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Unusual deactivation in the asymmetric hydrogenation of itaconic acid☆

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ABSTRACT

The formation of unusual Rh(III) substrate complexes from $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid has been detected which leads to the deactivation of the catalyst. The influence of different parameters on the formation of such complexes, namely substrate concentration, reaction time, temperature, acidic and basic additives, was investigated with different NMR methods. Two different Rh(III) substrate complexes are formed whose ratio is strongly dependent on substrate concentration and reaction time. The pH value of the solution shows a strong influence on the chemical shifts of the ^{31}P NMR signals of such complexes. A catalyst-mediated esterification of itaconic acid in methanol was detected. Extended investigations provide detailed ^{1}H, ^{13}C and ^{31}P NMR data for the Rh(III) complexes and information about their stability in solution.

1. Introduction

Enantioselective hydrogenation is an effective way to transform itaconic acid and its derivatives into optically active methyl succinates [1], which are also pharmaceutically relevant compounds [2]. However, when hydrogenation is carried out with the Rh-DIPAMP system we [3] and others [4] observed deactivation of the catalyst. A similar effect was reported when using a rhodium catalyst modified with the Me-DuPhos ligand, thus suggesting that such deactivation might be a common feature of Rh-diphosphane catalysts for this type of substrate [3]. So far the reason for deactivation of the catalyst during hydrogenation of itaconic acid was unknown. Prochiral olefins like dehydroamino acids and dimethyl itaconate coordinate to the Rh-catalyst via the C–C double bond and the oxygen atom of the carbonyl group available in such compounds [5,6] (Scheme 1 (**1**)). The same type of complexes is probably formed between itaconic acid and Rh-diphosphane catalysts. However, from a solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid we recently isolated an unusual Rh(III) alkyl complex (Scheme 1 (**2**)) (CCDC-690298) which is formed in a parallel running side reaction [3]. Due to the high stability of the terdentate coordination mode of the substrate to rhodium [7], the metal center is blocked and thus cannot participate in hydrogenation which explains the unusual behavior of the hydrogenation of itaconic acid promoted by the Rh-DIPAMP system [8].

The objective of this paper is to investigate the effect of different parameters, namely substrate concentration, reaction time and pH on the formation of complexes between catalyst and itaconic acid. This investigation has been supported by an extended NMR study.

2. Experimental

2.1. General procedures

All experiments were carried out according to Schlenk techniques [9] under argon. CH_3OH was dried with Mg and distilled under argon, CD_3OD was dried with molecular sieves, distilled under argon and then subjected to three cycles of freeze/thaw to remove any residual oxygen.

2.2. Materials

$[Rh(DIPAMP)(MeOH)_2]BF_4$ was generated from [Rh(DIPAMP)(NBD)]BF_4 (UMICORE) via hydrogenation [10,11]. Itaconic acid was recrystallized under argon prior to use. NEt_3 was dried with NaOH overnight and freshly distilled from Na prior to use. $HBF_4{*}2Et_2O$ (Fluka) was stored under argon.

2.3. Complex formation

Unless otherwise stated, catalyst-substrate complexes were formed by either mixing itaconic acid and the aryl-bridged dimer [Rh(DIPAMP)$(BF_4)]_2$ [11] in CH_3OH (CD_3OD in case of NMR experiments) or by adding a solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ to itaconic acid, to yield clear orange solutions. At room temperature the orange color of the solutions

☆ Part II, for part I see Reference [3].

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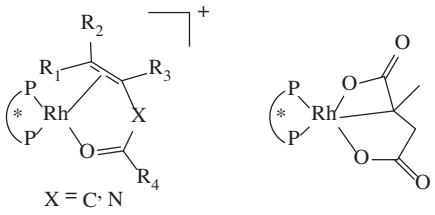


Scheme 1. Cationic Rh(I)- complex (**1**) and neutral Rh(III) complex (**2**).

always fades away within a few minutes, indicating the conversion from complex (**1**) to the substrate complex (**2**) (Scheme 1). All NMR spectra recorded at room temperature therefore contain almost exclusively catalyst-substrate complexes of type **2** (Scheme 1) [12].

2.4. Isolation of [Rh(DIPAMP)(methyl succinate)](2)

Single crystals of [Rh(DIPAMP)(methyl succinate)] (**2**) could be isolated from a solution of 0.01 mmol $Rh(DIPAMP)(MeOH)_2]BF_4$ and 0.05 mmol itaconic acid in 1 mL MeOH either by slow diffusion of diethyl ether (5 mL) or by addition of 0.05 mmol NEt_3.

2.5. NMR experiments

Samples containing rhodium complexes were prepared under argon in deoxygenated and dry CD_3OD using Young NMR tubes (Rotec Spintec GmbH). The catalyst concentration was 0.04 mmol/mL unless otherwise stated. NMR experiments were carried out either on a Bruker ARX-300 or on a Bruker ARX-400 spectrometer.

3. Results and discussion

3.1. Influence of the substrate concentration

As previously highlighted [3], the hydrogenation kinetics of itaconic acid catalyzed by $[Rh(DIPAMP)(MeOH)_2]BF_4$ is dependent on substrate concentration: reaction rate decreases with increasing substrate concentration under otherwise identical conditions. Fig. 1 shows the ^{31}P NMR spectra of a solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid at different Rh/substrate ratios, recorded immediately after sample preparation.

