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Cationic products from *O*-protonation reaction of 2-acylnorbornadiene complexes of rhodium with hydrogen chloride in ether: structure, reactivity and nature of hydrogen bond

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Abstract

The cationic hydroxyallylolefin complexes of rhodium, $[Rh(\eta^{2,3}\text{-}C_7H_7\text{-}2\text{-}CR{=}OH)(\eta^5\text{-}C_5H_4R^1)]^+Cl^-$ (II–IV), were prepared as stable salts from the reaction of $Rh(\eta^4\text{-}C_7H_7\text{-}2\text{-}COR)(\eta^5\text{-}C_5H_4R^1)$ (Ia, b, d) (where R = H, Me, R^1 = H; R = H, R^1 = Me) with HCl in absolute ether. The structure of these cations was deduced from their IR, ^1H NMR and ^{13}C NMR spectra. The dimeric dichlorocyclopentadienylrhodium complex, $[(\eta^5\text{-}C_5H_5)RhCL_2]_2$, was isolated from Ic (R = Ph, R^1 = H) under the same conditions. In view of the IR and ^1H NMR spectral data of cations II–IV, the presence of an interionic hydrogen bond of the O–H ··· Cl type was postulated. The likelihood that a similar hydrogen bond is present in *O*-protonated acylferrocene and in some π-enol iron complexes is discussed. Certain reactions of the hydroxyallylolefin cations were studied. Intramolecular oxidative addition of Cl^- to the cationic complexes in CH_2Cl_2 solution gave *endo/exo* isomeric 2-acyl-5-norbornenes and the dimeric complexes $[(\eta^5\text{-}C_5H_4R^1)RhCl_2]_2$ (where R^1 = H, Me) as the main products. Hydrogenation of protonated carbonyl group of complex II to give methyl group proceeds under the action of Et_3SiH in CH_2Cl_2 solution. The mechanisms of these reactions are described.

Introduction

Depending on the nature of the metal atom, the coordinated diene and the strength of acid used are one of a number of factors that affect the protonation of non-substituted diene π-complexes of transition metals, which as is known normally proceeds along two lines: (a) at the metal atom [1,2], and (b) at the carbon of the double ligand bonds [1,3,4]. This reaction is often stepwise with hydrogen migration from the metal to the coordinated diene [5,6].

If the diene ligand has a carbonyl function, proton attack usually occurs at the oxygen atom. Subsequent hydrogen migration to the carbon atom of the diene can

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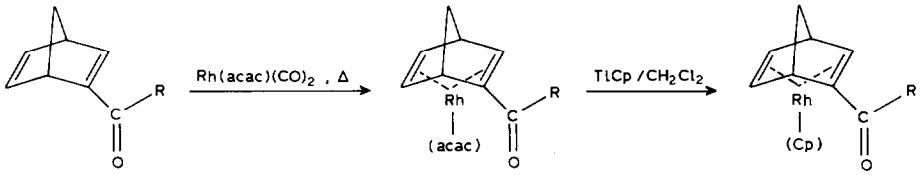
however be followed [7,8]. As a rule, the *O*-protonation product of the acyl derivatives of σ- or π-complexes can be observed only in acidic solutions using ^{1}H NMR and UV spectroscopy [9–13]. Examples of stable crystalline compounds of this type are rare [16], with the exception of some carbene complexes (for example see [14,15]).

Recently we obtained unusually stable *O*-protonated products from the reaction of (2-formylnorbornadiene)cyclopentadienylrhodium with HCl or F_2POOH [17]. This study has now been further extended to the 2-acyl derivatives of complexes $Rh(\eta^4\text{-}C_7H_8)(Cp)$, where $Cp = \eta^5\text{-}C_5H_4Me$ and $\eta^5\text{-}C_5H_5$. Spectral properties and reactivity of *O*-protonated cationic complexes have also been investigated.

Results and discussion

Initial π-complexes (Ib–d) were prepared from corresponding acetylacetonato-rhodium complexes by the convenient exchange method which was used previously to synthesize (2-formylnorbornadiene)cyclopentadienylrhodium (Ia) [18]. With the exception of low melting point Id, all the compounds are stable and crystallize well. Their structures were deduced from IR, ^{1}H NMR, mass spectral data and from elemental analysis (see Experimental).



(Ia–Ic, R = H, Me, Ph; Cp = η^5-C_5H_5;
Id, R = H; Cp = η^5-C_5H_4Me)

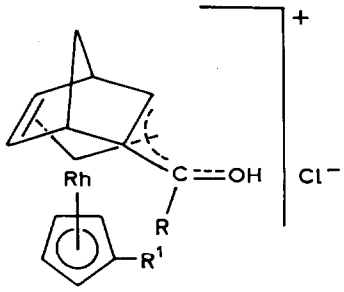
The protonation of 2-formyl derivatives (Ia, d) with gaseous HCl in ether produced crystalline adducts formulated as $C_{13}H_{14}ClORh$ (II) and $C_{14}H_{16}ClORh$ (III), respectively. The adducts appeared to be stable in a dry atmosphere of Ar. Thus, compound II after recrystallization from CH_2Cl_2 at −40 °C or from mixture CH_2Cl_2/hexane has a definite melting point, 103 °C (without dec.) and its composition did not change after 5 h in vacuo at 56 °C.

The reaction of ketone Ib with HCl under similar conditions also leads to a 1 : 1 adduct (IV), whose stability, however, is markedly lower than that of adducts II and III. The vacuation of sample IV within 5 h leads to a complete lose of HCl to form the initial complex Ib.

Treatment of the 2-benzoyl derivative Ic with HCl in ether gives the Rh^{III} product, $[(\eta^5\text{-}C_5H_5)RhCl_2]_2$.

^{1}H NMR and IR spectra of II–IV show that the protonation of complexes Ia, Ib and Id occurs at the oxygen atom of an acyl function. These data together with the ^{13}C NMR spectra of complexes II and III revealed the allylolefinic structure of the *O*-protonated cationic products.

