Enantioselective hydrogenation in the presence of the rhodium(I) complex with (+)-4*S*,5*S*-N^4,N^4,N^5,N^5,2,2-hexamethyl-1,3-dioxolane-4,5-dimethaneamine

L. O. Nindakova, B. A. Shainyan, and A. I. Albanov*

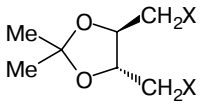
A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 39 6046. E-mail: bagrat@irioch.irk.ru

Hydrogenation of α-acetamidocinnamic and itaconic acids and their esters was carried out in the presence of the cationic Rh^I triflate complex with (+)-4*S*,5*S*-N^4,N^4,N^5,N^5,2,2-hexamethyl-1,3-dioxolane-4,5-dimethaneamine (DIODMA). The optical yields depended on the nature of the solvent and the hydrogen pressure and reached 30%. The catalytically active forms of the complexes and their transformations in the presence of phosphines, molecular hydrogen, and the substrate were studied by ^1H and ^{31}P NMR spectroscopy.

Key words: metal complex catalysis, rhodium complexes, chiral diamine ligands, enantioselective hydrogenation.

Recently, nitrogen- and oxygen-containing chelate ligands, which are more resistant to oxidation and destruction compared to mono- and diphosphine ligands, have attracted growing interest of researchers concerned with metal complex catalysis. Thus, optically active phenanthroline derivatives, amino alcohols, and, particularly, C_2-symmetrical *N*,*N*-alkyldiamines, which are used as modifying ligands in transition metal complexes, proved to be very efficient in enantioselective reduction of ketones.[1—3]

Nitrogen-containing analogs of (±)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP), *viz.*, optically active diamines of type **1** (X = NH_2 or NR_2), were described in the literature. The latter are used as ligands in chiral catalysts for the preparation of polymers, which are characterized by a high degree of helicity,[4] and in platinum(II) complexes possessing antitumor properties.[5,6]

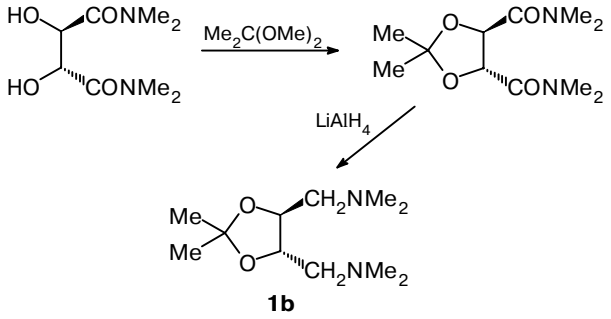


1a,b

X = NH_2 (**a**), NMe_2 (**b**)

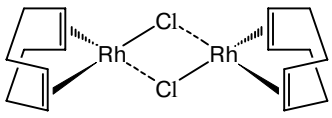
In the present study, we examined hydrogenation of α-acetamidocinnamic and itaconic acids and their esters in the presence of the cationic Rh^I triflate complex with the nitrogen analog of DIOP, *viz.*, with (+)-4*S*,5*S*-N^4,N^4,N^5,N^5,2,2-hexamethyl-1,3-dioxolane-4,5-dimethylamine (DIODMA, **1b**), established the structures of catalytically active forms of the complex, and investigated their transformations. Compound **1b** was prepared by cyclization of diamide of (+)-*R*,*R*-tartaric acid with 2,2-dimethoxypropane followed by reduction with lithium aluminum hydride.[7]

In the presence of DIODMA, the dimeric bis(cyclooctadiene)rhodium dichloride complex $[(1,5\text{-COD})RhCl]_2$



1b

(**2**) (COD is cyclooctadiene) exhibits no catalytic activity in hydrogenation of α-acetamidocinnamic acid (α-AACA) under mild conditions. According to the ^1H NMR spectral data, DIODMA is inert in the ligand exchange reaction with complex **2**. No noticeable shifts of the signals of the coordinated cyclooctadiene in **2** were observed upon the addition of DIODMA to a solution of the complex in deuterobenzene. In this case, the diamine is presumably a weaker nucleophile with respect to soft Rh^+ acid compared to triphenylphosphine, which cleaves the chloride bridge in dimer **2**, and, hence, the former



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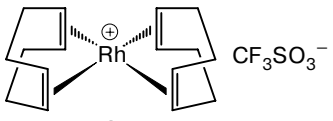

