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SYNTHESIS OF CATIONIC METALLOCYCLOPHANES WITH ARENE AND CYCLOPENTADIENYL LIGANDS

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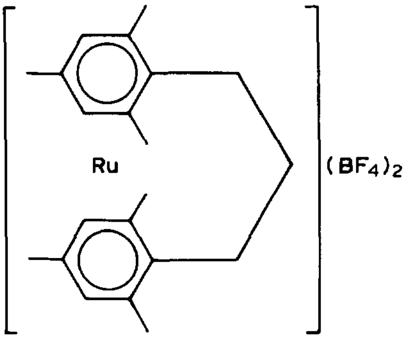
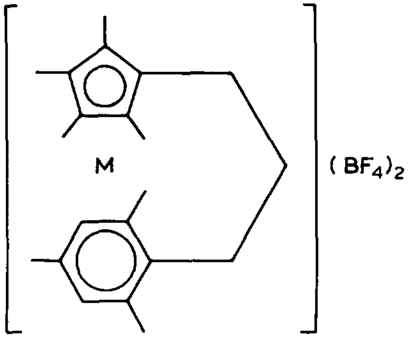
Summary

Previously unknown bridged cationic complexes (metallocyclophanes) with arene and cyclopentadienyl ligands have been obtained by ligand exchange in trifluoroacetic acid:





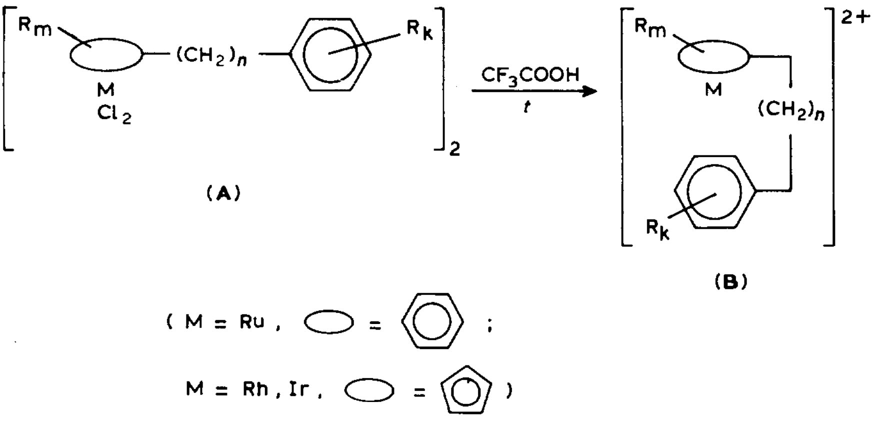
(M = Co , Rh , Ir)

Introduction

Cationic complexes are the least studied among the bridged cyclopentadienyl and arene complexes of transition metals, which have long attracted the attention of some chemists [1–5]. The synthesis of such compounds is thus of substantial interest and we have obtained a number of previously unknown compounds of this type by a simple and convenient method, developed in our laboratory for the synthesis of cationic complexes by exchanging ligands for arenes in strong protonic acids [6,7].

We have demonstrated previously that halogen ligands in dimeric complexes $[M(\eta\text{-}L)Cl_2]_2$ ($M = Ru$, $L =$ arene, $M = Rh, Ir$, $L = C_5Me_5$) are easily substituted by arenes in CF_3COOH with the formation of cationic complexes [6].

One might then expect that the metallocyclophanes (**B**) could be formed by intramolecular replacement of the halogen ligands (in complex **A**) by an arene fragment (eq. 1).

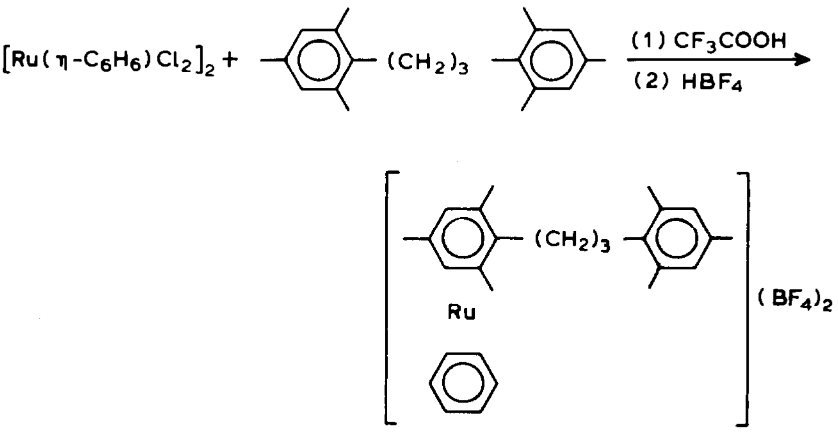


(1)

Results and discussion

A direct synthesis of type **A** dimers is difficult for ruthenium, thus, an indirect method was developed to obtain them. At first, we obtained the asymmetric cationic complex of ruthenium, I, by a technique developed earlier [6] (eq. 2). Complex I was then reduced to the neutral derivative II (eq. 3). From mass spectrometric data, only the unsubstituted benzene ligand was reduced, as had been observed previously [8]. After reaction with HCl, compound II was transformed into the desired dimer III (eq. 4).