In the ^{1}H NMR spectrum of cation II all the signals (with the exception of the H(8) signal) are shifted significantly downfield compared with those in the spectrum of the aldehyde Ia, which is typical of cationic norbornadiene rhodium complexes [19]. The shielding of the signal from H(8) proton corresponds to a decrease in the anisotropic effect by the protonated carbonyl group [20]. In the highly characteristic

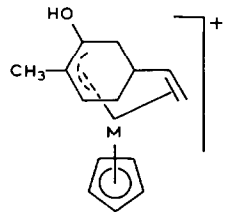


(II , R = R^1 = H ;
III , R = H , R^1 = Me ;
IV , R = Me , R^1 = H)

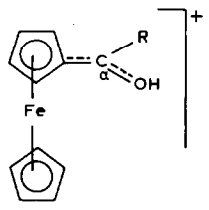
upfield region of the metal-hydride protons (upfield from TMS) no signal is observed in the cation II spectrum, whereas at 11 ppm a relatively broad $\Delta\nu_{1/2} \approx 35$ Hz) one-proton resonance appeared. Since this signal disappears with the addition of D_2O we assigned it to the OH-group proton.

Small changes in the ^1H NMR spectra are observed in the transition from 2-(α-carbonyl) derivatives Ib, d to the corresponding *O*-protonated complexes IV and III. However, the value of the downfield shift of the signals in the spectrum of cation IV compared with Ib is considerably less than those in the cases of the other pairs of complexes Ia and II or Id and III. Besides, all the signals in the spectrum of cation IV are broad, with the usual narrow doublet signal of the cyclopentadienyl protons, as well as the singlet of the methyl group; the OH-group signal in the spectrum of IV showed a broad π-like line (δ 6.07–6.88 ppm) typical of protons which exchange at intermediate rates. Such a feature in the spectrum of cation IV can be interpreted in terms of the existence of an equilibrium Ib ⇋ IV which is consistent with the IR spectral data of this cation in CH_2Cl_2 solution (see below).

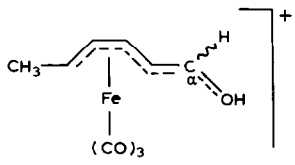
Interestingly, in the ^1H NMR spectra of *O*-protonated carbon complexes, Va, Vb, the structures of which are formally close to the cations II–IV, the OH resonances occur significantly more upfield at 6.12 and 5.66 ppm, respectively [6], in comparison with those of similar signals in the spectra of complexes II–IV. At the same time in the low temperature spectra of *O*-protonated acylferrocene VI [9] or *syn*- and *anti*-isomeric *trans*-cations VII [11] and in spectra II and III, (δ(OH) 9.15 ppm) above signals display very similar chemical shifts. Such a difference in the shielding of OH protons in the spectra of the above compounds evidences a substantially large involvement by the oxygen atom in the latter complexes in stabilizing the positive charge on the neighbouring electron-deficient α-carbon centre.



(Va , M = Rh ; Vb, M = Ir)



(VI , R = Me , Ph etc.)



(VII)

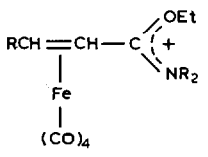
Table 1

^{13}C NMR spectral data of 2-acylnorbornadiene and hydroxyallylolefinrhodium complexes (δ in ppm downfield from TMS in CD_2Cl_2; $J(^{13}C-^{103}Rh)$ (Hz) in parentheses)

Compound	C((1)4)	C(2)	C(3)	C(4(1))	C(5(6))	C(6(5))	C(7)	C(8)	$C_5H_4R^1$	R (or R^1)
Ia	42.0 (2.2)	47.9 (9.8)	30.7 (11.0)	47.2 (2.2)	32.7 (10.6)	34.3 (10.6)	55.0 (5.2)	188.2 (3.0)	85.2 (4.4)	–
Ib	44.4 (2.9)	43.3 (8.8)	29.8 (10.3)	47.6 (2.9)	32.1 (10.3)	34.2 (10.3)	55.2 (5.9)	201.8 (2.9)	86.1 (4.4)	25.0 (s)
Ic	46.9 (2.9)	43.7 (10.3)	28.1 (10.3)	47.0 (2.9)	32.0 (8.8)	33.8 (10.3)	55.3 (4.4)	198.9 (2.9)	86.5 (4.4)	[a]
Id	41.9 (1.9)	48.1 (9.5)	31.5 (10.5)	47.7 (1.9)	34.2 (9.5)	35.7 (9.5)	54.8 (4.7)	187.8 (2.8)	[b]	12.8 (s)
II	39.3 (s.)	61.7 (5.6)	32.0 (11.0)	46.6 (s)	39.6 (8.1)	43.5 (9.3)	53.4 2.9)	142.0 (s br) [d]	89.1 (4.4)	–
III	39.6 (s br) [d]	?	31.8 (11.4)	46.5 (s)	42.1 (m)	44.9 (m)	53.7 (3.0)	143.4 (m)	([c])	12.8 (s)
VIII	39.8 (s)	60.1 (5.7)	31.6 (10.7)	46.8 (s)	39.4 (8.0)	43.0 (8.3)	53.6 (2.6)	149.0 (s br) [d]	88.8 (4.6)	–

[a] C_m 127.8, C_o 128.4, C_p 131.0, C_i 140.1. [b] C_i 73.2 (4.8), C(2–5) 71.8 (4.8), 72.0 (4.8), 74.0 (4.8), 74.4 (4.8). [c] C_i ?, C(2–5) 86.8, (s br), 89.2 (s br), 90.0 (s br) (fourth signal is overlapped). [d] $\Delta\nu_{1/2} \sim 1.1$ Hz.

It is known that the presence in organic carbocations in the α-position of the resonance-stabilizing substituents such as OH or OR (R = Alk) counteracts the effect of direct participation by the neighbouring C-containing groups in stabilizing α-C^+ [21]. It is believed that a similar situation may be present in the cationic complexes of VI and VII where the stabilization of the α-cationic centre occurs by a conjugative mechanism, i.e. without the direct participation of the metal atom [10]. However, as shown in the example of two cationic complexes II and $[Rh(\eta^2,\eta^3\text{-}C_7H_7\text{-}2\text{-}CH{=}OH)(\eta^5\text{-}C_5H_5)]^+F_2POO^-$ (VIII), the stabilization of α-C^+ in the *O*-protonated acyl-substituted π-complexes proceeds with the participation of the oxygen and the metal atom [17]. We arrived at this conclusion on the basis of ^{13}C NMR and IR spectral data for these complexes. Indeed, in the case of the stabilization of α-C^+ in cations II–IV and VIII in accord with the conjugative mechanism, the positive charge in the complexes is delocalized mainly between the oxygen and carbon C(8) atoms. One should thus expect to observe some kind of downfield shift of the carbon C(8) signal relative to those in the spectra of the initial 2-(α-carbonyl) compounds in the ^{13}C NMR spectra for these cationic complexes. In realizing the allylolefinic structure in cations II–IV and VIII owing to direct interaction of the rhodium with α-C^+, this signal in the ^{13}C NMR spectra, by contrast, should show an upfield shift when compared to that in the spectra of Ia, Ib, Id. The validity of such a consideration is supported by the ^{13}C NMR spectral data on nitrogen-containing π-olefin iron complexes (IX) and their cyclic allylic analogs (X) [22] as well as by the spectral data on ferrocenylimines (XI) and their salts (XII) [23].