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Table 1. Hydrogenation of prochiral substrates[a] in the presence of the $[(1,5\text{-COD})_2Rh]^+CF_3SO_3^-$ complex (**3**) with (+)-*S*,*S*-DIODMA

Entry	Substrate[b]	Substrate/Rh ratio	*T*/°C	DIODMA/Rh ratio	Arene	Time /h	Degree of conversion (%)	Optical yield (%) (configuration)
1	α-AACA	50	40	1	Benzene	12	Traces	—
2	α-AACA	40	40	1	Benzene	72	30.2	10.5 (*S*)
3	α-AACA	20	20	2	Benzene	24[c]	51.2	14.4 (*S*)
4	α-AACA	40	20	2	Benzene	1[d]	100	6.3 (*S*)
5	α-AACA	40	40	1	*p*-Xylene	72	21.3	12.8 (*S*)
6	α-AACA	40	40	1	Mesitylene	72	11.5	29.9 (*S*)
7[e]	α-AACA	50	40	2	Benzene	24	15.3	30.0 (*S*)
8[f]	MSA	40	40	1	Benzene	48	73.0	17.4 (*R*)
9[g]	α-AACA	40	20	1	Benzene	4	100	48.2 (*R*)

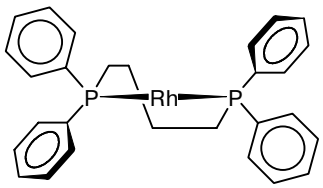
[a] Conditions: a 1 : 2 arene—MeOH mixture as the solvent; $c_{Rh} = (1—2) \cdot 10^{-3}$ mol L^{-1}; $p_{H_2} = 1$ atm.
[b] α-AACA is α-acetamidocinnamic acid, MSA is methylsuccinic acid.
[c] $r_{spec} = 0.04$ mol H_2/(g-at. Rh).
[d] After 1 h, the reaction mixture was transferred into an autoclave, $p_{H_2} = 35$ atm.
[e] The complex $[Rh(DIODMA)_2]^+CF_3SO_3^-$ was used as the catalyst.
[f] One equivalent of PPh_3 was added.
[g] One equivalent of DIOP was added.

compound cannot be involved in the ligand exchange reaction, which should proceed by the association S_N2 mechanism in the case of an unsaturated 16-electron rhodium complex.

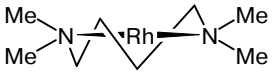
Unlike covalently bound chloride complex **2**, which we have prepared previously,[8] the cationic triflate rhodium complex $[(1,5\text{-COD})_2Rh]^+CF_3SO_3^-$ (**3**) in the presence of DIODMA is active in hydrogenation with molecular hydrogen. The results of hydrogenation of selected prochiral substrates in the presence of complex **3** with DIODMA are given in Table 1.

Under mild conditions, the catalyst is moderately active in hydrogenation of α-acetamidocinnamic and itaconic (methylsuccinic) acids. The optical yield of *N*-(+)-*S*-acetylphenylalanine increased as the diamine/Rh ratio was increased from 1 to 2, the degree of conversion of the substrate being also increased. The initial specific rate of hydrogenation was 0.04 mol H_2/(g-at. Rh h) (Table 1, entries *2* and *3*). When the nature of the arene component of the medium was changed (from benzene to mesitylene), hydrogenation slowed down so that the error of the measurement of the rate of H_2 absorption was sharply increased; however, the optical yield of the product in mesitylene reached 30% (entry *6*).

In all cases, except for hydrogenation in the presence of DIOP (entry *9*), (+)-*S*-*N*-acetylphenylalanine was formed as the major product in contrast to hydrogenation in the presence of the diphosphine complex $[(1,5\text{-COD})Rh\text{-}(-)\text{-}R,R\text{-DIOP}]^+CF_3SO_3^-$, which afforded (−)-*R*-*N*-acetylphenylalanine in high optical yield.[8] In our opinion, this is attributable to the difference in the conformation of the rhodium complexes with DIOP and DIODMA. The model MM2 calculations demonstrated that the diphosphine and diamine complexes adopt different conformations, *viz.*, a *twist*-boat and a chair, respectively (according to the nomenclature proposed in Ref. 9). Previously, it has been demonstrated (see Refs. 9—12 and references cited therein) that the enantioselectivity of the process is determined by the helicity of the chiral ligand, the chair conformation resulting in the formation of the *S* enantiomer of the hydrogenation product, whereas the *twist*-boat conformation giving rise to the *R* enantiomer. Our results agree well with this rule. The diphosphine exhibits higher enantioselectivity due to the fact that the helically oriented bulky diphenylphosphine groups are located closer to the reaction center.



