

## NORBORNADIENE COMPLEXES OF TRANSITION METALS

### III \*. STEREOSPECIFICITY IN THE GENERATION OF CATIONIC COMPLEXES $[\text{Rh}(2,3,8 : 5,6-\eta\text{-C}_7\text{H}_7\text{CHR})(\eta\text{-C}_5\text{H}_5)]^+$ (R = Me, Ph, FERROCENYL), AND MOLECULAR STRUCTURE OF $[\text{Rh}(2,3,8 : 5,6-\eta\text{-C}_7\text{H}_7\text{CH}_2)(\eta\text{-C}_5\text{H}_5)]^+\text{PF}_6^-$

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(Received August 14th, 1980)

#### Summary

Treatment of (2-hydroxymethylnorbornadiene)cyclopentadienylrhodium (V) with sulfuric acid offers the stable cationic complex XI, which can be isolated as  $\text{PF}_6^-$  or  $\text{BF}_4^-$  salts.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data indicate that in cation XI the bicyclic ligand is bound to the metal via  $\eta^2$ -ethylene and  $\eta^3$ -allyl bonds, including an exocyclic methylene carbon. The structure of complex XI is supported by a single-crystal X-ray diffraction study of its  $\text{PF}_6^-$  salt.

Reaction of diastereomeric carbinols  $\psi$ -*exo*-VI and  $\psi$ -*endo*- $\text{Rh}\{\eta^4\text{-C}_7\text{H}_7\text{CH}(\text{OH})\text{Me}\}(\eta^5\text{-C}_5\text{H}_5)$  (VII) proceeds with absolute stereospecificity to form *syn*-XII and *anti*- $[\text{Rh}(\eta^5\text{-C}_7\text{H}_7\text{CHMe})(\eta^5\text{-C}_5\text{H}_5)]^+$  (XIII) isomers, respectively. Similarly, cation  $[\text{Rh}(\eta^5\text{-C}_7\text{H}_7\text{CHPh})(\eta^5\text{-C}_5\text{H}_5)]^+$  (XV), derived from  $\psi$ -*endo*- $\text{Rh}\{\eta^4\text{-C}_7\text{H}_7\text{CH}(\text{OH})\text{Ph}\}(\eta^5\text{-C}_5\text{H}_5)$  (IX), has the *syn* configuration. However, the same reaction of the ferrocenyl-substituted carbinol  $\psi$ -*endo*- $\text{Rh}\{\eta^4\text{-C}_7\text{H}_7\text{CH}(\text{OH})\text{Fc}\}(\eta^5\text{-C}_5\text{H}_5)$  (X) leads to a mixture of two isomeric complexes, *syn*-(XVI) and *anti*- $[\text{Rh}(\eta^5\text{-C}_7\text{H}_7\text{CHFc})(\eta^5\text{-C}_5\text{H}_5)]^+$  (XVII), in a ratio of 4/1.

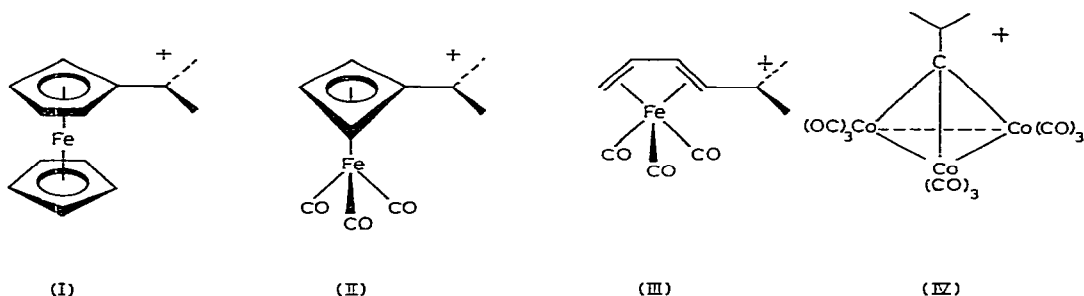
The absolute stereospecificity and the relative facility with which the formation of cationic  $\eta^3$ -allylic complexes from carbinols VI, VII and IX takes place are due to the nucleophilic participation of a rhodium atom in stabilizing the electron-deficient center during the reaction. The disturbance of stereospecificity during the conversion of carbinol X to a cationic complex assumes the formation of an  $\alpha$ -ferrocenylcarbenium ion (XIX) as an intermediate (a product of kinetic control). Owing to the relative non-hindrance of rotation around the exocyclic

\* For part II see ref. 1.

carbon—carbon bond C(2)—C(8) in the carbenium ion XIX, the formation of a non-equal mixture of complexes XVI and XVII, the products of thermodynamic control of the reaction, takes place.

## Introduction

Transition metal-stabilized carbenium ions have been the subject of great interest in recent years [2]. The first and most thoroughly studied species are ferrocenylcarbenium ions (I), other examples are cyclobutadienetricarbonyliron (II), butadienetricarbonyliron (III) and nonacarbonyltricobaltcarbon-substituted (IV) carbenium ions.



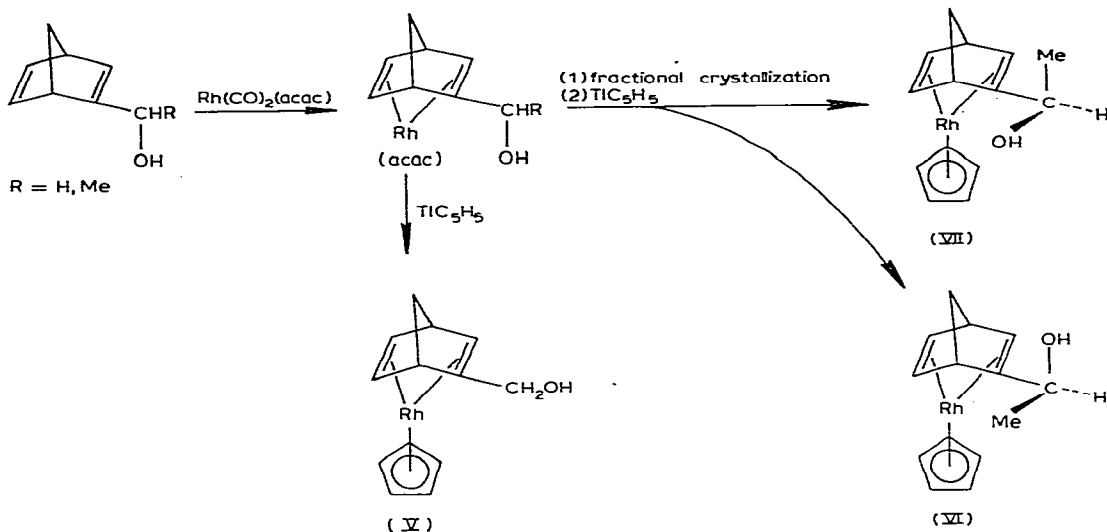
A number of controversial studies have been devoted to the reasons for the remarkable stabilization of ferrocenylcarbenium and related ions. Their enhanced stability is ascribed either to direct metal participation [3—5] or to conjugation [6,7]. Only quite recently has the first convincing evidence of direct metal participation been obtained in a  $^{13}\text{C}$ - $\{^1\text{H}, ^{57}\text{Fe}\}$  and  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR study of ferrocenylcarbenium ions and organoiron complexes enriched with iron-57 [8]. Further work along these lines will be required to determine the degree of direct metal participation in stabilizing the above carbenium ions.

In connection with this problem, in the present work we have studied the behaviour of diastereomeric {2-( $\alpha$ -carbinol)norbornadiene}cyclopentadienylrhodium complexes (containing Me, Ph and ferrocenyl substituents at the carbinol carbon) in acid media. Some preliminary results have already been reported [9,10].

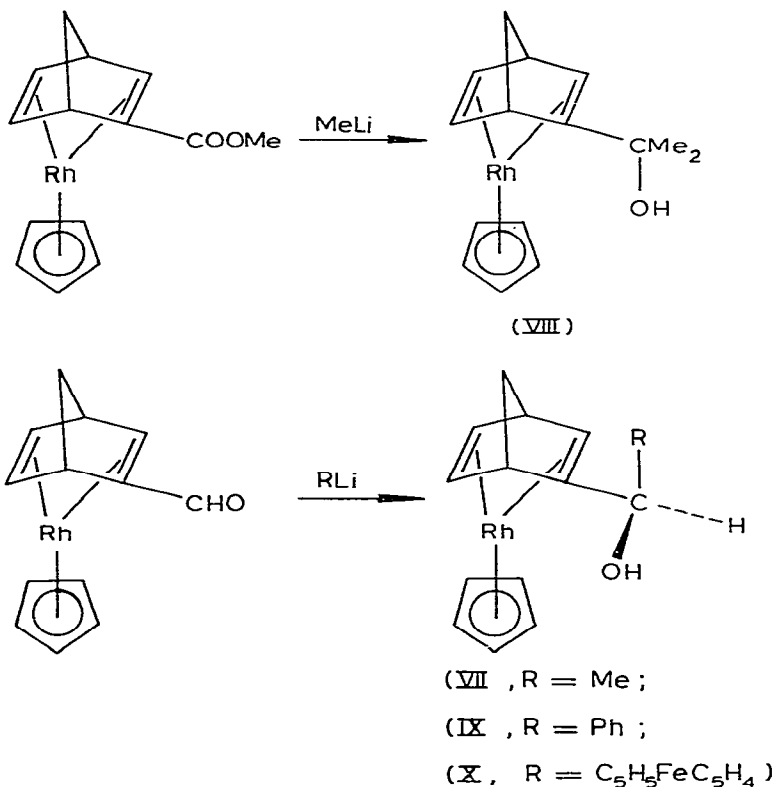
## Results and discussion

{2-( $\alpha$ -Carbinol)norbornadiene}cyclopentadienylrhodium complexes were synthesized by two methods.

i) The action of thallos cyclopentadienide on the corresponding dienol(acetyl-acetonate)rhodium complexes (where the secondary carbinols VI and VII represent a pair of diastereoisomers):



ii) The interaction of 2-carbomethoxy- and 2-formyl-norbornadiene(cyclopentadienyl)rhodium with organolithium reagents:



We have previously reported the preparation of complexes V–VII and the relative stereochemistry of isomers VI and VII [1,11]. It was shown that the reaction of  $\text{Rh}(\eta^4\text{-C}_7\text{H}_7\text{CHO})(\eta^5\text{-C}_5\text{H}_5)$  with methyllithium proceeds stereospeci-

fically to form preferably the  $\psi$ -endo-isomer (VII) (The diastereoisomers are designated  $\psi$ -endo- and  $\psi$ -exo according to the preferred conformation of the hydroxy group relative to the metal [12]).

