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Hybrid NH_2-Benzimidazole Ligands for Efficient Ru-Catalyzed Asymmetric Hydrogenation of Aryl Ketones†

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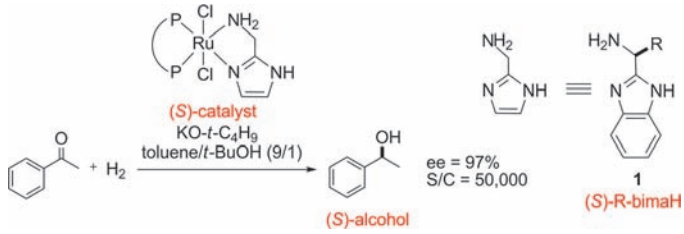
ABSTRACT



Readily available hybrid NH_2/benzimidazole ligands (R-bimaH, 1) dramatically influence the outcome of established Ru-based catalysts during asymmetric hydrogenation of aryl ketones. The benzimidazole functionality results in reversal of the typically observed chiral induction and allows for hydrogenation to be uncharacteristically conducted in nonprotic solvents. The developed systems efficiently catalyzed the AH of a number of ketones in up to 99% ee.

The nonbiological generation of chiral alcohols by asymmetric hydrogenation (AH) of ketones has been best achieved using transition-metal-based catalysts comprised of well-designed chiral ligand(s).[1] For AH of simple aryl ketones, the utilization of *trans*-$RuCl_2$(diphosphane)(1,2-diamine) catalysts have yielded the most efficient systems to date,[2] where the unique reactivity stems from the coorperative action of the Ru−H and NH_2 components operating through a metal−ligand bifunctional mechanism.[3−5] More recently, this concept has been furthered by development of several unsymmetrical hybrid amino-ligands for AH.[6,7] Of present relevance is the NH_2/pyridine combination,[7,8] where the functional and structural characteristics of the hybrid ligand are believed responsible for the high catalytic performance. In this connection, we considered that integration of the structurally related imidazole moiety would further influence the catalysis by virtue of its unique acid/base properties, best exemplified by the various functions of histidine during

† This work is dedicated to Professor Ryoji Noyori in honor of his 70th birthday.

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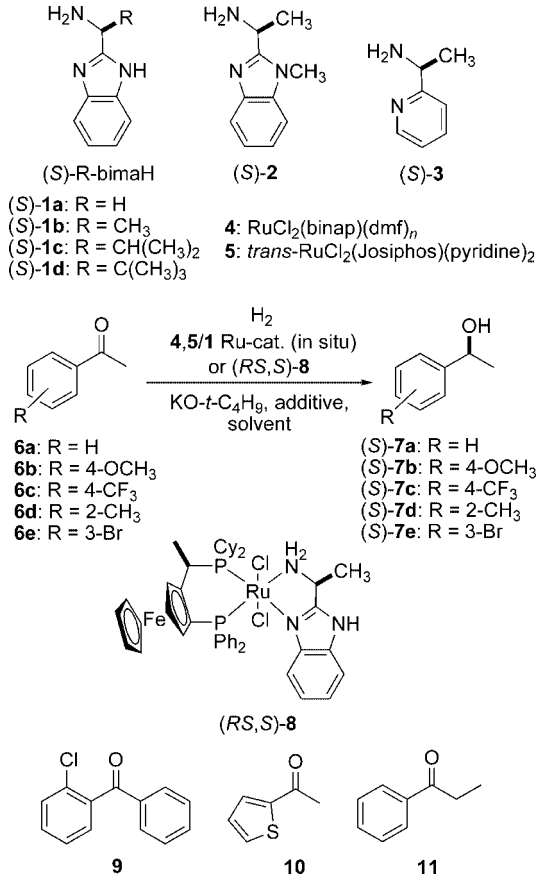
Scheme 1. Asymmetric Hydrogenation of Aryl Ketones Catalyzed by in Situ Generated Ru Complexes (**4**,**5**/**1**) or $RuCl_2$[(*R*,*S*)-Josiphos)][(*S*)-Me-bimaH)] [(*RS*,*S*)-**8**] Complex (Idealized Configuration Shown)



enzymatic processes and catalyzes.[9] Accordingly, we herein report the application of NH_2/benzimidazole hybrid ligands, α-R-1*H*-benzimidazole-2-methanamine [R-bimaH, **1**], for Ru-based aryl ketone AH.

