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New rhodium complexes with *P*,*N*-ligands possessing a hydroxy or methoxy group. Synthesis, characterization and application to hydroformylation of styrene

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Abstract

Two new cationic rhodium(I) complexes containing a phosphino amino alcohol ligand and a methoxy amino phosphine, respectively, have been prepared. According to IR and NMR data the ligands are *P*,*N*-bonded and coordination of the hydroxy or the methoxy group to the metal does not take place. The complexes were applied to the hydroformylation of styrene and displayed a quantitative chemoselectivity for aldehydes with a very good branched:linear ratio. The reaction rate is higher using the complex possessing the methoxy group as opposed to the hydroxy group.

Keywords: Phosphine; Hemilabile ligand; Rhodium; Catalysis; Hydroformylation

1. Introduction

Rhodium complexes containing nitrogen-substituted phosphine ligands have been the subject of some recent studies due to their applications in important homogeneous catalytic processes, such as hydroformylation [1]. In general, the use of *P*,*N*-bidentate ligands can be expected to improve the catalytic activity of some complexes [2]. In particular, hemilabile *P*,*N*,*O*-tridentate ligands exhibit interesting coordination chemistry and have been successfully applied to homogeneous catalysis [3]. In addition, phosphine ligands possessing a hydroxy or a methoxy group deserve particular attention, and the influence of these groups as hemilabile ligands in seven-membered (diphosphane)Rh(I) chelates on the asymmetric hydrogenation have been studied [4].

Our group has recently reported the synthesis of a phosphino amino alcohol ligand which, in solution, exhibits double hemilabile character for both the nitrogen and the oxygen functions in its Cu(I) complex, while on reaction of this ligand with an alkylpalladium(II) complex, an unusual proton transfer from the alcohol to the amino group of the ligand appears to take place, yielding a dinuclear palladium complex [5]. In contrast to this, the ligand **4**, reported in this paper, exhibits a different coordination chemistry in a rhodium(I) complex **8**. The characterization of the coordination mode in **8** and a study of its catalytic activity towards hydroformylation is of significant interest as the number of known rhodium complexes with ligands containing P, N and OH function is limited [6] and such complexes have not been tested before as hydroformylation catalysts. In order to investigate the influence of the hydroxy group on the catalyst behavior of the complex in the hydroformylation reaction, we have also synthesized and characterized the rhodium(I) complex **9**, with the analogous methoxy ligand **7**. Both **8** and **9** were successfully applied as homogeneous catalysts to the hydroformylation of styrene and a comparison of their catalytic activity is discussed.

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2. Results and discussion

2.1. Preparation of the ligands

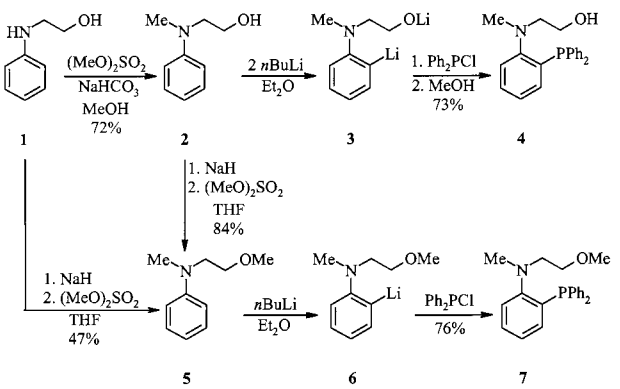
Ligands **4** and **7** were prepared starting from 2-anilinoethanol (**1**) according to the synthetic sequence shown in Scheme 1. [*N*-(2-Hydroxyethyl)-*N*-methyl]-aniline (**2**) was prepared by methylation of **1**. Subsequent reaction of the sodium alkoxide of **2** with dimethyl sulfate afforded [*N*-(2-methoxyethyl)-*N*-methyl]aniline (**5**) (overall yield, 60%). Amine **5** was prepared also by one-pot methylation of **1** in a lower yield (47%).

