



The first example of asymmetric hydrogenation of imines with $\text{Co}_2(\text{CO})_8/(\text{R})\text{-BINAP}$ as catalytic precursor

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ABSTRACT

The first example of asymmetric hydrogenation of imines using $\text{Co}_2(\text{CO})_8/(\text{R})\text{-BINAP}/\text{H}_2/\text{CO}$ system was developed. The reaction conditions were screened with a wide range of N-aryl benzophenone ketimines, obtaining products with excellent yields and good enantiomeric excess. Moreover, a pathway is suggested based on the isolation and characterization of several catalyst intermediates.

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1. Introduction

Asymmetric catalysis is one of the most important tools for the synthesis of enantiopure chemicals [1], due to its high atom economy when compared to methods based on the resolution of racemates. In this context, the enantioselective reduction of prochiral ketimines is among the most reliable and efficient approaches to obtain the corresponding optically active amines [2–4], which are themselves found in various natural or medicinal compounds [5–8]. Likewise, several methodologies have been developed for the enantioselective reduction of imines [9–28], the asymmetric hydrogenation of functionalized imines such as acyclic aromatic N-aryl imines [29], α -fluorinated iminoesters [30,31] and acyclic imines [32], with a variety of complexes of Ir [32,33], Ru [34], Rh [19] and organocatalysts [35,36] have been employed in asymmetric hydrogenations and/or transfer hydrogenations of imines. Noteworthy, $\text{Co}_2(\text{CO})_8$ /modified phosphine complexes have never been used as catalysts in asymmetric hydrogenation of imines, even though, phosphine dicobalt octacarbonyl derivatives play an important role as catalytic promoters in other organic transformations, for example: hydroformylation of alkenes (also known as oxo process discovered in 1938 by Otto Roelen) [37,38], amidocarbonylation reaction [39,40], synthesis of quinolines [41], synthesis of β -lactams [42] and the Pauson–Khand reaction (PKR) [43–45].

Overall, the last reaction was applied in the synthesis of asymmetric 2-cyclopentanones using $\text{Co}_2(\text{CO})_8$ modified with chiral bidentate phosphines as catalytic precursor. Furthermore, in 2003, Gibson's group studied the PKR mechanism of $\text{Co}_2(\text{CO})_8/\text{BINAP}$ system using the synthesis of bicyclic cyclopentenones; based on their results (they reported yields above 80% and ee up to 70%), postulated the existence of $(\text{BINAP})(\text{CO})\text{Co}-\mu-(\text{CO})_2-\text{Co}(\text{CO})_3$ as catalyst precursor [46] and the isolation of a cobalt hydride $(\text{BINAP})(\text{CO})_2\text{CoH}$ [47]. Therefore, we became interested in using of this hydride as a precursor in the reduction of prochiral imines, leading us to the first example of the catalytic asymmetric hydrogenation of imines with $\text{Co}_2(\text{CO})_8/(\text{R})\text{-BINAP}$.

2. Experimental

2.1. General

All reactions and manipulations were carried out under nitrogen atmosphere by using Schlenk-type techniques. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were obtained on a JEOL GX300 Bruker-Avance 300, Varian Unity 300 (300, 75 and 121 MHz respectively) spectrometers in CDCl_3 as solvent at 25 °C. IR spectra were recorded on a Nicolet FTIR Magna 750 spectrophotometer. Optical rotations were measured on a Perkin–Elmer 343 spectropolarimeter. Mass spectra were obtained using a JEOL JMS-SX102A instrument with m-nitrobenzyl alcohol as the matrix (FAB⁺ mode). Elemental analyses for some compounds were obtained on an Elemental Analyzer CE-440. HPLC analyses were performed on a Hewlett Packard 1100 system with UV-DAD. Separations were achieved on a

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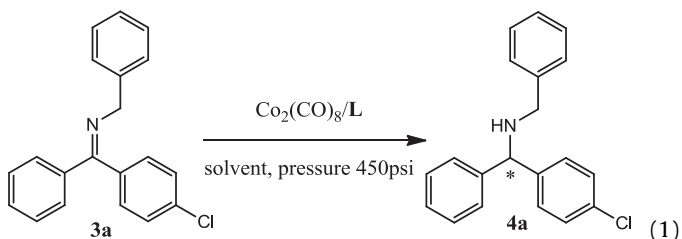
Daicel Chiracel OD-H (25 mm × 4.6 mm) column. X-ray determination was collected on a Bruker SMART APEX CCD area diffractometer by the ω -scan method.

2.2. Hydrogenation of imines

Imines were synthesized according to a literature procedure [48]. Typical procedure: in a Schlenk tube under nitrogen atmosphere, a solution of imine (100 mg), $\text{Co}_2(\text{CO})_8$ (1 mol%) and (R)-BINAP (2 mol%) in THF (10 mL) was transferred to a 45 mL stainless Steel Parr vessel which was pressurized at 450 psi with a H_2/CO mixture in a 1/3 ratio. The reactor was placed in a preheated oil bath at 120 °C with magnetic stirring for 15 h. The reaction mixture was purified by column chromatography using hexane and ethyl acetate as eluents.

3. Results and discussion

In our preliminary studies, we determined the influence of solvent, temperature, and carbon monoxide pressure, in the hydrogenation of imine **3a** (Eq. (1)) with $\text{Co}_2(\text{CO})_8/\text{rac-BINAP}$ (Table 1). The reduction of **3a** was not observed when working only with hydrogen (H_2) (entry 1), however, in the presence of CO/H_2 mixtures (3:1) (entries 2–4 and 7) good yields were obtained, behavior that suggests the stabilization of the catalytic species by CO partial pressure [40].