Both the (*S*)- and (*R*)-configuration of **1** were readily obtained from simple condensation of 1,2-diaminobenzene with the corresponding amino acid via established methods.[10] Trials using in situ generated catalysts derived from **1**−**3** and $RuCl_2$[(*S*)-binap](dmf)$_n$ [(*S*)-**4**][11] or *trans*-$RuCl_2$[(*R*,*S*)-Josiphos](pyridine)$_2$ [(*R*,*S*)-**5**][12] for AH of acetophenone (**6a**) revealed that systems based on **1** uncharacteristically performed well in both protic and nonprotic solvents (toluene, Et_2O, THF), Table 1.[13,14] Previous reactivity in nonprotic solvents for related systems has been limited to reactive Ru−hydride complexes representative of the active catalyst.[4a,7b,c,15,16] Better catalytic performance was obtained for homochiral combinations, (*S*)-**4**/(*S*)-**1** and (*R*,*S*)-**5**/(*S*)-**1**, noting that the latter generally gave higher enantiomeric excess (ee) values for **7a**. Only a small influence on enantioselectivity was exerted by the R group in **1**. In addition, for (*R*,*S*)-**5**/(*S*)-**1b** systems, the optical purity of product alcohol was largely influenced by phosphine additives (regardless of the solvent media). Thus, the obtained ee for (*S*)-**7a** varied from 82−98% depending on the phosphine additive used. Despite of the structural similarities

Table 1. Asymmetric Hydrogenation of Acetophenone (**6a**) Catalyzed by in Situ Generated Catalysts Comprised of $RuCl_2$(binap)(dmf)$_n$ (**4**) or *trans*-$RuCl_2$[(*R*,*S*)-Josiphos](pyridine)$_2$ [(*R*,*S*)-**5**] and Hybrid Ligands (**1**−**3**)[a]

	catalyst components				time	yield	ee[b] (%)
entry	complex	ligand	additive	solvent	(h)	(%)	(config)
1	(*S*)-**4**	**1a**		toluene	8	100	77 (*S*)
2	(*S*)-**4**	**1a**		*i*-PrOH	8	100	25 (*S*)
3	(*S*)-**4**	(*S*)-**1b**		toluene	8	100	91 (*S*)
4	(*R*)-**4**	(*R*)-**1b**		toluene	8	100	91 (*R*)
5	(*S*)-**4**	(*S*)-**1b**		*i*-PrOH	8	100	28 (*S*)
6	(*S*)-**4**	(*S*)-**1c**		toluene	12	100	87 (*S*)
7	(*S*)-**4**	(*S*)-**1d**		toluene	10	100	91 (*S*)
8	(*R*,*S*)-**5**	**1a**	$P(C_6H_5)_3$	toluene	9	100	82 (*S*)
9	(*R*,*S*)-**5**	(*S*)-**1b**		toluene	9	95	91 (*S*)
10	(*R*,*S*)-**5**	(*S*)-**1b**	$P(C_6H_5)_3$	toluene	9	100	96 (*S*)
11	(*R*,*S*)-**5**	(*S*)-**1c**	$P(C_6H_5)_3$	toluene	9	100	96 (*S*)
12	(*R*,*S*)-**5**	(*S*)-**1d**	$P(C_6H_5)_3$	toluene	9	50	93 (*S*)
13	(*R*,*S*)-**5**	(*S*)-**2**		*i*-PrOH	9	100	30 (*R*)
14[c]	(*R*,*S*)-**5**	(*S*)-**3**		*i*-PrOH	10	92	95 (*R*)
15	(*R*,*S*)-**5**	(*S*)-**1b**	$P(C_6H_5)_3$	*i*-PrOH	9	100	78 (*S*)
16	(*R*,*S*)-**5**	(*S*)-**1b**	$P(C_6H_5)_3$	*t*-BuOH	8	100	93 (*S*)
17	(*R*,*S*)-**5**	(*S*)-**1b**	$P(C_6H_5)_3$	THF	9	100	89 (*S*)
18	(*R*,*S*)-**5**	(*S*)-**1b**	$P(C_6H_5)_3$	Et_2O	9	100	92 (*S*)
19	(*R*,*S*)-**5**	(*S*)-**1b**	$P(4\text{-}ClC_6H_4)_3$	toluene	12	100	90 (*S*)
20	(*R*,*S*)-**5**	(*S*)-**1b**	$P[3,5\text{-}(C_6H_5)_2C_6H_3]_3$	toluene	12	100	82 (*S*)
21	(*R*,*S*)-**5**	(*S*)-**1b**	$P(CH_2CH_2CH_2CH_3)_3$	toluene	18	52	98 (*S*)

[a] Hydrogenation conditions: [**6a**] = 0.33 M, [**4** or **5**] = 0.33 mM, [**1**, **2**, or **3**] = 0.33 mM, $P(H_2)$ = 8 atm, [KO-*t*-C_4H_9] = 20 mM, [additive] = 1.0 mM (3 equiv), T = 25 °C. [b] Enantiomeric excess (ee) determined by GC analysis; absolute configuration (config) determined from $[\alpha]_D$ measurement. [c] $P(H_2)$ = 2 atm, [NaO-*t*-C_4H_9] = 20 mM.