The IR spectra of the  $\psi$ -exo and  $\psi$ -endo isomers in the region of OH stretching vibrations are quite different. The  $\psi$ -endo isomer (VII) has a sharp band at  $3515\text{ cm}^{-1}$  in the solid state (Figure 1, curve IIa), which shifts slightly to higher frequencies in dilute  $\text{CCl}_4$  solution (curve IIb). The  $\psi$ -exo-isomer (VI) shows an intense absorption in the  $3600\text{--}2300\text{ cm}^{-1}$  region in the solid state, centered at about  $3100\text{ cm}^{-1}$  (curve Ia). In dilute  $\text{CCl}_4$  solution the pattern changes dramatically, and a band with three maxima then appears (curve Ib). These results allow us to conclude that the OH groups of the  $\psi$ -exo isomers form a strong intermolecular hydrogen bond. The approximate enthalpy value for this

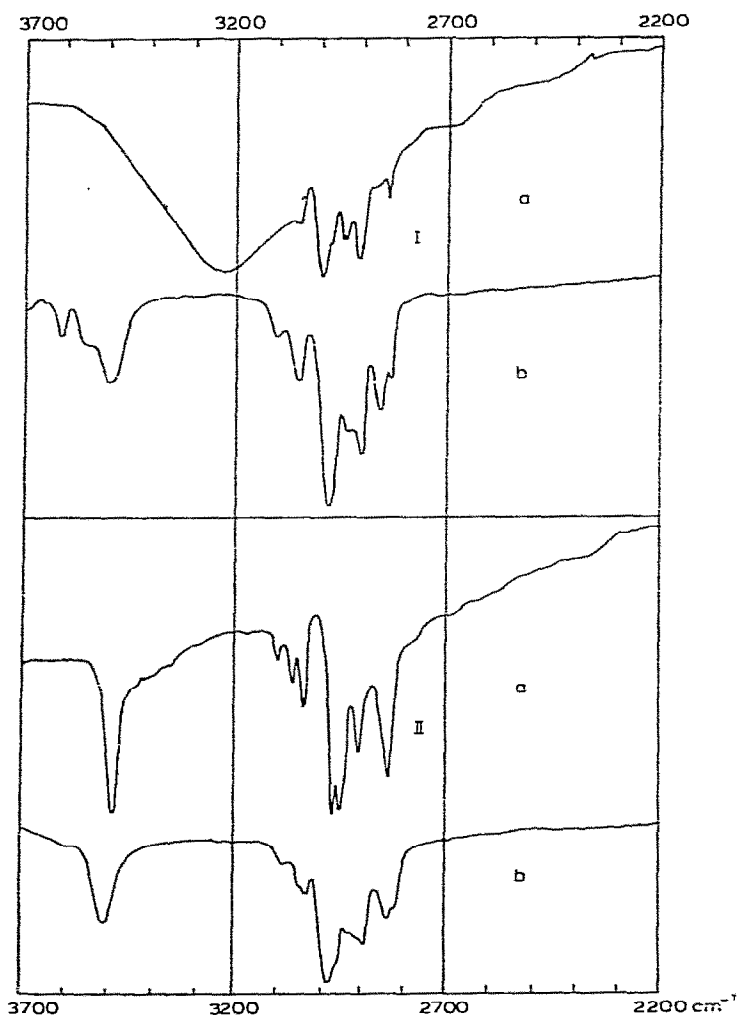


Fig. 1. IR spectra of  $\psi$ -exo-VI (curves Ia, b) and  $\psi$ -endo-VII (curves IIa, b) carbinols in the  $\nu(\text{OH})$  region (a, KBr; b,  $\text{CCl}_4$  solution).

TABLE 1

IR SPECTRA OF  $\{2-(\alpha\text{-CARBINOL})\text{NORBORNADIENE}\}$  CYCLOPENTADIENYL RHODIUM COMPLEXES

Compound	$\nu(\text{OH})$ ( $\text{cm}^{-1}$ ) (KBr)	$\nu(\text{OH})$ ( $\text{cm}^{-1}$ , in $\text{CCl}_4$ )
Rh $\{\eta^4\text{-C}_7\text{H}_7\text{CH}(\text{OH})\text{Me}\}(\eta^5\text{-C}_5\text{H}_5)$ $\psi$ - <i>exo</i> isomer (VI)	2300—3600 <sup>a</sup>	3512s, 3570w(sh) 3622w 3535s
$\psi$ - <i>endo</i> isomer (VII) Rh $\{\eta^4\text{-C}_7\text{H}_7\text{CH}(\text{OH})\text{Ph}\}(\eta^5\text{-C}_5\text{H}_5)$	3515	3518s
$\psi$ - <i>endo</i> isomer (IV) Rh $\{\eta^4\text{-C}_7\text{H}_7\text{CH}(\text{F})\text{C}_6\text{H}_5\}(\eta^5\text{-C}_5\text{H}_5)$	3510—3530	3518s
$\psi$ - <i>exo</i> isomer (XVIII)	3520	3500s, 3545s 3615w 3518s
$\psi$ - <i>endo</i> isomer (X)	3510—3540	3518s

<sup>a</sup> The band is very broad with its centre of gravity at  $3100 \text{ cm}^{-1}$ .

hydrogen bond, estimated from the frequency shift, is about 6 kcal/mole, i.e. larger than that for ordinary alcohols. The sterically hindered hydroxyl of the  $\psi$ -*endo* isomer VII is not associated, therefore the spectral patterns of the solid state and the diluted solution are alike.

The behaviour of the OH stretching bands for phenyl- (IX) and ferrocenyl-substituted (X) carbinols is similar to that of VII. The bands are sharp and do not shift significantly on going from solid mulls to  $\text{CCl}_4$  solution spectra (see Table 1). These facts indicate that the OH groups in IX and X are sterically hindered and thus confirm their  $\psi$ -*endo* structure.

The picture observed for diluted solution of the *exo*-isomer VI (curve Ib), is surprising. The presence of three maxima under conditions excluding both intermolecular and intramolecular associations is not easily explained and calls for further investigation. However, it is interesting to note that this picture resembles that of ferrocenylcarbinols, where three analogous maxima are explained by the existence of a "free" OH group and of two types of intramolecularly hydrogen-bonded OH groups,  $\pi$ -bonded and metal-bonded [13,14].

The distinction of isomers is also noticeable in mass-spectrometric investigation of diastereomeric pairs (and will be discussed in a separate paper). The

(Continued on p. 381)

TABLE 2

<sup>1</sup>H NMR SPECTRA OF THE RHODIUM COMPLEXES V—XII

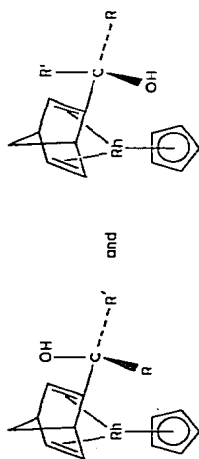
Compound	Chemical shift <sup>a</sup> (ppm) (multiplicity <sup>b</sup> , relative intensity, coupling constant <sup>c</sup> in Hz, assignment)
V	5.13 (d, 5, $J(\text{H-Rh}) = 1.1$ , $\text{C}_5\text{H}_5$ ); 3.93 (d, br, 1, $J(\text{H}_A\text{-H}_B) = 11.3$ , $\text{CH}_A\text{H}_B\text{OH}$ ); 3.47 (d, br, obscured, 1, $\text{CH}_A\text{H}_B\text{OH}$ ); 3.44—3.16 (m, 4, H(1,4—6), 3.10 (m, 1, H(3)); 2.96 (s, br, 1, OH); 0.92 (m, 2, H(7 $\alpha$ , $\beta$ ))
VI	5.17 (d, 5, $J(\text{H-Rh}) = 0.82$ , $\text{C}_5\text{H}_5$ ); 3.71 (qw, br, 1, $J(\text{H}(8)\text{-(OH, CH}_3)}) = 6.3$ , H(8)); 3.38 (q, q, $J^* = 3.5$ , H(5)); 3.32 (td, 1, $J_1^* = 4.2$ , $J_2^* = 2.8$ , H(6)); 3.29 (m, 1, H(1)); 3.21 (m, 1, H(4)); 3.04 (t, br, 1, $J^* = 3.5$ , H(3)); 2.93 (d, br, 1, $J(\text{OH-H}(8)) = 5.3$ , OH); 1.33 (d, 3, $J(\text{CH}_3\text{-H}(8)) = 7.2$ , $\text{CH}_3$ ); 1.01 (dt, 1, $J(\text{H}(7\beta(\alpha))\text{-H}(7\alpha(\beta))) = 9.0$ ; $J(\text{H}(7\beta(\alpha))\text{-H}(1,4)) = 1.8$ , H(7 $\beta(\alpha)$ ); 0.97 (dt, 1, $J(\text{H}(7\alpha(\beta))\text{-H}(7\beta(\alpha))) = 9.0$ , $J(\text{H}(7\alpha(\beta))\text{-H}(1,4)) = 1.8$ , H(7 $\alpha(\beta)$ ))

TABLE 2 (continued)

