



# NMR at elevated gas pressures and its application to homogeneous catalysis<sup>1</sup>

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## Abstract

A selection of topics dealing with instrumentation and applications of NMR under high pressure of gases is presented, with emphasis on some recent advances in mechanistic studies of homogeneous hydrogenation and carbonylation reactions carried out in the laboratory of the author.

*Keywords:* Carbonylation; High pressure; Hydrogenation; NMR spectroscopy

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## 1. Introduction

An important aspect of studies in homogeneous catalysis consists of the unravelling of complex catalytic cycles in order to better understand and ultimately influence the outcome of the overall catalytic reactions. Importantly, information should be in part obtained from in situ studies or model studies mimicking the actual reaction conditions, which implies that many such studies should be carried out under high pressures of gases. One of the spectroscopic techniques that has been and continues to be successful in this realm is NMR under high gas pressure, which has recently been reviewed [1]. Advantages of using NMR are, for example, the fact that it is a non-invasive technique and that detailed structural information about compounds in solution can be obtained, which in a number of cases outweighs the inherent disadvantages of being a slow and insensitive technique as compared to, e.g., IR.

*Note: Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high pressure NMR cells (see below).*

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The main applications of high pressure NMR to catalysis include the following:

- monitoring reactions under conditions similar to the catalytic reaction
- stabilization and identification of intermediates
- measurement of kinetics
- study of exchange processes

High pressure NMR has been applied ever since the advent of NMR spectroscopy [2] but most of the early applications have dealt with very high hydrostatic pressures on liquid samples [3]. Here only studies at elevated gas pressures will be presented.

## 2. Apparatus

Glass tubes have been employed at high pressures, up to 300 bar for Pyrex tubes of 5 mm outer diameter (o.d.) and 0.5 mm inner diameter (i.d.) [4]. In practice, nowadays commercial thick-walled glass tubes of 5 mm o.d. and 2 mm i.d. are used at low to moderate pressure (up to about 20 bar) [5].

Recently, several adequate cells for carrying out NMR studies under high pressure have been designed and applied. These include static (i.e. non-rotating) probes

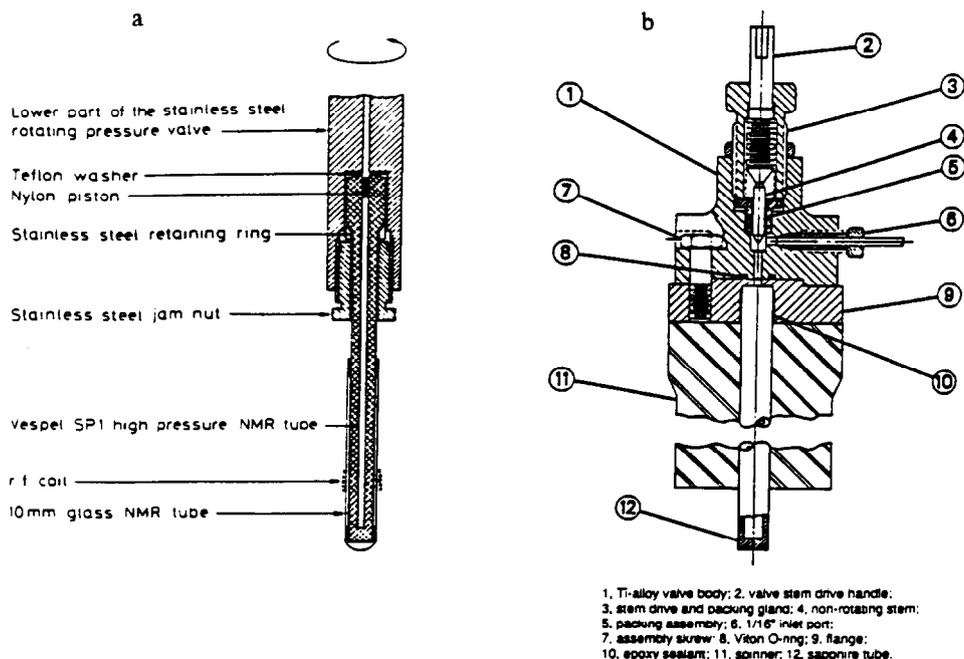


Fig. 1. Drawings of high pressure NMR cells (a) by Merbach and (b) by Roe. Reprinted with permission from [8] and [9].

[6,7] and rotatable assemblies (see Fig. 1): a polyimide tube by Merbach c.s. [8] and a sapphire tube by Roe [9]. The former [8] consists of a thick-walled (8 mm o.d., 2 mm i.d.) Vespel tube connected to a stainless steel high pressure valve, allowing measurements up to ca. 1000 bar. The resolution was approximately 2 Hz at 60 MHz. Deformations of the tubes required replacement after several experiments.

