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CHEMISTRY

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Supporting Information

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Unravelling the Reaction Path of Rhodium–MonoPhos-Catalysed Olefin Hydrogenation**

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Catalyst Precursors – NMR Data and Spectra

SI1 ^1H -NMR (400 MHz, CDCl_3 , 298 K) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{SbF}_6\}$ **8a**

SI2 ^{31}P -NMR (162 MHz, CDCl_3 , 298 K) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{SbF}_6\}$ **8a**

SI3 ^1H -NMR spectrum (400 MHz, CDCl_3 , 298 K) of $\{[\text{Rh}(\text{NBD})(R\text{-MonoPhos})_2]\text{BF}_4\}$ **8b**

SI4 ^{13}C -NMR spectrum (100 MHz, CDCl_3 , 298 K) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{BF}_4\}$ **8b**

SI5 ^{31}P -NMR spectrum (162 MHz, CDCl_3 , 298 K) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{BF}_4\}$ **8b**

{[Rh(NBD)(*R*)-MonoPhos₂]BF₄} **8b**

Table SI1 NMR data of complex **8b** in CD₂Cl₂

Proton signals A-4 and B-5 coincide, despite the clearly distinct coupling constants no exact value can be extracted. The assignment of carbon signals with * may be interchanged. Position A-3 approaches the olefinic proton at 6.01 ppm (positive NOE).

position	¹ H at 296 K	¹ H at 306 K	¹³ C at 306 K
A-1			123.23
A-2			147.88
A-3	7.06	7.07 (d, 8.6 Hz)	120.76
A-4	7.97	7.97 (d, <i>ca.</i> 9 Hz)	131.21
A-4a			132.19
A-5	8.10	8.10 (d, 8.3 Hz)	128.96
A-6	7.56	7.57 (ddd, 8.3/4.3/3.6 Hz)	126.49
A-7		7.32	127.36 *
A-8		7.32	127.44 *
A-8a			132.99
B-1			122.61
B-2			148.66
B-3	7.35	7.35 (d, 9.3 Hz)	120.76

B-4	8.03	8.04 (d, 8.9 Hz)	131.88
B-4a			132.0 ₅
B-5	7.97	7.97 (d, <i>ca.</i> 9 Hz)	129.03
B-6	7.49	7.49 (ddd, 8.1/6.0/2.0 Hz)	126.22
B-7	7.28	7.28	126.98
B-8		7.32	127.44 *
B-8a			132.77
NMe ₂	2.72	2.72 (“t”)	37.94 (“t”)
NBD, =CH	6.00	6.01	93.1
	5.21	5.21	96.5
NBD, CH	4.02	4.03	55.6
NBD, CH ₂	1.74	1.74	72.5

Table SI2 Chemical shifts δ /ppm of the “inorganic part” (297 K: spectrometer AV 400; 306 K: spectrometer AV 300, solvent dichloromethane)

position	$T = 297$ K	$T = 306$ K
F		−153.1 (¹¹ B isotopomer)
P	138.8	138.8
¹ <i>J</i> (Rh,P)	250 Hz	250 Hz
Rh [Ξ /MHz]	−268 [3.159154]

SI6 ¹H-NMR spectrum (400 MHz, CD₂Cl₂, 297 K) of {[Rh(NBD)(*R*)-MonoPhos₂]BF₄} **8b**

SI7 ³¹P-NMR spectrum (100 MHz, CD₂Cl₂, 297 K) of {[Rh(NBD)(*R*)-MonoPhos₂]BF₄} **8b**

SI8. 2D (^1H , ^{103}Rh) HMQC spectrum (400.1 MHz) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{BF}_4\}$ **8b**, in CD_2Cl_2 recorded at 297 K. The splitting of the signal along F_1 amounts to 250 Hz ($J_{\text{Rh,P}}$). The transfer delay was set to 250 ms (2 Hz coupling Rh,H).

SI9. 2D (^{31}P , $^{103}\text{Rh}\{^1\text{H}\}$) HMQC NMR spectrum (162.0 MHz) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{BF}_4\}$ **8b**, in CD_2Cl_2 recorded at 297 K.

