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Reactions of α-Diimino Ligands with the Chloro-bridged Dimer $[RhCl(COD)]_2$ (COD = 1,5-Cyclooctadiene

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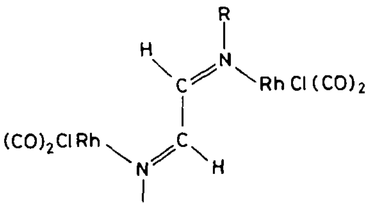
Abstract

The reactions of α-diimino ligands *N-N'* [*N-N'* = 2,2'-bipyridine (bipy), $C_5H_4N-2-CH{=}NR$ ($R = C_6H_4OMe$-*p*, PyCa), $RN{=}CH-CH{=}NR$ ($R = C_6H_4OMe$-*p*, DAB)] with $[RhCl(COD)]_2$ give rise to stoichiometry, solvent, ligand, and temperature dependent equilibria.

In general, the 1/1 ligand/dimer reaction yields the ionic product $[Rh(COD)(N\text{-}N')][RhCl_2(COD)]$, at room temperature. For *N-N'* = DAB, the ionic form is in equilibrium with the binuclear compound $[\{RhCl(COD)\}(\mu\text{-DAB})\{RhCl(COD)\}]$ (containing a σ,σ'-*N,N'* bridging α-diimine), which becomes the predominant species at low temperatures. In $[Rh(COD)(N\text{-}N')][RhCl_2(COD)]$, a fast exchange of the Rh(COD) unit between the cation and anion occurs at 30 °C for *N-N'* = PyCa and DAB (but not for *N-N'* = bipy). The 1/0.5 reaction leads to a product, generally formulated as $Rh(COD)(N\text{-}N')Cl$, which probably consists of an equilibrium mixture of the cationic $[Rh(COD)(N\text{-}N')]Cl$ and neutral $[RhCl(COD)(N\text{-}N')]$ species, in rapid interconversion even at −80 °C. The cationic complex largely predominates in polar solvents, such as methanol, from which it can be precipitated as a perchlorate salt (*N-N'* = bipy, PyCa). For $[Rh(COD)(PyCa)]ClO_4$, a low-energy process occurs which involves ligand site exchange (*cis–trans* isomerization) and cannot be frozen at the lowest explored temperature (−80 °C). Such dynamic behaviour is interpreted in terms of the formation of stereochemically non-rigid five-coordinate intermediates through association of the cation with the solvent or the counteranion. In $[Rh(COD)(N\text{-}N')]^+$, the σ,σ'-*N,N'* chelating abilities of *N-N'* appear to increase in the order: DAB < PyCa < bipy.

Introduction

The bridge-splitting reactions of the binuclear complexes $[RhCl(L_2)]_2$ [$L_2{=}(CO)_2$; η^2,η^2-1,5-cyclooctadiene (COD)] with α-diimino ligands *N-N'* (*N-N'* = 2,2'-bipyridine and 1,10-phenanthroline [1, 2], pyridine-2-carboxaldehyde-*N*-imines [3], 8-substituted quinoline-2-carboxaldehyde-*N*-methylimines [4], 1,2-bis(imino)ethanes [5, 6], 1,2-bis(imino)propylpalladium(II) and -platinum(II) derivatives [7, 8]) yield different products depending on the molar ratio of the reactants, the steric and electronic requirements of the *N-N'* ligand and of the coligands L_2. In the 1/1 reactions, the ionic product $[Rh(L_2)(N\text{-}N')][RhCl_2(L_2)]$, (**A**), is generally formed, in which the α-diimine is σ,σ'-*N,N'* chelate to the Rh(I) center of the cationic species. However, in the reaction of $[RhCl(CO)_2]_2$ with 1,2-bis(imino) ethanes bearing tertiary alkyl N-substituents, the binuclear complex (**B**) is obtained as the major product at low temperatures [6]



B

On the other hand, the 1/1 reaction of the imino carbon metallate ligand $RN{=}C(Me)-C(\textit{trans}\text{-}MCl(PPh_3)_2){=}NR'$ ($R = R'{=}C_6H_4OMe$-*p*; R = Me, $R' = C_6H_4OMe$-*p*; M = Pd, Pt) with $[RhCl(L_2)]_2$ gives initially an ionic intermediate of type **A**, which undergoes a further reaction involving PPh_3 and Cl^- ligand exchange between the cationic and anionic species (for L_2 = COD and M = Pd) [7, 8]:

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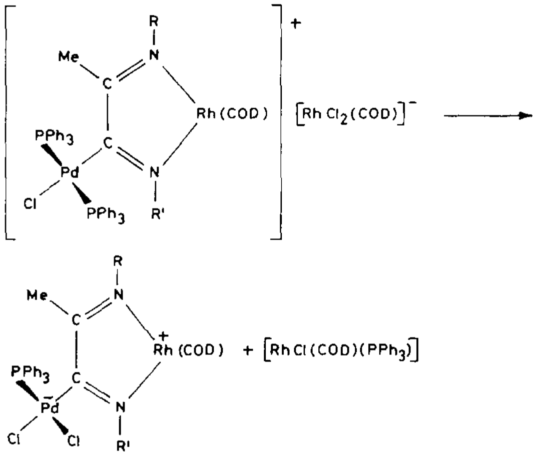
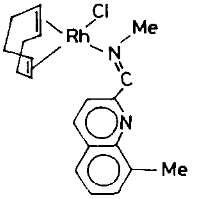
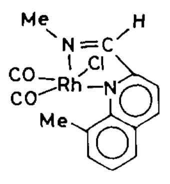


The reaction of *N-N'* with $[RhCl(CO)_2]_2$ (1/0.5 molar ratio) generally gives the five-coordinate product $[RhCl(CO)_2(N\text{-}N')]$ [2,4,9]. The complex $[RhCl(CO)_2(phen)]$ is in equilibrium with the four-coordinate cation $[Rh(CO)_2(phen)]Cl$, depending on the polarity of solvent [2], whereas the derivatives $[RhCl(CO)_2(RN{=}CH{-}CH{=}NR)]$ ($R = CMe_3$, CMe_2-Et) can be characterized only in solution by multinuclear NMR spectroscopy, as they are in equilibrium with the free α-diimino ligand, the ionic compound of type **A** and the binuclear species **B**. These five-coordinate products, however, are stabilized when one CO group is replaced by ethylene or when both CO ligands are replaced by PF_3 [9].

The reaction of *N-N'* with $[RhCl(COD)]_2$ (1/0.5) is usually followed by precipitation of $[Rh(COD)(N\text{-}N')]^+$ with bulky ClO_4^- and PF_6^- anions [3,7,8,10,11]. These cationic complexes are of interest as active catalysts (or catalyst precursors) in the hydrogenation of olefins and ketones, and in the hydrosilylation of ketones [3,10]. Only in one case, does the reaction afford a neutral four-coordinate complex with a σ-*N* monodentate ligand of type **C** [4]:



C



D

Interestingly, the corresponding reaction with $[RhCl(CO)_2]_2$ yields the stable five-coordinate complex (**D**).

The equilibria involved in the system *N-N'*/$[RhCl(COD)]_2$ at different ligand/dimer ratios are not studied in detail as for the related system *N-N'*/$[RhCl(CO)_2]_2$. In this context, we have undertaken an investigation of the reactions of $[RhCl(COD)]_2$ with various α-diimino ligands, such as $RN{=}CH{-}CH{=}NR$ ($R = C_6H_4OMe$-*p*, DAB), $C_5H_4N{-}2{-}CH{=}NR$ ($R = C_6H_4OMe$-*p*, PyCa), and 2,2'-bipyridine (bipy), which have different steric and electronic properties and give five-membered metallocycles of different stabilities when they are σ,σ'-*N,N'* chelate to d^8 metal centers, as in the cationic complexes $[M(\eta^3\text{-}2\text{-}RC_3H_4)(N\text{-}N')]^+$ ($M = Pd, Pt$; $R = H, Me$) [12].