The assembly designed by Roe [9] consists of a 5 mm o.d., 3.4 mm i.d. sapphire tube glued into a Ti (6Al-4V) alloy pressure head and allows measurements up to about 140 bar. It can be partly filled with a solution of an (organometallic) reagent, if necessary under nitrogen, and after fastening of the pressure head it is pressurized with the desired gas(es).

We have built and used this system since 1986, introducing the minor modification of employing 10.0 mm o.d., 8.0 mm i.d. sapphire tubes, the reason being that diffusion of the gas into solution takes place much more efficiently in the wider tube, which is a requirement in order to prevent limiting of reaction rates by slow diffusion of the gaseous reactant (particularly in kinetic studies). The resolution for the 10 mm tubes is about 1-2 Hz depending on the specific tube. Standard shim-files are regularly checked and updated. The weight of the valve assembly is about

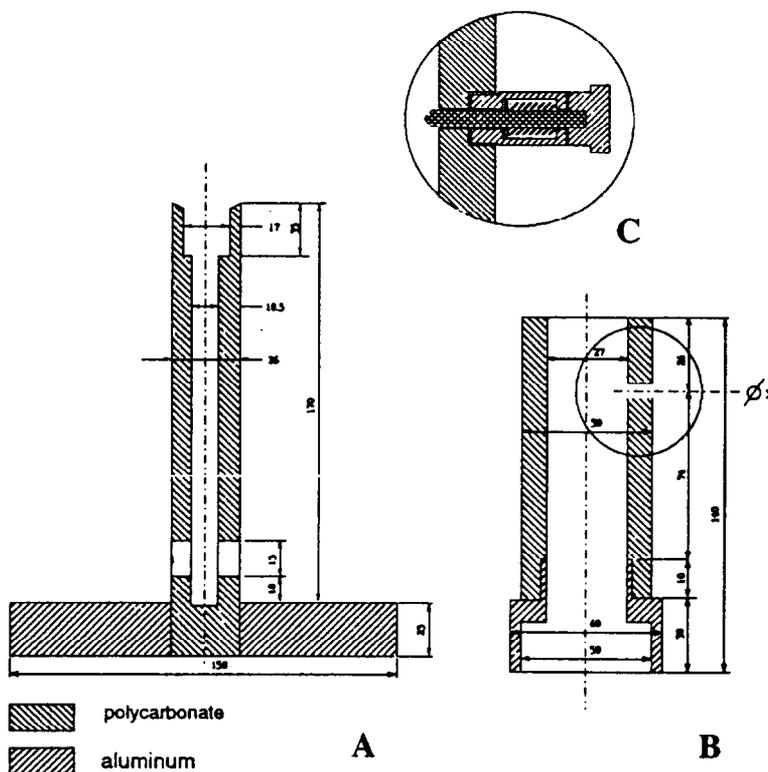


Fig. 2. Drawing of the polycarbonate safety cylinder used when pressurizing, transporting and mounting the high pressure tube.

100 g and it can be gently lowered into and raised from our magnets by employing the air or nitrogen lift-pressure at 5–6 bar. Recently, a slightly smaller and lighter variety of this assembly has been described [10] and several other assemblies for a number of applications are known, e.g. [11].

