Operando Infrared Spectroscopic and Quantum-chemical Studies on Iridium-catalyzed Hydroformylation

Dieter Hess^a, Bernd Hannebauer^b, Matthias König^a, Matthias Reckers^a, Stefan Buchholz^a, and Robert Franke^{a, c}

^a Evonik Industries AG, Paul-Baumann-Straße 1, 45772 Marl, Germany

^b AQura GmbH, Evonik Industries, Rodenbacher Chaussee 4, 63457 Hanau, Germany

^c Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Reprint requests to Prof. Dr. R. Franke. E-mail: robert.franke@evonik.com

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

Hydroformylation of 1-butene using a triphenylphosphine-modified iridium catalyst was investigated by operando infrared spectroscopy. The spectra were interpreted by comparison with quantumchemically calculated vibrational spectra at the density functional theory level. The processes during activation of the catalyst and hydroformylation were investigated in detail, and the results are discussed. The recently discovered phenomenon of activity enhancement in iridium-catalyzed hydroformylation by a preceding activation step, in which the reaction mixture is treated with synthesis gas containing an excess of carbon monoxide under pressure, could be correlated with the appearance of a complex HIr(PPh₃)(CO)₃. The similarities and differences between iridium- and rhodium-catalyzed hydroformylation are discussed.

Key words: Hydroformylation, Rhodium, Iridium, Triphenylphosphine, Operando Spectroscopy, Density Functional Theory

Introduction

Hydroformylation is the addition of synthesis gas (a mixture of carbon monoxide and molecular hydrogen) to an olefinic double bond in the presence of a catalyst. This results, in principle, in a 100% atomefficient conversion to aldehydes (disregarding some side reactions and the required regioselectivity), as shown in Scheme 1.

Hydroformylation is among the most important industrial-scale processes for the production of aldehydes. These are usually processed further to give alcohols, which are used as solvents, and in the production of surfactants and plasticizers. The capacity for oxygen compounds produced by hydroformylation was 10.4 m (10.4×10^6) metric tons in the year 2008. Typical production plants have annual capacities of several hundred thousand tons. In industrial processes, the reaction is exclusively homogeneously catalyzed, with cobalt and rhodium being used as catalysts. As for the cobalt, relatively high temperatures and pressures are required, typically 140 °C and syn-



Scheme 1. Linear and branched aldehydes formed by hydroformylation.

thesis gas pressures exceeding 200 bar. In the early 1970s the first rhodium-catalyzed processes were established commercially; these had considerable economic advantages in that the reaction could be carried out at relatively moderate temperatures of around $100 \,^{\circ}$ C and pressures below 100 bar. While the cobaltcatalyzed processes are mostly carried out without ligand modification, the rhodium-based processes typi-

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cally use phosphines or phosphites. Since the advent of the rhodium-catalyzed processes, research has concentrated mainly on this area. References [1] and [2], for example, provide an overview of the field. The reader is also referred to a recent review on applied hydroformylation [3]. The use of rhodium in hydroformylation always poses an economic risk, however: The material is one of the costliest of all precious metals. The already heavy demand for the metal is expected to increase still further in the future, not the least due to its use in automotive catalysts. Rhodium is obtained from only a few mines restricted to a single country (South Africa currently supplies over 80% of the rhodium demand), and the rhodium market is generally very small and narrow, resulting in massive price volatility, and thus providing incentive for research into the potential of alternative metals such as the precious metals Ru, Pd, Ir, and Pt and the commonly occurring Fe. So far, however, there has been little work in this field. One possible reason is the prevailing opinion on the activity of unmodified transition metal carbonyl complexes in hydroformylation [4]. According to this, the metals listed above show activity that is lower than that of rhodium by several orders of magnitude. Generalization of this result is clearly unwarranted, however, because the observation applies only to specific reaction conditions, and modification of the ligands or the use of special reaction conditions in particular can lead to different catalytic behavior. This has also been convincingly demonstrated very recently by Beller et al. for Pd [5] and Ir [6]. In the work on iridium, it was possible to formulate a generally applicable set of rules by which the hydroformylation of a wide range of substrates is possible, with activities at most only eight times lower than for rhodium catalysis. It is of particular commercial interest that this hydroformylation can be carried out with an easily accessible and very inexpensive ligand, triphenylphosphine (TPP). The solvents are those typically used in industrial organic chemistry, and the conditions are mild, with temperatures of around 100 °C and pressures below 50 bar. A key factor is a special preformation of the catalyst in either of two ways. In the first method, the mixture is initially treated with synthesis gas containing an excess of carbon monoxide, synthesis gas with a 1 : 1 CO/H₂ ratio being used only when the reaction mixture has attained the reaction temperature. Alternatively, a preformation step is performed with pure carbon monoxide before the hydroformylation reaction, and the resulting

