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SYNTHESIS AND REDUCTION OF CATIONIC BIS-ARENE-RUTHENIUM COMPLEXES

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Summary

A number of symmetrical and unsymmetrical bis-arene-ruthenium cations has been prepared and their reduction with sodium borohydride studied. Hydride hydrogen is shown to add preferentially to the less alkylated ring. The conditions are established, which allow the preparation of a new, previously unknown, cationic complex of arene-cyclohexadienyl-ruthenium by stepwise addition of hydride hydrogen.

Introduction

The arene complexes of ruthenium find wide application as catalysts in the hydrogenation of unsaturated compounds [1—3]. Although some of them are prepared from bis-arene-ruthenium cationic complexes [7], the methods for their synthesis and their properties have not been studied thoroughly. The Fischer method, involving the interaction of $RuCl_3$ with arene in the presence of $AlCl_3$ and Al [4—7], provides symmetrical bis-arene-ruthenium cations only. To prepare unsymmetrical cations the method of stepwise introduction of arenes, involving the interaction of $[C_6H_6RuCl_2]_2$ with $AgBF_4$ in acetone, to form a trisacetone complex is used [8,9]. Acetone is then removed from the latter by refluxing with arene in CF_3COOH:

$$[C_6H_6RuCl_2]_2 + AgBF_4 + S \rightarrow [C_6H_6RuS_3](BF_4)_2 \xrightarrow[CF_3COOH]{arene} [C_6H_6Ru\ arene](BF_4)_2$$

$(S = CH_3COCH_3)$

Results and discussion

We have prepared a number of symmetrical and unsymmetrical bis-arene-ruthenium cations. Following the Fischer method and using heptane as a solvent

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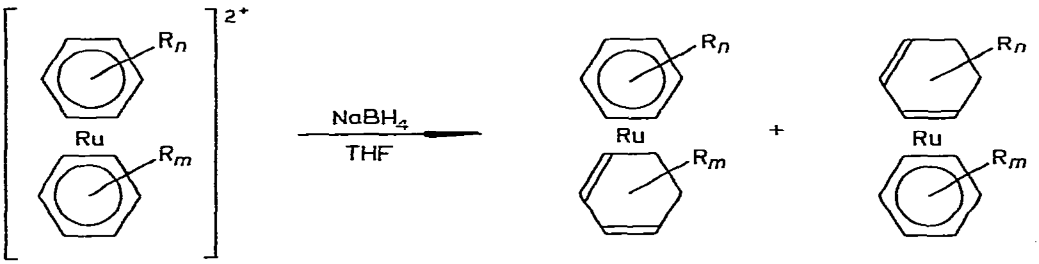
we obtained in good yield $[mes_2Ru](BPh_4)_2$ (complex I), where mes = 1,3,5-$(CH_3)_3C_6H_3$. For the preparation of unsymmetrical bis-arene-ruthenium cations we somewhat modified the method using silver salts, namely, the first step of reaction was carried out in water (S = H_2O) instead of acetone, and thus we obtained a number of bis-arene-ruthenium tetrafluoroborates IIa—IIg (see Table 1). The use of water as a solvent permitted use in the reaction not only of silver tetrafluoroborate, but of the more available silver nitrate as well, the salt being readily isolated in the form of the tetraphenylborate poorly soluble in water. Following this procedure we obtained $[C_6H_6Ru\ mes](BPh_4)_2$ (III). The obtained complexes I—III are air-stable, white or pale yellow compounds, insoluble in ether and benzene. Tetraphenylborates are soluble in acetone and nitromethane; tetrafluoroborates in nitromethane and dimethylsulphoxide.

The reduction of bis-arene-ruthenium cations to neutral arene-cyclohexadiene-ruthenium complexes has been earlier described only from bis-benzene-ruthenium dication [5], so it was of interest to investigate the effect of substituents in the arene rings on the direction of the hydride attack and estimate a possibility for conducting the process stepwise.