(*M*)-*TB*



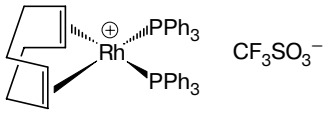
(*P*)-*C*

It was of interest to elucidate the nature of the complex responsible for the catalytic activity in hydrogenation. For this purpose, we studied the reaction of complex **3** with two equivalents of (+)-*S*,*S*-DIODMA in acetone and isolated the resulting complex. The latter was characterized by ^1H and ^{13}C NMR spectroscopy as a planar-square Rh^I bis-diamine complex, which does not contain the cyclooctadiene molecule in the coordination sphere and corresponds to the molecular formula $[Rh(DIODMA)_2]^+CF_3SO_3^-$ (**4**). Hydrogenation of

α-AACA with the use of this complex proceeded in 15% yield to give the (+)-*S* enantiomer of the product in 30% optical yield (entry *7*).

Under mild conditions, itaconic acid did not undergo hydrogenation in the presence of cationic complex **3** and DIODMA during 3 h. The highest degree of conversion was observed upon hydrogenation of this substrate in the presence of PPh_3. The latter was added for the purpose of stabilizing the catalyst, which is characterized by gradual reduction of Rh^I to Rh^0 and precipitation of rhodium metal. The optical yield of (+)-*R*-α-methylsuccinic acid was 17% (entry *8*). The composition of the precursor of the active catalyst in hydrogenation of itaconic acid was established by ^1H and ^{31}P NMR spectroscopy. The parameters of the ^1H NMR spectra of the corresponding complexes in acetone-d_6 are given in Table 2.

After the addition of one equivalent of PPh_3, the color of the solution of complex **3** in acetone-d_6 changed from red-orange to bright-orange and the signals of the coordinated cyclooctadiene ligand were shifted downfield ($\Delta\delta_{CH}$ 0.54, $\Delta\delta_{CH_A}$ 0.08, $\Delta\delta_{CH_B}$ 0.51), which indicates that the dative π-binding of the diene with the metal atom was weakened due to coordination of the phosphine ligand. The chemical shifts for the methine protons (δ_{CH}) lie between those of the corresponding signals in the spectra of complex **3** and free cyclooctadiene (δ_{CH} 5.50, δ_{CH_2} 2.32), whereas the positions of the signals for the methylene protons come closer together, which reflects an increase in the conformational lability of the diene molecule. Simultaneously, an intense doublet at δ 25.6 with the direct spin-spin coupling constant with the rhodium atom $^1J_{P-Rh}$ = 144.8 Hz appears in the ^{31}P NMR spectrum, *i.e.*, PPh_3 is coordinated to the central atom. The ratio of the integral intensities of the signals for the cyclooctadiene molecule and the aromatic protons (2 : 5) and the presence of only one doublet in the ^{31}P NMR spectrum are indicative of the probable planar-square structure of the resulting complex **5**.



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The ^{31}P NMR spectral characteristics of the phosphine complex remained virtually unchanged after the addition of one equivalent of chiral diamine **1b** (δ 25.6, $^1J_{P-Rh}$ = 145.5 Hz) with the only difference that a signal of triphenylphosphine oxide appeared at δ 24.6 near the doublet, the intensity of the new signal being approximately 8—10% of the intensity of the doublet.

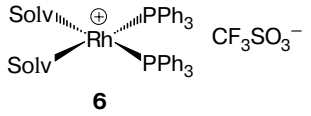
After treatment of this mixture with molecular hydrogen for 10 min, the ^1H signals belonging to DIODMA were shifted downfield ($\Delta\delta_{CH}$ 0.06, $\Delta\delta_{CH_A}$ 0.12, $\Delta\delta_{CH_B}$ 0.10, $\Delta\delta_{CH_3N}$ 0.11, and $\Delta\delta_{CH_3C}$ −0.01). In addition, signals of free diene and cyclooctane, which is the hydrogenation product of the diene, appeared in the ^1H NMR spectrum. The signals of rhodium hydrides were not observed at high field. In the ^{31}P NMR spectrum, a doublet signal at δ 26.89 with the constant $^1J_{P-Rh}$ = 145.53 Hz persisted and two doublets with approximately equal intensities appeared at δ 43.15 ($^1J_{P-Rh}$ = 202.0 Hz) and δ 55.88 ($^1J_{P-Rh}$ = 201.2 Hz). Since the