catalyst precursor is then used in a hydroformylation at the reaction temperature. These measures significantly suppress the side reaction of olefin hydrogenation. The regioselectivity of the aldehyde products lies in the range of values typical for rhodium-catalyzed hydroformylation with a similar ligand-to-metal ratio. Neither the nature of the iridium species formed in this process nor the reaction mechanisms involved in the advantageous modification of the iridium-catalyzed hydroformylation are as yet clear. This work therefore presents operando infrared spectroscopic studies and quantum-chemical calculations on the vibrational spectra, to help clarify these observations.

Results and Discussion

Reference [6] describes a catalyst system that shows the best known catalytic activity to date for iridiumcatalyzed olefin hydroformylation. The catalyst precursor used is Ir(COD)(acac) with 8 equivalents of PPh₃. The iridium catalyst system so generated shows a catalytic activity with a turnover frequency (TOF, the amount of reactant converted (turned over) divided by the amount of catalyst used and the time) of 163 h^{-1} ; this is lower only by a factor of 8 than the TOF of a comparable rhodium/triphenylphosphine catalyst for hydroformylation of 1-octene. The quantity of catalyst used in the reaction was 0.2 mol-% relative to the amount of 1-octene used. A prerequisite for good hydroformylation results is a preactivation in which 7 bar CO is applied at room temperature. After heating to the reaction temperature, 100 °C, synthesis gas (CO: H_2 in the molar ratio 1 : 1) is introduced under pressure. The reaction is carried out in tetrahydrofuran, which has good dissolving power for CO and H₂. In the present work, operando infrared spectroscopy supported by quantum-chemical calculations on the density functional theory (DFT) level are used to identify the processes occurring during activation of the catalyst as well as the nature of the corresponding intermediates in the activation.

Preliminary experiments were first carried out in which, by varying the pressure in the range 10-50 bar, the temperature between 20 and 100 °C, and the CO partial pressure, changes could be observed in the CO stretching region of the IR spectrum. 1-Butene, and not 1-octene as in reference [6], was used as the olefin for hydroformylation experiments. This was done with a view to possible industrial implementation: Due to its

