Pergamon

Tetrahedron Vol. 51, No. 41, pp. 11199-11206, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/95 $9.50+0.00

0040-4020(95)00687-7

Homogeneous Hydrogenation of Norbornadiene with Parahydrogen and Phosphonic Ester Phosphine Rhodium Complexes studied by in situ NMR Spectroscopy

A. Harthun, K. Woelk, and J. Bargon*
Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany
A. Weigt
Institute of Applied Chemistry, Rudower Chaussee 5, D-12489 Berlin, Germany

Abstract: 1) Homogeneous hydrogenation of norbornadiene with enriched parahydrogen (p-H_2) and phosphonic ester phosphine rhodium complexes is detected using in situ NMR spectroscopy. The obtained polarization spectra remain unchanged during the catalysis in thf-d_8 as a solvent but change with time when the hydrogenation is executed in acetone-d_6. **2)** The observed phenomenon is attributed to a change of the phase correlation of the transferred parahydrogen nuclei via nuclear singlet-triplet (S/T_0) mixing during the reaction. **3)** Simultaneously, ^{31}P NMR spectra change indicating a change in the nature of the original rhodium complex when the hydrogenation is carried out in acetone-d_6.

Introduction

The rhodium complexes $[Rh(pepe)(COD)]BF_4$ (**I**) and RhCl(pepe)(COD) (**II**) [pepe = 2-(diphenylphosphino) ethyl phosphonic acid dimethylester; COD = 1,5-cyclooctadiene] have already been applied successfully in the liquid-phase carbonylation of methanol to acetic acid [1]. During the carbonylation, coordination vacancies at the rhodium-organic catalysts were proposed to be of essential importance. Therefore, the complexes **I** and **II** were especially designed to incorporate the hemilabile pepe ligand that facilitates a reversible ring opening due to a weak donating effect of the double-bonded oxygen in the phosphonic ester group.

In this contribution, we elucidate the qualities of the catalysts **I** and **II** for homogeneous hydrogenation reactions, using 1,5-norbornadiene (NBD) as a model substrate. Different solvents, acetone-d_6 and thf-d_8, were used to demonstrate their role during the catalysis.

The hydrogenations were carried out with parahydrogen, i.e., H_2 that had been enriched in the nuclear singlet state and detected via in situ ^1H NMR spectroscopy. Using parahydrogen (p-H_2) leads to enhanced absorption and emission signals in ^1H NMR spectra of the hydrogenation products if the symmetry of the two transferred hydrogen atoms breaks during the reaction [2, 3]. However, as a prerequisite to observe polarization signals, the dihydrogen must be transferred pairwise to the product. The appearance of polarization signals in the NMR spectrum originates from a selective population of the product's nuclear spin levels that exhibit singlet character. This spin population deviates significantly from the Boltzmann distribution; therefore, and in contrast to normal ^{1}H NMR signals, polarization signals are enhanced by several orders of magnitude (up to 10^5). The method of nuclear spin polarization transferred by hydrogenation reactions has been termed "PASADENA" (Parahydrogen And Synthesis Allow Dramatically Enhanced Nuclear Alignment) [3] or "PHIP" (ParaHydrogen Induced Polarization) [4]. It allows the direct detection [5] and indirect characterization [6] of intermediates, the determination of stereo- and regioselectivity of hydrogenation reactions [7], and the measurement of reaction kinetics [8].

Results and Discussion

Hydrogenation of NBD with [Rh(pepe)(COD)]BF$_4$ (I) in thf-d$_8$

In situ hydrogenation of NBD in thf-d$_8$ with **I** leads to strong polarization signals of the hydrogenation product norbornene (NBN) indicating a pairwise transfer of dihydrogen. The polarization pattern remains the same during the entire reaction. This is exemplified in Figure 1, where polarization signals of the reaction are shown as observed **a)** at the beginning of the hydrogenation and **b)** close to the end. It is noted that at the end of the reaction (Figure 1b) regular ^{1}H NMR signals of the product NBN are visible, whereas in the beginning only polarization signals of NBN are detected. Since the absorption/emission pattern does not change during the reaction, a time-independent reaction mechanism is assumed. A similar result was obtained during the catalytic hydrogenation of NBD using the homogeneous rhodium(I)-catalyst [Rh(NBD)(PPh$_3$)$_2$]PF$_6$ in acetone-d$_6$ [9]. A comparison of the experimental with computer-simulated spectra (Figure 2) shows that the dihydrogen is transferred into a cis-endo position in the NBN.