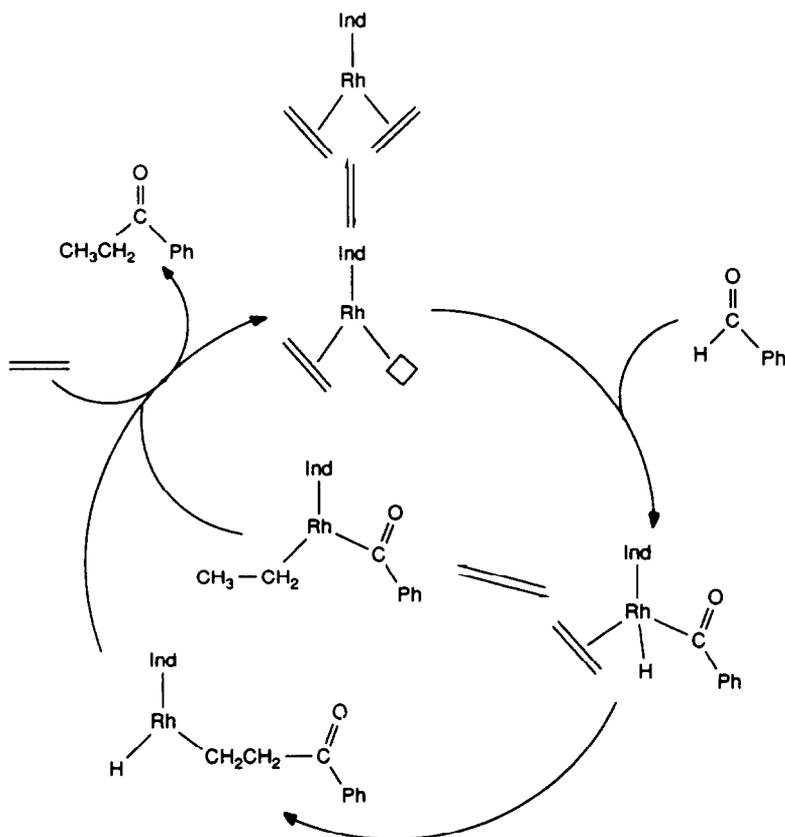
Special attention should be given to *the safety precautions*, as all manipulations are potentially hazardous! The tubes should be regularly tested at 150–200 bar static pressure; scratches in and bumping of the tube should be prevented: the use of velvet gloves and soft materials for storage of empty tubes is recommended. Personnel should never be directly exposed to pressurized tubes and all manipulations should be carried out behind a safety screen and/or in a *protective vessel* (for transport and mounting on the magnet). The vessel we designed consists of two coaxial thick-walled polycarbonate cylinders A and B (Fig. 2). The tube is inserted in this assembly in such a way that the pressure-head rests on lever C. Then the tube is pressurized behind an additional polycarbonate screen and subsequently transported to the spectrometer in the vessel A + B. The outer part B together with the tube is lifted from foot A and is placed and secured on top of the magnet. Under an adequate counter-stream of nitrogen or air, lever C is pulled and the tube is gradually lowered into the probehead by diminishing the lift-pressure.

### 3. Application of NMR at elevated gas pressures

The processes which have so far been most studied by NMR under high gas pressures involve (i) activation and addition reactions of C–H bonds, (ii) activation and addition reactions of H<sub>2</sub>, (iii) activation and insertion reactions of CO, and (iv) exchange of CO, CO<sub>2</sub>, H and Cp ligands. Recently, also homogeneous catalysis in supercritical fluids has become the subject of high pressure NMR studies. In the following parts, a selection of research conducted in these directions will be highlighted, with emphasis on studies from our laboratory.

#### 3.1. Activation and addition reactions of C–H bonds

The indenyl complex ( $\eta^5\text{-C}_9\text{H}_7$ )Rh( $\eta^2\text{-C}_2\text{H}_4$ )<sub>2</sub> is an active catalyst (precursor) for the addition of aldehydes to ethene, for instance the addition of benzaldehyde to ethene at 70 bar and 100°C [12]. It has been established by means of high pressure <sup>13</sup>C NMR that, when employing ca. 90% enriched C<sub>6</sub>H<sub>5</sub>-<sup>13</sup>CHO, only labeled benzaldehyde and propiophenone C<sub>6</sub>H<sub>5</sub>-<sup>13</sup>C(O)-C<sub>2</sub>H<sub>5</sub> were observed, whereas no resonances due to Rh-<sup>13</sup>CO or dissolved <sup>13</sup>CO were detected. This finding indicates that, after oxidative addition of the aldehyde C–H bond to Rh, no significant decarbonylation takes place. Deuterium labeling studies involving C<sub>6</sub>H<sub>5</sub>-CDO showed that virtually all propiophenone produced contained exactly one deuterium atom in the ethyl group, which was statistically scrambled between the methyl and methylene sites, whereas no deuterium incorporation in unreacted