The chemical shift $\delta(^{103}\text{Rh})$ is -268 ppm ($\Xi = 3.159154$ MHz).

SI10 ^1H -NMR (400 MHz, CDCl_3 , 298 K) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{PF}_6\}$ **8c**

SI11 ^{31}P -NMR (162 MHz, CDCl_3 , 298 K) of $\{[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{PF}_6\}$ **8c**

SI12 ^1H -NMR (400 MHz, CDCl_3 , 298 K) of $[\text{Rh}(\text{NBD})(R)\text{-MonoPhos}_2]\text{CF}_3\text{SO}_3$ **8d**

SI13 ^{31}P -NMR (162 MHz, CDCl_3 , 298 K) of $[\text{Rh}(\text{I})(\text{NBD})(R)\text{-MonoPhos}_2]\text{CF}_3\text{SO}_3$

{[Rh(*R*)-MonoPhos₄]BF₄} 9b

SI14 ¹H-NMR (300 MHz, CD₂Cl₂, 298 K) of **{[Rh(*R*)-MonoPhos₄]BF₄} 9b**

SI15 ^{31}P -NMR (121 MHz, CD_2Cl_2 , 298 K) of $\{[\text{Rh}(\text{R})\text{-MonoPhos}_4]\text{BF}_4\}$ 9b

Detection of Reaction Intermediates under Hydrogenation Conditions – NMR Data and Spectra

$[(\text{Rh}((\text{R})\mathbf{1a})_2)_2(\text{SbF}_6)_2 \mathbf{10}$

For this complex, four distinct naphthyl systems were identified by ^1H NMR (see **Table SI3**), the analysis was assisted by COSY and NOESY experiments. Although no complete assignment to molecular positions was achieved, it is evident that one of the naphthyl groups (D) differs from the others. This group is coordinated to the rhodium atom of the symmetry-related second part of the dinuclear complex. The signals due to this group, in particular those of the four-spin-system, 5-H to 8-H, exhibit detectable spin-spin-coupling to phosphorus (**SI17**) and rhodium (**SI18**). This is not the case for all other protons and brings us to the conclusion that coordination takes place from this six-membered ring.

Table SI3. Chemical shifts $\delta(^1\text{H})/\text{ppm}$ of the dinuclear complex **10** in CD_2Cl_2 . D represents the bridging naphthyl group.

naphthyl system	3-H	4-H	5-H	6-H	7-H	8-H
A	6.33	7.98	8.07	7.58	7.42	6.99
B	7.55	8.15	8.01	7.51	7.29	7.21
C	7.28	8.07	8.10	7.59	7.32	7.30
D	6.70	7.81	7.21	6.69	7.34	6.16

SI16 ^1H NMR spectra (400.1 MHz) of the dinuclear complex **10** in CD_2Cl_2 at ambient temperature. Labels indicate the resonances due to the bridging naphthyl group D. The signals due to the NMe_2 groups are not shown (2.63 ppm, d, $J_{\text{P,H}}$ 11 Hz; 2.38 ppm, d, $J_{\text{P,H}}$ 11 Hz; each of them represents 6 H).

SI17 2D (^1H , ^{103}Rh) HMQC (*left*) and (^1H , $^{103}\text{Rh}\{^{31}\text{P}\}$) HMQC (*right*) NMR spectra (400.1 MHz) of the dinuclear complex **10** in CD_2Cl_2 recorded at 297 K. The splitting of the signal along F_1 in the left, phosphorus-coupled spectrum amounts to 311 Hz (averaged value for $J_{\text{Rh,P}}$). The transfer delay was set to 250 ms (2 Hz coupling Rh,H) in both cases.

SI18 2D (^{31}P , $^{103}\text{Rh}\{^1\text{H}\}$) HMQC NMR spectrum (162.0 MHz) of the dinuclear complex **10** in CD_2Cl_2 recorded at 297 K.

The chemical shift $\delta(^{103}\text{Rh})$ is -620 ppm ($\Xi = 3.158041$ MHz).

