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Kinetic and mechanistic investigations in homogeneous catalysis using *operando* UV/vis spectroscopy

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ABSTRACT

This study presents three examples in which the methodological approach of *operando* UV/vis spectroscopy is demonstrated using both submersible optrodes and the stopped flow/diode array technique. First, the submersible optrode is applied for the monitoring of stoichiometric reactions, that is the hydrogenation of cyclooctadiene (cod) in the rhodium diphosphine complex [Rh(Me-DuPHOS)(cod)]BF_4 (Me-DuPHOS = 1,2-bis(-2,5-dimethyl-phospholano)benzene), which is a typical catalyst precursor in asymmetric hydrogenation. Second, the determination of stability constants for rhodium diphosphine arene complexes is shown. The third example presents UV/vis spectroscopy of zirconium and hafnium complexes with ethylene as a gaseous reaction partner using the stopped flow/diode array technique.

1. Introduction

Operando spectroscopy has become a valuable tool to monitor catalysts in action. In homogeneous catalysis with organometallic complexes, UV/vis spectroscopy offers a useful means of analysis due to the fact that such complexes are often coloured and thus show characteristic absorption spectra.

Typically, UV/vis spectroscopy is carried out in a cuvette. If conditions such as stirring, cell tempering or anaerobic conditions are required, reactors with submersible optrodes are advantageous. Furthermore, thermostable conditions and atmosphere control coupled with UV/vis spectroscopy is achievable with this technique. Additional reaction monitoring, e.g. gas consumption, pH, or electrical conductivity, may also be used to expand the range of observed parameters. Thus, the “fibreoptical sensors” serve practically as mobile cuvettes. An example of a reactor for the monitoring of UV/vis spectra and hydrogen consumption used in our group can be found in Ref. [1].

The combination of a diode array with a stopped flow technique allows the spectroscopic monitoring of very fast reactions. For our investigations the J&M Tidas MMS/100-1 and the Bio-Logic μ-SFM-20 were used allowing as little as 5–30 ms per spectrum. In addition, anaerobic conditions are gained using a glovebox, Fig. 1.

A drawback to this rapid method is that usually only solutions can be monitored, which are introduced via syringes, mixed in a mixing chamber and then pass to the cuvette. Reactions with gaseous reaction partners, e.g. hydrogenations, cannot be measured by this technique. However, this problem can be solved by using solutions that in the simplest case are saturated with the gaseous reaction partner.

2. Results and discussion

This study presents three examples in which the methodological approach of *operando* UV/vis spectroscopy is demonstrated using both submersible optrodes and the stopped flow/diode array technique. First, the submersible optrode is applied for the monitoring of stoichiometric reactions, that is the hydrogenation of cyclooctadiene (cod) in the rhodium diphosphine complex [Rh(Me-Du-PHOS)(cod)]BF_4 (Me-Du-PHOS = 1,2-bis(-2,5-dimethyl-phospholano)benzene), which is a typical catalyst precursor in asymmetric hydrogenation. Second, the determination of stability constants for rhodium diphosphine arene complexes is shown. The third example presents UV/vis spectroscopy of zirconium and hafnium complexes with ethylene as a gaseous reaction partner using the stopped flow/diode array technique.

3. Stoichiometric hydrogenation of a rhodium diphosphine diolefin complex

Asymmetric hydrogenation is still of both academic and industrial relevance [2]. Both the selectivity and the activity are important aspects of the hydrogenation process. In asymmetric hydrogenation with rhodium diphosphine complexes so-called

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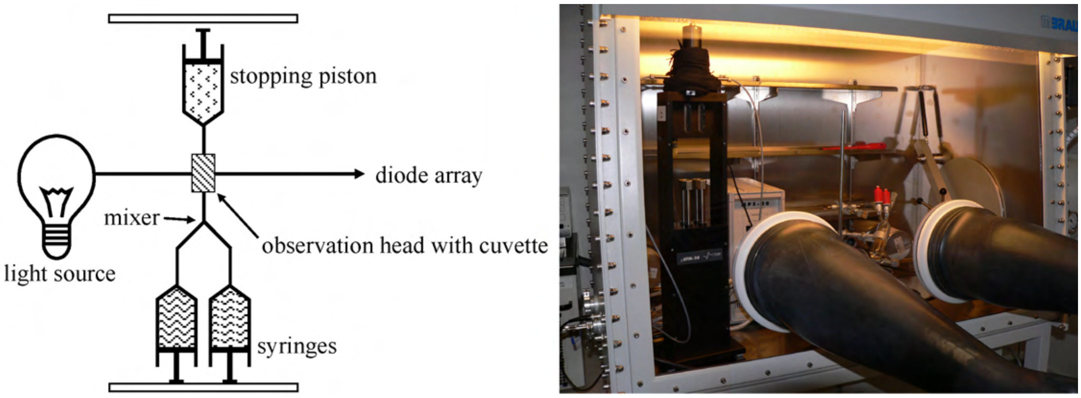
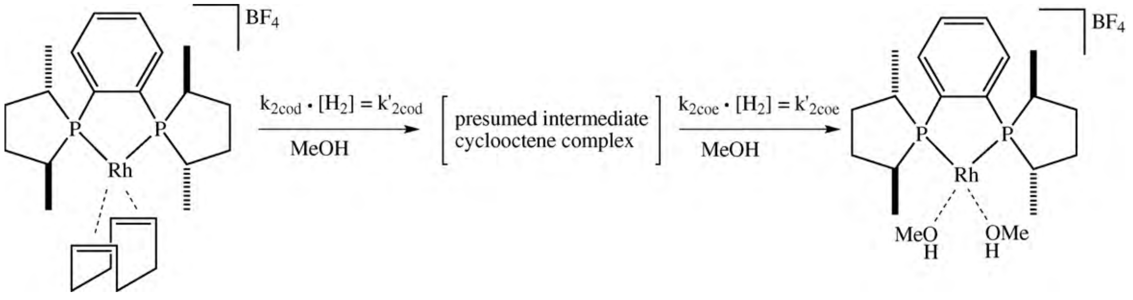


