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NMR STUDIES ON [Rh(η^6-ARENE)(P(OPh)$_3$)$_2$]ClO$_4$ IN THE PRESENCE OF ACETONE-d_6. ARENE DISSOCIATION AND DYNAMIC BEHAVIOUR OF THE SOLVENT COMPLEX

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Summary

Dissociation of the complexes [Rh(η^6-arene)L_2]ClO$_4$ (arene = mesitylene (Ia), toluene (Ib) and benzene (Ic); L = P(OPh)$_3$) with loss of the arene ligand in CD_2Cl_2/acetone-d_6 (95/5 mol/mol) has been studied by ^{31}P NMR spectroscopy; for initial 0.025 *M* concentrations of degrees of dissociation were 0.23, 0.33 and 0.85, respectively. The dissociations were first-order, with half-lifes of 31 (Ia), 1.2 (Ib) and 0.7 (Ic) h.

The solvent complex [Rh(acetone)$_m$L$_2$]ClO$_4$ produced by these dissociation reactions showed unusual dynamic structural behaviour. In dry acetone the two phosphorus nuclei were magnetically equivalent (species II-A$_2$), whereas in acetone solutions containing up to 3% water a new molecular species was formed having two non-equivalent phosphorus atoms (species II-AB). The molecules II-A$_2$ and II-AB undergo rapid interconversion on the NMR time scale with an activation barrier of $\approx$ 50 kJ/mol.

Introduction

The interest in π-arene complexes of the Co and Ni triads has increased in the last decade because the high reactivity of these compounds leads to arene exchange and to homogeneous catalytic activity in hydrogenation [1–7]. The labile metal–arene bond is broken in n-donor solvents with formation of solvent complexes. On the other hand, solvent complexes prepared in situ are important intermediates in the

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preparation of the arene complexes and in arene exchange reactions [6]. Although the properties of the intact metal-arene compounds have been studied by electron absorption spectroscopy, ^1H and ^{31}P NMR spectroscopy, IR spectroscopy and X-ray diffraction [8,9], knowledge of the solvent complexes is poor. Only in rare cases have stable solvent complexes been isolated and characterized [10], and normally neither the coordination number nor any other structural or dynamic feature of such species are known. In order to gain more information on the nature of the solvent interaction with rhodium complexes we have studied the dissociation and arene exchange reactions of the compounds $[Rh(\eta^6\text{-arene})L_2]^+$ (arene = mesitylene (Ia), toluene (Ib) and benzene (Ic); $L = P(OPh)_3$) [9] in solvent mixtures containing acetone as n-donor component. The solvent complex $[Rh(\text{acetone})_m L_2]^+$ (II) formed in situ was characterized by NMR spectroscopy. Under the influence of trace amounts of water (< 3 mol%) the complex II showed a ligand rearrangement which could be studied on the time scale of ^1H and ^{31}P NMR experiments.

Results and discussion

Dissociation and exchange of arene ligands

The NMR spectra show that in inert solvents (e.g. CD_2Cl_2) the complexes Ia–Ic are highly symmetrical over the temperature range from 303–198 K. The resonances of the arene- and arenemethyl protons are singlets (Table 1a) while a single 1/1 doublet (^1J(Rh–P) 323 Hz at 298 K) of ^{31}P NMR signals was obtained for the two magnetically equivalent phosphorus nuclei. Upon addition of acetone the arene ring begins to dissociate off. The appearance of free ligand signals can be observed in the ^1H NMR (Table 1a) and ^{13}C NMR spectra (Table 2), while in the ^{31}P NMR spectra

TABLE 1a

^1H CHEMICAL SHIFTS OF FREE AND COMPLEXED ARENE LIGANDS IN $[Rh(ARENE)(P(OPh_3)_2)]ClO_4$ COMPLEXES [a] IN CD_2Cl_2/ACETONE-d_6 (95/5 mol/mol)

Complex	δ(arene–methyl)		δ(arene)	
	free	bound	free	bound
Ia	2.22	1.98	6.76	6.12
Ib	2.26	1.75	[b]	≈ 5.77
Ic	–	–	[b]	5.91

[a] From 200 MHz spectra. [b] Hidden under the multiplet from the $P(OPh)_3$ protons (The resonances of the triphenylphosphite protons give a multiplet in the region 7.3–7.6 δ).