Compound	Chemical shift <sup>a</sup> (ppm) (multiplicity <sup>b</sup> , relative intensity, coupling constant <sup>c</sup> in Hz, assignment)
VII	5.21 (d, 5, $J(\text{H}-\text{Rh}) = 0.82$ , $\text{C}_5\text{H}_5$ ); 3.49 (q, br, 1, $J(\text{H}(8)-(\text{OH}, \text{CH}_3)) = 6.3$ , $\text{H}(8)$ ); 3.37 (m, 1, $J^* = 3.7$ , $\text{H}(5)$ ); 3.35 (m, 1, $\text{H}(1)$ ); 3.33 (m, 1, $J^* = 4.1$ , $\text{H}(6)$ ); 3.23 (m, 1, $\text{H}(4)$ ); 3.11 (t, br, 1, $J^* = 3.6$ , $\text{H}(3)$ ); 2.65 (d, br, 1, $J(\text{OH}-\text{H}(8)) = 2.7$ , $\text{OH}$ ); 1.15 (d, 3, $J(\text{CH}_3-\text{H}(8)) = 7.2$ , $\text{CH}_3$ ); 0.98 (dt, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 9.0$ , $J(\text{H}(7\beta(\alpha))-\text{H}(1.4)) = 1.8$ , $\text{H}(7\beta(\alpha))$ ); 0.93 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 9.0$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.8$ , $\text{H}(7\alpha(\beta))$ )
VIII	5.10 (d, 5, $J(\text{H}-\text{Rh}) = 1.0$ , $\text{C}_5\text{H}_5$ ); 3.30 (m, 4, $\text{H}(1.4-6)$ ); 2.91 (m, 1, $\text{H}(3)$ ); 2.30 (s, br, 1, $\text{OH}$ ); 1.31 (s, 3, $\text{CH}_3$ ); 1.10 (s, 3, $\text{CH}_3$ ); 0.96 (m, 2, $\text{H}(7\alpha, \beta)$ )
IX	7.43 (d, br, $J(\text{H}_o-\text{H}_m) = 7.2$ , $\text{C}_6\text{H}_5\text{-}o$ ); 7.30 (t, br, 2, $J(\text{H}_m-\text{H}_o) = J(\text{H}_m-\text{H}_p) = 7.2$ , $\text{C}_6\text{H}_5\text{-}m$ ); 7.18 (t, 1, $J(\text{H}_p-\text{H}_m) = 7.2$ , $J(\text{H}_p-\text{H}_o) = 1.36$ , $\text{C}_6\text{H}_5\text{-}p$ ); 5.29 (d, 5, $J(\text{H}-\text{Rh}) = 0.72$ , $\text{C}_5\text{H}_5$ ); 4.27 (s, 1, $\text{H}(8)$ ); 3.41 (q, br, 1, $J^* = 3.5$ , $\text{H}(5)$ ); 3.36 (td, obscured, 1, $J_1^* = 3.6$ , $J_2^* = 2.8$ , $\text{H}(6)$ ); 3.34 (td, 1, $J_1^* = 3.9$ , $J_2^* = 0.75$ , $\text{H}(3)$ ); 3.22 (m, 2, $\text{H}(1.4)$ ); 3.09 (d, br, 1, $J^* = 1.5$ , $\text{OH}$ ); 0.72 (dt, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 9.0$ , $J(\text{H}(7\beta(\alpha))-\text{H}(1.4)) = 1.8$ , $\text{H}(7\beta(\alpha))$ ); 0.38 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 9.0$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.8$ , $\text{H}(7\alpha(\beta))$ )
X <sup>d</sup>	5.27 (d, 5, $J(\text{H}-\text{Rh}) = 0.74$ , $\text{C}_5\text{H}_5$ ); 4.41 (m, 1, $\text{C}_5\text{H}_4$ ); 4.19 (s, 5, $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ); 4.10 (m, 1, $\text{C}_5\text{H}_4$ ); 4.03 (td, 1, $J_1^* = 2.3$ , $J_2^* = 1.25$ , $\text{C}_5\text{H}_4$ ); 3.94 (m, 1, $\text{C}_5\text{H}_4$ ); 3.92 (s, br, 1, $\text{H}(8)$ ); 3.43 (q, br, 1, $J^* = 3.5$ , $\text{H}(5)$ ); 3.34 (q, br, 1, $J^* = 3.5$ , $\text{H}(6)$ ); 3.25 (m, 1, $\text{H}(1)$ ); 3.19 (m, 1, $\text{H}(4)$ ); 3.13 (t, br, $J^* = 3.25$ , $\text{H}(3)$ ); 2.58 (s, 1, $\text{OH}$ ); 0.81 (dt, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 8.75$ , $J(\text{H}(7\beta(\alpha))-\text{H}(1.4)) = 1.6$ , $\text{H}(7\beta(\alpha))$ ); 0.49 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 8.75$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.6$ , $\text{H}(7\alpha(\beta))$ )
XI	6.00 (d, 5, $J(\text{H}-\text{Rh}) = 1.1$ , $\text{C}_5\text{H}_5$ ); 5.40 (s, br, 1, $\text{H}(8)\text{-syn}$ ); 4.90 (m, 1, $\text{H}(6)$ ); 4.56 (m, 1, $\text{H}(3)$ ); 4.30 (m, 1, $\text{H}(5)$ ); 3.98 (s, br, 1, $\text{H}(8)\text{-anti}$ ); 3.78 (m, 1, $\text{H}(4(1))$ ); 3.46 (m, 1, $\text{H}(1(4))$ ); 1.80 (d, br, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 10$ , $\text{H}(7\beta(\alpha))$ ); 1.67 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 10$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 2.0$ , $\text{H}(7\alpha(\beta))$ )
XII	5.85 (d, 5, $J(\text{H}-\text{Rh}) = 0.8$ , $\text{C}_5\text{H}_5$ ); 5.05 (q, br, 1, $J(\text{H}(8)-\text{CH}_3) = 6.0$ , $\text{H}(8)$ ); 4.88 (m, 1, $\text{H}(6)$ ); 4.44 (m, 1, $\text{H}(5)$ ); 4.20 (m, 1, $\text{H}(3)$ ); 3.72 (m, 2, $\text{H}(1.4)$ ); 2.31 (d, 3, $J(\text{CH}_3-\text{H}(8)) = 6.0$ , $\text{CH}_3$ ); 1.85 (d, br, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 10$ , $\text{H}(7\beta(\alpha))$ ); 1.59 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 10.0$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.6$ , $\text{H}(7\alpha(\beta))$ )
XIII	6.80 (qd, 1, $J(\text{H}(8)-\text{CH}_3) = 7.0$ , $J(\text{H}(8)-\text{Rh}) = 1.5$ , $\text{H}(8)$ ); 5.80 (d, 5, $J(\text{H}-\text{Rh}) = 1.0$ ; $\text{C}_5\text{H}_5$ ); 4.88 (m, 1, $\text{H}(3)$ ); 4.74 (td, 1, $J_1^* = 3.6$ , $J_2^* = 2.0$ , $\text{H}(6)$ ); 4.29 (m, 1, $\text{H}(5)$ ); 3.80 (m, 1, $\text{H}(1(4))$ ); 3.28 (m, 1, $\text{H}(1(4))$ ); 1.75 (dt, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 10$ , $J(\text{H}(7\beta(\alpha))-\text{H}(1.4)) = 1.2$ , $\text{H}(7\beta(\alpha))$ ); 1.60 (d, 3, $J(\text{CH}_3-\text{H}(8)) = 7.0$ , $\text{CH}_3$ ); 1.55 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 10.0$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.2$ , $\text{H}(7\alpha(\beta))$ )
XIV	5.64 (d, 5, $J(\text{H}-\text{Rh}) = 0.7$ , $\text{C}_5\text{H}_5$ ); 4.66 (m, 1, $\text{H}(6)$ ); 4.46 (m, 2, $\text{H}(5,3)$ ); 3.71 (m, 1, $\text{H}(4(1))$ ); 3.55 (m, 1, $\text{H}(1(4))$ ); 2.51 (s, 3, $\text{CH}_3\text{-syn}$ ); 1.84 (dt, obscured, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 10.0$ , $J(\text{H}(7\beta(\alpha))-\text{H}(1.4)) = 1.8$ , $\text{H}(7\beta(\alpha))$ ); 1.77 (s, 3, $\text{CH}_3\text{-anti}$ ); 1.55 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 10.0$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.8$ , $\text{H}(7\alpha(\beta))$ )
XV	7.96 (d, 1, $J(\text{H}(8)-\text{Rh}) = 1.7$ , $\text{H}(8)$ ); 7.51 (d, br, 2, $J(\text{H}_o-\text{H}_m) = 7.2$ , $\text{C}_6\text{H}_5\text{-}o$ ); 7.37 (t, br, 2, $J(\text{H}_m-\text{H}_o) = J(\text{H}_m-\text{H}_p) = 7.2$ , $\text{C}_6\text{H}_5\text{-}m$ ); 7.31 (t, 1, $J(\text{H}_p-\text{H}_m) = 7.2$ , $J(\text{H}_p-\text{H}_o) = 1.4$ , $\text{C}_6\text{H}_5\text{-}p$ ); 5.70 (m, 1, $\text{H}(3)$ ); 5.39 (d, 5, $J(\text{H}-\text{Rh}) = 0.73$ , $\text{C}_5\text{H}_5$ ); 4.86 (td, $J_1^* = 3.6$ , $J_2^* = 2.4$ , $\text{H}(6)$ ); 4.60 (m, 1, $\text{H}(5)$ ); 4.00 (m, 1, $\text{H}(4(1))$ ); 3.50 (m, 1, $\text{H}(1(4))$ ); 1.82 (dt, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 10.2$ ; $J(\text{H}(7\beta(\alpha))-\text{H}(1.4)) = 1.65$ , $\text{H}(7\beta(\alpha))$ ); 1.79 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 10.2$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.65$ , $\text{H}(7\alpha(\beta))$ )
XVI	6.05 (s, 1, $\text{H}(8)$ ); 5.71 (d, 5, $J(\text{H}-\text{Rh}) = 0.73$ , $\text{C}_5\text{H}_5$ ); 4.99 (m, 1, $\text{H}(3)$ ); 4.82 (q, br, $J^* \approx 3$ , $\text{H}(5)$ ); 4.67 (m, 1, $\text{H}(4(1))$ ); 4.59 (m, 2, $\text{H}(1(4))$ ); 4.30 (s, 5, $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ); 4.20 (m, 1, ?); 4.16 (m, 1, ?); 3.68 (m, 1, ?); 1.88 (d, br, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 10.0$ , $\text{H}(7\beta(\alpha))$ ); 1.74 (dt, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 10.0$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.2$ , $\text{H}(7\alpha(\beta))$ )
XVII <sup>e, f</sup>	8.0 (s, 1, $\text{H}(8)$ ); 5.34 (d, 5, $J(\text{H}-\text{Rh}) = 0.73$ , $\text{C}_5\text{H}_5$ ); 4.26 (s, 5, $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ); ... 1.72 (dt, obscured, 1, $J(\text{H}(7\beta(\alpha))-\text{H}(7\alpha(\beta))) = 10.2$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.4$ , $\text{H}(7\beta(\alpha))$ ); 1.68 (dt, 1, $J(\text{H}(7\alpha(\beta))-\text{H}(7\beta(\alpha))) = 10.2$ , $J(\text{H}(7\alpha(\beta))-\text{H}(1.4)) = 1.4$ , $\text{H}(7\alpha(\beta))$ )