lower activity as compared with rhodium, the iridium catalyst system, even with the improvements described in reference [6], would not have come into question for the relatively challenging branched C8 olefin mixture. The catalyst system is, however, definitely of industrial interest for C4 mixtures. To 80 mmol of 1-butene were added 0.04 mol-% of metal precursor and 8 equivalents of PPh₃. The solvent used was isohexadecane, which is well suited for IR measurements, having a high boiling point and little absorption in the CO stretching region of the IR spectrum. Fig. 1 shows the spectra obtained after compression of synthesis gas to 10 bar in an autoclave during the heating phase. Absorption bands developed at 2073, 2044, 1998, 1981, 1945, and 1936 cm⁻¹, some of which appeared on treatment with pressurized synthesis gas even at room temperature. When the pressure was increased to 20 bar, the absorption bands at 2044 and 1981 cm⁻¹became more intense. We assign these to a complex HIr(CO)₃PPh₃ (complex A), described by Drakesmith and Whyman as having absorption bands at 2046 (mw), 1982 (s), and 1948 cm⁻¹ (w) [7]; conversely, the bands at 2073, 1998, 1945, and 1936 cm^{-1} , for which we postulate a complex $HIr(CO)_2(PPh_3)_2$ (complex B), decrease in intensity. Cooling from 120 to 50 °C does not change the spectra appreciably. On the other hand, a change in the pressure of the synthesis gas from 20 to 5 bar led to significant intensification of the bands of complex B and a weakening of those of complex A. Fig. 2 shows spectra recorded after a change of CO partial pressure to 16.25 bar at a total pressure of 25 bar (65 vol.-% CO) and a temperature of 50 °C. The absorption bands of complex A were significantly stronger while the intensity of the remaining bands was



Fig. 2. Preliminary experiment: metering of 7.5 bar CO and compression to 25 bar at 50 $^{\circ}$ C; CO excess with CO to H₂ ratio of 65 to 35.

reduced, in some cases almost to extinction. A change of partial pressure to 14 vol.-% CO for a total pressure of 25 bar at 80 °C led to the opposite effect, an intensification of the bands of complex B and a weakening of those of complex A (Fig. 3). In reference [6] treatment with CO was carried out before applying pressurized synthesis gas. In line with these experiments, we carried out the following hydroformylation experiments at 100 and 120 °C and total pressure 20 bar, using 0.04 mol-% of iridium, a 2.5-fold excess of triphenylphosphine, 1-butene as the olefin, and isohexadecane as solvent. In these experiments, 7 bar CO was first applied. Under this pressure, the mixture was heated to the reaction temperature and treated with 20 bar synthesis gas, and the reaction was initiated by metering in 1butene. Fig. 4 shows first the spectra taken during the



Fig. 1. Preliminary experiment: heating to $100 \,^{\circ}$ C under 10 bar synthesis gas.



Fig. 3. Followed by H_2 addition up to 25 bar H_2 at 80 °C, resulting in excess H_2 with H_2 to CO ratio of 86 to 14.



Fig. 4. New experiment: 7 bar CO, heating to 120 °C.

heating phase under CO; in contrast to earlier studies, no hydrogen was present. Absorption bands were observed at 2073, 2044, 1999, and 1981 cm⁻¹. After feeding in synthesis gas to a final pressure of 20 bar (Fig. 5), only the absorption bands at 2044 and 1981 cm^{-1} remained. During the period of the reaction with 1-butene there were no significant variations in the CO stretching region of the IR spectrum. A notable feature here is that the absorption bands that were ascribed to complex B in the preliminary experiment did not appear distinctly when the catalyst was preactivated with CO and the reaction carried out with a $CO:H_2$ ratio of 2:1. Fig. 6 shows the spectrum obtained when synthesis gas was fed in at 7 bar without CO preactivation, the reactants heated to 80 °C at this pressure, and the gas pressure then increased to 20 bar. Absorption bands appeared at 2073, 2044, 1999, and 1981, with a shoulder at 1945 cm⁻¹. The complex B of the preliminary experiments was therefore also formed here in significant amounts.

In order to be able to interpret the complex vibrational spectroscopic results, we use quantum-chemical calculations at the DFT level. Comparison of the theoretical spectra with those from quantum-chemical calculations allows inferences to be drawn on the structure of the species present in the experiment. We cite here as an example a study on rhodium complexes with a new diphosphite that is highly selective in hydroformylation [8]. We carried out theoretical investigations on a number of iridium species as potential candidates from which we will document and discuss below the structures relevant to the present work.

The band pattern of Fig. 4 (obtained after addition of 7 bar CO at room temperature followed by heat-



Fig. 5. Treatment with synthesis gas to 20 bar at 120 °C.