[Rh ((*R*)-MonoPhos)₂(MAC)](SbF₆) **11-Maj + **11-min****

SI19. Normalized proportion of the substrate complex **11-min** as determined from temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (sum of **11-min** and **11-Maj** = 100). At higher temperatures, no quantification is possible because of strong line broadening.

SI20 Reaction of the dinuclear complex **10** with 1.2 MAC in dichloromethane- d_2 : Formation of the diastereomeric substrate complexes **11**. ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra (400.1 MHz) taken at 221 K, annotated the signals of the coordinated prochiral alkene (olefinic CH group). Tentative assignment: **11-Maj** 6.53 ppm; **11-min** 6.32 ppm. The signals at 5.98 and 4.76 ppm do correlate to carbon signals between 120 and 130 ppm, hence they do *not* represent coordinated arenes.

SI21. Reaction of the dinuclear complex **10** with 1.2 MAC in dichloromethane- d_2 : Formation of the diastereomeric substrate complexes **11**. 2D (^1H , ^{13}C) HMQC NMR spectrum (400.1 MHz) taken at 221 K, signals of the coordinated prochiral alkene (olefinic CH group). Tentative assignment: **11-Maj** 6.53 ppm; **11-min** 6.32 ppm.

[Rh((*R*)-MonoPhos)₂(*S*)-(MACH₂)](SbF₆) (*R,R*)(*S*)-12

Table SI4. Chemical shifts δ /ppm of the coordinated product at ambient temperature (quaternary C atoms were not detected)

group	¹ H, CD ₂ Cl ₂	¹ H, (CD ₂ Cl) ₂	¹³ C, (CD ₂ Cl) ₂
Methoxy	3.49	3.45	52.7
Acetyl	1.84	1.81	22.9
NH	5.88	5.82	
CH	4.33	4.26	53.2
CH ₂	2.35 1.94	2.25 1.84	36.4
<i>ortho</i> -Ph	6.69 6.12	6.65 6.08	107.1 103.4
<i>meta</i> -Ph	6.85 6.16	6.86 6.15	105.4 100.5
<i>para</i> -Ph	6.35	6.37	103.9

Chemical shifts δ /ppm of the RhP₂ core)

position	297 K, CD ₂ Cl ₂	297 K, (CD ₂ Cl) ₂	250 K, CD ₂ Cl ₂
P	145.9	145.9	145.9
¹ <i>J</i> (Rh,P)	308 Hz	308 Hz	308 Hz
Rh [Ξ/MHz]	−849 [3.157317]	−851 [3.157311]	−883 [3.157211]

Solutions for characterizing the product complex [Rh((*R*)-MonoPhos)₂((*S*)-MAC(H)₂)]SbF₆ ((*R,R*)(*S*)-12) were prepared by hydrogenating MAC **2a** and [Rh(I)((*R*)-MonoPhos)₂(NBD)]SbF₆ **8a** in either dichloromethane-*d*₂ or 1,2-dichloroethane-*d*₄ (molar ratio substrate:Rh = 1.2). The solutions were analyzed without further workup and thus contain also the hydrogenation product norbornane and further complexes that could not be characterized. From the proton NMR spectra it is evident that about half of the hydrogenation product is coordinated to the Rh((*R*)-MonoPhos)₂ core, whereas the ³¹P NMR spectra show only the resonance of **12** (SI22), the signals due to the remainder of the Rh complexes are not resolved. As the reaction proceeds with a high *ee* to the (*S*)-configured phenylalanine derivative, the resonances due to the diastereomeric complex of the (*R*)-configured product are not detected.

SI22 Hydrogenation of $\text{MAC}/[\text{Rh}(\text{I})((R)\text{-MonoPhos})_2(\text{NBD})]\text{SbF}_6$, molar ratio 1.2, in dichloromethane- d_2 . Sections of ^{31}P NMR spectra (taken after complete conversion) at two temperatures.

At ambient temperature, the ^1H NMR signals are rather broad, but sharpen a little upon cooling down the solution. The reason is the exchange between the η^6 -coordinated and the residual free reaction product in solution. This process is detectable by ^1H exchange spectroscopy (**SI23**, **SI24**, **SI25**). All ^1H resonances of the coordinated amino acid ester (and the connected ^{13}C signals by indirect detection) were identified, they are clearly shifted to lower frequencies as compared to the free product (*cf.* **Table SI4**). No attempt was made to analyze the signals due to the MonoPhos ligands.