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between **1** and **3**, the observed sense of chiral induction for corresponding catalysts was opposite! While hydrogenation in *i*-PrOH using the (*S*)-phosphine/(*S*)-**3** combination gave the expected (*R*)-**7a** in 46% and 95% ee for (*S*)-**4** and (*S*)-**5**,[8] respectively,[17] the analogous (*S*)-phosphine/(*S*)-**1b** systems gave the opposite (*S*)-**7a** as the major isomer in 28 and 78% ee. In toluene solvent, the latter similarly induced the (*S*)-configured alcohol in significantly higher ee, 91% for (*S*)-**4** and 91/96% (no PPh_3/added PPh_3) for (*S*)-**5**, while poor performance was observed for (*S*)-phosphine/(*S*)-**3** combinations.[14] For systems comprised of the methylated bimaH-analogue **2**, the reactivity and sense of chiral induction resembled the (*S*)-**5**/(*S*)-**3** combination, although (*R*)-**7a** was obtained in poor ee. Thus, although the reasons for the dramatic change in prochiral face discrimination are not clear at present, they are considered to originate from the added functionality provided by the benzimidazole moiety in **1**.

The air-stable isolated precatalyst (*RS*,*S*)-**8** was readily synthesized by simply mixing (*S*)-Me-bimaH (**1b**) and an appropriate Ru-Josiphos precursor (e.g., **5**) at elevated temperature (100 °C).[14] The ^{31}P NMR spectrum in DMSO-d_6 indicated the presence of several isomers, predominantly exhibiting two sets of resonances at δ 65.1 and 41.3 ppm ($^2J_{P,P}$ = 41.0 Hz) and δ 72.3 and 41.0 ppm ($^2J_{P,P}$ = 44.0 Hz).[14] The AH of **6a** proceeded smoothly when catalyzed by (*RS*,*S*)-**8** (conditions: [**8**] = 0.33 mM, [**6a**] = 0.33 M, $P(H_2)$ = 8 atm, [KO-*t*-C_4H_9] = 20 mM, [PPh_3] = 1.0 mM, toluene solvent), giving (*S*)-**7a** in the same 96% ee (cf. Table 1, entry 10). Under analogous conditions, the hydrogenation rate expectedly increased with increasing pressure giving 4, 51, 95, and 100% conversion after 1 h at 2, 4, 8, and 16 atm, respectively. Importantly, however, the chiral induction was independent of pressure within this range, with (*S*)-**7a** obtained in the same 96% ee (>80% conv). Hydrogenation proceeded efficiently throughout the [K-O-*t*-C_4H_9] range of 15−50 mM (*t* = 1 h, 95−96% ee, toluene solvent), while reduced reactivity was found at lower (5 mM, <5% conv, *t* = 1 h) or higher (100 mM, 57% conv, *t* = 1 h, 87% ee) base concentrations. Reaction in *i*-PrOH or *t*-BuOH proceeded considerably faster with complete conversion in under 1 h above 2 atm. For unknown reasons, reaction in methanol and ethanol was inferior (<5% conv), although the system was not sensitive to small amounts of water.[14]

Table 2. Asymmetric Hydrogenation of Simple Aryl Ketones (**6**, **9**−**11**) Catalyzed by $RuCl_2$[(*R*,*S*)-Josiphos)][(*S*)-Me-bimaH)][(*RS*,*S*)-**8**] Complex[a]

entry	sub	S/C ratio	P/H_2 (atm)	time (h)	yield[b] (%)	ee[b,c] (%)
1	**6a**	1000	8	2	100	96 (*S*)
2	**6a**	10000	20	12	100	96 (*S*)
3[d]	**6a**	50000	40	10	100	97 (*S*)
4	**6b**	5000	20	16	95	97 (*S*)
5	**6c**	5000	20	8	90	82 (*S*)
6	**6d**	5000	20	8	100	95 (*S*)
7	**6e**	5000	20	6	100	92 (*S*)
8[e]	**9**	5000	20	24	95	99 (*R*)
9	**10**	1000	8	12	92	94 (*S*)
10	**11**	1000	8	12	100	97 (*S*)

[a] Hydrogenation conditions: [**6**, **9**−**11**] = 0.3−1.9 M, [(*RS*,*S*)-**8**] = 0.04−0.3 mM, [KO-*t*-C_4H_9] = 15−20 mM, [PPh_3] = 1.0−3.4 mM, *T* = 25 °C, solvent = toluene/*t*-BuOH (9/1). [b] Determined by GC. [c] Determined from $[\alpha]_D$. [d] Toluene/*t*-BuOH (7/3). [e] Yield determined by ^{1}H NMR; ee determined by HPLC.

