Inorganica Chimica Acta, 29 (1978) 203–209

NMR and IR Studies of the Bonding Properties of the Ethylene–Rhodium Complexes $RhCl(C_2H_4)(L)(L')$, L = C_2H_4, CO, PR_3, and L' = 2,6-Lutidine

ANDRÉ MAISONNAT and RENÉ POILBLANC

Laboratoire de Chimie de Coordination du C.N.R.S., B.P. 4142, 31030 Toulouse Cedex, France

Received November 28, 1977

A series of complexes of general formula RhCl-(C_2H_4)(L)(2,6-lutidine), L = CO, C_2H_4, PR_3, has been studied by infrared and NMR spectroscopies. For L = C_2H_4, the ethylenic ligand molecules are non equivalent and in the cases L = CO and PR_3, two isomers are detected in solution; the spectroscopic data (ν CO, VTP of ^1H NMR, ^{13}C NMR) and the ligand exchange studies are discussed in terms of differences in lability, rotational mobility and σ-donor properties of the ethylene groups trans *to the chloride ligand and those* trans *to the amine ligand. The* trans *influence and* trans *effect of chloride appear to be smaller than those of 2,6-lutidine, and the σ donation from ethylene to rhodium(I) becomes more favorable in the order N < Cl.*

The synthesis of a dinuclear species of the type ($RhCl(C_2H_4)(PMe_3)$)$_2$, from $RhCl(C_2H_4)_2$(2,6-lutidine), by displacement of the sterically hindered amine ligand, is also reported.

Introduction

As previously reported [1], the nucleophilic attack by the very sterically hindered 2,6-lutidine ligand on the $(RhCl(CO)(C_2H_4))_2$ complex affords exclusively $RhCl(CO)(C_2H_4)$(2,6-lutidine) by bridge splitting. In the present paper we would like:

(i) to report the synthesis of a novel dissymetric diethylenic mononuclear compound, *cis*-$RhCl(C_2H_4)_2$ (2,6-lutidine) according to a similar nucleophilic attack by 2,6-lutidine on $(RhCl(C_2H_4)_2)_2$.

(ii) to report the reactivity of this complex toward carbonyl and phosphine ligands,

(iii) and to discuss the ^1H and ^{13}C NMR and IR spectrographic data.

Experimental

Preparation

The $(RhCl(C_2H_4)_2)_2$ [2] and $(RhCl(CO)(C_2H_4))_2$ [3] complexes were prepared as described previously. All solvents were distilled and used under nitrogen atmosphere. Microanalyses were carried out by the "Service Central de Microanalyses du C.N.R.S.". Molecular weight measurements were determined in benzene using a Mechrolab osmometer.

The *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) complex was prepared quantitatively from $(RhCl(C_2H_4)_2)_2$ in toluene solution, at room temperature, by addition of 2,6-lutidine in the molar ratio 2,6-lut.: Rh = 1. This complex was recrystallized at –20 °C, from a toluene hexane mixture, as red prismatic crystals. *Anal.* Calcd: C, 43.80; H, 5.69; N, 4.64; Cl, 11.75; mol. wt. 301. Found: C, 43.89; H, 5.71; N, 4.72; Cl, 11.72%; mol. wt. 318.

The $RhCl(C_2H_4)(CO)$(2,6-lutidine) complex may be prepared from $(RhCl(C_2H_4)(CO))_2$ by addition of 2,6-lutidine in the molar ratio L': Rh = 1 as previously described [1] or from *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) in toluene solution at room temperature by reaction with carbon monoxide. Fine yellow crystals were obtained after crystallization from a toluene–hexane solution. *Anal.* Calcd: C, 39.82; H, 4.35; N, 4.64; Cl, 11.75; mol. wt. 301. Found: C, 39.95; H, 4.58; N, 4.69; Cl, 11.60%; mol. wt. 308.

The $RhCl(C_2H_4)$(2,6-lutidine)(PMe_3) complex was prepared from a diluted toluene solution of *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) by addition at room temperature of trimethylphosphine in the molar ratio PMe_3:Rh = 1. This complex was recrystallized at –20 °C from a toluene–hexane mixture.

The $(RhCl(C_2H_4)(PMe_3))_2$ complex was prepared by precipitation from a concentrated toluene solution of *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) in which the added phosphine ligand was in the molar ratio PMe_3: Rh = 1. *Anal.* Calcd: C, 24.97; H, 5.41; Cl, 14.62; P, 12.77. Found; C, 25.44; H, 5.48; Cl, 14.57; P, 12.57%.