Experimental

The ligands $RN{=}CH{-}CH{=}NR$ ($R = C_6H_4OMe$-*p*, DAB) [13], $C_5H_4N{-}2{-}CH{=}NR$ ($R = C_6H_4OMe$-*p*, PyCa) [14], and the complexes $[RhCl(COD)]_2$ [15], $[RhCl_2(COD)]AsPh_4$ [7] were prepared by literature methods. The solvent 1,2-dichloroethane was distilled over anhydrous K_2CO_3 before use. All other chemicals and solvents were reagent grade, and were used without further purification. The reactions were carried out at room temperature, unless otherwise stated, under N_2 atmosphere. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

[{RhCl(COD)}₂(N-N')] (N-N' = bipy, PyCa, DAB)

A benzene solution of the ligand *N-N'* (0.5 mmol in 20 ml of solvent) was added dropwise to a stirred solution of the dimer $[RhCl(COD)]_2$ (0.246 g, 0.5 mmol in 30 ml of benzene). A deeply coloured precipitate (red for bipy, dark blue for PyCa, red–violet for DAB) began to separate in a few minutes. After 30 min, the volume was reduced to *ca.* 10 ml and diethyl ether (*ca.* 40 ml) was added to complete the precipitation. The microcrystalline product was washed several times with Et_2O and dried *in vacuo*. The yields, based on the theoretical amount, ranged from 91% (bipy) to 85% (PyCa) and 77% (DAB).

Attempted Preparation of Rh(COD)(N-N')Cl

A benzene solution of the ligand *N-N'* (0.5 mmol in 10 ml of solvent) was added dropwise to a stirred solution of the dimer $[RhCl(COD)]_2$ (0.123 g, 0.25 mmol in 20 ml of benzene). The reaction mixture was worked up as above to yield a microcrystalline precipitate, identified as $[\{RhCl(COD)\}_2(N\text{-}N')]$ by IR and ^1H NMR spectroscopy.

[Rh(COD)(N-N')]ClO₄ (N-N' = bipy, PyCa)

The ligand *N-N'* (1 mmol) and the complex $[RhCl(COD)]_2$ (0.246 g 0.5 mmol) were stirred in 30 ml of methanol until complete dissolution. A solution of $NaClO_4{\cdot}H_2O$ (0.40 g) in 10 ml of water was added dropwise, and the mixture was set aside for 2 h. The coloured microcrystalline precipitate (red for bipy, and dark violet for PyCa) was filtered off and washed with distilled H_2O, then with a mixture H_2O/MeOH (1/1, *v*/*v*), and finally with cold MeOH (yield: 0.37 g, 79.3% for bipy; 0.33 g, 63.1% for PyCa).

Attempted Preparation of [Rh(COD)(DAB)]ClO$_4$

(a) The reaction of DAB (0.27 g, 1 mmol) with $[RhCl(COD)]_2$ (0.246 g, 0.5 mmol) and $NaClO_4 \cdot H_2O$ (0.40 g) was carried out as described above for the preparation of $[Rh(COD)(N\text{-}N')]ClO_4$. The resulting red–brown solution was cooled at −60 °C for 2 h to give a red–violet precipitate (0.35 g), identified as $[\{RhCl(COD)\}_2(DAB)]$.

(b) The ligand DAB (0.40 g, 1.5 mmol) and the dimer $[RhCl(COD)]_2$ (0.246 g, 0.5 mmol) were mixed in 15 ml of MeOH. Some red–violet solid began to precipitate within a few minutes. After addition of $NaClO_4 \cdot H_2O$ (0.40 g in 10 ml of H_2O), the mixture was stirred for 1 h. The red–brown solid was filtered off and washed with H_2O and with MeOH/H_2O (3/1, *v*/*v*). This product (0.56 g) was identified as a mixture of unreacted DAB and $[\{RhCl(COD)\}_2(DAB)]$.

Physical Measurements

The conductivity measurements were carried out with a CDM 83 conductivity meter at 20 °C. The ^1H NMR spectra were recorded on a Varian FT80A and on a Bruker WP 80SY FT spectrometer.

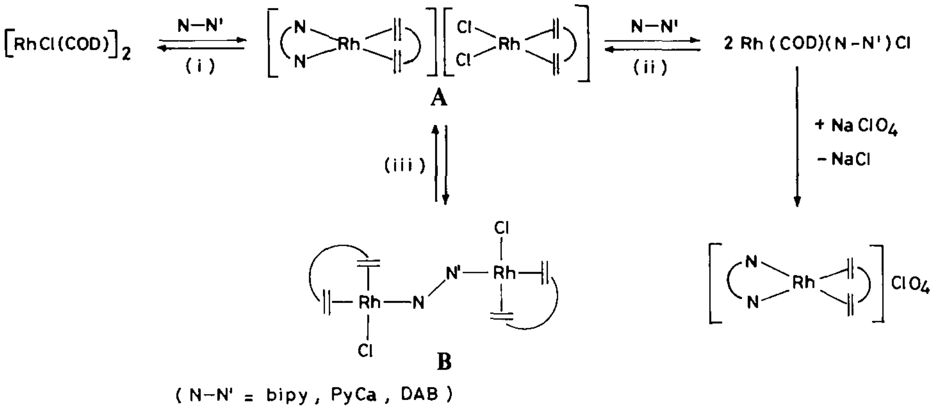
The electronic spectra in solution were recorded with a Bausch-Lomb Spectronic 210UV and with a Cary 219 spectrophotometer in the range 700–250 nm at 25 °C, using quartz cells of 1 cm path length. Infrared spectra were recorded with a Perkin-Elmer 983 G instrument, using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}, and CaF_2 cells of 0.5 mm width for CH_2Cl_2 and C_6H_6 solutions in the range 1800–1500 cm^{-1}.

Results and Discussion

The reactions of α-diimino ligands *N-N'* with the chloro-bridged dimer $[RhCl(COD)]_2$ are shown in Scheme 1. Two successive equilibria take place depending on the ligand/dimer molar ratio. The bridge-splitting products of equilibrium (i) can be isolated as solids from the 1/1 reaction in benzene (see 'Experimental') and have a composition of $[\{RhCl(COD)\}_2(N\text{-}N')]$. The products of equilibrium (ii), generally formulated as $Rh(COD)(N\text{-}N')Cl$, can be studied only in solution. Addition of $NaClO_4$ to the system $N\text{-}N'/[RhCl(COD)]_2$ (1/0.5) in methanol brings about the precipitation of the cationic complexes $[Rh(COD)(N\text{-}N')]ClO_4$ (*N-N'* = bipy, PyCa). Any attempt to prepare the corresponding DAB compound by the same method (even at lower temperature or with an excess of DAB) failed, because in the preparative conditions (concentration of reactants higher than 10^{-2} mol dm^{-3}) the least soluble product $[\{RhCl(COD)\}_2(DAB)]$ precipitates. Elemental analyses, molar conductivities, and selected IR and electronic spectral data are listed in Table I, while some selected ^1H NMR spectral data at variable temperature are reported in Table II.