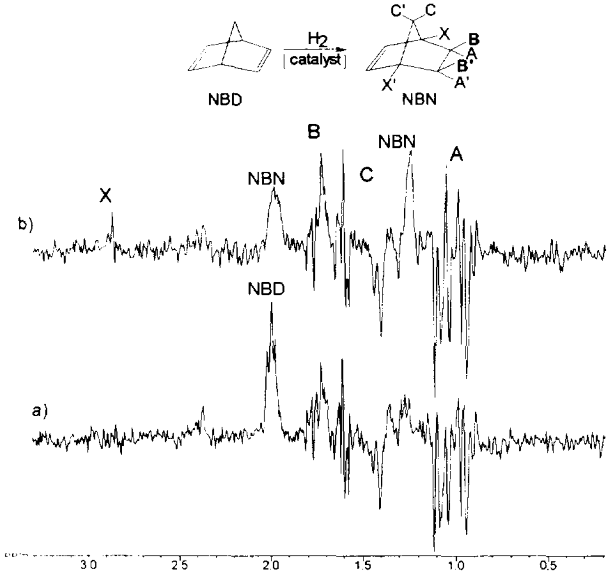


Figure 1: Polarization spectra obtained during the selective hydrogenation of 30 μl NBD to NBN in 1 ml thf-d$_8$ using 17 mg of **I**;
a) accumulation of the first five FIDs after starting the hydrogenation; **b)** accumulation of five FIDs (36-40) at the end of the hydrogenation.
The spectra were recorded with a $\pi/4$ pulse and a delay time between transients of 20 s;

S/T_0-mixing during the hydrogenation of NBD with (I) in acetone-d_6

Similar to the hydrogenation of NBD in thf-d_8, catalyst **I** was used in acetone-d_6 as a solvent. However, in contrast to the reaction in thf-d_8, now the polarization pattern continuously changes with time. Comparing experimental spectra with computer simulations [10] indicates that the change is due to a changing degree of admixture of triplet character to the originally pure singlet state of parahydrogen during the catalytic cycle (singlet/triplet mixing).

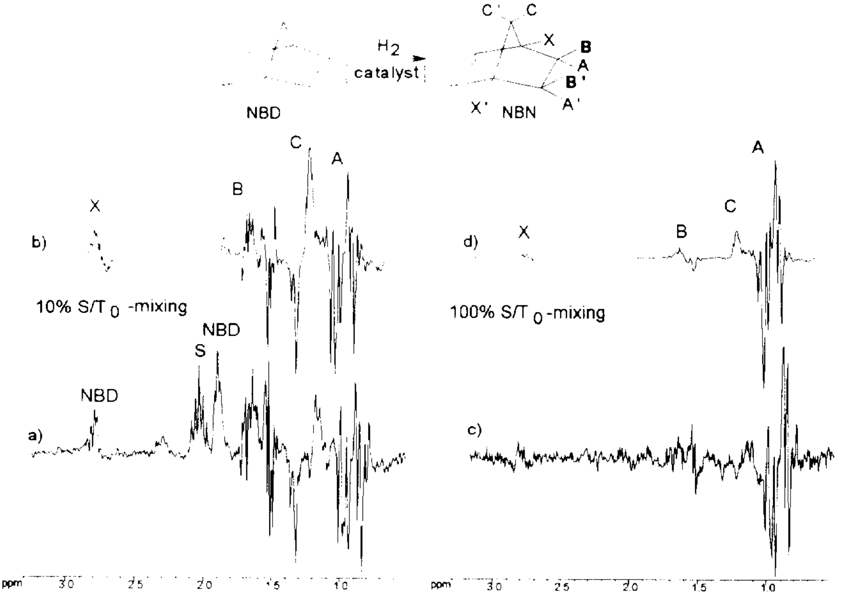


Figure 2: Comparison between experimental spectra recorded during the p-H_2 hydrogenation of 30 µl NBD and 13.3 mg **I** dissolved in 1 ml acetone-d_6 and computer-simulated spectra: **a)** experimental spectrum from the accumulation of the first FIDs 1-5 (s = solvent); **b)** simulation considering 10% S/T_0 mixing and a subsequent transfer of hydrogen into a cis-endo position of NBN; **c)** spectrum of the FIDs 21-25 (for better visualization of the polarization signals, the strong NMR signals of unpolarized reaction product NBN have been subtracted); **d)** simulation as in b) but considering 100% S/T_0 mixing ($S : T_0$ = 50% : 50%).

