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NMR STUDY OF THE BONDING CHARACTER IN BIS(ETHYLENE)RHODIUM(I)—4-IMINO-2-PENTANONE CHELATES

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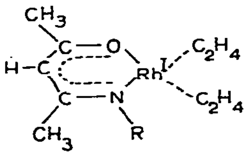
Summary

The NMR spectra of the ethylene protons in bis(ethylene)rhodium—4-imino-2-pentanone chelates have been analyzed. The ethylenic ligand molecules are physically and chemically nonequivalent; the ethylene *trans* with respect to nitrogen is more reactive for exchange with other ligands and is more sensitive to structural effects in the chelate moiety; substitution by electron-acceptor groups in the iminopentanone part leads to a lowering of π-electron density in the ethylene ligands.

Introduction

As previously reported [1], asymmetric chelates of monovalent rhodium of type (A) have been prepared where R is H (II), CH_3 (III), C_6H_5 (IV), $C_6H_4CH_3$ (V), C_6H_4Cl (VI), C_6H_4Br (VII), $C_6H_4OCH_3$ (VIII), $C_6H_4NO_2$ (IX). The NMR spectra of protons of coordinated ethylene in these compounds are more complicated than in the analogous spectra of symmetric chelates [2,3]. In symmetric (e.g. acetylactonate or cyclopentadienyl [3]) chelates at room temperature, the ethylene protons exhibit two broad signals, which upon cooling to −20° or −60° are split into well-resolved multiplets corresponding to an AA'XX' system (or AA'BB'X system if spin coupling to ^{103}Rh has to be considered.) In asymmetric chelates of type (A), the room temperature spec-



(A)

trum of the ethylene protons exhibits a larger number of broad lines, indicating non-equivalence of the two ethylene ligand molecules. The spectra change strongly upon substitution in the iminopentanone part of the chelate, and analysis of the ethylene proton signals can therefore yield information on the transfer of the electronic perturbation through the ligand field and on the native of the bonding in these asymmetric chelates.

Results and discussion

Analysis of the spectra of ethylene protons

The spectrum of the methylimino derivative (III), shown in Fig. 1a, is relatively well resolved even at room temperature. In addition to the sharp signals of the C—H, CH_3—N and both CH_3C group protons of the methyliminopentanone part of the molecule, it exhibits four broader doublets of ethylenic protons, marked $\alpha - \delta$; in all cases the doublet spacing is about 14 Hz. Upon cooling to −60°, fine structure with a spacing of about 2 Hz become evident in the broad doublet components. Non-specific exchange of ethylene for dideuterioethylene leads to a collapse of all the doublets, as shown in Fig. 1b. The extent of exchange in this experiment was 60%, and from the resulting spectra it is clearly evident that the broad doublets are due to *trans*-coupling of ethylenic protons. The doublet pairs were assigned to the respective ethylene molecules by double resonance (NMDR). The proximity of the strong solvent signal precludes the application of a sufficiently high amplitude of the saturating alternating field for complete decoupling, because the spectrum in such a case is modified by the strong dispersion signal originating from interaction of solvent proton resonance with the perturbing field [4]. Nevertheless, static irradiation of various doublet components by an alternating field of about 0.52 mG causes a significant decrease of intensity of some other lines in the spectrum. As this effect is symmetrical, it can be described as the consequence of a "generalized" Overhauser effect [5,6] and it is likely that transitions connected by this effect correspond to protons of the same molecule. Transitions exhibiting mutual interdependence in NMDR are linked by dashed lines in Fig. 1a.

Based on these experiments, and in analogy with the spectra of symmetrical chelates, the ethylenic proton spectrum of (III) can be interpreted as a superposition of two AA′XX′systems. Its form corresponds well to theoretical spectra calculated for the values ν_α to ν_δ, shown in Table 1, and to the coupling constants $J_{AX'}$ 10 Hz (vicinal, *cis*),J_{AX} 14 Hz (vicinal, *trans*) and $J_{AA'}=$ $J_{XX'}$ 2 Hz (*geminal*), which are normal for ethylenic systems [7]. The lines are somewhat broadened, even at lower temperatures; this might be caused by rotation of ethylenic molecules about the axis of the coordination bond [2,3], as will be discussed further.