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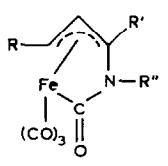

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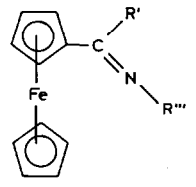

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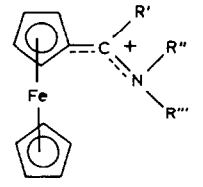


(XII)

The C(8) carbon signals in the ^{13}C NMR spectra of the cationic complexes II, III and VIII [17] are considerably shielded relative to those in the spectra of aldehydes (Ia, Id); while other carbon signals, particularly those from carbons C(2), C(3) and C(5), C(6) are deshielded (Table 1). Interestingly, the observed changes in the chemical shifts of the latter carbons, as well as values of the $J(^{103}Rh\text{–}^{13}C)$ in passing from Ia, d to II and VIII is rather insignificant.

Typical uniformity is also observed for $J(^{103}Rh\text{–}^{13}C(8))$, whose values are consistent well with the spectra of the cationic complexes and the initial aldehydes.

On passing from $Rh(\eta^4\text{-}C_7H_7\text{-}2\text{-}CH(OH)R)(\eta^5\text{-}C_5H_5)$ (XIII, R = H, Alk, Ar, etc.) to the allyllolefinic complexes of the type $[Rh(\eta^{2,3}\text{-}C_7H_7\text{-}2\text{-}CHR)(\eta^5\text{-}C_5H_5)]^+PF_6^-$ (XIV) which were studied by us earlier [19], the changes in the parameters of the carbon signals relevant to the norbornadiene ligand in ^{13}C NMR spectra are significantly stronger. For example, the downfield shifts of the carbon signals C(2), C(3) and C(8) are 32.7, 11.5 and 22.5 ppm, respectively on passing from XIII (R = Me, ψ-*exo*) to *syn*-XIV; in this case the values of $J(^{103}Rh\text{–}^{13}C(8))$ increases from 1.8 to 7.3 Hz [19].

Table 2

IR spectral data of 2-acylnorbornadiene and cationic rhodium complexes (ν in cm^{-1})

Compound	Medium	ν(C=O)	$\nu(C^3 \cdots C^2 \cdots C^8 \cdots O)$	ν(OH)
Ia	KBr	1642	–	–
	CCl_4	1658	–	–
	CH_2Cl_2	1648	–	–
Ia-^{18}O	CCl_4	1630, 1658	–	–
	CH_2Cl_2	1620, 1648	–	–
Ib	KBr	1630	–	–
	CH_2Cl_2	1642	–	–
Ic	KBr	1627	–	–
XVII	CH_2Cl_2	1712	–	–
II	Nujol	–	1557	2100–2700
	CH_2Cl_2	1648, 1712	1562	2000–2800
II-^{18}O	Nujol	–	1557	2000–2700
	CH_2Cl_2	1620, 1648, 1678, 1712	1562	2000–2800
III	Nujol	–	1565	2100–2600
IV	Nujol	–	1560	2000–2500
	CH_2Cl_2	1610, 1642 1708	1555–1565	–

The spectral differences between the cations XIII and II–IV, VIII are probably due to a substantial decrease in the degree of direct metal participation in stabilizing the carbocationic centre in the latter complexes. Evidently, this decrease is a result of the resonance-stabilizing effect of α-hydroxyl group competing in this respect with the metal atom.

Important information on the structure of the cationic complexes II–IV was obtained by IR spectroscopy. IR spectra of cationic complexes II–IV differ dramatically from those of 2(α-carbonyl)complexes (Ia, Ib, Id). Instead of the ν(C=O) bands which appear in the 1630–1660 cm^{-1} region in the IR spectra of aldehydes (Ia, Id) and ketone (Ib), new intense bands show up at 1540–1565 cm^{-1} in the spectra of the cationic complexes (Table 2). On the basis of a previous IR spectroscopy experiment of cation II enriched with ^{18}O-isotope, we assigned the bands to the mixed stretching mode of the oxoallyl fragment $C^3 \cdots C^2 \cdots C^8 \cdots O$ [17]. Moreover, in the IR spectra of the allylolefinic cations XIV (R = H or *syn*-Me) the only band in this region at 1532 cm^{-1} apparently assigned to the stretching vibration of the allylic fragment has an immeasurably smaller intensity as compared with those found for cations II–IV at 1540–1565 cm^{-1}.

Typically, an intense broad band of the hydroxyl group is observed in the IR spectra of the cationic complexes II–IV at 2000–2800 cm^{-1}. The same picture was observed previously for *O*-protonated acylferrocenes VI (An = Cl) where the absorption bands at 2200–2400 cm^{-1}, are assigned to the ν(OH) [24]. It is important that the position and shape of those bands both in the spectra of II–IV as well as that of VI evidence of the presence of a relatively strong hydrogen bond in these compounds.

Rubalkova and Thompson interpreted the results of an IR study of *O*-protonated acylferrocenes from the standpoint of the existence of an intramolecular H bond of

the O–H · · · Fe type in the complexes [24]. Later, Roberts and Silver came to the conclusion from Mössbauer spectra of the same ferrocene derivatives that such an interaction did not take place [25]. Thus, at the present time, the nature of the hydrogen bond in these ferrocene complexes is still unclear.