Singlet/triplet (S/T_0) mixing is a concept that explains a loss of phase correlation between two spins if they become exposed to different magnetic fields at some point during the reaction. In the hydrogenation reaction with p-H_2, this exposure to different fields becomes possible if the former p-H_2 hydrogen atoms coordinate in magnetically inequivalent positions at the metal center prior to the transfer to the substrate. If the duration of this coordination is long enough in comparison to the time scale defined by the difference of the chemical shifts and the magnetic field [6], a constant mixing rate of the S and T_0 states occurs (Figure 3). If S/T_0 mixing must be assumed to explain polarization patterns, the hydrogenation is called non-spontaneous; in contrast to the spontaneous mechanism proposed by Bowers and Weitekamp [11]. The presence of a S/T_0 mixing is considered an indirect proof for the occurrence of a dihydride complex as reaction intermediate [6]. This has been studied extensively for the hydrogenation of 1,4-dihydro-1,4-epoxy naphthalene using Wilkinson's catalyst in a benzene-d_6 solution. A constant S/T_0-mixing rate of $S : T_0$ = 60% : 40% was found.

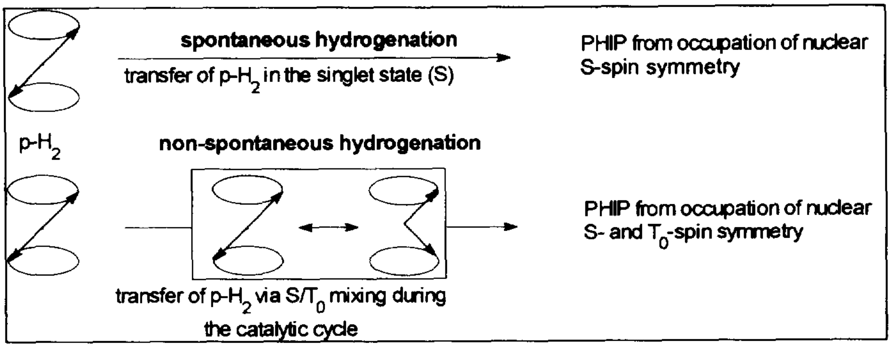


Figure 3: Scheme of two possible pathways of catalytic hydrogenation comparing a spontaneous and a non-spontaneous alternative, where the latter leads to S/T_0 mixing via changing the original phase correlation. The antiparallel arrows arranged on double cones characterize nuclear spins that precess in an external magnetic field.

From the discussion above, it is evident that the hydrogenation of NBD with **I** in thf-d_8 proceeds with a fixed S/T_0 mixing, while during the same hydrogenation in another solvent (acetone-d_6) the S/T_0 mixing rate changes. Considering the theory of non-spontaneous hydrogenation [6], an increasing S/T_0 mixing must be a result of an increasing lifetime of the intermediate dihydrogen complex. To elucidate whether this increase of stability of the dihydrogen complex in acetone-d_6 is due to changes of the ligand sphere, e.g., changes of the hemilabile pepe ligand, ^{31}P NMR spectra of the reactive solution were recorded.

For this purpose, catalyst **I** was dissolved in thf-d_8 or acetone-d_6, and ^{31}P NMR spectra were monitored before and after the hydrogenation. Prior to each measurement, 30 µl NBD were added to the solution to substitute COD with NBD. The spectroscopic data are depicted in Table 1. They reveal that the chemical shifts and coupling constants of the hemilabile ligand are different before and after the hydrogenation of NBD in acetone-d_6, whereas they remain constant in thf-d_8.

Table 1: ^{31}P NMR data observed after the addition of 30 µl NBD to the complex **I** dissolved in acetone-d_6 or thf-d_8. The spectra were recorded before and after the hydrogenation. The data correspond to the two P nuclei of the pepe ligand as follows: $(H_3CO)_2P^1O(CH_2)_2P^2(Ph)_2$.