Even at a Rh/substrate ratio of 2:1 (Fig. 1a) about half of the catalyst (48%) is complexed by the substrate (red, orange underlined signals), forming complexes of type **2** (Scheme 1). The other signals belong to the η^6-bridged dimer $[Rh(DIPAMP)BF_4]_2$ (blue underlined) and to the solvent complex $[Rh(DIPAMP)(MeOH)_2]BF_4$ (brown underlined): the equilibrium between these species is concentration-dependent [11]. At variance with what observed with dimethyl itaconate, at a ratio of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid of 1:1 (Fig. 1b) neither the solvent complex nor aryl-bridged dimers are detectable a proof that the Rh-DIPAMP/substrate complex of itaconic acid is more stable than the one formed by dimethyl itaconate [6]. At room temperature, the Rh/substrate complex of type **1** (Scheme 1) was not observed, independent of the relative amount of itaconic acid present in solution. Two different, probably diastereomeric, substrate complexes of type **2** (Scheme 1) can be detected in the NMR spectra. Surprisingly, their relative amounts depend on the substrate concentration: at a catalyst-substrate ratio of 1:40 (Fig. 1d) [13] the share of the minor signals is 10% and therefore more than twofold the share at ratio 1:1 (4%). Furthermore, a drift of the chemical shift of the major signals with variation of substrate concentration is visible and very prominent when changing from a catalyst-substrate ratio of 2:1 to 1:1.

The solution behavior of the Rh-DIPAMP system in the presence of itaconic acid as observed by ^{31}P NMR spectroscopy is different from the one reported in the presence of either (*Z*)-(*N*)-methyl acetamido cinnamate or dimethyl itaconate: these substrates coordinate to $[Rh(DIPAMP)(MeOH)_2]BF_4$ to form two diastereomeric substrate-adducts whose relative amounts and ^{31}P NMR chemical shifts are independent of the substrate concentration [6,10].

3.2. Time dependence of the ^{31}P NMR spectra

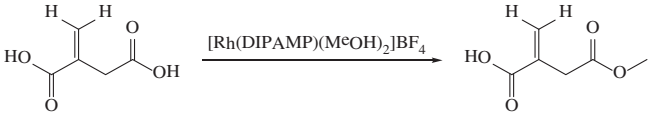
As pointed out, a color change after preparation of the catalyst-substrate complexes provides the hint that the solution composition changes over time. In order to investigate the time dependence of the ^{31}P NMR spectra, we recorded a series of NMR spectra of solutions of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid in CD_3OD at two different catalyst/substrate ratios 1:5 (Fig. 1 Supplementary information.) and 1:40 (Fig. 2) over a time interval of several days. The latter solution shows a dramatic change of the ratio between the two catalyst-substrate complexes. Thirty minutes after sample preparation, the relative amounts of the two catalyst-substrate complexes (both type **2**) are 90% and 10% respectively (Fig. 2a). Already after three days (Fig. 2c), the amount of the former "minor" substrate complex is higher (60%) than that of the initial "major" diastereomer (40%). Furthermore, new signals appear which, to the best of our knowledge do not correspond to complexes of itaconic acid with $[Rh(DIPAMP)(MeOH)_2]BF_4$. After six days (Fig. 2d), the relative amount of the initial "minor" complex has raised to 75%. The concentration of the unknown species increases over time.

3.3. Origin of the new-appearing signals

As shown in Fig. 2 and Fig. 1 Supplementary information, new signals emerge within a time range of several days in the ^{31}P NMR spectra of a solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid in CD_3OD, independent on the substrate concentration. In the ^1H NMR spectra (ratio 1:5) the changes in the signals of the vinylidenic CH_2 protons over time are more informative (Fig. 3). In the spectrum recorded immediately after sample preparation (spectrum a, Fig. 3) mainly the signal set of uncoordinated itaconic acid CH_2 is visible, already after five days (spectrum b, Fig. 3) the concentration of a newly-formed species slightly exceeds that of itaconic acid. In this species, the vinylidenic CH_2 protons must have a chemical environment similar to that experienced in itaconic acid as the differences in the chemical shifts of the peaks are low. After 13 days (Fig. 3c) the concentration of the new species is threefold that of itaconic acid. Additionally, an H/D exchange of the vinylidenic CH_2 protons is observed, leading to additional peaks.

Due to the similarity of the signals of the newly-formed species with those of itaconic acid we hypothesized that one of the possible *mono*methyl itaconates had been formed (Scheme 2). To confirm our assumption we let $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid equilibrate in undeuterated methanol for 5 days and compared the ^1H NMR spectrum with that of a solution of itaconic acid with no added catalyst which had been left standing for 5 days as well (Fig. 4).

No new signals were observed in the absence of the catalyst. The identity of the new species was confirmed by comparison with the



Scheme 2. $[Rh(DIPAMP)(MeOH)_2]BF_4$ catalyzed esterification of itaconic acid.