SI23 Hydrogenation of $\text{MAC}/[\text{Rh}(\text{I})((R)\text{-MonoPhos})_2(\text{NBD})]\text{SbF}_6$, molar ratio 1.2, in dichloromethane- d_2 . Sections of ^1H NMR spectra (taken after complete conversion) at ambient temperature. *Left*: COSY-45 spectrum showing the five-spin system of the coordinated arene. The signals within the boxes are due to the dinuclear complex **10** (minute amounts, but sharp signals). *Right*: NOESY (mixing time 1.5 s, positive signals in black, negative signals in red) showing the exchange between free and η^6 -coordinated phenylalanine (arrows) as well as the two inequivalent *ortho* (and *meta*) positions in the arene complex effected by the reaction sequence dissociation-rotation-association.

SI24. Hydrogenation of MAC/[Rh(I)((*R*)-MonoPhos)₂(NBD)]SbF₆, molar ratio 1.2, in 1,2-dichloroethane-*d*₄. Sections of ¹H NMR spectra, aromatic region (taken after complete conversion) at ambient temperature. *Left*: NOESY (mixing time 0.3 s, positive signals in black, negative signals in red). *Right*: ROESY (mixing time 0.3 s, positive signals in black, negative signals in red). At that short mixing time, the signals for exchange between free and ⁶-coordinated phenylalanine dominate (arrows).

SI25. Hydrogenation of MAC/[Rh(I)((*R*)-MonoPhos)₂(NBD)]SbF₆, molar ratio 1.2, in 1,2-dichloroethane-*d*₄. Sections of ¹H NMR spectra, aliphatic region (taken after complete conversion) at ambient temperature. *Left*: NOESY (mixing time 0.3 s, positive signals in black, negative signals in red). *Right*: ROESY (mixing time 0.3 s, positive signals in black, negative signals in red). At that short mixing time, the signals for exchange between free and ⁶-coordinated phenylalanine dominate (arrows), but few cross peaks due to NOE show up (*cf.* the diastereotopic methylene group). Only the signals of the coordinated product are labelled.

Qualitative Compound Report

Instrument Name	ESI-TOF/MS	Date Filename	D:\MassHunter\Data\1010\10102208.d
Acq Method	HRMS Pos oS.m	Sample Name	EA 251
DA Method	HRMS.m	Position	Vial 41
User Name	Fischer	Comment	MeOH/0.1%HCOOH in H2O 90:10

Compound Table

Name	RT	Abund	Formula	Ion Mass	Ionization Mode
1	0.168	414425	C88H72N4O8P4Rh	1539.3356	Positive

MS Spectrum

MS Zoomed Spectrum

MS Spectrum Peak List

Ion	Abund	Formula	Calculated Mass	Measured Mass	Difference	Diff (ppm)
M*+	414425	C88 H72 N4 O8 P4 Rh	1539.335	1539.3391	4.08	2.65
M*+	414315	C88 H72 N4 O8 P4 Rh	1540.3383	1540.3425	4.17	2.71

--- End Of Report ---

SI26 HRMS spectrum of {[Rh(*R*)-MonoPhos₄]BF₄} 9b

ESI-MS analyses of [Rh(*R*)-MonoPhos₂(NBD)]X complexes **8** and corresponding intermediates under hydrogenation conditions.

Experimental conditions:

Mass spectrometric analyses were performed on LCQ Deca XP ion trap MS (ThermoFisher, Bremen, Germany)

Samples dissolved in dichloromethane were introduced with a syringe via direct infusion at 10 μ l/min.

Electrospray ionization(ESI) in positive ion mode was used to analyze the cations, and negative ion mode was used for the anions.