Fig. 1. Design of the stopped flow/diode array technique (left) and glove box with the stopped flow/diode array (right).



Scheme 1. Reaction scheme for the generation of the solvate complex [Rh(Me-DuPHOS)(MeOH)$_2$]BF$_4$.

solvate complexes are regarded as the catalytically active species. The solvate complexes are generated by stoichiometric hydrogenation of diolefin precursor complexes, Scheme 1.

If the presumed intermediate (a cyclooctene (coe) complex) is only present in a very small concentration since $k'_{2\mathrm{coe}} = k_{2\mathrm{coe}} \cdot [\mathrm{H_2}]$ is greater than $k'_{2\mathrm{cod}}$, see also Ref. [3], the formally consecutive reaction can be reduced to a pseudo-first order reaction.

Thus, the question of how long diolefin complexes have to be hydrogenated to gain solvate complexes can be reduced to the determination of the pseudo-rate constants $k'_{2\mathrm{cod}}$. Due to the fact that there is a dependence on diphosphine ligand, diolefin, solvent, temperature and hydrogen pressure, the pseudo-rate constants have to be determined experimentally. This can be accomplished by either stoichiometric hydrogenation of the diolefin in the diolefin complex, e.g. by UV/vis spectroscopy, or by catalytic hydrogenation of an excess of diolefin which is also present in the precatalyst. The latter method is described in full detail in Ref. [4].

For the stoichiometric hydrogenation of [Rh(Me-DuPHOS)(cod)]BF$_4$ in MeOH, the UV/vis reaction spectra result as shown in Fig. 2.

Four isosbestic points are visible and corresponds to a kinetically uniform reaction. So-called extinction diagrams (as “graphical factor analysis”) confirm this, Fig. 3(top) [5]. According to Ref. [3] two absorbing species are in solution: the solvate complex is formed from the diolefin complex, corresponding to a pseudo-first order reaction. From the non-linear curve fit as pseudo-first order reaction of the wavelength dependent absorbance-time-data the desired pseudo-rate constant $k'_{2\mathrm{cod}}$ can be calculated, Fig. 3(bottom). The overall fit with Specfit/32 [6] results in a pseudo-rate constant of 0.119 min^{-1}.

A very interesting possibility to process reaction spectra is the so-called factor analysis. In this analysis the separate spectra of the single reaction partners and thus their progression as a function of time are accessible merely by mathematical routines applied to experimental reaction spectra—without the use of any *a priori* information.

If the Bouguer-Lambert-Beer law is valid, reaction spectra (total absorption) can be described as linear superposition of the absorbances of the participating species in form of a matrix. A rank analysis of this matrix finally provides the desired information. An introduction to this analytic method can be found in Ref. [7]. Concrete applications with several mathematical algorithms and programs are described. A representative application is the Band Target Entropy Minimization (BTEM) from Garland et al., examples for IR spectroscopy can be found in Ref. [8].

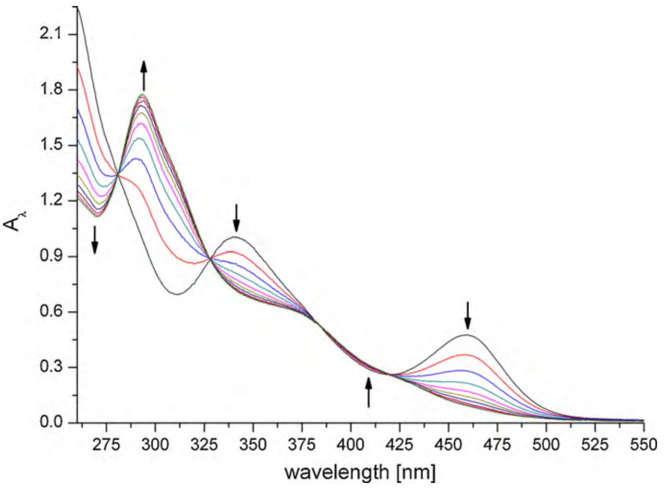


Fig. 2. Reaction spectra for the stoichiometric hydrogenation of 0.01 mmol [Rh(Me-DuPHOS)(cod)]BF$_4$ in 15 mL MeOH at 25 °C and 1 bar overall pressure (cycle time 3 min, layer thickness 0.5 cm).