Spectroscopic Measurements

Infrared spectra were recorded on a Perkin-Elmer 225 grating spectrometer either in hexadecane solutions or in caesium bromide pellets. In the carbonyl stretching region, the spectra were calibrated by water vapor lines.

^1H NMR spectra were obtained with Varian A60 and Varian HA 100 NMR spectrometers in dichloro-

TABLE I. PMR, CMR and IR Parameters of Mono and Diethylenic Chloro Rhodium(I) Complexes.

Compound	PMR parameters[a]						$\{^1H\}^{13}C$ NMR parameters[c]			
	δH (CH_3)	C_2H_4 δH	J_{Rh-H}	PMe_3 δH	$^2J_{P-H}$	$^3J_{Rh-H}$	δC (CH_3)	δC (C_2H_4)	$^1J_{Rh-C=}$	νCO[d]
1	3.37 (s)[b]	3.37 (s) 2.55 (s)					26.3 (s)	67.5 (d) 58.0 (d)	11.0 ± 0.5 13.2 ± 0.5	
IIa	3.21 (s)	2.83 (s)		1.23 (dd)	9.58	1.0				
IIb	2.45 (s)	2.22 (t)	2	1.20 (dd)	10.24	1.0				
IIIa[e]	3.13 (s)	4.16 (s)								1990
IIIb[e]	3.13 (s)	3.42 (d)	2							2023
$(RhCl(C_2H_4)(PMe_3))_2$		2.71 (s)		1.18 (dd)	10.08	1.1				

[a] CH_2Cl_2 solution; units of ppm relative to TMS as internal standard for δ and Hz for J parameters. [b] Abbreviations: s, singlet; d, doublet; t, triplet: dd, doublet of doublets. [c] $CDCl_3$ solution. [d] Hexadecane solutions; unit of cm^{-1}. [e] Reference 1.

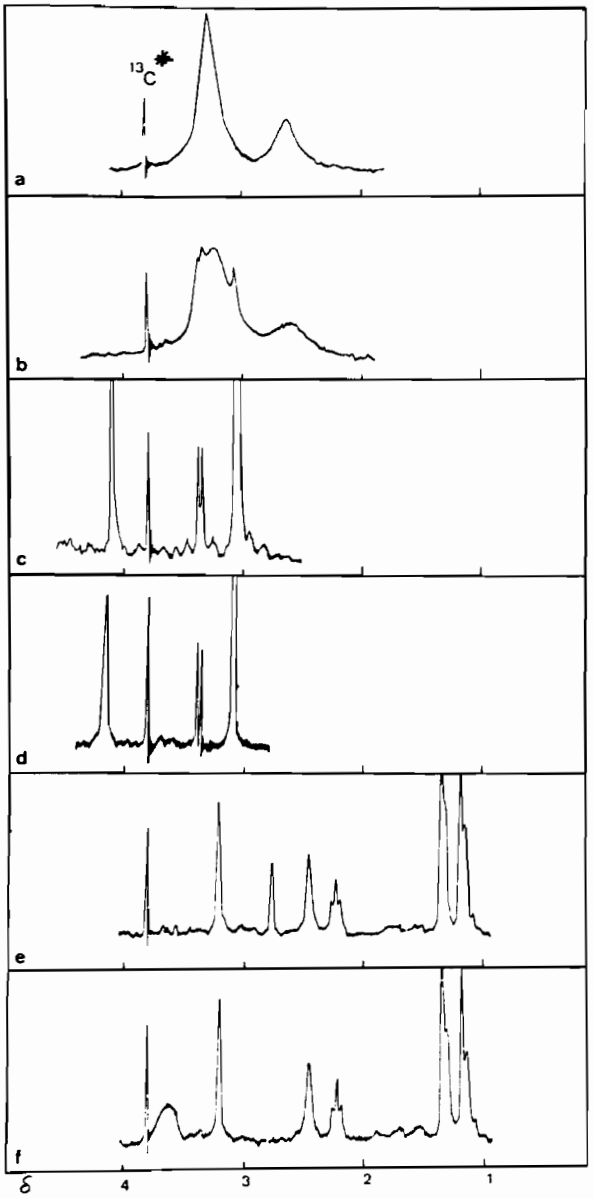

Figure 1. 60 MHz ^1H NMR spectra in the ethylene and methyl groups region in CH_2Cl_2 of a) *cis*-$RhCl(C_2H_4)_2$ (2,6-lutidine), b) *cis*-$RhCl(C_2H_4)_2$ (2,6-lutidine) with free carbon monoxide, c) $RhCl(C_2H_4)(CO)$(2,6-lutidine), d) $RhCl(C_2H_4)(CO)$(2,6-lutidine) with free ethylene, e) $RhCl(C_2H_4)(PMe_3)$(2,6-lutidine) and f) $RhCl(C_2H_4)(PMe_3)$(2,6-lutidine) with free ethylene.
*Due to $^{13}C-^1H$ coupling in CH_2Cl_2.