MS Conditions:

Full scan mode : (positive ion mode): mass range 150-2000 Dalton
(negative ion mode): mass range 60-300 Dalton
Scan time : 200 msec

Zoom scan mode: center mass 821, width 10 Dalton
Scan time: 50 msec

ESI source conditions:

Sheath gas 35
Aux/sweep gas 5
Spray voltage 4kV
Capillary temperature 50⁰C
Capillary voltage 5V
Tube lens offset 10V

Selected fragments for compound **8a-d** and **9a-d**: Positive ion mode

<i>Compound (cation)</i>	<i>Fragment</i>	<i>z</i>	<i>m/z</i>
[Rh(MonoPhos) ₂ (NBD)] ⁺	[Rh(MonoPhos) ₂ (NBD)] ⁺	1	913.18
	[Rh(MonoPhos) ₂] ⁺	1	821.12
	[Rh(MonoPhos)(NBD)] ⁺	1	554.08
[Rh(MonoPhos) ₄] ⁺	[Rh(MonoPhos) ₄] ⁺	1	1539.34
	[Rh(MonoPhos) ₃] ⁺	1	1180.23

Negative ion mode

<i>Anion</i>	<i>z</i>	<i>m/z</i>
BF ₄	1	87.00
SbF ₆	1	234.89
PF ₆	1	144.96
CF ₃ SO ₃	1	148.95

$\{[\text{Rh}(\text{R})\text{-MonoPhos})_2(\text{NBD})]\text{SbF}_6\}$ 8a

Pos ion mode

SI27 cap. temp. 40 °C

SI28 cap temp 70 °C

SI29 cap temp 100 °C

SI30 cap temp 150 °C

SI 31 cap temp 200 °C

SI 32 cap temp 275 °C

SI 33 measured isotopic cluster for $m/z = 913$

SI 34 simulated isotopic cluster

Neg ion mode

SI35

SbF₆⁻

100414-02 #3-9 RT: 0.06-0.22 AV: 7 NL: 1.13E7
T: -p ESI Full ms [150.00-2000.00]

SI 36 simulation of isotopic cluster SbF₆

SbF6: Sb1 F6 p(gss, s/p:40) Chrg 1R: 0.5 Da @FWHM

$[\text{Rh}(\text{R-MonoPhos})_2(\text{NBD})]\text{BF}_4$ 8b

Pos ion mode

SI37

100415-08 #57-72 RT: 2.34-2.95 AV: 16 SB: 21 0.09-0.92 NL: 7.94E8
T: + p ESI Full ms [150.00-2000.00]

SI38 zoom in on m/z 821

100415-08 #57-72 RT: 2.34-2.95 AV: 16 SB: 21 0.09-0.92 NL: 9.93E7
T: + p ESI Full ms [150.00-2000.00]

SI 39 zoom scan:

100415-08_100415121307 #2-10 RT: 0.02-0.14 AV: 9 NL: 2.80E7
T: + p ESI Z ms [816.00-826.00]

Neg ion mode

SI40

BF₄⁻

100415-09 #137-163 RT: 1.69-1.99 AV: 27 SB: 1 0.72 NL: 7.38E6
T: - p ESI Full ms [60.00-300.00]

SI41 simulated spectrum for BF₄

BF₄: B1 F4 p(gss, sip:40) Chrg 1R: 0.4 Da @FWHM

[Rh(*R*)-MonoPhos)₂(NBD)]PF₆ 8c

Pos ion mode

SI 42

100415-06 #56-71 RT: 2.32-2.93 AV: 16 SB: 10 0.20-0.57 NL: 9.88E8
T: + p ESI Full ms [150.00-2000.00]

SI43 zoom in on m/z 821:

Neg ion mode

SI44

PF₆⁻

$[\text{Rh}(\text{R-MonoPhos})_2(\text{NBD})]\text{CF}_3\text{SO}_3$ 8d

Pos ion mode

SI45

Compound **9d** $[\text{Rh}(\text{R-MonoPhos})_4]\text{CF}_3\text{SO}_3$ is present in less than 5% as shown in ^1H -NMR spectrum SI12.