The structure of complex III was confirmed by elemental analysis (see Table 1). Prolonged refluxing of a dilute solution of III in CF_3COOH (molar ratio ~ 1 : 1000)



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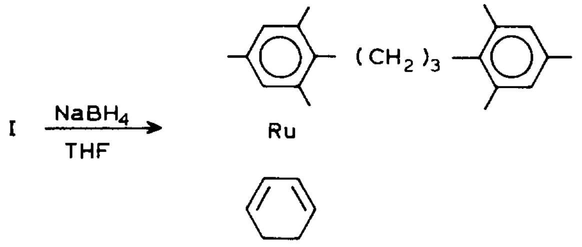
(I)



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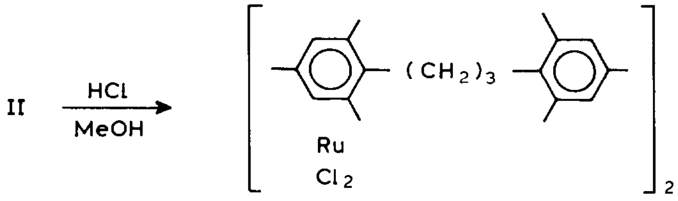

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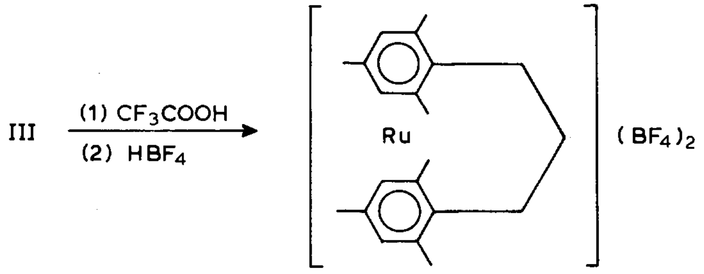


(5)

(IV)

resulted in intramolecular exchange of chloride ligands for arene fragments giving a bridged bisarene cation which was isolated in the form of the borofluoride, IV, in 90% yield [9] (eq. 5)

During product formation, the original orange color of the solution fades and after approximately 40 hours the solution is completely colorless. Complex IV was crystallized from $MeNO_2/EtOH$ as large colorless prisms. Its structure was confirmed by elemental analysis and ^1H NMR spectroscopy, in which 4 singlets with an intensity ratio of 2 : 3 : 3 : 6 are observed (see Table 2). It should be emphasized that as in previously known trimethylene bridges of ferrocenophane [10] and ruthenocenophane [11], in our case the bridged protons appear in the form of singlets. This can be accounted for by the fast bridge inversion which averages proton orientation and distances to the metal atom and, consequently, the magnetic environment of protons [12].

In order to rule out dimeric structure for complex IV, it was reduced with $NaBH_4$ in THF to a neutral bridged complex V, η^6-arene-η^4-cyclohexadiene (eq. 6).

$$\mathrm{IV} \xrightarrow[\mathrm{THF}]{\mathrm{NaBH_4}} \underset{\mathrm{(V)}}{[\eta^6\text{-}Me_3C_6H_2(CH_2)_3C_6H_4Me_3\text{-}\eta^4]Ru} \qquad (6)$$