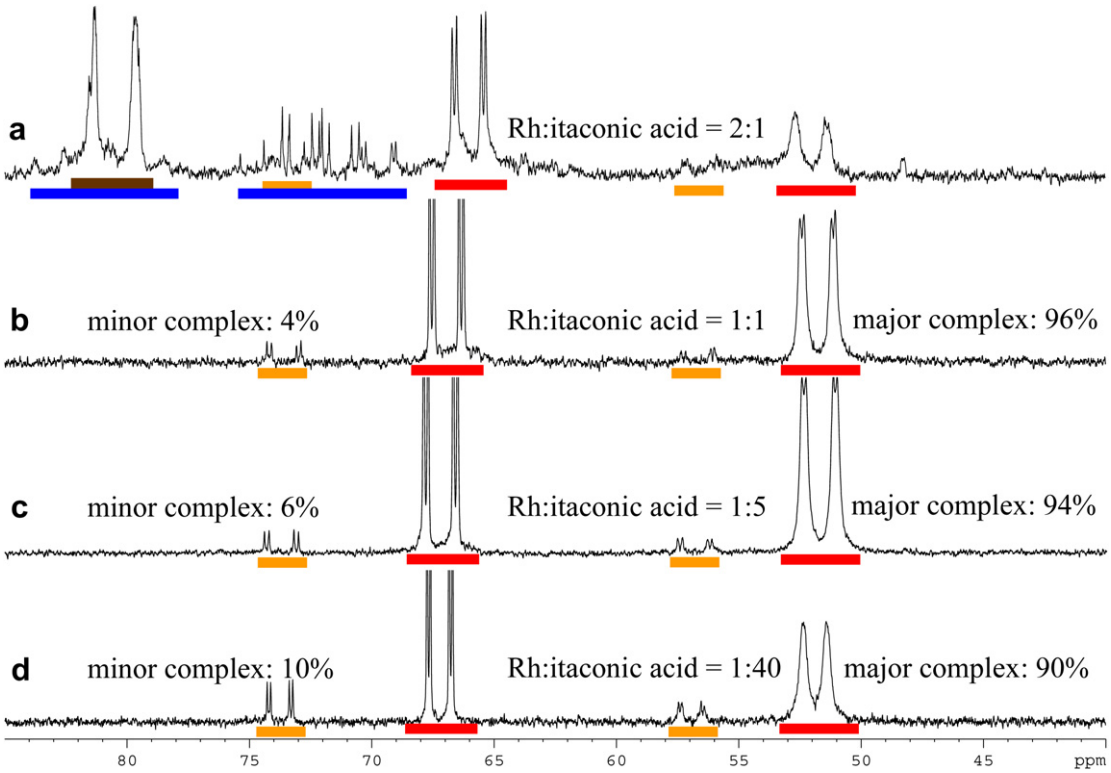


Fig. 1. Room temperature ^{31}P NMR spectra of solutions of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid in CD_3OD at different Rh/substrate ratios, recorded immediately after sample preparation. Red, orange: catalyst-substrate complexes of type **2** (Scheme 1), brown: $[Rh(DIPAMP)(MeOH)_2]BF_4$, blue: dimeric η^6-complexes of type $[Rh(DIPAMP)BF_4]_2$ [11].

^1H NMR spectrum of an authentic sample of β-methyl itaconate (reference spectrum in Fig. 2 Supplementary information). Metal promoted esterification of itaconic acid with a titanium catalyst [14] and of other organic carboxylic compounds [15] has been previously reported in the literature.

A comparison of the ^{31}P NMR spectrum of a solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and β-methyl itaconate in CD_3OD (Fig. 3 Supplementary information) proves that the newly-formed species observed in spectra c and d (Fig. 2, framed signals) is the catalyst-substrate complex with β-methyl itaconate.

3.4. Low-temperature NMR investigations of the formation of catalyst-substrate complexes

In an attempt to intercept the formation of intermediates we [3] and Brown *et al.* [16] tried to freeze out the irreversible formation of

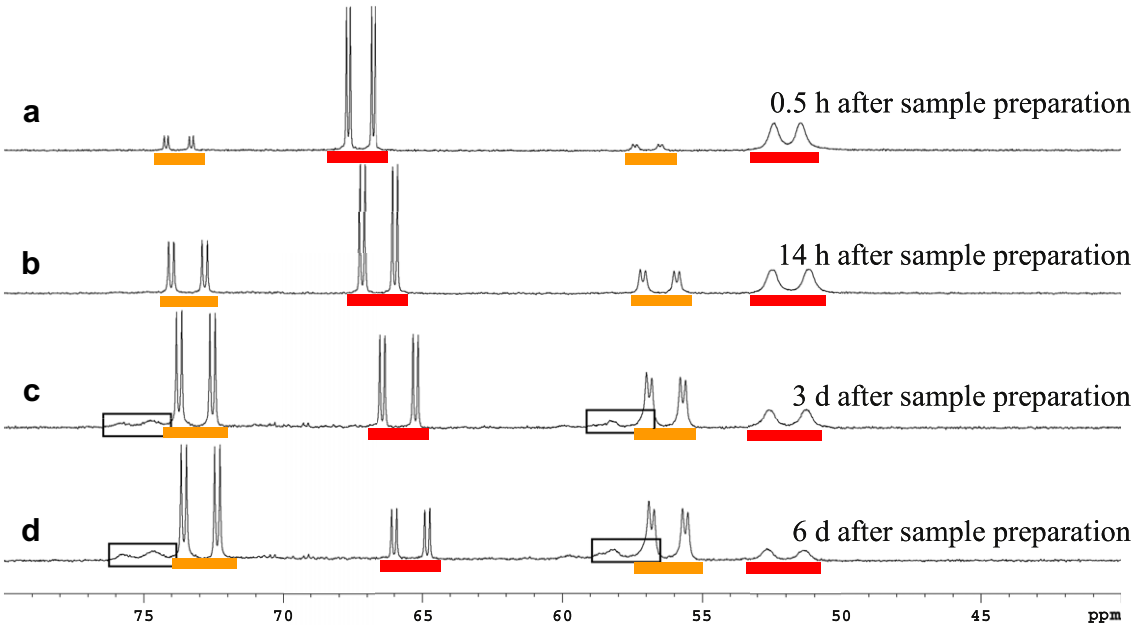


Fig. 2. Time-dependent ^{31}P NMR spectra of a solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid (Rh:substrate = 1:40). The additional appearing signals are framed.

