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Synthesis of optically active 2-aminotetraline derivatives via enantioselective ruthenium-catalyzed hydrogenation of ene carbamates

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Abstract—The enantioselective hydrogenation of prochiral ene carbamates, directly derived from 2-tetralone, was completed using a catalytic ruthenium system generated from $Ru(COD)(methallyl)_2$, an optically pure diphosphine and a strong acid containing a non-coordinating counter anion.

1. Introduction

Optically active amine derivatives represent an important class of biologically active compounds and homochiral amines are often used as resolving agents or as auxiliaries in enantioselective synthesis.[1] Therefore, the development of practical methods to directly produce such derivatives is of great interest. Catalytic enantioselective hydrogenation has become a competitive route[2] with respect to traditional methods such as resolution or enzymatic processes. Many efforts have been directed towards the enantioselective hydrogenation of enamides in the presence of ruthenium[3] and rhodium[4–6] catalytic precursors. The highly enantioselective syntheses of 2-aminotetraline derivatives which are building blocks for biologically active compounds and pharmaceutical intermediates via the hydrogenation of enamides using ruthenium complexes have been reported.[7]

Although first described in 1975 by Kagan et al.,[8] the enantioselective hydrogenation of ene carbamates is far less documented in comparison with the equivalent reaction of enamides; this is despite the advantageous facile deprotection of carbamates under mild conditions to yield amines. During the synthesis of alkaloid precursors, ruthenium catalysts were shown to be active for the enantioselective hydrogenation of the exocyclic C=C bond of ene carbamates,[9] and recently, rhodium–diphosphine complexes[10] were used to reduce highly functionalized ene carbamates. At the same time, we reported the synthesis of optically active carbamates through the hydrogenation of the endocyclic C=C bond of ene carbamates in the presence of chiral ruthenium complexes.[11] However, none of the previously reported catalytic systems based on stable well-defined ruthenium and rhodium catalyst precursors were able to hydrogenate the ene carbamates derived from 2-tetralone itself.

We now report the transformation of 2-tetralone into optically active amine derivatives via catalytic enantioselective hydrogenation of ene carbamates using a catalytic system based on $Ru(COD)(methallyl)_2$ (COD = 1,5-cyclooctadiene), an optically pure diphosphine and HBF_4.

2. Preparation of ene carbamates from 2-tetralone and primary carbamates

Starting from 2-tetralone **1**, the ene carbamates **2**–**7** were obtained in one step in the presence of an excess of primary carbamate (2.5 equiv.) and a catalytic amount of *para*-toluenesulfonic acid (PTSA) (0.1 equiv.) in refluxing toluene in a Dean–Stark apparatus under inert atmosphere for 20 h.[11] After purification by flash chromatography over silica gel with an ether/pentane mixture, the ene carbamates **2**–**7** were isolated in 50–93% yield. Because of their low stability, they were immediately hydrogenated or stored under an inert atmosphere at 6°C (Scheme 1).

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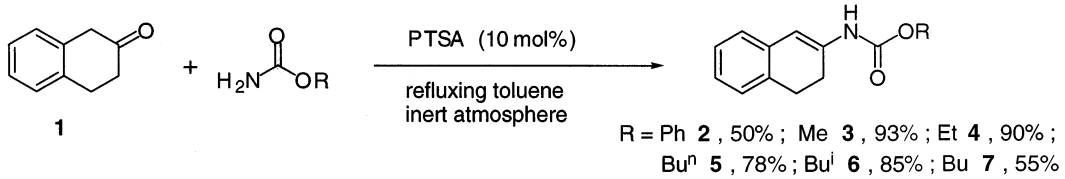
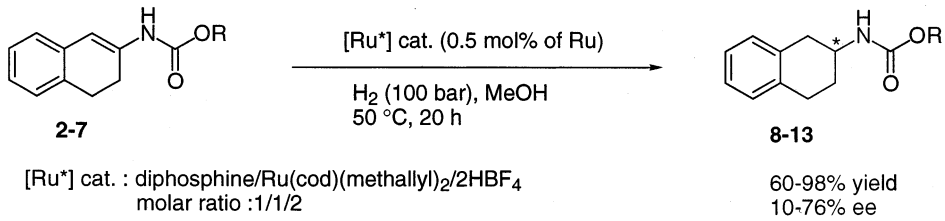


Scheme 1.