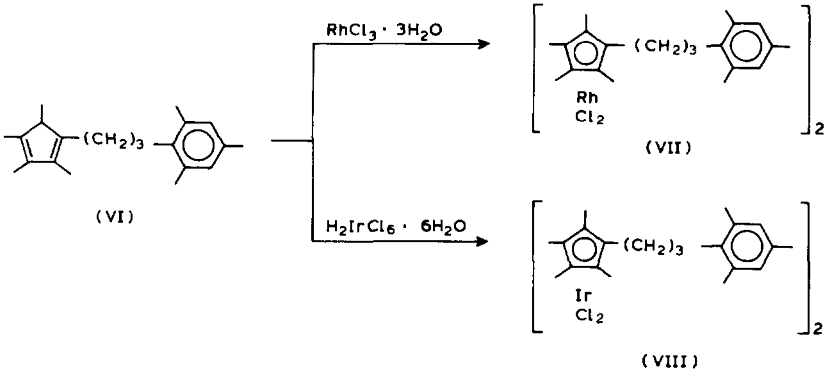
TABLE 1

YIELD AND ELEMENTAL ANALYSIS OF THE BRIDGED CYCLOPENTADIENYL OR ARENE CATIONIC COMPLEXES

No	Empirical formula	Yield (%)	Analysis (Found (calc) (%)) C	H	B/P	F/Cl
I	$C_{27}H_{34}B_2F_8Ru$	88	48.42 (48.44)	5.28 (5.37)	3.24 (3.11)	21.66 (21.89)
$III \cdot 2CHCl_3$	$C_{44}H_{58}Cl_{10}Ru_2$	91	46.69 (46.21)	5.20 (5.11)	–	–
IV	$C_{21}H_{28}B_2F_8Ru$	91	45.10 (45.43)	4.89 (5.08)	3.91 (3.89)	26.60 (27.38)
V	$C_{21}H_{30}Ru$	88	65.72 (65.76)	7.79 (7.88)	–	–
$VII \cdot CHCl_3$	$C_{43}H_{59}Cl_7Rh_2$	89	50.13 (50.14)	5.85 (5.77)	–	24.09 (24.10)
$VIII \cdot CHCl_3$	$C_{43}H_{59}Cl_7Ir_2$	84	42.89 (42.73)	5.10 (4.92)	–	20.67 (20.53)
$IX \cdot MeNO_2$	$C_{22}H_{32}B_2F_8NO_2Rh$	79	42.67 (42.68)	5.23 (5.21)	3.44 (3.49)	24.58 (24.55)
$X \cdot MeNO_2$	$C_{22}H_{32}B_2F_8IrNO_2$	81	37.49 (37.30)	4.45 (4.55)	3.09 (3.05)	21.51 (21.46)
XIII	$C_{23}H_{29}CoO_2$	64	70.22 (69.68)	7.66 (7.37)	–	–
XIVa	$C_{21}H_{29}B_2CoF_8$	68	49.42 (49.07)	5.59 (5.69)	4.11 (4.21)	29.83 (29.57)
$XIVb \cdot MeNO_2$	$C_{22}H_{32}CoF_{12}NO_2P_2$	69	38.33 (38.22)	4.40 (4.67)	8.83 (8.96)	32.93 (32.98)

The mass spectrum of the compound obtained shows a set of peaks with $[M]^+ = 381–386$ which corresponds to a natural mixture of ruthenium isotopes ^{99}Ru–^{104}Ru, confirming the monomeric structure of the neutral complex V and, consequently, of the cationic complex IV.

Dimers of type A have turned out to be more accessible for Rh and Ir because we succeeded in obtaining a diene ligand VI by a general method, that of preparing organyl-tetramethyl-cyclopentadienes [13]. Reaction of VI with $RhCl_3 \cdot 3H_2O$ or $H_2IrCl_6 \cdot 6H_2O$ directly produced the corresponding chlorides, VII and VIII (eq. 7).



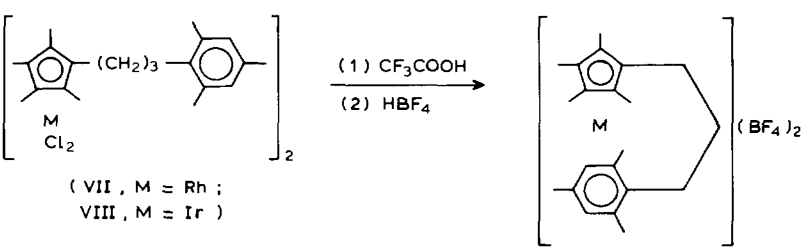
(7)

TABLE 2

^{1}H NMR SPECTROSCOPIC DATA (200 MHz)