1/1 Reactions

With a 1/1 ligand/dimer molar ratio, only the equilibrium (i) occurs for *N-N'*=bipy and PyCa, whereas for DAB a temperature-dependent equilibrium (iii) is also present. The product $[\{RhCl(COD)\}_2(N\text{-}N')]$ has a ionic structure of type A both in solution and in the solid for *N-N'*=bipy and PyCa. In the far-infrared spectra, two ν(Rh–Cl) bands are detected at close frequencies to those of the anionic complex $AsPh_4$-$[RhCl_2(COD)]$ (Table I). Furthermore, the compounds $[Rh(COD)(PyCa)]ClO_4$ and $[Rh(COD)$-$(PyCa)][RhCl_2(COD)]$ exhibit comparable ν(C=N)



Scheme 1.

values in the narrow range 1617–1613 cm^{-1} in the solid state and in CH_2Cl_2 solution. The corresponding DAB derivative has predominantly an ionic structure (**A**) (with extensive cation–anion association) in concentrated dichloromethane solution, where a ν(C=N) vibration is found at 1577 cm^{-1}. In the solid state, this band occurs at a lower frequency (1544 cm^{-1}), and also the ν(Rh–Cl) values (280 and 272 cm^{-1}) are rather different from those of $AsPh_4[RhCl_2(COD)]$ (270 and 249 cm^{-1}). These changes, however, cannot be taken as a conclusive evidence for a binuclear structure (**B**) with a σ,σ'-N,N' bridging DAB ligand, since they might also arise from solid state effects in [Rh(COD)(DAB)] $[RhCl_2(COD)]$.

In methanol, the equilibrium (i) is completely shifted to the right: the electronic spectra show no evidence of free *N-N'* even at very low concentrations. The electronic spectra of [Rh(COD)(*N-N'*)]-$[RhCl_2(COD)]$ are very similar to those of [Rh(COD)(*N-N'*)]ClO_4 (*N-N'* = bipy, PyCa), and obey the Lambert–Beer law down to the lowest explored concentration (5×10^{-5} mol dm^{-3}). Accordingly, the molar conductivities values in MeOH are in the expected range for uni-univalent electrolytes [16]. For $[\{RhCl(COD)\}_2(DAB)]$, some slight deviations from the Lambert–Beer law are observed in the range 5×10^{-4}–5×10^{-5} mol dm^{-3}, and the conductivity in MeOH is significantly lower (52.2 ohm^{-1} cm^2 mol^{-1}). This may be due to the occurrence of equilibrium (iii) and also to some cation–anion association (*cf.*, the solution behaviour of Rh(COD)(DAB)-Cl). Unfortunately, the DAB product is not sufficiently soluble in CD_3OD for ^1H NMR studies.

In 1,2-dichloroethane, the position of equilibrium (i) is markedly dependent on the α-diimino ligand. For [Rh(COD)(bipy)] $[RhCl_2(COD)]$, no dissociation towards the starting materials is observed in the range 10^{-3}–5×10^{-5} mol dm^{-3}, whereas the PyCa and DAB derivatives are largely dissociated at low concentration. Analysis of the electronic spectra of Fig. 1 in comparison with those of the free *N-N'* ligands [17] and those of [Rh(COD)(*N-N'*)]ClO_4 in 1,2-dichloroethane (Table I) shows that, at a concentration of 5×10^{-5} mol dm^{-3}, the dissociation is almost complete for $[\{RhCl(COD)\}_2(DAB)]$, whereas it is *ca.* 80% for [Rh(COD)(PyCa)] $[RhCl_2(COD)]$. Thus, the chelating abilities of the α-diimino ligands in the system *N-N'*/$[RhCl(COD)]_2$ (1/1) appear to increase qualitatively in the order: DAB < PyCa < bipy which corresponds to the order of increasing stability (measured from dissociation constants) of the cationic complexes $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(N\text{-}N')]$-$ClO_4$ [12].

The lower molar conductivity of [Rh(COD)-(bipy)] $[RhCl_2(COD)]$ (23.7 ohm^{-1} cm^2 mol^{-1}) relative to that of [Rh(COD)(bipy)]ClO_4 (40.8 ohm^{-1} cm^2 mol^{-1}) suggests that cation–anion association occurs in 1,2-dichloroethane, probably

TABLE I. Analyses, Conductivity, and Selected IR and Electronic Spectral Data

Compound	Analyses[a] (%)				Molar conductivity (ohm^{-1} cm^2 mol^{-1})[b]	Infrared bands (cm^{-1})[c]				Electronic spectra (nm)[d]
	C	H	N	Cl		ν(C=N)	ν(Cl–O)	δ(Cl–O)	ν(Rh–Cl)	λ_{max} (ϵ (mol^{-1} dm^3 cm^{-1}))
[Rh(COD)(bipy)]ClO_4	46.1 (46.32)	4.2 (4.32)	5.9 (6.00)	7.7 (7.60)	101.2 [40.8]		1090vs	624s		474(720), 340sh, 323(14400), 314sh [485(960), 345sh, 324(17900), 314sh]
[Rh(COD)(PyCa)]ClO_4	48.1 (48.24)	4.6 (4.63)	5.30 (5.36)	6.8 (6.78)	92.6 [39.9]	1616m [1617m][e]	1095vs	623s		522(440), 366(8400) [550(480), 382(8800)]
[Rh(COD)(bipy)] $[RhCl_2(COD)]$	48.0 (48.10)	4.9 (4.97)	4.3 (4.32)	10.8 (10.92)	87.2 [23.7]				275m, 252ms	472(690), 340sh, 323(14700), 314sh [482(770), 346(6480), 324(13800), 313(12500)]
[Rh(COD)(PyCa)] $[RhCl_2(COD)]$	49.3 (49.38)	5.1 (5.14)	4.0 (3.97)	10.1 (10.05)	83.0 [8.3]	1613ms [1615ms][e]			280sh, 258s	520(420), 365(9600)
$[\{RhCl(COD)\}_2(DAB)]$	50.8 (50.48)	5.3 (5.30)	3.7 (3.68)	9.2 (9.31)	52.2 [0.2]	1544m [1577ms][e]			280ms 272s	416(13800)
$AsPh_4[RhCl_2(COD)]$	57.5 (57.77)	4.8 (4.85)		10.7 (10.66)	87.5				270sh, 249s	

[a] Calculated values in parenthesis. [b] For 10^{-3} mol dm^{-3} MeOH solution at 20 °C; molar conductivities in square brackets refer to 10^{-3} mol dm^{-3} 1,2-dichloroethane solution at 20 °C. [c] As Nujol mulls. [d] Absorption maxima in MeOH solution at 25 °C; the absorption maxima in square brackets refer to 1,2-dichloroethane solution at 25 °C. [e] For 5×10^{-2} mol dm^{-3} CH_2Cl_2 solution.

TABLE II. Selected ^1H NMR Data[a]