<sup>a</sup> Solvent is  $(\text{CD}_3)_2\text{CO}$  unless otherwise indicated. <sup>b</sup> s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, q<sub>w</sub> = quintet, dt = doublet of triplets, tt = triplet of triplets, qd = quadruplet of doublets,  $J^*$  is the signal splitting magnitude. <sup>d</sup> In  $\text{CDCl}_3$  solvent. <sup>e</sup> XVI and XVII were examined as a mixture, ratio ~4/1, respectively. <sup>f</sup> Other signals: 4.61 (t, br, 1,  $J^* = 2$ ), 4.58 (m, obscured, 1), 4.54 (m, 1,  $J^* = 2.4$ ), 4.52 (m, 1,  $J^* = 2.4$ ), 4.45 (m, 1), 4.27 (m, 1, Fc), 3.85 (m, 1, Fc), 3.31 (m, 1, Fc).

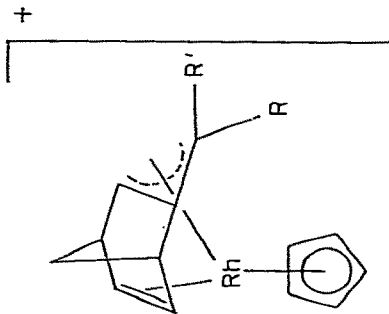
TABLE 3  
<sup>13</sup>C NMR SPECTRA OF RHODIUM COMPLEXES



Compound <sup>13</sup>C chemical shifts (ppm downfield from TMS, in CH<sub>2</sub>Cl<sub>2</sub>) and *J*(<sup>13</sup>C—<sup>103</sup>Rh) (Hz) in parentheses

Compound	C(1,4)	C(2)	C(3)	C(5,6)	C(7)	C(8)	R	R'	C <sub>5</sub> H <sub>5</sub>
V	47.3 (3.1)	53.6 (11.4)	28.2 (11.6)	30.0 (11.4)	30.5 (10.4)	56.6 (6.7)	63.6 (1.8)		84.6 (4.9)
VI	47.4 (2.9)	59.8 (11.0)	26.4 (11.0)	29.9 (10.3)	31.0 (10.3)	56.7 (6.6)	67.5 (1.5)	21.3 (s)	84.9 (4.9)
VII	46.6 (2.9)	59.2 (10.3)	26.7 (10.3)	30.4 (10.3)	31.2 (10.3)	56.7 (7.3)	68.0 (1.5)	20.8 (s, br)	84.6 (4.4)
VIII	47.2 (2.9)	64.7 (11.0)	25.3 (10.3)	30.0 (10.3)	30.7 (10.3)	56.6 (7.5)	69.0 (s)	28.3 (s)	85.1 (4.4)
IX	46.9 (2.9)	59.6 (11.0)	27.6 (10.3)	31.2 (10.3)	32.3 (11.0)	56.3 (6.6)	73.8 (1.5)	C <sub>i</sub> 141.9, C <sub>o</sub> 126.0, C <sub>m</sub> 127.9, C <sub>p</sub> 126.8	84.8 (3.7)
X	46.5 (3.0)	58.8 (11.8)	26.8 (11.8)	30.9 (10.3)	32.1 (11.8)	56.5 (6.7)	71.2 (s, br)	C <sub>α,α'</sub> 65.6, 67.7 C <sub>β,β'</sub> 67.2, 67.5, C <sub>5</sub> H <sub>5</sub> 68.8	84.8 (4.4)
XVIII	47.3 (2.9)	57.6 (11.0)	25.7 (10.3)	30.1 (10.1)	31.3 (10.3)	56.6 (5.9)	70.5 (s, br)		85.1 (5.9)
									66.5 67.0 67.5 68.8

TABLE 4  
 $^{13}\text{C}$  NMR SPECTRA OF CATIONIC RHODIUM COMPLEXES



Compound	$^{13}\text{C}$ chemical shifts (ppm downfield from TMS, in $\text{CH}_2\text{Cl}_2$ , $J(^{13}\text{C}-^{103}\text{Rh})$ (Hz) in parentheses										
	C(1,4)	C(2)	C(3)	C(5,6)	C(7)	C(8)	$\text{R}$	$\text{R}'$	$\text{C}_5\text{H}_5$		
XI	41.7 (s)	96.3 (4.3)	41.6 (8.6)	47.7 (6.7)	54.9 (3.0)	66.9 (7.3)			91.0 (4.9)		
XII	38.2 (s)	92.5 (u)	37.8 (8.8)	45.5 (7.3)	54.6 (1.2)	89.9 (7.3)	20.0 (s)		95.5 (4.4)		
XIII	42.5 (s)	91.1 (s)	38.8 (7.3)	45.2 (7.3)	55.3 (u)	95.2 (7.3)		19.7 (s)	92.1 (5.9)		
XIV	40.2 (s)	86.8 (5.9)	35.7 (9.8)	44.4 (5.9)	54.6 (1.2)	119.9 (5.9)	28.5 (s)	26.6 (s)	92.6 (5.3)		
XV	44.8 (s)	87.5 (2.9)	41.0 (7.3)	47.0 (7.3)	54.6 (1.2)	97.1 (5.9)			93.6 (5.9)		
XVI	40.0 (s)	83.5 (3.7)	36.7 (9.5)	44.0 (5.5)	54.5 (2.9)	98.7 (3.7)	$c$		91.6 (5.2)		
XVII	44.2 (s)	83.2 (s)	39.1 (8.8)	49.4 (7.4)	54.9 (7.3)	103.5 (3.7)		$b$	92.6 (4.4)		

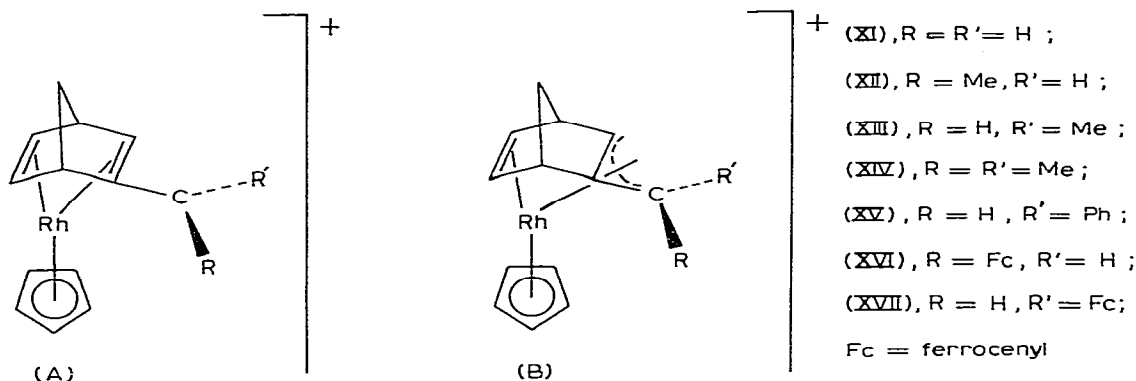
$a$  Phenyl group signals:  $\text{C}_i$  135.6,  $\text{C}_o$ ,  $\text{C}_m$  127.4, 129.6,  $\text{C}_p$  130.1.  $b$  Ferrocenyl group signals:  $\text{C}_{80,1}$ ,  $\text{C}_{\alpha,\alpha'}$  63.8, 71.4,  $\text{C}_{\beta,\beta'}$  72.3, 72.6,  $\text{C}_5\text{H}_5$  70.5.  $c$  Ferrocenyl group signals:  $\text{C}$  79.8,  $\text{C}_{\alpha,\alpha'}$  68.4, 71.7,  $\text{C}_{\beta,\beta'}$  72.6, 73.0  $\text{C}_5\text{H}_5$  70.5.



$^1\text{H}$  and  $^{13}\text{C}$  NMR data of carbinols V–X are listed in Tables 2 and 3.

The most interesting results were obtained when studying the behaviour of the carbinols in an acid medium. When treating an ether solution of carbinols V–X with concentrated sulfuric acid an oily deposit appears, from which stable  $\text{PF}_6^-$  or  $\text{BF}_4^-$  salts of cationic complexes XI–XVII precipitate after dilution with water and subsequent addition of aqueous  $\text{NH}_4\text{PF}_6$  or  $\text{AgBF}_4$  solution.

$^1\text{H}$  and  $^{13}\text{C}$  NMR data on the cationic complexes (see Tables 2 and 4) indicate that they are not carbenium ions (A), but rather that they are allylic complexes (B), where the bicyclic ligand is bound to the rhodium atom via  $\eta^2$ -ethylene and  $\eta^3$ -allyl bonds including the exocyclic carbon C(8).