	^{31}P NMR data of **I**			
	before hydrogenation		after hydrogenation	
	P1	P2	P1	P2
thf-d_8	δ = 41,99 ppm J_{PP} = 11,3 Hz	δ = 26,14 ppm J_{PP} = 11,3 Hz, J_{PRh} =171,79 Hz	δ = 41,99 ppm J_{PP} = 11,3 Hz	δ = 26,14 ppm J_{PP} = 11,3 Hz, J_{PRh} =171,79 Hz
acetone-d_6	δ = 41,54 ppm J_{PP} = 9,9 Hz	δ = 25,55 ppm J_{PP} = 9,9 Hz, J_{PRh} = 164,89 Hz	δ = 40,6 ppm J_{PP} = 12,8 Hz; J_{PRh} = 3,45 Hz	δ = 22.56 ppm J_{PP} = 12,8 Hz, J_{PRh} = 151,1 Hz

To prove whether ring opening of the chelated pepe ligand is the origin of the formation of a new complex during the hydrogenation of NBD in acetone-d_6, reactions with the second complex (**II**) were investigated. In **II**, the pepe ligand is mono-coordinated by the phosphine group but not chelated. The ^{31}P NMR spectrum of this complex (Figure 4a) shows similar signals compared with those of free pepe substrate in the same solution [1], while a bis-coordinated pepe chelat shows entirely different signals (Table 1). When $AgBF_4$ is added to a solution of **II**, chlorine becomes displaced and the mono-coordinated pepe ligand is forced to form a chelat ring via the phosphonic ester group (complex **A**). ^{31}P NMR spectra of **A** exhibit the same signals as obtained from **I** before the hydrogenation.

A solution of **II** and NBD in acetone-d_6, which has been primed with $AgBF_4$ in the above-mentioned way, was hydrogenated with p-H_2 at a pressure of 3 bar. ^{31}P NMR spectra recorded in situ from this solution show a new complex **B** that evolves from complex **A** (Figure 4b, 4c and Table 2).

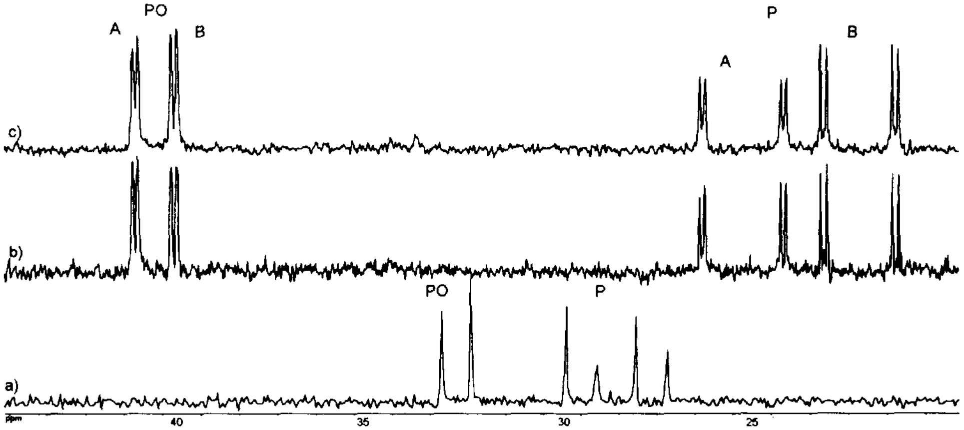


Figure 4: **a)** Experimental ^{31}P NMR spectrum of a solution containing 17 mg complex **II** and 30 μl NBD dissolved in acetone-d_6; **b)** as a) but after addition of $AgBF_4$, observed during the hydrogenation at 3 bar p-H_2 pressure; **c)** as b) but the spectrum was recorded 30 min later.

Table 2: ^{31}P NMR data of complex **II** and 30 μl NBD dissolved in acetone-d_6. Addition of $AgBF_4$ to the solution leads to ring closure, upon which complex **A** is detected. The spectra recorded during the hydrogenation reveal that complex **B** evolves from complex **A**.