Fig. 6. Additional experiment without CO activation: direct treatment with synthesis gas to 20 bar at $80 \,^{\circ}$ C.



Fig. 7. IR spectrum of the iridium compound after preactivation with CO at 7 bar and heating to 100 °C (pure component spectrum after BTEM analysis) and comparison with results of DFT calculations for possible complex structures. ("acac^m" = singly coordinated acac).

ing) can be explained by a combination of structures: One probable complex is $Ir(COD)(acac)(PPh_3)(CO)$, for which the calculation gives a band position of 1983 cm⁻¹. If the COD is removed, the complex $Ir(acac)(PPh_3)(CO)_3$ results, for which band positions are calculated at 2066, 2018 and 1990 cm⁻¹. Agreement with the experimental spectrum is good for a combination of the two structures (Figs. 7, 8 and 9). An interesting feature of the complex in Fig. 9 is that one oxygen atom of the acetylacetonate is no longer bound to the metal but forms a bond in the direction of a CO molecule, with deformation of the metal C-O axis. After activation of the catalysts under synthesis gas is complete, three



Fig. 8. Molecular structure of $Ir(COD)(acac)(PPh_3)(CO)$ with singly bonded acac as obtained by geometry optimization.



Fig. 9. Molecular structure of Ir(acac)(PPh₃)(CO)₃ with singly bonded acac as obtained by geometry optimization.

complexes are essentially observed (Figs. 10 to 12): first, the complex $HIr(PPh_3)(CO)_3$ (Fig. 10) with axial coordination of the triphenylphosphine ligand (calculated band positions 2041, 2026 and 1981 cm⁻¹; this corresponds well to complex A of the preliminary experiment (Fig. 13); the complex with equatorial ligand coordination does not fit so well with calculated band positions at 2082, 2023, 1989, and



Fig. 10. Molecular structure of $HIr(PPh_3)(CO)_3$ (ax) as obtained by geometry optimization.



Fig. 11. Molecular structure of $HIr(PPh_3)_2(CO)_2$ (eq/ax) as obtained by geometry optimization.



Fig. 12. Molecular structure of HIr(PPh₃)₂(CO)₂ (eq/eq) as obtained by geometry optimization.

1966 cm⁻¹); second, the complex HIr(PPh₃)₂(CO)₂ with the TPP ligands in eq-eq positions (Fig. 12); and third, the complex $HIr(PPh_3)_2(CO)_2$ with the TPP ligands in eq-ax positions (Fig. 11). The second and third complex have calculated band positions at 2071, 1983 and 1945 cm⁻¹ and at 2045, 1982 and 1947 cm^{-1} , respectively (Fig. 14). Such complexes have been described by Yagupsky and Wilkinson [9] with assignment of peaks at 2085 (w), 1992 (s) and 1944 cm⁻¹ (s) ("species A") and 2070 (sh), 1980 (w) and 1935 cm^{-1} (m) ("species B"). Complexes of the type HIr(PPh₃)₃CO with eq-eq-ax [calculated band positions 2076 and 1936 cm⁻¹ (Fig. 15)] and eq-eqeq [calculated band positions 2031 and 1914 cm⁻¹ (Fig. 16)] configurations may also be present (Fig. 17). The former has been described by Bath and Vaska [10], bands at 2068 and 1930 cm^{-1} being assigned to the complex.

For comparison with the work of reference [6], hydroformylation experiments were carried out with 1-butene using the metal precursor Ir(COD)(acac). The results of these experiments are collected in Table 1. An experiment with 1-butene as reactant and Rh(acac)(CO)2 as metal precursor was used for com-

Table 1. Ir- and Rh-catalyzed hydroformylation of 1-butene.



^a Determined by GC; ^b 80 mmol 1-butene, 0.04 mol-% metal precursor, 2.5 eq. PPh₃, 20 bar CO/H₂ = 2/1, 7 bar CO at r. t. and 13 bar syngas introduced at 100 °C, 40 g isohexadecane; ^c 19 h; ^d 17.5 h; ^e 110 mmol 1-butene, 0.018 mol-% metal precursor, 100 eq. PPh₃, 20 bar syngas, 40 g toluene; f 12 h.