It was found in all experiments that reduction with sodium borohydride in THF led to formation of neutral arene-cyclohexadiene complexes in more than 70% yield. Generally, a mixture of isomers IV and V was expected to be obtained; the ratio of isomers was determined by mass spectrometry of the reduction products. The mass spectrum of IVa indicates that the diene ring is always the first to be lost. As might be expected, the treatment of complexes of various arenes by $NaBH_4$ resulted in prevailing hydrogenation of the less alkylated benzene ring which becomes a diene ring and is seen to be lost in the mass spectrum. Using mesitylene as a second arene results in the formation of complex IVb exclusively, while with toluene and *p*-xylene a mixture of IVc, d and Vc, d, respectively, is formed (ratio ~ 70 : 30).



(IVa–IVd) (Va–Vd)

a, R_n = R_m = 1,3,5-$(CH_3)_3$
b, R_n = 1,3,5-$(CH_3)_3$; R_m = H
c, R_n = 1,4-$(CH_3)_2$; R_m = H
d, R_n = CH_3 ; R_m = H

Complexes IV and V are practically colourless, unstable, solid, low-melting compounds.

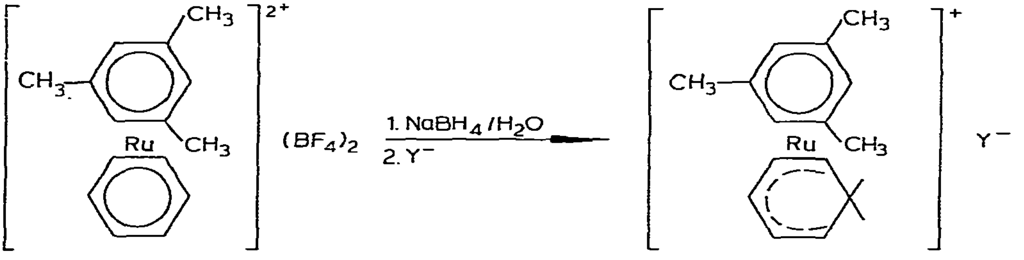
We found that when the reduction process is carried out in water an unknown intermediate monocationic arene-cyclohexadienyl-ruthenium can be isolated

TABLE 1

YIELDS AND ANALYTICAL DATA FOR COMPLEXES $[C_6H_6Ru\text{-arene}](BF_4)_2$

No.	Arene	Yield (%)	Anal. (Found (calc.) (%))			
			C	H	B	Ru
IIa	$1,3,5\text{-}(CH_3)_3C_6H_3$	73	38.11 (38.09)	4.17 (3.84)	4.55 (4.57)	21.00 (21.26)
IIb	$1,4\text{-}(CH_3)_2C_6H_4$	77	36.91 (36.64)	3.94 (3.51)	4.68 (4.71)	21.92 (22.02)
IIc	$CH_3C_6H_5$	74	34.87 (35.09)	3.47 (3.17)	4.87 (4.86)	22.15 (22.71)
IId	$n\text{-}C_5H_{11}C_6H_5$	78	—	—	4.26 (4.32)	20.19 (20.17)
IIe	$C_{10}H_8$(naphthalene)	70	—	—	4.37 (4.50)	21.24 (21.01)
IIf	$C_6H_5OC_2H_5$	76	—	—	4.32 (4.55)	21.10 (21.28)
IIg	$1,3,5\text{-}(CH_3)_3C_6H_2(CH_2)_3COOH$	84	—	—	3.90 (3.87)	18.30 (18.08)

along with a small amount of neutral arene-cyclohexadiene-ruthenium, for instance:



(IIa) (VI)

a; Y = BPh_4, b; Y = PF_6

Further reduction of VIa with sodium borohydride in THF yields the complex IVb. The ^1H NMR spectrum of complex VIb corresponds to the structure suggested. In particular, signals can be seen from aromatic protons of mesitylene (δ = 6.01 ppm, singlet), methyl groups (δ = 2.25 ppm, singlet) and cyclohexadienyl ring (H(4): δ = 6.02 ppm, triplet, J = 6 Hz; H(3,5): δ = 5.07 ppm, triplet, J = 6 Hz; H(2,6): δ = 3.18 ppm, triplet, J = 6 Hz; H_β(*exo*): δ = 2.62 ppm, double triplet, J_1 = 15 Hz, J_2 = 6 Hz; H_α(*endo*): δ = 2.22 ppm, doublet, J = 15 Hz).