^{31}P NMR data of **II**					
before hydrogenation		after $AgBF_4$ addition and hydrogenation			
		complex A		**complex B**	
p1	p2	p1	p2	p1	p2
δ = 32,2 ppm J_{PP} = 66 Hz	δ = 28,94 ppm J_{PP} = 66 Hz, J_{PRh} =149,6 Hz	δ = 41,62 ppm J_{PP} = 11,3 Hz	δ = 25,6 ppm J_{PP} = 11,3 Hz, J_{PRh} =171,8 Hz	δ = 40,6 ppm J_{PP} = 12,8 Hz J_{PRh} =2,96 Hz	δ = 22,56 ppm J_{PP} = 12,8 Hz J_{PRh} =151,6 Hz

Comparing the spectra 4b and 4c with 4a indicates that no free or mono-coordinated ligand is detected during the hydrogenation. Accordingly, both **A** and **B** contain the hemilabile pepe ligand as a bis-chelat. The ^{31}P NMR data of complex **B** (Figure 4) are very similar to those obtained after the hydrogenation of complex **I** in acetone-d_6. After the hydrogenation in thf-d_8, however, a formation of complex **B** was not detected. Unfortunately, complex **B** could not be isolated, and therefore, was not characterized more precisely [12]. Nevertheless, it appears that the change of S/T_0 mixing rate is related to the evolution of the new complex **B** during the hydrogenation.

Further experiments, like a preceding hydrogenation of **I** before the addition of the substrate NBD or the hydrogenation of a mixture of NBD and NBN did not effect the polarization pattern at the beginning of the hydrogenation; therefore, the initial conditions do not effect the changing S/T_0 mixing rate.

Conclusion

The rhodium(I)-complex $[Rh(pepe)(COD)]BF_4$ is an active catalyst for the selective hydrogenation of NBD to NBN. The H_2 atoms are transferred pairwise into a cis-endo position of the substrate. In acetone-d_6, a change of the S/T_0 mixing rate is observed during the hydrogenation with p-H_2 via in situ NMR spectroscopy and is correlated to a formation of a new complex **B**. ^{31}P NMR spectra reveal that the hemilabile ligand pepe is closed, i.e., chelated, in this new complex **B**. In thf-d_8, neither a change of the S/T_0 mixture nor the formation of a new complex is monitored.

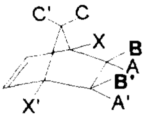
For the first time, a changing S/T_0 mixing rate has been observed during a hydrogenation reaction with p-H_2 indicating a change of the reaction mechanism. In addition, it has been shown that this change coincides with the evolution of a new catalyticly active species. Accordingly, using p-H_2 for hydrogenation reactions is not only helpful for the elucidation of reaction intermediates but also for the in situ detection of changing reaction mechanisms.

Experimental Part

The ^1H NMR spectra were obtained at 80 MHz (Varian CFT 20) and the ^{31}P NMR spectra at 200 MHz (Bruker AC 200). The ^{31}P NMR spectra are referenced to H_3PO_4 (80%) as internal standard. The solvents acetone-d_6 (Eurisotop) and thf-d_8 (Eurisotop) were used without further work-up.

^1H NMR simulation of NBN

The simulation spectra of NBN were calculated for a simplified, i.e., for the olefinic-decoupled spin system AA'BB'CC'XX' [13]. The chemical shifts and coupling constants are depicted in Figure 5. Best agreements between the simulations and the experimental NMR spectra were obtained when additional cross-polarization effects were considered; in particular, W_0 (AB`/A`B) with a rate of 0.26 sec^{-1} and W_2 (AB/A`B`) with a rate of 0.1 sec^{-1} [13].