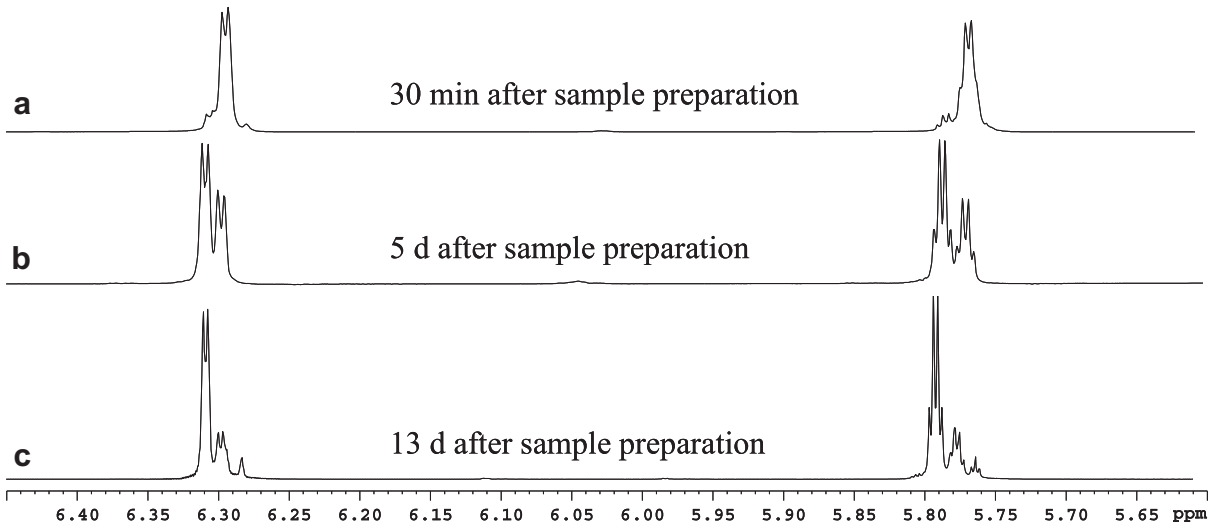


Fig. 3. Section of the time-dependent ^{1}H NMR spectra of a solution of $[Rh(Dipamp)(MeOH)_2]BF_4$ and itaconic acid (1:5) in CD_3OD (the signals correspond to the vinylidenic CH_2 protons of the uncoordinated substrate).

the colorless Rh(III) alkyl complex ((**2**) in Scheme 1), whose X-ray structure we had previously reported [3].

A solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ in CD_3OD was cooled to −60 °C and transferred to a precooled Schlenk tube containing a solution of itaconic acid in the same solvent (Rh/substrate ratio 1:5). After stirring for 1 h, the orange solution was transferred to a Young NMR tube and a ^{31}P NMR spectrum was immediately recorded at −60 °C (Fig. 5, spectrum a).

Beside the signals of the aryl-bridged Rh-DIPAMP dimers [11] characteristic signals of a catalyst-substrate complex were found, whereas the solvent complex could not be detected [17]. The $J(^{31}P, ^{31}P)$ coupling of the observed substrate complex is 41 Hz and thus in the range of the $J(^{31}P, ^{31}P)$ coupling observed in the Rh-DIPAMP substrate complex with dimethyl itaconate [6]. Additionally, a doublet (purple) is detected ($\delta = 73.1$ ppm, $J(^{31}P, ^{103}Rh) = 208$ Hz) whose origin is unknown.

Warming of the sample to room temperature leads to fading of the orange color: the ^{31}P NMR spectrum of the colorless solution is the same as spectrum c reported in Fig. 1. If the solution is cooled back to −60 °C, the ^{31}P NMR spectrum (spectrum b, Fig. 5) does not reproduce spectrum a in Fig. 5. Spectrum b from Fig. 5 is the low-temperature spectrum of the colorless Rh(III) alkyl species (Fig. 4 Supplementary information). The value of the $J(^{31}P, ^{31}P)$ coupling 20.7 Hz and the color change give evidence of a drastic change in substrate coordination. In accordance with results by Brown *et al.* [16], our findings confirm the proposed formation of a bis-chelate complex of itaconic acid with the Rh-DIPAMP solvent complex, followed by its irreversible transformation into a Rh(III) alkyl complex [3].

3.5. Influence of acidic and basic additives and of the BF_4^- anion on the ^{31}P NMR signals

From preliminary investigations (see Supp. info of Reference [3]) we noticed that the chemical shifts of the ^{31}P NMR signals of a solution of $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid in CD_3OD differ from those observed in the ^{31}P NMR spectrum of a solution obtained dissolving single crystals of the complex [Rh(DIPAMP)(methyl succinate)] in CD_3OD. In the former sample, formation of the complex [Rh(DIPAMP)(methyl succinate)] releases HBF_4 in solution which is absent in the latter sample.

Fig. 6 shows the ^{31}P NMR spectra of complexes [Rh(DIPAMP)(methyl succinate)] measured at different pH value or in the presence of variable amounts of BF_4^-. The complexes are either formed "*in situ*" by reacting $[Rh(DIPAMP)(MeOH)_2]BF_4$ and itaconic acid in the ratio of 1:1 (d) or by dissolving single crystals of [Rh(DIPAMP)(methyl succinate)] in CD_3OD (a). NEt_3 was chosen as basic additive, a solution of HBF_4 in diethyl ether as the acidic one.

