

## PREPARATION AND CHARACTERISTICS OF 2-IMINO-4-PENTANONE CHELATES OF BIS(ETHYLENE)RHODIUM(I)

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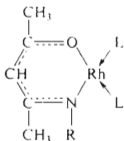
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Chelates of the  $[\text{CH}_3\text{C}(\text{NR})\text{CHCOCH}_3]\text{Rh}(\text{C}_2\text{H}_4)_2$  type were synthesized. From these, complexes of the  $[\text{CH}_3\text{C}(\text{NR})\text{CHCOCH}_3]\text{Rh}(\text{L}_1\text{L}_2)$  type were obtained by reactions with 1,5-cyclooctadiene and CO; their NMR spectra were recorded and the difference between the signals of ethylenic protons in complexes with various R substituents in the chelate ligand was explained qualitatively.

An exchange of 1,3-substituents in 1,3-diketone chelate ring of the complexes of Rh(I) leads in the first place to the exchange of  $\pi$ -bonding component of the coordination bond of a nonspecified donor with the rhodium atom<sup>1</sup>. In complexes with ethylenic ligands, both spectral characteristics and the exchange capacity of both coordinated ethylene molecules are affected<sup>1,2</sup>. If on the other hand Schiff's bases of salicylaldehyde and 2,4-pentanedione are used as the ligands of Rh(I) and Ir(I), the different donor capacity of the nitrogen and oxygen atoms becomes visible as nonequivalency of the coordination bonds between two identical nonspecified donors<sup>3,4</sup>.

In our earlier papers<sup>2,5</sup> we reported the preparation and properties of various 1,3-disubstituted 1,3-propanedione chelates of bis(ethylene)rhodium(I) and of corresponding complexes in which ethylene had been replaced by chloro-substituted dienes.



- II; R=H, L=C<sub>2</sub>H<sub>4</sub>  
 III; R=CH<sub>3</sub>, L=C<sub>2</sub>H<sub>4</sub>  
 IV; R=C<sub>6</sub>H<sub>5</sub>, L=C<sub>2</sub>H<sub>4</sub>  
 V; R=C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, L=C<sub>2</sub>H<sub>4</sub>  
 VI; R=C<sub>6</sub>H<sub>4</sub>Cl, L=C<sub>2</sub>H<sub>4</sub>  
 VII; R=C<sub>6</sub>H<sub>4</sub>Br, L=C<sub>2</sub>H<sub>4</sub>

- VIII; R=C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>, L=C<sub>2</sub>H<sub>4</sub>  
 IX; R=C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, L=C<sub>2</sub>H<sub>4</sub>  
 X; R=CH<sub>3</sub>, L=CO  
 XI; R=CH<sub>3</sub>, L=COD  
 XII; R=C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, L=CO  
 XIII; R=C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, L=COD

This paper is dealing with the preparation of a number of analogous complexes of Rh(I) with variously N-substituted 2-imino-4-pentanone. The NMR spectra of complexes obtained in this work were used to evaluate the effect of various N-substituents in the chelate ring of Schiff's base on the character of coordination of ethylenic ligands with the central rhodium atom. The chemical reactivity of ethylenic ligands was investigated during exchange reactions with 1,5-cyclooctadiene and carbon monoxide.

The reaction of dichlorotetraethylenedirrhodium (I) with the respective Schiff's bases of 2,4-pentanedione in the presence of potassium hydroxide was used for the preparation of complexes of the A(II-IX) type; their physical properties, elemental analyses and characteristic bands of the infrared spectra are given in Table I.

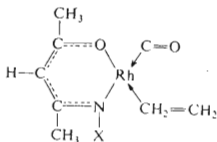
The above complexes are crystalline compounds, with a sharp melting point in most cases; decomposition takes place at temperatures above 150°C with formation of ethylene. They are low-soluble in nonpolar organic solvents, but readily dissolve in ether and chloroform. According to the molecular weights determined osmotically in toluene solution (Table I), complexes II-IX are monomeric in these solutions. All identified complexes are sufficiently stable at reduced pressure, which allows the determination of their mass spectra.