Phosphino amino alcohol ligand **4** was prepared in a 73% yield via *ortho*-lithiation of **2** [7] with two equivalents of *n*-BuLi and subsequent reaction of the lithioxyaryllithium **3** with one equivalent of Ph_2PCl, according to the literature procedure [5]. An analogous metallation of **5** with one equivalent of *n*-BuLi and subsequent reaction of the organolithium **6** with one equivalent of Ph_2PCl afforded phosphine **7** in a 76% yield.

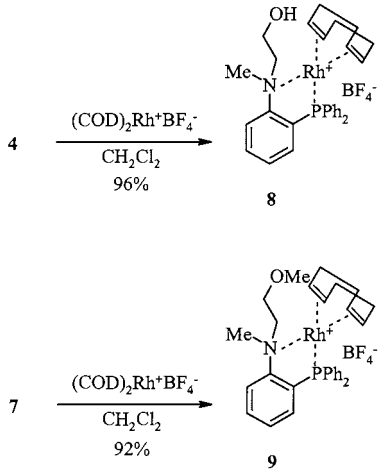
2.2. Synthesis and characterization of the complexes

When $(COD)_2Rh^+BF_4^-$ was treated in dichloromethane solution with one equivalent of ligand **4** or **7**, the cationic rhodium complex, **8** or **9** respectively, was isolated in high yield (Scheme 2).

The coordination mode in rhodium complexes **8** and **9** was determined by spectroscopic techniques. In the ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **8** and **9**, the NMe resonances are shifted to low field compared to the corresponding resonances in the free ligands. This observation is strong evidence for Rh–N coordination [8]. In complex **9** on the other hand, the OCH_3 resonances are at almost the same position as those of the free ligand **7**, indicating the absence of Rh–O coordination. In the ^{31}P{^{1}H}-NMR spectra in CD_2Cl_2 at 303 K, complex **8** shows a doublet at δ 40.52 ($J_{RhP} = 149.6$ Hz) and complex **9** a doublet at δ 39.05 ($J_{RhP} = 155.6$ Hz). At temperatures down to 220 K for **8** and 233 K for **9**,



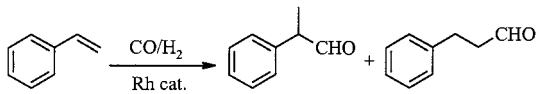
Scheme 1.



Scheme 2.

no significant change was observed in the ^{31}P{^{1}H}-NMR spectra, indicating that the η^2-coordination mode of the ligands is retained even at low temperatures, because a probable change in the coordination mode of a complex possessing a hemilabile ligand should result in a change in the ^{31}P{^{1}H}-NMR spectrum [4,5]. In the IR spectra of complex **8**, the band corresponding to OH is shifted to a higher wavenumber compared to that in the free ligand **4**. This is extra evidence that there is no coordination between rhodium and the hydroxy group; in rhodium complexes with no coordination between the metal and the hydroxy group, the OH band is shifted to a higher wavenumber compared to those in the free ligands [9], while in complexes with Rh–O coordination it is shifted to a lower wavenumber [10]. In the ^{1}H-NMR spectrum of **8** the hydroxy proton has a chemical shift close to that of the free ligand **4**, while in rhodium complexes with Rh–O coordination the hydroxy proton resonance is shifted to a considerably lower field compared to that of the free ligand [10]. From all these data it can be concluded that in the rhodium complexes **8** and **9** association of the hydroxy or the methoxy group to the metal does not take place. This is most likely because they are very poor ligands for rhodium(I).

In the ^{1}H- and ^{13}C-NMR spectra of **8** and **9**, the resonances of COD deserve some comment. In the ^{1}H-NMR spectrum of **8** at 303 K, three of the four olefinic protons are observed as a very broad resonance at δ 4.20. On lowering the temperature to 233 K, the olefinic protons give three single resonances at δ 5.43, 5.05 and 3.93, respectively. From 253 to 308 K, in the ^{13}C-NMR spectrum of **8** the COD olefinic carbons are not observable and the aliphatic carbons afford two resonances of low intensity at δ 31.52 and 29.76, at room temperature (r.t.). In the ^{1}H-NMR spectrum of **9** at 300 K, only one olefinic proton signal is apparent as a very broad resonance at δ 5.32. On lowering the



Scheme 3.

temperature to 233 K, this sharpens slightly and shifts to δ 5.12. In the ^{13}C-NMR spectrum of **9** at 300 K, the signals for the olefinic carbons are not observable and the aliphatic carbons give two resonances of very low intensity at δ 32.19 and 28.31; the latter changed to four sharp signals on lowering the temperature (δ 32.37, 31.99, 28.11 and 27.53, at 253 K). The above-mentioned behavior of complexes **8** and **9** suggests a fluxional process within the molecules. This fluxionality could be due to inversion at the nitrogen atom and this would account for the inequivalence of the COD resonances.