The α and β doublets in the NMR spectra of (III) lie very close to the analogous doublets of the ethylenic protons of the symmetrical acetylacetonate chelate. Because of symmetry, the electronic perturbation arising in the molecule due to the exchange of nitrogen for oxygen myst be exhibited in the opposite direction to the coordination bond; therefore we assign the α and β

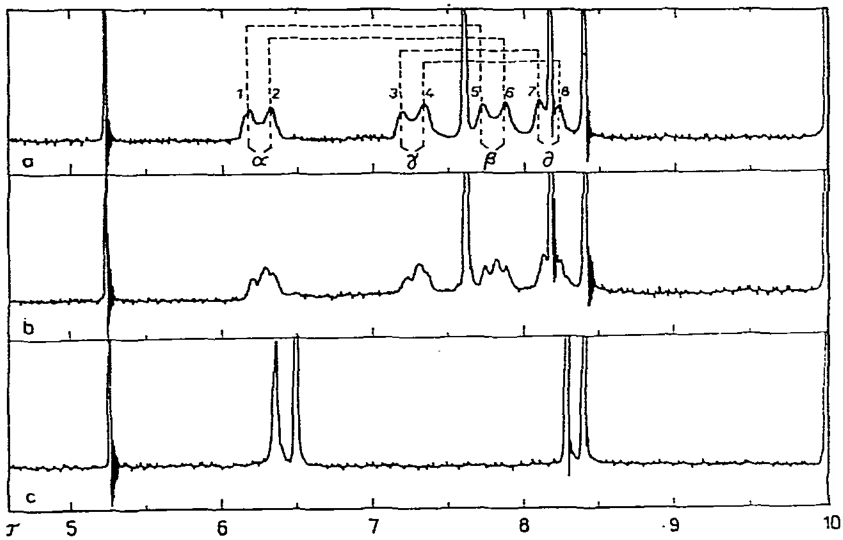
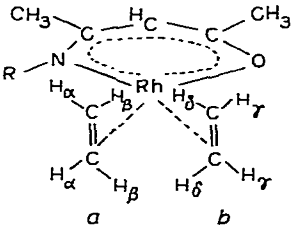


Fig. 1. NMR spectra of bis(ethylene)rhodium - 4-(methylimino)-2-pentanone chelate: a, with two molecules of ethylene; b, with two molecules of ethylene-*cis*-d_2 (60% enrichment); c, with one molecule of ethylene and one molecule of CO.

doublets to the ethylene molecule in the *cis*-position with respect to nitrogen [i.e. to molecule *a* in formula (B)], and the remaining two doublets to the molecule in the *trans*-position [i.e. *b* in formula (B)].



(B)

By analogy with Cramer's interpretation [2,3] of spectra of symmetrical complexes, we assume that the "internal" ethylene protons are more shielded by the other ligand molecule, so that individual doublets can be assigned to proton pairs as indicated in formula (B).

Exchange of one molecule of ethylene in the chelate for CO leads to the collapse of the quartet of the remaining molecule to a singlet, as shown in Fig. 1c; the singlet lies at τ 6.48 ppm, near to the centre of the α-doublet (τ 6.31 ppm), and its intensity corresponds to four equivalent protons. Cooling of the solution down to the limit of solubility of this mixed chelate at −30° does not influence significantly the shape of the signal, so that it is not clear if the remaining ethylene molecule is relatively rigid and surrounded by a uniform shielding field (due to the less effective long range shielding of the CO group), or if, on the contrary, it rotates rapidly about the axis of the coordination bond. Due to its position, this signal can be assigned to molecule *a*, i.e. to the "*cis*" position with respect to nitrogen. According to our interpretation, ethylene in a "*trans*" position with respect to nitrogen is thus more reactive towards replacement by another ligand.