TABLE 1b

$^{31}P\{^1H\}$ CHEMICAL SHIFTS [a] AND ^1J(RhP) COUPLING CONSTANTS FOR THE COMPLEXES I AND II IN CD_2Cl_2/ACETONE-d_6 (95/5 mol/mol) AT 298 K

Complex	δ	J (Hz)
Ia	116.3	323.0 ± 3
Ib	120.4	323.0
Ic	123.8	323.0
II	122.3	312.0

[a] Relative to an aqueous solution of H_3PO_4 as external standard.

TABLE 2

^{13}C CHEMICAL SHIFTS, C–H COUPLING CONSTANTS AND ASSIGNMENTS FOR THE RESONANCES OF II AND FREE MESITYLENE GENERATED FROM Ia IN ACETONE-d_6 (T 220 K)

δ	^1J(C–H) (Hz)	Assignment	
121.3 (d)	162±3	C(3,5)	triphenylphosphite
126.0 (d)	162	C(4)	
130.8 (d)	162	C(2,6)	
151.7 (s)	–	C(1)	
137.8 (s)	–	$C_{quart.}$	free mesitylene
127.3 (d)	152	$C_{tert.}$	
21.0 (q)	126	C_{methyl}	

the resonances of the solvent complex II can be distinguished from those of the starting compounds (Table 1b).

For kinetic measurements of the dissociation ^{31}P NMR spectroscopy offers two advantages: (i) it is more sensitive by several orders of magnitude than ^{13}C NMR spectroscopy, and (ii) information can also be obtained on the dissociation of Ic, whereas the aromatic signals of free toluene and benzene cannot be observed by ^{1}H NMR spectroscopy (Table 1a).

In Fig. 1a the degree of dissociation x, $[x = c_{II}/(c_I + c_{II})]$ relating to an initial concentration of 0.025 M, is plotted against the reaction time. The data indicate (Fig. 1b) that the dissociation is a first order process which reaches an equilibrium:

$$\underset{(I)}{[Rh(arene)L_2]^+} \underset{+\text{arene}}{\overset{+\text{acetone}}{\rightleftharpoons}} \underset{(II)}{[Rh(acetone)_mL_2]^+}$$

The half-life and equilibrium degrees of dissociation are substantially different for the three arene ligands.

By use of ^{31}P NMR spectra it was also possible to monitor the arene exchange reactions in dichloromethane. In a solution containing equimolar quantities of the benzene complex Ic and free mesitylene the formation of the mesitylene complex Ia was complete after 2 h, while under the same conditions with the toluene complex (Ib) as starting material only $\approx$ 50% of arene ligands were exchanged. These results are in excellent agreement with observations reported in the literature; according to Sievert and Muetterties [6] and Brown et al. [11] the arene–metal bond enthalpy in a homologous series of η^6-arenemetal complexes is proportional to the number of methyl substituents on the aromatic ring. In agreement with these data solution equilibrium studies showed a coordination preference of mesitylene > toluene > benzene, and the exchange of η^6-toluene $\rightleftharpoons$ η^6-mesitylene for the system $(C_6F_5)_2$Ni(toluene) was found to be first order in both directions [5]. Moreover, solvolytic displacements observed for (C_5Me_5)M(arene) cations (M = Rh, Ir) [10] showed that alkyl substitution of the η^6-arene lowered the lability of the metal–arene bond.

Dynamic behaviour of the acetone complex II under the influence of water

While mixtures of complexes I and II are obtained in CD_2Cl_2/acetone-d_6 (95/5)