Compound	Solvent $(mol\ dm^{-3})$	Temperature (°C)	α-Diimino ligand protons[b]					COD protons[c]	
			N=CH	H^3	H^6	AA′	OMe	CH olefinic	$-CH_2-$
$[Rh(COD)(bipy)]ClO_4$	CD_2Cl_2 (4×10^{-2})	30		8.36M	7.85M			4.57	2.9–1.9M
$[Rh(COD)(bipy)][RhCl_2(COD)]$	CD_2Cl_2 (5×10^{-2})	30		8.78M	7.87M			4.57[d] 4.10[e]	2.9–1.3M
	CD_2Cl_2 (5×10^{-2})	−50		8.74M	7.80M			4.51[d] 4.02[e]	2.9–1.3M
$Rh(COD)(bipy)Cl$[f]	CD_2Cl_2 (5×10^{-2})	30		8.83M(br)	7.91M(br)			4.52[d] 4.10[e]	2.8–1.3M
	CD_2Cl_2 (5×10^{-2})	- 50		8.91M	7.78M			4.49[d]	2.8–1.8M
	CD_3OD (5×10^{-2})	30		8.45M	8.00M			4.68[d]	3.0–1.9M
$[Rh(COD)(PyCa)]ClO_4$	CD_2Cl_2 (3×10^{-2})	30	8.40D $^3J(Rh-H) = 2.4$	8.20M	7.89M	7.15M	3.79S	4.35	2.9–1.9M
	CD_2Cl_2 (3×10^{-2})	−50	8.37D $^3J(Rh-H) = 2.4$	8.12M	7.83M	7.11M	3.75S	4.25(br)	2.8–1.8M
$[Rh(COD)(PyCa)][RhCl_2(COD)]$	CD_2Cl_2 (5×10^{-2})	30	8.93S	8.30M[g]	8.30M[g]	7.41M	3.81S	4.14(br)	2.7–1.4M
	CD_2Cl_2 (5×10^{-2})	−50	8.85D $^3J(Rh-H) = 2.4$	8.67M	7.86M	7.22M	3.75S	4.15 3.95	2.7–1.3M
$Rh(COD)(PyCa)Cl$[f]	CD_2Cl_2 (5×10^{-2})	30	8.90S	8.18M	8.60M	7.53M	3.83S	4.0	2.6–1.5M
	CD_2Cl_2 (5×10^{-2})	−70	8.57D $^3J(Rh-H) = 1.8$	8.1M[g]	8.0M[g]	7.34M	3.73S[g]	3.75(sh)[g]	2.6–1.5M
	CD_3OD (5×10^{-2})	−60	8.58D(br) $^3J(Rh-H) \sim 2$	8.1M[g]	8.05M[g]	7.27M	3.79S	4.28	2.7–1.5M
$[\{RhCl(COD)\}_2(DAB)]$	CD_2Cl_2 (5×10^{-2})	30	8.9S(br)			7.65M(br)	3.86S	4.15(br)	2.7–1,5M
	CD_2Cl_2 (5×10^{-2})	−50	10.1S[h] 10.0S[h]			8.15M[h]	3.87S[h]	4.65[h] 3.50[h] 3.25[h]	2.6–1.3M
			9.01S[i]			7.71M[i]	3.81S[i]	4.10[i] 3.95[i]	
	$CDCl_3$ (5×10^{-2})	30	10.1(w,br)[h] 8.85S(br)[i]			8.0M(br)[h] 7.6M(br)[i]	3.88S	4.17(br)	2.7–1.5M

(continued)

TABLE II. *(continued)*

Compound	Solvent (mol dm^{-3})	Temperature (°C)	α-Diimino ligand protons[b]					COD protons[c]	
			N=CH	H^3	H^6	AA′	OMe	CH olefinic	$-CH_2-$
	$CDCl_3$ (5 x 10^{-2})	−30	10.15S[h]			8.15M[h]	3.96S[h]	4.8[h] 3.6[h] 3.3[h]	2.7−1.4M
			8.95S[i]			7.71M[i]	3.90S[i]	4.2[i] 4.1[i]	
Rh(COD)(DAB)Cl[f]	CD_2Cl_2 (5 x 10^{-2})	30	10.1(w,br)[h]					4.7(br)[h] 3.4(br)[h]	2.7−1.4M
			8.8S(br)			7.55M(br)	3.85S	4.1	
	CD_2Cl_2 (5 x 10^{-2})	−50	10.1S[h] 10.0S[h]			8.12M[h]	3.87S[h]	4.65[h] 3.50[h] 3.25[h]	2.6−1.4M
			9.02D $^3J(Rh-H) = 1$			7.72M	3.82S	3.95	
			8.37S[j]			7.32M[j]	3.78S[j]		
$AsPh_4[RhCl_2(COD)]$	CD_2Cl_2 (4 x 10^{-2})	30						4.08	2.6−1.3M

[a] ^{1}H Chemical shifts in ppm from TMS; S = singlet, D = doublet, M = multiplet, sh = shoulder, br = broad, w = weak; coupling constants in Hz; satisfactory integration values are obtained. [b] The protons of the 2-pyridyl group give rise to second-order spectra, in which each proton appears as a multiplet of characteristic pattern; the H^4 and H^5 protons resonate in the narrow ranges 8.0−8.3 and 7.5−7.8 ppm, respectively; the *ortho* and *meta* protons of the C_6H_4OMe-*p* group appear as a symmetrical AA′BB′ system; numbering scheme:

[c] The olefinic protons of the coordinate 1,5-cyclooctadiene give rise to unresolved multiplets and are observed as rather broad singlets. [d] Signals of the cationic complex Rh(COD)-(*N*-*N*′)$^+$. [e] Signals of the anion $RhCl_2(COD)^-$. [f] Reaction mixture *N*-*N*′/$[RhCl(COD)]_2$ in the molar ratio 1/0.5. [g] Overlapping signals. [h] Signals of the binuclear species **B** (see Scheme 1). [i] Signals of the ionic species $[Rh(COD)(DAB)][RhCl_2(COD)]$. [j] Signals of the uncoordinate DAB ligand.

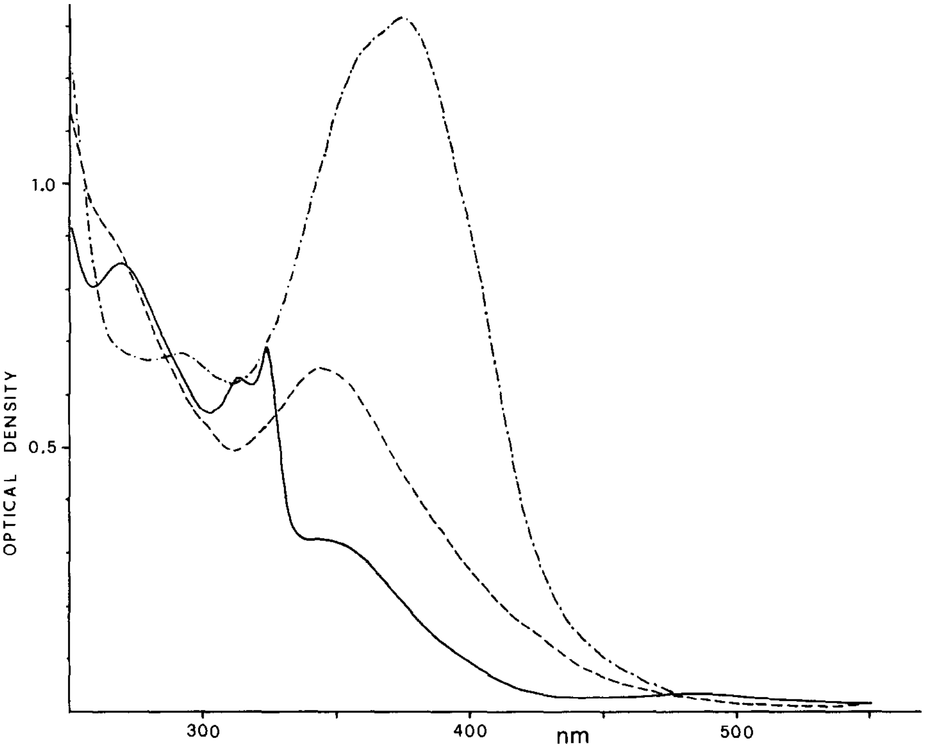


Fig. 1. Electronic spectra of 5 × 10^{-5} mol dm^{-3} solutions of [{RhCl(COD)}$_2$(*N-N'*)] in 1,2-dichloroethane at 25 °C: *N-N'* = bipy (——); PyCa (– – –); DAB (– · –).