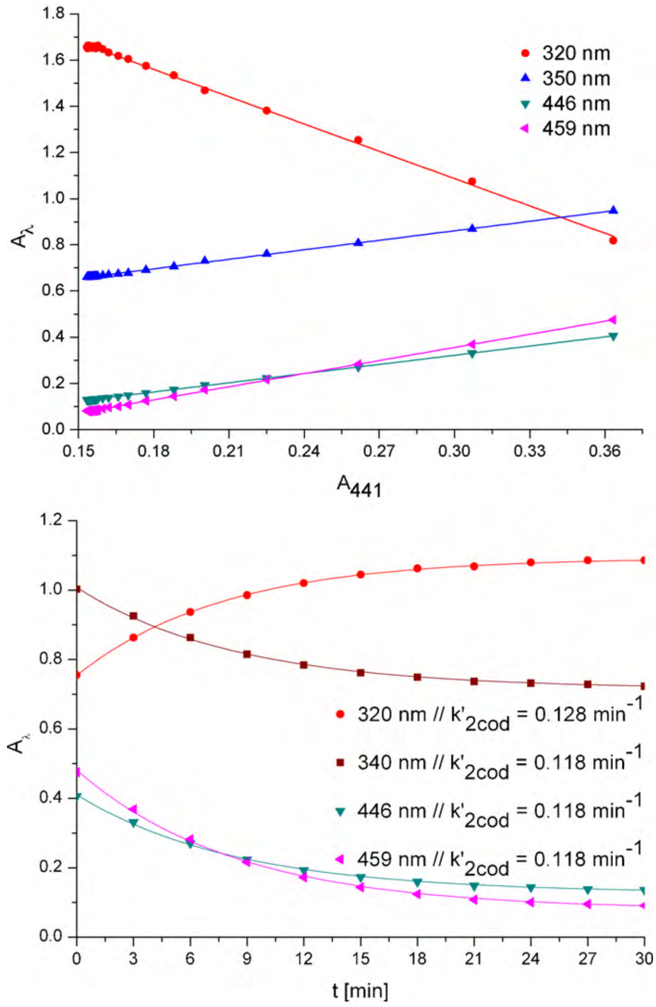


Fig. 3. Extinction diagram (top) and comparison of spectroscopic values (points) and values fitted as pseudo-first order (solid line) for several wavelengths, cp. Scheme 1.

However, this factor analysis (principal component analysis) is already implemented in some analysis packages, for example in Specfit/32 used in our investigations [6].

In addition, the program Pure Component Decomposition (PCD), which was developed at the Institute for Mathematics at the University of Rostock, was included in the calculations of single component spectra [9].

Applying pure component analysis (PCD or Specfit/32) to the example of Scheme 1 and Fig. 2, concentration-time data results are shown in Fig. 4.

Fitting the concentration-time data as a pseudo-first order reaction gives the desired pseudo-rate constant. Due to the fact that both the spectrum of the educt and the product can be measured separately, the result of the pure component analysis can be experimentally validated [10].

4. Determination of stability constants

Besides the investigation of catalytically active species also insights into deactivation phenomena are of interest in homogeneous organometallic catalysis as they might help to understand reaction mechanisms. In asymmetric hydrogenation with rhodium diphosphine complexes, aromatic solvents such as benzene and toluene have the potential to inhibit reactions [11]. For example, the asymmetric hydrogenation of ethyl (*E*/*Z*)-1-methyl-2-benzoyloxy acrylate with [Rh(Et-DuPHOS)(cod)]OTf (Et-DuPHOS = 1,2-bis(-2,5-diethylphospholano)benzene) did not proceed in benzene, whereas in non-aromatic solvents such as MeOH, THF or dichloromethane, the reaction proceeded smoothly [12]. From ^{31}P NMR measurements the authors reasoned that the formation of a stable arene complex [Rh(Et-DuPHOS)(η^6-benzene)]OTf caused the observed inactivity. In fact, systematic investigations on the influence of aromatic solvents in the asymmetric hydrogenation with rhodium diphosphine complexes confirmed the results. Single crystals of the proposed benzene complex with Et-DuPHOS as a chiral ligand could also be isolated and were analyzed by X-ray crystallography [13].

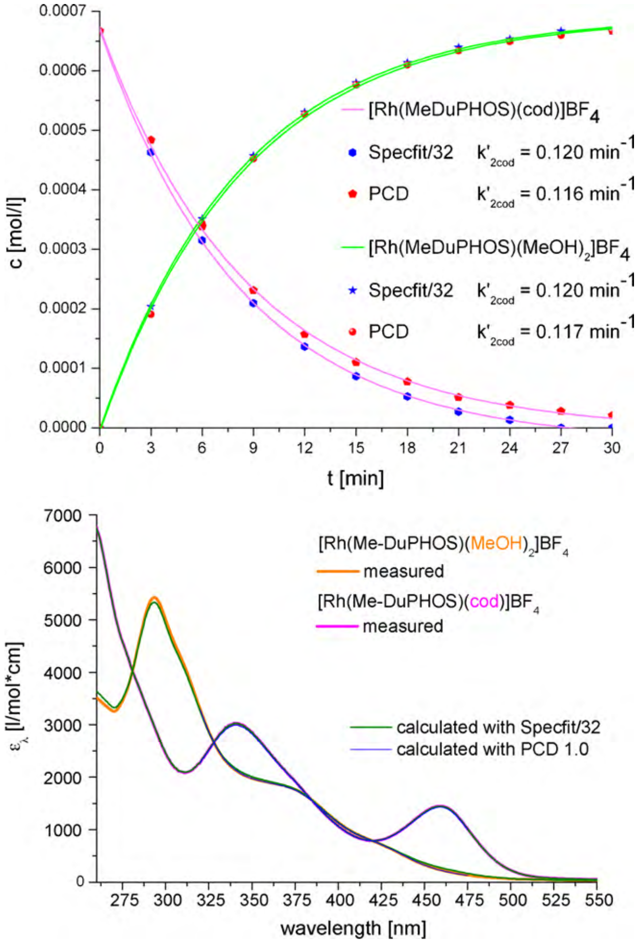
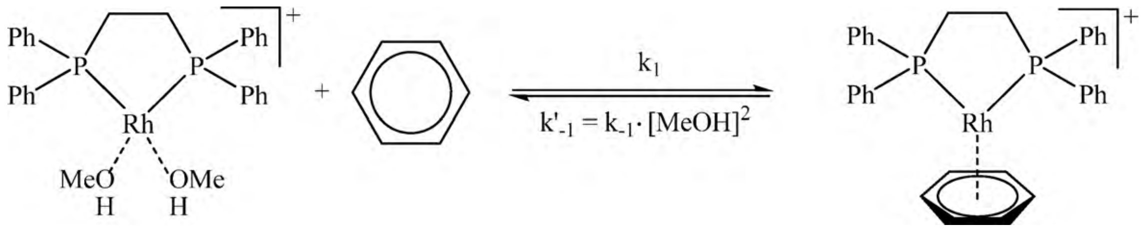