methane solutions. Tetramethylsilane was used as internal standard. Temperatures were adjusted with a V 4343 variable temperature probe accessory.

^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker WH 90 apparatus (22.62 MHz) operating in Fourier transform mode, with full proton decoupling. ^{13}C chemical shift were measured relative to the internal solvent resonance and are given in ppm downfield positive from TMS.

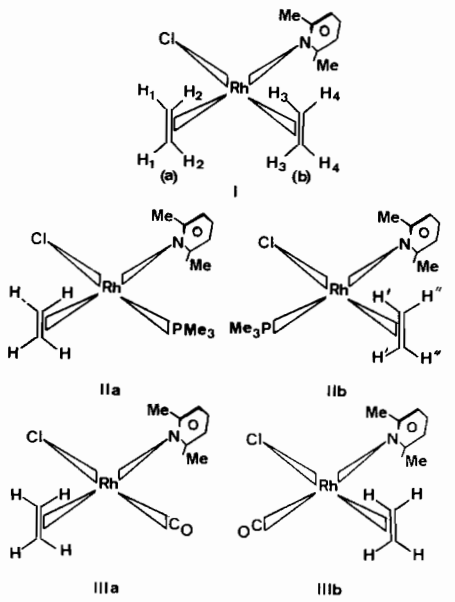

Figure 2. The proposed configurations.

The infrared and NMR data are listed in Table I.

Results and Discussion

Analysis of the Infrared and NMR Data of the RhCl(C_2H_4)(L)(2,6-lutidine) Complexes, L = C_2H_4, CO, and PMe_3

Addition at room temperature of the stoichiometric quantity of 2,6-lutidine to di-μ-chlorotetraethylenedirhodium in toluene gives, after crystallization at –20 °C, red crystals in quantitative yield. Elemental analysis and molecular weight determination are consistent with the $RhCl(C_2H_4)_2$ (2,6-lutidine) formula.

The ^1H NMR room temperature spectrum in dichloromethane exhibits, in addition to the signals of the aromatic protons, two broad singlets at 3.37 ppm and 2.55 ppm relative to tetramethylsilane, (Figure 1a) in the ratio 10:4. Thus, the apparently simple signal at 3.37 ppm is attributed to the six methyl protons of the lutidine ligand in addition to the four protons of one of the coordinated ethylene and the signal at 2.55 ppm is due to the protons of the other coordinated ethylene. The equivalence of the four protons of each ethylene ligand is commonly ascribed to the rapid rotation of the C_2H_4 group about the coordination bond [4]: this aspect will be discussed after we have assigned the observed signals to each ethylene ligand. The dissymetric configuration I (Figure 2, I) is proposed for this compound.

The $RhCl(C_2H_4)(CO)$(2,6-lutidine), II, and $RhCl(C_2H_4)(PMe_3)$(2,6-lutidine), III, complexes have been prepared by the nucleophilic attack of $RhCl(C_2H_4)_2$ (2,6-lutidine) by CO or PMe_3. Concerning the

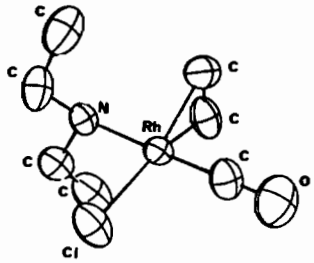

Figure 3. The molecular geometry of $RhCl(C_2H_4)(CO)(NHEt_2)$. (From ref. 5)

synthesis of complex II, another route has been reported [1] by cleavage of the bridges in $(RhCl(CO)(C_2H_4))_2$ by 2,6-lutidine. A mixture of two isomers is delected in solution for each complex II or III by NMR and IR; from consideration of intensities the following characteristics are unambiguously attributed to each isomer. For complex II, isomer A: δC_2H_4 = 2.83 ppm; δCH_3 = 3.21 ppm; δPR_3 = 1.23 ppm and isomer B: δC_2H_4 = 2.22 ppm; δCH_3 = 2.43 ppm and δPR_3 = 1.20 ppm; for complex III, isomer A: νCO = 1990 cm^{-1}; δC_2H_4 = 4.16 ppm; δCH_3 = 3.13 ppm and isomer B: νCO = 2023 cm^{-1}; δC_2H_4 = 3.42 ppm; δCH_3 = 3.13 ppm. (From infrared experiments, the change from hexadecane to dichloromethane solvents does not modify either the nature of the isomers of III or significantly their molar ratio).

