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η^6-Arene-η^5-Cyclopentadienylruthenium Complexes and Related Systems

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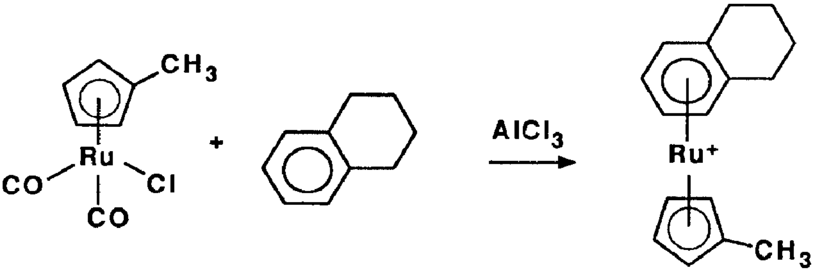
1. Introduction

The ability of ruthenium to form stable complexes with π-hydrocarbons is well reported and plays a significant role in various aspects of analytical, biological, theoretical, catalytic and general chemistry. It is the aim of this article to review η^6-arene-η^5-cyclopentadienylruthenium(II) and related bis(arene)ruthenium(II) complexes, outlining the generalities of the subject matter. We hope to introduce the area to synthetic as well as heterocyclic chemists and biochemists and stimulate their activity in the field, and lead to the synthesis of complex organic and bioorganometallic molecules.

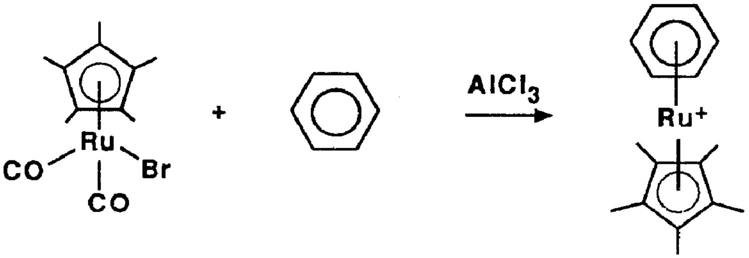
2. η^6-Arene(η^5-cyclopentadienyl)ruthenium(II) Complexes

2.1. Synthesis using $CpRuL_3$ complexes

Coffield et al [1] isolated the first mixed ruthenium sandwich complex having a Cp and an arene ligand. A reaction between tetralin and (η^5-methylcyclopentadienyl) dicarbonylruthenium chloride in the presence of $AlCl_3$ yielded the (η^6-tetralin) (Cp)ruthenium(II) complex (eq. 1) which was precipitated by the addition of sulfate anion (Na_2SO_4). However, the details of this work are not available except as described in a brief patent. Recently, this method has been successfully used for the synthesis of (η^6-benzene)(η^5-pentamethylcyclopentadienyl)ruthenium(II) complex from (η^5-C_5Me_5) dicarbonylruthenium bromide (eq. 2). The resulting complex has been isolated as its hexafluorophosphate salt in 34% yield [2]. In a different approach, Haines et al [3a-c]

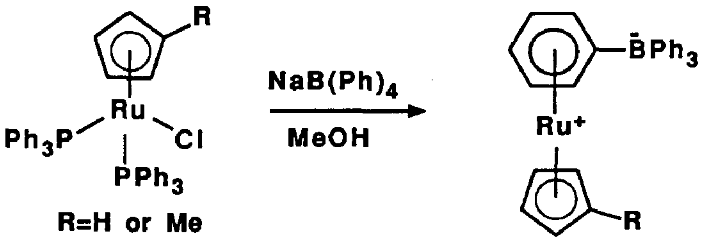


(eq. 1)



(eq. 2)

isolated the zwitterionic (η^6-tetraphenylborate)(η^5-Cp)ruthenium(II) from the reaction between (η^5-Cp)bis(triphenylphosphine) ruthenium chloride and sodium tetraphenylborate in methanol. They also carried out a similar reaction with (η^5-methylcyclopentadienyl)bis(triphenylphosphine)ruthenium chloride (eq. 3).

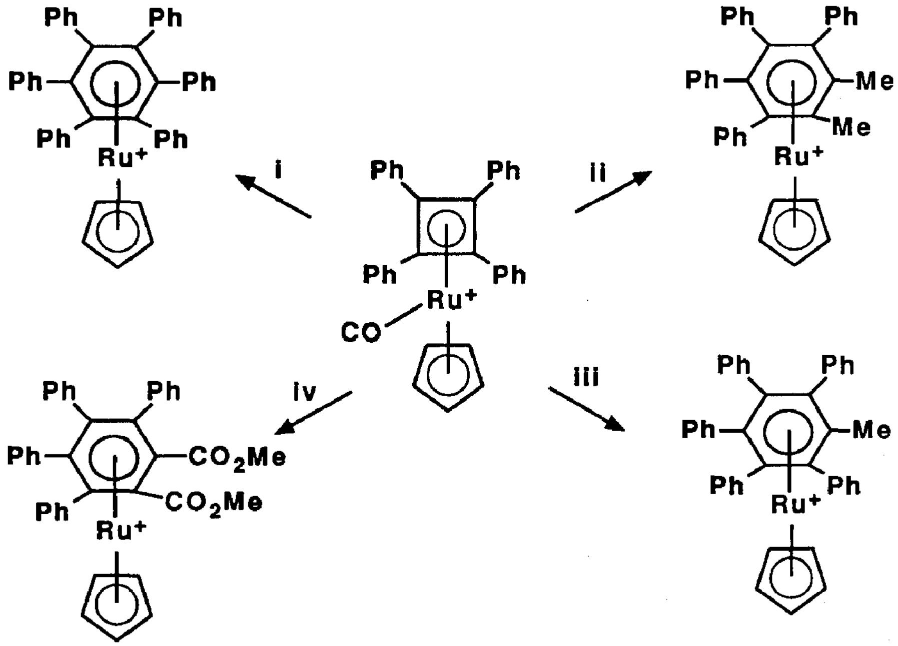


(eq. 3)