The exchange of ethylenic ligands was verified on complexes III and V. By treating them with carbon monoxide or 1,5-cyclooctadiene ethylene was released, and corresponding dicarbonyl complexes X and XII or 1,5-cyclooctadiene complexes XI and XIII were isolated from the reaction mixture. Their chemical analyses and physical constants are given in Table II. The possibility of replacing coordinated ethylene molecules by another ligand is in agreement with the explanation given for the cause of exchange reactions of 1,3-propanedione chelates of bis(ethylene)rhodium(I) (ref.<sup>6</sup>). The number of electrons in the central metal atom region is lower by two than in the electron shell of xenon; therefore, another ligand may contribute by its electrons to the electron region of rhodium(I) and also replace the originally coordinated ethylene. In contrast with the comparatively easy preparation of 1,3-propanedione chelates (1,6-dichloro-1,5-cyclooctadiene) of rhodium(I) by an exchange reaction of 1,3-propanedione chelates of bis(ethylene)rhodium(I) with 1,6-dichloro-1,5-cyclooctadiene<sup>2</sup>, ethylene was released during reactions III and V with this diene; however, the reaction products could not be divided into individual compounds even by elution chromatography on a column of active Al<sub>2</sub>O<sub>3</sub>. Neither was it possible to obtain defined products by treating ether solutions of III and V with tetrafluoroethylene. The reaction between complexes III and X, and V and XII respectively in chlorobenzene was investigated by means of the NMR spectra. It can be deduced therefrom that a mixed complex is formed in solution:

TABLE I  
 Characteristics of N-Substituted 2-Imino-4-pentanone Chelates of Bis(ethylene)rhodium(I)

Complex Yield, %	M.p., °C Colour	Formula m. w.	Calc./Found			$M_{\text{osm}}$ m/e	Infrared spectra $\text{cm}^{-1}$
			%C	%H	%N		
<i>H</i>	104 orange	$\text{C}_9\text{H}_{16}\text{NORh}$ (257.1)	42.0	6.6	5.45	260	1 575(s) <sup>a</sup> , 1 545(s), 1 515(s)
<i>III</i>	110 orange	$\text{C}_{10}\text{H}_{18}\text{NORh}$ (271.1)	42.15 44.27	6.5 6.65	5.32 5.18	257 280	1 570(s), 1 550(s), 1 520(s)
<i>IV</i>	132 orange	$\text{C}_{11}\text{H}_{20}\text{NORh}$ (333.3)	43.97 54.04	6.60 6.05	5.23 4.19	271 350	1 591(s), 1 572(m) <sup>b</sup> , 1 540(w) <sup>c</sup> , 1 510(m)
<i>V</i>	120 yellow	$\text{C}_{16}\text{H}_{22}\text{NORh}$ (347.2)	53.9 55.4	6.02 6.40	4.10 4.04	333 360	1 600(m), 1 575(m), 1 540(s), 1 520(m)
<i>VI</i>	180 <sup>f</sup> yellow	$\text{C}_{15}\text{H}_{19}\text{ClNORh}^d$ (367.7)	49.40 49.60	5.20 5.36	3.83 3.70	380 269; 367	1 590(m), 1 525(m), 1 508(s), 1 508(s)
<i>VII</i>	122 yellow	$\text{C}_{15}\text{H}_{19}\text{BrNORh}^e$ (412.1)	43.90 44.05	4.65 4.70	3.40 3.52	420 413; 411	1 590(m), 1 545(s), 1 520(s), 1 555(s)
<i>VIII</i>	165 yellow	$\text{C}_{16}\text{H}_{22}\text{NO}_2\text{Rh}$ (363.2)	53.10 53.00	6.14 6.01	3.85 3.70	370 363	1 580(s), 1 595(s), 1 515(s), 1 505(s)
<i>IX</i>	150 <sup>f</sup> orange	$\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_3\text{Rh}$ (378.2)	47.60 47.5	5.08 5.05	7.40 7.30	<i>g</i> 378	1 600(m), 1 570(s), 1 530(s)

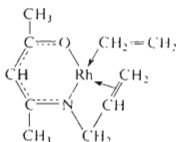
<sup>a</sup> s = strong, <sup>b</sup> m = medium, <sup>c</sup> w = weak, <sup>d</sup> calculated 9.72% Cl, found 9.45% Cl, <sup>e</sup> calculated 19.40% Br, found 19.52% Br, <sup>f</sup> decomposition temperature, <sup>g</sup> complex unstable in solution.



( $X = \text{CH}_3$  in *XV*,  $X = \text{CH}_3\text{C}_6\text{H}_4$  in *XVI*) the structure and properties of which are the object of further study.

The  $m/e$  values found for molecular ions of complexes *II–IX* correspond to the calculated molecular weights of the complexes (Table I). Their fragmentation (Fig. 1a) begins with the splitting-off of one or both ethylenic ligands similarly to that of molecular ions of dicarbonyl complexes *X* and *XII* which begins by the splitting-off of the CO ligands (Fig. 1c).