Identification of Each Isomer of Compounds II and III

Three isomers are to be considered *a priori* for the complexes II and III. From spectrographic comparison one of them, in the case of III, may be identified.

The crystal structure of a parent compound of III, *i.e.*, $RhCl(CO)(C_2H_4)(NHEt_2)$ has been reported [5]. In this complex, the rhodium atom lies in a square planar surrounding with the diethylamine and chloride ligands *trans* with respect to the carbonyl and ethylene ligands respectively (Figure 3). The space group is $P\bar{4}2_1c$ with eight units per unit cell and by application of the site group method, three infrared active CO stretching modes are expected for this compound in the solid state. In fact, two bands at 2003 (vs) and 2018 cm^{-1} (s) appear for the crystalline solid whereas the spectrum of an hexadecane solution of this complex exhibits two bands at 2024 and 1986 cm^{-1}. It may be expected that the νCO absorptions, obtained from the crystal, lie in a region shifted towards lower frequency compared with the single νCO absorption obtained from the solution. By taking this shift into consideration, the absorption at 2024 cm^{-1} is univocally assigned to the species obtained in the crystalline state and that at 1986 cm^{-1} to another isomer. Thus, by analogy,

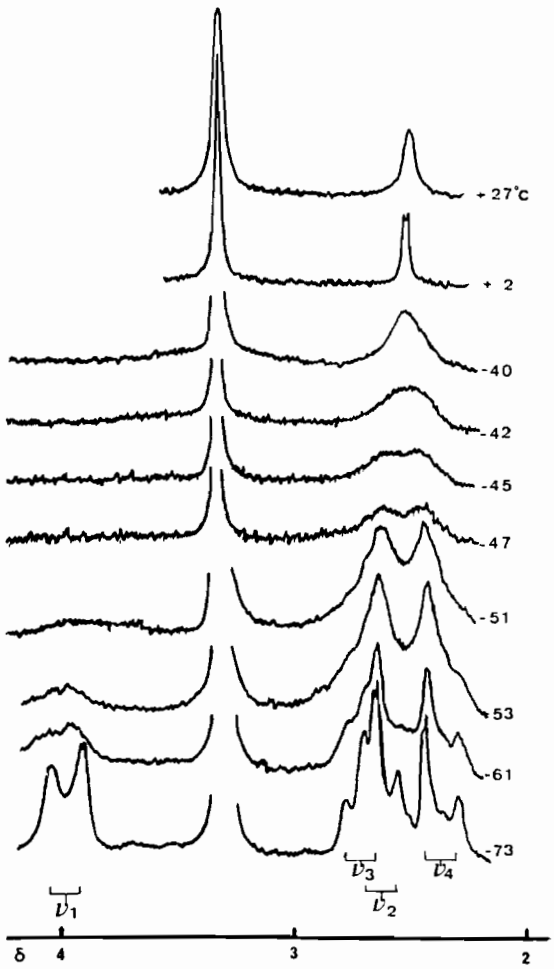

Figure 4. 100 MHZ ^{1}H NMR spectrum in the ethylene and methyl groups region of *cis*-RhCl(C_2H_4)$_2$(2,6-lutidine) as a function of temperature in dichloromethane.

isomer B of complex III which has a CO stretching frequency at 2023 cm^{-1} must have the configuration IIIb* (Figure 2).

Alternatively, by considering the synthetic processes involved, configuration IIIa may be proposed for isomer A of complex III. Complex III may be prepared by nucleophilic attack of (RhCl(CO)(C_2-H_4))$_2$ by 2,6-lutidine. Moreover since the nucleophilic attack of (RhCl(C_2H_4)$_2$)$_2$ by the same ligand leads only to the dissymmetric complex I, we expect as a result of the bridge splitting of (RhCl(CO)(C_2H_4))$_2$ the kinetic isomers having the ethylene and carbonyl groups in *cis* positions. It is noteworthy that this assignment is quite similar to those previously retained from nuclear generalized Overhauser effect consideration [1].