Scheme 2.

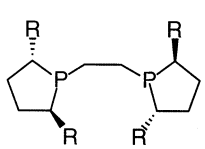
3. Enantioselective hydrogenation of ene carbamates

Whereas ene carbamates derived from functionalized 2-tetralones were successfully hydrogenated in the presence of [(*R*)-Binap]Ru(O_2CCF_3)$_2$, no conversion of the ene carbamate **4** derived from the non-substituted tetralone **1** was observed using the same catalyst precursor.[11] With this type of catalyst precursor, the presence of another functional group on the molecule favoring the coordination of the substrate to the ruthenium center appeared to be essential for hydrogenation in these conditions.[12] The hydrogenation of the ene carbamates **2**–**7** was achieved using ruthenium catalyst precursors produced by treatment in dichloromethane of an equimolar mixture of the ruthenium complex Ru(COD)(methallyl)$_2$ and an optically pure diphosphine: the BPE- or Duphos-type ligand, with 2 equiv. of tetrafluoroboric acid. This catalytic system is inspired from the ruthenium system recently developed by Genêt, Rautenstrauch et al. for the hydrogenation of a tetrasubstituted endocyclic C=C bond to produce methyl dihydrojasmonate,[13] but differs by the use of 2 equiv. of acid and the absence of $BF_3{\cdot}Et_2O$ as additive.

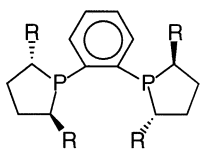
The catalytic hydrogenation reactions were performed in methanol at 50°C under 100 bar pressure of hydrogen in the presence of 0.5 mol% of ruthenium and went to completion within 20 h (non-optimized reaction times) (Scheme 2).

In the presence of BPE–ruthenium precursors, phenyl **8** and *tert*-butyl **13** carbamates were obtained with low enantioselectivity (21–23% e.e.), probably as a result of electronic and steric factors, respectively. Better results were observed for carbamates bearing a linear alkyl chain such as **10** (R = ethyl, 56% e.e.) and **11** (R = *n*-butyl, 40 and 50% e.e.) (Table 1). The hydrogenation of alkyl derivatives at 50°C under 100 bar hydrogen pressure, using the more rigid Duphos bis-phosphine ligands, generally led to a significant increase in enantioselectivity (Table 2). Carbamates **9**–**13** were thus obtained in 66–76% e.e. with Et-Duphos as a ligand, which led to slightly better enantioselectivities than Me-Duphos. In comparison with other alkyl derivatives, the *tert*-butyl carbamate **13** was still obtained with lower selectivity (66% e.e.). Decreasing the reaction temperature to 20°C did not significantly improve the enantioselectivity in the hydrogenation of **5** (77% e.e. at 20°C as compared to 76% e.e. at 50°C).

It is noteworthy that the use of the atropoisomeric Binap and Biphemp ligands led to no activity for the hydrogenation of these ene carbamates, which might be explained by the transformation of these ligands into monophosphines and the generation of new ruthenium species in the presence of strong acids.[14] Similarly, hydrogenation did not occur in the presence of the cationic [(Duphos)Rh(COD)]BF_4 and [(BPE)Rh-(COD)]BF_4 complexes.



R= Me : (S,S)-Me-BPE
R= Et : (S,S)-Et-BPE



R= Me : (S,S)-Me-Duphos
R= Et : (S,S)-Et-Duphos

Table 1. Enantioselective hydrogenation of ene carbamates using BPE-type ligands

R (substrate)	Diphosphine	Product	Yield[a] (%)	E.e.[b] (%)
Ph **2**	(*S*,*S*)-Me-BPE	**8**	76[c]	21 (+)
Et **4**	(*S*,*S*)-Et-BPE	**10**	98	56 (+)
n-Bu **5**	(*S*,*S*)-Me-BPE	**11**	96	40 (+)
n-Bu **5**	(*S*,*S*)-Et-BPE	**11**	97	50 (+)
tert-Bu **7**	(*S*,*S*)-Me-BPE	**13**	98	10 (+)
tert-Bu **7**	(*S*,*S*)-Et-BPE	**13**	97	23 (+)

General conditions: [Ru*] cat.: (diphosphine)/Ru(COD)(methallyl)$_2$/$2HBF_4$ in molar ratio 1:1:2, 0.5 mol% of Ru, H_2 (100 bar), MeOH, 50°C, 20 h, total conversion observed by ^{1}H NMR.