To investigate the NMR spectra of complexes of the given type complex *XIV* was obtained:



The most intensive band in the mass spectrum of complex *XIV* (Fig. 1b) is that for  $m/e$  241 corresponding to the splitting-off of one ethylenic ligand; the band  $m/e$  213 which would correspond to the splitting-off of two ethylenic ligands does not appear in the spectrum at all. The mass spectra are in accordance with the results of elemental analysis (Table II), and also with the observation that approximately one ethylenic ligand per rhodium atom was released during the preparation of *XIV* from dichlorotetraethylenedirhodium(I). In the given complex, the allyl substituent is obviously coordinated with the metal atom through the nitrogen atom; this is in agreement with the finding that allyl amine acts as a bifunctional ligand toward transition metals<sup>7–9</sup>. For instance, in the platinum complexes allyl amine was first assigned coordination of the chelate type<sup>7</sup>; later however it was found that allyl amine acted as a bridge ligand<sup>8</sup>. The coordination of  $\text{Cu}^+$  with allyl amine in neutral medium proceeds with formation of a chelate structure<sup>9</sup>. The  $m/e$  and molecular weight values de-

terminated for complex *XIV* suggest that the structure of the allyl amine ligand is rather of the chelate than of the bridge type. The bridge structure of complex *XIV* cannot however be ruled out under conditions different from those used for the determination of  $m/e$  and molecular weight.

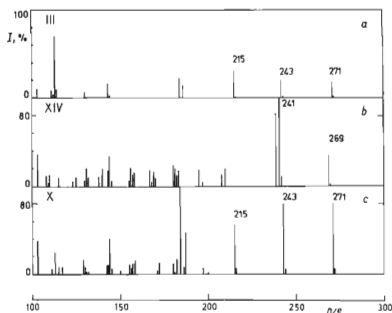


FIG. 1

Mass Spectra (*III*) of Bis(ethylene)(2-methylimino-3-pentene-4-olate)rhodium(I), (*X*) Dicarboxyl(2-methylimino-3-pentene-4-olate)rhodium(I) and (*XIV*) (Ethylene) (2-allylimino-3-pentene-4-olate)rhodium(I)

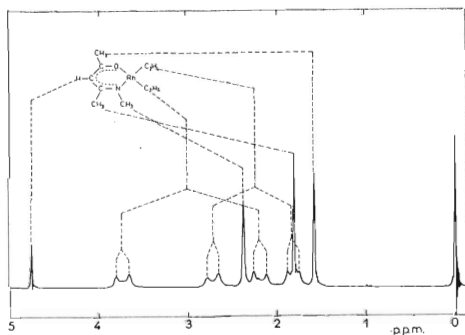


FIG. 2

NMR Spectrum of Bis(ethylene)(2-methylimino-3-pentene-4-olate)rhodium(I)

TABLE II  
Characteristics of N-Substituted 2-Imino-4-pentanone Rhodium(I) Chelates

Complex L <sub>1</sub> ; L <sub>2</sub>	M. p., °C Colour	Formula mol. weight	Calc./Found			M <sub>osm</sub> <sup>a</sup> m/e
			%C	%H	%N	
X CO; CO	141 yellow	C <sub>8</sub> H <sub>10</sub> NO <sub>3</sub> Rh (271·1)	35·40	3·72	5·17	285
			35·10	3·57	5·05	271
XI 1,5-cyclooctadiene	125 orange	C <sub>14</sub> H <sub>22</sub> NORh (323·2)	52·00	6·80	4·33	340
			52·30	6·75	4·20	323
XII CO; CO	132 <sup>b</sup> yellow	C <sub>14</sub> H <sub>14</sub> NO <sub>3</sub> Rh (347·2)	48·40	4·10	4·00	347
			48·15	4·25	3·90	347
XIII 1,5-cyclooctadiene	205 <sup>b</sup> yellow	C <sub>20</sub> H <sub>22</sub> NORh (395·3)	60·80	6·60	3·50	380
			60·42	6·50	3·40	—
XIV C <sub>2</sub> H <sub>4</sub> ; <sup>c</sup>	121 orange	C <sub>10</sub> H <sub>16</sub> NORh (269·8)	45·00	6·10	5·20	290
			45·25	6·24	5·09	269

<sup>a</sup> Osmometry, <sup>b</sup> melting points correspond to the published values<sup>4</sup>, <sup>c</sup> cf. set of structures.