In this connection it should be noted that in the π-enol cationic complexes of iron $[\eta^5\text{-}C_5H_5Fe(CO)_2(CH_2{=}COHR)]^+X^-$ (XV, R = H, Me; X = Cl, Br), in which the hydrogen bond was also revealed by IR spectroscopy, bands of the ν(OH) vibration were observed in IR spectra in the same region as in those for the complexes II–IV or VI, namely at 2400–2800 cm^{-1} [26]. The authors [26] consider these data to be in accord both with the intra- (O–H · · · Fe) and intermolecular hydrogen bonds in complexes XV. It is known, however, that the OH groups binding with the halide ions by H bonding appear in the same region of the spectrum. A similar H bond type was found, in the series of phosphonium salts, $[Ph_3P^+C(COR){=}C(OH)Me]\ X^-$ (R = MeO, Ph, etc; X = Cl, Br) (ν(OH) 2000–2800 cm^{-1} [27,28]); in the two above cases the presence of an O–H · · · Cl bond in the complexes was confirmed by an X-ray diffraction study [29,30]. On the basis of these data we came to the conclusion that a similar type of the interionic hydrogen bond O–H · · · X must exist in the cationic complexes II–IV and VIII and possibly also in cations VI and XV. Such a conclusion is in good agreement with the data on the IR spectrum of the neutral π-enol platinum complex, (acac)PtCl(CH_2=CHOH) [31] in which the absence of the halide-anion leads to a change in the shape, and on to a noticeable shift of the ν(OH) band to higher field. Finally, a comparison of ^{1}H NMR data in the OH resonance region of cationic complexes II, III and VIII, (see [17]) and the phosphonium salts (in the spectra of the latter ones, δ(OH) 10–12 ppm) can also serve as evidence of similar H-bonding nature in these compounds.

As was previously mentioned, the interaction of (2-benzoylnorbornadiene)cyclopentadienylrhodium (Ic) with HCl under conditions similar to those for Ia, Ib and Id leads to the dimeric complex $[\eta^5\text{-}C_5H_5RhCl_2]_2$ (XVI). It is logical to presume that the intermediate stage of the reaction of Ic with HCl is that of *O*-protonation of ketone, whereas the isolated complex XVI is a product of the thermodynamic control of this reaction *. When studying the reactivity of the cationic complexes II–IV in solution we obtained evidence confirming this supposition.

It was found that when a solution of cation II in CH_2Cl_2 was allowed to stand, the IR spectrum revealed the oxoallylic band (1562 cm^{-1}) together with absorption bands at 1648 and 1712 cm^{-1}. Two successive recordings of the spectrum one after 2, 4 and the other after 20 h showed that the intensity of these last two bands increases significantly, whilst the intensity of the first band decreases. The spectrum of cation II enriched with ^{18}O isotope recorded under similar conditions revealed new bonds of a carbonylic nature (Fig. 1). Furthermore, comparison of the IR spectra of the cation II and the aldehyde Ia in CH_2Cl_2 solution allowed us to assign the band at 1648 cm^{-1} in the spectrum of II to the aldehyde Ia ν(C=O) mode.

* In the intermediate of reaction Ic with HCl of similar nature with complexes II–IV, the direct interaction of Rh–C(8) could be substantially weakened due to an additional resonance-stabilizing effect of the phenyl group, leading apparently to a decrease in the thermodynamic stability of this compounds.

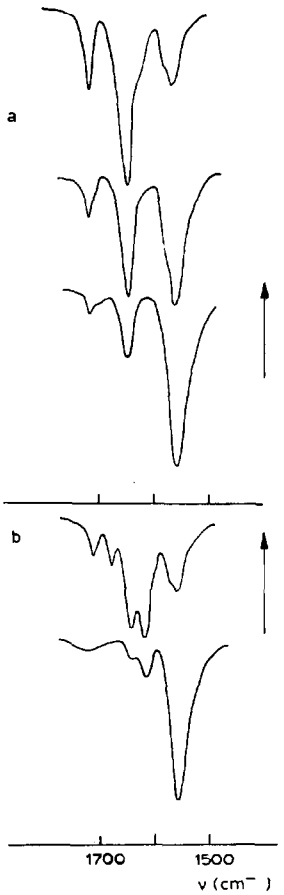
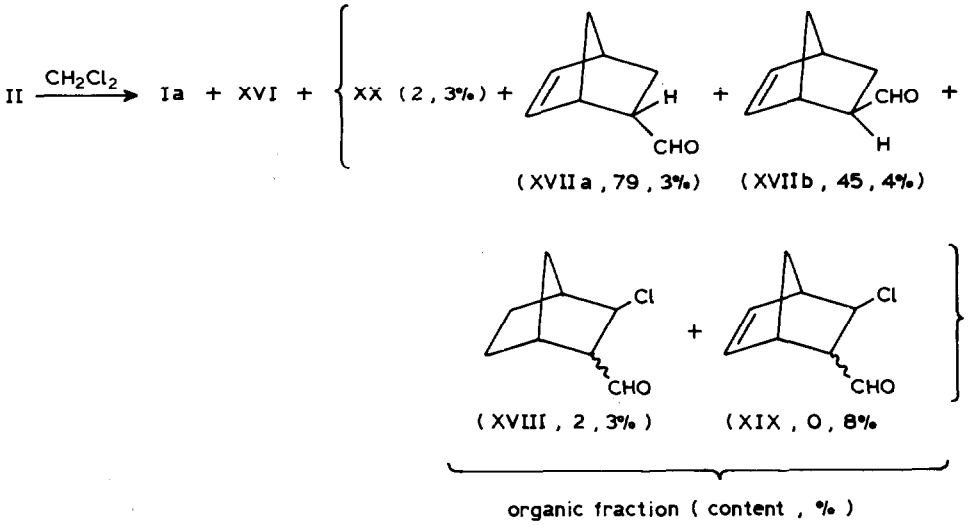


Fig. 1. IR spectra of complexes II (a) and ^{18}O-II (b) in CH_2Cl_2 solution, 2, 4 and 20 h (a) or 2 and 20 h (b) after preparation of samples.