No.	Solvent	δ C_6H_2	δ *o*-Me	δ *p*-Me	δ C_5Me_4	δ ($-CH_2CH_2CH_2-$) $C_5Me_4\underset{a}{CH_2}\underset{b}{CH_2}\underset{c}{CH_2}Me$	δ S [a]
IV	CF_3COOD	6.25 (4H) [b]	2.27 (12H)	2.34 (6H)	–	2.58 (6H)	–
VII·$CHCl_3$	$CDCl_3$	6.80 (2H)	2.21 (9H)		1.63 (6H) 1.66 (6H)	1.48 (2H), m (b) 2.43 (2H), t, *J* = 8 Hz (a) 2.62 (2H), t, *J* = 8 Hz (c)	7.27
VIII·$CHCl_3$	$CDCl_3$	6.79 (2H)	2.22 (9H)		1.60 (6H) 1.63 (6H)	1.52 (2H), m (b) 2.28 (2H), t, *J* = 8 Hz (a) 2.62 (2H), t, *J* = 8 Hz (c)	7.26
IX·$MeNO_2$	CF_3COOD	7.09 (2H)	2.45 (6H)	2.67 (3H)	2.08 (6H) 2.26 (6H)	2.35 (2H), broad s. (b) 2.61 (4H), (a,c)	4.40
X·$MeNO_2$	CF_3COOD	7.21 (2H)	2.52 (6H)	2.75 (3H)	2.16 (6H) 2.38 (6H)	2.33 (2H), m (b) 2.59 (4H) (a,c)	4.61
XIII	C_6D_6	6.76 (2H)	2.16 (9H)		1.65 (12H)	1.39 (2H), m (b) 2.24 (2H), m (a) 2.46 (2H), m (c)	–
XIVa	CF_3COOD	6.79 (2H)	2.51 (6H)	2.63 (3H)	1.93 (6H) 2.12 (6H)	2.30 (2H), broad s. (b) 2.79 (4H), broad s. (a,c)	–

[a] Chemical shift of solvent in crystal-solvate system. [b] Singlets in all cases if not otherwise specified.



(8)

(VII , M = Rh ;
VIII , M = Ir)

(IX , M = Rh ;
X , M = Ir)

The structure of complexes VII and VIII is confirmed by elemental analysis and by ^{1}H NMR spectroscopy. Subsequent refluxing in CF_3COOH induces cyclization as a result of the intramolecular coordination of an arene fragment to the metal atom and this favors the formation of arene-cyclopentadienyl cationic metallocyclophanes which can be isolated as the borofluorides, IX and X (eq. 8). Completion of reaction is indicated by disappearance of the initial characteristic color. It should be noted that in the case of rhodium and iridium the reaction proceeds faster than in the case of ruthenium. The structure of the bridged complexes IX and X is confirmed by elemental analysis and by ^{1}H NMR spectroscopy (see Tables 1 and 2). Non-equivalence of cyclic ligands in these complexes leads to magnetic non-equivalence of the methylene protons and this is reflected in the ^{1}H NMR spectra.

In the case of cobalt, the dimeric chloride $[C_5Me_5CoCl_2]_2$ is less readily available than the carbonyl complex $C_5Me_5Co(CO)_2$ (XI) [14,15]. So, we tried to use the more readily available complex XI as starting compound for the synthesis of the cationic arene complexes $[Co(\eta\text{-}C_5Me_5)(\eta\text{-arene})]X_2$. It was found that the desired η-arene-η-pentamethyl-cyclopentadienyl complexes of cobalt could be obtained from XI in one step by refluxing with arenes in CF_3COOH in an inert atmosphere [7]:

$$\underset{(XI)}{Co(\eta\text{-}C_5Me_5)(CO)_2} \xrightarrow[CF_3COOH]{\text{arene}} \underset{(XIIa-XIId)}{[Co(\eta\text{-}C_5Me_5)(\eta\text{-arene})]X_2} \qquad (9)$$

(XIIa : arene = $1,3,5\text{-}Me_3C_6H_3$, X = BF_4 ;
XIIb : arene = $1,3,5\text{-}Me_3C_6H_3$, X = PF_6 ;
XIIc : arene = C_6Me_6 , X = BF_4 ;
XIId : arene = C_6Me_6 , X = PF_6)

The structure of the compounds obtained is confirmed by elemental analyses and by ^{1}H NMR spectroscopy (see Table 3). In this reaction formation of cationic arene complexes is accompanied by oxidation of Co^I to Co^{III}. It should be emphasized that under such conditions a similar rhodium complex also produces arene complexes, for example see eq. 10.

$$Rh(\eta\text{-}C_5Me_5)(CO)_2 + 1,3,5\text{-}Me_3C_6H_3 \xrightarrow[(2)\ HPF_6]{(1)\ CF_3COOH} [Rh(\eta\text{-}C_5Me_5)(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)](PF_6)_2 \qquad (10)$$

However, the yield (60%) in this case is less than when $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ is used