TABLE III  
Chemical Shifts (τ) of Protons in the NMR Spectra of 2-Imino-4-pentanone Chelates of Bis(ethylene)rhodium(I)

Group	II	III	IV	V	VI	VII	VIII	IX
CH <sub>3</sub> (1) <sup>a</sup>	8·24	8·22	8·19	8·16	8·18	8·19	8·15	8·19
CH <sub>3</sub> (5) <sup>a</sup>	8·46	8·45	8·69	8·65	8·73	8·75	8·62	8·73
CH	5·37	5·27	5·13	5·10	5·13	5·13	5·05	5·10
		6·24	6·20	6·17	6·21	6·21	6·16	6·21
		6·38	6·34	6·32	6·35	6·35	6·30	6·33
		7·27	7·63	7·56	—	—	7·53	7·76
C <sub>2</sub> H <sub>4</sub>	7·03	7·39	7·76	7·69	7·78	7·76	7·65	7·91
		7·79	7·92	7·78	7·91	7·90	7·73	8·09
		7·94	—	7·92	—	—	7·88	8·29
		7·78	8·17	8·25	8·15	8·27	8·26	8·21
CH <sub>3</sub> (N) <sup>b</sup>	—	8·30	8·34	8·38	8·40	8·40	8·33	9·08
		7·66	—	8·09	—	—	6·72	—

<sup>a</sup> 1,5-Positions of methyl groups in 2-imino-3-pentene-4-olate ligand. <sup>b</sup> Methyl group on N or in the position *para* of a phenyl bonded to N.

TABLE IV

Hypothetic Chemical Shifts of Protons\* of the Ethylenic Ligands in *N*-(*p*-Y-phenyl)-2-imino-4-pentanone Chelates of Bis(ethylene)rhodium(I) in Correlation with Hammett's Constants ( $\delta_p$ ) of the Substituents Y

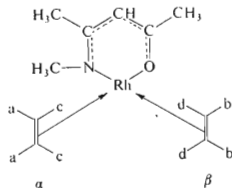
Complex	Y	$\delta_p$	$\tau_\alpha$	$\tau_\beta$
VIII	CH <sub>3</sub> O	-0.26	7.02	7.92
V	CH <sub>3</sub>	-0.16	7.05	7.94
IV	H	0	7.06	8.00
VII	Br	0.23	7.07	8.10
VI	Cl	0.23	7.07	8.12
IX	NO <sub>2</sub>	0.79	7.08	8.59

\* For free-rotating ligand molecule, from the statistically weighted mean,  $\tau$ , of the protons of a rigid molecule.

The infrared spectra of complexes II–IX in the region 1500–1600 cm<sup>-1</sup> (Table I) characterize qualitatively the chelate ring of Schiff's bases. This region includes characteristic valency vibrations of the groups<sup>10</sup> C=O, C=C and C=N. Since the bond vibrations in the chelate ring strongly interact similarly to the 1,3-diketone chelates<sup>2</sup>, the absorption bands cannot be assigned unambiguously to a certain bond type.

The NMR spectra reflect the bonding conditions in molecules of the complexes in a complicated way; a detailed analysis of these conditions will be dealt with in a separate communication. This paper contains a brief description of the spectra and qualitative conclusions ensuing from their analysis.

A typical NMR spectrum of compound III is shown in Fig. 2. The 2-imino-4-pentanone part yields a simple spectrum, but protons of ethylenic ligands give a complex system of signals in the form of four greatly broadened doublets. According to an NMDR study<sup>6</sup> the signals belong to four pairs of protons split by spin interaction and broadened mainly by the slow rotation of the ligand about the axis of the coordination bond. With increasing  $\tau$ , the individual doublets correspond to protons of the a, b, c, d type in the formula of complex III:



The spectra of the other complexes differ from that of complex *III* in the chelate part only by small changes in  $\tau$  of the individual proton groups. With varying substitution the position and also the shape of the signals of ethylenic protons change more owing to mutual superposition (Table III gives chemical shifts of the individual pronounced maxima). Static weighting of nonsuperimposed signals yielded hypothetical shifts for free-rotating ligand molecules; the data for a number of complexes with 2-phenylimino-4-propanone ligands having different substituents in the position *para* of phenyl are summarized in Table IV.

Both molecules of the ethylenic ligand are clearly not magnetically equivalent. Similarly to the coordination-enhanced shielding of the ethylenic protons, here too the nonequivalency is due to the different decrease in the density of the  $\pi$ -electrons, and consequently to a change in shielding.

