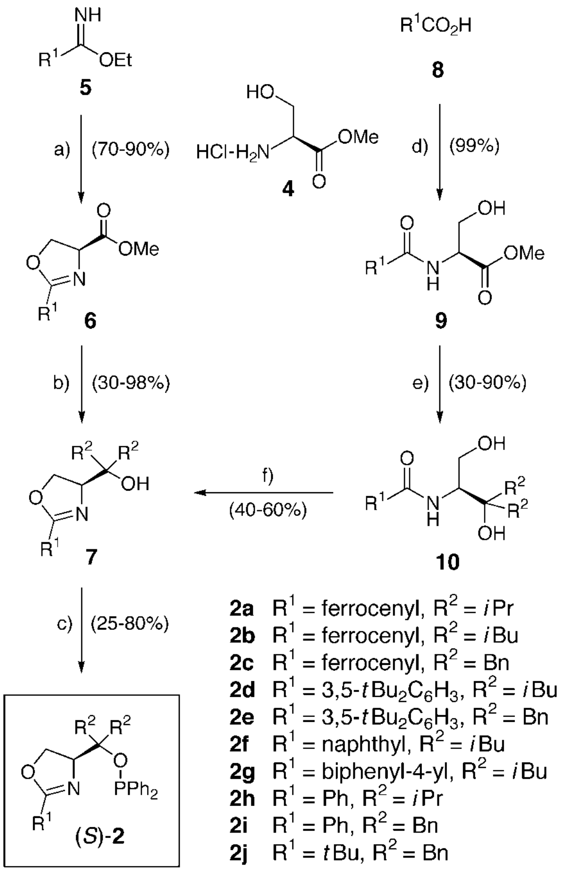
Both enantiomers of the phosphinite–oxazoline ligands **2** are readily prepared in three to four steps, starting from imidates **5** or carboxylic acids **8** and L-serine methyl ester hydrochloride (**4**) or the corresponding D isomer (Scheme 1). Special precautions had to be taken in the peptide coupling (step d) to avoid racemization.[4] The addition of Grignard reagents to **9** sometimes gave complex mixtures, so that in general the (hydroxymethyl)oxazolines **7** were preferentially synthesized by means of the imidate route.[5] The modular nature of **2** with its three permutable structural units (R^1, R^2, and the P-substituents) is an attractive feature of these ligands. Especially the selection of the R^1 group, which is derived from a carboxylic acid, is essentially unlimited.



2a R^1 = ferrocenyl, R^2 = *i*Pr
2b R^1 = ferrocenyl, R^2 = *i*Bu
2c R^1 = ferrocenyl, R^2 = Bn
2d R^1 = 3,5-tBu$_2$C$_6$H$_3$, R^2 = *i*Bu
2e R^1 = 3,5-tBu$_2$C$_6$H$_3$, R^2 = Bn
2f R^1 = naphthyl, R^2 = *i*Bu
2g R^1 = biphenyl-4-yl, R^2 = *i*Bu
2h R^1 = Ph, R^2 = *i*Pr
2i R^1 = Ph, R^2 = Bn
2j R^1 = *t*Bu, R^2 = Bn

Scheme 1. Synthesis of compounds **2** for which R^3 = Ph. a) **4**, $ClCH_2CH_2Cl$, reflux; b) R^2MgX, −78 °C; c) *n*BuLi, NEt_3, $ClPPh_2$, −78 °C; d) **4**, EDC, HOBT, CuCl, DMF; e) R^2MgX, −78 °C; f) (1) NEt_3, TsCl, (2) H_2O. EDC = *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride, HOBT = 1-hydroxybenzotriazole.

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[*] Prof. A. Pfaltz, Dr. J. Blankenstein
Department Chemie
Universität Basel
St.-Johanns-Ring 19, 4056 Basel (Switzerland)
Fax: (+41)61-2671103
E-mail: andreas.pfaltz@unibas.ch