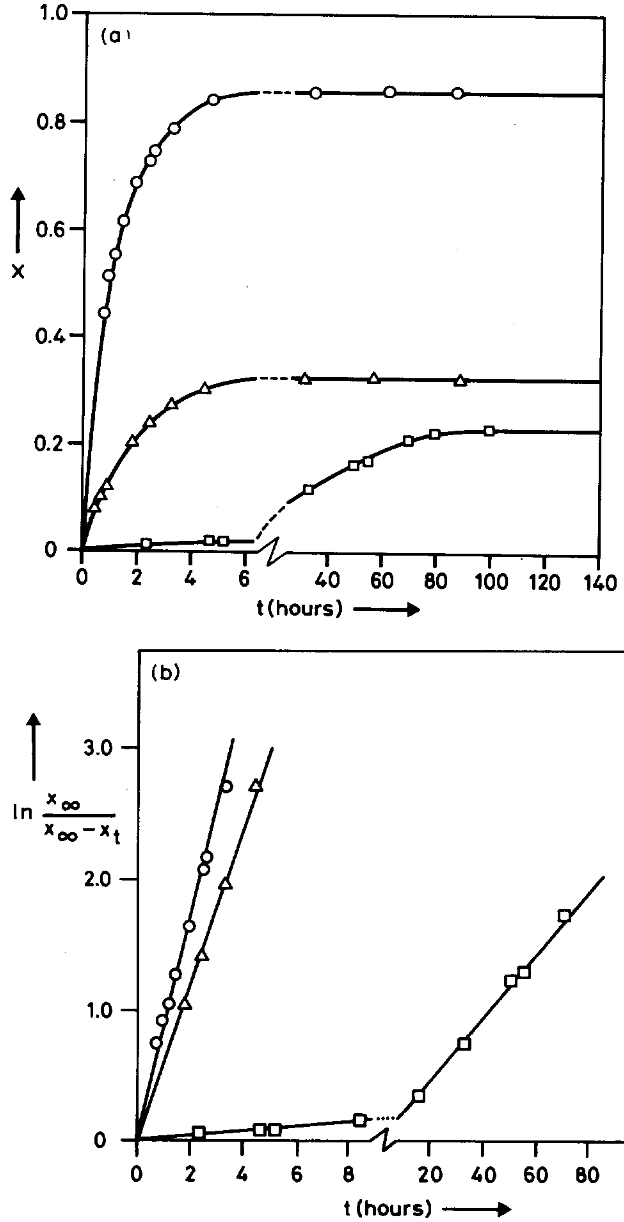

Fig. 1. (a) Plot of the degree of dissociation x ($= c_{II}/(c_I + c_{II})$) against time for complexes Ia (□), Ib (△) and Ic (○) in CD_2Cl_2/acetone-d_6 (95/5, mol/mol). Logarithmic plot of $x_\infty/(x_\infty - x_t)$ vs. time. (x is the equilibrium dissociation degree).

(Fig. 1), dissociation is complete in pure acetone. Under these conditions, the ^{31}P NMR spectrum of II consists of a single doublet with ^1J(Rh–P) 312.0 Hz (298 K), the chemical shift of which changes from 122 to 127 δ upon lowering the temperature from 298 to 198 K. Upon addition of trace amounts of water to the solutions ($<$ 3 mol%) eight new ^{31}P signals appear in the low temperature spectra at 198 K, in addition to this doublet (Fig. 2). The ^{31}P spectrum of the solvent complex now