2.3. Hydroformylation

The rhodium complexes **8** and **9** were applied to the hydroformylation of styrene (Scheme 3; Table 1). The conversion of styrene was quantitative after 22 h using complex **8**, under mild reaction conditions (P(CO/H_2) = 100 bar; T = 40°C), and with a high styrene:**8** ratio (1484:1), while the corresponding aldehydes were the only products detected by GC–MS and ^{1}H-NMR spectroscopy. Noteworthy is the very good selectivity (94%) obtained for the formation of the branched aldehyde. Hydroformylation of styrene for 4 h at 40°C gave poor conversion (17%) while the branched:linear ratio was the same. Under identical reaction conditions, the rhodium complex **9** possessing the methoxy group afforded a higher reaction rate (conversion 55% after 4 h) while the regioselectivity did not change. Hydroformylation by complex **8** or **9** is temperature dependent. After 4 h at 60°C, hydroformylation of styrene by complex **8** gave a considerably higher conversion (70%) compared to that at 40°C after 4 h, while the selectivity towards the branched aldehyde decreased to 89%. The conversion of styrene by complex **9** under the same conditions is almost complete (conversion 99%) after 4 h while the regioselectivity towards the branched aldehyde also decreased to 89%.

As mentioned above, replacement of the methoxy by the hydroxy group lowers the reaction rate of hydroformylation while the chemoselectivity and regioselectivity is identical. However, the role of a hydroxy group in the ligand throughout the course of the hydroformylation reaction has not been clarified yet. A decelerating effect of the hydroxy group has also been noted by other authors for hydrogenation [4,11].

3. Conclusions

We have synthesized two new five-membered chelate rhodium(I) complexes with P,N-ligands posssessing hydroxy or methoxy groups. The latter groups do not coordinate to the metal. Examination of the catalytic activity of these complexes on the hydroformylation of styrene has shown promising results. Quantitative selectivity for aldehydes and a very good branched:linear ratio were observed. The rhodium complex possessing the methoxy group gave higher reaction rates than that with the hydroxy group.

4. Experimental

4.1. General

2-Anilinoethanol (**1**) was commercially available. $(COD)_2RhBF_4$ was prepared from rhodium trichloride hydrate according to the literature procedure [12–14]. n-BuLi was prepared from lithium metal and n-BuCl in methylcyclohexane or was commercially available (1.6 M in hexane). All preparations and hydroformylations were carried out under argon by using dry and degassed

Table 1
Hydroformylation of styrene catalyzed by rhodium complex **8** or **9** [a]

Catalyst [b]	T (°C)	Time (h)	Conversion (%)	R_c [c] (%)	R_{br} [d] (%)	TON [e]
8	40	4	16.8	100	94.4	249
9	40	4	55.3	100	94.5	821
8	40	22	100	100	94.3	1484
9	40	22	100	100	95.0	1484
8	60	4	70.1	100	89.4	1032
9	60	4	98.9	99.6 [f]	89.2	1462

[a] Reaction conditions: initial total pressure of CO/H_2 (1/1) = 100 bar; styrene:cat. = 1484:1.
[b] A 4 mM solution in CH_2Cl_2.
[c] R_c = chemoselectivity towards aldehydes.
[d] R_{br} = regioselectivity towards branched aldehyde.
[e] Turnover no. (TON) = % aldehydes × substrate:catalyst ratio.
[f] There was a trace (0.4%) of ethylbenzene (hydrogenation product).