through a bridging chloride ligand. The conductivity is even more reduced for [Rh(COD)(PyCa)] [RhCl$_2$(COD)], and is negligible for [{RhCl(COD)}$_2$(DAB)] (Table I). This trend can be rationalized in terms of increased cation–anion association and of occurrence of the dissociation equilibrium (i), particularly for the less stable DAB compound. Further evidence for such cation–anion association comes from the ^{1}H NMR spectra in CD_2Cl_2, and in particular from the downfield shifts of the imino N=C–H and pyridyl H^3 proton resonances of [Rh(COD)(*N-N'*)] [RhCl$_2$(COD)] relative to the corresponding signals of [Rh(COD)(*N-N'*)]ClO_4 (see Table II). A similar effect was already noted and discussed for the ^{1}H NMR spectra of the complexes [M(η^3-2-MeC_3H_4)(PyCa)]-[MCl_2(η^3-2-MeC_3H_4)] and [M(η^3-2-MeC_3H_4)(PyCa)]-ClO_4 (M = Pd, Pt) [12b]. The ^{1}H NMR spectrum of [Rh(COD)(bipy)] [RhCl$_2$(COD)] is hardly affected by lowering the temperature: two distinct resonances are detected for the cyclooctadiene olefinic protons of the cationic and anionic species, both at 30 and –50 °C (see Table II). In contrast, the ^{1}H NMR spectra of PyCa and DAB derivatives are significantly temperature-dependent. For [Rh(COD)(PyCa)]-[RhCl$_2$(COD)] at –50 °C, the N=C–H signal at 8.85 ppm appears as a doublet, due to the coupling constant with ^{103}Rh (2.4 Hz), and the COD olefinic protons resonate at 4.15 ppm for [Rh(COD)(PyCa)]$^+$ and at 3.95 ppm for [RhCl$_2$(COD)]$^-$. At higher temperature (30 °C), the ^3J(Rh–H) coupling disappears for the N=C–H proton, and the two olefinic proton signals merge into a single resonance at 4.14 ppm. Correspondingly, only one olefinic carbon signal at 79.7 ppm (with a ^1J(Rh–C) of 13.0 Hz) is detected in the ^{13}C NMR spectrum at 30 °C. Thus, a fast exchange of the Rh(COD) unit takes place at 30 °C between the cationic and anionic species, with breaking of the Rh–imino bond (but without breaking of the Rh–cyclooctadiene bond). This dynamic behaviour can be rationalized in terms of a fast dissociation equilibrium (i) (Scheme 1), which becomes slower and shifts progressively towards the ionic form **A** as the temperature is lowered. (At –50 °C, no trace of free PyCa is actually observed).

The variable-temperature ^{1}H NMR spectra of [{RhCl(COD)}$_2$(DAB)] (Table II and Fig. 2) can be interpreted by taking into account the equilibrium (iii) of Scheme 1, between the ionic (**A**) and the binuclear species (**B**), the latter compound being characterized by markedly low-field δ(N=C–H) signals (*ca.* 10 ppm), as in the case of the corresponding carbonyl complexes [{RhCl(CO)$_2$}$_2$(RN=CH–CH=NR)] (R = CMe$_3$, CMe$_2$Et) [6]. At 30 °C [spectrum (a) of Fig. 2], the ionic form [Rh(COD)(DAB)]-[RhCl$_2$(COD)] predominates, as can be inferred by the observation of a single, broad imino proton resonance at 8.9 ppm, very close to the N=C–H chemical shift of **A** at lower temperatures (9.01

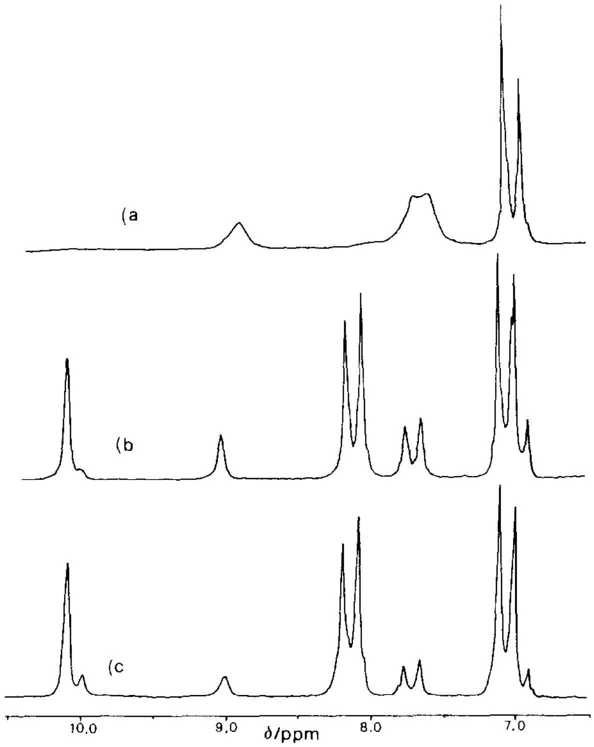
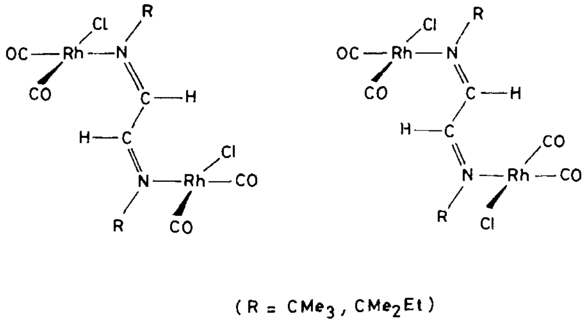


Fig. 2. Variable-temperature ^1H NMR spectra of 5×10^{-2} mol dm^{-3} solution of $[\{RhCl(COD)\}_2(DAB)]$ in CD_2Cl_2 in the range 10.5–6.5 ppm: (a) 30 °C; (b) −25 °C; (c) −50 °C.

ppm). A single, broad resonance appears also for the C_6H_4OMe-*p ortho* protons at 7.65 ppm, and for the COD olefinic protons at 4.15 ppm, suggesting that the species **A** is in a rather fast exchange with small amounts of dissociation products [equilibrium (i)] and of the binuclear complex **B** [equilibrium (iii)]. At lower temperatures, the equilibrium (i) is completely shifted to the right (there is no evidence for free DAB in the range −25 to −75 °C), whereas the equilibrium (iii) shifts progressively in favour of **B**, with a **B**/**A** molar ratio of *ca.* 7/3 at −25 °C, 8/2 at −50 °C, >9/1 at −75 °C. The exchange of the Rh(COD) unit between the cation and anion of **A** is fast at 30 °C and slow at lower temperatures (at −50 °C, two distinct olefinic proton signals are detected at 4.10 and 3.95 ppm for $[Rh(COD)(DAB)]^+$ and $[RhCl_2(DAB)]^-$, respectively). Two (N=C–H) singlets of different intensity are observed for **B** at 10.1 and 10.0 ppm, indicating the presence of two stereoisomers of different concentration. The isomer ratio is also temperature-dependent: at −25 °C the isomer with δ(N=C–H) at 10.1 ppm predominates, whereas the concentration of the second isomer with δ(N=C–H) at 10.0 ppm increases with decreasing temperature.

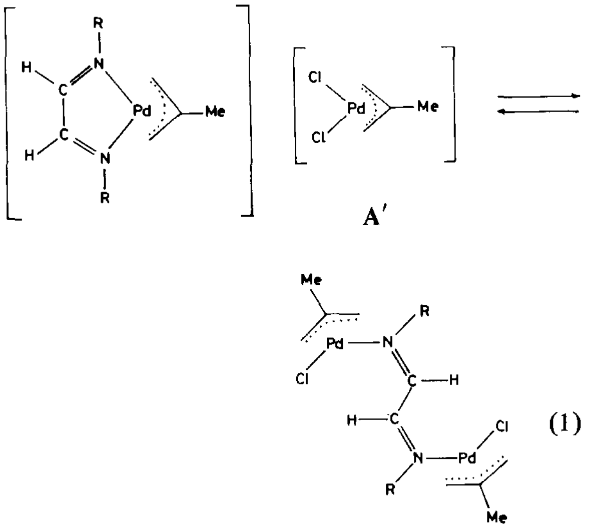
The variable-temperature ^1H NMR spectra of $[\{RhCl(COD)\}_2(DAB)]$ in $CDCl_3$ (Table II) are similar to those in CD_2Cl_2 at comparable concentrations. However, at 30 °C the broad δ(N=C–H) signal of **A** at 8.85 ppm is flanked by a much weaker and broad δ(N=C–H) signal of **B** at 10.1 ppm, with an integration ratio of *ca.* 9/1. At lower temperatures, the relative amount of **B** increases, but only one stereoisomeric form is observed, characterized by a δ(N=C–H) singlet at 10.15 ppm.

