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Highly Efficient Asymmetric Hydrogenation of Alkyl Aryl Ketones Catalyzed by Iridium Complexes with Chiral Planar Ferrocenyl Phosphino-Thioether Ligands

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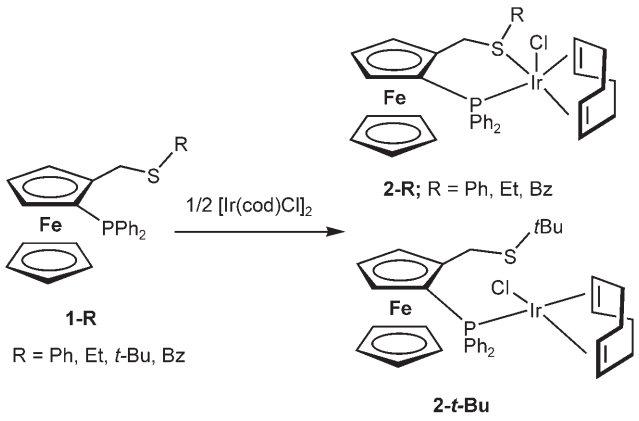
Abstract: Iridium complexes of planar-chiral ferrocenyl phosphine-thioether ligands were tested in the hydrogenation of simple ketones. Optimization of the conditions led to a highly active catalytic system with turnover numbers up to 915 and turnover frequencies up to *ca.* 250 h^{-1}. Furthermore, very high enantioselectivities (up to >99%) together with complete conversions were obtained for the asymmetric hydrogenation of various acetophenones at 10 °C.

Keywords: alkyl aryl ketones; asymmetric catalysis; ferrocene ligands; hydrogenation; iridium; P,S ligands

The development of new asymmetric catalytic systems is still a major challenge because of its importance in synthetic organic chemistry and fine chemicals manufacturing.[1] For instance, enantiomerically pure secondary alcohols, which are very valuable synthetic intermediates for pharmaceuticals or materials, can often be obtained by asymmetric ketone hydrogenation. The catalytic hydrogenation of unfunctionalized ketones, i.e., those lacking additional heteroatoms for secondary interactions of the substrate with the metal center, have long been a major challenge[2,3] until Noyori et al. introduced new ruthenium-based [(diphosphine)$RuCl_2$(diamine)][4] complexes which proved outstanding in terms of both activities and enantioselectivities. Although many ruthenium-based catalytic systems have been developed during the last decade,[5] the use of other metals in this reaction have been rather rarely described.[6–8] Herein, we report a highly active and highly enantioselective catalytic system for the hydrogenation of various substituted acetophenones, based on Ir complexes of ferrocenyl phosphine-thioether ligands. We have recently developed syntheses of new chiral ferrocenyl P,S ligands in both racemic and enantiomerically pure form (*R* or *S* configuration), and briefly reported on their application to asymmetric catalysis, namely in palladium-catalyzed allylic substitution.[9,10] We have also described iridium complexes **2-R** (R = Ph, Et, *t*-Bu, see Scheme 1), obtained in high yields (85–90%) and with complete diastereoselectivity *via* the addition of the bidentate ligands **1-R** to $[Ir(cod)Cl]_2$.[11] The coordination number of **2-R** is controlled by the size of R (5-coordinate for the smaller Ph and Et, square planar 4-coordinate for the bulkier *t*-Bu), both in the solid state and in solution, while the absolute configuration at the coordinated sulfur atom is in turn controlled by the ferrocene planar chirality (only one diastereoisomer is obtained).[11a] By using the same procedure, we have now prepared the benzyl analogue



Scheme 1. Synthesis of complexes **2**.

(**2-Bz**) starting from ligand **1-Bz**[9] and $[Ir(cod)Cl]_2$. NMR data for **2-Bz** are similar to those of **2-Et** and **2-Ph**. In particular, the ^{31}P signal (−9 ppm) is close to the corresponding signals of **2-Et** and **2-Ph** (respectively −3.1 ppm and −4.2 ppm) but not to the signal of **2-*t*-Bu** (15.7 ppm). The ^1H NMR data (δ and $J_{H,H}$) of the two diastereotopic protons of the methylene group between the ferrocene moiety and the sulfur atom are also much more affected by coordination than in the case of **2-*t*-Bu**. This suggests that the sulfur atom is coordinated to the iridium center and therefore that **2-Bz** is pentacoordinated like **2-Et** and **2-Ph**.