*The validity of this argument rests on the fact that CO groups *trans* to an aliphatic or an aromatic amine have force constants of the same magnitude [6].

From another point of view, owing to the σ–π synergism, νCO might be expected to provide a measurement of the metal–CO bond strength. Also, it appears from the above infrared attribution, that the chloride ligand has a smaller *trans influence* than the 2,6-lutidine ligand. (The *trans influence* concept is used here according to Pidcock *et al.* 's definition, that is to the extent that a ligand weakens the bond *trans* to itself in a metal complex).

Concerning complex II, we similarly attribute the configurations IIa and IIb to the isomers A and B respectively.

Returning to the *cis*-RhCl(C_2H_4)$_2$(2,6-lutidine) complex, we assign therefore the upfield ethylenic signal to the ethylene group in *trans* position to the chloride ligand and the downfield ethylenic signal to the ethylene group in *trans* position to the amine ligand.

Low Temperature NMR Spectrum of the RhCl(C_2-H_4)(L)(2,6-Lutidine) Complexes, L = C_2H_4, PMe_3

The evolution of the 100 MHz proton NMR spectrum of the *cis*-RhCl(C_2H_4)$_2$ (2,6-lutidine) complex between +27 °C and –73 °C is shown in Figure 4.

At –73 °C, the spectrum is relatively well resolved. In addition to the sharp signal of the methyl protons at 3.37 ppm, it exhibits four broad doublets ν_1, ν_2, ν_3, and ν_4 for the ethylenic protons and this pattern is consistent with the superposition of two AA'BB'X spin systems. These signals are symmetrically arranged pairwise – first, with respect to 3.37 ppm: two doublets ν_1 = 3.98 ppm, ν_2 = 2.61 ppm with a doublet spacing of 14.5 Hz and – second, with respect to 2.55 ppm: two other doublets ν_3 = 2.70 ppm, ν_4 = 2.34 ppm with a doublet spacing of 13.5 Hz. A fine structure with a spacing of about 2 Hz appears in doublet components. Unlike the cases of symmetric [4, 8, 9] and dissymmetric [10] bis-ethylenerhodium(I) chelates we do not obtain the fully resolved low temperature limiting spectrum and we are not able to calculate the coupling constants vicinal *cis*, vicinal *trans* and geminal between ethylenic protons.

When the temperature is raised, the four doublets broaden. The two ethylene (b) doublets ν_3 and ν_4 (Figure 2, I) broaden and coalesce at –42 °C into a single signal. At 0 °C, this signal appears as a single doublet with a ^{103}Rh–^{1}H spin–spin coupling constant of 1.7 Hz. This doublet coalesces into a sharp line when the temperature is raised above 0 °C.

For ethylene (a), the coalescence temperature is more difficult to evaluate. Indeed the two doublets ν_1 and ν_2 coalesce into a single signal which appears exactly at the same chemical shift as the methyl protons of the amine ligand. But, by integration of the signal at 3.37 ppm at each temperature, we are able to determine roughly, by a non ambiguous

graphical process, the coalescence temperature: we situate it between –37 °C and –40 °C.

Our observations on ethylene (b) are in agreement with an intramolecular exchange phenomenon since J_{Rh-H} is maintained above the coalescence temperature. Our observations in ^{13}C NMR (see later) confirm this point of view for both ethylene ligands (a) and (b).

Cramer explained the temperature dependence of the ^1H NMR spectrum of $C_5H_5Rh(C_2H_4)_2$ in terms of hindered internal rotation of the ethylene group about the coordination bond, and he assumed that "inside" protons of coordinated olefin are more strongly shielded than "outside" protons by a second olefin coordinated to the same metal atom [4, 8]. In the present case, we assign by analogy doublets ν_1, and ν_2 to the protons H_1 and H_2 of ethylene (a) and doublets ν_3 and ν_4 to the protons H_3 and H_4 of ethylene (b).

The changes in line position as a function of temperature were used to compare the rates of rotation of the coordinated ethylene (a) and (b) of complex (I)*. We thus found that the rotation barrier for each kind of ethylene groups has roughly the same magnitude and cannot be differentiated significantly by this parameter. We tentatively attribute this to a steric effect which couples the rotation of the two ethylene molecules by some kind of a gear effect. We tried to ascertain this hypothesis by the study of homologous complexes having various different anionic ligands, without success so far.