Two stereoisomers were also observed for the binuclear systems $[\{RhCl(CO)_2\}_2(RN{=}CH{-}CH{=}NR)]$ containing a σ,σ′-*N,N′* bridging α-diimine, in a solvent-dependent ratio at low temperatures, and the following structures were proposed [6]:



It is interesting to note that the compound $[\{RhCl(CO)_2\}_2(RN{=}CH{-}CH{=}NR)]$ (R = 2,6-$Me_2C_6H_3$) was reported to exist only in the ionic structure **A** [6], whereas the complex $[\{RhCl(COD)\}_2(DAB)]$, containing a related 1,2-bis(*N*-arylimino)ethane, can be present in solution with both structures **A** and **B**. Thus, the capability of α-diimines RN=CH–CH=NR to act as σ,σ′-*N,N′* bridging ligands cannot be entirely ascribed to the presence of bulky nitrogen substituents, as it was earlier suggested for the complexes $[\{RhCl(CO)_2\}_2(RN{=}CH{-}CH{=}NR)]$ [6], but other factors, such as the steric and/or electronic properties of different rhodium coligands, can also play an important role.

In this context, we have reinvestigated more accurately the variable-temperature ^1H NMR spectra of the complex $[\{PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\}_2(DAB)]$ [12a] in CD_2Cl_2 (Fig. 3). As can be seen, the solution behaviour of this compound closely parallels that of $[\{RhCl(COD)\}_2(DAB)]$ in the same solvent, and can be understood from the temperature-dependent equilibrium (1). At 30 °C, the ionic form **A′** [δ(N=C–H) as a rather broad singlet at 8.8 ppm] predominates, but with decreasing temperature equilibrium (1) shifts progressively in favour of the binuclear complex **B′**, characterized by imino proton resonances at lower field (*ca.* 9.5 ppm). Also in this case, the occurrence of two δ(N=C–H) singlets of comparable intensity (at 9.49 and 9.41 ppm respectively at −50 °C) points to the presence of two stereoisomers for **B′** in solution.



A′

B′

(1)

(R = C_6H_4OMe-*p*)

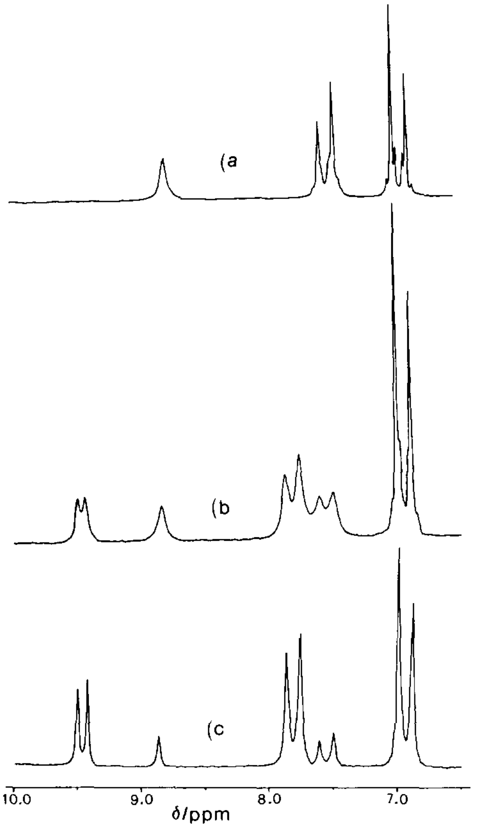


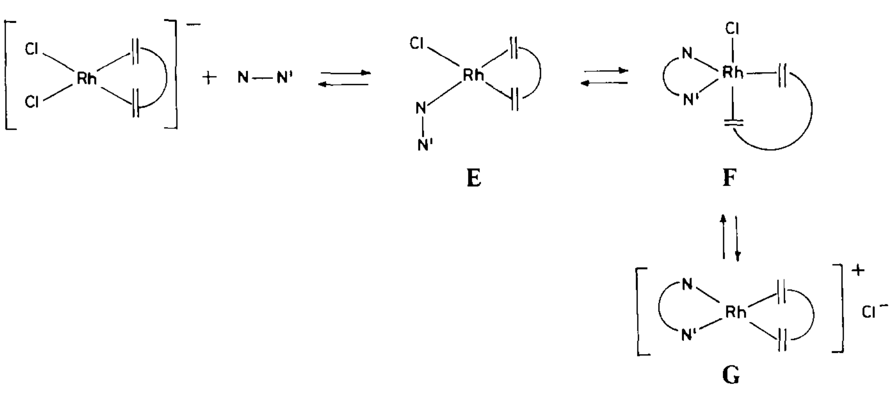
Fig. 3. Variable-temperature ^1H NMR spectra of 5×10^{-2} mol dm^{-3} solution of [{PdCl(η^3-2-MeC_3H_4)}$_2$(DAB)] in CD_2Cl_2 in the range 10.0–6.5 ppm: (a) 30 °C; (b) −25 °C; (c) −50 °C.

1/0.5 Reactions

With a ligand/dimer molar ratio higher than 1/1, the successive equilibrium (ii) of Scheme 1 takes place, in which a product generally formulated as Rh(COD)(*N*-*N*′)Cl is formed. This equilibrium consists essentially in a reversible substitution of the chloride ligands of the $[RhCl_2(COD)]^-$ anion by the α-diimino ligand, and is likely to occur through intermediates (or transients) of the type **E** and **F** (see below). Intermediates similar to **E** and **F** have been observed in the replacement of chelate DAB ligand in $[PtCl_2(DAB)]$ by dimethylsulfoxide [18]. In the present case, however, the species **E** and **F** cannot be frozen in the ^1H NMR spectra (even at the lowest examined temperature of −80 °C), probably because the equilibria (2) are fast (on the NMR time scale), and shift to the right as the temperature is lowered.

As expected, the formation of the ionic product **G** is strongly favoured in polar solvents, such as methanol. Actually, the electronic spectra of the system *N*-*N*′/$[RhCl(COD)]_2$ (1/0.5) in MeOH closely match those of [Rh(COD)(*N*-*N*′)]$[RhCl_2(COD)]$ in the range 700–250 nm, and the molar conductivities (calculated for a theoretical 10^{-3} mol dm^{-3} concentration of **G** vary from 72.7 (*N*-*N*′ = bipy), to 73.5 (PyCa), and to 48.0 ohm^{-1} cm^2 mol^{-1} (DAB). The significantly lower value for the DAB system suggests that non-conducting species (such as **E** and **F**) are present in the equilibrium mixture.

Consistently, the ^1H NMR spectra of the 1/0.5 reaction mixtures in CD_3OD (for bipy and PyCa) are



E

F

G

(2)

in a good agreement with those of the cationic complexes [Rh(COD)(*N-N'*)]ClO$_4$ in CD$_2$Cl$_2$ (Table II).

