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CATIONIC ALKOXYALLYLOLEFIN COMPLEXES OF RHODIUM, $[Rh(\eta^2\text{-}5,6\text{-}\eta^3\text{-}2,3,8\text{-}C_7H_7\text{-}2\text{-}CHOR)(\eta^5\text{-}C_5H_5)]^+ An^-$, AS KEY INTERMEDIATES IN THE SYNTHESIS AND HYDROLYSIS OF 2-FORMYLNORBORNADIENE-CYCLOPENTADIENYLRHODIUM DIALKYLACETALS

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Summary

The cationic alkoxyallylolefin complexes of rhodium, $[Rh(\eta^2\text{-}5,6\text{-}\eta^3\text{-}2,3,8\text{-}C_7H_7\text{-}2\text{-}CHOR)(\eta^5\text{-}C_5H_5)]^+ An^-$ (II) were prepared as stable salts from the reaction of $Rh(\eta^4\text{-}C_7H_7\text{-}2\text{-}CHO)(\eta^5\text{-}C_5H_5)$ (I) with ROH (R = Me, Et) in the presence of HBF_4 or HPF_6. A preliminary X-ray study of the cation IIa (R = Me, An = PF_6) confirms the metal–ligand bonding of the η^2-5,6-η^3-2,3,8-allylolefinic type with a significant participation of the oxygen atom of the methoxy group in stabilization of the C(8) cationic centre. The above-mentioned cationic complexes were found to be key intermediates in the formation and hydrolysis of the dialkylacetals of the corresponding aldehyde.

When studying the reactivity of 2-formylnorbornadienecyclopentadienylrhodium (I), we encountered an unexpected difficulty in preparation of the aldehyde acetals. Attempts to carry out its direct acetalization with alcohols or the *ortho*-ester under conditions of acid catalysis (TsOH, NH_4NO_3) were unsuccessful.

Taking into account a strong stabilizing effect of the norbornadienerhodium cyclopentadienyl group on the neighbouring cationic centre [1,2] we supposed that the initially formed semiacetals (see eq. 1) underwent a facile ionization under the action of an acidic catalyst to produce cationic intermediates of the type II. Due to certain electronic factors the latter are incapable to participate in further reaction with alcohols leading to the formation of the desired acetals.

$$RCHO + R^1OH \rightleftarrows RCH(OH)OR^1 \xrightarrow{H^+} \underset{(II)}{[RCH \cdots OR^1]^+} \xrightarrow{R^1OH} RCH(OR^1)_2 \qquad (1)$$

$R = (\eta^5\text{-}C_5H_5)Rh(\eta^4\text{-}C_7H_7\text{-}2\text{-})$

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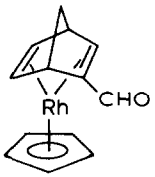
By using the stoichiometric reaction of the aldehyde I in alcohols with strong protonic acids such as HBF_4 or HPF_6 (eq. 2), we finally succeeded in isolating cationic compounds of this type.

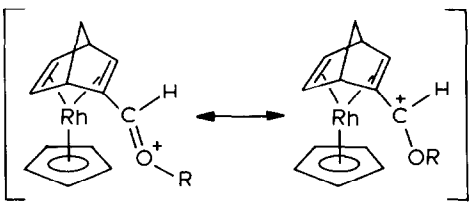


(I)

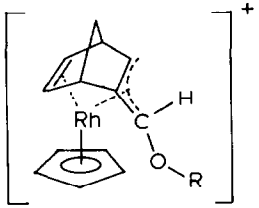
$$\xrightarrow{ROH/AnH} [Rh(C_7H_7CHOR)(C_5H_5)]^+ An^- \qquad (2)$$

(IIa–c : a, R = Me, An = PF_6; b, R = Et, An = PF_6 ; c, R = Et, An = BF_4)

The ^1H NMR spectra of complexes IIa–IIc reveal an additional singlet ($\delta = 3.99$ ppm) or a triplet ($\delta = 1.45$ ppm) and a doublet of quadruplets ($\delta_A = 4.29$ ppm, $\delta_B = 4.18$ ppm; $J_{AB} = 10$ Hz), respectively, from the methyl or ethyl group at the oxygen atom. The olefinic proton signals, as well as the signal of the cyclopentadienyl ring, exhibit a downfield shift of 0.4–0.8 ppm, which is typical of cationic complexes. At the same time, the signal of proton H(8) is shifted upfield by 1.6 ppm, probably due to the decrease of the anisotropic effect of the carbonyl group on passing from the aldehyde I to cations IIa–IIc [3]. However, in our opinion, the changes observed in the ^1H NMR and ^{13}C NMR spectra (see Table 1) on transition from I to IIa–IIc do not allow one to make an unambiguous choice between the structures A and B, feasible from consideration of the resulting cationic complexes.