Fig. 13. IR spectrum of the Iridium hydride complex $HIr(PPh_3)(CO)_3$ (pure component spectrum after BTEM analysis) compared with spectra of possible structures from DFT calculations.

parison with the analogous rhodium system. Reference [6] gives, for 120 °C and 20 bar with 0.02 mol-% iridium, an aldehyde yield of 65 mol-%, an *n* to iso ratio for the 1-octene starting material of 76 to 24, an *n*-octane yield from hydrogenation of 19%, and a TOF of $163 h^{-1}$. These values are of the same order of magnitude as the data in Table 1. The TOF for iridium-catalyzed hydroformylation is lower than that for the rhodium system by a factor of 52; this means that the iridium catalyst is nowhere near as inactive as suggested by the earlier literature, in which an activity 1000 to 10000 times lower than for rhodium was indicated [11]. For the experiment with rhodium, a ligand excess of about 100 was typically used to strongly inhibit isomerization to internal olefins. The reaction curves for 1-butene for experiments 1 and 2 (Table 1) with the iridium catalyst were linearized assuming first-order kinetics. For a reaction temperature of 100 °C this gives a rate constant of

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Fig. 14. IR spectrum of the Iridium hydride complex (PPh₃)₂(CO)₂ (pure component spectrum after BTEM analysis) compared with spectra of possible structures from DFT calculations.



Fig. 15. Molecular structure of $HIr(PPh_3)_3CO$ (eq/eq/ax) as obtained by geometry optimization.

 $k = 4.8 \times 10^{-3} \text{ min}^{-1}$, and for a reaction temperature of 120 °C a value of $7.9 \times 10^{-3} \text{ min}^{-1}$. An Arrhenius plot then gives an activation energy of 30 kJ mol⁻¹. Murzin *et al.* investigated propene hydroformylation with a rhodium catalyst and a ligand very similar to triphenylphosphine, cyclohexyldiphenylphosphine [12]. The authors have modelled the catalysis cycle with a mixture of two catalysts: The complex with two phosphine ligands leads to linear products due to stronger steric shielding of the rhodium; the complex with one phosphine ligand yields also the internally hydroformylated product 2-methylpropanal.



Fig. 16. Molecular structure of $HIr(PPh_3)_3CO$ (all-eq) as obtained by geometry optimization.



Fig. 17. IR spectrum of the Iridium hydride complex $HIr(PPh_3)_3(CO)$ (pure component spectrum after BTEM analysis) compared with spectra of possible structures from DFT calculations.

By fitting to the kinetic model, the authors obtained a value of $25.2 \text{ kJ} \text{ mol}^{-1}$ for the activation energy. This value is also similar to that we obtained for the activation energy of 1-butene hydroformylation with iridium and triphenylphosphine. In volume [2] edited by van Leeuwen, Casey and Whiteker the authors discuss phosphines as ligands for the hydroformylation of olefines with rhodium. With regard to influences on activity and selectivity, they emphasize the problems associated with the variety of possible complexes and their interconversion, which depends on the reaction conditions. For this reason there have been few systematic investigations at the structural level for the phosphinemodified rhodium hydridocarbonyl complexes. In reference [2], Claver and van Leeuwen describe Rh systems containing triphenylphosphine as a ligand. At $-100 \,^{\circ}\text{C}, 5 - 20 \,\text{bar}, [Rh] = 1 \,\text{mM}, \text{ and } PPh_3/Rh = 5,$ the only absorption bands found by in-situ transmission spectroscopy were those corresponding to the $RhH(PPh_3)_2(CO)_2$ complexes. For the same ligand-tometal ratios as in these IR studies and pressures of up to 4 bar, but significantly higher ligand concentrations of approx. 10 mM, Oswald et al. [13] found in NMR studies that the predominant complex species is then the tris-triphenylphosphine complex. Under standard conditions, therefore, the complex $RhH(PPh_3)_2(CO)_2$ is the predominant species. The dependence on CO partial pressure generally shows a negative reaction order, indicating that the formation of a RhH(PPh₃)(CO)₃ species reduces the catalytic activity.