In order to assess the efficiency of these complexes in ketone hydrogenation, the experimental conditions were first optimized for the hydrogenation of acetophenone as a model substrate with the racemic catalysts **2-R**, followed by the asymmetric hydrogenation of various substituted alkyl aryl ketones with the enantiomerically pure complexes. The asymmetric hydrogenation of simple ketones is commonly carried out in alcoholic solvents, typically isopropyl alcohol, in the presence of a base.[4-8] Therefore, the hydrogenation of acetophenone was first studied in isopropyl alcohol (see Table 1). In the absence of a base, **2-Et** showed no catalytic activity (run 1). The addition of KI had no effect on the reaction rate[12] (run 2), whereas I_2 had a positive but limited effect (run 3).[13] On the other hand, the addition of a strong base (NaOMe, KO-*t*-Bu or KOH; 5 equivalents) efficiently promoted catalysis (runs 4–6). The weaker base NEt_3 had no significant effect (run 7), contrary to former observations by Dahlenburg and Götz for related iridium-based catalytic systems.[8d] The iridium/substrate ratio could be decreased to 1/1500 while maintaining significant conversions after 5 h (61% corresponding to a turnover number of 915; run 8). The optimized conditions for **2-Et** were finally applied to the other **2-R** complexes. All proved to be efficient catalysts, with complete conversion after 5 h in all cases (runs 9–11). These activities appear to compare quite favorably with those reported for other Ir complexes under similar conditions.[8] The reason for this difference may be related to a greater hemilability of these P,S ligands,[11b] relative to the other chelating ligands used so far.

The solvent influence on the catalytic activity has also been investigated (see Table 2). The runs in alcoholic solvents were stopped after 2 h in order to better compare the catalytic activities. The catalytic activity depends on the nature of the alcohol (runs 12–16). In particular, the reactivity dropped dramatically in *tert*-butanol (*cf.* runs 15 and 16 for the **2-Et** catalyst), in contrast again with the system developed by Dahlenburg and Götz.[8d] This observation raised the question of the intervention of a transfer hydrogenation pathway, with the alcoholic solvent as the hydride source. However, the reaction could be efficiently carried out in toluene, which cannot be a hydride source (runs 18 and 19), ruling out this mechanism under these conditions. Furthermore, the activity in isopropyl alcohol dropped dramatically when the

Table 1. Influence of the additives on the hydrogenation of acetophenone in isopropyl alcohol.[a]

Run	Catalyst	Additive	Time [h]	Conversion [%][b]	TOF $[h^{-1}]$[c]
1	**2-Et**	None	5	0	0
2	**2-Et**	KI	5	0	0
3	**2-Et**	I_2	5	2	1
4	**2-Et**	NaOMe	5	>99	>99
5	**2-Et**	KO-*t*-Bu	5	>99	>99
6	**2-Et**	KOH	5	>99	>99
7	**2-Et**	NEt_3	5	0	0
8[d]	**2-Et**	NaOMe	5	61	183
9	**2-Ph**	NaOMe	5	>99	>99
10	**2-*t*-Bu**	NaOMe	5[e]	>99	>99
11	**2-Bz**	NaOMe	5	>99	>99

[a] *Reaction conditions:* racemic catalyst, 6.4×10^{-3} mmol; additive, 3.2×10^{-2} mmol; acetophenone, 3.2 mmol; (1/5/500) under 30 bars at 27 °C in 2 mL of isopropyl alcohol.
[b] Conversions determined by GC; 100% selectivity in (*R/S*)-1-phenylethan-1-ol.
[c] Global turnover frequency.
[d] Amount of acetophenone increased to 9.6 mmol (S/C ratio = 1500).
[e] The conversion was 91% after 2 h.