The band at 1712 cm^{-1} was due to 2-formyl-5-norbornene (XVII); corresponding signals of the *endo/exo*-isomers (XVIIa, XVIIb) in the ratio of 5/1 were recorded in the ^{1}H NMR spectrum of cation II in CH_2Cl_2 solution 8–10 h after the sample had been prepared: δ 9.76 (d, 1, $J(H^8–H^2)$ 2.1 Hz, CHO-*exo*); 9.40 (d, 1, $J(H^8–H^2)$ 2.1 Hz, CHO-*endo*), 6.18 (m, 1, $H^{5(6)}$-*endo*); 5.98 (m, 1, $H^{6(5)}$-*endo*); 3.23 (m, 1 H^1-*endo*); 3.08 (m, 1, H^1-*exo*); 2.96 (m, 1, H^4-*endo*); 2.87 (m, 1, $H^{(2,exo)}$-*endo*); 1.87 (m, 1, $H^{(3,exo)}$-*endo*). The other signals of XVIIa, b were overlapped by signals from II; the assignment of the signals was in accordance with the data from [32]. During the course of the quantity experiment with cation II, (a solution of II in CH_2Cl_2 was allowed to stand for 4 d at 22°C), the following products were obtained from the reaction mixture: dimer XVI (19%), aldehyde Ia (45%), and an organic fraction. Based on GC/MS data the organic fraction consisted of *endo/exo*-isomers (XVIIa, b), 2-formyl-3-chloronorbornane (XVIII), 2-formyl-3-chloro-5-norbornene (XIX) and an unidentified product (XX) with $M^+ = 210$; compounds XVIII–XX were present in small quantities.

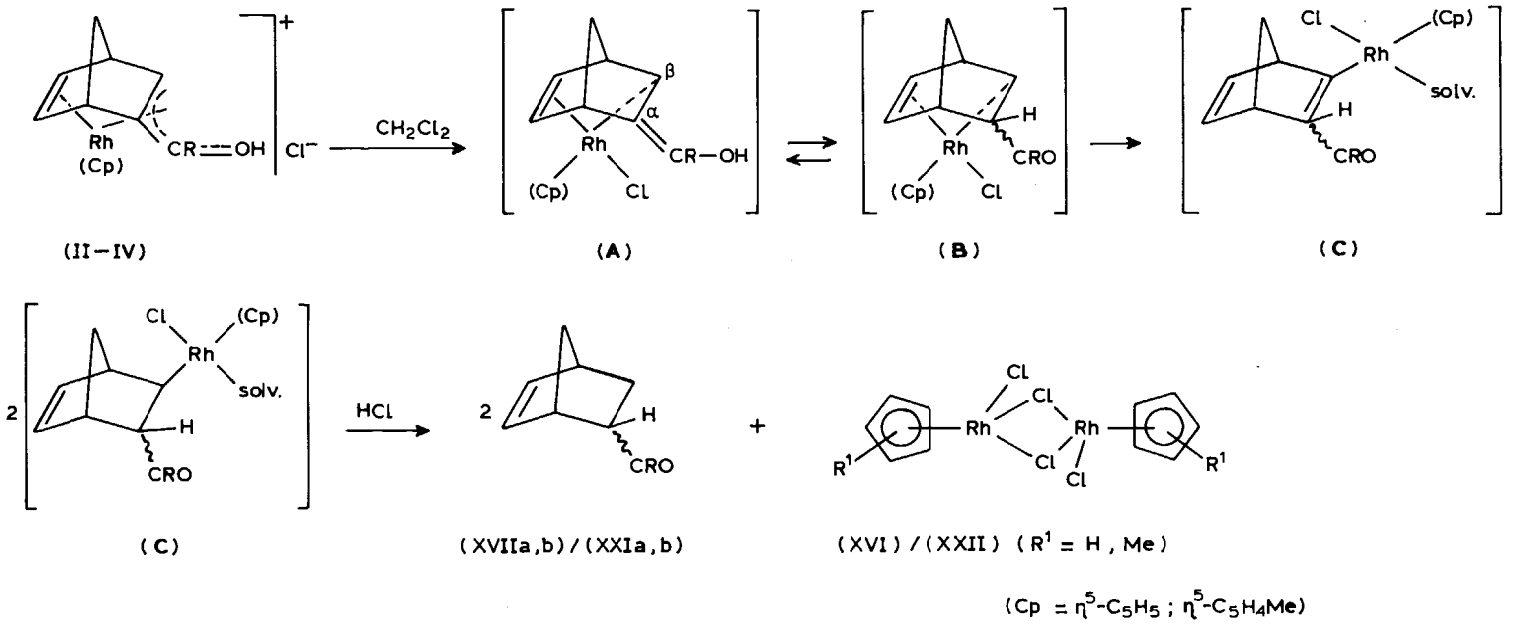
Thus, it has been established that in CH_2Cl_2 solution the cationic complex II undergoes the following conversion:



Cation IV and III apparently decompose in solution CH_2Cl_2 according to the same scheme. The ^1H NMR spectrum of IV after 8 h or III immediately after dissolution in CD_2Cl_2 show *endo/exo*-isomer signals of XVIIa and XVIIb) or 2-acetyl-5-norbornene (XXIa, XXIIb), as well as the corresponding dimers $[(\eta^5\text{-}C_5H_4Me)RhCl_2]_2$ XXII or XVI respectively. Complex XXII was isolated from the reaction mixture and analysed (see Experimental).

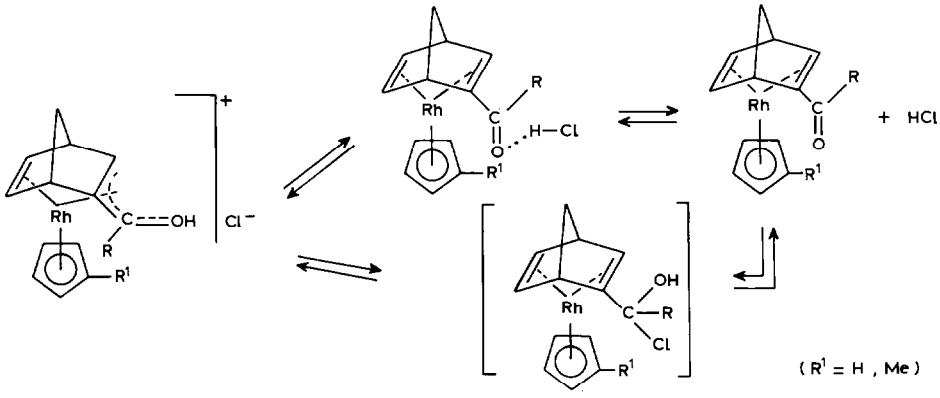
Although the IR spectra of cations II–IV in CH_2Cl_2 solution show the presence of unprotonated α-carbonyl complexes *, only single sets of signals were observed in their ^1H NMR spectra (recorded at 22°C in the above indicated time interval. Very likely, this is due to an equilibrium between the protonated and unprotonated forms of the carbonyl complexes with averaged J and δ values on the NMR scale. Changes observed in the ^1H NMR spectra of the cations over a period of time after the NMR samples had been prepared confirm the existence of this equilibrium. Thus, after 10 h the signal from the H(8) proton in the spectrum of cation II is shifted downfield by 0.35 ppm; a slightly broadened signal from the C_5H_5 ligand, on the other hand, is shifted upfield ($\Delta\delta$ 0.12 ppm). The other signals also reveal an upfield shift of about 0.04–0.05 ppm over the same time interval.