Table 2. Parameters of the ^1H NMR spectra of the rhodium complexes in acetone-d_6 (δ, *J*/Hz)

Complex	CH	CH_A in CH_2	CH_B in CH_2	NCH_3	CCH_3
3	4.16 (COD)	2.50 (COD)	1.77 (COD)		
3 + PPh_3	4.70 (COD)	2.58 (COD)	2.28 (COD)		
3 + PPh_3 + DIODMA	4.68 (COD)	2.53 (COD)	2.29 (COD)		
	3.82 (DIODMA)	2.53 (DIODMA), J_{AC} = 3.65, J_{AB} = 12.9	2.42 (DIODMA), J_{BC} = 5.48	2.23	1.32
3 + PPh_3 + DIODMA + H_2	5.50 (COD_{free})	2.32 (COD_{free})[a]	2.32 (COD_{free})[a]		
	4.70 (COD_{bound})	2.53 (COD_{bound})[b]	2.29 (COD)[a]		
	3.88 (DIODMA)	2.65 (DIODMA), J_{AC} = 4.03, J_{AB} = 12.9	2.52 (DIODMA), J_{BC} = 5.48	2.32	1.31
3 + PPh_3 + DIODMA + + H_2 + 3 MSA[c]	4.21 (DIODMA)	3.37 (DIODMA)	3.12 (DIODMA)	2.79	1.38
	5.85 (MSA)[d]	5.37 (MSA)[e]	3.14 (CH_2, MSA)		
DIODMA	3.80	2.52, J_{AC} = 3.65, J_{AB} = 12.9	2.37, J_{BC} = 5.48	2.21	1.29
MSA	6.26,[d] 5.78[e]	3.33 (CH_2)			

[a] The signal is overlapped with an intense signal of NCH_3 of DIODMA.
[b] The signal is overlapped with a signal for H_B of DIODMA.
[c] MSA is methylsuccinic (itaconic) acid.
[d] The vinylic proton in the *cis* position with respect to the CH_2 group.
[e] The vinylic proton in the *trans* position with respect to the CH_2 group.

^{1}H NMR spectral data provide evidence that the diene molecule coordinated to Rh^I is hydrogenated and released from the coordination sphere, the doublets with the large spin-spin coupling constants of ~200 Hz are, apparently, attributable to the generation of complexes **6** and **7** from complex **5**. An increase of the constants $^1J_{P-Rh}$ to ~200 Hz has been observed previously[13–16] upon the formation of tetrafluoroborate and perchlorate diphosphine solvate rhodium complexes of type **6** [13,14] and of diphosphine diamine complexes of type **7**.[14–16] A comparison of the ^{31}P chemical shifts for the acetone triethylamine (δ 43.53 and 53.90) and bis-triethylamine (δ 51.60) diphosphine rhodium complexes[14] made it possible to assign the high-field signal at δ 43.15 and the low-field signal at δ 55.88 to diacetone complex **6** and complex **7**, respectively.



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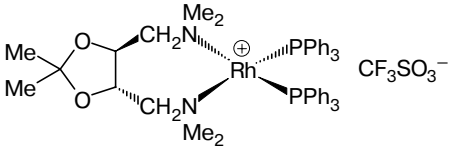

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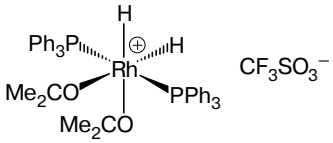

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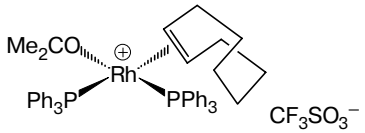

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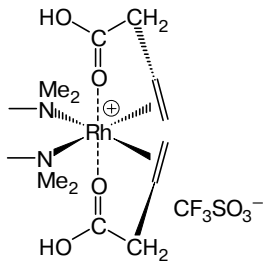
The formation of complex **7** was observed only upon treatment of complex **5** with hydrogen in the presence of diamine. After hydrogenation of complex **5** in the absence of DIODMA, the ^{31}P NMR spectrum had a doublet at δ 45.30 ($^1J_{P-Rh}$ = 118.1 Hz) and a doublet of doublets at δ 39.91 ($^1J_{P-Rh}$ = 114.0 Hz and $^2J_{P-P}$ = 18.2 Hz); the intensity of the latter signal was an order of magnitude lower than that of the doublet. According to the data published in the literature,[13] the low-field doublet (δ 45.3) belongs to dihydride solvate complex **8**, which has the low constant $^1J_{P-Rh}$ due to the *trans* effect of the triphenylphosphine groups. A monodentate complex of type **9** was assumed[13] as a precursor of dihydride complex **8**; however, no evidence for the formation of complex **9** was obtained. The signal at δ 39.91 with the nonequivalent phosphorus nuclei detected by us can be considered as the supporting evidence for the scheme of transformations proposed previously.[13]