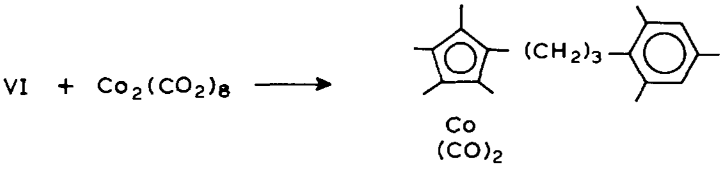
TABLE 3

ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES XIIa–XIId

No	Yield (%)	Analysis (Found (calc)(%))		Empirical formula	^{1}H NMR spectra			
		C	H		δ C_5Me_5	δ Me (in arene)	δ arom.	Solvent
XIIa	72	46.67 (46.96)	5.62 (5.60)	$C_{19}H_{27}B_2CoF_8$	2.13	2.49	6.80	CF_3COOD
XIIb	69	38.34 (37.89)	4.15 (4.52)	$C_{19}H_{27}CoF_{12}P_2$	2.15	2.64	6.98	CF_3COOD
XIIc	78	49.52 (50.04)	6.35 (6.30)	$C_{22}H_{33}B_2CoF_8$	1.52	2.16	–	CD_3COCD_3
XIId	79	40.63 (40.88)	4.98 (5.15)	$C_{22}H_{33}CoF_{12}P_2$	2.03	2.60	–	CD_3COCD_3

as starting material [6], besides, $C_5Me_5Rh(CO)_2$ is obtained from the dichloride by treating it with CO in the presence of zinc dust [16]. Therefore, it must be said that the method based on $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ is more preferable for preparing cationic $[Rh(\eta\text{-}C_5Me_5)(\eta\text{-arene})]^{2+}$ complexes [6].

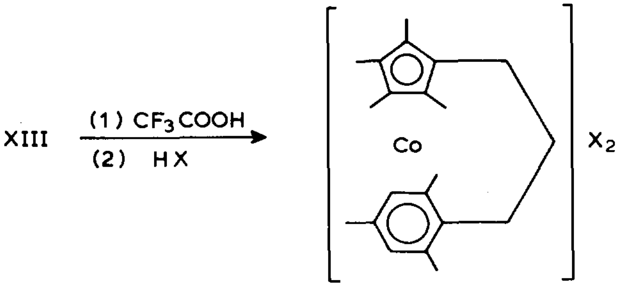
The exchange reaction of carbonyl ligands for arenes, discovered by us, was used to obtain cobalt derivatives similar to IX and X. At first, the initial complex, XIII, was obtained by reaction of VI with $Co_2(CO)_8$:



(XIII)

(11)

Its structure is confirmed by elemental analysis and from its IR, ^{1}H NMR and mass spectra. Refluxing a dilute solution of this complex in CF_3COOH produced a metallocyclophane cation which was isolated as the borofluoride or as the hexafluorophosphate:



(12)

(XIVa : X = BF4 ; XIVb : X = PF6)

The structure of both products is confirmed by elemental analysis and by ^{1}H NMR spectroscopy. All cationic metallocyclophanes obtained in this work are crystals which are stable in air and neither melt nor decompose at temperatures up to 250 °C.

Thus, the method developed for synthesis of cationic arene complexes with the use of strong protonic acids proved to be a convenient route to some new metallocyclophanes.

Experimental

Synthesis and isolation of substances were carried out in absolute solvents, while the neutral complexes Ru^0 and Co^I were treated under argon. Experiments performed in refluxing CF_3COOH were protected from moisture in the air. ^1H NMR spectra were obtained on Bruker WP-200 SY (200MHz) and Perkin–Elmer R-12 (60 MHz) instruments, with TMS as internal reference. IR spectra were recorded on a UR-20 spectrophotometer. Mass spectra were recorded on an AEI MS-30 spectrometer equipped with a DS-50 data processing system at an ionizing energy of 70 eV.

Preparation of 1,3-dimesitylpropane

To a mixture of $LiAIH_4$ (6,6 g, 0.175 mol) and anhydrous $AICI_3$ (46.7 g, 0.35 mol) in ether (300 ml) was added dropwise a solution of 1,3-dimesitylpropanon-1 [17] (29.4 g, 0.1 mol) in ether (150 ml), with stirring for 0.5 h. The reaction mixture was then stirred for another 2 h under reflux, then cooled with ice, and unchanged reactants decomposed by successively adding ethylacetate, water and dilute H_2SO_4. The ether layer was separated, dried with $CaCl_2$, and filtered off. The solvent was then removed in vacuo and the residue recrystallized from alcohol. 1,3-Dimesitylpropane was obtained as colorless crystals, (24.8 g, 88%) m.p. 125–126 °C. Found: C 89.46, H 10.22. $C_{21}H_{28}$ calc: C 89.94, H 10.06%. ^1H NMR spectrum (60 MHz, $CDCI_3$): 1.58 (m, 2H, $CH_2\mathit{CH_2}CH_2$), 2.25 (c, 6H, *p*-Me), 2.29 (c, 12H, *o*-Me), 2.67 (t, 4H, $\mathit{CH_2}CH_2\mathit{CH_2}$), 6.96 (c, 4H, C_6H_2).