* 4 Bands at 1555–1565, 1610, 1642 and 1708 cm^{-1} (Table 2) in ν(C=O) region are observed in IR spectra of cation IV in CH_2Cl_2 solution recorded immediately after preparing the sample. The first band assigned to $\nu(C^3{=}C^2{-}C^8{=}O)$ reveals a weak intensity which practically disappears with time. Bands at 1642 and 1708 cm^{-1} are assigned to ν(C=O) of ketone Ib and to 2-acetyl-5-norbornenes respectively; the band at 1610 cm^{-1} as is seen occupies an intermediate position between the corresponding bands of the protonated and "free" ketone Ib, and could be assigned to $\nu(C{=}O)$ of the H-complex ML-2-CMe=O→HCl, where Ml = Rh (η^4-C_7H_7)(η^5-Cp).


Rh
(Cp)
CR=OH
Cl⁻
+
CH2Cl2
β
α
CR—OH
H
CRO
Cl
solv.
(II–IV)
(A)
(B)
(C)
2
HCl
(XVIIa,b)/(XXIa,b)
R¹
(XVI)/(XXII) (R¹ = H, Me)
(Cp = η⁵-C5H5 ; η⁵-C5H4Me)

Scheme 1

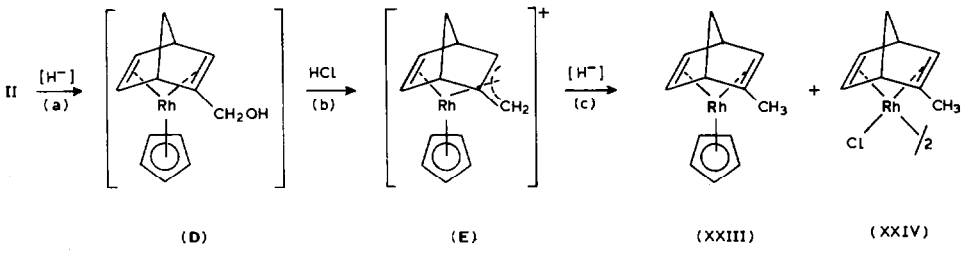
The formation of 2-(α-carbonyl) complexes, as a result of the decomposition of cations II–IV in $CHCl_2$ may take place as a result of partial dissociation of the latter owing to traces of moisture in the solvent, or as a result of an intramolecular nucleophilic attack of Cl^- at the C(8) carbon atom of the exocyclic allylic system. The latter route should lead to labile hemichlorocarbinols which after being dehydrochlorinated may revert to their initial carbonyl complexes. Such a reversible conversion of aldehydes and ketones due to hydrogen halides is well known [33].



At the same time, the fact that formation of the dimeric M-chloro complexes XVI and XXII as well as 2-acyl-5-norbornenes occurs, evidences the progress of the competing reaction which probably has a mechanism as shown in Scheme 1.

Since the rhodium atom in cations II–IV has some positive charge, the most likely first stage of the competing process is the nucleophilic attachment of Cl^- to the metal atom. The π,σ-enol complex **A** which is formed as a result, can readily and, apparently stereoselectively, be subjected to a prototropic rearrangement into its corresponding tautomer **B**. When passing from initial cationic complexes to complexes **A** and **B**, Rh^I oxidizes to Rh^{III}, confirmed experimentally by a change in colour of the solution from yellow to purple-red, a colour typical of rhodium(III) complexes. The stereochemical control in the predominant formation of the *endo*-2-acyl-5-norbornenes is apparently realized at this stage owing to the formation of the metal–β-carbon bond in the π,σ-complexes **A** and **B**. Such a conclusion is consistent with ref. 34 where the linear structure of π-olefin-σ-alkylrhodium complexes is rigid, forming complexes of the type η^5-$C_5H_5Rh(CH{=}CHR)_2$ (where R is a functional group) during protonation with HCl. It is also known that such π,σ-complexes readily lose the olefin molecule at low temperatures, to become coordination-unsaturated σ-complexes [35]. It is quite likely that in the case of π,σ-complex **B** a similar conversion takes place. The resulting σ-complex **C** is decomposed by HCl and forms either dimer XVI or XXII along with a 2-acyl-5-norbornene.

In the presence of a hydride ion source, such as Et_3SiH, the reaction of cation II proceeds along a different line to form the 2-methyl-substituted complexes XXIII and XXIV. The latter complex whose identity confirmed by separate experiment, is formed from complex XXIII by the action of HCl.



(D) (E) (XXIII) (XXIV)

The reaction scheme of cation II presupposes the formation of an intermediate carbynol (**D**) and a cationic complex (**E**). However, even with a 1/1 ratio of Et_3SiH to II, no carbynol **D** could be isolated; only complex XXIII, aldehyde Ia and dimer XVI were obtained from the reaction mixture. It is likely that under such conditions the rates of reaction for stages (c) and (b) exceed the rate of hydration of cation II at stage (a). The latter may be related to the high stability of the allylolefinic cation **E**; such compounds have been isolated by us as PF_6 or BF_4 salts [19]. It should be mentioned that the same uniformity is observed in the ionic hydration reaction of the carbonyl compounds in the ferrocene [36] and cymantrene [37] series of which the high stability of α-carbocations is also typical.

Experimental

A UR-20 spectrometer was used to record IR spectra in the range 400–3700 cm^{-1}; ^1H NMR and ^{13}C NMR spectra were recorded on Bruker WH-200-SY spectrometer. The solvents for preparing the IR samples were carefully dried over 4 Å molecular sieves of and distilled in argon. The course of the reaction was controlled by TLC on silufol with a ether/hexane (1/1) mixture as eluent.