Table 2. Influence of the solvent and additives on the hydrogenation of acetophenone.[a]

Run	Catalyst	Additive	Solvent	Time [h]	Conversion [%][b]	TOF $[h^{-1}]$[c]
12	**2-Ph**	NaOMe	MeOH	2	68	170
13	**2-Ph**	NaOMe	EtOH	2	16	40
14	**2-Ph**	NaOMe	*i*-PrOH	2	>99	>247
15	**2-Et**	NaOMe	*i*-PrOH	2	94	234
16	**2-Et**	NaOMe	*t*-BuOH	2	1	2
17[d]	**2-Et**	NaOMe	*i*-PrOH	2	1	2
18	**2-Et**	NaOMe	Toluene	5	44	44
19	**2-Et**	KO-*t*-Bu	Toluene	5	94	94
20	**2-Et**	NaOMe	CH_3CN	5	58	58
21	**2-Et**	KO-*t*-Bu	CH_3CN	5	52	52
22	**2-Et**	NaOMe	CH_2Cl_2	5	0	0
23	**2-Et**	NaOMe	THF	5	1	1

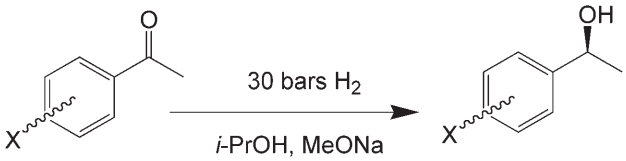
[a] *Reaction conditions:* racemic catalyst, 6.4×10^{-3} mmol; additive, 3.2×10^{-2} mmol; acetophenone, 3.2 mmol; (1/5/500) under 30 bars at room temperature in 2 mL of solvent.
[b] Conversions determined by GC; 100% selectivity in (*R/S*)-1-phenylethan-1-ol.
[c] Global turnover frequency.
[d] Identical conditions as in[a] except $P(H_2) = 2$ bars.

reaction was carried out under reduced H_2 pressure (2 bars, run 17). These two independent observations strongly support the hydrogenation mechanism in alcoholic solvents. Acetophenone could also be hydrogenated efficiently in acetonitrile but not in dichloromethane or THF (runs 20–23). The replacement of NaOMe with KO-*t*-Bu increased significantly the activity of **2-Et** in toluene, probably because of the higher solubility of the latter base. In MeCN, where both bases are completely soluble, the observed activity is comparable.

The asymmetric hydrogenation using enantiomerically pure **(*S*)-2-R** has been studied under the optimized conditions (i.e., those of Table 2, run14). In contrast with the catalytic activities, the enantioselectivities for the acetophenone hydrogenation strongly depend on the R substituent on sulfur, going from 43% with **(*S*)-2-Ph** to 77% with **(*S*)-2-Bz** (Table 3, runs 24–27). For substituted acetophenones, enantioselectivities depend also strongly on the R substituent, especially for 2-substituted compounds where, with the more crowded complexes **(*S*)-2-Ph** and **(*S*)-2-*t*-Bu**, low enantioselectivities were observed (Table 3, runs 29, 30 and 33, 34). However, good levels of enantioselectivities (over 70%) were observed for the 3- and 4-substituted acetophenones (runs 36–51). For each substrate, complex **(*S*)-2-Bz** gives the best enantioselectivities (*cf.* runs 27, 31, 35, 39, 43, 47 and 51). The two best ligands in terms of enantioselectivity for the acetophenone hydrogenation [i.e., **(*S*)-1-Et** and **(*S*)-1-Bz**] were selected for further studies at lower temperature (10 °C, see Table 4). This resulted in much higher enantioselectivities (up to >99% for 4-fluoroacetophenone, Table 4, runs 52–57), while the catalytic activities remained acceptably high. This outstanding increase is much greater than expected on the basis of a simple Arrhenius relationship for a mononuclear catalyst. It is therefore likely that several catalytically active species are involved. This hypothesis is in agreement with a preliminary investigation of the *ee* of the product as a function of enantiomeric purity of the catalyst, which shows a negative non-linear effect.[14] This aspect of the catalytic process is under further investigation.

In conclusion, we have shown that iridium complexes with planar chiral P,S ligands are effective catalysts for the asymmetric hydrogenation of various alkyl aryl ketones with high activities (TOF up to *ca.*

Table 3. Asymmetric hydrogenation of alkyl aryl ketones.[a]