Fig. 4. Concentration-time profile for the hydrogenation of [Rh(Me-DuPHOS)(cod)]BF$_4$ in MeOH (top) and pure component spectra of [Rh(Me-DuPHOS)(cod)]BF$_4$ and [Rh(Me-DuPHOS)(MeOH)$_2$]BF$_4$ (bottom) after pure component analysis. Overall fit of absorbances with Specfit/32: $k'_{2cod} = 0.119\,\text{min}^{-1}$.

However, to the best of our knowledge only one publication exists in which the stability of such rhodium diphosphine arene complexes has been reported [11]. For the achiral ligand DPPE (DPPE = 1,2-bis(diphenylphosphino)ethane) the solvate complex [Rh(DPPE)(MeOH)$_2$]BF$_4$ was titrated with arenes in methanol and the equilibrations were each monitored by UV/vis spectroscopy. Stability constants [Rh(DPPE)(arene)]BF$_4$ with arene = benzene 18 L/mol, toluene 97 L/mol and xylene ca. 500 L/mol were determined.

In order to obtain stability constants for other rhodium diphosphine arene complexes, the static (only equilibrated solutions are measured) method as described in Ref. [11] was used with a modern dosage technique. The applied micro-annular gear pump [14] allows for dosing in the microliter range under anaerobic conditions. The device was tested on the system described in Ref. [11], Scheme 2.



Scheme 2. Equilibrium between solvate complex [Rh(DPPE)(MeOH)$_2$]BF$_4$ and arene complex [Rh(DPPE)(η^6-benzene)]BF$_4$.

Analysis of the reaction spectra for the titration of [Rh(DPPE)(MeOH)$_2$]BF$_4$ with benzene, Fig. 5, by linearization (e.g. Benesi-Hildebrand equation, Fig. 6) [15] gives the desired stability constant of 18 L/mol.

The agreement with the literature data proves the practicability of our measurements. Applying Spectfit/32 for the titration of [Rh(DPPE)(MeOH)$_2$]BF$_4$ with benzene gives the overall stability constant (18 L/mol).

The pure component analysis (PCD or Specfit/32) of the example gives the pure component spectra for [Rh(DPPE)(MeOH)$_2$]BF$_4$ and [Rh(DPPE)(η^6-benzene)]BF$_4$, which are in very good agreement with the experimental spectra, Fig. 7.

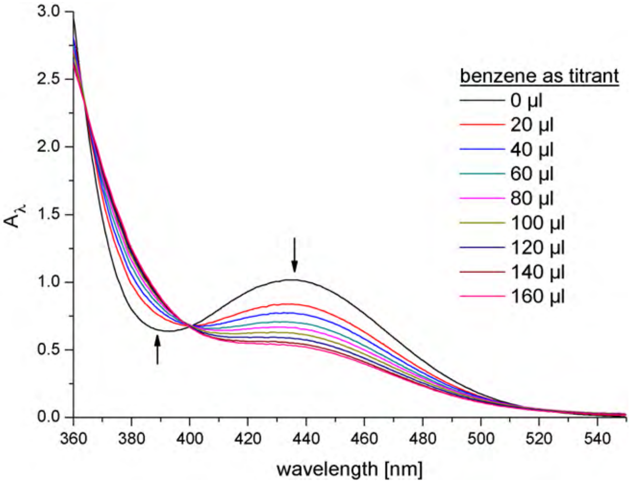


Fig. 5. Titration of benzene to a solution of 0.02 mmol [Rh(DPPE)(MeOH)$_2$]BF$_4$ in 15 mL MeOH; 25.0 °C. To verify equilibration, after ca. 10 min, an identical spectrum was recorded.