The temperature dependence of the 100 Mz ^1H NMR spectrum of a mixture of isomers IIa and IIb was studied from –40 °C to +20 °C (Figure 5). Solubility problems precluded measurements at lower temperatures. It is noteworthy that the margin between the coalescence temperature of each isomer's ethylenic proton signal is greater than in the case of ethylene (a) and (b) of complex I. The coalescence temperatures are –32 °C for isomer IIa and –2 °C for isomer IIb.

The slow exchange limit signals corresponding to the ethylene group of the isomer IIb consist of two dissymetric broad doublets centered at $\nu' = 2.47$ ppm and $\nu'' = 1.97$ ppm with a doublet spacing of 13 Hz and with a dissymetric fine structure with a spacing of 2 Hz in the doublet components. When the temperature is raised these signals coalesce into a single signal which appears unexpectedly as a triplet with a spacing of 2 Hz (at 60 and at 100 MHz). The multiplicity of this signal and the dissymmetry of signals ν' and ν'' in the slow exchange limiting spectrum may be explained taking into account the coupling between the ethylenic protons and the ^{103}Rh nucleus

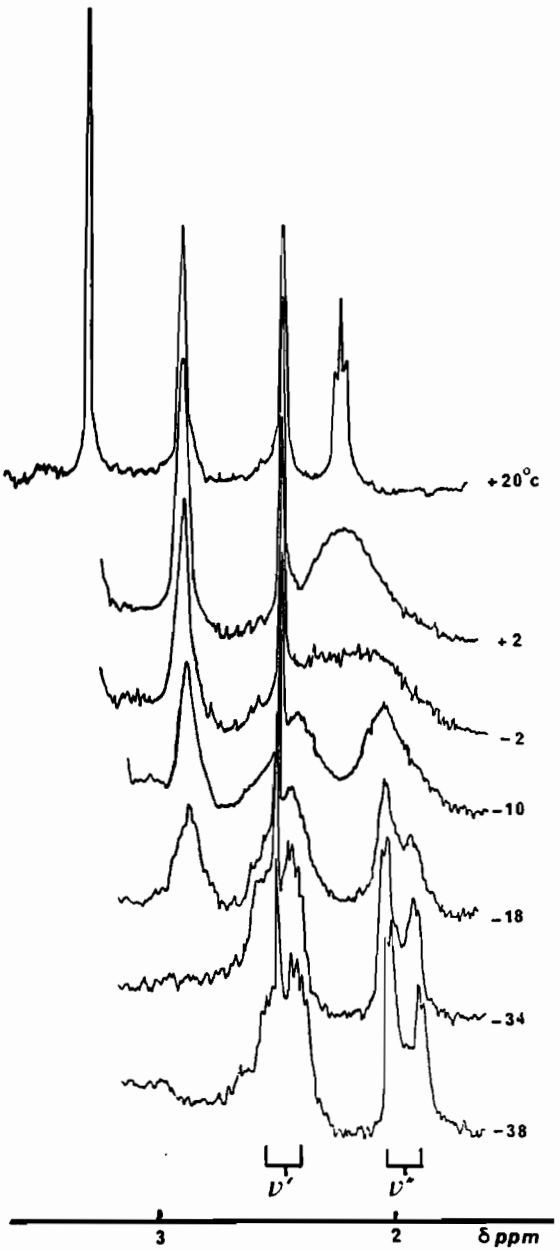

Figure 5. 100 MHz ^1H NMR spectrum of the C_2H_4 and of the CH_3 groups of 2,6-lutidine in $RhCl(C_2H_4)(PMe_3)$(2,6-lutidine) as a function of temperature in CH_2Cl_2.

in addition to the coupling between the two ethylenic protons and the ^{31}P nucleus and assuming that these couplings are accidentally of the same magnitude, *i.e.* 2 Hz. In the rapid exchange range, the ethylenic protons of this isomer IIb are equally coupled with the ^{31}P nucleus whereas in the slow exchange zone, our observations are rationalized if only the two protons in the vicinity of the phosphine ligand are coupled with ^{31}P nucleus. Thus the downfield signal ν' which appears as a doublet of doublets of doublets is assigned to the H' ethylenic protons whereas the

*The aim of this estimate is only to give relative values of the activation energies since the absolute values are highly underestimated by this method [8].