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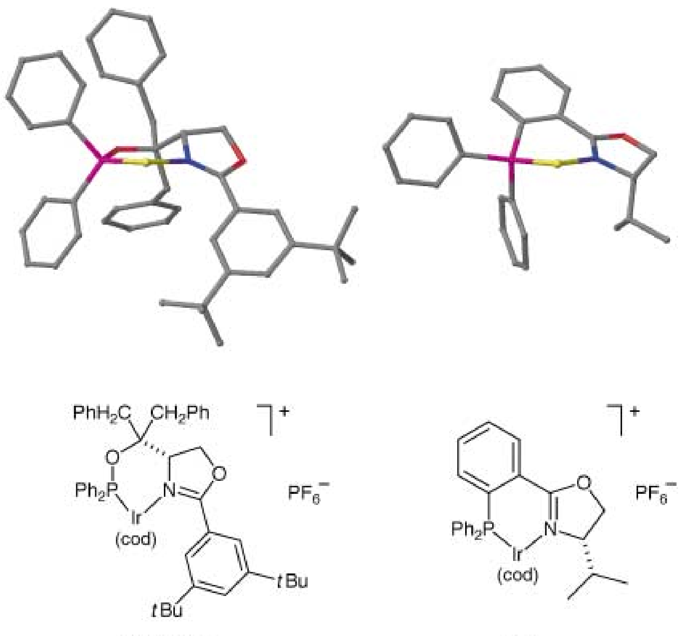
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

Structurally related ligands **3** have been recently synthesized by Burgess et al.; in Ir-catalyzed hydrogenations they were found to give results similar to those of the phox ligands **1**.[6]

For evaluating the phosphinite–oxazoline ligands in Ir-catalyzed hydrogenations, a set of ten derivatives **2a–j** (see Scheme 1) was synthesized from six different precursors of either type **5** or **8** and three different Grignard reagents (R^2MgX). The corresponding Ir complexes were prepared by using the standard procedure developed for Ir–phox catalysts.[2]

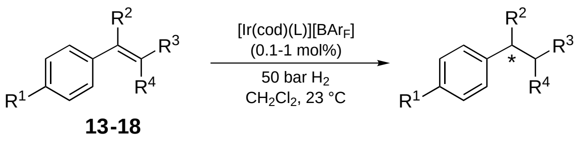
Single crystals could be obtained from the iridium complex **11e**-PF_6, and the result of the X-ray structure analysis is shown in Figure 1.[7] Comparison with the structure of the analogous Ir–phox complex **12**[8] reveals two distinct differences. In contrast to the typical axial–equatorial disposition of the two P-phenyl groups in Ir–phox complexes, the two P–Ph bonds in complex **11e** form a nearly symmetrical arrangement with respect to the coordination plane defined by the P-Ir-N core (dihedral angles N-Ir-P-C: 111° and 126°). In the phox complex **12**, the substituent at the stereogenic center is quite remote from the Ir atom, whereas the bis(*tert*-butyl)phenyl group in complex **11e** extends towards the coordination sphere and, therefore, is expected to interact with reactants bound at the adjacent coordination sites. This implies that the chiral environment of the Ir atom is substantially different in the two complexes.



11e-PF_6 **12**

Figure 1. Structures of the iridium complex **11e** (as PF_6 salt) and the analogous phox complex **12** in the crystal (H atoms, PF_6^- ions, and cod ligands have been omitted for clarity).

In initial studies [Ir(cod)L][BAr$_F$] complexes **11**-BAr$_F$ (L = **2a–j**; cod = cyclooctadiene, BAr$_F$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were tested in the hydrogenation of alkene **13** [Eq. (1)]. The counterion BAr$_F$ was chosen because of its beneficial effect on catalyst reactivity and stability.[2] In general the reactions were run in CH_2Cl_2 under 50 bar of H_2; in toluene very similar results were obtained. With enantioselectivities ranging from 89–98% *ee* for the hydrogenation of **13**, the new ligands proved to be as effective as the phox ligands **1**[2] (Table 1). The ferrocenyl- and 3,5-bis(*tert*-butyl)-phenyl-substituted ligands **2a–e** proved to be superior to the other derivatives. These differences became more pronounced in the hydrogenation of the monoaryl-substituted alkenes **14–17** (for **14** the enantioselectivity ranged from 45–96% *ee* for **2a–j**). The structure of the backbone substituents (R^2) had a minor but still significant influence; however, no general trend could be derived from the data. With 96% *ee* for the hydrogenation of **14** and 85–90% *ee* for **15–17**, the new ligands clearly outperform the phox ligands **1** (maximum enantioselectivity for reactions of **14**: 61% *ee*, **15**: 42% *ee*, **16**: 61% *ee*, **17**: 84% *ee*).[9]



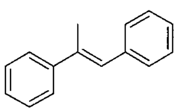
(1)

Table 1. Hydrogenation of substrates **13–17**.[a]