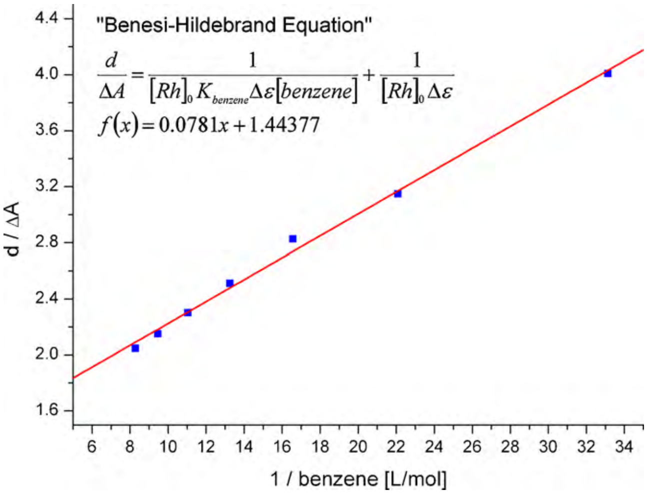


Fig. 6. Analysis of the arene complex formation by linearization (with d = layer thickness = 0.5 cm).

5. UV/vis spectroscopy of fast reactions with gaseous reaction partners

In the selective oligomerization of ethylene, metallacycles are key intermediates on the way to linear α-olefins (LAO's). Metallacycles of group 4 metals (Ti, Zr, Hf) can serve as model complexes for active catalysts [16].

Here, fast UV/vis spectroscopy in combination with conventional NMR measurements shall be presented as a useful method to investigate the reactions of complexes *rac*-(ebthi)M(η^2-Me$_3$SiC$_2$-SiMe$_3$) (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl), **1-Zr**: M = Zr, **1-Hf**: M = Hf) with ethylene that form metallacyclopentanes [17].

NMR-spectroscopic investigations revealed that **1-Zr** readily reacts with ethylene at room temperature to give **3-Zr** exclusively. Only at low temperature (−63 °C) **2-Zr** can be detected as an intermediate by NMR, Scheme 3. Upon heating **2-Zr**, which is unstable at room temperature, disproportion occurs to give **1-Zr** and **3-Zr** in a ratio 1:1 [18].

Given that **2-Zr** is only stable at low temperature and that the reaction is carried out with an excess of ethylene, a pseudo-first order reaction (A → C) with the pseudo-rate constant $k' = k \cdot$[ethylene] should be observed instead of a consecutive reaction. Thus, a uniform reaction with isosbestic points in the UV/vis reaction spectra is to be expected.

Applying the stopped flow/diode array technique requires that ethylene as the gaseous reaction partner is dissolved in the toluene solvent. With the limiting factor of ethylene solubility in toluene [19] and a desired extinction of not much higher than 1, cell thickness and concentration of **1-Zr** were optimized. Ratios of **1-Zr** to ethylene between 1:10 and 1:35 were determined and can be regarded as pseudo-conditions.

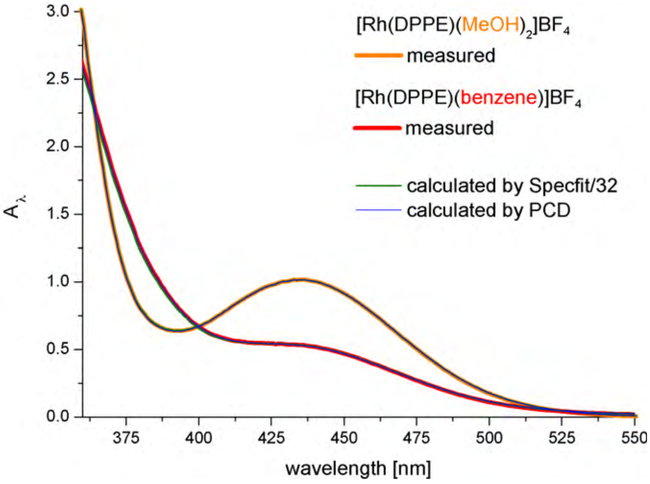
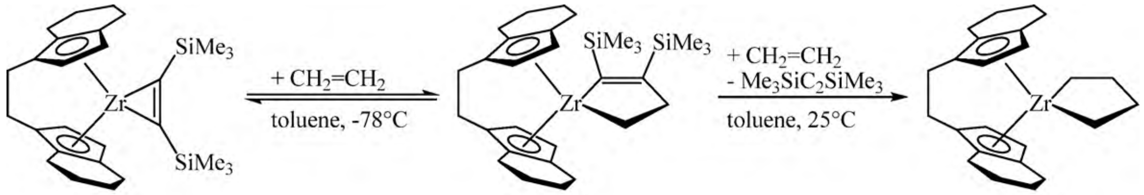


Fig. 7. Agreement between calculated and measured spectra: pure component spectra for the titration of [Rh(DPPE)(MeOH)$_2$]BF$_4$ with benzene as determined by pure component analysis.



1-Zr **2-Zr** **3-Zr**

Scheme 3. Reaction of **1-Zr** with ethylene.