After the addition of three equivalents of itaconic acid and additional treatment with hydrogen, the signals of the coordinated diamine molecule in the ^{1}H NMR spectrum were further shifted downfield ($\Delta\delta_{CH}$ 0.39, $\Delta\delta_{CH_A}$ 0.84, $\Delta\delta_{CH_B}$ 0.72, $\Delta\delta_{CH_3N}$ 0.56, and $\Delta\delta_{CH_3C}$ 0.06), whereas the signals of itaconic acid, on the contrary, were shifted upfield ($\Delta\delta_{=CH_A}$ −0.41, $\Delta\delta_{=CH_B}$ −0.41, and $\Delta\delta_{CH_2}$ −0.19); signals for the protons of cyclooctane and diene were also observed. In the ^{31}P NMR spectrum, the signals of complexes **6** and **7** disappeared; a low-intensity doublet of complex **5** and a signal of free phosphine oxide (both at δ ~28) persisted. The signals of the rhodium hydride and alkyl hydride complexes were absent. The equivalence of two $CH-CH_2$ fragments in DIODMA and the ratio of the integral intensities of the signals of itaconic acid and DIODMA are indicative of the possible formation of symmetrical complex **10**.



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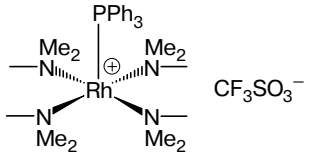

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Therefore, treatment of achiral complex **5** with H_2 in the presence of DIODMA afforded achiral complex **6** and the chiral complex $[Rh(S,S\text{-DIODMA})(PPh_3)_2]^+CF_3SO_3^-$ (**7**), complex **6** being, apparently, a precursor of complex **7**. The chiral diamine molecule was retained in the coordination sphere of olefin complex **10** and was responsible for enantioselectivity of the process, *i.e.*, for the formation of an excess of (+)-*R*-α-methylsuccinic acid upon hydrogenation of itaconic acid.

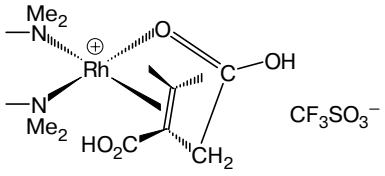
In the presence of two equivalents of DIODMA, complex **11** can be formed. The latter was obtained in the reaction of complex **4** with one equivalent of PPh_3. In the ^{1}H NMR spectrum, the positions of signals of the coordinated diamine molecule differ only slightly from the positions of the corresponding signals in the spectrum of complex **4**; the signals for the protons of the CH_2 groups are somewhat shifted and coalesce into one multiplet. In the ^{31}P NMR spectrum, a signal of phosphine oxide at δ 31.93 and a doublet at δ 25.97 ($^1J_{P-Rh}$ = 144.6 Hz) appear. The latter doublet indicates that the triphenylphosphine ligand is coordinated to the Rh^I atom. Hence, the use of individual diamine rhodium complexes **4** and **11** should be more efficient in enantioselective hydrogenation compared to the complexes generated *in situ*. The reason is that complexes **4** and **11** reduce the possibility of the presence of achiral rhodium complexes in the reaction mixture (the latter complexes can also exhibit catalytic activity with respect to the substrates thus decreasing the optical yields of the products).