General method for synthesis of 2-acylnorbornadiene complexes of rhodium (Ia–d)

(2-Acetylnorbornadiene)cyclopentadienylrhodium (Ib). A mixture of 0.52 g (3.8 mmol) of 2-acetylnorbornadiene [38] and 0.5 g (1.93 mmol) of $Rh(acac)(CO)_2$ in 25 ml of C_6H_6 is refluxed for 6–8 h until disappearance of $Rh(acac)(CO)_2$ is complete (TLC control). After the reaction has gone to completion the solvent is evaporated in vacuum, the residue is recrystallized from MeOH to give 0.62 g (1.84 mmol, 95%) of $Rh(acac)(\eta^4\text{-}C_7H_7\text{-}2\text{-}COMe)$ as red crystals, m.p. 124–125°C (Found: C, 62.67; H, 5.06. $C_{14}H_{17}O_3Rh$ calc: C, 62.63; H, 4.67%). Mass spectrum: M^+ 336. A suspension of 0.45 g (1.3 mmol) of the isolated compex and 0.45 g (1.6 mmol) of C_5H_5Tl in 30 ml of CH_2Cl_2 (distilled under argon) was refluxed under argon with stirring until the reaction is complete (TLC control), the solvent is evaporated, the residue is thoroughly extracted with ether (3 × 30 ml), filtered and allowed to stand for 2–3 h at −78°C, then refiltered to free it from precipitated thallium salts, evaporated and the crude product purified by chromatography on a column of silica gel using an ether/hexane mixture (1/1) as eluent. Yield (Ib) (0.31 g, 0.102 mmol, 76%), m.p. 91–92°C (n-hexane). (Found: C, 55.64; H, 5.07. $C_{14}H_{15}ORh$ calc: C, 55.62; H, 4.96%). Mass-spectrum: M^+ 302. ^1H NMR ($CDCl_3$): 5.05 (d, 5, $J(^{103}Rh\text{–}^1H)$ 0.85 Hz, C_5H_5), 3.73 (m, 1, H(1(4))), 3.62 (m*, 1, H(5(6))), 3.47 (m*, 1,

H(6(5))), 3.41 (m, 1, H(3)), 3.38 (m, 1, H(4(1))), 1.80 (s, 3, Me), 1.06 (d br, 1, J_{AB} 8.9 Hz, H(7A)), 0.92 (d br, 1, J_{AB} 8.9 Hz, H(7B)) *.

(2-Benzoylnorbornadiene)cyclopentadienylrhodium (Ic). A mixture of 0.5 g (2.5 mmol) of 2-benzoylnorbornadiene [39] and 0.52 g (2.0 mmol) of Rh(acac)$(CO)_2$ in 35 ml of C_6H_6 is refluxed until the reaction is complete (TLC control), the solvent is evaporated, and the oil-like product is transformed into Ic, as described for Ib without additional purification; yield (Ic) (0.39 g, 0.108 mmol, 54%), m.p. 112–113° C (n-hexane), (Found: C, 62.67; H, 5.06. $C_{19}H_{17}ORh$ calc: C, 62.63; H, 4.67%). Mass spectrum: M^+ 364.

(2-Formylnorbornadiene)methylcyclopentadienylrhodium (Id). Id was prepared from Rh(η^4-C_7H_7-2-CHO)(acac) [18] and C_5H_4MeTl, as a yellow-orange oil, yield 65%. Mass spectrum M^+ 302. ^{1}H NMR (CD_2Cl_2): 8.53 (s, 1, H(8)), 5.24, 5.20, 5.09, 5.01 (m, 1 + 1 + 1 + 1, C_5H_4Me), 3.73 (m, 1, H1(4)), 3.52 (m*, 1, H(5(6))), 3.47 (m, 1, H(4(1))), 3.39 (m*, 1, H(6(5))), 3.33 (m, 1, H(3)), 1.80 (s, 3, Me), 1.14 (d br, 1, J_{AB} 9.2 Hz, H(7A)), 1.01 (d t, 1, J_{AB} 9.2, J_t 1.2 Hz, H(7B)).

Methylcyclopentadienylthallium was obtained in the form of yellow hygroscopic powder according to the procedure for C_5H_5Tl [40].

(2-Formylnorbornadiene)cyclopentadienylrhodium (Ia) had been prepared previously [18]. ^{1}H NMR spectral data are presented in [17]; the assignment of H(3) signal in the spectrum of Ia was made by using the 1,4,5,6,7,7′-deuterium-labeled analog obtained from C_7HD_6-2-CHO according to the procedure for Ia. Synthesis of the deuterated 2-formylnorbornadiene was carried out by condensation of C_5D_6 and CH≡CCHO [41].

General procedure for synthesis of cationic hydroxyallylolefin complexes II–IV

A slow current of HCl is passed through a solution of 0.43 g (1.49 mmol) aldehyde Ia in 30 ml absolute ether until an amorphous orange product separates out and the solution becomes colorless. The solution is decanted, the residue washed twice with 10 ml absolute ether, dried in vacuum at 56° C/1.5 mmHg over P_2O_5, yield cation II (0.39 g, 1.22 mmol, 82%), m.p. 103° C (without dec.). Analytical data and ^{1}H NMR spectrum (II) data are listed in [17].

Cation III was prepared from aldehyde Id by the same procedure in 73% yield. (Found: C, 49.75; H, 4.73; Rh, 30.18. $C_{14}H_{16}ClORh$ calc: C, 49.63; H, 4.70; Rh, 30.42%). ^{1}H NMR (CD_2Cl_2): 9.72 (s br, 1, OH), 7.64 (s, 1, H(8)), 5.83, 5.65, 5.50, 5.43 (m, 1 + 1 + 1 + 1, C_5H_4Me), 4.04 (m*, 1, H(5(6))), 3.90 (m*, 1, H(6(5)), 3.85 (m, 1, H(1)) 3.65 (m, 1, H(4)), 3.52 (m, 1, H(3)), 1.90 (s, 3, Me), 1.60 (dt br, 1, J_{AB} 10, J_t 1.4 Hz, H(7A)). 1.44 (dt, 1, J_{AB} 10, J_t 1.4 Hz, H(7B)). ^{1}H NMR spectrum of III recorded 8 h after preparing the sample: 8.24 (s, 1, H(8)), 5.53, 5.48, 5.42, 5.27, (m, 1 + 1 + 1 + 1, C_5H_4Me), 3.76 (m, 2, H(1(4)), H(5(6)), 3.57 (m, 2, H(4(1)), H(6(5)), 3.40 (m, 1, H(3)), 1.82 (s, 3, Me), 1.40 (d br, 1, J_{AB} 9.4 Hz, H(7A)), 1.20 (dt, 1, J_{AB} 9.4, J_t 1.3 Hz, H(7B)). Additional signals of complexes XXII and the isomers XVIIa, XVIIb (ratio *endo/exo* equal to 6.6/1, see text) are also present in the spectrum, XXII: 1.87 (s, C_5H_4Me (signals of C_5H_4Me group are overlapped)). After 24 h the complex XXII was isolated from the solution of NMR tube. (Found:

* This and further m* represent a quadruplet-like signal.