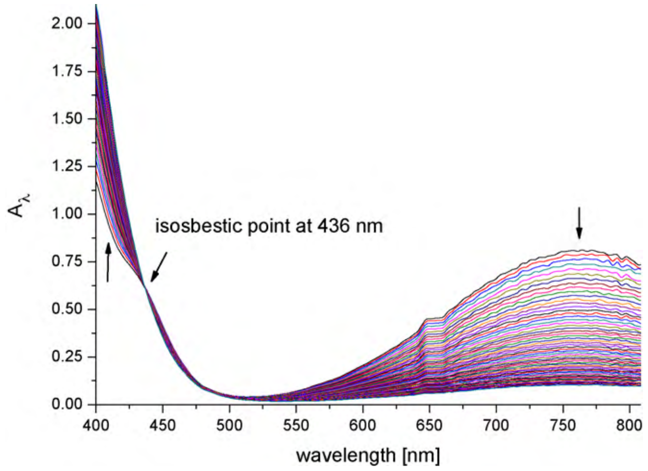


Fig. 8. Sample reaction spectra for the reaction of **1-Zr** with ethylene (conditions: 0.0065 mol/L **1-Zr**, 0.10125 mol/L ethylene, solvent toluene, 25 °C, interval of spectra 8 ms, overall time 2.0 min, $k' = 0.0365\ \mathrm{s}^{-1}$).

The UV/vis reaction spectra for the reaction of **1-Zr** with ethylene at room temperature and a ratio of **1-Zr** to ethylene of 1:15.5 is shown in Fig. 8.

As expected, the reaction spectra possess an isosbestic point; extinction diagrams confirm pseudo-first order. Non-linear curve fit (cp. Example 1, Fig. 3) affords pseudo-rate constants k'. From the plot k' vs. ethylene concentration the desired rate constant k of $0.35\ \mathrm{L\,mol^{-1}\,s^{-1}}$ for the formation of **3-Zr** from **1-Zr** and ethylene at 25 °C can be derived from the slope of the straight line, Fig. 9.

The reaction of the respective hafnium complex **1-Hf** with ethylene proceeds in a similar manner to that of **1-Zr** as deduced from NMR measurements [17]. However, in contrast to **1-Zr**, **1-Hf** reversibly reacts with ethylene to give **2-Hf** at room temperature, whereas the consecutive reaction yielding **3-Hf** requires temperatures of 100 °C. Thus, at 25 °C a simple – eventually reversible – pseudo-first order reaction from **1-Hf** to **2-Hf** should be observed with an excess of ethylene. Again, ratios **1-Hf** to ethylene between 1:10 and 1:30 were determined from the UV/vis measurements.

However, isosbestic points are not observed, Fig. 10. In fact, extinction diagrams, which show two distinct straight lines, indicate a simple consecutive reaction (Fig. 11). The circumstance that the first reaction is extremely fast and the second much slower allows for the separate treatment of both reactions.

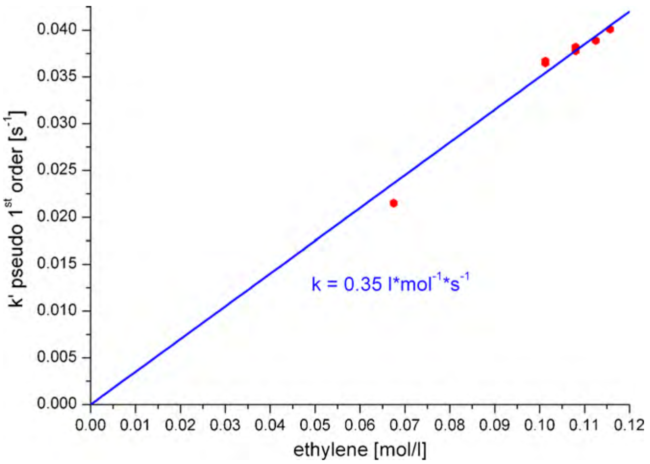


Fig. 9. Pseudo-rate constants k' for the formation of **3-Zr** from **1-Zr** and ethylene at 25 °C as a function of the ethylene concentration. From the slope of the linear regression the rate constant k is determined.

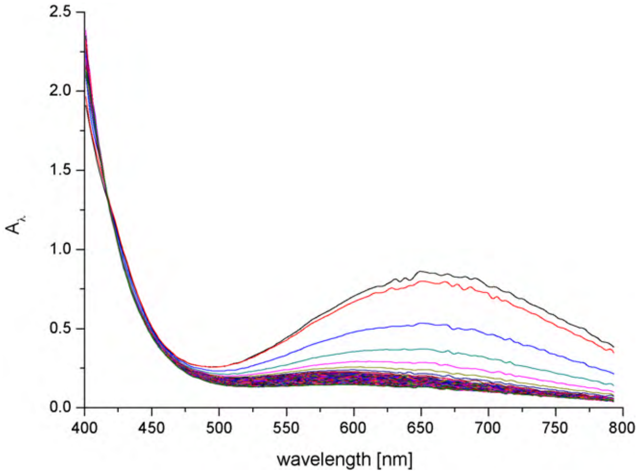


Fig. 10. Sample reaction spectra for the reaction of **1-Hf** with ethylene (conditions: 0.0104 mol/L **1-Hf**, 0.0804 mol/L ethylene, solvent toluene, 25 °C, interval of spectra 5 ms, overall time 2.5 s, $k'_{\mathrm{obs.1}} = 78.6\ \mathrm{s}^{-1}$, $k'_{\mathrm{obs.2}} = 2.4\ \mathrm{s}^{-1}$).