NBN

Figure 5: δ = A, A' 1.677; B, B'1.062; C 1.074; C'1.314; X, X' 2.843 ppm.
$J_{AA'}$ = 9.02; J_{AB} = $J_{A'B'}$ = -11.29; $J_{AB'}$ = $J_{A'B}$ = 3.91; J_{AC} = $J_{A'C}$ = 0.25; $J_{AC'}$ = $J_{A'C'}$ = 2.37; J_{AX} = $J_{A'X'}$ = 0.55; $J_{AX'}$ = $J_{A'X}$ = -0.08; $J_{BB'}$ = 9.38; J_{BX} = $J_{B'X'}$ = 3.66; $J_{BX'}$ = $J_{B'X}$ = -0.15; $J_{CC'}$ = -8.03; J_{CX} = $J_{CX'}$ = 1.51; $J_{C'X}$ = $J_{C'X'}$ = 1.83; $J_{XX'}$ = 1.19 Hz

Hydrogenation of NBD with [Rh(pepe)(COD)]BF$_4$ (I) in acetone-d$_6$ and thf-d$_8$

The hydrogenations were carried out at room temperature in open 5-mm NMR tubes within the NMR probe of the 80 MHz NMR spectrometer. Para-enriched dihydrogen containing about 50 % p-H_2 was prepared by passing H_2 through activated charcoal at 77 K, and bubbled through a capillary in an interrupted mode into the spinning NMR tube containing the reaction solution [14]. Prior to their use, the deuterated solvents were deoxygenated with argon for about 5 min.

Hydrogenation of NBD with RhCl(pepe)(COD) (II) and AgBF$_4$ in acetone-d$_6$

Hydrogenation of NBD with **II** and $AgBF_4$ was carried out at 3 bar p-H_2 pressure in a 5 mm NMR tube equipped with a Teflon pressure valve. The tube was closed, shaken, and placed into the probe of the 200 MHz magnet at room temperature.

Acknowledgement

Financial support was obtained from the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF), the Deutsche Forschungsgemeinschaft (DFG, SFB 334), the Volkswagenstiftung, and the Fonds der Chemischen Industrie. We thank S. Klages, University of Bonn, for assistance in the measurement of ^{31}P NMR spectra.

References and Notes

1 Freiberg, J.; Weigt, A.; Dilcher, H. *J. prakt. Chem.* **1993,** *335*, 337-344; and references therein.

2 Eisenschmid, T.C.; Kirss, R. U.; Deutsch, P. P.; Hommeltoft, S. I.; Eisenberg, R.; Bargon, J.; Lawler, R. G.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 8089-8091.

3 Bowers, C. R.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541-5542.

4 Kirss, R. U.; Eisenschmid, T. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1988**, *110*, 8564-8566.

5 Duckett, S. B.; Eisenberg, R. *J. Am. Chem. Soc.* **1993**, *115*, 5292-5293, and references therein.

6 Bargon, J.; Kandels, J.; Kating, P. *J. Chem. Phys.* **1993**, *98*, 6150-6153; Kating, P.; Wandelt, A.; Bargon, J.; Selke, R. *J. Phys. Chem.* **1993**, *97*, 13313-13317.

7 Harthun, A.; Bargon, J.; Selke, R. *Tetrahedron Lett.* **1994**, *35*, 7755-7758 and references therein.

8 Chinn, M. S.; Eisenberg, R. *J. Am. Chem. Soc.* **1992**, *114*, 1908-1909; Woelk, K.; Bargon, J. *Z. Phys. Chem.* **1993**, *182*, 155-165.

9 Bargon, J.; Kating, P.; Kandels, J.; Thomas, A.; Woelk, K. *Tetrahedron Lett.* **1990**, *31*, 5721-5724.

10 The simulations were performed using the computer program PHIP9 as developed by J. Kandels, *Ph.D. Thesis*, University of Bonn, Germany, **1992**.

11 Bowers, C. R.; Weitekamp, D.P. *Phys. Rev. Lett.* **1986**, *57*, 2645-2648.

12 Complexes with hemilabile ligands of the type $Ph_2P(CH_2)_nP(X)Ph_2$ [X = O, n = 1, 2; S, n = 1] are described in the literature to form dimers: Blagborough, T. C.; Davis, R.; Ivison, P. *J. Organometal. Chem.* **1994**, *467*, 85-94, and references therein.

13 Thomas, A.; Haake, M.; Grevels, F. W.; Bargon, J. *Angew. Chem.* **1994**, 7, 820-822; Thomas, A. *Ph.D. Thesis*, University of Bonn, Germany **1994**.

14 Bargon, J.; Kandels, J.; Woelk, K. *Z. Phys. Chem.* **1993**, *180*, 65-93.

(*Received in Germany* 18 *July* 1995; *accepted* 23 *August* 1995)