Based on the analysis of the spectrum of (III) and its analogues, the NMR spectra of the series of *para*-substituted bis(ethylene)rhodium-4-(phenylimino)-2-pentanone chelates can be interpreted, with the aid of NMDR, as shown in Fig. 2. The mutual dependence of signals in NMDR, indicated by dashed lines, again corresponds to a superposition of two AA'XX'systems, arising from the two non-equivalent molecules of coordinated ethylene in each of the chelates. The chemical shifts of various ethylenic protons derived by this analysis are summarized in Table 1.

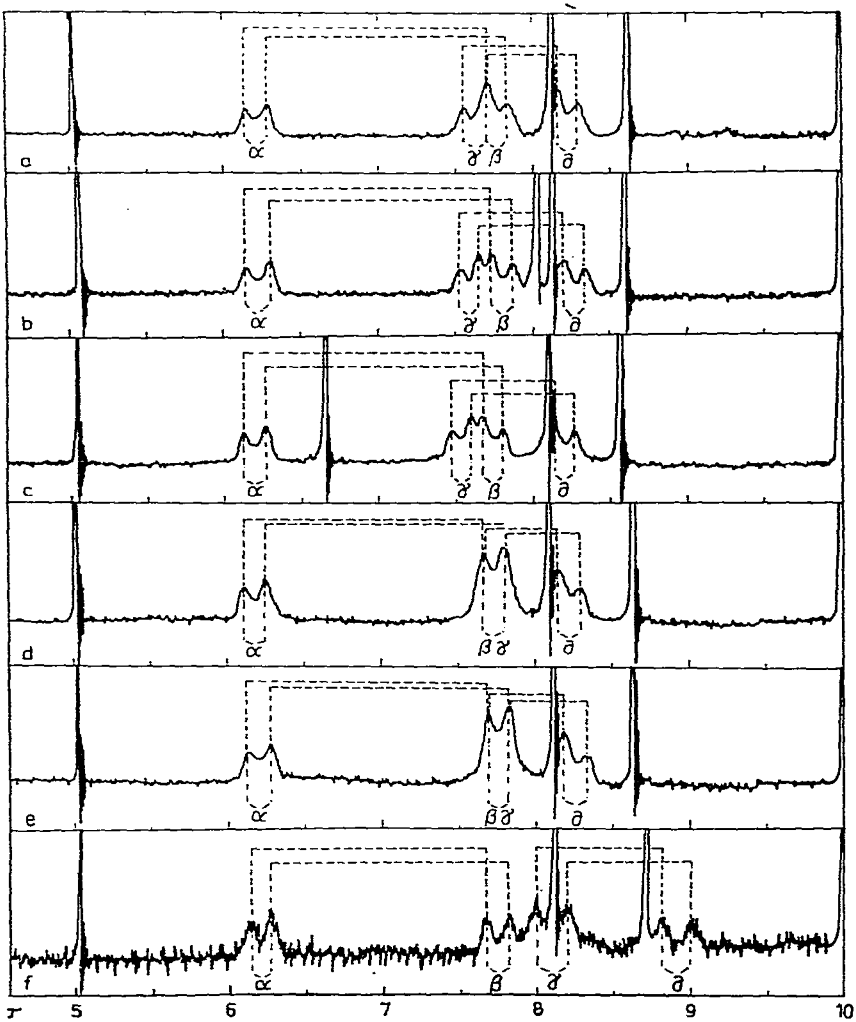


Fig. 2. NMR spectra of solutions of bis(ethylene)rhodium - 4-(phenylimino)-2-pentanone chelates in chlorobenzene. Substituent: a, H; b, CH_3; c, CH_3O; d, Cl; e, Br; f, NO_2.

