Catalyst–Substrate Complexes of Chiral Seven-membered Ring Chelates of Rhodium(ı)-bis(phosphinites)

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Line-shape analysis of ^{31}P NMR spectra of catalyst substrate complexes of seven-membered ring rhodium(ı)-bisphosphinites indicate for the first time a quantifiable preference of the intramolecular major–minor isomerisation of both diastereoisomeric chelates of dimethyl itaconate over the slow intermolecular interconversion.

Rhodium(ı)–diphosphine catalysts prefer one enantiotopic face of prochiral olefinic substrates forming the more stable major complex. However, the thermodynamically less favoured minor complex has been shown to be considerably more reactive towards hydrogen.[1,2] In the interconversion of these two complexes both the inter- and intra-molecular ligand exchange processes are occurring.[3,4] We investigated seven-membered bis(phosphinite) rhodium ring chelate complexes[5,6] because of their industrial importance. The catalyst–solvent complexes 2 are obtained as usual by hydrogenation of the corresponding COD, or better NBD complexes in methanol, Scheme 1.†,[7]

Except for 2b, complexes 2 have been unequivocally characterised by ^{1}H and ^{13}C NMR spectroscopy. The spectra show only resonances consistent with the solvent complexes 2 and cyclooctane, or norbornane, respectively. The ^{31}P NMR spectra show the characteristic signals of 2. The coupling constants $^1J_{103Rh-31P}$ are in the range of 220–230 Hz, and downfield shifts of ca. 35 ppm relative to the free ligands are typical.[8]

Addition of a four- to seven-fold excess of substrate olefin to solutions of 2 at room temperature cause, in almost all cases, no sharp but broadened ^{1}H, ^{13}C and ^{31}P resonances. This is again the case when studying the reaction of 2b with methyl (Z)-2-N-acetamidocinnamate in [2H8] THF, and of 2c with methyl (Z)-2-N-benzoylamidocinnamate in [2H6] acetone, at room temperature from +30 to −80 °C; the lines remained broadened due to exchange processes. However, when studying the reaction of the C_2-symmetric complex 2a with itaconic acid dimethylester (ItMe₂) in CD₃OD by ^{31}P NMR spectroscopy by appropriate lowering of the temperature we have been able to observe characteristic line form alterations consistent with (i) the intermolecular exchange process solvent complex 2a ⇌ substrate complexes 3a' + 3a" and likewise, upon further lowering of temperature, with (ii) the intramolecular major-complex 3a' ⇌ minor-complex 3a" exchange, as displayed as follows:

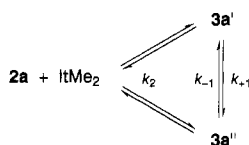Fig. 1 shows the experimental and the calculated low-temperature ^{31}P{^{1}H} NMR spectra. At room temperature only a doublet from [103]Rh–[31]P coupling of the solvent complex 2a is observed. This is also confirmed by ^{1}H and ^{13}C NMR spectroscopy. Hints for low complexation of dimethyl itaconate with seven-membered ring chelates have been given previously.[9] Lowering the temperature to 238 K causes signals of the mixture of diastereoisomers 3a' + 3a" to appear. These remain, by fast exchange, averaged at >197 K.

Further lowering to 187 K causes splitting and two groups of multiplets, arising from 3a' and 3a", respectively. The signal assignment was done on the basis of coupling constants and
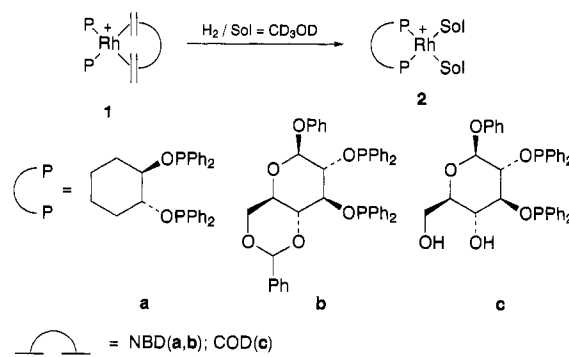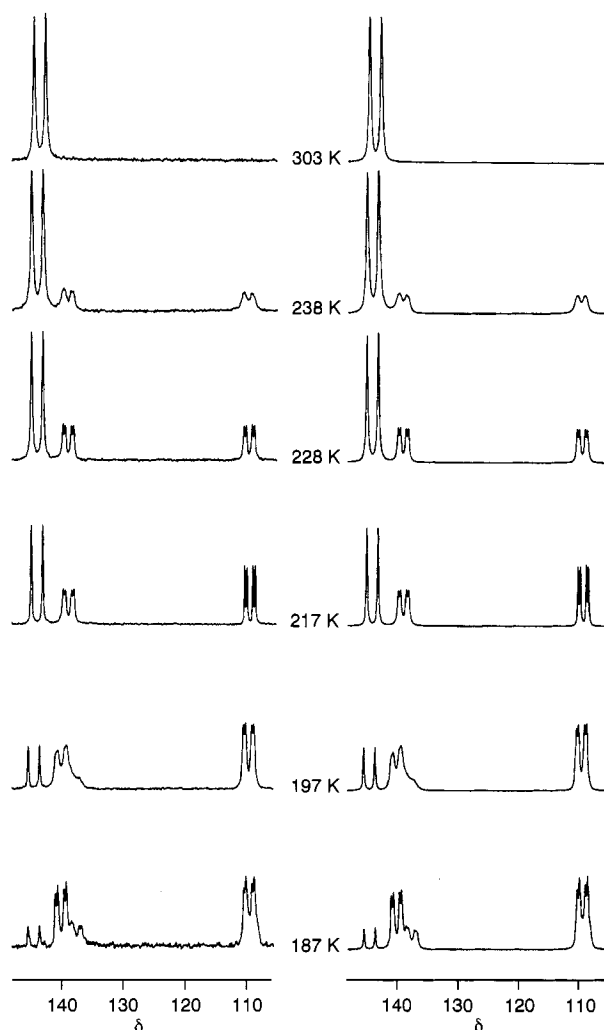