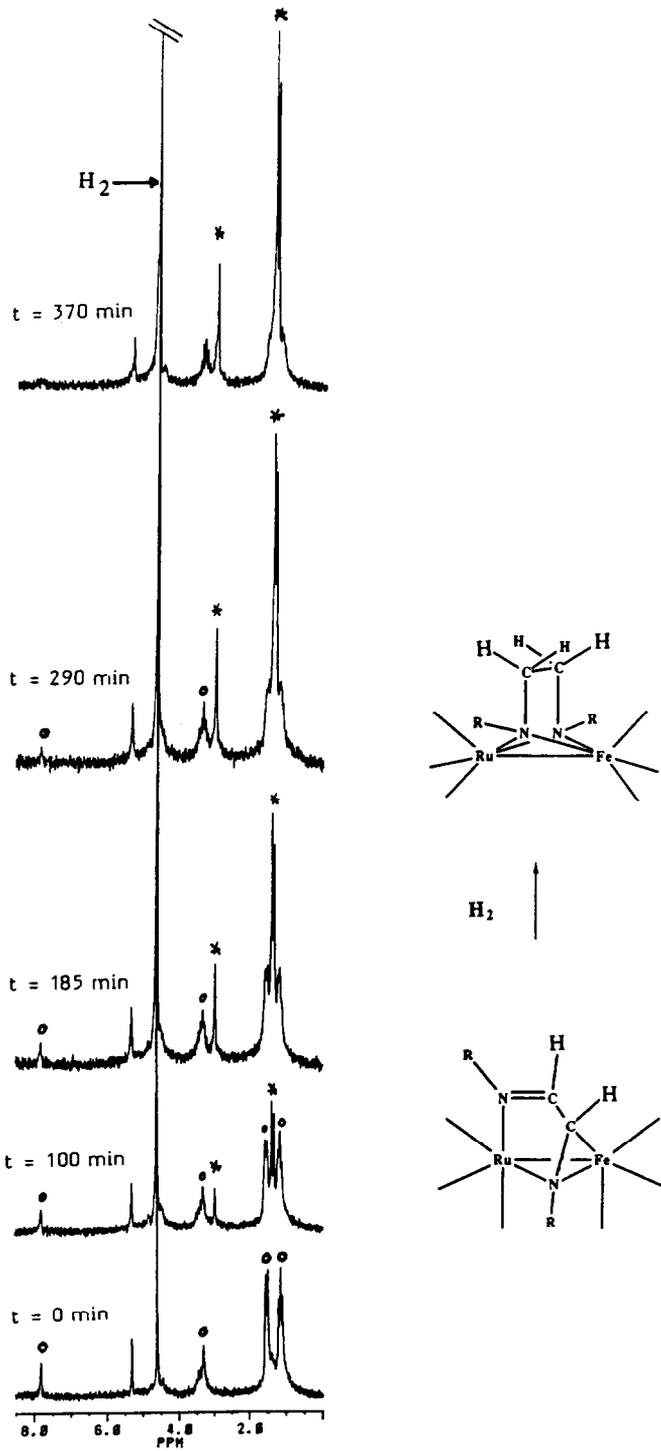


Scheme 1. Proposed catalytic cycle for the Rh-catalyzed hydroacylation of aldehydes (Ind = indenyl =  $\eta^5$ -C<sub>9</sub>H<sub>7</sub>), adapted from [13].

ethene took place. Hence, insertion of ethene into the Rh–D bond must take place rapidly and reversibly and must be faster than any subsequent step. As no product of  $\beta$ -H elimination, i.e. H<sub>2</sub>C=CH–C(O)C<sub>6</sub>H<sub>5</sub>, was detected, ethene insertion into the Rh–H bond is the process taking place (upper part of cycle in Scheme 1). The results also suggest that only one ethene molecule is coordinated to Rh during the C–H activation step.

### 3.2. Activation and addition reactions of H<sub>2</sub>

The photochemical activation of H<sub>2</sub> by Fe(CO)<sub>5</sub> has been studied by high pressure NMR and ESR [13]. The rate of H<sub>2</sub> elimination from the labile molecular hydrogen complex ( $\eta^2$ -H<sub>2</sub>)Cr(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> was followed at 10–55 bar H<sub>2</sub> by <sup>1</sup>H inversion–recovery techniques [14], its independence on the pressure showed that the elimination is a first order process. Calculation of thermodynamic data revealed that the enthalpy of activation for the dissociation of H<sub>2</sub> is lower for the studied



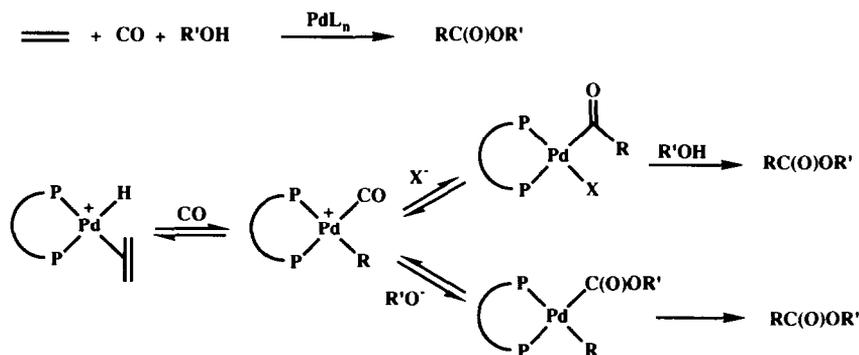
chromium complex than for the analogous known tungsten complex ( $\Delta H^\ddagger = 50.8$  and  $80.0$  kJ/mol, respectively). The coordination mode of hydrogen was established by  $T_1$  measurements.