[a] Isolated yield.

[b] Determined by HPLC (Chiralcel OD 25 column).

[c] Partial conversion observed by ^{1}H NMR.

Table 2. Enantioselective hydrogenation of ene carbamates using Duphos-type ligands

R (substrate)	Diphosphine	Product	Yield[a] (%)	E.e. (%)[d]
Ph **2**	(*R*,*R*)-Me-Duphos	**8**	60[b]	17 (−)
Me **3**	(*R*,*R*)-Me-Duphos	**9**	95	68 (−)
Me **3**	(*S*,*S*)-Et-Duphos	**9**	96	73 (+)
Et **4**	(*R*,*R*)-Me-Duphos	**10**	97	61 (−)
Et **4**	(*S*,*S*)-Et-Duphos	**10**	98	76 (+)
n-Bu **5**	(*S*,*S*)-Et-Duphos	**11**	97	76 (+)
n-Bu **5**[c]	(*S*,*S*)-Et-Duphos	**11**	98	77 (+)
iso-Bu **6**	(*S*,*S*)-Et-Duphos	**12**	98	73 (+)
tert-Bu **7**	(*S*,*S*)-Et-Duphos	**13**	95	66 (+)

General conditions: [Ru*] cat.: (diphosphine)/Ru(COD)(methallyl)$_2$/2HBF$_4$ in molar ratio 1:1:2, 0.5 mol% of Ru, H_2 (100 bar), MeOH, 50°C, 20 h, total conversion observed by ^{1}H NMR.

[a] Isolated yield.

[b] Partial conversion observed by ^{1}H NMR.

[c] 20°C, 20 h.

[d] Determined by HPLC (Chiralcel OD 25 column).

The influence of the nature of the acid used to generate the ruthenium precursors was investigated in the presence of (*S*,*S*)-Et-Duphos as a ligand in the hydrogenation of **5** (Table 3). Similar results were obtained with tetrafluoroboric and triflic acids (100% conversion, 76 and 74% e.e.), but no conversion was observed when hydrochloric and hydrobromic acids were used.[15] The strong coordinating properties of halide anions are presumably responsible for the dramatic change in the catalytic activity of these ruthenium systems, indicating that different organometallic species are formed depending on the acid.[13,15]

The *tert*-butyl carbamate **13** was deprotected without racemization using a procedure based on the classical method, which involved stirring the carbamate in dichloromethane at 25°C for 1.5 hours in the presence of 10 equiv. of trifluoroacetic acid. The 2-aminotetraline hydrochloride **14** was obtained in 90% yield after treatment with 1N HCl (Scheme 3).

4. Conclusions

We have shown that the enantioselective hydrogenation of 2-tetralone derived ene carbamates containing an endocyclic C=C bond can be achieved using ruthenium precursors generated upon protonation of Ru(COD)(methallyl)$_2$ with HBF$_4$ or triflic acid in the presence of a BPE or Duphos ligand.

The activities of these precatalysts dramatically depends on the nature of the diphosphine and the acid used to generate the active catalytic species. Hydrogenated carbamates were thus obtained with e.e.s of up to 77%, depending on the ligand used and also on the nature of the carbamate moiety. With the objective of producing optically active amines, these results are still less attractive than those obtained from the corresponding amides,[7c] and thus provide impetus for the search for more active catalytic systems.

5. Experimental

^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained using a Bruker AM 200 spectrometer with TMS as a reference. Silica gel column chromatography was carried out using Si 60 Merck silica gel. Analytical HPLC analyses were performed using a Waters instrument equipped with UV detection and a Chiralcel OD 25 column.