According to the investigations in reference [6] and our own experience, it is necessary in any process modification with triphenylphosphine to work with excess CO in order to obtain good activity of the iridium complexes. The equilibrium is also shifted by an increasing or decreasing triphenylphosphine concentration for a given metal concentration relative to the quantity of CO dissolved; it follows that for a reduction of metal concentration, an increase in activity can be expected if the more active complex $HIr(PPh_3)(CO)_3$ is formed. This could be the subject of a systematic study of the kinetics of the iridium-triphenylphosphine system, and goes beyond the scope of the present study.

Conclusion and Outlook

In our hydroformylation studies with iridium catalysts following the findings of Beller *et al.* [6] we have contributed toward clarifying the chemistry of the reaction by the use of operando infrared spectroscopy combined with quantum-chemically calculated vibrational spectra. We have succeeded in showing that hydroformylation with iridium and triphenylphosphine differs significantly from that of the rhodium system. For rhodium-catalyzed hydroformylation of 1-olefins, it is known that complexes with two phosphine ligands produce higher yields of terminal aldehydes. Increasing the partial pressure of CO shifts the equilibrium toward complexes with one phosphine ligand and so decreases the *n*-selectivity. Further, it is known that an increase of the CO partial pressures in phosphine-modified rhodium catalysts retards the reaction rate [14]. Complexes with a single phosphine ligand thus have a lower hydroformylation activity than those with two phosphine ligands. The optimum reaction conditions for such systems lie in the region of a slight excess of hydrogen. In the case of a triphenylphosphine-modified iridium catalyst, a 2:1 excess of CO has a positive effect on the activity of the catalyst system, as was shown for the first time in reference [6]. Our investigations now reveal that in this case, as also for the analogous rhodium complex, the complex with a single PPh₃ ligand is favored as the CO partial pressure increases. From this we deduce that, in contrast to the rhodium system, the complex with a single phosphine ligand is the more active. We have thus supplemented the empirical findings of reference [6] by a structurally substantiated hypothesis for clarifying activity enhancement in iridium-catalyzed hydroformylation with the use of excess CO in the activation stages. A detailed quantitative study with systematic investigation of the kinetics of iridium-catalyzed hydroformylation would now be of interest. This would entail, in addition to operando spectroscopic studies, a mathematical modeling in the form of kinetic differential equations and a support of these studies by quantum-chemical calculations for the catalysis cycle. We will be reporting on such studies in the future.

Experimental Section

All oxygen- and moisture-sensitive reagents were handled under argon atmosphere. Syringes and cannulas were purged with nitrogen before use. The autoclave was subjected to a leak test using a CO warning device and purging several times with argon.

Autoclave experiments were performed in Parr 5500 100mL microreactors. The autoclave can be operated up to 150 °C and 60 bar. In the sampling circuit to the infrared transmission cell and back to the autoclave a micro annular gear pump mzr-7255 (HNP Mikrosysteme GmbH, Parchim) was used. This pump has 48 μ L displacement volume. The maximum volumetric flow rate is 17.28 L h⁻¹ at a speed of 6000 min⁻¹. The pump is controlled by the Faulhaber Motion Manger software.

The infrared spectrometer is a Tensor 27 (Bruker Optik GmbH) equipped with a DigiTect-DTGS detector. The spectrometer is operated with the OPUS 6.5 software by Bruker. The infrared transmission liquid cell which can be heated up to 200 °C was manufacured by Bruker. The windows are made of silicon. The cell thickness is 400 μ m. The cell windows are wedged to prevent fringes.