Substrate	Ligand	Cat. [mol%]	Conv. [%][b]	*ee* [%][c]
13	**2a**	0.1	100	97 (*R*)
13	**2e**	0.4	100	98 (*R*)
14	**2a**	1.1	100	93 (*R*)
14	**2c**	0.1	100	96 (*R*)
14	**2e**	1.0	100	95 (*R*)
15	**2a**	0.4	100	85 (*S*)
15	**2e**	0.4	100	77 (*S*)
16	**2a**	0.5	100	85 (*S*)
16	**2e**	0.5	100	81 (*S*)
17	**2b**	0.5	100	90 (*R*)
17	**2e**	0.3	100	62 (*R*)

[a] Conditions: see Equation (1); experimental procedures: see ref. [2]. [b] Determined by GC (Restek RTX-1701). [c] Determined by HPLC: for substrates **13**, **14**, **15**, **17** see ref. [2], for **16** Chiracel OD-H was used (0.46 × 25 cm, 20 °C, 0.5 mL min^{-1}, heptane/*i*PrOH 99.8:0.2, $R_t(R) = 12.6$, $R_t(S) = 14.8$ min).

Terminal alkenes such as **18** are particularly demanding substrates. The highest selectivity for the hydrogenation of **18** has been observed with an *ansa*-bis(cyclopentadienyl)lanthanide catalyst (64% *ee* at 25 °C, 96% *ee* at −80 °C).[10] With ruthenium-diphosphane complex (Ru-(MeDuPhos)) catalyst in the presence of *t*BuOK, Noyori et al. recently obtained 81–89% *ee* for the hydrogenation of 2-phenylbutene and several



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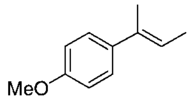

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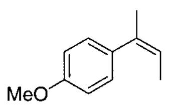

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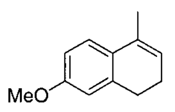

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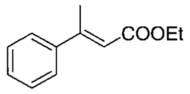

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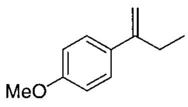

18

m- and *p*-substituted derivatives.[11] In our studies with the (phosphinite – oxazoline)Ir complexes **11** a strong dependence of the enantioselectivity on the hydrogen pressure was observed (Table 2). The highest enantioselectivities (up to 88% *ee*) were obtained at ambient pressure, which compares favorably with the best results reported to date.[3, 10, 11]

Table 2. Hydrogenation of 2-(4-methoxyphenyl)butene (**18**).[a]

Ligand	Cat. [mol%]	H_2 [bar]	*ee* [%][b]
2a	0.2	50	46 (*S*)
2a	0.2	10	59 (*S*)
2a	0.1	1	78 (*S*)
2e	0.2	50	53 (*S*)
2e	0.2	10	77 (*S*)
2e	0.1	1	88 (*S*)

[a] Conditions: see Equation (1); 100% conversion in all reactions; experimental procedures: see ref. [2]. [b] Determined by HPLC, see ref. [2].

The new phosphinite – oxazoline ligands **2** significantly expand the scope of enantioselective hydrogenation to classes of substrates for which no efficient catalysts were previously available. The modular construction and the facile synthesis of these ligands should make it possible to tailor their structure for other substrates and other metal-catalyzed reactions.

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Synthesis of Highly Magnetic, Air-Stable Iron – Iron Carbide Nanocrystalline Particles by Using Power Ultrasound[**]

Sergei I. Nikitenko, Yuri Koltypin, Oleg Palchik,
Israel Felner, Xiao N. Xu, and Aharon Gedanken[*]

Coated magnetic nanoparticles may have important applications as materials for magnetic data storage, xerography, and magnetic resonance imaging.[1] A protective layer on the surface of the particles prevents interactions between closely

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[*] Prof. Dr. A. Gedanken, Dr. Yu. Koltypin, O. Palchik
Department of Chemistry, Bar-Ilan University
Ramat-Gan 52900 (Israel)
Fax: (+972) 3-5351250
E-mail: gedanken@mail.biu.ac.il

Prof. Dr. I. Felner
Racah Institute of Physics, Hebrew University
Jerusalem (Israel)

Dr. S. I. Nikitenko
Institute of Physical Chemistry, RAS
Leninskii Pr.31, 117915 Moscow (Russia)

Dr. X. N. Xu
Department of Physics, Nanjing University
Nanjing 210093 (China)

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