SI46 zoom in on m/z 821

Neg ion mode

SI47

SI48 measured spectrum zoom in:

SI49 simulated spectrum

$\{[\text{Rh}(\text{R})-(\text{MonoPhos})_2]_2(\text{SbF}_6)_2\}$ 10

Compound	Fragment	z	m/z
$\{[\text{Rh}(\text{R})-(\text{MonoPhos})_2]_2(\text{SbF}_6)_2\}$	$\{[\text{Rh}(\text{R})-(\text{MonoPhos})_2]_2(\text{SbF}_6)\}^+$	1	1877.14
	$[\text{Rh}(\text{R})-(\text{MonoPhos})_2]_2^{++}$	2	821.12

SI50

100415-10 #38-52 RT: 1.54-2.12 AV: 15 SB: 5 0.08-0.25 NL: 1.24E9
T: + p ESI Full ms [150.00-2000.00]

SI 51 zoom in on m/z 821:

100415-10 #38-52 RT: 1.54-2.12 AV: 15 SB: 5 0.08-0.25 NL: 1.24E9
T: + p ESI Full ms [150.00-2000.00]

SI52 zoom scan:

100415-10 #71-93 RT: 2.61-2.94 AV: 23 NL: 3.82E8
T: + p ESI Z ms [816.00-826.00]

{[Rh (R)-(MonoPhos)₂]₂(BF₄)₂} 10b

Compound	Fragment	z	m/z
[Rh (R)-(MonoPhos) ₂] ₂ (BF ₄) ₂ }	[Rh (R)-(MonoPhos) ₂] ₂ (BF ₄) ₂ } ⁺	1	1729.24
	[Rh(R)-(MonoPhos) ₂] ₂	2	821.12

SI53

100415-11 #33-51 RT: 1.36-2.09 AV: 19 SB: 11 0.19-0.60 NL: 9.86E8
T: + p ESI Full ms [150.00-2000.00]

SI54 zoom in on m/z 821

SI55 zoom scan:

Selected fragments for compounds **11**: Positive ion mode

Compound (cation)	Fragment	z	m/z
[Rh(MonoPhos) ₂ (MAC)] ⁺	[Rh(MonoPhos) ₂ (MAC)] ⁺	1	1040.21
	[Rh(MonoPhos) ₂] ⁺	1	821.12

(MAC = (Z)- α -acetamidocinnamic methyl ester)

[[Rh(R)-(MonoPhos)₂(MAC)](SbF₆)] 11

SI56

100418 #51-62 RT: 2.11-2.56 AV: 12 SB: 7 0.38-0.63 NL: 1.93E9
T: + p ESI Full ms [150.00-2000.00]

SI57 zoom scan on m/z 821:

100418 #69-83 RT: 2.72-2.93 AV: 15 NL: 4.47E8
T: + p ESI Z ms [816.00-826.00]

The solution still contain some dimer **[[Rh(R)-(MonoPhos)₂]₂(SbF₆)₂] 10**

The relative intensity of the peak due to the substrate adduct fragment m/z 1039.9 has been shown to increase when the speed of injection increases. By injecting a bigger amount of solvent per unit of time the probe is cooled down to a lower temperature because of the rapid evaporation of the solvent. This is beneficial for the time of survival of fragment m/z 1039.9 before it breaks down.

$[\text{Rh}(\text{R})-(\text{MonoPhos})_2(\text{MAC})](\text{BF}_4)$ 11b

SI58

100417a #5-19 RT: 0.19-0.76 AV: 15 NL: 2.00E9
T: + p ESI Full ms [150.00-2000.00]

SI59 zoom scan on m/z 821:

100417b #3-18 RT: 0.03-0.26 AV: 16 NL: 4.29E8
T: + p ESI Z ms [816.00-826.00]

Selected fragments for compounds **12**: Positive ion mode

Compound	Fragment	z	m/z
$[\text{Rh}(\text{MonoPhos})_2(\text{MAC}(\text{H})_2)]^+$	$[\text{Rh}(\text{MonoPhos})_2(\text{MAC}(\text{H})_2)]^+$	1	1042.23
	$[\text{Rh}(\text{MonoPhos})_2]^+$	1	821.12

(MAC(H)₂ = N-Acetyl- phenylalanine methyl ester)