5.1. Typical procedure for the preparation of a ruthenium precatalyst

An equimolar mixture containing 0.33 mmol of Ru(COD)(methallyl)$_2$ and 0.33 mmol of the ligand was dissolved in degassed CH_2Cl_2 (6 mL) in a Schlenk tube under an inert atmosphere. The solution was then cooled down to 0°C and 2 equiv. (0.66 mmol) of HBF$_4$ (54 wt% in Et_2O) were slowly added. After stirring at 0°C for 0.5 h the reaction mixture was evaporated to dryness and afforded an orange solid which was directly used for hydrogenation of the ene carbamates.

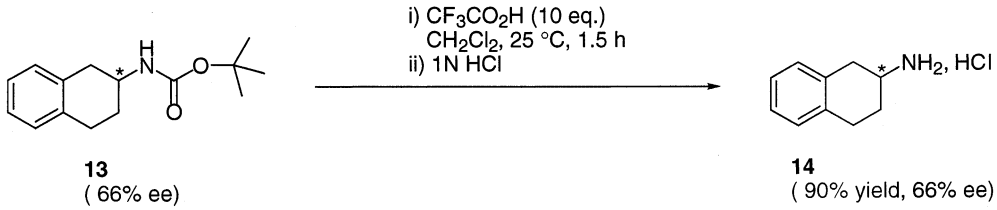
Table 3. Influence of the acid on the enantioselective hydrogenation of ene carbamate **5**

Acid	Conversion[a] (%)	E.e.[b] (%)
HBF$_4$	100	76 (+)
HOTf	100	74 (+)
HCl	0	
HBr	0	

General conditions: [Ru*] cat.: (*S*,*S*)-Et-Duphos/Ru(COD)(methallyl)$_2$/2HBF$_4$ in molar ratio 1:1:2, 0.5 mol% of Ru, H_2 (100 bar), MeOH, 50°C, 20 h.

[a] Conversion of the ene carbamate observed by ^{1}H NMR.

[b] Determined by HPLC (Chiralcel OD 25 column).



13
(66% ee)

14
(90% yield, 66% ee)

Scheme 3.

5.2. General procedure for the enantioselective hydrogenation of ene carbamate

A solution of the ene carbamate (1 mmol) and the ruthenium precatalyst (0.005 mmol based on the initial $Ru(COD)(methallyl)_2$ complex) in degassed MeOH (8 mL) was placed in a 125 mL autoclave under an inert atmosphere. After removing the inert gas with hydrogen, a pressure of 100 bar of hydrogen was applied. The autoclave was mechanically stirred at 50°C for 20 h and the conversion was then determined by ^1H NMR. The carbamates were purified by flash chromatography over silica gel (ether/pentane (1:4) mixture used as eluent). The enantiomeric excesses were determined by HPLC using a Chiralcel OD 25 column (eluent: hexane/*iso*-propanol, 85:15).

5.2.1. *N*-(1,2,3,4-Tetrahydronaphthalen-2-yl) phenylcarbamate 8. ^1H NMR (200.130 MHz, $CDCl_3$), δ 1.70–1.97 (m, 1H, CH_2), 2.01–2.25 (m, 1H, CH_2), 2.73 (dd, *J* 16.3 and 8.0 Hz, 1H, CH_2), 2.91 (t, *J* 6.6 Hz, 2H, CH_2), 3.19 (dd, *J* 16.3 and 5.0 Hz, 1H, CH_2), 3.95–4.25 (m, 1H, CHN), 5.07 (d, *J* 6.8 Hz, 1H, NH), 6.95–7.20 (m, 7H, H ar.), 7.23–7.45 (m, 2H, H ar.). ^{13}C NMR $\{^1H\}$ (50.323 MHz, $CDCl_3$), δ 27.2 (CH_2), 28.84 (CH_2), 35.86 (CH_2), 47.15 (CHN), 121.73 (2 CH ar.), 125.36 (CH ar.), 126.08 (CH ar.), 126.33 (CH ar.), 128.94 (CH ar.), 129.37 (2CH ar.), 129.58 (CH ar.), 134.00 (C quat. ar.), 135.46 (C quat. ar.), 151.09 (C quat. ar.), 154.11 (CO).