solvents. THF and diethylether were distilled from $LiAlH_4$ and Na–K alloy/benzophenone, respectively. Styrene was distilled from CaH_2 and kept under argon. Hydroformylation studies were performed in a stainless steel autoclave (300 ml) with magnetic stirring. The syngas CO/H_2 (1/1) (CO, 1.8; H_2, 3.0) was purchased from Messer Griesheim GmbH. IR: Nicolet Impact 420. NMR: Bruker AC 300 (300.13 MHz, 75.47 MHz, and 121.50 MHz for ^1H, ^{13}C and ^{31}P, respectively); ^1H- and ^{13}C-NMR shifts were referenced to the solvents, the ^{31}P-NMR shifts were referenced to external 85% H_3PO_4 in D_2O. The assignments of the aliphatic carbons were made on the basis of 2D{^1H, ^{13}C} and DEPT NMR. ESI MS: Finnigan MAT TSQ 7000. GC–MS (EI): Varian Saturn 2000 with a 30 m × 0.25 mm DB5-MS column. GC: Varian Star 3400 CX with a 30 m × 0.53 mm DB5 column. Elemental analyses: Mikroanalytisches Laboratorium Kolbe, Mülheim a.d. Ruhr, Germany.

4.2. [N-(2-Hydroxyethyl)-N-methyl]aniline (**2**) [7]

Dimethyl sulfate (53 ml, 0.56 mol) was added dropwise to a suspension of 2-anilinoethanol (**1**) (63 ml, 0.50 mol) and $NaHCO_3$[2] (83.6 g, 0.99 mol) in methanol (300 ml), after which the mixture was stirred at r.t. for 90 h. Methanol was removed by evaporation, an aqueous solution of NaOH 50% (10 ml), water (500 ml) and dichloromethane (250 ml) were added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (5 × 100 ml), the combined organic layers were dried over Mg_2SO_4, filtered and evaporated to dryness, yielding 61.4 g of the crude product. Purification was carried out by distillation, yielding **2** (54.5 g, 72%), b.p. 96°C (0.1 mmHg). ^1H-NMR ($CDCl_3$): δ 7.28–7.22 (m, 2H, Ar), 6.82–6.73 (m, 3H, Ar), 3.81–3.78 (m, 2H, CH_2O), 3.47 (t, $^3J = 5.6$ Hz, 2H, CH_2N), 2.96 (s, 3H, NCH_3), 1.93 (brs, 1H, OH). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 150.07, 129.17, 117.21 and 113.04 (Ar), 60.05 and 55.43 (NCH_2CH_2O), 38.70 (NCH_3). GC–MS (EI): m/z (relative intensity) 151 (M^+, 35), 120 (100), 91 (9), 77 (20).

4.3. o-Diphenylphosphino-[N-(2-hydroxyethyl)-N-methyl]aniline (**4**)

To a solution of **2** (6.2 g, 41.06 mmol) in ether (35 ml) under argon, was added *n*-butyllithium (1.76 M in methylcyclohexane, 50 ml, 88 mmol) at −78°C. The reaction mixture was stirred at r.t. overnight and subsequently refluxed for 3 h, yielding the organolithium **2**. A solution of chlorodiphenylphosphine (7.8 ml, 43.45 mmol) in ether (25 ml) was added dropwise with ice-water bath cooling, and the mixture then stirred at r.t. overnight. Methanol (50 ml) was introduced. The mixture was stirred for 1 h, volatile materials were removed by evaporation, water was added, the product was extracted with toluene (3 × 100 ml), dried over Mg_2SO_4, filtered and evaporated to dryness. Purification was carried out by recrystallization from ether–hexane, yielding **4** as a white solid (10 g, 73%), m.p. 123–127°C. IR ($CHCl_3$): ν 3392 (OH). ^1H-NMR ($CDCl_3$): δ 7.40–6.82 (m, 14H, Ar), 3.53 (t, $^3J = 4.6$ Hz, 2H, CH_2O), ca. 3.5 (coincides with signal of CH_2O, 1H, OH, exchangeable with D_2O), 3.03 (t, $^3J = 4.6$ Hz, 2H, CH_2N), 2.28 (s, 3H, NCH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 156.35–123.43 (Ar), 60.08 (CH_2N), 59.26 (CH_2O), 43.42 (NCH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −17.74 (s). GC–MS (EI): m/z (relative intensity) 336 ($[M+H]^+$, 9), 318 (6), 304 (24), 291 (100), 261 (5), 200 (65), 122 (10), 91 (14), 77 (13). Anal. Calc. for $C_{21}H_{22}NOP$ (335.38): C, 75.21; H, 6.61; N, 4.18; P, 9.24. Found: C, 75.18; H, 6.66; N, 4.15; P, 9.27%.