TABLE 1

FREQUENCIES OF DECOUPLED TRANSITIONS[a] OF RIGID LIGAND PROTONS, AND HYPOTHETICAL TRANSITION FREQUENCIES OF FREELY ROTATING LIGANDS[b] IN NMR SPECTRA OF BIS(ETHYLENE)RHODIUM(I)—4-IMINO-2-PENTANONE CHELATES

Compound	Subst.	ν_α	ν_β	ν_γ	ν_δ	Freely rotating molecule	
						ν_a	ν_b
(II)	H					7.03	7.78
(III)	CH_3	6.31	7.87	7.33	8.24	7.09	7.81
(VIII)	$CH_3OC_6H_4$	6.23	7.81	7.59	8.25	7.02	7.92
(V)	$CH_3C_6H_4$	6.25	7.85	7.63	8.25	7.05	7.94
(IV)	$H—C_6H_4$	6.27	7.84	7.70	8.30	7.06	8.00
(VII)	BrC_6H_4	6.28	7.84	7.83	8.37	7.07	8.10
(VI)	ClC_6H_4	6.28	7.85	7.85	8.38	7.07	8.12
(IX)	$NO_2C_6H_4$	6.27	7.89	8.19	8.99	7.08	8.59

[a] Transition. frequencies are given in τ (ppm) units; frequencies of decoupled signals were obtained by spectrum analysis, for real signal positions see ref.1. [b] The frequency was calculated as a weighted mean of line positions of α, β and γ, δ protons, respectively.

Magnetic shielding and bonding character of Rh^I complexes

The high symmetry (at least C_{2v}) of Rh^I complexes with four or six equal ligands indicates a high degree of hybridization of its electrons in *N* and *O* shells, particularly $5s4d4p^2$ for D_{4h} symmetry (planar RhL_4 complexes) and $5s4d^2 4p^3$ for O_h (octahedral RhL_6). By analogy to other bonding types, it can be assumed that this hybridization is roughly preserved even at the lower symmetry brought about by the introduction of unequal ligands.

In assumed hybridization types sp^2d or sp^3d^2, the 4*d* electrons of rhodium partly participate in the bonding with the ligand, and partly occupy the non-bonding orbitals. By the introduction of ethylene into the complex, part of its original π-electron density is transferred into the bonding orbitals of the central metal. As documented in the Appendix, this change leads to a relative increase of the shielding of ethylenic protons in our chelates. Most non-bonding *d*-orbitals of rhodium undoubtedly contribute more by their diamagnetic term to the shielding, so that the total effect of coordination of ethylene with rhodium is a relative increase of proton shielding, as observed (the singlet of uncoordinated ethylene in the same medium at −60° lies at τ 4.98 ppm).

The type (A) chelate can be considered as a pseudo-conjugated system. If a decrease of electron density in one of the ligands is caused by substitution, the electronic perturbation spreads in all directions through the chelate. For reasons of symmetry it is manifested most strongly in the opposite hybrid orbital of the central metal, where to it is transferred along the hybrid bond by a system of exchange and repulsion interactions. This results in a decrease π-electron density of coordinated ethylene in the *trans* position, and consequently in a relatively higher shielding of its protons.

These conclusions are summarized in Table 1, in which hypothetical proton signal positions of freely rotating ethylene molecules are given; these were obtained as a weighted average of the measured lines of the protons of each ethylene molecule. The decrease of the shielding of molecule *b* [see (B)] upon substitution of the aromatic ring attached to nitrogen in the chelate moiety, in accord with our interpretation, is clearly evident. Of course, the effects of substitution can be studied in detail only in the series of various substituted (phenylimino)pentanone complexes, i.e. beginning by compound (VIII) in Table 1. As assumed, the substitutent with larger electron affinity causes larger magnetic shielding of protons in ethylenic ligands, and this effect is stronger in molecule *b* than in *a*. With the exception of compound (IX), the changes are generally larger in protons γ than in protons δ, where this effect is probably compensated by the shielding by molecule *a*.

On the whole it can be concluded that in the chelates investigated, the ligand molecules are non-equivalent especially in π-electron density, and that this density can be significantly influenced by substitution in the iminopentanone part of the chelate. This conclusion may be of some consequence for the interpretation of the influence of substitution upon the stability and reactivity of the chelates.