In contrast to the solution behaviour in methanol, where no trace of free *N-N'* ligand can be detected even at high dilution, substantial amounts of unreacted *N-N'* and [RhCl$_2$(COD)]$^-$ are present in less polar solvents (1,2-dichloroethane or dichloromethane) also at the concentration of 5×10^{-2} mol dm^{-3} used in the ^{1}H NMR spectra. In the ^{1}H NMR spectrum of the system bipy/[RhCl(COD)]$_2$ (1/0.5 in CD$_2$Cl$_2$ at 30 °C (Fig. 4), the two COD olefinic proton signals at 4.52 and 4.10 ppm (with a relative integration ratio of *ca.* 7/3) are assigned to the product Rh(COD)(bipy)Cl, mainly in the ionic form **G** (*cf.*, the corresponding signals of [Rh(COD)-(bipy)]ClO$_4$ and [Rh(COD)(bipy)][RhCl$_2$(COD)] at 4.57 ppm), and to the anion [RhCl$_2$(COD)]$^-$, respectively. On cooling, the [RhCl$_2$(COD)]$^-$ resonance decreases in intensity and eventually disappears, as the equilibria (2) shift to the right.

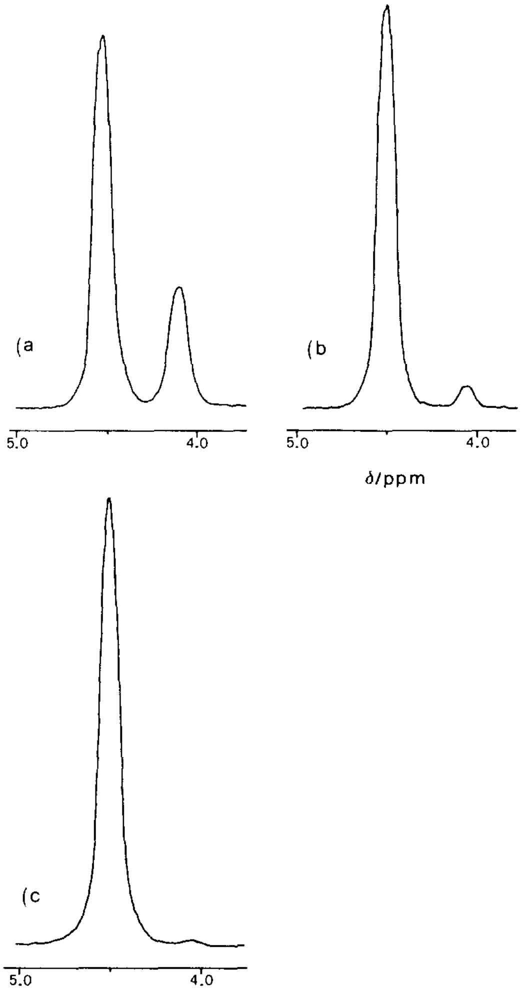


Fig. 4. Variable-temperature ^{1}H NMR spectra of the system bipy/[RhCl(COD)]$_2$ (1/0.5 molar ratio) in CD$_2$Cl$_2$ (with a bipy concentration of 5×10^{-2} mol dm^{-3}) in the olefinic proton range: (a) 30 °C; (b) −25 °C; (c) −50 °C.

The presence of free bipy cannot be detected in the ^{1}H NMR spectrum at 30 °C because it is in a rather fast exchange with the coordinate ligand. However, it can be observed as a weak band at 282 nm in the electronic spectrum in 1,2-dichloroethane. For the same reason, the unreacted PyCa ligand is not detected in the ^{1}H NMR spectrum of the system PyCa/[RhCl(COD)]$_2$ (1/0.5) at 30 °C, but its presence in the equilibrium mixture is confirmed by the IR spectra in CH$_2$Cl$_2$ at comparable concentration. At room temperature, the free ligand is characterized by a medium-weak ν(C=N) band at 1625 cm^{-1}, which disappears when the solution is cooled to −30 °C.

The variable-temperature ^{1}H NMR spectra of the system DAB/[RhCl(COD)]$_2$ (1/0.5) in CD$_2$Cl$_2$ (Table II and Fig. 5) can be interpreted on the basis of the temperature-dependent equilibria (ii) and (iii) of Scheme 1. At 30 °C (see Table II), two broad δ(N=C–H) signals are observed at 10.1 and 8.8 ppm, with a relative integration ratio of *ca.* 1/9. The low-field resonance is assigned to the binuclear complex **B**, whereas the signal at 8.8 results from fast exchange between the free and the coordinate DAB ligand of **A** and Rh(COD)(DAB)Cl. As the temperature is

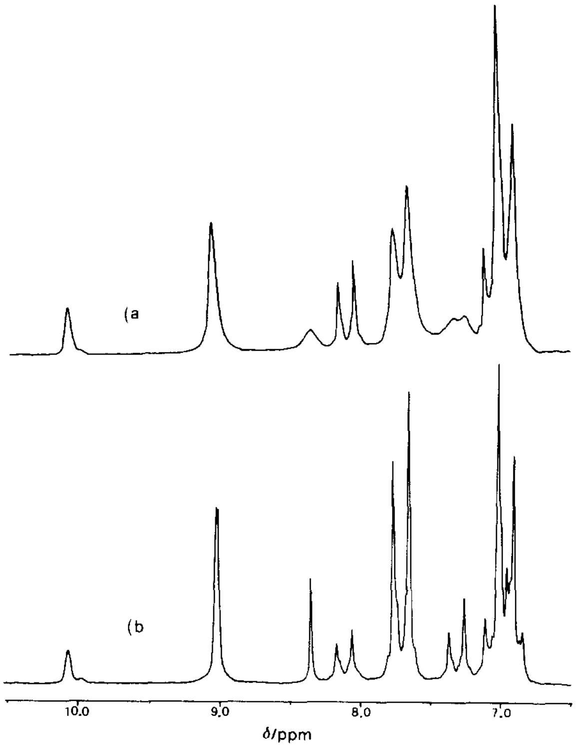


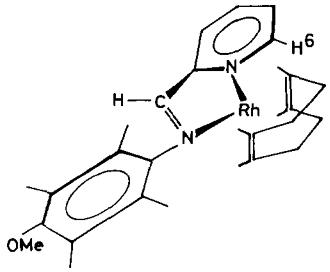
Fig. 5. Variable-temperature ^{1}H NMR spectra of the system DAB/[(RhCl(COD)]$_2$ (1/0.5 molar ratio) in CD$_2$Cl$_2$ (with a DAB concentration of 5×10^{-2} mol dm^{-3}) in the range 10.5–6.5 ppm: (a) −25 °C; (b) −50 °C.

lowered, the rate of such exchange is reduced, and the equilibria (ii) and (iii) shift in favour of Rh(COD)(DAB)Cl and of **B**, respectively. This leads to the progressive disappearance of the species **A**: at −25 °C, the equilibrium mixture practically consists of **B** (δ(N=C–H) at 10.1 ppm), of free DAB (δ(N=C–H) at 8.37 ppm), and of Rh(COD)(DAB)Cl (δ(N=C–H) at 9.04 ppm) with a relative ratio of *ca.* 1/1/4.5, which remains unchanged at lower temperatures. The close similarity of the low-temperature ^{1}H NMR spectra of [Rh(COD)(DAB)][RhCl$_2$(COD)] and Rh(COD)(DAB)Cl (see Table II) suggests that the ionic species **G** predominates in the latter compound.

Solution Behaviour of [Rh(COD)(N-N')]ClO₄

In the complex [Rh(COD)(PyCa)]ClO$_4$, the α-diimino ligand is σ,σ'-*N,N'* bonded to the central metal, as is shown by the deshielding of the imino carbon and most of the pyridyl carbon resonances in the ^{13}C NMR spectrum, relative to the free ligand (Table III). The same coordination mode was also found in the related compound [Rh(COD)(C$_5$H$_4$N-2-CH=NR]PF$_6$ (R = (*S*)-CHMePh) by an X-ray structural analysis [10].