The ligand molecule, which according to our interpretation is situated in the *trans* position to the nitrogen atom and is designated by  $\beta$  in the formula of complex *III*, is more reactive toward another ligand. The substitution of one ethylene molecule with CO in the molecule of *III* or *V* leads to a contraction of the whole ethylene spectrum to yield a single signal corresponding to the free rotation of the ethylene molecule. Its position is closer to those of hypothetical  $\tau_a$  in mother homoligand molecules, and still more close to the  $\tau_a$  values (which probably is related to the less effective long range shielding observed for CO than that observed for  $C_2H_4$ ): for *XV*, this value is 6.48 compared to 7.09 ( $\tau_a$ ) or 6.31 ( $\tau_a$ ) for *III*, while for *XVI* it is 6.41 compared to 7.05 ( $\tau_a$ ) or 6.25 ( $\tau_a$ ) for *V*.

As shown in Table IV, the shielding of protons in the *trans*-ethylenic ligand is more sensitive by an order of magnitude to a change in the substituent in the chelate residue than the shielding in *cis*-ethylene, which corresponds to the quantum chemical requirements to the expansion of the electron disturbance along the pseudoconjugated system. According to our interpretation this change is connected with the various degrees of the density transfer of  $\pi$ -electrons to the coordination bond. The electron acceptor substituents cause the largest reduction of the  $\pi$ -density and consequently also the largest decrease in negative shielding. An elucidation of the effect of this disturbance on the stability and reactivity of complexes will be dealt with in further communications.

## EXPERIMENTAL

The infrared spectra of the complexes were recorded by the KBr techniques with a UR-10 (C. Zeiss) spectrometer; the NMR spectra were measured in chlorobenzene solutions of complexes (HMDS as the internal standard) with a JEOL-PS-100 spectrometer. The molecular weights were determined with a Vapour-Pressure-Osmometer Hitachi Perkin-Elmer 115; an AEI Mass Spectrometer MS 902 was used for the mass spectra determinations.



## Chemicals

Dichlorotetraethylenedirrhodium(I) (*I*) was synthesized after Cramer<sup>11</sup> (m.p. 116°C). 2,4-Pentanedione was purified by extractive distillation with water and rectified on drying (b.p. 139°C,  $n_D^{20}$  1.4521). The physical constants of Schiff's bases obtained<sup>10,12</sup> from 2,4-pentanedione and ammonia, methyl amine and substituted aromatic amines were in accordance with the literature data. 2-Allylimino-4-pentanone, not described in the literature, was obtained by condensation of allylamine (b.p. 55–6°C) with acetylacetone; the product after isolation was purified by distillation (b.p. 97–98°C/15 Torr,  $n_D^{20}$  1.5322, molecular ion  $m/e$  139). 1,5-Cyclooctadiene (98%) was used without further modifications.

## Preparation of Complexes

Bis(ethylene) (2-imino-3-pentene-4-olate)rhodium(I) (*II*). To a suspension of 0.386 g (*I*) in 25 ml ether, 0.2 g of 2-imino-4-pentanone was added, the mixture was cooled to  $-20^\circ\text{C}$  and 1 ml 20% KOH was added dropwise to the mixture with vigorous shaking. After stirring at  $0^\circ\text{C}$  for 15 min, the ether layer was separated, dried with anhydrous  $\text{Na}_2\text{SO}_4$  and cooled to  $-80^\circ\text{C}$ . The crystals thus obtained, 0.35 g (68%), were recrystallized from the ether-hexane mixture (1 : 1); m.p.  $104^\circ\text{C}$ . Complexes *III-IX* were obtained similarly to complex *II*. During the preparation of (ethylene) (2-allylimino-3-pentene-4-olate)rhodium(I) by a procedure similar to that described above, approximately 40 ml of ethylene was released per one mole of complex *I*. (1,5-Cyclooctadiene)2-methylimino-3-pentene-4-olate)rhodium(I) (*XI*). To a mixture of 0.27 g (*III*) (1 mmol) in ether 0.3 ml of 1,5-cyclooctadiene was added. The reaction proceeded with a fast evolution of ethylene (42 ml within 15 min). After filtration and cooling of the filtrate to  $-80^\circ\text{C}$  crystals were obtained, the melting point of which after recrystallization from ether was  $125^\circ\text{C}$ . Dicarbonyl(2-methylimino-3-pentene-4-olate)rhodium(I) (*X*). A vigorous stream of carbon monoxide was introduced into a solution of 1 mol (*III*) in ether for 60 min. The crystalline fraction was filtered off, dried, and sublimated. The yield was 0.17 g, m.p.  $141^\circ\text{C}$ .

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