4.4. [N-(2-Methoxyethyl)-N-methyl]aniline (**5**) [15]

4.4.1. Procedure A

A solution of **2** (30.2 g, 200 mmol) in THF (50 ml) was added dropwise to a suspension of NaH (previously washed three times with THF to remove the mineral oil, 8.9 g, 80% in NaH, 297 mmol) in THF (50 ml) cooled with an ice-water bath, after which the reaction mixture was stirred at r.t. for 1 h. A solution of dimethyl sulfate (22 ml, 232 mmol) in THF (30 ml) was then added dropwise with ice-water bath cooling. After stirring at r.t. overnight, THF was removed by evaporation, water was added, the product was extracted from CH_2Cl_2 (3 × 100 ml), dried over Na_2SO_4, filtered and evaporated to dryness. Purification was carried out by distillation, yielding **5** (27.8 g, 84%), b.p. 112°C (5 mmHg).

4.4.2. Procedure B

A solution of **1** (6.3 ml, 50 mmol) and dimethyl sulfate (10 ml, 105 mmol) in THF (150 ml) was added dropwise to a suspension of NaH (previously washed three times with THF to remove the mineral oil, 5.2 g, 80% in NaH, 173 mmol) in THF (50 ml) cooled with an ice-water bath, after which the reaction mixture was stirred at r.t. overnight. The workup procedure was as described above, yielding **5** (3.9 g, 47%), b.p. 118°C (7 mmHg).

4.4.3. Analytical data for **5**

^1H-NMR ($CDCl_3$): δ 7.26–7.21 (m, 2H, Ar), 6.75–6.68 (m, 3H, Ar), 3.61–3.49 (m, 4H, NCH_2CH_2O), 3.36 (s, 3H, OCH_3), 2.98 (s, 3H, NCH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 149.29, 129.15, 116.30 and 112.17 (Ar), 70.18 (CH_2), 59.01 (CH_3), 52.45 (CH_2), 38.89 (CH_3). GC–MS (EI): m/z (relative intensity) 165 (M^+, 29), 120 (100), 91 (8), 77 (18).

[2] Na_2CO_3 was also sufficient, yielding **2** (71%) after 3 h at r.t. followed by 0.5 h under reflux.

4.5. o-Diphenylphosphino-[N-(2-methoxyethyl)-N-methyl]aniline (7)

To a solution of **5** (6.75 g, 40.91 mmol) in ether (35 ml) under argon, was added *n*-butyllithium (1.6 M in hexane, 28 ml, 44.80 mmol). The reaction mixture was subsequently stirred at r.t. for 27 h, yielding the organolithium **6**. A solution of chlorodiphenylphosphine (7.8 ml, 43.45 mmol) in ether (25 ml) was then added dropwise with ice-water bath cooling and the mixture then stirred at r.t. overnight. The volatile materials were removed by evaporation, water was added, the product was extracted with toluene (3×100 ml), dried over Na_2SO_4, filtered and evaporated to dryness. Purification was carried out by recrystallization from ether, yielding **7** as a white solid (10.85 g, 76%), m.p. 70–73°C. ^{1}H-NMR ($CDCl_3$): δ 7.35–6.76 (m, 14H, Ar), 3.18 (t, $^3J = 6.5$ Hz, 2H, CH_2O), 3.18 (s, 3H, OCH_3), 3.02 (t, $^3J = 6.5$ Hz, 2H, CH_2N), 2.64 (s, 3H, NCH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 157.36–122.21 (Ar), 71.12 (CH_2O), 58.53 (OCH_3), 56.31 (CH_2N), 43.68 (NCH_3). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ −13.80 (s). GC–MS (EI): m/z (relative intensity) 350 ($[M+H]^+$, 12), 304 (49), 291 (100), 261 (7), 200 (64), 122 (9), 91 (17), 77 (13). Anal. Calc. for $C_{22}H_{24}NOP$ (349.41): C, 75.62; H, 6.92; N, 4.01. Found: C, 75.55; H, 7.06; N, 4.11%.