In contrast, the imino and the H^6 pyridyl protons are shielded of 0.2 and 0.8 ppm, respectively, compared to the corresponding signals of free PyCa [19]. A shielding of 0.7 ppm also occurs for the H^6 proton of bipy in [Rh(COD)(bipy)]ClO$_4$. The above chemical shifts result essentially from two opposite factors: a deshielding effect due to σ,σ'-*N,N'* chelation and a prevailing shielding effect, which arises, for the N=C–H proton, from the phenyl ring current of the C$_6$H$_4$OMe-*p* group (the plane of which is forced out of the $N\overset{\cdots}{-}C{-}C{=}N$ plane by steric hindrance with the COD ligand), and, for the H^6 proton, from its close proximity to the *cis* positioned C=C double bond of cyclooctadiene (out of the $H\diagdown C{=}C\diagup H$ olefinic plane) [10]:



In spite of the asymmetric nature of PyCa, only one olefinic proton (and carbon) resonance is observed at 4.35 ppm (and at 86.6 ppm), which broadens when the temperature is lowered from 30 to −80 °C. This is indicative of a low-energy process taking place in solution and involving a fast ligand site exchange (*cis–trans* isomerization). The observation of ^{103}Rh coupling constants for the imino proton (2.4 Hz) and for the cyclooctadiene carbons (12.2 Hz) rules out any dissociative mechanism with breaking of the Rh–N(imino) or of the Rh–COD bonds. On the other hand, a rapid exchange between coordinate and free PyCa is observed at 30 °C, upon addition of a small amount of PyCa to a CD$_2$Cl$_2$ solution of [Rh(COD)(PyCa)]ClO$_4$. The rate of the latter process decreases rapidly on cooling and becomes very slow at −50 °C, whereas a much faster *cis–trans* isomerization is still present at the same temperature.

The observed dynamic behaviour can be accommodated into a mechanism involving an association equilibrium (iv) of the cationic substrate with the solvent, the counteranion and, if present, also with the free PyCa ligand to form stereochemically nonrigid five-coordinate intermediates, in which the ligand site exchange probably occurs through Berry pseudorotations (Scheme 2). A similar solvent promoted *cis–trans* isomerization through a five-coordinate intermediate was earlier proposed for the neutral complexes [Rh(diene)(O-S)] (O-S$^-$ = monothio-β-diketonate anion) [20].

The equilibrium (v) of Scheme 2 accounts for the exchange between free and chelate PyCa via a higher-energy transient (or transition state), in which both the entering and leaving α-diimine is σ-*N* monodentate to the rhodium center.

An intermolecular associative mechanism, analogous to that of Scheme 2, has recently been proposed for the *syn–syn,anti–anti* exchange of allylic protons and for the exchange between free and chelate PyCa in the cationic complex [Pd(η^3-2-MeC$_3$H$_4$)(PyCa)]$^+$ [12b].

In very dilute acetonitrile solution, the complex [Rh(COD)(PyCa)]ClO$_4$ undergoes a slight dissociation of the α-diimino ligand according to equilibrium (3)

$$[\mathrm{Rh(COD)(PyCa)}]^+ + 2\mathrm{MeCN} \rightleftharpoons [\mathrm{Rh(COD)(NCMe)_2}]^+ + \mathrm{PyCa} \qquad (3)$$

Non-linear regression analysis of the spectral changes with dilution [12] at 25 °C gives a dissociation constant of $(4.0 \pm 0.9) \times 10^{-6}$ mol dm^{-3}, comparable to the value of $(5.6 \pm 1.8) \times 10^{-6}$ mol dm^{-3} measured for the dissociation of [Pd(η^3-2-MeC$_3$H$_4$)(PyCa)]ClO$_4$ in the same solvent at 25 °C [12b]. No dissociation is observed for the complex [Rh(COD)(bipy)]ClO$_4$ under the same experimental conditions.

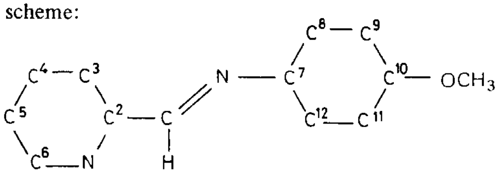
Conclusions

The α-diimino ligands *N-N'* (bipy, PyCa, DAB) give bridge-splitting reactions with [RhCl(COD)]$_2$ in the same way as with the chloro-bridged dimer [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ [12]. The dynamic behaviour

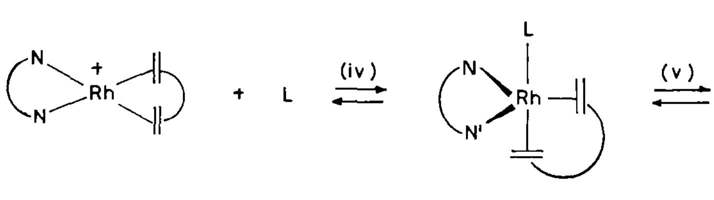
TABLE III. $^{13}C\{^1H\}$ NMR Data[a]

Compound	Temperature (°C)	Imino carbon N=C–H	2-Pyridyl carbons					N-substituent carbons					Cyclooctadiene carbons	
			C^2	C^3	C^4	C^5	C^6	C^7	$C^{8,12}$	$C^{9,11}$	C^{10}	O–CH_3	$C_{olefinic}$	–CH_2–
PyCa[b]	30	158.5	155.2	121.2	136.5	124.8	149.6	143.8	122.8	114.5	159.1	55.5		
[Rh(COD)(PyCa)]ClO$_4$	30	171.1	n.o.	129.7 or 129.4	141.4	129.4 or 129.7	149.5	n.o.	122.8	114.6	n.o.	55.7	86.6 ^1J(Rh–C) = 12.2	30.4
	–50	171.0	154.0	129.4 or 128.8	141.1	128.8 or 129.4	148.9	139.3	122.5	113.8	158.7	55.5	86.3(br)	30.2
[Rh(COD)(PyCa)] [RhCl$_2$(COD)]	–50	170.9	154.4	130.1 or 128.9	140.6	128.9 or 130.1	148.5	139.9	122.6	113.6	158.7	mk[c]	84.8[d] ^1J(Rh–C) = 12.0 77.3[e] ^1J(Rh–C) = 13.2	30.0[d] 30.6[e]
AsPh$_4$[RhCl$_2$(COD)]	30												76.3 ^1J(Rh–C) = 13.5	31.0

[a] ^{13}C Chemical shifts (ppm, relative to Me$_4$Si) measured in CD_2Cl_2/CH_2Cl_2 (1/1, v/v) solution; coupling constants in Hz; n.o. = not observed; br = broad. Carbon numbering scheme:



[b] Data from ref. 17. [c] Masked by the intense solvent signal. [d] Signals of the cationic species. [e] Signals of the anionic species. In the spectrum at 30 °C, these signals coalesce into a doublet at 79.7 ppm. (^1J(Rh–C) = 13.0 Hz), for the olefinic carbon, and into a singlet at 31.0 ppm, for the methylene carbons.



Scheme 2.

of the complexes [Rh(COD)(N-N')] [$RhCl_2$(COD)] and [Rh(COD)(N-N')]ClO_4, and the stability of the five-membered metallocycle Rh(N-N') (towards dissociation of the σ,σ'-N,N' chelate ligand closely parallel those of the corresponding complexes [Pd(η^3-2-MeC_3H_4)(N-N')] [$PdCl_2$(η^3-2-MeC_3H_4)] and [Pd(η^3-2-MeC_3H_4)(N-N')]ClO_4 [12]. Even though five-coordination is much easier for Rh(I) than for Pd(II) d^8 metal centers (and five-coordinate complexes [RhCl$(CO)_2$(N-N')] have actually been reported [2,4,9]), no five-coordinate product can be isolated (or detected in solution) in the N-N'/[RhCl(COD)]$_2$ (1/0.5) reaction mixture.

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