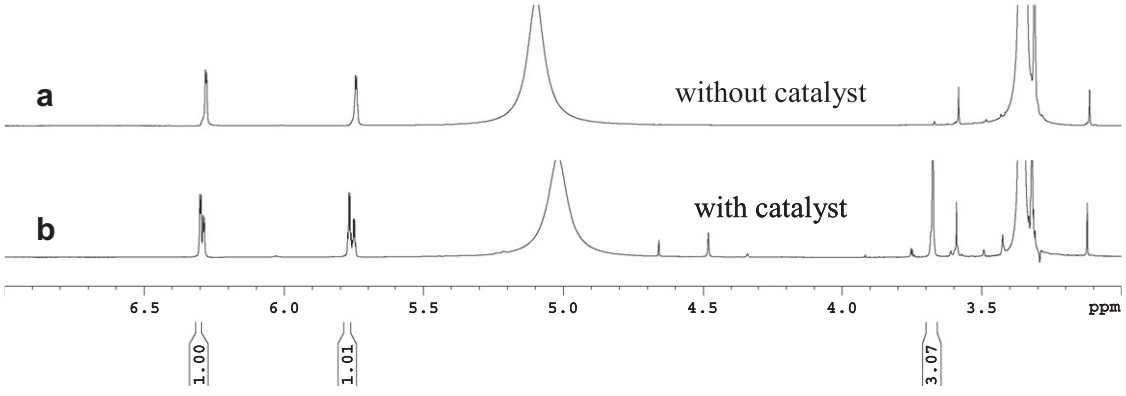


Fig. 4. ^{1}H NMR spectra of the solutions of itaconic acid (with no added $[Rh(DIPAMP)(MeOH)_2]BF_4$, spectrum a; in the presence of $[Rh(DIPAMP)(MeOH)_2]BF_4$), spectrum b) equilibrated over 5 days in CH_3OH, after solvent evaporation and dissolution in CD_3OD.

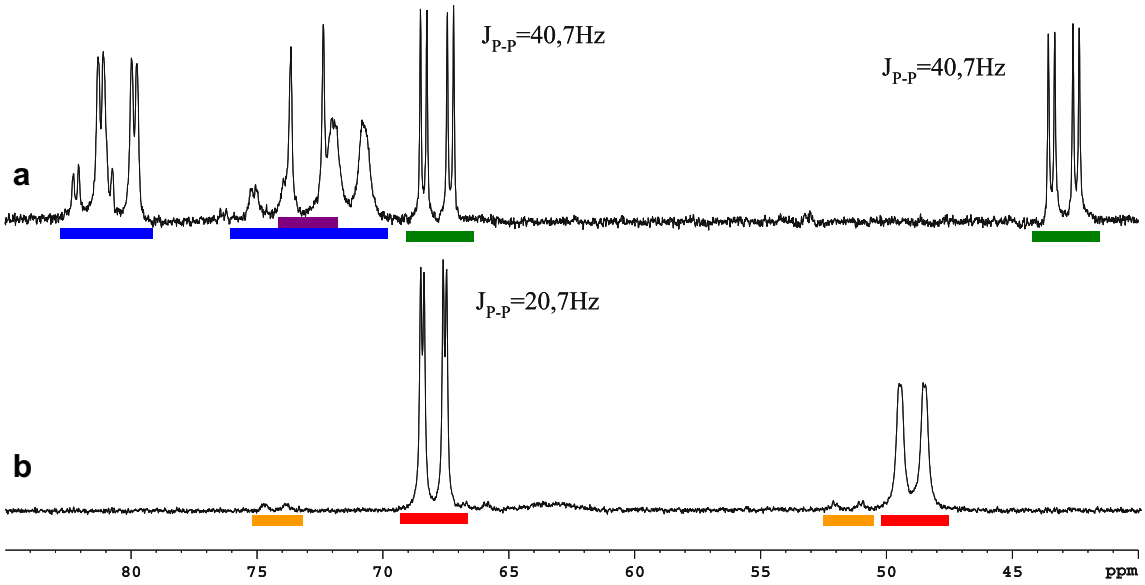


Fig. 5. ^{31}P NMR spectra of [Rh(DIPAMP)(MeOH)$_2$]BF$_4$ after addition of five equivalents of itaconic acid at −60 °C (a): measured after 1 h equilibration at −60 °C (b) measured after 2 h equilibration at 25 °C, followed by cooling to −60 °C. Green: catalyst-substrate complex type **1**, orange, red: catalyst-substrate complex type **2**, blue: [Rh(DIPAMP)(BF$_4$)]$_2$, purple: unknown species.