We have examined the mechanism of addition of  $H_2$  to the coordinated  $\alpha$ -diimine in  $RuM(CO)_6\{RN=CH-CR'=NR\}$  ( $M = Fe, Ru$ ;  $R' = H, Me$ ) which resulted in the addition product  $RuM(CO)_6\{RN-CH_2-CH(R')-NR\}$  [15,16]. By employing  $D_2$ , it has been shown that, unexpectedly, stereoselective *trans*-addition of  $D_2$  to the central C–C bond of the ligand takes place. The reaction proceeds measurably only at temperatures above  $70^\circ C$  at  $H_2$  pressures between 20 and 70 bar. Kinetic studies have revealed a first order dependence both on the concentration of the complex and of  $H_2$ . The conversion could conveniently be monitored e.g., at  $110^\circ C$  at 60 bar  $H_2$  (Fig. 3) by integration of appropriate signals [16]. Importantly, due to fast diffusion of the gas into solution (thanks to the use of an 8 mm i.d. tube) a constant high concentration of  $H_2$  in solution could be maintained for each experiment, i.e., the diffusion of  $H_2$  was fast compared to the rate of hydrogenation.

The mechanism of selective Rh-catalyzed hydrogenation of heterocycles, in particular of quinoline to 1,2,3,4-tetrahydroquinoline and of benzothiophene to 1,2-dihydrobenzothiophene, has been studied in detail [17]. Monitoring the reaction at 34 bar  $D_2$  pressure allowed indication of the sequence of reduction steps, reversibility in the reduction of the N=C and C=C bonds of six-membered N-heteroaromatic compounds, and the coordination of substrates to the catalyst.

### 3.3. Addition and insertion reactions of CO

An early application of high pressure NMR concerned the mechanistic aspects of the synthesis of ethylene glycol from CO and  $H_2$  catalyzed by rhodium–carbonyl clusters [6,18]. This on-line  $^{13}C$  NMR study was conducted at 580 bar CO pressure



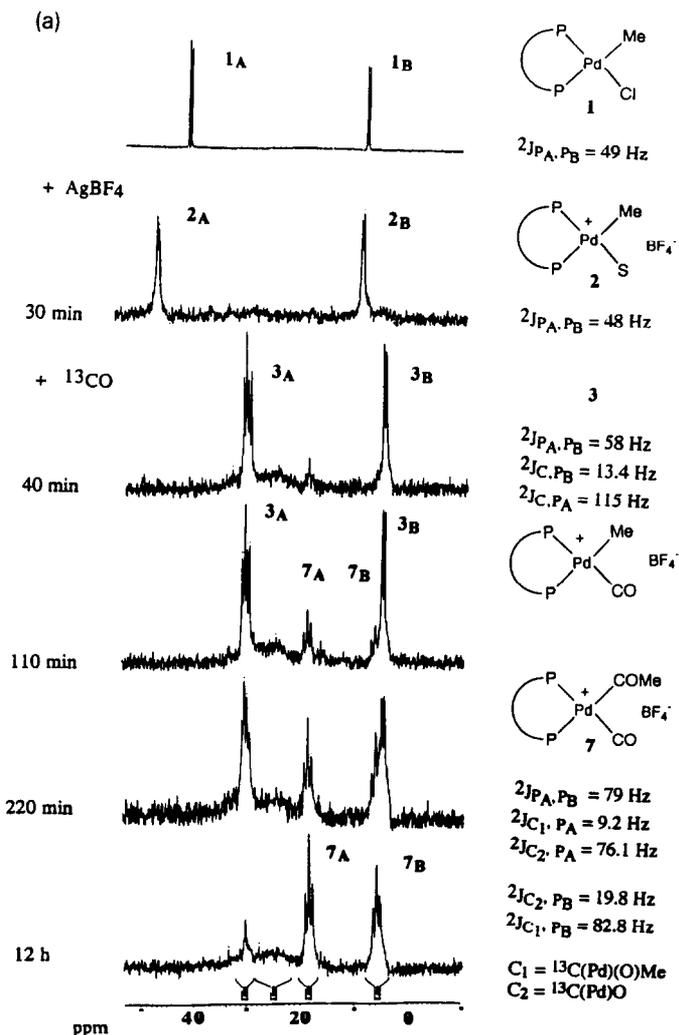
Scheme 2. Possible intermediates in hydrocarboxylation and alkoxy-carboxylation.

Fig. 3. High pressure  $^1H$  NMR spectra of the reaction of (○)  $FeRu(CO)_6\{iPr-N=CH-CH=N-iPr\}$  with  $H_2$  at  $110^\circ C/60$  bar to give (✱)  $FeRu(CO)_6\{iPr-N-CH_2CH_2-N-iPr\}$ . Reprinted with permission from [15].

in acetone- $d_6$  at  $-52^\circ\text{C}$  in the presence of  $[\text{PhCH}_2\text{NMe}_3]_2[\text{Rh}_{12}(\text{CO})_{30}]$  and revealed a progressive transformation of  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  into  $[\text{Rh}_5(\text{CO})_{15}]^-$ . After warming to  $25^\circ\text{C}$  and cooling to  $-33^\circ\text{C}$ , the formation of  $[\text{Rh}_5(\text{CO})_{15}]^-$  was complete.