At room temperature, the hydrogenation product was not observed (entry 5) but, a temperature increase (120 °C) favored conversion and reaction yields (entries 4 and 6). The use of a coordinating solvent (THF) led to the best enantiomeric excess (95%ee) (entry 11), that contrasts with lower values obtained when carrying out the reaction in other solvents such as: toluene (67%ee), benzene (75%ee) and methylene chloride (52%ee) (entries 8–10).

Table 1
Effect of the H_2/CO ratio, solvent and temperature in hydrogenation of imine **3a**.^a

Entry	Temperature (°C)	H_2/CO ratio	Yields (%) ^b	ee% ^g
1	120	1/0	0	0
2	120	1/1	0	0
3	120	1/2	0	0
4	120	1/3	87	0
5	25	1/3	0	0
6	100	1/3	20	0
7	120	1/4	73	0
8 ^c	120	1/3	91	67
9 ^d	120	1/3	75	75
10 ^e	120	1/3	80	52
11 ^f	120	1/3	86	95

^a Reaction time 24 h and 450 psi pressure, 100 mg of imine **3a**, 5 mol% $\text{Co}_2(\text{CO})_8/\text{rac-BINAP}$ (1/2) and dry tetrahydrofuran (THF, 10 mL) as solvent.

^b Isolated yield.

^c The reaction was carried out in dry toluene (10 mL) as solvent and (R)-BINAP.

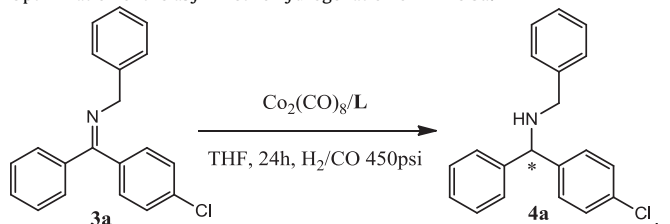
^d The reaction was carried out in dry benzene (10 mL) as solvent and (R)-BINAP.

^e The reaction was carried out in dry methylene chloride (10 mL) as solvent and (R)-BINAP.

^f The reaction was carried out in dry THF as solvent and (R)-BINAP.

^g Determined by HPLC.

Table 2
Optimization of the asymmetric hydrogenation of imine **3a**.^a



Entry	$\text{Co}_2(\text{CO})_8$ (mol%)	Ligand	Yield (%) ^b	ee (%) ^c
1	5	L1	31	–
2	2	L1	30	–
3	5	L2	79	–
4	3	L2	80	–
5	2	L2	79	–
6	1	L2	81	–
7	1	L3	86	93
8	1	L4	83	53
9	1	L5	40	5
10	1	L6	34	1
11 ^d	1	L3	89	92
12 ^e	1	L3	95	93
13 ^f	1	L3	82	90
14 ^g	1	L3	95	63

^a Reaction conditions: imine **3a** (100 mg), 1 mol% $\text{Co}_2(\text{CO})_8/\text{ligand}$ (1/2) in dry THF (10 mL), 24 h, 450 psi with a 1/3 ratio (H_2/CO), ligand: PPh_3 **L1**, *rac*-BINAP **L2**, (R)-BINAP **L3**, (R)-Tol-BINAP **L4**, (S,S)-Me-DUPHOS **L5**, (S,S)-DIOP **L6**.

^b Isolated yield.

^c Determined by HPLC.

^d 20 h.

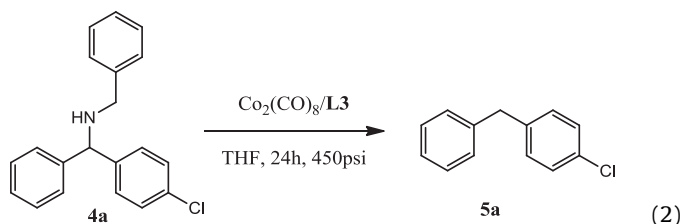
^e 15 h.

^f 12 h.

^g $\text{Co}_2(\text{CO})_8/\text{ligand}$ (ratio: 1/1), 15 h.

Our initial evaluation began with hydrogenation of imine **3a** as the model substrate, finding an optimal H_2/CO ratio (1:3) in THF. Afterwards, we tested the influence of different monodentate and bidentate phosphine ligands in the conversion yields; the results are summarized in Table 2.

The use of monophosphine ligand **L1** resulted in poor yields (entries 1 and 2), unlike the biphosphine ligands **L2–L6**, we found that low catalyst loading (1%) did not affect the conversion of **3a** (entries 3–6). However, low yields were obtained when using Me-DUPHOS **L5** or DIOP **L6** ligands (entries 9 and 10), compared to those observed for **L4** (entry 8) and (R)-BINAP **L3**, which achieved the best result (entry 7). After 24 h we found in this reaction a lower concentration of the by-product **5a** (less than 6%), which was isolated and fully characterized (Eq. (2)), same results were obtained using the fluorinated imine **2b** as substrate in catalytic amounts of $\text{Co}_2(\text{CO})_8/\text{L3}$ (1 mol%). Moreover, when we used previously prepared amine **4a** in the same reaction conditions, we found again the product **5a** (25%). Finally when this last reaction was carried out in the absence of $\text{Co}_2(\text{CO})_8/\text{L3}$ we did not find by-product **5a**. This by-product was not formed when the reaction time was reduced to 15 h (entries 11–13).



Noteworthy, the use of an equimolar mixture of $\text{Co}_2(\text{CO})_8/\text{ligand}$ resulted in good reaction yield but low enantioselectivity (entry 14), this lack of selectivity could be related to the existence of two hydride species, $\text{HCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_2\text{-BINAP}$

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