Table 3. Parameters of the ^{1}H NMR spectra of the diamine rhodium complexes in methanol-d_4 (δ, *J*/Hz)

Complex	CH	CH_A in CH_2	CH_B in CH_2	NCH_3	CCH_3
4	3.90	2.87, J_{AC} = 12.9	2.79, J_{BC} = 6.59, J_{AB} = 13.0	2.47	1.38
11 (**4** + PPh_3)	3.88	2.70—2.78	2.70—2.78	2.45	1.39
12 (**4** + MSA)	6.14[a]	3.38 (DIODMA),	3.23 (CH_2 in MSA)		
	5.61[b]	J_{AB} = 13.2	3.27 (DIODMA)	2.87	1.47
	4.18 (DIODMA)				
DIODMA	3.78	2.55, J_{AC} = 2.0, J_{AB} = 13.1	2.46, J_{BC} = 7.7	2.29	1.36

[a] The vinylic proton in the *cis* position with respect to the CH_2 group.
[b] The vinylic proton in the *trans* position with respect to the CH_2 group.

As a result of the reaction of two equivalents of itaconic acid with bis-diamine complex **4** in methanol, the signals of the coordinated diamine molecule were shifted downfield compared to those of the starting complex **4** ($\Delta\delta_{CH}$ 0.28, $\Delta\delta_{CH_A}$ 0.51, $\Delta\delta_{CH_B}$ 0.48, $\Delta\delta_{CH_3N}$ 0.40, and $\Delta\delta_{CH_3C}$ 0.09) and the signals of itaconic acid were shifted upfield ($\Delta\delta_{CH_A}$ −0.12, $\Delta\delta_{CH_B}$ −0.17, and $\Delta\delta_{CH}$ −0.10) (Table 3), which is indicative of the formation of an olefin complex. We assumed that the latter has structure **12**.



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Previously, we have reported[8] that hydrogenation of α-AACA on the cationic triflate complex $[(1,5\text{-COD})Rh\text{-}(-)\text{-DIOP}]^+CF_3SO_3^-$ afforded the (−)-*R* enantiomer of *N*-acetylphenylalanine with *ee* higher than 90%. The addition of one equivalent of (+)-*S*,*S*-DIODMA to the diphosphine complex resulted in a slight decrease in the rate of hydrogenation of α-AACA and in a substantial decrease in the optical yield of (−)-*R*-*N*-acetylphenylalanine (see Table 1, entry *9*), which is attributable to the fact that (−)-DIOP and (+)-*S*,*S*-DIODMA acting as ligands in the Rh^I complexes show opposite directions of asymmetric induction in hydrogenation of α-AACA (see above).

To enhance the degree of conversion of the substrates, we studied their hydrogenation in the presence of complex **3** with DIODMA and diamine complex **4** at high pressure. The results of the experiments are given in Table 4.

As can be seen from the data in Tables 1 and 4, not only the degrees of conversion but also the optical yields of the hydrogenation products of α-*N*-acetamidocinnamic and itaconic acids increased as the H_2 pressure was increased.

It can be noted that hydrogenation of the substrates at the hydrogen pressure of 1 atm prior to their hydrogenation in an autoclave resulted in a sharp decrease in the optical yields of the products (*cf.* entry *4* in Table 1

Table 4. Hydrogenation of the substrates on the diamine rhodium catalysts $[(1,5\text{-COD})_2Rh]^+CF_3SO_3^-$ (**3**) and $[Rh(DIODMA)_2]^+CF_3SO_3^-$ (**4**)[a]

Entry	Substrate	Substrate/Rh ratio	Catalyst	Time /h	Degree of conversion (%)	Optical yield (%) (configuration)
1	α-AACA	40	**3** + (+)-(*S*,*S*)-DIODMA	8	100	22.4 (*S*)
2	Methyl ether α-AACA	25	**3** + (+)-(*S*,*S*)-DIODMA	5	100	15.4 (*S*)
3	Methyl ether α-AACA	25	**3** + (+)-(*S*,*S*)-DIODMA	5[b]	100	4.3 (*S*)
4	MSA	50	**3** + (+)-(*S*,*S*)-DIODMA	8	100	28.0 (*R*)
5	α-AACA	40	**4**	8	100	20.3 (*S*)
6	MSA	50	**4**	8	100	20 (*R*)
7	MSA	50	**4** + PPh_3	6	100	14.2 (*R*)
8	Acetophenone	450	**4**	5	75	17.9 (*R*)

[a] Conditions: a 1 : 2 benzene—MeOH mixture as the solvent; $c_{Rh} = (1—2) \cdot 10^{-3}$ mol L^{-1}; p_{H2} = 35 atm; *T* = 20 °C, (+)-*S*,*S*-DIODMA/Rh = 2.
[b] The process was preceded by hydrogenation at 1 atm for 1 h.

and entry *3* in Table 4). Apparently, this is associated with the fact that in the absence of coordination of the hydrogen molecule to the metal atom (p_{H_2} = 1 atm), the diamine ligand is displaced from the coordination sphere by the substrate molecules and subsequent hydrogenation occurs at high pressure (p_{H_2} = 35 atm) in the presence of the resulting achiral rhodium complexes.