Preparation of $[Ru(\eta\text{-}C_6H_6)(\eta^6\text{-}Me_3C_3H_2C_3H_6C_6H_2Me_3)](BF_4)_2$ *(I)*

A mixture of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (1.0 g, 2 mmol) and 1,3-dimesitylpropane (11.2 g, 40 mmol) in CF_3COOH (300 ml) was refluxed for 2 h until the original orange color had disappeared. An excess of ligand was used so as to avoid formation of the binuclear product. After cooling, the excess of ligand was filtered off, and the filtrate reduced in volume to 10 ml. Aqueous HBF_4 (2 ml, 48%) was added to the filtrate, after which the solution was evaporated to dryness in vacuo. The residue was washed with ether and recrystallized from the $MeNO_2$/EtOH mixture. For the yield and elemental analysis see Table 1. The substance contains one $MeNO_2$ of crystallization, ^1H NMR spectrum (60 MHz, CF_3COOD): 2.12 (c, 3H, *p*-Me), 2.27 (c, 6H, *o*-Me), 2.49 (c, 3H, *p*-Me), 2.58 (c, 6H, *o*-Me), 4.36 (c, 3H, $MeNO_2$), 6.96 (c, 2H, C_6H_2), 7.00 (c, 6H, C_6H_6), 7.07 (c, 2H, C_6H_2).

Preparation of $Ru(\eta^6\text{-}Me_3C_6H_2C_3H_6C_6H_2Me_3)(\eta\text{-}C_6H_8)$ *(II)*

A mixture of complex I (1.4 g, 2 mmol) and $NaBH_4$ (0.2 g, 5.2 mmol) in THF (30 ml) was stirred at room temperature for 8 h. Pentane (30 ml) was added, the reaction mixture filtered off, and the filtrate evaporated to dryness in vacuo. The residue was extracted with pentane, and subjected to column chromatography on deactivated Al_2O_3(5% H_2O) with pentane as eluant. The pale yellow layer was collected and the solvent evaporated off in vacuo giving a pale yellow oil (0.79 g, 86%). Mass spectrum: 459–464 ($[M]^+$), 379–384 ($[M-C_6H_8]^+$).

Preparation of $[Ru(\eta^6\text{-}Me_3C_6H_2C_3H_6C_6H_2Me_3)Cl_2]_2$ *(III)*

To a solution of II (0.92 g, 2 mmol) in MeOH (20 ml) was added concentrated HCl (1 ml) and the mixture was stirred for 1 h. The precipitate was filtered off and recrystallized from a mixture of $CHCl_3$/EtOH. Dark red crystals (1.04 g) of complex III with two $CHCl_3$ of crystallization were obtained. The compound decomposed without melting at 210–230°C. For yield and elemental analysis see Table 1.

Preparation of $[Ru(\eta^{12}\text{-}Me_3C_6H_2C_3H_6C_6H_2Me_3)](BF_4)_2$ *(IV)*

A solution of complex III (0.57 g, 0.5 mmol) was refluxed in CF_3COOH (80 ml) for 40 h until the initial orange color had disappeared. Most of the CF_3COOH was distilled off, then 48% aqueous HBF_4 (0.5 ml) was added, and the mixture evaporated to dryness in vacuo. The residue was washed with ether and recrystallized from a $MeNO_2$/EtOH mixture. Complex IV (0.50 g, 91%) was obtained as large colorless prisms.

Reduction of complex IV

A mixture of complex IV (0.28 g, 0.5 mmol) and $NaBH_4$ (0.1 g, 2.6 mmol) in THF (20 ml) was stirred at room temperature for 20 h. Pentane (20 ml) was added and the solution filtered and evaporated to dryness in vacuo. The residue was recrystallized from pentane at −78°C. The complex, $Ru[\eta^6\text{-}Me_3C_6H_2(CH_2)_3\text{-}C_6H_4Me_3\text{-}\eta^4]$ (V) (0.17 g, 88%), was obtained in the form of pale yellow crystals, m.p. 130–135°C, $[M]^+ = 381$–386.

