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Preliminary communication

LIGAND EXCHANGE AT RUTHENOCENE

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Summary

The exchange of a ruthenocene Cp-ligand for an arene was realized for the first time. A set of cationic arene-Cp derivatives of ruthenium $[\text{AreneRuC}_5\text{H}_5]^+\text{X}^-$ (Arene = C_6H_6, $CH_3C_6H_5$, $C_6H_5C_6H_5$, ClC_6H_5) was obtained by this reaction. The structure of the complexes was determined by ^{1}H NMR spectroscopy.

Earlier we discovered a reaction leading to the replacement of one ferrocene Cp ligand (Cp = cyclopentadienyl) by an arene ligand [1,2]. This reaction has become a general convenient method for the synthesis of cationic arene-Cp derivatives of iron $[\text{AreneFeC}_5\text{H}_5]^+\text{X}^-$ [3,4].

In the present paper we describe several examples of an analogous exchange reaction of ruthenocene which is the first transformation of this kind in ruthenocene chemistry.

$$(C_5H_5)_2\text{Ru} + \text{Arene} \xrightarrow[\text{NaX}]{\text{AlHal}_3/\text{Al}} [\text{AreneRuC}_5\text{H}_5]^+\text{X}^- + \{C_5H_5\}_n$$

Arene = C_6H_6, $CH_3C_6H_5$, $C_6H_5C_6H_5$, ClC_6H_5; X^- = BF_4, PF_6, BPh_4
Hal = Cl, Br

The following compounds were synthesized by the use of this reaction (below are given: compound; yield (%); m.p. with decomposition (°C)): $[C_6H_6RuC_5H_5]PF_6$ ($I \cdot PF_6$), 7, does not melt; $I \cdot BPh_4$, —, 248—250; $[CH_3C_6H_5RuC_5H_5]BPh_4$ ($II \cdot BPh_4$), 6, ~260; $II \cdot BF_4$, 5, ~245; $[C_6H_5C_6H_5RuC_5H_5]PF_6$ ($III \cdot PF_6$), 3, 129—131; $[ClC_6H_5RuC_5H_5]BF_4$ ($IV \cdot BF_4$), 7, 160—162.

The reaction conditions and analytical data are given in Table 1. All the runs were carried out under an atmosphere of dry argon. A typical ratio of reagents was $(C_5H_5)_2$Ru : $AlHal_3$: Al : Arene = 1 : 3—5 : 1 : excess. In the synthesis of $[II]^+$ and $[IV]^+$ an excess of arene was used as a solvent; in the synthesis of $[I]^+$ and $[III]^+$ nonane and octane were used respectively. Aluminium chloride and aluminium bromide served as catalysts. There was no significant difference in their activity.

TABLE 1

CONDITIONS FOR THE SYNTHESIS OF [AreneRuC_5H_5]X AND ANALYTICAL DATA

π-Complex	Catalyst	Temperature (°C) and time (h) of the reaction	Found (calculated) (%)	
			C	H
$[C_6H_6RuC_5H_5]PF_6$	$AlBr_3$	100/12	33.20	3.12
			(33.93)	(2.85)
$[C_6H_6RuC_5H_5]BPh_4$	$AlBr_3$	100/2	74.52	5.47
			74.59	5.63
			(74.59)	(5.54)
$[CH_3C_6H_5RuC_5H_5]BPh_4$	$AlCl_3$	110/5	74.74	6.03
			74.72	5.68
			(74.84)	(5.76)
$[CH_3C_6H_5RuC_5H_5]BF_4$	$AlBr_3$	110/12	41.96	3.89
			41.72	4.08
			(41.75)	(3.79)
$[C_6H_5C_6H_5RuC_5H_5]PF_6$	$AlCl_3$	125/6.5	43.48	3.11
			43.59	3.23
			(43.87)	(3.24)
$[ClC_6H_5RuC_5H_5]BF_4$	$AlBr_3$	130/5.5	35.85	2.76
			35.86	2.70
			(36.14)	(2.76)

In the synthesis of $[III]^+$ and $[IV]^+$ some water (2—3 drops) was added to promote the reaction. However, in these cases there was no significant increase in the yield (cf. [5]).

In order to avoid an oxidation of ruthenocene to ruthenocenium cation aluminium powder was added to the reaction mixture. However, the reaction of ruthenocene with chlorobenzene was performed without aluminium powder to exclude dehalogenation [6]. In this case the cation $[(C_5H_5)_2Ru]^+$ formed was reduced with ascorbic acid after hydrolysis of the reaction mixture.

It can be seen from the data given above that the yields of the complexes $[AreneRuC_5H_5]^+X^-$ are lower than 10%. These results are in sharp contrast to the exchange reactions of ferrocene which give the salts $[AreneFeC_5H_5]^+X^-$ in 20—80% yields. It seems probable that the rupture of a C_5H_5—Ru bond in the presence of $AlCl_3$ is more difficult than the rupture of a C_5H_5—Fe bond.

All the salts of arene-Cp ruthenium cations obtained are pale-yellow or white crystalline diamagnetic compounds. Tetrafluoroborates of the cations are fairly soluble in water, ethanol, dichloroethane, acetone and acetonitrile; hexafluorophosphates of the cations are less soluble in the same solvents; tetraphenylborates of I and II are only slightly soluble in acetonitrile and acetone.

The only cation, $[C_6H_6RuC_5H_5]^+$, described hitherto [7] was synthesized by means of the reaction between C_5H_5Tl and the dimer $[C_6H_6RuCl_2]_2$.