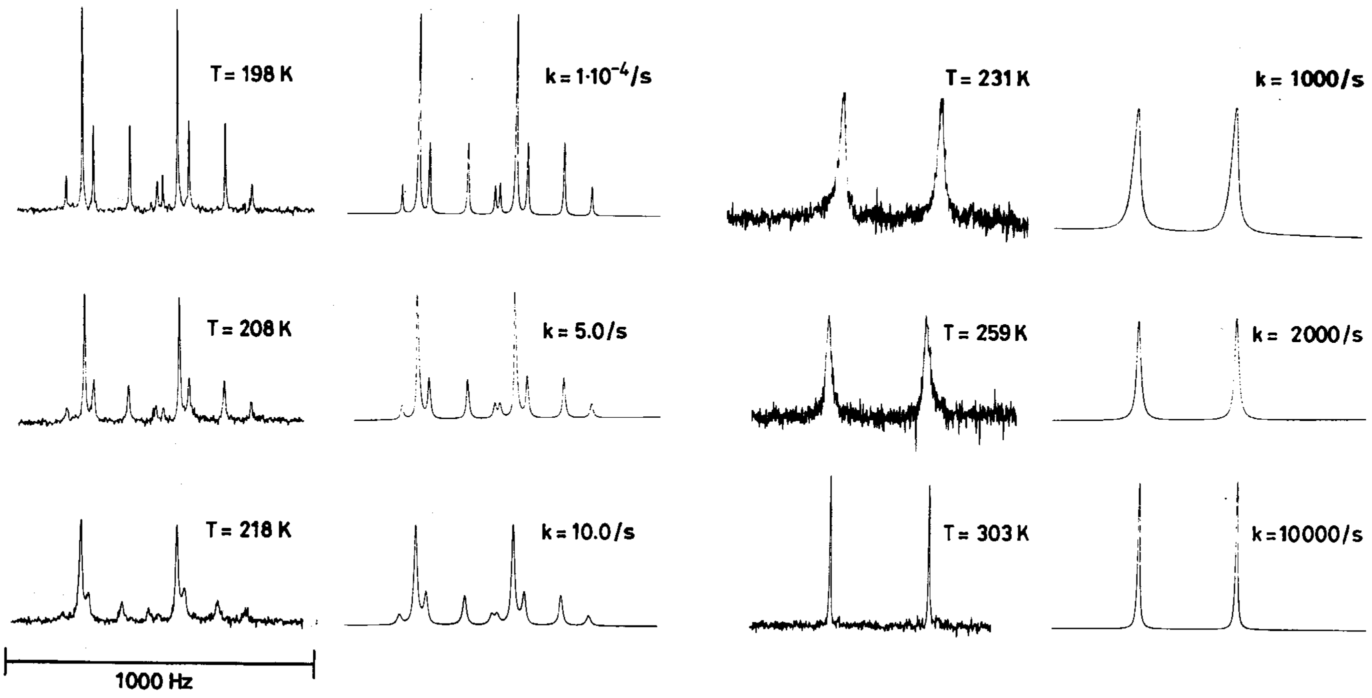

Fig. 2. Experimental and simulated ^{31}P NMR spectra. Experimental spectra were recorded for a solution of Ia in a mixture of D_2O and acetone-d_6 (0.3/99.7 mol/mol) in the temperature range from 198–303 K. Simulated spectra were calculated for the exchange rate constants shown on the graphs.

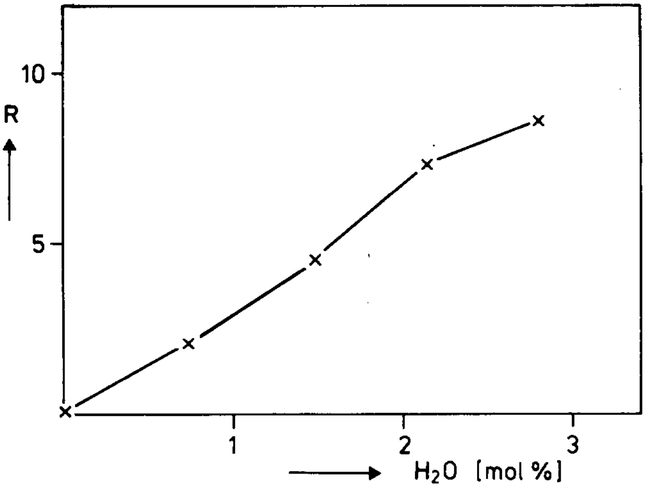

Fig. 3. Ratio of the intensity of the AB- to that of the A_2- ^{31}P NMR patterns at 198 K for solutions of Ia in acetone-d_6/water mixtures.

consists of the A_2 part of an A_2X spectrum and the AB part of an ABX spectrum. The molecular species giving rise to these signals are denoted by II-A_2 and II-AB, respectively. We assign II-A_2 to the acetone complex with a symmetrical environment of the ^{31}P nuclei, and II-AB to a species in which these nuclei are in an asymmetric environment. This assumption is confirmed by the fact that the ratio of concentration of II-AB over II-A_2 is proportional to the water content of the sample (Fig. 3) and that the same spectral pattern is observed in solutions of II obtained in the presence of $AgClO_4$ from $Rh_2L_4Cl_2$ in acetone containing trace amounts of water.