5.2.2. *N*-(1,2,3,4-Tetrahydronaphthalen-2-yl) methylcarbamate 9. ^1H NMR (200.130 MHz, $CDCl_3$), δ 1.60–1.85 (m, 1H, CH_2), 1.90–2.15 (m, 1H, CH_2), 2.63 (dd, *J* 16.1 and 8.0 Hz, 1H, CH_2), 2.86 (t, *J* 6.6 Hz, 2H, CH_2), 3.10 (dd, *J* 16.1 and 5.0 Hz, 1H, CH_2), 3.65 (s, 3H, OCH_3), 3.85–4.15 (m, 1H, CHN), 4.71 (broad s, 1H, NH), 6.90–7.20 (m, 4H, H ar.). ^{13}C NMR $\{^1H\}$ (50.323 MHz, $CDCl_3$), δ 27.32 (CH_2), 29.11 (CH_2), 36.05 (CH_2), 46.89 (CHN), 52.01 (OCH_3), 125.97 (CH ar.), 126.20 (CH ar.), 128.85 (CH ar.), 129.49 (CH ar.), 134.20 (C quat. ar.), 135.51 (C quat. ar.), 156.59 (CO). $[\alpha]_D^{20}=+37.0$ (*c* 0.010, CH_2Cl_2) (73% e.e.).

5.2.3. *N*-(1,2,3,4-Tetrahydronaphthalen-2-yl) ethylcarbamate 10. ^1H NMR (200.130 MHz, $CDCl_3$), δ 1.22 (t, *J* 7.1 Hz, 3H, CH_3), 1.60–1.90 (m, 1H, CH_2), 1.90–2.20 (m, 1H, CH_2), 2.63 (dd, *J* 16.3 and 8.2 Hz, 1H, CH_2), 2.86 (t, *J* 6.6 Hz, 2H, CH_2), 3.10 (dd, *J* 16.3 and 5.2 Hz, 1H, CH_2), 3.80–4.30 (m, 3H, OCH_2+CHN), 4.75 (broad s, 1H, NH), 6.90–7.20 (m, 4H, H ar.). ^{13}C NMR $\{^1H\}$ (50.323 MHz, $CDCl_3$), δ 14.70 (CH_3), 27.17 (CH_2), 29.03 (CH_2), 36.08 (CH_2), 46.66 (CHN), 60.73 (OCH_2), 125.96 (CH ar.), 126.19 (CH ar.), 128.86 (CH ar.), 129.52 (CH ar.), 134.16 (C quat. ar.), 135.52 (C quat. ar.), 156.12 (CO). $[\alpha]_D^{20}=+49.4$ (*c* 0.011, CH_2Cl_2) (76% e.e.).

5.2.4. *N*-(1,2,3,4-Tetrahydronaphthalen-2-yl) butylcarbamate 11. ^1H NMR (200.130 MHz, $CDCl_3$), δ 0.93 (t, *J* 7.1 Hz, 3H, CH_3), 1.20–1.47 (m, 2H, CH_2), 1.47–1.65 (m, 2H, CH_2), 1.65–1.90 (m, 1H, CH_2), 1.95–2.20 (m, 1H, CH_2), 2.64 (dd, *J* 16.3 and 8.3 Hz, 1H, CH_2), 2.87 (t, *J* 6.6 Hz, 2H, CH_2), 3.10 (dd, *J* 16.3 and 5.1 Hz, 1H, CH_2), 3.80–4.20 (m, 3H, OCH_2+CHN), 4.91 (broad s, 1H, NH), 6.90–7.20 (m, 4H, H ar.). ^{13}C NMR $\{^1H\}$ (50.323 MHz, $CDCl_3$), δ 13.86 (CH_3), 19.20 (CH_2), 27.32 (CH_2), 29.11 (CH_2), 31.20 (CH_2), 36.06 (CH_2), 46.75 (CHN), 64.68 (OCH_2), 125.96 (CH ar.), 126.18 (CH ar.), 128.86 (CH ar.), 129.50 (CH ar.), 134.25 (C quat. ar.), 135.54 (C quat. ar.), 156.32 (CO). $[\alpha]_D^{20}=+25.0$ (*c* 0.011, CH_2Cl_2) (76% e.e.).