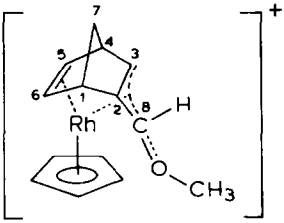


(A)



(B)

The structural assignment was made on the basis of an X-ray study of the cation IIa in the solid state. Some important structural data of this complex are given below.



PF_6^-

Rh—C(8)	2.39 Å
C(8)—O	1.35 Å
C(3)C(2)C(8)O	170°

The characteristic feature of this compound is an appreciable involvement of the oxygen atom of the methoxy group in stabilizing the neighbouring cationic centre with a simultaneous preservation of the bonding distance Rh–C(8) of 2.39 Å *. It

* In the previously investigated cationic complex $[Rh(\eta^2\text{-}5,6\text{-}\eta^3\text{-}2,3,8\text{-}C_7H_7\text{-}2\text{-}CH_2)(\eta^5\text{-}C_5H_5)]^+ PF_6^-$ of the allylolefinic type, the Rh–C(8) bond length is equal to 2.27 Å [2].

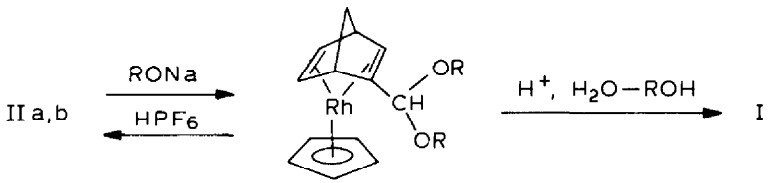
TABLE 1

^{13}C NMR SPECTRA OF COMPLEXES I AND II IN CH_2Cl_2

Compound	Chemical shift, δ (ppm) ($J(^{13}C-^{103}Rh)$ (Hz))									
	Cl(4)	C(2)	C(3)	C4(1)	C5(6)	C6(5)	C(7)	C(8)	R	C_5H_5
I	41.98	47.87	30.74	47.21	32.67	34.32	55.01	188.22	–	85.21
	(2.2)	(9.8)	(11.0)	(2.2)	(10.6)	(10.6)	(5.2)	(3.0)		(4.4)
IIa	39.52	63.07	32.32	47.00	43.77	47.55	54.38	131.85	14.94	89.38
	(s)	(4.5)	(10.5)	(s)	(7.4)	(7.4)	(2.2)	(3.0)	(s)	(4.5)
IIb	39.30	68.77	32.12	47.74	43.13	46.87	53.71	132.20	14.48 (Me)	89.30
	(s)	(4.5)	(10.3)	(7.4)	(7.4)	(10.3)	(3.7)	(2.2)	(s)	(6.0)
									72.47 (CH_2)	
									(s)	

should be noted that in the cation IIa the methoxy group occupies a *syn* position, and in view of the absence of additional signals due to possible *anti* isomers in the ^{1}H NMR spectra of IIa–IIc, one may conclude that the reaction involved is highly stereospecific.

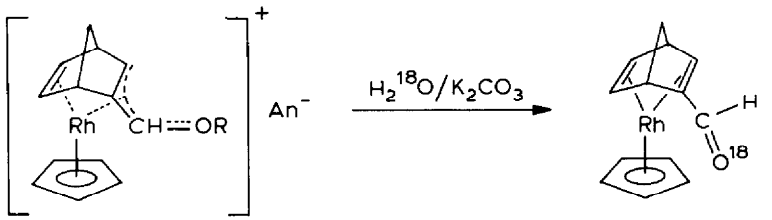
Interaction of the cations IIa–IIc with solid RONa in absolute diethyl ether gives rise to the relatively stable dialkylacetals IIIa, b, whose structure is confirmed by the ^{1}H NMR (IIa, H(8) $\delta = 4.41$ ppm; Me(1), $\delta = 3.38$ ppm; Me(2), $\delta = 3.27$ ppm) and mass spectra.



(IIIa,b : a, R = Me ; b, R = Et)

The acetals are readily hydrolyzed to the aldehyde I under the action of catalytic quantities of mineral acids in aqueous alcoholic solutions. At the same time, we succeeded in carrying out a partial hydrolysis of the acetals in the presence of salts of strong acids (e.g. $NaPF_6$). The qualitative transformation of IIIa,b to IIa,b was effected by treatment of ethereal solutions of the acetals with 70% HPF_6.

By a special experiment it was shown that cations IIa,b hydrolyze slowly to the initial aldehyde I even in aqueous solutions. The hydrolysis is accelerated appreciably in the presence of K_2CO_3. The use of H_2O^{18} (with 85% content of the oxygen label) leads to the formation of the O^{18}-labelled aldehyde I. The content of the O^{18} label in the products amounts to 73–78% according to mass spectrometry.



(IIa,b) (I)

This result confirms the nucleophilic attack of the hydroxide ion at the α-carbon centre of the cationic complexes and together with the ^{13}C NMR data of the latter is consistent with preservation of the solid state structure of these compounds in solution.

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