All the cyclic ligand protons of the cationic complexes give well-resolved signals in the  $^1\text{H}$  NMR spectra, and in comparison with the proton signals of the starting carbinols, they are shifted downfield, which indicates a delocalization of the positive charge throughout the entire rhodium complex, including the cyclopentadienyl ring.

The exocyclic protons at C(8) of the complex  $[\text{Rh}(\eta^5\text{-C}_7\text{H}_7\text{CH}_2)(\eta^5\text{-C}_5\text{H}_5)]^+$  (XI) reveal some broadened singlets at  $\delta$  3.98 and 5.40 ppm. Such a difference in the chemical shifts of geminal protons with an extremely small coupling constant is characteristic of *syn-anti* protons in  $\eta^3$ -allyl metal complexes [15]. The difference in the chemical shifts ( $\Delta\delta = 1.42$  ppm) of protons at C(8) remains constant in the temperature range of 30–150°C for nitrobenzene solution and indicates the absence of rotation around the C(2)–C(8) bond under such conditions. No temperature dependence was observed also for the spectrum of complex XIV under the same conditions.

The chemical shifts of the phenyl and ferrocenyl group protons in the cationic complexes XV and XVII are similar to those in the uncharged benzene and ferrocene derivatives with electron-withdrawing substituents, showing the relatively small contribution of these groups to the delocalization of the positive charge.

Strong evidence for bonding of the rhodium atom to carbon C(8) in cationic complexes is provided by the coupling constants  $J(^{103}\text{Rh}-^{13}\text{C})$  for carbons C(2), C(3) and C(8) in the  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectra, when passing from carbinols to cationic complexes. For example, in the primary carbinol V these constants have values of 10.4, 10.4, and 1.8 Hz, respectively, whereas in the cationic

TABLE 5  
 ATOMIC COORDINATES ( $\times 10^5$  FOR Rh AND  $\times 10^6$  FOR OTHERS) AND THEIR ANISOTROPIC TEMPERATURE FACTORS ( $\times 10^2$  FOR Rh AND  
 $\times 10$  FOR OTHERS) IN THE FORM  $T = [\exp - 1/4(B_{11}h^2a^*2 + \dots + 2D_{23}hb^*c^*)]$

Atom	x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Rh	78451(7)	-4253(6)	-562(6)	363(3)	325(2)	299(2)	-7(3)	19(3)	-19(3)
C(1)	5455(13)	859(14)	-640(11)	43(6)	69(7)	103(9)	3(6)	-11(6)	-22(7)
C(2)	6655(14)	330(13)	-1216(7)	98(8)	58(6)	44(4)	33(6)	-33(5)	-14(6)
C(3)	7779(14)	1151(13)	-1081(9)	76(7)	66(6)	57(5)	8(7)	-12(6)	12(5)
C(4)	7216(15)	2188(11)	-379(10)	70(6)	40(5)	102(8)	5(6)	21(7)	3(5)
C(5)	7117(15)	1412(10)	514(8)	82(7)	42(5)	57(5)	18(7)	9(6)	-14(4)
C(6)	6040(13)	580(13)	410(9)	53(6)	70(7)	69(6)	7(6)	26(5)	-3(6)
C(7)	5739(16)	2320(13)	-729(13)	75(8)	60(7)	135(12)	25(6)	-16(8)	9(7)
C(8)	6777(20)	-953(16)	-1474(10)	152(13)	91(13)	71(7)	17(10)	-50(9)	-15(7)
C(9)	8356(12)	-2480(10)	202(9)	64(6)	45(4)	69(7)	1(4)	-9(5)	6(6)
C(10)	9423(11)	-1861(11)	-330(8)	57(6)	48(5)	57(5)	17(5)	6(5)	-0(4)
C(11)	9988(10)	-851(11)	238(8)	38(4)	60(5)	64(6)	1(4)	-1(4)	15(5)
C(12)	9269(11)	-805(11)	1141(7)	50(5)	66(6)	49(5)	1(5)	-10(4)	6(6)
C(13)	8266(14)	-1843(12)	1122(8)	86(8)	57(6)	57(6)	1(6)	-6(5)	25(5)
F	7975(4)	-4698(3)	-2537(2)	57(1)	49(1)	43(1)	0(2)	2(1)	-8(1)
F(1)	7952(9)	-4803(8)	-1383(4)	113(5)	103(5)	44(2)	-4(5)	-7(8)	-3(3)
F(2)	7078(9)	-4612(9)	-3679(4)	112(6)	131(6)	46(3)	31(6)	11(3)	1(4)
F(3)	7079(11)	-3473(7)	-2502(7)	150(6)	62(3)	100(5)	42(5)	13(7)	-5(4)
F(4)	8815(9)	-5932(9)	2572(9)	125(8)	98(6)	102(6)	68(6)	-14(6)	-16(6)
F(5)	6666(7)	-5543(11)	-2591(7)	67(4)	93(5)	85(4)	-16(4)	-8(4)	-8(5)
F(6)	9243(9)	-3852(12)	-2439(9)	100(5)	168(8)	126(7)	-74(6)	10(6)	-11(8)

complex XI they are 4.3, 8.6 and 7.3 Hz, respectively. The same picture is seen for the other compounds investigated.

The assignment of structure B to the cationic complexes is supported by an X-ray analysis of the  $\text{PF}_6^-$  salt of cation XI. A single crystal suitable for an X-ray study was obtained by slow crystallization from a dilute alcohol solution at 0–5°C.

The crystals of hexafluorophosphate XI are orthorhombic,  $a$  9.998(1),  $b$  10.372(1),  $c$  13.589(11) Å,  $V$  1409.2(5) Å<sup>3</sup>,  $M$  = 418.1.  $D_{\text{calc}}$  1.98 g cm<sup>-3</sup> for  $Z$  = 4; space group  $P2_12_12_1$ . The unit cell parameters and intensities of 1288 reflections with  $I > 2\sigma$  were measured with a Synthex P2<sub>1</sub> four-circle diffractometer (Mo- $K_\alpha$  radiation, graphite monochromator,  $\theta/2\theta$  scan,  $\theta_{\text{max}} \leq 22^\circ$ ). Absorption corrections were neglected ( $\mu(\text{Mo}) = 13.6 \text{ cm}^{-1}$ ). The structure was solved by the heavy atom technique and refined by the least-squares procedure in a full-matrix anisotropic approximation,  $R = 0.041$ ,  $R_w = 0.433$  (disregarding hydrogen atoms, no attempt being made to localize them). The absolute configuration of the complex was determined by the Hamilton test, the  $R$  factor for the inverted structure is equal to 0.050. The atomic coordinates and their temperature factors are given in Table 5, bond angles in Table 6, and equation of some individual molecular planes in Table 7.

The structure of complex XI, with interatomic distances, is illustrated in Figure 2. The complex is chiral due to the molecular asymmetry (in the sense of absence of reflection symmetry elements). Considering the carbon C(1) as a chiral centre and using  $R$ ,  $S$  nomenclature, one should assign the  $R$  configuration to the complex.

It is notable that the single crystal is built up of molecules of one configuration. The same fact has been previously noted in an X-ray structure determination of  $\beta$ -ferrocenylacrylonitrile [16]. However, complex XI, unlike the ferrocene derivative, is configurationally stable and should display optical activity both in the crystal state and in solution.

In complex XI the rhodium atom is bound to the cyclopentadienyl (Cp) ring, and to the bicyclic ligand via the C(5)–C(6)  $\eta^2$ -ethylene bond and the C(3)–C(2)–C(8)  $\eta^3$ -allyl system and in this manner the outer rhodium 18-electron shell is completed. The Cp ring is planar with an average value of C–C

TABLE 6  
BOND ANGLES,  $\omega$  (°)

Angle	$\omega$	Angle	$\omega$	Angle	$\omega$
C(2)C(1)C(6)	96.6(1.0)	C(1)C(6)C(5)	102.2(1.1)	F(1)PF(6)	88.1(5)
C(2)C(1)C(7)	100.1(1.1)	C(1)C(7)C(4)	93.4(1.1)	F(2)PF(3)	89.2(5)
C(6)C(1)C(7)	100.8(1.1)	C(9)C(10)C(11)	110.5(1.0)	F(2)PF(4)	90.8(5)
C(1)C(2)C(3)	109.5(1.1)	C(10)C(11)C(12)	107.1(9)	F(2)PF(5)	89.2(5)
C(1)C(2)C(8)	123.0(1.2)	C(11)C(12)C(13)	107.8(9)	F(2)PF(6)	93.0(5)
C(3)C(2)C(8)	122.7(1.3)	C(12)C(13)C(9)	108.2(1.0)	F(3)PF(4)	178.1(6)
C(2)C(3)C(4)	102.1(1.1)	C(13)C(9)C(10)	106.4(1.0)	F(3)PF(5)	88.8(5)
C(3)C(4)C(5)	98.8(1.0)	F(1)PF(2)	178.9(5)	F(3)PF(6)	90.4(6)
C(3)C(4)C(7)	102.6(1.1)	F(1)PF(3)	91.0(5)	F(4)PF(5)	89.3(5)
C(5)C(4)C(7)	103.7(1.1)	F(1)PF(4)	88.9(5)	F(4)PF(6)	91.5(6)
C(4)C(5)C(6)	108.1(1.1)	F(1)PF(5)	89.7(5)	F(5)PF(6)	177.6(6)

TABLE 7  
PLANAR FRAGMENTS OF THE MOLECULE

a) Deviations of atoms from mean planes  $\Delta$  (Å)