C, 28.34; H, 2.74; Cl, 28.09. $C_{12}H_{14}Cl_4Rh_2$ calc: C, 28.42; H, 2.85; Cl, 28.03%). IR (KBr; ν, cm^{-1}): 3105, 1420 (C_5H_4Me); 1440, 1470, 2935 (Me).

Cation IV was derived from Ib by the same procedure in 66% yield. (Found: C, 49.57; H, 4.70; Cl, 10.68. $C_{14}H_{16}ClORh$ calc: C, 49.63; H, 4.70; Cl, 10.48%). ^1H NMR (CD_2Cl_2): 6.88–6.07 (π-like signal, 1, OH) 5.26 (s br, 5, C_5H_5), 3.93 (m, 1, H(5(6))), 3.85 (m, 1, H(6(5))), 3.72 (m, 2, H(1(4)), H(3)), 3.53 (m, 1, H(4(1))), 2.16–2.11 (s br, 3, Me), 1.25 (d. br., 1, J_{AB} 9.9 Hz, H(7A)), 1.10 (d br, 1, J_{AB} 9.9 Hz, H(7B)). Signals from complex XVI are also present in the spectrum: 5.60 (s br, C_5H_5) and signals from the *endo/exo*-isomeric complexes XXIa, XXIb: 6.13 (m*, 1, H(5(6)-*endo*), 5.84 (m*, 1, H(6(5)-*endo*)), 3.22 (m, 1, H(1)-*endo*)), 2.87 (m, 1, H(4-*endo*)), 2.18 (s, –, COMe-*exo*), 2.09 (s, 3, COMe-*endo*), 1.70 (m, 2, H(3,3′-*endo*)), 1.43 (d br, 1, J_{AB} 7.9 Hz, H(7A)), 1.32 (d br, 1, J_{AB} 7.9 Hz, H(7B)). (The other signals of XXIa, XXIb are overlapped or only weakly seen in the spectrum; the assignment of the signals is made according to [42]).

Decomposition of cation II in solution CH_2Cl_2 at room temperature

A solution of 0.46 g (1.4 mmol) of cation II in 7 ml of dry CH_2Cl_2 is allowed to stand 96 h at room temperature. The colour of the solution changes gradually from yellow-orange to purple-red and dark-red crystals appear on the flask walls. These are then removed, washed with ether, dried, to give 0.13 g (0.27 mmol, 19%) dimer XVI. (Found: C, 25.47; H, 2.09; Cl, 30.12. $C_{10}H_{10}Cl_4Rh_2$ calc: C, 25.10; H, 2.09; Cl, 29.70%). IR (KBr; ν, cm^{-1}): 3100, 1418 (C_5H_5), 288 (Rh–Cl, terminal), 231, 248 (Rh–Cl, bridging). ^1H NMR (Me_2SO-d_6): 6.02 (d, $J(^{103}Rh–^1H)$ 0.48 Hz, C_5H_5). The mother solution is evaporated, the residue is chromatographed on a column of silica gel eluting with hexane to give an organic fraction (0.05 g) which is analyzed by GC/MS. The substance, retention time per min, content of the substance in % relative to XVIIa and fragmentations are given: XVIIb, 1.86, 20, 122 (M^+, 3.8%), 93 ($M^+ - CHO$, 3.6%), 91 ($M^+ - CH_3O$, 8.5%), 77 ($C_6H_5^+$, 11.9%), 66 ($C_5H_6^+$, 100%); XVIIa, 2.02, 100, 122 (M^+, 3.9%), 93 ($M^+ - CHO$, 3.20%), 91 ($M^+ - CH_3O$, 7.2%), 77 ($C_6H_5^+$, 10.5%), 66 ($C_5H_6^+$, 100%); XVIII, 2.18, 3.5, 129 ($M^+ - CHO$, 2.5%), 122 ($M^+ - HCl$, 36%), 121 ($M^+ - HCl–H$, 5.6%), 104 ($M^+ - HCl–H_2O$, 13.5%), 91 ($C_3H_4ClO^+$, 80%), 77 ($C_6H_5^+$, $C_3H_6Cl^+$, 100%); XIX, 4.64, 1, 156 (M^+, 3.5%), 127 ($M^+ - CHO$, 4.4%), 121 ($M^+ - Cl$, 7.1%), 120 ($M^+ - HCl$, 4.4%), 103 ($M^+ - Cl - H_2O$, 7.1%), 91 ($C_3H_4ClO^+$, 38.1%), 77 ($C_6H_5^+$, $C_3H_6Cl^+$, 20.4%), 66 ($C_5H_6^+$, 100%). After elimination of the organic fraction, the residue is eluted with a mixture of hexane/ether (1/1) yielding 0.18 g (0.63 mmol, 45%) aldehyde Ia, m.p. 122°C [18].

Hydrogenation of cation II by Et_3SiH in CH_2Cl_2 solution

0.35 g (3.0 mmol) Et_3SiH is added to a solution of 0.2 g of cation II in 4 ml of dry CH_2Cl_2 and the resulting mixture stirred for 24 h at room temperature. The solvent is evaporated, the residue is chromatographed on a silica-gel column, eluting with pentane to give a yellow-fraction from which 0.05 g (0.18 mmol, 29.6%) an oil (XXIII) was obtained. Mass spectrum: 274 (M^+), 259 ($M^+ - Me$), 168 ($C_5H_5Rh^+$), 103 (Rh^+). Further chromatography eluting with hexane/ether (1/1) mixture yields 0.13 g (0.27 mmol, 44%) dimer XXIV (Found: C, 39.22; H, 4.09; Cl, 14.80. $C_{16}H_{20}Cl_2Rh_2$ calc: C, 39.26; H, 4.09; Cl, 14.52%).

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