Experimental

IR spectra were recorded on a UR-20 spectrometer. ^1H NMR spectra were obtained on a Hitachi-Perkin-Elmer R-20 instrument (60 MHz) in acetone-d_6 using HMDS as internal reference. The chemical shifts are cited on the δ scale in ppm. Mass spectra were recorded on an AEI MS-30 spectrometer equipped with a DS-50 data processing system at 70 eV ionizing energy.

Preparation of [mes$_2$Ru](BPh$_4$)$_2$ (I)

To $RuCl_3$ (0.5 g, 2.4 mmol) was added Al (0.065 g, 2.4 mmol), mesitylene (3 ml) and an excess of $AlCl_3$ (3 g, 22.5 mmol) in heptane (20 ml). The mixture was stirred under reflux for 8 hours in an argon atmosphere. After decomposing the mixture with water, the solution was filtered, the aqueous layer separated, and aqueous solution of sodium tetraphenylborate was added. The precipitate was filtered off, washed with water, dried in vacuo over P_2O_5 and precipitated twice from acetone by ether to give a solid (1.29 g, 55%), m.p. 198—200°C (decomp.). Found: C, 80.85; H, 6.66; B, 2.19; Ru, 10.07. $C_{66}H_{64}B_2Ru$ calcd.: C, 80.90; H, 6.58; B, 2.21; Ru, 10.31%.

Preparation of [C$_6$H$_6$Ru arene](BF$_4$)$_2$ (II) complexes

To $[C_6H_6RuCl_2]_2$ (0.25 g, 0.5 mmol) was added $AgBF_4$ (0.39 g, 2 mmol) in water (10 ml) and the mixture was stirred at room temperature for 10 min. The precipitate was filtered off and the solution was evaporated in vacuo. The residue was dissolved in CF_3COOH (5 ml), arene (~0.5 g) was added and the mixture was refluxed for an hour. After removing the solvent in vacuo the residue was washed with ether and precipitated from nitromethane by ether. All of the prepared complexes are slowly decomposed without melting in the 240—270°C range. Table 1 lists yields and elemental analysis data. IR spectrum (KBr) of IIg: 1740 cm^{-1} [ν(C=O)].

Preparation of [C$_6$H$_6$Ru mes](BPh$_4$)$_2$ (III)

To $[C_6H_6RuCl_2]_2$ (0.25 g, 0.5 mmol) was added $AgNO_3$ (0.34 g, 2 mmol) in water (10 ml) and the mixture was stirred at room temperature for 10 min. The solution was filtered and evaporated in vacuo. The residue was dissolved in CF_3COOH (5 ml), mesitylene (0.5 ml, 4.3 mmol) was added and the reaction mixture was kept under reflux for an hour. After removal of the solvent in vacuo the residue was dissolved in water and treated with an excess of an aqueous solution of $NaBPh_4$. The formed precipitate was washed with water, dried over P_2O_5 and precipitated from acetone by ether to give 0.6 g (64%) of solid compound, m.p. 120—122°C (decomp.). Found: B, 2.28; Ru, 10.75. $C_{63}H_{58}B_2Ru$ calcd.: B, 2.31; Ru, 10.78%.