Exchange of free CO in solution with  $\text{Co}_2(\text{CO})_8$  and  $\text{CH}_3\text{C}(\text{O})-\text{Co}(\text{CO})_4$  [19], which is relevant to the mechanism of cobalt-catalyzed hydroformylation, was studied by  $^{13}\text{C}$  magnetization transfer techniques at CO pressures up to ca. 80 bar, up to which the rates for dissociation of CO were independent of CO pressure. Some high pressure NMR experiments involving rhodium(phosphine)carbonyl complexes have also been carried out recently [20].

We have studied several addition and exchange reactions of CO with organometallic compounds, among which feature studies of ruthenium complexes con-



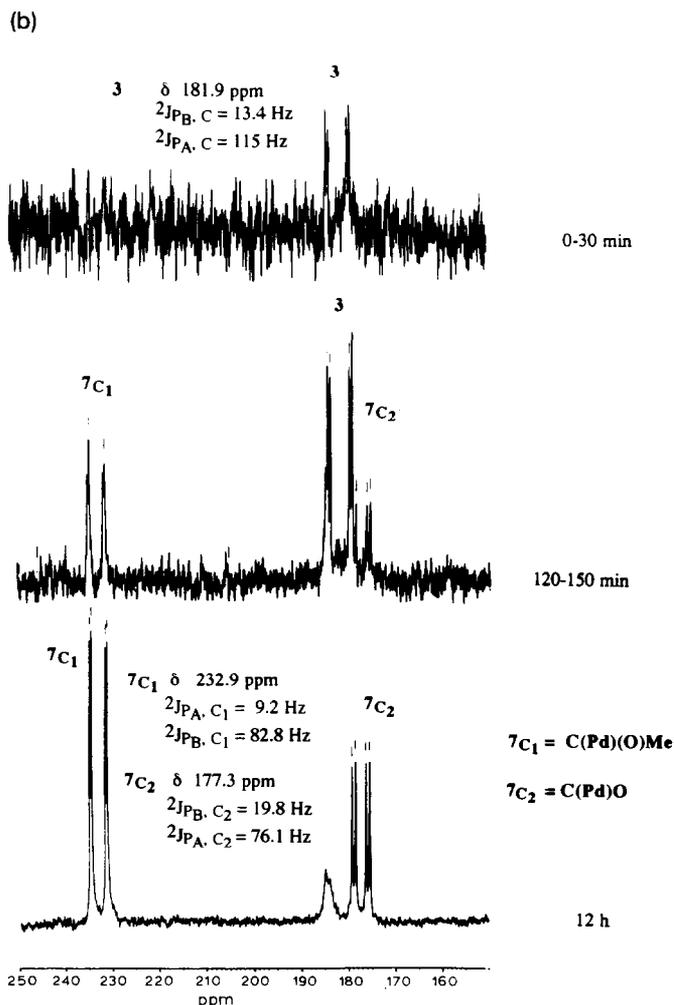


Fig. 4. Monitoring by high pressure (a)  $^{31}\text{P}$  NMR (121.5 MHz) and (b)  $^{13}\text{C}$  NMR (25 MHz) of the reaction of (diphos)Pd(Me)Cl (1) with  $\text{AgBF}_4$  at  $20^\circ\text{C}$  followed by carbonylation of [(diphos)Pd(Me)(MeOH)] $\text{BF}_4$  (2) with  $^{13}\text{CO}$  at  $-90^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ -MeOH to give [(diphos)Pd(Me)( $^{13}\text{CO}$ )] $\text{BF}_4$  (3) and [(diphos)Pd-{ $^{13}\text{C}(\text{O})\text{Me}$ }( $^{13}\text{CO}$ )] $\text{BF}_4$  (7). Reprinted with permission from supplementary material to [29].

taining monoazadiene ligands [21,22]. It was shown that under exclusion of light the linear tetranuclear complex  $\text{Ru}_4(\text{CO})_{10}\{\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{N}-i\text{Pr}\}_2$  stepwise adds four equivalents of CO at ambient temperature, whereby the  $\pi$ -bonding of the monoazadienyl ligands is progressively substituted by CO molecules, resulting in a linear chain of four ruthenium atoms with three Ru-Ru bonds which are not supported by any bridging ligand [22].