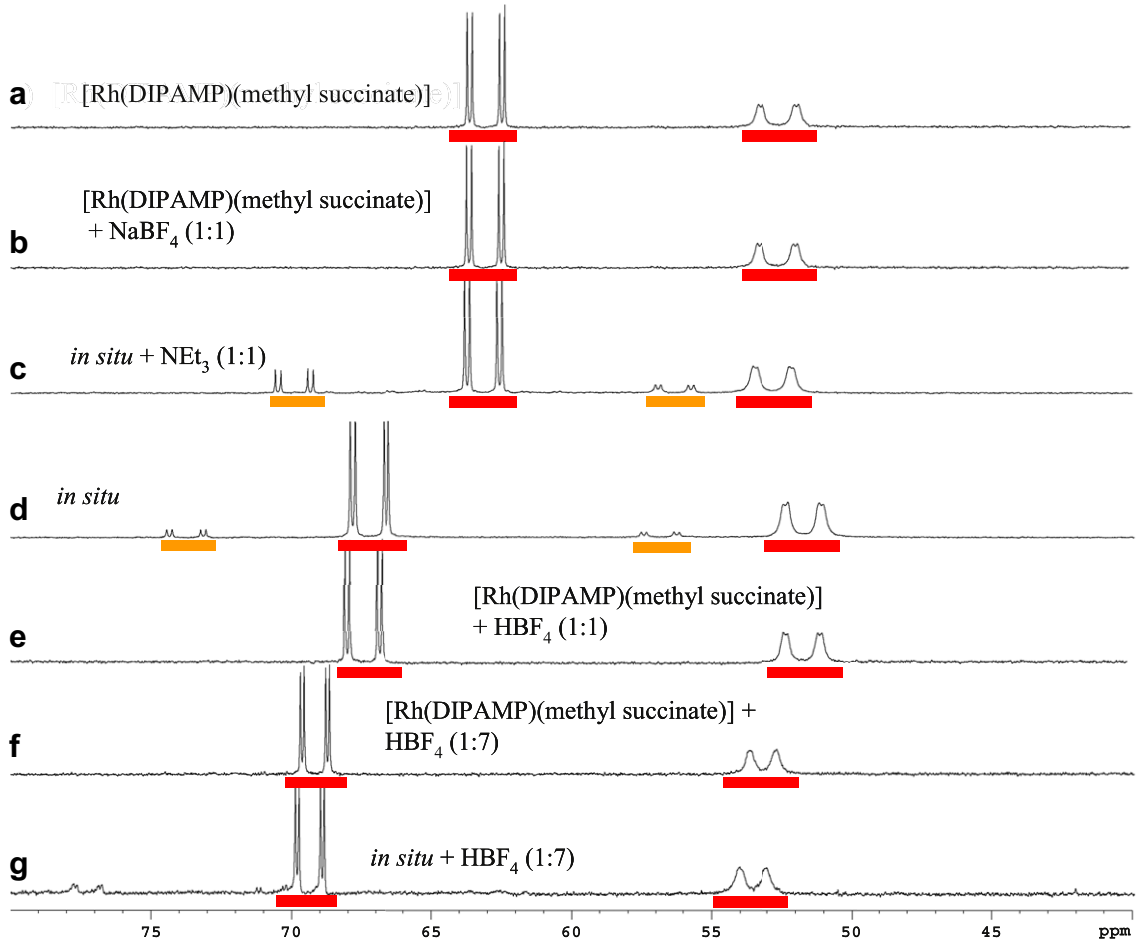


Fig. 6. Influence of basic and acidic additives and/or BF_4^- anion concentration on the ^{31}P NMR spectra: a), b), e), f): single crystals of [Rh(DIPAMP)(methyl succinate)] dissolved in CD$_3$OD; c), d) g): *in situ*-preparation [Rh(DIPAMP)(MeOH)$_2$]BF$_4$ and itaconic acid (1:5) in CD$_3$OD.

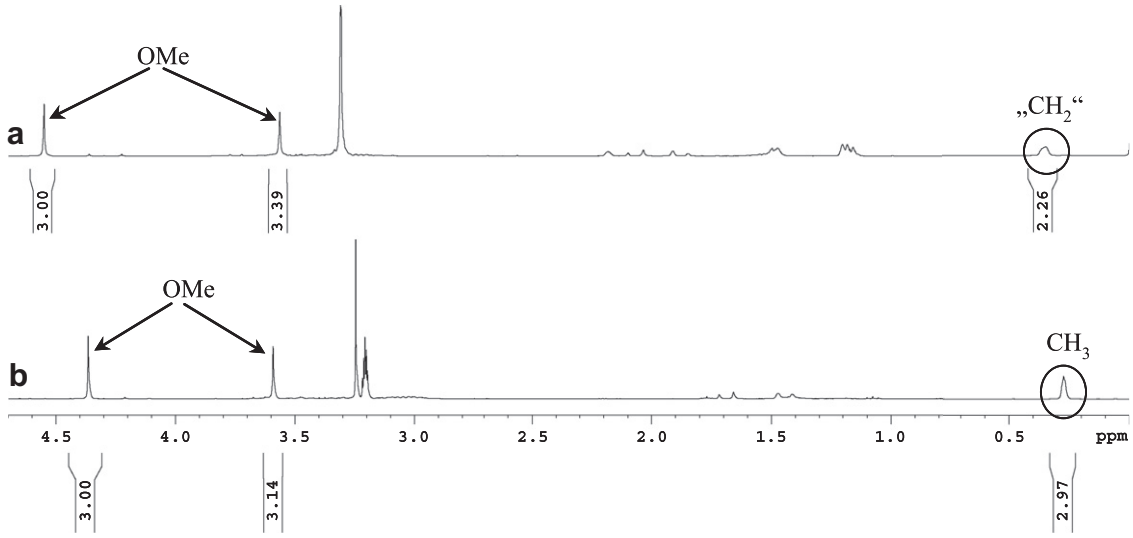


Fig. 7. ^{1}H NMR spectrum sections (0–4.7 ppm) of a) [Rh(DIPAMP)(MeOH)$_2$]BF$_4$ and itaconic acid (1:5), b) dissolved single crystals of [Rh(DIPAMP)(methyl succinate)] in CD$_3$OD.

Examples are reported in the literature showing the influence of counterions on the chemical shifts of cationic complexes [18]. In the present case, the addition of NaBF$_4$ to a solution of [Rh(DIPAMP)(methyl succinate)] has no influence on the ^{31}P NMR signals (compare spectra a and b, Fig. 6). Therefore we assume no strong interaction of the anion with the investigated catalyst-substrate complex.

However, the pH of the solutions strongly influences the chemical shifts. Spectra a–c, d and e, f and g refer to solutions which have comparable pH values, respectively [19]. Consistently, the major signals in the spectra of each group have almost the same shift. The left major signal is shifted to lower fields with increasing acid concentration. The same shift is observed for both minor signals. However, the shift of the right major signal changes irregularly.