Preparation of tetramethyl-γ-mesityl-propyl-cyclopentadiene (VI)

To chipped lithium (3.1 g, 0.44g-a) in ether (500 ml) was added a small amount of 2-bromobut-2-ene (29.7 g in all, 0.22 mmol) with stirring. After reaction initiation, 2-bromobut-2-ene was added at a rate so as to keep ether under steady reflux, the mixture was then stirred for 1 h. A solution of the ethyl ester of γ-mesityl-butyric acid (23.4 g, 0.1 mol) (obtained by esterification of acid [18] (b.p. 98–99°C/0.01 ml) in ether (100 ml)) was then added dropwise. The mixture was stirred for 2 h and poured into the saturated aqueous NH_4Cl (300 ml). The ether layer was separated off, the water layer acidified with HCl to a pH ~ 9, and extracted three times with ether. The combined ether layers were dried over Na_2SO_4 and the volume reduced to ~ 100 ml. The concentrate obtained was added rapidly, with vigorous stirring to a $p\text{-}MeC_6H_4SO_3H \cdot H_2O$ (2 g) in ether (100 ml). This was almost immediately followed by vigorous boiling and separation of water. When boiling had subsided, the mixture was stirred for 15 min and poured into a solution of Na_2CO_3 (1 g) in saturated aqueous $NaHCO_3$ (100 ml). The ether layer was separated and the water layer extracted three times with ether. Combined ether extracts were dried over Na_2SO_4, ether was evaporated off, and the residue distilled in vacuo (131–132°C/0.01 mm). The yield of compound was 23.7 g, 84%. Found: C, 89.08; H, 10.53. $C_{21}H_{30}$ calc: C, 89.29; H 10.71%. Mass spectrum: $[M]^+ = 282$.

Preparation of $[Rh(\eta^5\text{-}C_5Me_4C_3H_6C_6H_2Me_3)Cl_2]_2$ (VII)

The mixture of $RhCl_3 \cdot 3H_2O$ (1.05 g, 4 mmol) and compound VI (1.4 g, 5 mmol) in MeOH (30 ml) was refluxed under argon for 8 h with stirring. After cooling the solvent was removed in vacuo, and the residue washed with ether and recrystallized from $CHCl_3$/EtOH. Dark red crystals of complex VII (1.83 g), with one $CHCl_3$ of crystallization, were obtained, m.p. 138–143°C.

Preparation of $[Ir(\eta^5\text{-}C_5Me_4C_3H_6C_6H_2Me_3)Cl_2]_2$ (VIII)

As for complex VII, orange crystals of complex VIII (1.02 g), with one $CHCl_3$ of crystallization were obtained by treating $H_2IrCl_6 \cdot 6H_2O$ (1.03 g, 2 mmol) with compound VI (2.3 g, 8 mmol). The compound neither melts nor decomposes when heated to 250°C.

Preparation of $[Rh(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2$ (IX)

The solution of complex VII (0.52 g, 0.5 mmol) in CF_3COOH (80 ml) was refluxed for 3 h until the initial orange color had disappeared. After most of the solvent had distilled off, 48% aqueous HBF_4 (0.5 ml) was added to the residue, and the mixture evaporated to dryness in vacuo. The residue was washed with ether and recrystallized from $MeNO_2$/EtOAc. Pale yellow crystals (0.49 g) of complex IX, with one $MeNO_2$ of crystallization, were obtained.

Preparation of $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2$ (X)

As for the previous case, colorless crystals of complex X (0.57 g), with one $MeNO_2$ of crystallization, were obtained from complex VIII (0.6 g, 0.5 mmol) in CF_3COOH (80 ml) after refluxing for 1 h.

Preparation of $[Co(\eta\text{-}C_5Me_5)(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)](BF_4)_2$ (XIIa)

A solution of $Co(\eta\text{-}C_5Me_5)(CO)_2$ (0.125 g, 0.5 mmol) (XI) and mesitylene (0.5 ml) in CF_3COOH was refluxed for 18 h and cooled. 48% aqueous HBF_4 (0.3 ml) was added to the solution and the mixture evaporated to dryness in vacuo. The residue was washed with ether and reprecipitated from $MeNO_2$ with ether. A yellow solid, XIIa, was obtained. For data see Table 3. Hexamethylbenzene complex XIIc was obtained in a similar way.

Preparation of $[Co(\eta\text{-}C_5Me_5)(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)](PF_6)_2$ (XIIb)

A solution of complex XI (0.125 g, 0.5 mmol) and mesitylene (0.5 ml) in CF_3COOH (3 ml) was refluxed for 18 h. The solvent was then removed in vacuo and the residue dissolved in water (~ 5 ml). After addition of NH_4PF_6 (0.2 g) a yellow precipitate of complex XIIb separated. It was filtered off, washed with water, dried in air, and reprecipitated from nitromethane with ether.