	$\Delta$	$\Delta/\sigma$		$\Delta$	$\Delta(\sigma)$
Plane (1)			Plane (3)		
C(9)	0.005	0.44	C(1)	0.004	0.29
C(10)	0.001	0.10	C(2)	-0.005	0.47
C(11)	-0.006	0.56	C(3)	0.006	0.45
C(12)	0.009	0.80	C(4)	-0.004	0.28
C(13)	-0.100	0.83	C(7) <sup>a</sup>	0.853	52.61
Plane (2)			Plane (4)		
C(2)	0.011	0.85	C(4)	-0.005	0.38
C(3)	0.012	0.91	C(5)	0.006	0.53
C(5)	0.011	0.90	C(6)	-0.007	0.53
C(6)	-0.012	0.90	C(1)	0.005	0.36
C(1) <sup>a</sup>	0.912	65.08	C(7) <sup>a</sup>	-0.816	53.56
C(4) <sup>a</sup>	0.899	70.19			

b) Coefficients of plane equations  $A^x + B^y + C^z - \nu = 0$ 

Plane	A	B	C	$\nu$
1	-0.6575	0.6401	-0.3974	-7.2535
2	-0.5693	0.7797	-0.2607	-3.1018
3	-0.2759	0.5470	-0.7903	-0.3375
4	0.6131	0.6848	-0.3943	3.0774

## c) Dihedral angles (°)

(1)-(2)	12.3	(2)-(4)	38.7
(2)-(3)	37.9	(3)-(4)	103.4

<sup>a</sup> Atoms are not included in calculations of the plane equation.

bond lengths of 1.43(2) Å; all the carbon atoms are equidistant from the rhodium atom, and the average Rh—C(Cp) bond length of 2.21(1) Å is comparable with those found in other cyclopentadienyl rhodium complexes [17,18].

The rhodium atom is asymmetrically bound to the  $\eta^3$ -allylic fragment: Rh—C(3), Rh—C(2) and Rh—C(8) distances are 2.15(1), 2.12(1) and 2.27(1) Å, respectively. The increase of the latter distance is due to the rigidity of the bicyclic ligand, although in this case the exocyclic carbon, C(8), is bent away from the plane C(1)C(2)C(3)C(4) towards the rhodium (the angle between the C(8)—C(2) bond and the above plane is 20.5°). The C(5) and C(6) atoms of the double bond are located at the same distance from the rhodium, the value of 2.18(1) Å being slightly greater than that observed, for example, in Rh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(acac) (2.13 and 2.14 Å) [19]. The length of the double bond is 1.39 Å, towards the lower end of the range for C=C distances observed in ethylene complexes of rhodium.

The geometry of the norbornadiene skeleton is unexceptional revealing a typical decrease in the bond angle at the bridged C(7) atom in comparison with the rest of endocyclic angles.

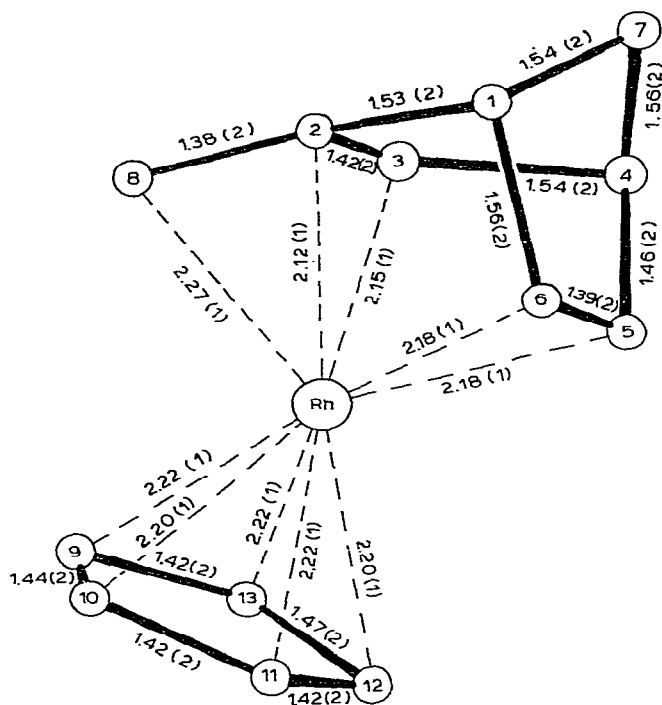
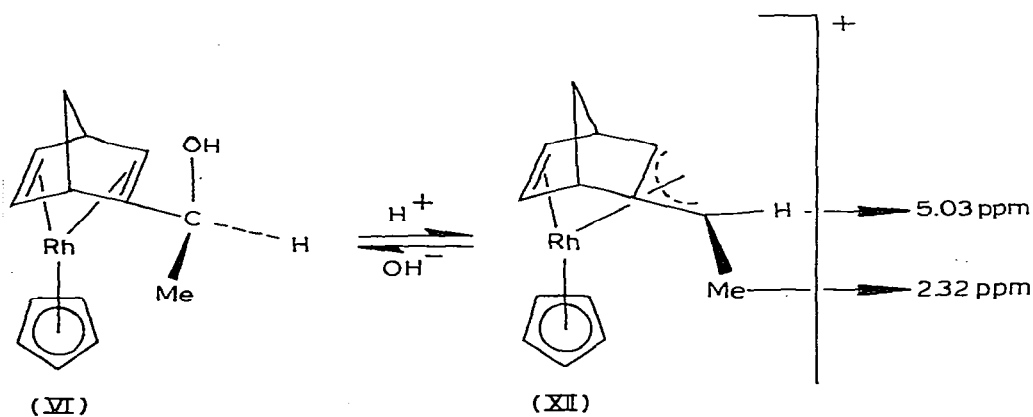
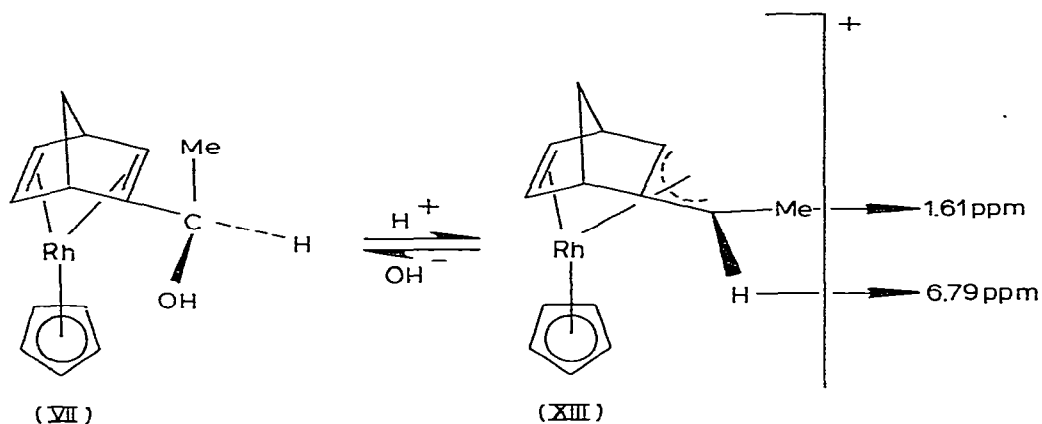


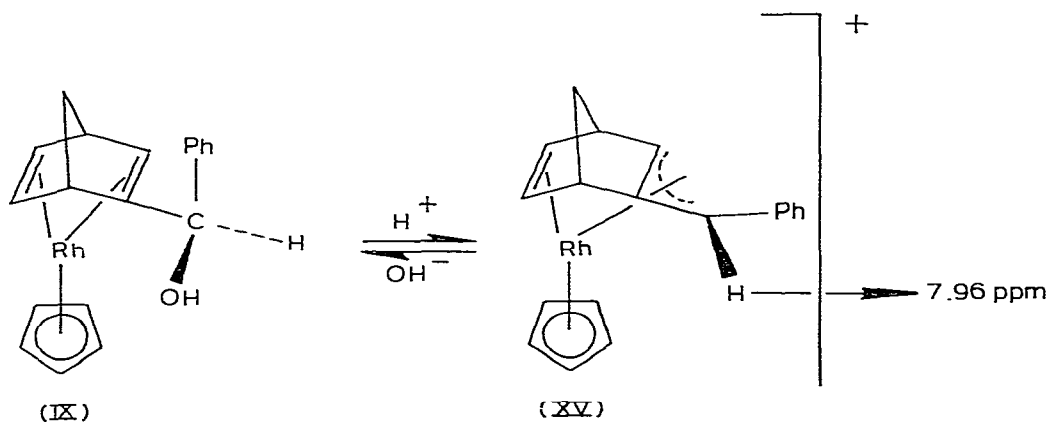
Fig. 2. The molecular structure of  $[\text{Rh}(\eta^5\text{-C}_7\text{H}_7\text{CH}_2)(\eta^5\text{-C}_5\text{H}_5)]^+$ .

An important criterion in establishing the configuration of the secondary carbinols VI and VII was the absolute stereospecificity found for them in the generation of the cationic complexes XII and XIII, respectively, in acid media. As was pointed out, the alkaline hydrolysis of these complexes led to carbinol precursors [1,10].

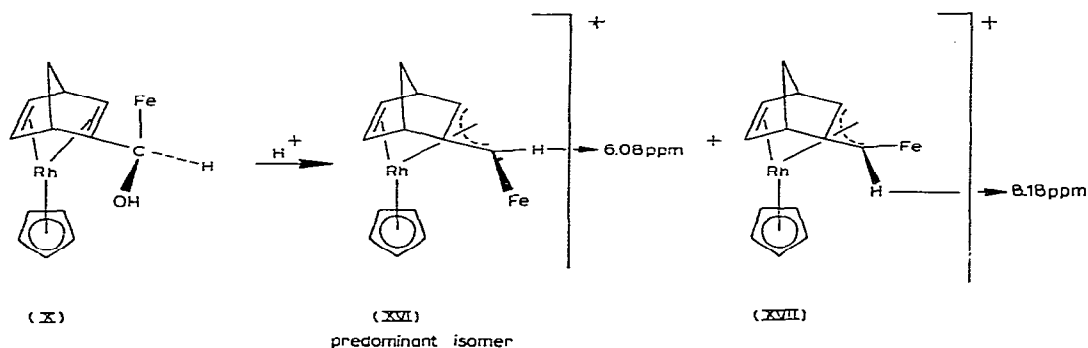




In this work it was established that the same stereospecificity is present in the reaction of the phenyl-substituted  $\psi$ -endo carbinol IX.