Ir(COD)(acac) was used as an iridium metal precursor. The complex was dissolved in isohexadecane after taking a reference spectrum of the solvent. At 30 °C triphenylphosphine was added in a molar excess of 2.5 relative to iridium. In the next step the solution was compressed up to 7 bar with pure CO, followed by heating to the final temperature (100 or 120 °C). The system was held at this temperature and pressure until no further change was observed in the IR spectrum (about 30 min). Then synthesis gas (molar ration CO:H₂ = 1 : 1) was added at 120 °C until a final pressure of 20 bar was reached. Again the system was allowed to equilibrate for some minutes. Finally the reaction was started by addition of 4.5 g 1-butene.

Pure component spectra were extracted from raw data with the BTEM program (M. Garland, ICES Singapore [15]).

- M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, J. Mol. Catal A: Chem. 1995, 104, 17.
- [2] P. W. N. M. van Leeuwen, C. Claver (Eds.), *Rhodium Catalyzed Hydroformylation*, Springer, Dordrecht, 2002.
- [3] R. Franke, D. Selent, A. Börner, *Chem. Rev.* 2012, 112, doi:10.1021/cr3001803.
- [4] F. P. Pruchnik, Organometallic Chemistry of the Transition Elements, Plenum Press, New York, 1990, p. 691.
- [5] R. Jennerjahn, I. Piras, R. Jackstell, R. Franke, K.-D. Wiese, M. Beller, *Chem. Eur. J.* **2009**, *15*, 6383.
- [6] I. Piras, R. Jennerjahn, R. Jackstell, A. Spannenberg, R. Franke, M. Beller, *Angew. Chem. Int. Ed.* 2011, 50, 280.
- [7] A. J. Drakesmith, R. Whyman, J. Chem. Soc., Dalton Trans. 1972, 362.
- [8] D. Selent, R. Franke, C. Kubis, A. Spannenberg, W. Baumann, B. Kreidler, A. Börner, *Organometallics* 2011, *30*, 4509.
- [9] G. Yagupsky, G. Wilkinson, J. Am. Chem. Soc. (A) 1969, 725.
- [10] S. S. Bath, L. Vaska, J. Am. Chem. Soc. 1963, 85, 3500.
- [11] G. Protzmann, K.-D. Wiese, *Erdöl Erdgas Kohle* 2001, 117, 235.

For all quantum-chemical calculations on model structures in the gasphase the TURBOMOLE program package [16] was used. The geometry was optimized with the BP86 functional [17-19] and the def-SV(P) basis set [20]. Computational vibration wave numbers were corrected by multiplication with the empirical factor 0.99 [21]. The computational result gives the infrared spectrum of the complexes in the gasphase.

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- [12] D. Yu. Murzin, A. Bernas, T. Salmi, *AIChe J.* 2011, in print.
- [13] A. A. Oswald, J. S. Merola, E. J. Mozeleski, R. V. Kastrup, J. C. Reisch, *Adv. Chem. Series* **1981**, *104*, 503.
- [14] N. S. Imyanitov, Hydroformylation of Olefins with Rhodium Complexes – A Review, Rhodium Express 10/11, 3, Russ. Sci. Res. Inst. Petrochem. Proc. St. Petersburg, 1995.
- [15] E. Widjaja, C. Li, M. Garland, Organometallics 2002, 21, 1991.
- [16] TURBOMOLE (version 6.3 2011), A Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, **1989–2007**; TURBOMOLE GmbH (since 2007). See also: R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165. http://www.turbomole.com.
- [17] S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200.
- [18] A. D. Becke, Phys. Rev. A 1988, 38, 3098.
- [19] J. Perdew, Phys. Rev. B 1986, 33, 8822.
- [20] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571.
- [21] A. P. Scott, L. Radom, J. Phys. Chem. 1996, 100, 16502.