Complex XIId was obtained in a similar way.

Preparation of $Co(\eta\text{-}C_5Me_4C_3H_6C_6H_2Me_3)(CO)_2$ (XIII)

A mixture of $Co_2(CO)_8$ (1.03 g, 3 mmol) and compound VI (1 g, 6 mmol) was refluxed in CH_2Cl_2 (10 ml) for 1 h, the solvent was removed in vacuo, and the residue chromatographed on a column with deactivated Al_2O_3 (5% H_2O). A bright red layer which was eluted with hexane yielded dark red crystals (1.53 g, m.p. 48–50°C) of complex XIII after evaporation in vacuo, and crystallization from pentane at −78°C. Mass spectrum: $[M]^+ = 396$.

Preparation of $[Co(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2$ *(XIVa)*

A solution of complex XIII (0.4 g, 1 mmol) in CF_3COOH (80 ml) was refluxed for 8 h until evolution of gas had ceased. After most of the solvent had been removed 48% aqueous HBF_4 (0.5 ml) was added and the mixture evaporated to dryness in vacuo. The residue was washed with ether and recrystallized from $MeNO_2/EtOAc$. Pale yellow crystals of complex XIVa (0.35 g) were obtained.

Preparation of $[Co(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](PF_6)_2$ *(XIVb)*

The reaction was similar to that above. The solvent was removed in vacuo, the residue dissolved in water (5 ml), and an excess of NH_4PF_6 added. The precipitate was filtered off, washed with water (~ 5 ml), dried, and recrystallized from $MeNO_2/EtOAc$. Pale yellow crystals (0.48 g) of complex XIVb, with one $MeNO_2$ of crystallization, were obtained.

References

1 A.N. Nesmeyanov, L.P. Yur'eva, N.N. Zaitseva, G.A. Domrachev and V.D. Zinov'ev, J. Organomet. Chem., 153 (1978) 181

2 T.N. Sal'nikova, V.G. Andrianov, Yu.T. Struchkov, L.P. Yur'yeva and N.N. Zaitseva, Koord. Khim., 4 (1978) 288.

3 A.R. Koray, M.L. Ziegler, M.E. Blak and M.W. Haenel, Tetrahedron Lett., (1979) 2465.

4 C. Elschenbroich, R. Möckel and U. Zenneck, Angew. Chem. Int. Ed. Engl., 17 (1978) 531.

5 A.N. Nesmeyanov, M.V. Tolstaya, M.I. Rybinskaya, G.B. Shul'pin, N.G. Bokii, A.S. Batsanov and Yu. T. Struchkov, J. Organomet. Chem., 142 (1977) 89.

6 M.I. Rybinskaya, A.R. Kudinov and V.S. Kaganovich, J. Organomet. Chem., 246 (1983) 279.

7 M.I. Rybinskaya, V.S. Kaganovich and A.R. Kudinov, in O.A. Reutov (Ed.), Advances in Organometallic Chemistry, MIR, Moscow, 1984, 117–127.

8 M.I. Rybinskaya, V.S. Kaganovich and A.R. Kudinov, J. Organomet. Chem., 235 (1982) 215.

9 M.I. Rybinskaya, V.S. Kaganovich and A.R. Kudinov, Izv. AN SSSR, Ser. Khim., (1984) 1672.

10 M. Rosenblum, A.K. Banerjee, N. Daniele and R.W. Fish, J. Amer. Chem. Soc., 85 (1963) 316.

11 S. Kamiyama, T.M. Suzuki, T. Kimura and A. Kazahara, Bull. Soc. Chem. Jap., 51 (1978) 909.

12 E.W. Abel, M. Booth, C.A. Brown, K.G. Orrell and R.L. Woodford, J. Organomet. Chem., 214 (1981) 93.

13 R.S. Threlkel and J.E. Bercaw, J. Organometal. Chem., 136 (1977) 1.

14 L.M. Cirjak, R.E. Ginsburg and L.F. Dahl, Inorg. Chem., 21 (1982) 940.

15 M.J. Macazaga, S. Delgado, R.M. Medina and J.R. Masaguer, J. Organomet. Chem., 277 (1984) 423.

16 J.W. Kang and P.M. Maitlis, J. Organomet. Chem., 26 (1971) 393.

17 R.C. Fuson and C.H. McKeever, J. Amer. Chem. Soc., 62 (1940) 2088.

18 R.C. Fuson and J.S. Meek, J. Org. Chem., 10 (1945) 551.