IR spectra of $[AreneRuC_5H_5]X$ are very similar to the spectra of the corresponding iron salts, $[AreneFeC_5H_5]X$ [8]. The IR spectrum of IV·BF_4 contains a band at 700 cm^{-1} which corresponds to the vibrations of a C—Cl bond.

^1H NMR spectra of the $[AreneRuC_5H_5]X$ complexes synthesized and corresponding $[AreneFeC_5H_5]X$ complexes are given in Table 2. From these data it can be seen that the spectra of ruthenium derivatives are very similar to the spectra of the related π-complexes of iron. A sandwich structure of $[AreneRuC_5H_5]^+$, similar to $[AreneFeC_5H_5]^+$ [4,10], with planar undisturbed cyclic ligands seems to be reasonable on the basis of NMR spectra.

TABLE 2

^{1}H NMR DATA OF [AreneRuC_5H_5]X AND [AreneFeC_5H_5]X^{a,b}
(R-12, 60 MHz, deuterioacetone, δ 2.07 ppm)

π-Complex	δ (Cp) (ppm)	δ (Arene) (ppm)	δ (Substituent) (ppm)
$(C_5H_5)_2Ru$	4.60s (5)		
$(C_5H_5)_2Fe$	4.20s (5)		
$[C_6H_6RuC_5H_5]PF_6$ ^{c}	5.45s (5)	6.20s (6)	
$[C_6H_6FeC_5H_5]PF_6$	5.23s (5)	6.44s (6)	
$[CH_3C_6H_5RuC_5H_5]BF_4$	5.45s (5)	6.16s^d (5)	2.43s (3)
$[CH_3C_6H_5FeC_5H_5]PF_6$	5.27s (5)	6.56s (5)	2.56s (3)
$[C_6H_5C_6H_5RuC_5H_5]PF_6$	5.49s (5)	6.34—6.85m (5)	7.34—7.87m (5)
$[C_6H_5C_6H_5FeC_5H_5]BF_4$	5.14s (5)	6.51—7.09m (5)	7.42—8.11m (5)
$[ClC_6H_5RuC_5H_5]BF_4$	5.71s (5)	6.36—6.69m (3) 6.76—6.98m (2)	
$[ClC_6H_5FeC_5H_5]BF_4$	5.40s (5)	6.54—7.07m^e (5)	
C_6H_6 ^{f}			7.27 (6)

^{a} s = singlet, m = multiplet. ^{b} Intensities of the signals are given in parentheses. ^{c} Literature data [7]: δ 5.35 (5), 6.12 ppm (6). ^{d} Broadened singlet. ^{e} Two superimposed multiplets. ^{f} Ref. 9.

The signal for the cyclopentadienyl protons in the spectrum of I·PF_6 is shifted downfield by 0.85 ppm as compared with the respective signal in the spectrum of ruthenocene.

The downfield shift of the Cp protons of $[C_6H_6FeC_5H_5]PF_6$ is even higher than that with ferrocene. This phenomenon for iron derivatives was explained [10] as being due to delocalization of the cation positive charge on the ligands. This explanation would seem to be applicable for the ruthenium derivatives also. On the contrary, the signal of the benzene ligand protons in the spectrum of I·PF_6 is shifted upfield by 1.07 ppm as compared with the spectrum of non-coordinated benzene [9]. The corresponding value for iron derivative is 0.89 ppm. The upfield shift of coordinated arene protons is a well-known phenomenon [9]. This shift for the cations [AreneMC_5H_5]$^+$ (M = Fe, Ru) is weaker because of the influence of the π-complex positive charge (see data for $C_6H_6MC_5H_5$, where M = Mn, Re [12]). The downfield shift of the Cp protons and the upfield shift of the arene protons in comparison with the spectra of the corresponding iron derivatives is characteristic of all the complexes [AreneRuC_5H_5]X obtained.

From an analysis of the data given above it is possible to arrive at a preliminary conclusion that the positive charge of the cations is delocalized on the ligands to a lesser extent for [AreneRuC_5H_5]$^+$ as compared with [AreneFeC_5H_5]$^+$.

References

1 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 149 (1963) 615.
2 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Tetrahedron Lett., (1963) 1725.
3 A.N. Nesmeyanov, Adv. Organometal. Chem., 10 (1972) 44.
4 N.A. Vol'kenau, in A.N. Nesmeyanov and K.A. Kocheshkov (Eds.), Methods of elementoorganic chemistry, Nauka, Moscow, 1976, 127.
5 A.N. Nesmeyanov, N.A. Vol'kenau, I.N. Bolesova and L.S. Polkovnikova, Koord. Khim., 1 (1975) 1252.
6 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 166 (1966) 607.
7 R.A. Zelonka and M.C. Baird, J. Organometal. Chem., 44 (1972) 383.
8 A.N. Nesmeyanov, B.V. Lokshin, N.A. Vol'kenau, I.N. Bolesova and L.S. Isaeva, Dokl. Akad. Nauk SSSR, 184 (1969) 358.
9 A. Gordon and R. Ford, The Chemist's Companion, J. Wiley and Sons, New York, 1972.
10 A.N. Nesmeyanov, I.F. Leshchova, Yu.A. Ustynyuk, R.I. Sirotkina, I.N. Bolesova, L.S. Isaeva and N.A. Vol'kenau, J. Organometal. Chem., 22 (1970) 689.
11 V.S. Khandkarova, S.P. Gubin and B.A. Kvasov, J. Organometal. Chem., 23 (1970) 509.
12 E.O. Fischer and H.W. Wehner, Chem. Ber., 101 (1968) 454.