From the values of the Rh–P and P–P coupling constants it is possible to draw some conclusions about the coordination at the metal atom. It is known that ^1J(Rh–P) depends on the *s*-electron densities on the metal and the phosphorus atoms, and that the value of ^1J(Rh–P) decreases with increasing coordination number due to the distribution of the metal *s*-electrons among a greater number of orbitals [13,14]. When comparing the coupling constants in Table 3 with literature values we find close agreement with a pseudo-planar complex (η^3-pentamethylben-

TABLE 3

^{31}P NMR SPECTRAL PARAMETERS OF THE SOLVENT COMPLEXES II-A_2 AND II-AB IN ACETONE-d_6/D_2O (99/1 mol/mol) AT 198 K [a]

Complex	δ	^1J(RhP) (Hz)	^2J(PP) (Hz)
II-A_2	127.8	303.4±3	–
II-AB	127.9 122.5	310.0 310.0	87.0±3

[a] The spectra were normally recorded at 36.43 MHz (Bruker WH 90). The spectral assignment was confirmed by measurements at 80.9 MHz (varian XL 200).

zyl)RhL$_2$ [15] with a geometric mean value of $\langle {}^1J(\text{Rh–P}) \rangle$ 320 Hz and ${}^2J(\text{P–P})_{cis}$ $\approx$ 82 Hz while a significantly lower value of $\langle {}^1J(\text{Rh–P}) \rangle$ 181 Hz has been reported for the trigonal bipyramidal environment [16] of Rh. These observations favour a square-planar coordination with *cis*-arrangement of the phosphite ligands in the solvent complexes II-A$_2$ and II-AB.

When the temperature is raised, characteristic changes in the line-shapes of the spectrum in Fig. 2 indicate rapid reversible interconversion of species II-A$_2$ and II-AB, with an activation barrier between them of 50 kJ/mol. The molecular rearrangement is also evident in the ^{1}H NMR pattern of the triphenylphosphite ligands. As shown in Fig. 4a (complex IIa in acetone-D$_2$O), the aromatic region of the proton spectrum of water-containing sample changes significantly when the temperature is lowered from 268 to 200 K. In the low temperature region the proton signals due to the phenoxy rings cover the range from 6.8–7.7 δ, while in the high temperature region the resonance is much narrower (7.3–7.6 δ). When dry acetone is used as a solvent the phenoxy part of the spectrum (7.3–7.6 δ) is completely independent of temperature (Fig. 4b). This indicates that there is a decrease in the overall symmetry of the molecule upon lowering the temperature in the presence of water, and is consistent with the conclusions drawn from the ^{31}P NMR measurements.

In contrast, the ^{13}C NMR spectra of II in mixtures of acetone-d_6 and D$_2$O did not show any significant change upon lowering the temperature from 273 to 220 K,

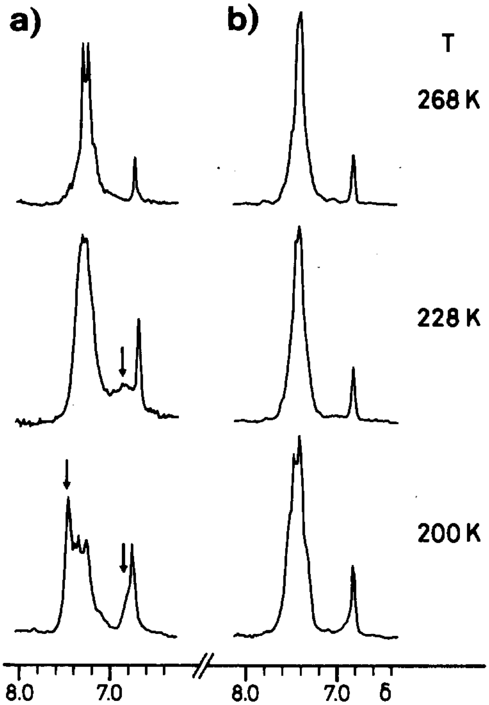

Fig. 4. Aromatic region of ^{1}H NMR spectra of (IIa) in acetone-d_6/water (99/1, mol/mol) (a) and in dry acetone (b). The spectrometer frequency was 90 MHz. The arrows indicate the new signals which appeared at low temperature in the water-containing sample.