Mobility of ligand molecules

If the chelate molecule is preserved as a whole, then the principal degree of freedom of the ethylenic ligands is assumed to correspond to their rotation about the axis of the coordination bond [2,3]. This assumption, based on energy considerations, is supported by the following reasoning [2,3], which is partly confirmed by our experiments: The spectra of ethylenic protons in these chelates exhibit in various temperature ranges a reversible change from the pattern of one or two AA'XX'systems down to the singlet of equivalent protons (in pentadienyl chelates at 67°, in 2,4-pentanedione chelates at room temperature, in 4-imino-2-pentanone chelates, the coalescence cannot be achieved below decomposition temperature); this change is first order with respect to the concentration of the chelate, and is caused neither by chemical exchange of individual protons nor by exchange of whole ligand molecules for uncoordinated ehtylene; the only other possible reason for a reversible temperature change of the spectrum, namely mutual exchange of ligands without dissociation, is excluded by excessive requirement for rehybridization of the orbitals of the central metal atom.

Because of the lower stability of our asymmetric chelates, the reversibility of the spectral change cannot be checked over the whole temperature range. Nevertheless, the applicability of the ligand rotation hypothesis can be supported, in addition to the above qualitative arguments, by the results of NMDR experiments. As already stated, the decrease of intensity of one doublet component can be explained only by relaxation effects causing population redistribution on various energy levels ("generalized" Overhauser effect); however, in such a case the intensity of the other line of the doublet should be increased. Since this is not the case, as observed, then it can be explained only by slow exchange between the irradiated and measured protons; in our case this can only be caused by rotation of the moelcule.

In Fig. 3 the temperature change of the spectrum of complex (III) ($R = CH_3$) is shown. This change can be regarded as reversible up to 35°, but at higher temperatures it is accompanied by irreversible changes due to decomposition of the compound. It is evident that the α, β protons are more mobile than the γ, δ protons.

It can therefore be concluded that the mobility of coordinated ethylene

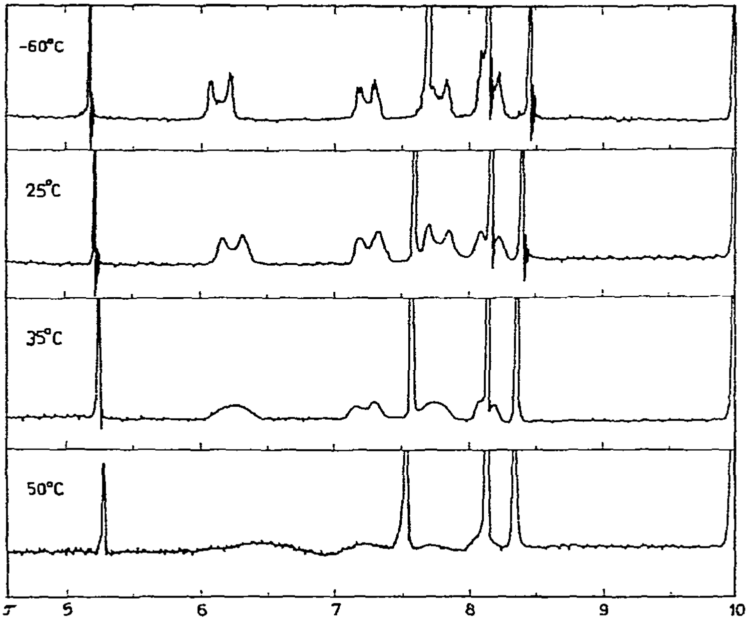


Fig. 3. Temperature change of the NMR spectrum of bis(ethylene)rhodium-4-(methylimino)-2-pentanone chelate in chlorobenzene.

about the coordination bond is greater in 2,4-pentanedione complexes than in 4-imino-2-pentanone chelates; in the latter, ethylene "*cis*" to nitrogen is more mobile than in the "*trans*" position. However, this mobility is evidently not connected with the strength of the coordination bond. Symmetrical 2,4-pentanedione chelates are generally less reactive than asymmetric iminopentanone chelates. The less mobile ethylene in the "*trans*" position is evidently more reactive with respect to exchange with another ligand, as shown.