The results of multinuclear NMR spectroscopy demonstrated that olefin is coordinated to complex **4** (or **11**) giving rise to olefin intermediates of type **10** (or **12**) in the absence of hydrogen and also, apparently, at the H_2 pressure of ~1 atm. Taking into account this fact and the absence of signals of rhodium hydrides upon treatment of complex **4** with hydrogen, the substrate mechanism of hydrogenation on the bis-amine complex under study can be proposed. The optical yield of (+)-*R*-α-methylsuccinic acid increased and the optical yield of (+)-*S*-*N*-acetylphenylalanine slightly decreased as the H_2 pressure was increased, which may be associated with the decrease in the difference between the rates of hydrogenation of diastereomeric olefin intermediates. By varying substituents at the N atom in the ligands of **1**, the mechanism of hydrogenation on diamine rhodium complexes can be investigated in more detail.

Experimental

The IR spectra were recorded on an IKS-29 instrument in a thin layer. The ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were measured on a Bruker DPX 400 spectrometer (400, 100, 376, and 162 MHz, respectively) for solutions in acetone-d_6 with HMDS as the internal standard. The chemical shifts are given relative to Me_4Si. The GLC analyses were carried out on an LKhM-80 chromatograph equipped with a 1 m×3-mm column packed with 5% SE-30 on Chromaton N-AW-DMCS (a thermal conductivity detector; helium as the carrier gas). The degrees of conversion of the substrates were determined by GLC. The specific optical rotation was measured on a Polamat A instrument at 546 nm and was scaled to the wavelength of 589 nm using the coefficient of 1.17543.

(4*R*,5*R*)-*N*^{4},*N*^{4},*N*^{5},*N*^{5},2,2-Hexamethyl-1,3-dioxolane-4,5-dicarboxamide was prepared according to a procedure described previously.[7] M.p. 82 °C (*cf.* lit. data[6]: 83—84 °C). ^1H NMR, δ: 1.44 (s, 6 H, Me_2C); 2.95 and 3.16 (both s, 6 H, NMe_2); 5.22 (s, 2 H, CH) [*cf.* lit. data[7]: (CCl_4): 1.38, 2.92, 3.16, 5.09 (all s)].

(+)-4*S*,5*S*-*N*^{4},*N*^{4},*N*^{5},*N*^{5},2,2-Hexamethyl-1,3-dioxolane-4,5-dimethaneamine (1b) was prepared according to a procedure described previously.[7] B.p. 41 °C (1 Torr) (*cf.* lit. data[7]: 54 °C (0.8 Torr)). ^1H NMR ($CDCl_3$), δ: 1.39 (s, 6 H, Me_2C); 2.28 (s, 12 H, NMe_2); 2.38 (d, 2 H, H_A in CH_2); 2.50 (dd, 2 H, H_B in CH_2, $^2J_{H_AH_B}$ = 12.6 Hz, $^3J_{HH}$ = 6.8 Hz); 3.77 (m, 2 H, CH); in C_6D_6: 1.35 (s, 6 H, Me_2C); 2.13 (s, 12 H, NMe_2); 2.37 (d, 2 H, H_A in CH_2, $^3J_{HH}$ = 5.67 Hz); 2.47 (dd, 2 H, H_B in CH_2, $^2J_{H_AH_B}$ = 12.9 Hz, $^3J_{HH}$ = 3.47 Hz); 3.91 (m, 2 H, CH); in acetone-d_6: 1.29 (s, 6 H, Me_2C); 2.21 (s, 12 H, NMe_2); 2.37 (d, 2 H, H_A in CH_2, $^3J_{HH}$ = 6.03 Hz); 2.52 (dd, 2 H, H_B in CH_2, $^2J_{H_AH_B}$ = 13.0 Hz, $^3J_{HH}$ = 3.64 Hz); 3.80 (m, 2 H, CH); *cf.* lit. data[7]: (in CCl_4): 1.32 s, 3.34* m, 3.50 m, 3.85 m. ^{13}C NMR (acetone-d_6), δ: 27.66 ($C\underline{C}H_3$); 46.74 (NCH_3); 62.77 (CH_2); 79.63 (CH); 109.11 ($\underline{C}CH_3$).