(^{13}C chemical shifts of a sample containing complex II in acetone-d_6/D_2O (99/1, mol/mol) at 220 K are given in Table 2).

A simple model to explain the distortion of the originally highly symmetric complex II in the presence of water is based upon the assumption that a rhodium-bound acetone molecule is reversibly replaced by a water molecule:

$$\underset{\text{(II-A}_2\text{)}}{[\mathrm{L_2Rh(acetone)}_m]^+} \underset{+\,\text{acetone}}{\overset{+\,\mathrm{H_2O}}{\rightleftharpoons}} \underset{\text{(II-AB)}}{[\mathrm{L_2Rh(acetone)}_{m\text{-}1}(\mathrm{H_2O})]^+}$$

All our attempts to detect a proton signal for the bound water molecule in II-AB failed. This might be due to a rapid proton exchange between bound and free water molecules. However, it would also be consistent with an alternative model lacking bound water. In principle, it cannot be ruled out that conformational changes of II upon increase in solvent polarity might occur without direct binding of water to the metal atom. The solvatation sphere of the hydrophobic phenoxy part of complex II could be disturbed by the presence of water and a second molecular conformation with asymmetric arrangement of the phenoxy groups might be stabilized.

In conclusion, we can say that because of the high sensitivity and the spectral simplicity ^{31}P NMR spectroscopy provides is an excellent method of studying arene dissociation and exchange in compounds of type I. Such spectroscopy revealed the influence of small amounts of water on the molecular geometry of the acetone complex II and gave valuable information about a water-induced reversible molecular rearrangement of II. Details of the molecular mechanisms of this process are not yet known.

Experimental

Preparations

The [Rh(η^6-arene)L_2]ClO_4 complexes were prepared by adding $AgClO_4$ to a solution of the dimer complex $Rh_2L_4Cl_2$ in a mixture of CH_2Cl_2 and arene [9].

NMR experiments

^{1}H and ^{31}P NMR spectra were recorded on a Bruker WH 90 or on a Varian XL 200 spectrometer, and ^{13}C NMR spectra were recorded on a Bruker WP 200. The sample concentrations were 0.025 *M* ($\approx$ 20 mg/ml). For ^{1}H NMR spectra 20–100 and for ^{31}P NMR spectra about 500–800 transients with a pulse sequence of 3 sec and a pulse angle of 60° were accumulated, while 5000–50000 accumulations were necessary for the ^{13}C spectra. NMR line-shape calculations were carried out with the D-NMR program of Kleier and Binsch [17].

Dissociation of arenes

Samples of the arene complexes Ia–Ic (0.025 *M* CD_2Cl_2 were thermostated at 273 K. At zero time acetone was added to the solution (acetone-d_6/CD_2Cl_2 = 5/95 mol/mol). ^{31}P NMR spectra were recorded at 193 K. The progress of the dissociation was followed by integration of the signals of the solvent complex II and of undissociated complexes I. The degree of dissociation x, given by [$x = c_{II}/(c_I + c_{II})$], was plotted against the reaction time. At 193 K the dissociation reaction was very slow compared to that at 273 K, which means that the dissociation was interrupted during the NMR measurements.

Arene exchange reactions

Equimolar amounts of mesitylene were added to samples of complexes Ib and Ic (0.025 *M* in CD_2Cl_2). The mixtures were kept at 273 K and the degree of arene exchange was determined from the ^{31}P NMR spectrum at 193 K.

Stability of the acetone complex

Solutions of Ia–Ic in acetone-d_6 are not stable at 298 K; decomposition yields a dark solid and free triphenylphosphite. However, when the samples were kept at 220 K the rate of decomposition was low; under those conditions ca. 10% of free triphenylphosphite could be detected after 3 weeks. The temperature dependent effects in the ^{31}P and ^1H NMR spectra of II were fully reversible, and independent of the amount of decomposition product present ($< 10\%$). A typical NMR sample contained 20 mg Ia and 2 μl water in 1 ml acetone-d_6 (1 mol% water); this corresponds to a molar ration of 1/5/500 for Ia/H_2O/acetone-d_6.

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