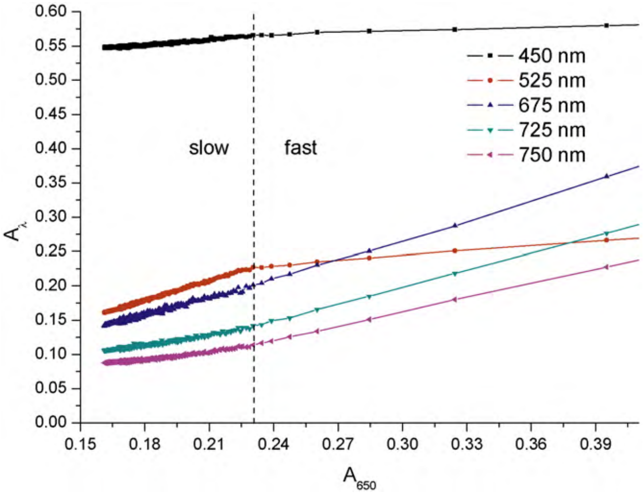


Fig. 11. Extinction diagram for the formation of **2-Hf** from **1-Hf** and ethylene.

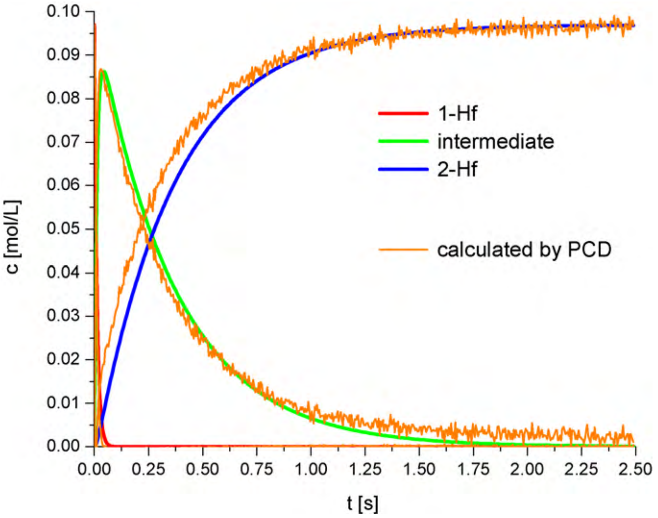


Fig. 12. Comparison between as a consecutive reaction calculated concentration-time profile and those determined with PCD, calculated in a model-free manner.

Fig. 12 shows the concentration-time profiles calculated from the determined rate constants for the starting material, the product, as well as the intermediate, compare Ref. [17]. The model-free decomposition of the reaction spectra in the single components as a function of the time shows a practically analogous result after standardization (Fig. 12). This finding confirms the model of the consecutive reaction. The measured spectra for the starting material and the product also agree very well with the pure component spectra.

Plotting the observed rate constants $k'_{obs.i}$ vs. the ethylene concentration results in the rate constants $k_{obs.i}$ for both reactions. Surprisingly, *both* reactions depend on the ethylene concentration, Fig. 13.

This stepwise reaction presumably proceeds as shown in Scheme 4. A hitherto unknown intermediate, most likely **B**, could be detected. Although further investigations are necessary as to elucidate its true nature, Fig. 12 suggests its existence which would have escaped observation with NMR experiments. Bis–π complexes as **B** have been previously described and discussed as intermediates in reactions of other group 4 metallocene complexes [17].

However, this sequence does not describe how the second step depends on the ethylene concentration.

Two explanations may be given which are related to the dynamic behavior of the metallacyclopentenes **2**. Both the Zr and Hf complexes are kinetically labile and exhibit a fast exchange of the incorporated with free ethylene, as shown by NMR experiments (Refs. [17,18]). Hence their formation was regarded as reversible (equilibria formulated in Schemes 3 and 4), but the mechanism for this exchange is unknown.

The first explanation is that the reverse reaction **2** → **B** is ethylene-assisted (in the manner of a S_N2 reaction) that would introduce an ethylene influence on the overall observed formation rate of **2**. The reaction of **2** in this manner would produce an intermediate **B** with the alkene and the alkyne having changed places after C–C bond reformation. Since **2** is chiral, an isomerization of the metallacyclopentene would be expected to occur. This isomerization should be detectable by an apparent interchange of the chemically inequivalent tetrahydroindenyl moieties A and B. Indeed, such an exchange was observed (Fig. 14 right).