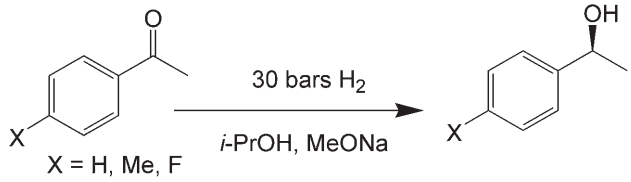


Run	Catalyst	X (position)	Time [h]	Conversion [%][b]	*ee* [%][b]
24	**(*S*)-2-Et**	H	2	94	**68**
25	**(*S*)-2-Ph**	H	2	>99	43
26	**(*S*)-2-*t*-Bu**	H	2	92	59
27	**(*S*)-2-Bz**	H	2	95	**77**
28	**(*S*)-2-Et**	Cl(2)	2	96	**51**
29	**(*S*)-2-Ph**	Cl(2)	2	>99	33
30	**(*S*)-2-*t*-Bu**	Cl(2)	2	98	30
31	**(*S*)-2-Bz**	Cl(2)	2	>99	**56**
32	**(*S*)-2-Et**	F(2)	2	71	**37**
33	**(*S*)-2-Ph**	F(2)	2	>99	11
34	**(*S*)-2-*t*-Bu**	F(2)	2	47	17
35	**(*S*)-2-Bz**	F(2)	2	82	**47**
36	**(*S*)-2-Et**	Me(3)	2	18	**66**
37	**(*S*)-2-Ph**	Me(3)	2	94	41
38	**(*S*)-2-*t*-Bu**	Me(3)	2	20	55
39	**(*S*)-2-Bz**	Me(3)	2	31	**72**
40	**(*S*)-2-Et**	Me(4)	2	85	67
41	**(*S*)-2-Ph**	Me(4)	2	97	72
42	**(*S*)-2-*t*-Bu**	Me(4)	2	72	68
43	**(*S*)-2-Bz**	Me(4)	2	81	**73**
44	**(*S*)-2-Et**	Cl(4)	2	92	61
45	**(*S*)-2-Ph**	Cl(4)	2	>99	31
46	**(*S*)-2-*t*-Bu**	Cl(4)	2	68	55
47	**(*S*)-2-Bz**	Cl(4)	2	88	**76**
48	**(*S*)-2-Et**	F(4)	2	16	61
49	**(*S*)-2-Ph**	F(4)	2	>99	74
50	**(*S*)-2-*t*-Bu**	F(4)	2	72	57
51	**(*S*)-2-Bz**	F(4)	2	64	**75**

[a] *Reaction conditions:* catalyst, 6.4×10^{-3} mmol; NaOMe, 3.2×10^{-2} mmol; substrate, 3.2 mmol (1/5/500) at 27 °C.

[b] Conversion and *ee* determined by GC. In each case, the absolute configuration configuration of the product is *S* (assigned by comparison of optical rotation sign with literature data).

Table 4. Asymmetric hydrogenation of alkyl aryl ketones.[a]



Run	Catalyst	X	Time [h]	Conversion [%][b]	*ee* [%][b]
52	**(*S*)-2-Et**	H	8	>99	78
53	**(*S*)-2-Bz**	H	8	99	87
54	**(*S*)-2-Et**	Me	8	86	93
55	**(*S*)-2-Bz**	Me	8	84	93
56	**(*S*)-2-Et**	F	8	>99	>99
57	**(*S*)-2-Bz**	F	8	96	>99

[a] *Reaction conditions:* catalyst, 6.4×10^{-3} mmol; NaOMe, 3.2×10^{-2} mmol; substrate, 3.2 mmol (1/5/500) at 10 °C.

[b] Conversion and *ee* determined by GC. In each case, the absolute configuration configuration of product is *S* (assigned by comparison of optical rotation sign with literature data).

250 h^{-1}) and ees up to >99% with conversions up to >99%). To the best of our knowledge, these activities and enantioselectivities are the best ones reported so far for the iridium-catalyzed hydrogenation of ketones. Future work will focus on investigating the reaction mechanism and on expanding the substrate scope. Only four **(*S*)-1-R** ligands have been used in this study, but a variety of analogues can be easily synthesized,[9a] opening the way to a search for the best complex for each substrate. Therefore, we hope that the fine tuning of the complex stereoelectronic properties, in particular by modification of the R group, will lead to a more efficient asymmetric hydrogenation of a large variety of simple ketones.