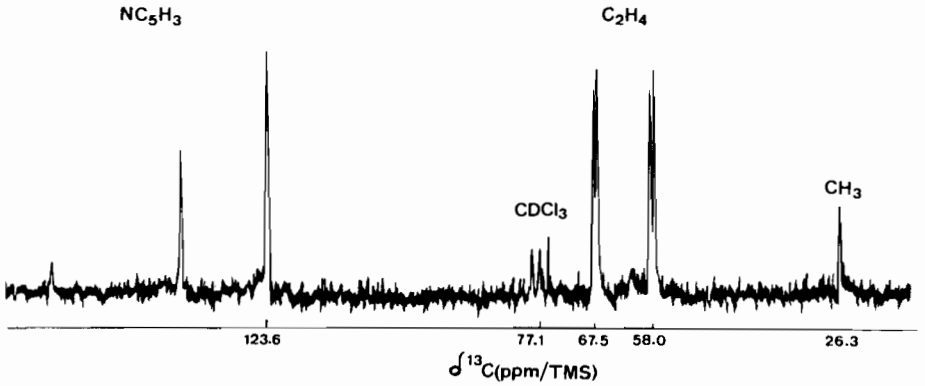

Figure 6. The ^1H decoupled Fourier transform pulsed ^{13}C spectrum of *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) in $CDCl_3$ solution at 22.62 MHz (20400 scans, pulse = 8.0 μs).

upfield signal ν "which appears as a doublet of doublets is assigned to the H" protons (Figure 2, II).

The limiting signal for the ethylene groups of isomer IIa was not obtained. On the other hand, the Rh–H coupling is not observed above the coalescence temperature. The existence of intermolecular lability of this ethylene ligand, shown further, can influence the line shape variations of the NMR signal. But at a very low concentration of free ethylene the coalescence temperature is practically unchanged. Therefore, owing to the coalescence temperatures, it is clear that the ethylene group of isomer IIa is rotating more easily than the ethylene group of isomer IIb.

^{13}C NMR Study of the cis-*$RhCl(C_2H_4)_2$(2,6-lutidine) Complex*

Besides the ^{13}C methyl signal of the amine ligand, at 26.30 ppm the upfield signals consist of two doublets at 67.50 and 58.00 ppm which are attributed to the ^{13}C nuclei of the coordinated ethylene (a) and (b) respectively (Figure 6). The measured values for $^1J_{(Rh-C=)a}$, *i.e.* 11.0 ± 0.5 Hz and for $^1J_{(Rh-C=)b}$, *i.e.*, 13.2 ± 0.5 Hz, differ significantly (the subscripts a and b refer to the (a) and (b) positions of the ethylene groups as shown in Figure 2, I.). It has generally been accepted that bonding in olefin–metal complexes consists of both σ donation from olefin to metal and of π-back donation from metal to olefin [11–13], according to the Chatt–Dewar–Duncanson model [14, 15]. The variation in coupling between directly bound nuclei M–L is consistently explained in terms of variations in the s-character of the hybrid orbitals used by M in the M–L bond [16]. Consequently, M–L coupling constants can be related to the *trans* influence in these terms, and thus it is expected that the direct coupling constant $^1J_{(Rh-C=)}$ decrease as the σ donor ability of the *trans* influencing ligand increases [17]. Therefore, from our experimental data it appears that the chloride ligand has a smaller σ donor ability than the 2-6-lutidine ligand, and this observation is in agreement with previous reports in platinum–ethylene bond studies [18–20].

It would be useless to correlate the ^{13}C or ^1H chemical shifts of ethylenic ligands with the total strength of the Rh–ethylene bonds for lack of quantitative information about the magnitude of the magnetic anisotropy due to the ring current of the lutidine ligand. We consider that an evaluation of this magnetic anisotropy effect by a Johnson and Bovey calculation [21], in this particular case, would be too approximate to be significant.

Ligand Exchange Studies

Coordinated–free ethylene exchange

In the *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) compound, experiments with different concentrations of free ethylene induce no shift of both ethylene ligands and free ethylene signals. Therefore the compound seems to exhibit no detectable exchange phenomenon. Nevertheless in absence of ethylene, at 27 °C, the coupling is no longer seen and the peak (b) broadens. The reason for this apparent discrepancy has not been studied.

Concerning the mixture of isomers IIa, IIb or IIIa, IIIb, we find that in the presence of free ethylene in each case the position of the lowfield ethylene signal is shifted towards the absorption of free ethylene and that the intensity of this signal increases, whereas the upfield ethylene signal remains unchanged as shown in Figure 1, d, f.