During rotation of ethylene, no marked changes of overlap of its π-orbitals with the hybrid orbital of the central atom take place. The strength of the coordination bond therefore cannot substantially influence the height of the rotation barrier. However, the overlap of π-orbitals with the non-bonding 4*d* orbitals of the central metal does change during rotation. The asymmetry of electron density distribution in these orbitals, caused by the asymmetry of the ligand field, evidently leads to an increase of the rotation barrier.

Experimental

Preparation of compounds

Type (A) chelates were prepared by the method described in an earlier communication [1]. The mixed [4-(methylimino)-2-pentanonato](ethylene)(carbonyl)rhodium was prepared by mixing equimolar amounts of solutions of compound (III) and of [4-(methylimino)-2-pentanonato)(dicarbonyl)rhodium; the dicarbonyl chelate used was prepared by exchange of both ethylenic ligands in (III) by reaction with CO, and purified by sublimation at 70°/10^{-2} mmHg.

cis-Dideuterioethylene was prepared by reduction of acetylene by activated Zn in D_2O; by mass spectrometry, the content of dideuterioethylene was about 65%. The exchange of ethylene for *cis*-dideuterioethylene in (III) was achieved by saturation of a 5% solution of (III) in chlorobenzene with deuterated ethylene at 20°.

Measurement of NMR and NMDR spectra

All chelates were measured in the form of 5% solutions in chlorobenzene, in which they are relatively stable and where paramagnetic effects which disturb NMR spectra are absent. The spectra were measured at 100 MHz on the PS-100 (Jeolco, Japan) NMR spectrometer. The NMDR spectra were measured in the variable frequency- fixed field mode. The PS-100 spectrometer operates with a relatively high modulation frequency (8 kHz) and consequently the NMDR spectra were not perturbed by the modulation effects in the measured range [8,9]. The amplitude of the perturbing field was calibrated by the method of Anderson [4], and also by decoupling of a simple AX system.

Appendix

The Ramsey equation [10] for the scalar shielding constant is:

$$\sigma = (e^2/3m \cdot c^2)\langle 0|\sum_k r_k^{-1}|0\rangle -$$

$$2/3 \sum_\lambda \sum_n (E_n - E_o)^{-1} \cdot \Big\{ \langle 0|\sum_k m_{\lambda k}|n\rangle\langle n|\sum_k m_{\lambda k} \cdot r_k^{-3}|0\rangle +$$

$$\langle 0|\sum_k m_{\lambda k} \cdot r_k^{-3}|n\rangle\langle n|\sum_k m_{\lambda k}|0\rangle \Big\} \quad ; \lambda = x, y, z \tag{1}$$

(with r_k designating the position of the k-th electron, m_k the corresponding component of momentum and $\langle 0|$ and $|n\rangle$ the corresponding vectors of the ground and excited states) can be rewritten in the form;

$$\sigma = e^2/m \cdot c^2 \sum_{\mu < \nu}\sum P_{\mu\nu} \cdot S_{\mu\nu} \left\{ \langle\mu|r^{-1}|\nu\rangle - \frac{\langle\mu|m_{z\mu} \cdot m_{z\nu} \cdot r_\nu^{-3}|\nu\rangle\ \langle\mu|x_\mu \cdot r_\nu^{-3}|\nu\rangle}{\langle\mu|m_{z\mu} \cdot p_{y\nu} \cdot r_\nu^{-3}|\nu\rangle} \right\} \tag{2}$$

using the mean excitation energy approximation with simultaneous conservation of gauge invariance [11,12], and with the LCAO molecular integral approximation [13]; $\langle\mu|, |\nu\rangle$ are the vectors of the corresp. atomic orbitals, $S_{\mu\nu} \equiv \langle\mu|\nu\rangle$, and $P_{\mu\nu}$ is an element of the density matrix represented in the space of the given basis set. Results of more precise calculations indicate [13] that the largest contributions in the integrals of eqn. (2) correspond to terms with $\mu = \nu$, or, in other words, the contribution of each atomic orbital is *roughly* given by its net localized electron density. As in ethylene the π-electrons contribute mostly by the paramagnetic term [13,14], a small decrease of their net density will lead to a relative increase of the shielding of ethylenic protons.

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