Experimental Section

General Remarks

All reactions were carried out under dry argon by using Schlenk glassware and vacuum line techniques. Commercial samples were used as received. Solvents were freshly distilled from standard drying agents. ^{1}H, $^{13}C\{^{1}H,^{31}P\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 500 instrument operating at 500, 200, and 125 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were obtained on a Nermag R10–10 instrument (DCI, FAB) and on a Applied Biosystem API 365 instrument (APCI). Optical rotations were measured with a Perkin–Elmer 241 polarimeter.

Synthesis of Complex 2-Bz

Complex **2-Bz** was synthesized following the published procedure[11a] from ligand **1-Bz**.[9] ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.45$ (br s, 2H, Ar), 7.64–7.60 (m, 3H, Ar), 7.43–7.38 (m, 5H, Ar), 7.27–7.22 (m, 3H, Ar), 7.03–6.99 (m, 2H, Ar), 4.85 [br d (AB syst.), $J_{H,H} = 12$ Hz, 1H, CH_2-Cp], 4.24 (dd, $J_{H,H} = 2.2$ Hz, $J_{H,H} = 1.5$ Hz, 1H, subst Cp), 4.14 (t, $J_{H,H} = 2.5$ Hz, 1H, subst Cp), 4.12 [d (AB syst.), $J_{H,H} = 13{,}2$ Hz, 1H, CH_2-Ph], 3.95 (m, 1H, subst Cp), 3.94 [d (AB syst.), $J_{H,H} = 13.2$ Hz, 1H, CH_2-Ph), 3.65(s, 5H, Cp), 3.62–3.56 (m, 2H, CH/COD), 3.56–3.50 (m, 2H, CH/COD), 3.32 [br d (AB syst.), $J_{H,H} = 12$ Hz, 1H, CH_2-Cp], 2.81–2.69 (m, 2H, CH_2/COD), 2.18–2.03 (m, 4H, CH_2/COD), 1.47–1.36 (m, 2H, CH_2/COD); $^{13}C\{^{1}H\}$ RMN (500 MHz, $CDCl_3$): $\delta = 135.6$ (d, $J_{C,P} = 14.3$ Hz, Ar), 135.3 (s, quat Ar), 135.2 (d, $J_{C,P} = 45$ Hz, quat Ar), 133.9 (d, $J_{C,P} = 51.9$ Hz, quat Ar), 131.7 (d, $J_{C,P} = 8.5$ Hz, Ar), 130.6 (d, $J_{C,P} = 3$ Hz, Ar), 129.6 (s, Ar), 128.9 (s, Ar), 128.8 (s, Ar), 128.0 (s, Ar), 127.8 (d, $J_{C,P} = 10.4$ Hz, Ar), 127.1 (d, $J_{C,P} = 8.9$ Hz, Ar), 87.8 (d, $J_{C,P} = 18.8$ Hz, quat Cp), 72.5 (d, $J_{C,P} = 7.0$ Hz, subst Cp), 72.4 (s, subst Cp), 70.7 (d, $J_{C,P} = 44.5$ Hz, quat Cp), 70.5 (s, Cp), 68.8 (d, $J_{C,P} = 4.6$ Hz, subst Cp), 66.12 (s, CH/COD), 63.40 (d, CH/COD, $J_{C,P} = 14.7$ Hz), 40.13(d, $J_{C,P} = 5.7$ Hz, CH_2Ph), 36.61 (d, $J_{C,P} = 3$ Hz, CH_2/COD), 31.1 (s, CH_2-Cp), 28.25 (s, CH_2/COD); ^{31}P NMR (500 MHz, $CDCl_3$): $\delta = -9.00$; MS (DCI, NH_3): $m/z = 843$ ($M + H^+$, 2%); 807 ($M - Cl^-$, 28%).

General Procedure for Asymmetric Hydrogenation

In a glove-box, a solution of 6.4×10^{-3} mmol of catalyst, 3.2×10^{-2} mmol of additives (5 equivs.) and 3.2 mmol of substrate (500 equivs.) in 2 mL of the desired solvent was transferred into a 5-mL glass ampoule which was then placed into a stainless steel autoclave. The reaction vessel was pressurized to the required H_2 pressure and stirred with a magnetic bar for the desired time at a controlled temperature (±2 °C). The reaction was stopped by release of pressure and quenching of the solution with CH_2Cl_2 at room temperature. The crude materials were obtained by evaporation of the solvent on a rotavapor. The product was finally analyzed by chiral GC (Supelco BETA DEX™ 225).

Acknowledgements

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