Ethylene–CO exchange

The exchange reaction between CO and the ethylene groups in *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) was monitored in dichloromethane by 60 MHz ^1H NMR. The carbon monoxide was introduced with a syringe in the NMR tube. Immediately after homogenisation of the solution the NMR spectrum revealed besides the two broad characteristic signals of complex I, the signals of isomer IIIb, *i.e.*, a signal at 3.13 ppm for the methyl group of the lutidine ligand and a

doublet at 3.42 ppm for the protons of the ethylenic group (Figure 1, b.). Better than in the case of the exchange between free and coordinate ethylene this observation demonstrates the intrinsic lability of ethylene (a).

Therefore from these exchange processes, it appears that in each case studies the ethylene group *trans* to the nitrogen donor ligand is more labile than the other ethylene group which is *trans* to the chloride ligand. In other words, the chloride ligand has a smaller *trans effect* than the 2,6-lutidine ligand as compared to free ethylene or carbon monoxide molecules.

Ethylene–Phosphine exchange

One of the two ethylene groups of the *cis*-$RhCl(C_2H_4)_2$(2,6-lutidine) complex is displaced by a phosphine molecule to give the isomers IIa and IIb. It is noteworthy that these isomers evolved in solution as in the solid state to give, by dissociation of the 2,6-lutidine, the dinuclear chloride bridged $(RhCl(C_2H_4)(PMe_3))_2$ according to the following sequence:

$$RhCl(C_2H_4)_2(2,6\text{-lutidine}) \xrightarrow[-C_2H_4]{+PMe_3} RhCl(C_2H_4)(PMe_3)(2,6\text{-lutidine})$$

$$RhCl(C_2H_4)(PMe_3)(2,6\text{-lutidine}) \xrightarrow{-2,6\text{-lutidine}} \tfrac{1}{2}(RhCl(C_2H_4)(PMe_3))_2$$

The spectroscopic data concerning this complex are listed in Table I. A similar dinuclear species, $(RhCl(C_2H_4)(PPh_3))_2$, has been previously obtained by a direct nucleophilic attack by triphenylphosphine on the $(RhCl(C_2H_4)_2)_2$ complex [22].

Acknowledgments

We are indebted to Professor J. Barrans and Mrs Boisdon for the use of the HA 100 Spectrometer.

References

1 A. Maisonnat, P. Kalck and R. Poilblanc, *Inorg. Chem., 13,* 2996 (1974).
2 R. D. Cramer, *Inorg. Chem., 1,* 722, (1962).
3 J. Powell and B. L. Shaw, *J. Chem. Soc. A,* 211 (1968).
4 R. Cramer, *J. Am. Chem. Soc., 86,* 217 (1964).
5 J. J. Bonnet, Y. Jeannin, A. Maisonnat, P. Kalck and R. Poilblanc, *C.R. Acad. Sc. Paris Serie C,* 15 (1975).
6 R. J. Angelici and M. D. Malone, *Inorg. Chem., 6,* 1731 (1967).
7 A. Pidcock, R. E. Richard and L. M. Venanzi, *J. Chem. Soc. A,* 1707 (1966).
8 R. Cramer, J. B. Kline and J. D. Roberts, *J. Am. Chem. Soc., 91,* 2519 (1969).
9 K. Moseley, J. W. Kang and P. M. Maitlis, *J. Chem. Soc. A,* 2875 (1970).
10 J. Kriz and K. Bouchal, *J. Organomet. Chem., 64,* 255 (1974).
11 F. R. Hartley, *Angewandte Chem. Internat. Ed., 11,* 596 (1972).
12 M. Herberhold, "Metal π complexes", II, Elsevier (1972).
13 J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev., 6,* 27 (1973).
14 J. Chatt and L. A. Duncanson, *J. Chem. Soc.,* 2939 (1953).
15 M. J. S. Dewar, *Bull. Soc. Chim. France, 18,* C79 (1953).
16 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev., 10,* 335 (1973).
17 F. R. Hartley, *J. Chem. Soc. Rev., 2,* 163 (1973).
18 T. Iwayanagi and Y. Saito, *Inorg. Nucl. Chem. Letters, 11,* 459 (1975).
19 M. A. M. Meester, D. J. Stufkens and K. Vrieze, *Inorg. Chim. Acta,* 16, *191 (1976).*
20 M. A. M. Meester, D. J. Stufkens and K. Vrieze, *Inorg. Chim. Acta, 21,* 251 (1977).
21 C. E. Johnson and F. A. Bovey, *J. Chem. Phys., 29,* 1012 (1958).
22 S. Otsuka, A. Nakamura and H. Minamida, *Chem. Comm.,* 191 (1969).