Therefore, it was rather surprising to observe the formation of a mixture of isomeric cations XVI and XVII from the ferrocenyl-substituted  $\psi$ -endo carbinol (X) under the same conditions. Moreover, the syn-allylic isomer XVI is the predominant product. According to the  $^1\text{H}$  NMR spectrum of this mixture, the *syn/anti* ratio is  $\sim 4/1$ .



The configurations of isomeric complexes XVI and XVII were assigned on

the basis of the different screening of protons H(8) in the  $^1\text{H}$  NMR spectrum of this mixture. For isomer XVII the chemical shift of the H(8) proton,  $\delta$  8.18 ppm, is close to 7.96 ppm in the complex XV, (the H(8) hydrogen signal of isomer XVI appears at 6.08 ppm) and is consistent with the general tendency to less screening of the *syn*-substituent in the  $\eta^3$ -allylic system [15]. Moreover, alkaline hydrolysis of the resulting XVI and XVII mixture affords a  $\psi$ -*exo* carbinol (XVIII). (No isomeric  $\psi$ -*endo* carbinol was found as the reaction product, probably due to irreversible loss during work-up, which one might expect when taking into account the relatively small anti-isomer (XVII) content in the initial mixture).

In the  $^{13}\text{C}$  NMR spectra of complexes X and XVIII certain (though not significant, see Table 4) differences are seen, which together with IR and mass-spectrometric data, are in good agreement with their assigned configuration.

The final and most convincing evidence for the accuracy of our interpretation of the chemical results obtained was the X-ray analysis of the predominant  $\eta^3$ -allylic isomer. The cationic complex XVI has *syn*-configuration (Fig. 3).

The stereospecificity of the generation of cationic complexes from the secondary carbinols VI, VII and IX indicates that the water molecules leave from that side which is *trans* to the rhodium, and that in the transition state of the reaction the rotation around the C(2)–C(8) bond is restricted. The observed absolute stereospecificity of the reactions together, with their relative facility (carbinols transform readily into cationic complexes even in weak acetic and formic acids), suggests a nucleophilic participation of the rhodium atom in the

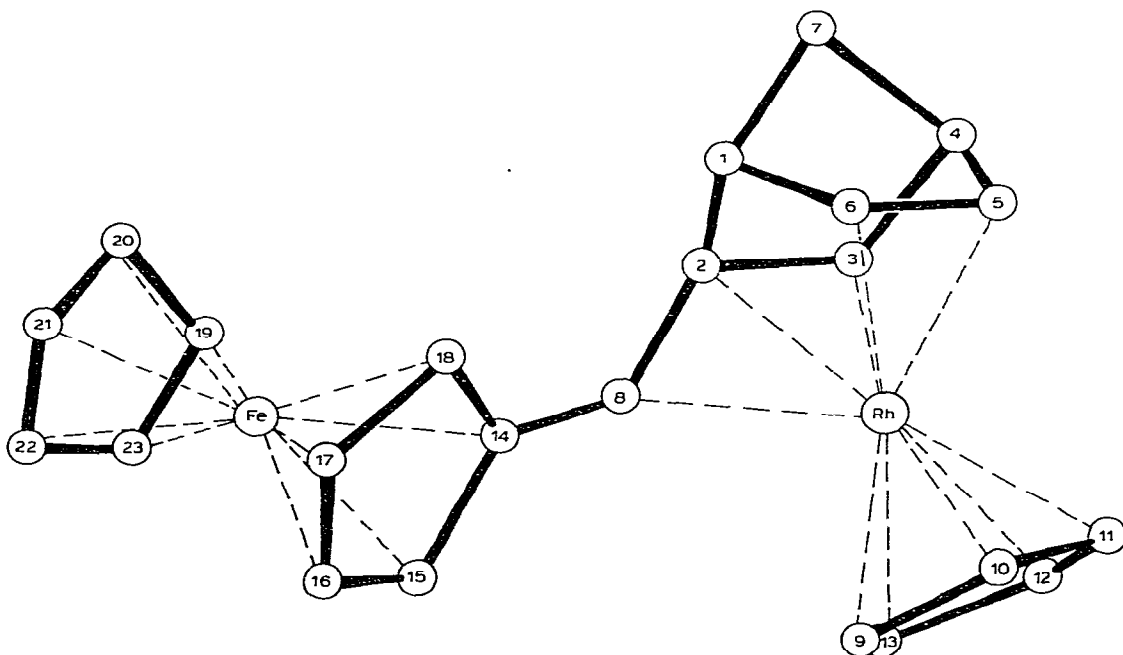


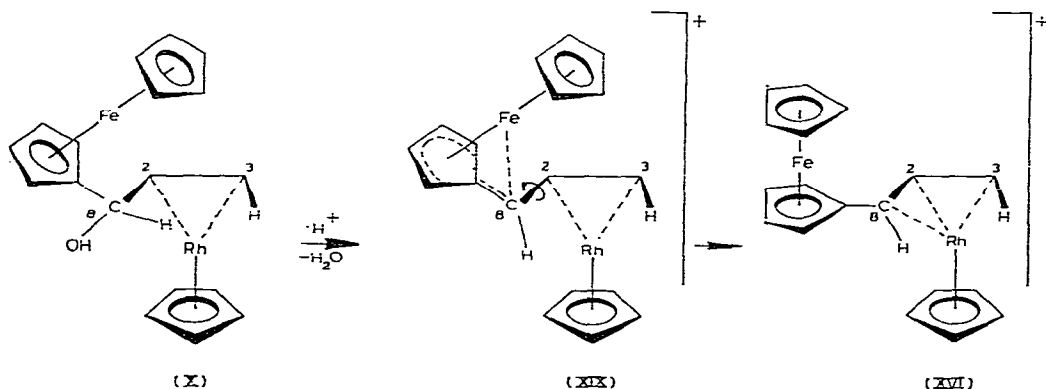
Fig. 3. The molecular structure of  $\text{syn-}[\text{Rh}(\eta^5\text{-C}_7\text{H}_7\text{CHFc})(\eta^5\text{-C}_5\text{H}_5)]^+$ .

transition state of the reaction. The same explanation for the stereospecificity and rate differences between  $\psi$ -*exo* and  $\psi$ -*endo* isomers in a solvolytic reaction of ferrocenylcarbinyl acetates has been given previously [12]. Unlike ferrocenyl-substituted carbenium ions, for which the direct metal participation has only quite recently been confirmed [8], the metal-*exo*-carbon bond is obvious in the complexes of rhodium (XI–XVII).

Finally, it is necessary to comment on the disturbance of the stereospecificity in the reaction of the  $\psi$ -*endo* carbinol (X) leading to the predominant formation of the *syn*-cationic complex (XVI). With this aim in view, we consider the conformation of the initial carbinol X (the principal approach to the analysis of the conformations of diastereomeric carbinols VI and VII [1] most probably also extends to the phenyl- and ferrocenyl-substituted carbinols IX, X and XVIII).

It is generally accepted that ferrocenyl carbinols exhibit intramolecular hydrogen bonding between the hydroxyl group and the iron atom, which leads to the appearance of an additional band of hydroxyl stretching absorption in the 3560–3580  $\text{cm}^{-1}$  region. However, in the IR spectrum of  $\psi$ -*endo* carbinol X, one can see only one narrow absorption band at 3518  $\text{cm}^{-1}$ , which fully coincides with the same absorption band in the spectrum of the  $\psi$ -*endo* phenyl-substituted carbinol IX. This fact indicates that the hydroxyl group in complex X is *exo*-positioned relative to the iron atom in the ferrocenyl substituent, and is at the same time *endo*-oriented relative to the rhodium atom. Therefore, during protonation of the hydroxyl group and generation of the cationic centre at the exocyclic carbon C(8), the leaving group departs from the *exo*-position relative to the iron atom rather than to the rhodium atom, as is the case in the formation of complexes XI–XV.

Thus, the stereochemistry of carbinol X favours the direct participation of the iron atom in stabilizing the generated electron-deficient centre at carbon C(8). As a result, the  $\alpha$ -ferrocenylcarbenium ion  $[\text{Rh}(\eta^4\text{-C}_7\text{H}_7\text{CHFc})(\eta^5\text{-C}_5\text{H}_5)]^+$  (XIX) is formed in the first stage. In this ion the rotation about the C(8)–C(Fc) bond will be hindered, while the rotation about C(8)–C(2) will encounter no substantial hindrances. Such a rotation gives the mixture of  $\eta^3$ -allylic complexes XVI and XVII (products of thermodynamic control), the ratio of which is accounted for by the steric hindrances in the  $\alpha$ -ferrocenylcarbenium ion XIX.





In addition, the formation of a mixture of cationic complexes XVI and XVII can be due to the competition that arises between the iron and rhodium atoms to participate in stabilizing the generated cationic centre at an earlier stage of carbinol ionization, i.e. at the stage where the leaving group can occupy both an *endo* and possibly an *exo* position relative to the rhodium atom.

### Experimental

The  $^1\text{H}$  NMR spectra were recorded on Perkin-Elmer R-32 and Bruker WH-360 spectrometers.  $^{13}\text{C}$  NMR spectra analysis were performed on a Bruker HX-90 instrument. IR spectra were recorded using a UR-20 spectrometer.