4.6. [Rh(COD)–4]BF_4 (8)

A solution of the phosphine **4** (0.4062 g, 1.21 mmol) in CH_2Cl_2 (15 ml) was added dropwise to the dark red solution of $(COD)_2Rh^+BF_4^-$ (0.4923 g, 1.21 mmol) in CH_2Cl_2 (15 ml) with ice-water bath cooling, after which the mixture was stirred at r.t. for 2 h. The volatile materials were evaporated under reduced vacuum, the residue washed with hexane and dried, yielding **8** (0.7373 g, 96%) as a pale yellow solid, m.p. 192–194°C. IR ($CHCl_3$): ν 3684 (OH, free), 3477 (OH, H-bonded), 1067 (BF_4^-). ^{1}H-NMR (CD_2Cl_2, 303 K): δ 7.81–7.29 (m, 14H, Ar), 4.20 (brs, 3H, COD–CH), 3.69 (s, 1H, OH, exchangeable with D_2O), 3.65, 3.46, 3.37–3.28 and 3.14–3.08 ($4 \times$ m, 4×1H, NCH_2CH_2O), 3.43 (s, 3H, NCH_3), 2.56–2.48, 2.36, 2.16–2.12 and 1.97–1.91 ($4 \times$ m, 4×2H, COD–CH_2). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 294 K): δ 157.59–123.22 (Ar), 63.96 and 58.93 (NCH_2CH_2O), 53.35 (NCH_3), 31.52 and 29.76 (COD–CH_2). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 303 K): δ 40.52 (d, $J_{RhP} = 149.6$ Hz). ESI MS: m/z (relative intensity) 546 ($[M-BF_4]^+$, 100). Anal. Calc. for $C_{29}H_{34}BF_4NOPRh$ (633.28): C, 55.00; H, 5.41; N, 2.21. Found: C, 55.10; H, 5.47; N, 2.20%.

4.7. [Rh(COD)–7]BF_4 (9)

The reaction of **7** with $(COD)_2Rh^+BF_4^-$ according to the procedure described for the synthesis of **8** yielded the complex **9** (92%) as an orange solid, m.p. (dec.) 197–200°C. ^{1}H-NMR (CD_2Cl_2, 300 K): δ 7.76–7.28 (m, 14H, Ar), 5.32 (brs, 1H, COD–CH), 3.63–3.58 (m, 1H, part of NCH_2CH_2O), 3.49–3.36 (m, 2H, part of NCH_2CH_2O), 3.34 (s, 3H, NCH_3), 3.09–3.02 (m, 1H, part of NCH_2CH_2O), 2.98 (s, 3H, OCH_3), 2.44 and 2.10 ($2 \times$ brs, 8H, COD–CH_2). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 300 K): δ 157.46–123.16 (Ar), 68.60 and 62.97 (NCH_2CH_2O), 59.59 (OCH_3), 54.15 (NCH_3), 32.19 and 28.31 (COD–CH_2). ^{31}P{^{1}H}-NMR (CD_2Cl_2, 303 K): δ 39.05 (d, $J_{RhP} = 155.6$ Hz). ESI MS: m/z (relative intensity) 560 ($[M-BF_4]^+$, 100). Anal. Calc. for $C_{30}H_{36}BF_4NOPRh$ (647.30): C, 55.67; H, 5.61; N, 2.16. Found: C, 55.79; H, 5.66; N, 2.14%.

4.8. Hydroformylation

Styrene (3.4 ml, 29.67 mmol) and a 4 mM solution of rhodium complex in dichloromethane (5 ml, 0.02 mmol) was placed under argon in an oven-dried autoclave, which was then closed, pressurized with syngas ($CO:H_2 = 1:1$) to 100 bar and brought to the required temperature. After the required reaction time, the autoclave was cooled to r.t., the pressure was carefully released and the solution was passed through celite and analyzed by GC, GC–MS and ^{1}H-NMR spectroscopy. Conversions were determined by GC.

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