Table 2describes the AH of a number of aryl ketones catalyzed by (*RS*,*S*)-**8** using a toluene/*t*-BuOH (9/1) solvent mixture. For the simple **6a**, the hydrogenation proceeded efficiently even at an S/C (substrate-to-catalyst) ratio of 50000 giving (*S*)-**7a** in 97% ee. Ring substitution influenced the enantioselectivity. Most notably, alcohol (*S*)-**7c** was obtained in only moderate ee (82%), with others ranging from 92−96%. Significantly, AH of biaryl ketone **9** (although less reactive) proceeded with excellent enantioselectivity giving alcohol product in 99% ee. Heteroaromatic **10** (94% ee) and **11** (97% ee) were considerably less reactive.

Reaction profiles for AH of **6a** showed that addition of PPh_3 influences the general performance of (*RS*,*S*)-**8** in terms of both reactivity and selectivity, Figure 1. In toluene solvent,

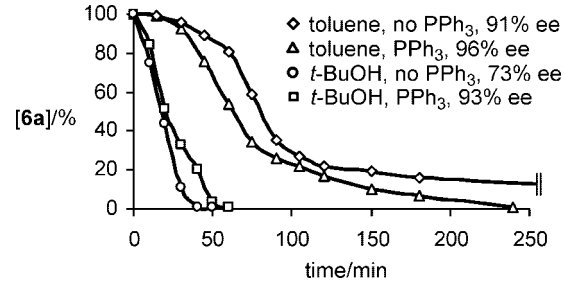

Figure 1. Reaction profiles for the asymmetric hydrogenation of acetopheneone (**6a**) catalyzed by $RuCl_2$[(*R*,*S*)-Josiphos)][(*S*)-Me-bimaH)] [(*RS*,*S*)-**8**] complex. Conditions: [(*RS*,*S*)-**8**] = 0.33 mM; [**6a**] = 0.33 M; $P(H_2)$ = 4 atm; [KO-*t*-C_4H_9] = 15.0 mM; [PPh_3] = 0 or 1.0 mM.

the presence of PPh_3 resulted in overall enhanced reactivity and a small (but consistent) increase in (*S*)-**7a** ee (91−96%).

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(17) Similarly, use of related (*S*)-**4**/(*S*)-1,2-diamine[2b] and (*R*,*S*)-**5**/(*S*)-1,2-diamine (Leong, C. G.; Akotsi, O. M.; Ferguson, M. J.; Bergens, S. H. *Chem. Commun.* **2003**, 750−751) catalysts give (*R*)-**7a**.

In *t*-BuOH, overall AH rates were similar but the increase in ee for (*S*)-**7a** was more pronounced (73−93%). No further improvements were observed for higher [PPh_3].[14] Accordingly, we consider the predominantly active catalyst (solvent independent) to be coordinatively saturated monohydride species RuH[(*R*,*S*)-Josiphos)][(*S*)-Me-bima)](PPh_3). In nonprotic solvent, AH most likely proceeds through intramolecular H_2 heterolytic cleavage,[3−5,7b,15b−d,19] while in alcoholic solvents the available protons allow for other more kinetically favorable pathways.[3,15c,d,20] The highly acidic nature (particularly upon metal coordination) of **1** is critical, assisting precatalyst activation in nonprotic solvents, and providing an anionic-chelate during hydrogenation which allows for (neutral) PPh_3 coordination. Furthermore, the enhanced basic strength of the amino moiety largely facilitates the intramolecular cleavage of H_2.

In conclusion, efficient ketone asymmetric hydrogenation catalysts based on Ru-complexes utilizing readily available hybrid NH_2/benzimidazole bimaH (**1**), and C_1- (JOSIPHOS) or C_2-symmetric (BINAP) diphosphane ligands have been developed. Resulting systems show unique enantioselection properties giving product alcohol in up to 99% ee and high reactivity in protic and nonprotic solvents (up to S/C = 50000) and display potential for further combinatorial development. The origin of such significant features lies in the added functionality provided by the benzimidazole moiety in **1**. Further work is now in progress to develop the practical aspects of these systems and to further understand the nature of the catalysis.

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Supporting Information Available: Synthetic and hydrogenation procedures; hydrogenation data and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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