#### {2-( $\alpha$ -Hydroxyisopropyl)norbornadiene}cyclopentadienylrhodium (VIII)

(2-Carbomethoxynorbornadiene)cyclopentadienylrhodium [11] (0.35 g, 0.11 mmol) in 20 ml of abs. ether is added dropwise to a stirred solution of MeLi in ether (3.2 ml, 0.78 N, 0.25 mmol) in an inert gas atmosphere at 0–5°C. The mixture is stirred and allowed to reach room temperature, then refluxed for 5 h, cooled, and poured into water. The ether layer is removed, and the aqueous layer extracted with ether (2  $\times$  10 ml). The combined extracts are washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The residue (0.32 g, 0.10 mmol) is crystallized from hexane at –78°C, yielding light-yellow crystals (0.21 g, 0.066 mmol, 60%), m.p. 45–46°. (Found: C, 56.48; H, 5.97; Rh, 32.38.  $\text{C}_{15}\text{H}_{19}\text{ORh}$  calcd.: C, 56.60; H, 5.97; Rh, 32.39%).

#### {2-( $\alpha$ -Hydroxybenzyl)norbornadiene}cyclopentadienylrhodium (IX)

A solution of PhLi (2.66 ml, 0.94 N, 0.25 mmol) in hexane is added slowly to a stirred solution of (2-formylnorbornadiene)cyclopentadienylrhodium [11] (0.29, 0.10 mmol) in abs. ether (15 ml) in an inert gas atmosphere at –30°C. The mixture is allowed to reach room temperature, and then refluxed for 2 h, the reaction mixture is cooled, and poured into water. The ether layer is separated and the aqueous layer is extracted with ether (2  $\times$  15 ml). The combined ether solutions are washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The residue is dissolved in a minimum amount of hexane and cooled at –78°C. for 12 h. The resulting crystals are filtered and recrystallized from hexane yielding yellow IX (0.23 g, 0.063 mmol, 63%), m.p. 89–90°C (Found: C, 62.35; H, 5.19; Rh, 28.16.  $\text{C}_{19}\text{H}_{19}\text{ORh}$  calcd.: C, 62.29; H, 5.19; Rh, 28.14%).

#### {2-( $\alpha$ -Hydroxyferrocenylmethyl)norbornadiene}cyclopentadienylrhodium, $\psi$ -*endo* isomer (X)

An ether solution of n-BuLi (1.76 ml, 1.14 M, 0.20 mmol) is added dropwise to a stirred solution of iodoferrrocene [20] (0.624 g, 0.20 mmol) in ether at –70°C. The mixture is stirred for 1/2 h and (2-formylnorbornadiene)cyclopentadienylrhodium (0.46 g, 0.16 mmol) in 25 ml ether is rapidly added. The cooled mixture is stirred for another 1/2 h, allowed to rise to room temperature and poured into 40 ml of water. The ether layer is removed, and the aqueous layer extracted with ether (2  $\times$  35 ml); the combined extracts are washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. Pale orange crystals are obtained, which after crystallization from acetone afford  $\psi$ -*endo* carbinol X

(0.68 g, 0.142 mmol, 89%), m.p. 165–167.5°C (Found: C, 58.35; H, 5.06;  $C_{23}H_{23}OFeRh$  calcd.: C, 58.23; H, 4.85%).

*General method for synthesis of  $PF_6^-$  or  $BF_4^-$  salts of  $\eta^3$ -allyl cationic complexes XI–XVII*

Concentrated  $H_2SO_4$  (1 or 2 drops) is added under stirring to a solution of IX (0.15 g, 0.05 mmol) in dry ether (10 ml) in an inert gas atmosphere. The stirring is stopped, and after 10 min the solution is decanted from the dark-red oily residue obtained, which is washed with 20 ml of dry ether and dissolved in 1–1.5 ml of distilled water. To the resulting aqueous solution,  $AgBF_4$  (0.1 g, 0.05 mmol) in 0.5 ml of water is added dropwise while stirring. The precipitate obtained is extracted with  $CH_2Cl_2$  ( $2 \times 5$  ml), the combined dichloromethane solution is dried ( $Na_2SO_4$ ) and slowly poured into 150 ml of dry ether. After 1/3 h golden-orange crystals begin to precipitate, they are filtered, washed with dry ether and recrystallized from abs. ethanol, affording the tetrafluoroborate salt of XV (0.16 g, 0.037 mmol, 90%). (Found: C, 52.36; H, 4.14; D, 17.21; Rh, 23.65.  $C_{19}H_{18}BF_4Rh$  calcd.: C, 52.32; H, 4.13; F, 17.44; Rh, 23.63%). The change of  $AgBF_4$  for  $NH_4PF_6$  leads to the  $PF_6^-$  salt of XV (72% yield), (Found: C, 44.41; H, 3.58; Rh, 20.88.  $C_{19}H_{18}F_6PRh$  calcd.: C, 46.15; H, 3.64; Rh, 20.85%). The hexafluorophosphate salt of XI is obtained in the same manner (89% yield). (Found: C, 37.51; H, 3.52; F, 26.95.  $C_{13}H_{14}F_6PRh$  calcd.: C, 37.32; H, 3.34; F, 27.27%). (The formation of the cationic complex XI is also observed when formic acid is used instead of sulphuric acid). Hexafluorophosphate salt of XII (yield 93%). (Found: C, 38.80; H, 3.65; Rh, 23.92.  $C_{14}H_{16}F_6PRh$  calcd.: C, 38.89; H, 3.70; Rh, 23.96%). Hexafluorophosphate salt of XIII (yield 91%), (Found: C, 38.75; H, 3.74; F, 25.78.  $C_{14}H_{16}F_6PRh$  calcd.: C, 38.89; H, 3.70; F, 26.38%). Hexafluorophosphate salt of XIV, (yield 88%) (Found: C, 40.31; H, 4.22; Rh, 23.01.  $C_{15}H_{18}F_6PRh$  calcd.: C, 40.36; H, 4.04; Rh, 23.09%). Mixture of the tetrafluoroborate salts of XVI and XVII (yield 76%), (Found: C, 50.76; H, 4.33; Rh, 19.14.  $C_{23}H_{23}BF_4Rh$  calcd.: C, 50.76; H, 4.04; Rh, 18.93%).

*General method for alkaline hydrolysis of  $\eta^3$ -allyl cationic complexes*

Aqueous sodium hydroxide (5 N, 1.2 ml) is added dropwise to a stirred solution of XII (0.26 g, 0.06 mmol) in water (30 ml) at 50°C. The suspension obtained is cooled to room temperature and extracted with ether ( $2 \times 30$  ml). The combined ether extracts are washed with water, dried ( $Na_2SO_4$ ), and evaporated. The residue is crystallized from hexane at  $-76^\circ C$  yielding complex VII [1].

*{2-( $\alpha$ -Hydroxyferrocenylmethyl)norbornadiene} cyclopentadienylrhodium,  $\psi$ -exo isomer (XVIII)*

A mixture of tetrafluoroborate salts of XVI and XVII (0.3 g, 0.55 mmol) is dissolved in boiling distilled water (100 ml). Aqueous sodium hydroxide (5 N, 1.6 ml) is added with stirring, the reaction mixture is cooled to room temperature and extracted with ether ( $3 \times 30$  ml). The ethereal solutions are washed with water, dried ( $Na_2SO_4$ ) and evaporated. The residue is dissolved in hot hexane (10 ml), filtered and cooled to  $-78^\circ C$ . After 12 h the precipi-

tated crystals are filtered, yielding *exo*-carbinol XVIII, (0.19 g, 0.039 mmol, 72%), m.p. (dec.) 157–158°C.

## References

- 1 I.T. Chizhevsky, A.A. Koridze, V.I. Bakhmutov and N.E. Kolobova, *J. Organometal. Chem.*, **206** (1981) 361.
- 2 R. Pettit and L.W. Hanes in G.A. Olah and P. von R. Schleyer (Eds.), *Carbonium Ions*, Vol. 5, Intersciences, New York, N.Y., 1976, p. 2263.
- 3 E.A. Hill and J.H. Richards, *J. Amer. Chem. Soc.*, **81** (1959) 3483; **83** (1961) 3840.
- 4 M. Cais, J.J. Dannenberg, A. Eisenstadt, M.I. Levenberg and J.H. Richards, *Tetrahedron Lett.*, (1966) 1695.
- 5 J.J. Dannenberg, M.I. Levenberg and J.H. Richards, *Tetrahedron*, **29** (1973) 1575.
- 6 J.C. Ware and T.G. Traylor, *Tetrahedron Lett.*, (1963) 1295.
- 7 T.G. Traylor and J.C. Ware, *J. Amer. Chem. Soc.*, **89** (1967) 2304.
- 8 A.A. Koridze, N.M. Astakhova, P.V. Petrovskii and A.A. Lutsenko, *Dokl. Akad. Nauk SSSR*, **242** (1978) 117.
- 9 I.T. Chizhevsky and A.A. Koridze, *J. Organometal. Chem.*, **153** (1978) C28.
- 10 A.A. Koridze, I.T. Chizhevsky, P.V. Petrovskii and N.E. Kolobova, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, (1979) 2395.
- 11 I.T. Chizhevsky, A.A. Koridze, P.V. Petrovskii and N.E. Kolobova, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, in press.
- 12 E.A. Hill and J.H. Richards, *J. Amer. Chem. Soc.*, **83** (1961) 4216.
- 13 D.S. Trifan and R. Bacskai, *J. Amer. Chem. Soc.*, **82** (1960) 5010.
- 14 A.W. Baker and D.E. Bublitz, *Spectrochim. Acta*, **22** (1966) 1787.
- 15 L.A. Fedorov, *Usp. Khim.*, **39** (1970) 1389.
- 16 T.E. Borovyak, V.E. Shklover, A.I. Gusev, S.P. Gubin, A.A. Koridze and Yu.T. Struchkov, *Zh. Strukt. Khim.*, **11** (1970) 1087.
- 17 L.J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, **94** (1972) 3779.
- 18 M.G.B. Drew, S.M. Nelson and M. Sloan, *J. Organometal. Chem.*, **39** (1972) C9.
- 19 J.A. Evans and D.R. Russel, *Chem. Commun.*, (1971) 197.
- 20 R.W. Fish and M. Rosenblum, *J. Org. Chem.*, **30** (1965) 1253.