It has to be mentioned that the minor catalyst-substrate complex is never observed in the spectra of solutions obtained by dissolving single crystals of [Rh(DIPAMP)(methyl succinate)] (spectra a, b, e, f, Fig. 6). This provides evidence that the interconversion between the catalyst-substrate complexes is kinetically hampered. This behavior, which is at variance with what observed with α- and β-dehydroamino acid derivatives whose catalyst-substrate adducts do interconvert, can be explained by the terdentate substrate coordination.

Under basic conditions, the major catalyst-substrate complex precipitates from the solution. Its crystal structure has been previously reported [3]. This explains the higher relative amount of the minor diastereomer observed in spectrum c compared to spectrum d. Because both the J(^{31}P, ^{103}Rh) and J(^{31}P, ^{31}P) couplings do not vary with pH, we assume that the same complex type is observed in all spectra, namely type **2** (Scheme 1). The drift of the chemical shifts with pH is attributed to the chemical environment of those complexes.

3.6. Structure of the catalyst-substrate complexes in solution

As the ^{31}P NMR spectra of the *in situ* generated major substrate-complex and of the dissolved single crystals of [Rh(DIPAMP)(methyl succinate)] differ, we set out to investigate the complex

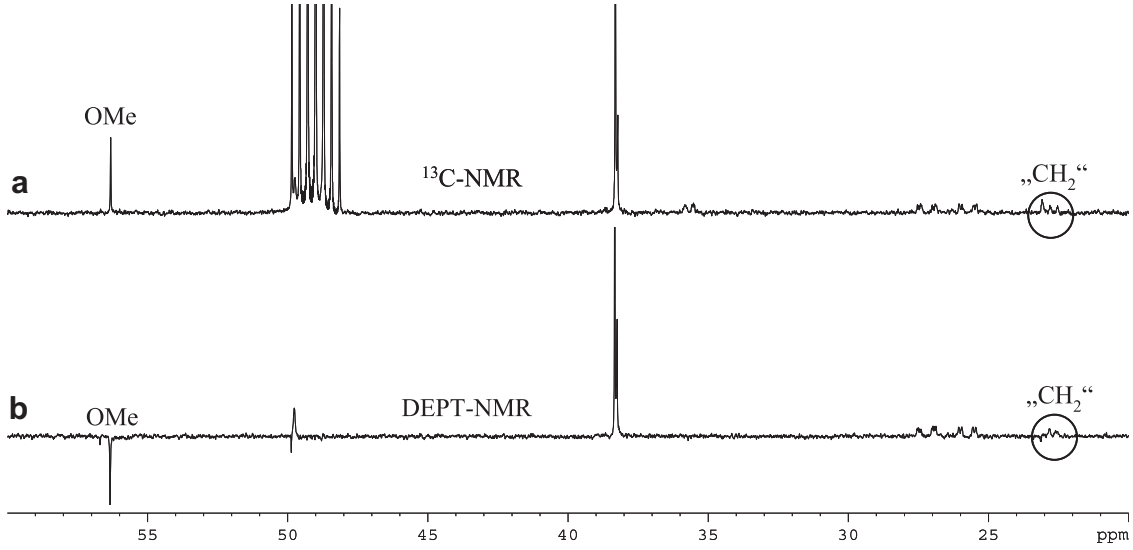


Fig. 8. Section of ^{13}C NMR and DEPT-NMR measurements (20–60 ppm) of a solution of [Rh(DIPAMP)(MeOH)$_2$]BF$_4$ and itaconic acid (1:5) in CD$_3$OD.

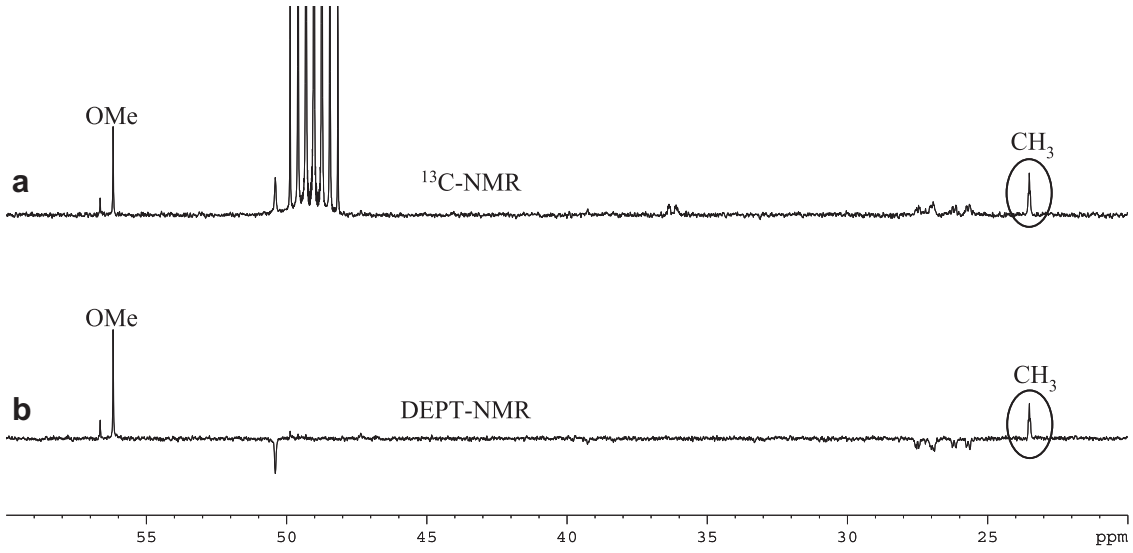


Fig. 9. Sections of ^{13}C NMR and DEPT-NMR measurements (20–60 ppm) of a solution of single crystals of [Rh(DIPAMP)(methyl succinate)] in CD_3OD.

formation in more detail. One problem to be addressed concerns the mode of substrate coordination in solution: according to Brown and coworkers it takes place through the C–C double bond [16], whereas our findings show that coordination involves the formation of a Rh–C bond (and the consequent formation of a CH_3 group). Such binding mode has been confirmed by X-ray analysis [3]. In this section we discuss only selected NMR data. For extensive NMR data, please refer to the Supplementary information.