Insertion reactions of CO into transition metal to carbon bonds, as model reactions for several Ru-, Rh-, Pd- and Pt-catalyzed carbonylations, have been widely studied by means of high pressure NMR in Amsterdam [23–30]. For instance, we

have conducted kinetic and equilibrium studies of CO insertions into Pd–CH<sub>3</sub> bonds of complexes stabilized by bidentate phosphine and nitrogen ligands, mixed P–N ligands and tridentate nitrogen ligands [23,24]. Successive CO-insertion into  $\sigma$ -allenyl–Pd complexes [25] has been monitored by high pressure <sup>1</sup>H and <sup>13</sup>C NMR which together with IR measurements has provided evidence for the occurrence of Pd–vinylketene intermediates [26]. Furthermore, high pressure NMR studies concerning enantioselective hydroformylation of alkenes catalyzed by chiral Pt–diphosphine complexes in the presence of SnCl<sub>2</sub> have been studied [27].

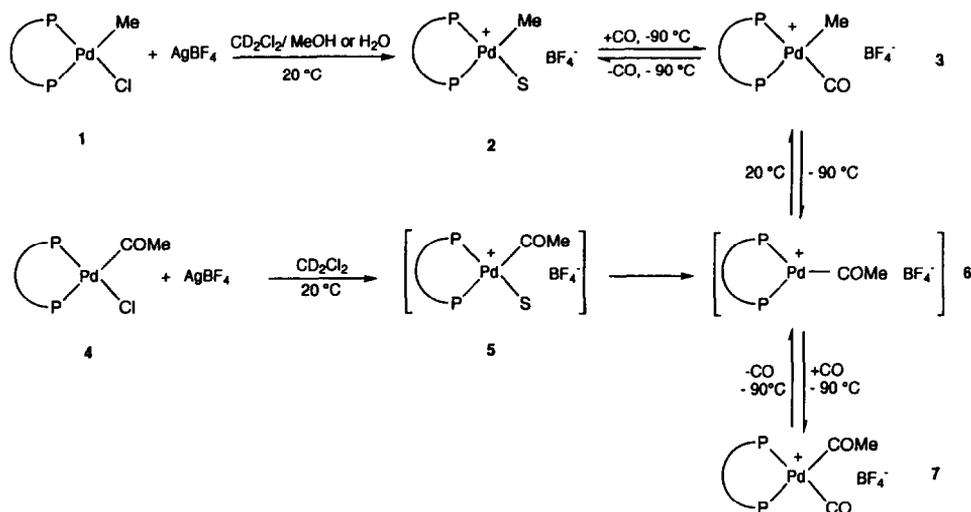
Recently, much effort has been put into the study of CO-insertion and related model reactions pertaining to enantioselective alkoxy carbonylation of prochiral alkenes catalyzed by chiral Pd–diphosphine complexes [28–30], some aspects of which will be presented below.

In (diphosphine)Pd-catalyzed hydro-carboxylation and -alkoxy carbonylation of alkenes several routes to the product (acids and) esters, proceeding through key intermediates like the ones depicted in Scheme 2, may be envisaged.

When monitoring the hydrocarboxylation of *p*-i-butylstyrene catalyzed by (diphos)PdCl<sub>2</sub> at 50 bar CO pressure and 80°C in dioxane-d<sub>8</sub>/water (i.e., under conditions similar to those during actual catalysis) by high pressure <sup>1</sup>H and <sup>31</sup>P NMR, the formation of (diphos)Pd{C(O)R}Cl was observed and (diphos)PdCl<sub>2</sub> was the only other detectable compound (diphos = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane). In stoichiometric reactions under pressure of <sup>13</sup>CO, the linear as well as both diastereomers of the branched acyl complexes have been observed by <sup>13</sup>C NMR. After complete conversion of the alkene to phenylpropanoic acids, only (diphos)PdCl<sub>2</sub> was detected in the <sup>31</sup>P NMR, confirming precatalyst stability under catalytic conditions [28]. No other intermediates could be detected under these conditions, hence stoichiometric and model studies were carried out.

Model studies included monitoring by high pressure <sup>31</sup>P and <sup>13</sup>C NMR (Fig. 4) of the reactions shown in Scheme 3, i.e., of [(diphos)Pd(Me)(H<sub>2</sub>O)]BF<sub>4</sub>, **2**, with <sup>13</sup>CO at low temperature. The idea was that by proceeding at low temperatures we might be able to monitor by NMR the formation of palladium(II) carbonyl coordination complexes containing a methyl group in *cis*-position. Although such intermediates have been proposed as intermediates on the way to palladium–acyl species, they have never been observed. We succeeded in authenticating the existence of this thus far elusive, crucial intermediate *cis*-palladium(methyl)carbonyl complex, **3**, for the first time; it was formed instantaneously in a stoichiometric amount from **2** at –90°C at pressures of 3–10 bar <sup>13</sup>C labeled CO and was subsequently converted into the relatively stable *cis*-palladium(acyl)carbonyl complex **7** in several hours [29].