{[Rh(R)-(MonoPhos)₂(MAC(H)₂)](SbF₆)} 12

SI60

100422 #38-57 RT: 1.61-2.38 AV: 20 NL: 1.38E9
T: + p ESI Full ms [150.00-2000.00]

SI61 and SI62 zoom scan on m/z 821 and 1042

100422a #3-40 RT: 0.04-0.59 AV: 38 NL: 2.82E8
T: + p ESI Z ms [816.00-826.00]

100422a #89-113 RT: 1.32-1.68 AV: 25 NL: 1.37E8
T: + p ESI Z ms [1037.00-1047.00]

$\{[\text{Rh}(\text{R})-(\text{MonoPhos})_2(\text{MAC}(\text{H})_2)](\text{BF}_4)\}$ 12b

SI63

100423 #32-45 RT: 1.36-1.89 AV: 14 SB: 10 0.27-0.64 NL: 3.77E8
T: + p ESI Full ms [150.00-2000.00]

SI64 and SI65 zoom scan on m/z 821 and 1042

100423a #4-40 RT: 0.05-0.59 AV: 37 NL: 2.35E8
T: + p ESI Z ms [816.00-826.00]

100423a #66-122 RT: 0.98-1.81 AV: 57 NL: 1.13E8
T: + p ESI Z ms [1037.00-1047.00]

$\{[\text{Rh}(\text{R})\text{-(MonoPhos)}_2(\text{MAC}(\text{H})_2)](\text{SbF}_6)\}$ 12 + 5 equivalents of MAC

SI66

SI67 and SI68 zoom scan on m/z 821 and 1040

Fresh substrate MAC is able to displace the product $\text{MAC}(\text{H})_2$ from the catalyst to regenerate the catalyst-substrate adduct $\{[\text{Rh}(\text{R})\text{-(MonoPhos)}_2(\text{MAC})](\text{SbF}_6)\}$ 11

GC analysis

SI69 Chiral GC of solution containing [Rh(R)-MonoPhos₂((S)-MAC(H)₂)]SbF₆ **12** deriving from *in-situ* detection of reaction intermediates under hydrogenation conditions.

```
=====
Acq. Operator   : Buchholz                      Seq. Line :    1
Acq. Instrument : GC 9                          Location  : Vial 5
Injection Date  : 18-Jan-10, 07:51:56           Inj       :    1
                                           Inj Volume: Manually

Method          : D:\HPCHEM\1\METHODS\AME.M
Last changed    : 1/18/2010 7:49:42 AM by Buchholz
Method Info     : 25m Chiralsil Val
=====
```

Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.547	BV	0.1402	20.25946	2.22465	3.42120
2	14.169	VB	0.1547	571.91431	46.44578	96.57880
Totals :				592.17377	48.67043	

Handwritten notes: 13.47, 96.53, 93.06% ee

60m AS

*** End of Report ***

Kinetic: Hydrogen Consumption Curves

Hydrogen consumptions were monitored using the device described in H.-J. Drexler, A. Preetz, T. Schmidt, D. Heller, in *Handbook of Homogeneous Hydrogenation* (eds.: J. G. de Vries, C. J. Elsevier), WILEY-VCH, **2007**, ch. 10, pp. 257-293.

[Rh] = 0.01 mmol, MAC = 1 mmol, DCE = 15 ml, 1.01 bar total pressure, 25.0 °C

SI70 Hydrogen consumption curves for the catalytic hydrogenation of methyl *Z*-2-acetamidocinnamate **2a** (MAC):

the red curve refers to the experiment in which the catalyst precursor $[Rh((R)\text{-}\mathbf{1a})_2(\text{NBD})]\text{SbF}_6$ **8a** is prehydrogenated to reduce NBD (this leads to formation of the species $[(Rh((R)\mathbf{1a})_2)_2(\text{SbF}_6)_2]$ **10**, MAC is added and hydrogen consumption monitoring is started;

the green curve refers to the experiment in which all reagents $[Rh((R)\text{-}\mathbf{1a})_2(\text{NBD})]\text{SbF}_6$ **8a** and substrate MAC **2a** are placed in the reactor at the same time and hydrogen consumption monitoring is started immediately afterwards.