Scheme 1

Fig. 1 Experimental and calculated ^{31}P{^{1}H} NMR spectra of the complexes 2a, 3a' and 3a" in CD₃OD

Table 1 ^{31}P NMR data (δ, rel. 85% H_3PO_4 ext.), J/Hz and population (%) of the complexes **2a**, **3a'** and **3a"** in CD_3OD

T/K	2a δ(P₁/P₂)	¹J_{Rh–P}	(%)	3a' + 3a" δ(P₁)	δ(P₂)	¹J_{Rh–P}	²J_{P–P}	(%)	3a' δ(P₁)	δ(P₂)	¹J_{Rh–P}	²J_{P–P}	(%)	3a" δ(P₁)	δ(P₂)	(%)
303	144.3	228	>99					< 1ᵃ								
271	144.5		92					8								
260	144.6		88					12								
249	144.6		80	139.5	110.7			20								
238	144.6		67	139.6	110.5			33								
228	144.6		52	139.5	110.3			48								
217	144.6	228	35	139.2	110.1	164	48	65								
197	144.6	228	12						140.2	110.0			63	137.7	109.4	25
187	144.6	228	5						140.2	109.9	164	48	68	137.7	109.3	27

ᵃ The low population of catalyst substrate complexes found for ItMe₂ at room temp. distinctly increases for methyl (Z)-2-N-acetamido- cinnamate as substrate. Both substrates are hydrogenated in methanol with comparable enantioselectivities of 66% e.e. (S) or 72% e.e. (R), respectively.

Table 2 Kinetic and thermodynamic data of the complexation reaction **2a** + ItMe₂ ⇌ **3a'** + **3a"** and the major–minor complex isomerisation **3a'** ⇌ **3a"**

T/K	2a + ItMe₂ ⇌ 3a' + 3a" k₂obs	K_{ass}/ dm³ mol⁻¹	3a' ⇌ 3a" k₁obs/ s⁻¹	k₊₁/ s⁻¹	k₋₁/ s⁻¹	ΔG₊₁‡/ kJ mol⁻¹	ΔG₋₁‡/ kJ mol⁻¹	K₁	ΔG₁°/ kJ mol⁻¹
303	(2000)	(0.02)							
271	488								
260	266	0.4							
249	143	0.7							
238	96	1.5							
228	47	2.9							
217	(30)	6.1	(2500)	(700)	(1800)				
197		25	168	48	120	41.2	39.7	0.40	1.5
187		66	39	11	28	41.4	40.0	0.40	1.4

The K- and k-values in parentheses were determined by simulation, all others by iterative fitting to the experimental spectra. $K_{ass} = ([3a'] + [3a"])/[2a][ItMe_2]$; $k_{1obs} = k_{+1} + k_{-1}$; $K_1 = [3a"]/[3a']$.

chemical shifts (Table 1), as they arise from the coordination of the substrate via the olefinic double bond and the β-ester carbonyl group, respectively.[10]

By using the program DNMR5[11] we successfully attempted to quantitatively track down these dynamic processes. The kinetic and thermodynamic data, as obtained, are given in Table 2. Here the rate constant k_2(obs) fits the intermolecular process **2a** + ItMe₂ ⇌ (**3a'** + **3a"**).

The $\Delta G^{\ddagger}$ values of the isomerisation **3a'** ⇌ **3a"** of about 40 kJ mol⁻¹ are within the observable temperature range and are considerably lower than those dissociative processes in which the activation enthalpy approaches the binding energy. The value of the bond dissociation energy of the Rhᴸ–olefin bond has been found to be ca. 130 kJ mol⁻¹.[12,13] In the case of the five-membered ring chelate [Rh(DIPAMP)(BMe)]⁺ an isomerisation rate constant of k_1(obs) = 0.65 s⁻¹ has been found at 325 K,[3] corresponding to a $\Delta G^{\ddagger}$ value of ca. 80 kJ mol⁻¹; hence the energetic barrier for intramolecular isomerisation is in the case of the seven-membered Rhᴸ–bis(phosphinite)-olefin complexes considerably lower. In the former, the rate constants k_1(obs) and k_2(obs) are of similar magnitude[4,14] whereas the data from Table 2 suggests that with our bis-phosphinite chelates the isomerisation of the diastereoisomeric substrate complexes **3a'** ⇌ **3a"** proceeds much faster by the intramolecular than by the intermolecular pathway.

Footnote

† An orange solution of the COD or NBD complexes **1** (0.05 mmol) in 0.8 ml degassed CD_3OD was stirred under hydrogen for 5–15 min and then hydrogen was replaced by argon. The yellow–brown solution of solvent complex was filtered to 0.25 mmol of the substrate in a 5 mm NMR tube which was then sealed under vacuum. Temperature dependent ^{31}P NMR spectra were recorded with a BRUKER ARX-300 spectrometer (121.5 MHz).

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