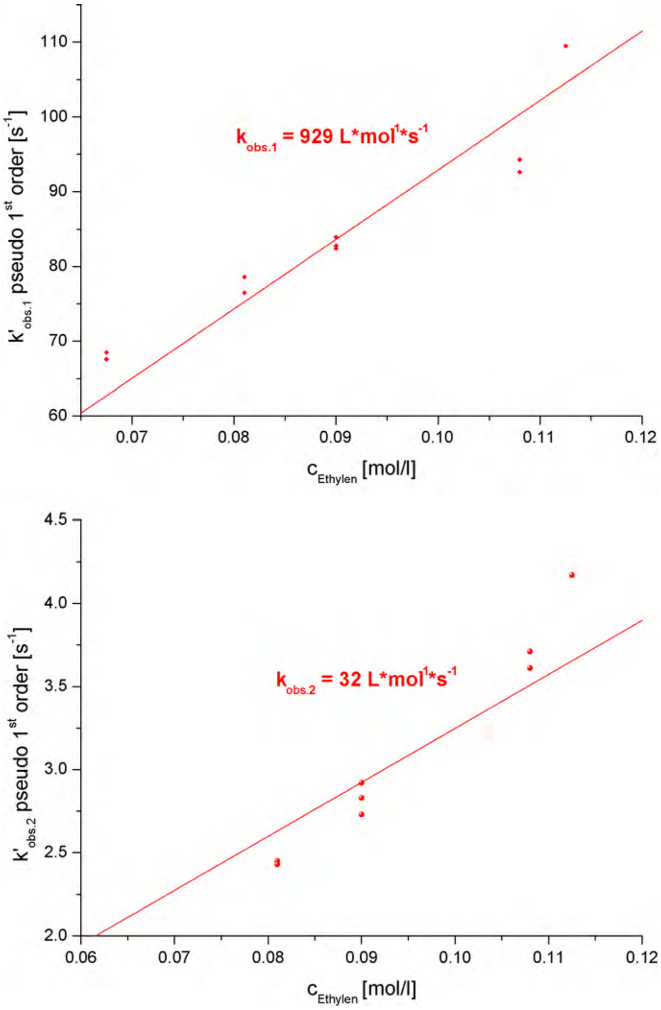
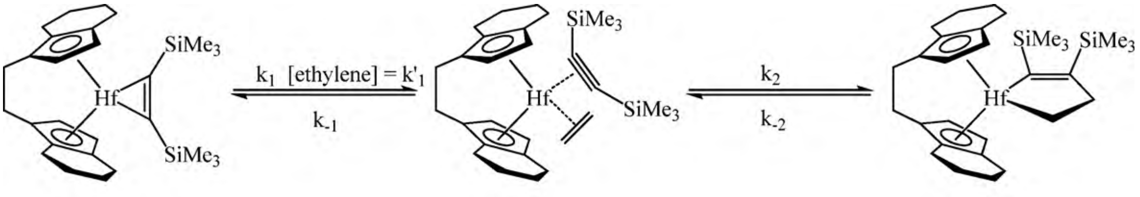


Fig. 13. Dependence of the pseudo-rate constants $k'_{obs.i}$ on ethylene concentration for the consecutive reaction of **1-Hf** with ethylene (top: fast first step, bottom: second slow step).

The second explanation is that the conversion **B** → **2** (going from an 18- to a 16-electron species) is ethylene-assisted. This weak coordination would be expected to be very labile and thus difficult to detect the alkene–metal interaction.

Although speculative, both explanations require the close proximity of a second ethylene to the metal, which is also a



1-Hf **B** **2-Hf**

Scheme 4. Reaction of **1-Hf** and ethylene resulting in **2-Hf** in toluene at 25 °C via postulated intermediate **B**.

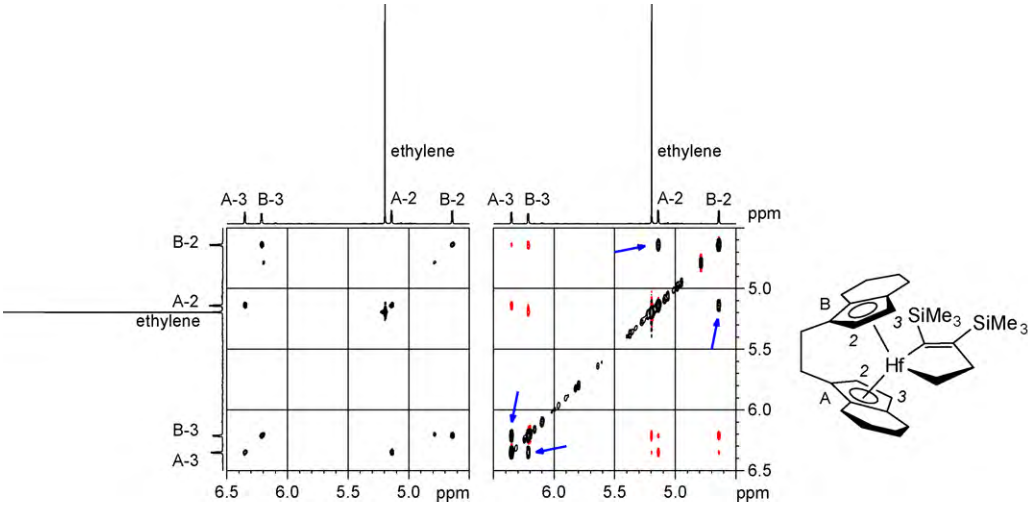


Fig. 14. Sections from ^{1}H NMR spectra (400 MHz, ambient temperature, toluene-d_8, excess ethylene) of **2-Hf**. Left, COSY-45, right, NOESY (mixing time 1.5 s, signals with positive phase drawn in black, signals with negative phase drawn in red). Cross-peaks marked with arrows indicate the dynamic process as described in the text; they are absolutely uncommon with this ligand system. Weak signals at 4.8 and 6.2 ppm are due to minute amounts of **3-Hf** (Ref. [17]).

prerequisite for the observed decomposition of **2-Zr** to equal amounts of **1-Zr** and **3-Zr**, as described above.

6. Summary

Three examples were shown in which the UV/vis technique was presented as a useful tool in observing homogeneous catalysts *in operandi*. Submersion optrodes as well as the stopped flow/diode array technique allow for the monitoring of very slow to very fast reactions. Very fast reactions with gaseous reaction partners can be investigated by stopped flow/diode array using solutions of the dissolved gas.

Finally, pure component analysis allows the reconstruction of spectra and if applicable also concentration-time diagrams for the pure compounds, thus providing important kinetic information such as reaction order and rate constant without any *a priori* information.

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