Reduction of [mes$_2$Ru](BPh$_4$)$_2$ (I)

The mixture of complex I (0.99 g, 1 mmol) and $NaBH_4$ (0.1 g, 2.6 mmol) in dry THF (10 ml) was stirred in an argon atmosphere at room temperature for 20 hours. Pentane (20 ml) was added and the solution was filtered and evaporated in vacuo. The residue was extracted with pentane and chromatographed on a column with disactivated Al_2O_3 (5% H_2O) with pentane. The pale yellow fraction was collected, evaporated in vacuo and the residue was recrystallized from pentane at —78°C to give complex IVa (0.12 g, 35%), m.p. 85—87°C (decomp.). Mass spectrum, *m/e* (ion): 341—346 * (M^+), 219—224 ($[M - C_6H_5(CH_3)_3]^+$).

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* Corresponds to the value calculated for the natural mixture of ruthenium isotopes ^{99}Ru—^{104}Ru.

Reduction of [C_6H_6Ru mes]$(BF_4)_2$ (IIa)

The reaction was carried out as described previously. After 8 hours of stirring the solution was treated similarly to give complex IVb, 76%, m.p. 53—54°C. The same product was obtained on reduction of complex III. Mass spectrum: 299—304 (M^+), 219—224 ($[M - C_6H_8]^+$). There are no $[M - C_6H_5(CH_3)_3]^+$ peaks.

Reduction of [$C_6H_6RuC_6H_4(CH_3)_2$-p]$(BF_4)_2$ (IIb)

The reaction was carried out as described previously to give a mixture of complexes IVc and Vc with total yield 76%, m.p. 75—76°C (decomp.). Mass spectrum: 285—290 (M^+), 205—210 ($[M - C_6H_8]^+$), 177—182 ($[M - C_6H_6(CH_3)_2]^+$). IVc : Vc ratio ~70 : 30.

Reduction of [$C_6H_6RuC_6H_5CH_3$]$(BF_4)_2$ (IIc)

The IVd and Vd mixture was obtained in the same way in 72% total yield, m.p. 6—8°C. Mass spectrum: 271—276 (M^+), 191—196 ($[M - C_6H_8]^+$), 177—182 ($[M - C_6H_7CH_3]^+$). IVd : Vd ratio ~70 : 30.

Reduction of IIa in water

$NaBH_4$ (0.38 g, 10 mmol) was added stepwise under stirring in an argon atmosphere over a period of 2 hours to the mixture of [C_6H_6Ru mes]$(BF_4)_2$ (0.47 g, 1 mmol), water (20 ml) and pentane (20 ml). After stirring for an hour the layers were separated. The pentane layer was chromatographed on an Al_2O_3 column and the residue after evaporation was recrystallized from pentane to give 35 mg (12%) of mesRuC_6H_8 (IVb). After filtering the aqueous layer an excess of $NaBPh_4$ was added. The precipitate formed was filtered off, washed with water, dried over P_2O_5 and precipitated from acetone by ether to give 0.36 g (58%) of a pale yellow fine crystalline compound [mesRuC_6H_7]BPh_4 (VIa), m.p. 150—160°C (decomp.). Found: C, 75.67; H, 6.35; B, 1.97. $C_{39}H_{39}BRu$ calcd.: C, 75.60; H, 6.34; B, 1.74%.

If an excess of saturated NH_4PF_6 solution is added instead of $NaBPh_4$ solution, 0.21 g (47%) of [mesRuC_6H_7]PF_6 (VIb), m.p. 227—228°C (decomp.) will be formed. Found: C, 40.90; H, 4.43; P, 6.54. $C_{15}H_{19}F_6PRu$ calcd.: C, 40.45; H, 4.30; P, 6.95%.

Reduction of [mesRuC_6H_7]BPh_4 (VIa)

The mixture of complex VIa (0.31 g, 0.6 mmol) and $NaBH_4$ (0.05 g) in THF (10 ml) was stirred in an argon atmosphere at room temperature for 8 hours. Further treatment was carried out as previously described for reduction of complexes I—III to give 56 mg (37%) of IVb, m.p. 52—54°C.

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