Fig. 7 shows a comparison between the ^{1}H NMR spectra of a freshly prepared solution of [Rh(DIPAMP)$(MeOH)_2$]BF_4 and itaconic acid (1:5) in CD_3OD and a solution of single crystals of the complex [Rh(DIPAMP)(methyl succinate)] in CD_3OD. As integral reference the more downfield shifted methoxy signal of the DIPAMP ligand was used.

While in case of the *in situ* generated catalyst-substrate complex (spectrum a, Fig. 7) the integral of the CH_2 group is 2,26 (which corresponds more to a methylene than a methyl group), in case of the dissolved crystals of the isolated substrate complex (spectrum b, Fig. 7) an integral of 2.97 (methyl group) is found.

These findings are confirmed by the measurement of ^{13}C- and DEPT-NMR spectra (Fig. 8 [20]). Again, the *in situ* generated complex provides a CH_2 signal which is, however, a triplet. The spectra of the dissolved single crystals of [Rh(DIPAMP)(methyl succinate)] give a CH_3 signal (Fig. 9). Obviously, the chemical shifts of both signals are almost identical as is also true for the discussed signals in the ^{1}H NMR.

The presence of different groups (either $-CH_2-$ or $-CH_3$) seems to be inconsistent, as the single crystals of [Rh(DIPAMP)(methyl succinate)] were isolated from the *in situ* generated solution.

This however can be explained by an H/D exchange of the carboxylic protons with the deuterated solvent, followed by a D-transfer to the methylene group of the coordinated substrate upon formation of the Rh(III) alkyl complex. The detected CH_2 unit is in fact a CH_2D group. This explanation is consistent with the triplet pattern observed in the ^{13}C- and DEPT-spectra recorded after *in situ* complex generation. The complex [Rh(DIPAMP)(methyl succinate)] was isolated from undeuterated methanol, thus explaining the presence of a CH_3 group.

Further evidence for deuterium incorporation from CD_3OD is provided by isolation of single crystals of [Rh(DIPAMP)(methyl succinate)] from a solution of [Rh(DIPAMP)$(CD_3OD)_2$]BF_4 and itaconic acid in CD_3OD: the ^{1}H NMR spectrum of the solution obtained by dissolving such crystals in CD_3OD [21] shows the presence of a vinylidenic CH_2 unit (Fig. 5 Supplementary information). When the complexes are prepared *in situ* in CD_2Cl_2 NMR investigations indicate the presence of a methyl group (Figs. 6–8 Supplementary information).

Because no H/D exchange takes place when single crystals of [Rh(DIPAMP)(methyl succinate)], isolated from undeuterated methanol, are dissolved in CD_3OD, complex formation must be *irreversible*.

4. Conclusions

Itaconic acid forms two very stable, colorless Rh(III) alkyl complexes (type **2**) with [Rh(DIPAMP)$(MeOH)_2$]BF_4 at room temperature, that are probably diastereomers. The ratio of the formed complexes varies with time and substrate concentration, unlike similar known complexes of the Rh-DIPAMP system with dehydroamino acid derivatives, which can be attributed to type **1**. Furthermore, esterification of the β-carboxylic group of the substrate with the solvent methanol was observed. The chemical shift of the complex signals in the ^{31}P NMR spectra is influenced by acidic and basic additives but not by the BF_4^- anion concentration. The structure of the isolated catalyst-substrate complex [Rh(DIPAMP)(methyl succinate)] as shown by X-ray analysis is retained in solution, independent of the mode of sample preparation (*in situ* formation vs. dissolution of single crystals of preformed complex). An H/D exchange in CD_3OD is responsable for the dependence of the metheyl group signal shape on the mode of sample preparation.

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Appendix A

Supplementary material CCDC 690298 (2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix A. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.12.020.

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[7] The X-ray structure of the complex surprisingly revealed that the substrate is not coordinated via the C–C double bond and one carboxylate oxygen, but instead via the two carboxylate oxygens and the quaternary carbon [C(2)] atom. Formally the acidic functions of the substrate had been completely deprotonated and the methylene group had been already converted into a methyl group via H-transfer. The tetrafluoroborate anion was no longer present in the crystal as the counterion. Thus, the complex represents a neutral Rh(III) alkyl complex, compare Reference [3].

[8] Since the substrate in the described Rh(III) alkyl complex contains a CH_3 group instead of the former vinylidenic CH_2 group we use *methyl succinate* instead of *itaconate*. A reasonable mechanism for the formation of this complex is proposed in Ref. [3].

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[19] Upon formation of [Rh(DIPAMP)(methyl succinate) from itaconic acid and [Rh(DIPAMP)$(MeOH)_2$]BF_4, 1 equivalent HBF_4 is released (for details refer to Ref. [3]). Because HBF_4 is a strong acid and NEt_3 is a strong base, we assume that an equimolar solution of the two species should be neutral.

[20] The correlation was carried out via $^1H–^{13}C$ measurements.

[21] The X-ray analysis of the complex isolated from CD_3OD shows that it is the same catalyst-substrate complex for which the X-ray structure had been previously reported in Ref. [3]. Unfortunately, it was impossible to conclude from the data whether an H or D atom had been transferred to the vinylidenic CH_2 group.