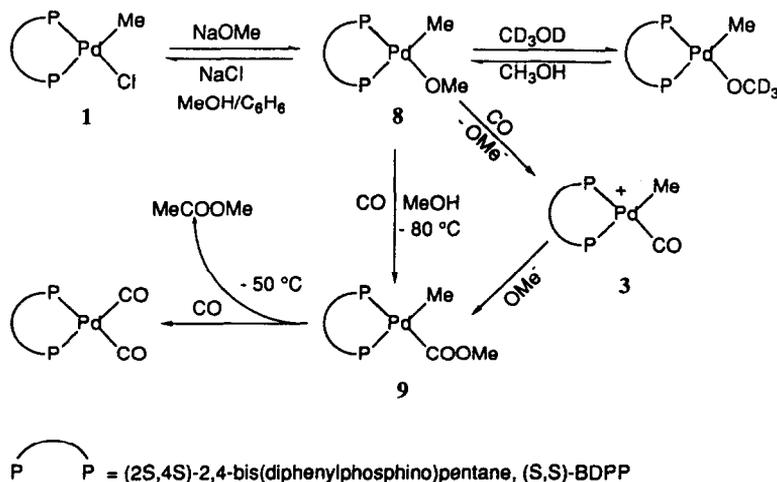
In another study we showed [30] that, in the presence of added sodium methoxide, palladium(methyl)carbomethoxy compound, **9**, (Scheme 4) is formed through the intermediacy of methoxypalladium complex, **8**, and that reductive elimination from this species leads to methyl acetate. However, the occurrence of



Scheme 3. Complexes observed in high pressure model studies of alkoxycarbonylation (complexes in square brackets were not observed). Reprinted with permission from [29].

compounds like **9** under catalytic conditions is unlikely, as (i) little or no methoxide is present under those circumstances and (ii) because **3** was not converted into **9** upon addition of sodium methoxide.

Exchange of free  $^{13}\text{CO}$  in solution and inserted CO in complexes such as **4** (Scheme 3), or of free  $^{12}\text{CO}$  and  $^{13}\text{C}(\text{O})\text{Me}$ -labeled **4**, was shown to be dependent on the anion X and the solvent [28]. For X = Cl in dioxane/water at 30 bar CO the reaction proceeded not at all at 20°C and barely measurably above 60°C, but at 20°C in toluene/methanol the exchange proceeded measurably and was dependent



Scheme 4. Complexes observed in high pressure model studies of alkoxycarbonylation in the presence of added methoxide. Reprinted with permission from [30].

on the CO pressure, whereas for  $X = \text{BF}_4$  the exchange already took place at  $-50^\circ\text{C}$ . These results indicate that the degree of dissociation of the anion  $X$  plays a determining role in the CO exchange process, which in turn will influence the degree of  $\beta$ -elimination from the palladium–alkyl complex.

For details of this and related high pressure NMR studies the reader is referred to several papers which have appeared and to some which will appear in the near future [27–30].

#### 4. Supercritical fluids

Supercritical fluids as the medium for homogeneous catalysis currently receives attention because of the advantage that in reactions with e.g. CO only one phase is involved. For instance, the Rh-catalyzed hydroformylation of propene to butyraldehydes in supercritical carbon dioxide has been studied [7]; by using high pressure NMR it was found that the rate of formylation and the steady state concentrations of intermediates like  $\text{Co}_2(\text{CO})_8$ ,  $\text{HCo}(\text{CO})_4$  and  $\text{RC}(\text{O})\text{--Co}(\text{CO})_4$  are comparable to those in non-polar liquid media. Dynamic processes were studied at temperatures up to  $205^\circ\text{C}$  at 340 bar by  $^{59}\text{Co}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR in a non-rotating probe. Due to reduced viscosity, line widths of quadrupolar nuclei like  $^{59}\text{Co}$  are appreciably reduced in supercritical fluids. For a 0.04 M solution of  $\text{Co}_2(\text{CO})_8$  in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$  the line width was 30.0 kHz, whereas in supercritical  $\text{CO}_2$  ( $d = 0.5 \text{ g/ml}$ ) at  $32^\circ\text{C}$  it was only 5.1 kHz. Hence, the distinction between Co-complexes with similar  $^{59}\text{Co}$  chemical shifts, like  $\text{C}_3\text{H}_7\text{C}(\text{O})\text{--Co}(\text{CO})_4$  and  $\text{Co}_2(\text{CO})_8$ , in  $^{59}\text{Co}$  NMR is facilitated in the supercritical fluid.

#### 5. Conclusion and outlook

It has been shown that high pressure NMR is a most powerful technique for in situ studies and model studies of (homogeneous catalytic) reactions involving high pressures of gases and it will certainly gain impetus in the next few years.

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