5.2.5. *N*-(1,2 3,4-Tetrahydronaphthalen-2-yl) isobutylcarbamate 12. ^1H NMR (200.130 MHz, $CDCl_3$), δ 0.91 (d, *J* 6.7 Hz, 6H, $2CH_3$), 1.60–1.95 (m, 2H, 1H CH_2+CH), 1.95–2.20 (m, 1H, CH_2), 2.63 (dd, *J* 16.5 and 8.2 Hz, 1H, CH_2), 2.87 (t, *J* 6.6 Hz, 2H, CH_2), 3.11 (dd, *J* 16.5 and 5.0 Hz, 1H, CH_2), 3.83 (d, *J* 6.7 Hz, 2H, OCH_2), 3.87–4.15 (m, 1H, CHN), 4.73 (broad s, 1H, NH), 6.90–7.20 (m, 4H, H ar.). ^{13}C NMR $\{^1H\}$ (50.323 MHz, $CDCl_3$), δ 19.16 ($2CH_3$), 27.22 (CH_2), 28.09 (CH), 29.05 (CH_2), 36.08 (CH_2), 46.72 (CHN), 70.99 (OCH_2), 125.96 (CH ar.), 126.19 (CH ar.), 128.87 (CH ar.), 129.52 (CH ar.), 134.19 (C quat. ar.), 135.54 (C quat. ar.), 156.31 (CO). $[\alpha]_D^{20}=+30.1$ (*c* 0.011, CH_2Cl_2) (73% e.e.).

5.2.6. *N*-(1,2,3,4-Tetrahydronaphthalen-2-yl) *tert*-butylcarbamate 13. ^1H NMR (200.130 MHz, $CDCl_3$), δ 1.43 (s, 9H), 1.60–1.85 (m, 1H, CH_2), 1.90–2.15 (m, 1H, CH_2), 2.64 (dd, *J* 16.2 and 8.0 Hz, 1H, CH_2), 2.86 (t, *J* 6.6 Hz, 2H, CH_2), 3.11 (dd, *J* 16.2 and 5.0 Hz, 1H, CH_2), 3.85–4.15 (m, 1H, CHN), 4.72 (s broad, 1H, NH), 6.90–7.20 (m, 4H, H ar.).

5.3. General procedure for carbamate deprotection

To a solution of *tert*-butylcarbamate **13** (1 equiv.) in dichloromethane was slowly added trifluoroacetic acid (10 equiv.) and the reaction mixture was stirred at room temperature for 1.5 h. It was then evaporated to dryness under vacuum. The residue was dissolved in dichloromethane and 1N HCl was then added. The biphasic mixture was vigorously stirred for 45 min. The aqueous phase was then evaporated to dryness to afford (1,2,3,4-tetrahydronaphthalen-2-yl)-amine chlorhydrate **14** as a white solid in 90% yield.

5.3.1. (1,2,3,4-Tetrahydronaphthalen-2-yl)-amine chlorhydrate 14. ^1H NMR (200.130 MHz, D_2O), δ 1.60–1.90 (m, 1H, CH_2), 1.95–2.15 (m, 1H, CH_2), 2.60–2.90 (m, 3H, 1H CH_2+CH_2), 3.09 (dd, *J* 16.1 and 5.2 Hz, 1H, CH_2), 3.40–3.65 (m, 1H, CHN), 7.10 (s, 4H, H ar.). ^{13}C NMR $\{^1H\}$ (50.323 MHz, D_2O), δ 26.42 (CH_2), 26.63 (CH_2), 32.79 (CH_2), 47.44 (CHN), 126.30 (CH ar.), 126.74 (CH ar.), 128.80 (CH ar.), 129.26 (CH ar.), 132.25 (C quat. ar.), 134.95 (C quat. ar.).

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