Complex [Rh(*S*,*S*-DIODMA)$_2$]$^+$CF$_3$SO$_3^-$. The reagent CF_3SO_3Ag (25.7 mg, 0.1 mmol) was added to a mixture of $[(1,5\text{-COD})RhCl]_2$ (0.05 mmol) and cyclooctadiene (0.1 mmol) in degassed acetone (50 mL). The flocculent AgCl precipitate that formed was filtered off and then *S*,*S*-DIODMA (1.2 equiv., 27.6 mg, 0.127 mmol) in acetone (3 mL) was added portionwise to the yellow solution of $[Rh(COD)_2]^+CF_3SO_3^-$. The resulting solution was concentrated to the volume of 3 mL. The complex was precipitated with diethyl ether, successively washed with diethyl ether and hexane, dried *in vacuo*, and sealed in tubes. The yield was 0.04 g (60% with respect to the theoretical value); m.p. 128—132 °C. ^1H NMR, δ: in a CD_3OD—C_6D_6 mixture: 1.38 (s, 6 H, Me_2C); 2.47 (s, 12 H, NMe_2); 2.79 (dd, 2 H, H_A in CH_2, $^3J_{HH}$ = 6.59 Hz, $^2J_{H_AH_B}$ = 13.2 Hz); 2.88 (d, 2 H, H_B in CH_2, $^2J_{H_AH_B}$ = 13.1 Hz); 3.90 (m, 2 H, CH); in acetone-d_6: 1.36 (s, 6 H, Me_2C); 2.68 (s, 12 H, NMe_2); 2.75 (m, 4 H, CH_2); 3.89 (m, 2 H, CH). ^{13}C NMR, δ: in acetone-d_6: 27.23 ($C\underline{C}H_3$); 45.68 (NCH_3); 60.60 (CH_2); 77.90 (CH); in a CD_3OD—C_6D_6 mixture: 27.23 ($C\underline{C}H_3$); 45.19 (NCH_3); 60.93 (CH_2); 77.20 (CH); 111.85 ($\underline{C}CH_3$). ^{19}F NMR (CD_3OD), δ: 76.99.

Hydrogenation of itaconic and α-acetylaminocinnamic acids and their esters. ***A.*** In a swinging flask. Hydrogenation was carried out with intense stirring in a glass temperature-controlled swinging flask connected with a manometer and a system for supplying hydrogen. The gas was purified and dried according to a standard procedure. Methanol (5 mL) and the substrate (~1 mmol) were placed under a stream of hydrogen in a swinging flask mounted on a shaker and the pressure was raised to 1.2—1.4 atm. Then a solution of the individual complex or the catalyst (c_{Rh} = 2 mmol L^{-1}), which was prepared *in situ* in an individual vessel under an atmosphere of argon in a 2 : 1 mixture of methanol and benzene (5 mL), was added with a syringe and the mixture was stirred.

B. In an autoclave. The complex $[(1,5\text{-COD})_2Rh]^+CF_3SO_3^-$ (0.02 mmol) was placed in a vessel, which was purged with dry argon, and dissolved in a mixture of C_6H_6 (3 mL) and MeOH (7 mL). Then two fractions of (+)-*S*,*S*-DIODMA were added. The reaction mixture was stirred for 10 min, a weighed sample of the substrate (0.13—0.22 g) was added, the mixture was placed in a pre-evacuated autoclave, hydrogen was fed to the autoclave under high pressure, and the autoclave was mounted on a shaker. The treatment of the reaction mixture and isolation of the products were carried out as described above.[8]

The chemical yield of the hydrogenation product was determined based on the ratio of the integral intensities of the signals for the acetyl groups in the ^1H NMR spectra of the initial substrate and the hydrogenation product (for α-AACA and its ester) or of the signals for the protons of the $=CH_2$ groups in the initial substrate and of the CH_3 group in the hydrogenation product (for itaconic acid). For α-AACA: $\delta(CH_3CO)_{sat}$ 1.88, $\delta(CH_3CO)_{unsat}$ 2.08; for methyl ester of α-AACA: $\delta(CH_3CO)_{sat}$ 1.92, $\delta(CH_3CO)_{unsat}$ 2.12. For itaconic acid, $\delta(=CH_2)$ 6.27. For α-methylsuccinic acid, $\delta(CH_3)$ 1.19 (d).

* The value is obviously erroneous; apparently, δ 2.34.

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