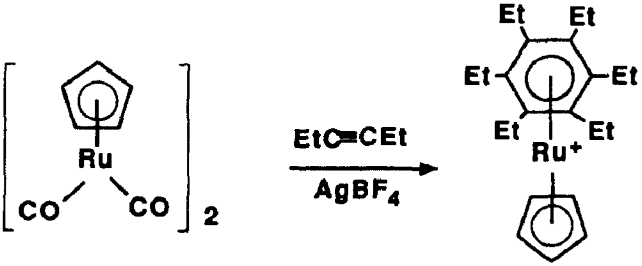
2.2. Synthesis using $CpRuL_2$ complexes

A number of sterically hindered (η^6-arene)(η^5-cyclopentadienyl)ruthenium(II)

Scheme I



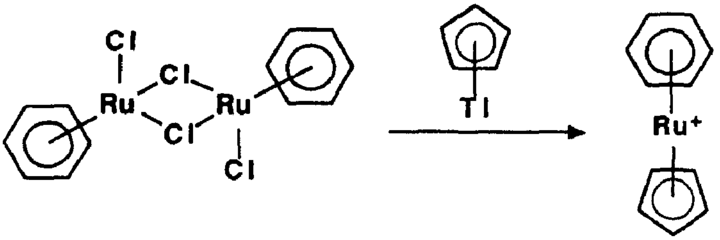
i) Ph_2C_2/UV, ii) Me_2C_2/UV, iii) PhC_2Me/UV, iv) $(MeO_2C)_2C_2$/UV complexes have been synthesized [4]. Under photochemical conditions, the cationic η^4-tetraphenylcyclobutadiene complex, $[(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}Cp)(CO)Ru]BF_4$ undergoes cycloaddition of alkyne $R^1\text{-}C{\equiv}C\text{-}R^2$ (R^1,R^2 = Ph, Me, CO_2Me; R^1 = Ph, R^2 = Me) accompanied by decarbonylation to give the arene sandwich complex $[(\eta^6\text{-}C_6(Ph)_4R^1R^2)(Cp)Ru]BF_4$ (Scheme 1). Interestingly, the (η^6-hexaethylbenzene)(Cp)ruthenium complex [4] has been obtained in a one pot reaction between cyclopentadienyldicarbonyl ruthenium dimer with excess EtC≡CEt in the presence of $AgBF_4$ (eq. 4).



(eq. 4)

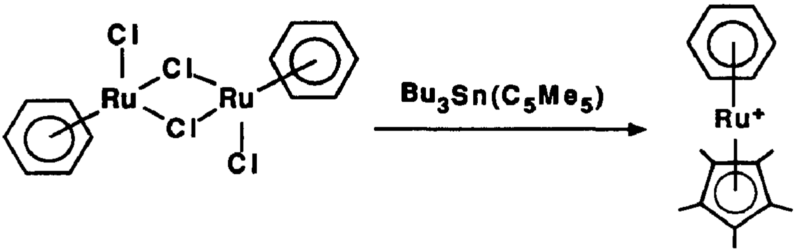
2.3. Synthesis using (η^6-arene)ruthenium dichloride dimer

In 1972, Zelonka and Baird [5] briefly described the reaction between (η^6-benzene)ruthenium dichloride dimer and cyclopentadienylthallium in MeCN at room temperature which produces the mixed sandwich complex, [(η^6-benzene)(η^5-cyclopentadienyl)ruthenium]Cl (eq. 5). Later this method was used by Robertson et al. [6]



(eq. 5)

for the synthesis of a series of new (η^6-arene)(Cp)ruthenium complexes (arene = benzene, p-cymene, anisole and hexamethylbenzene). Most of these complexes were precipitated as tetraphenylborate salts in 50-80% yields (eq. 5). Table 1 lists the complexes prepared according to the method of Zelonka and Baird. Utilizing a similar methodology, Mann et al. [2] reported a synthesis of a (η^6-benzene)(η^5-pentamethylcyclopentadienyl)ruthenium(II) complex from the reaction of (η^6-benzene)ruthenium dichloride dimer with $Bu_3Sn(C_5Me_5)$ in refluxing acetonitrile (Eq. 6) [2]. The major



(eq. 6)

drawback of Zelonka and Baird's procedure is the problem of obtaining appropriately substituted cyclohexadienes which are key chemicals for the preparation of the initial (η^6-arene)ruthenium dichloride dimers.

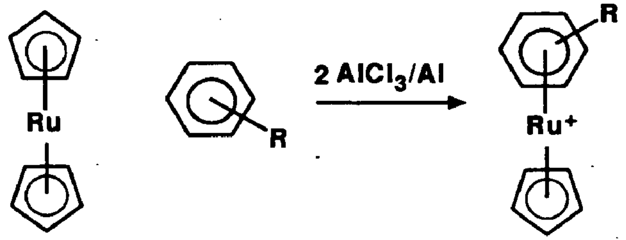
Table 1

[(η^6-Arene)(Cp)Ru]X Complexes Prepared via a Reaction Between [(η^6-arene)RuCl$_2$]$_2$ and CpTl

Arene	MP(°C)	X	Yield%	References
Benzene	161	Cl	83	5
	288~290	PF_6	61	11
Anisole	123~125	BPh_4	41	6
p-Cymene	168-169	BPh_4	82	6
Hexamethylbenzene	252	BPh_4	64	6

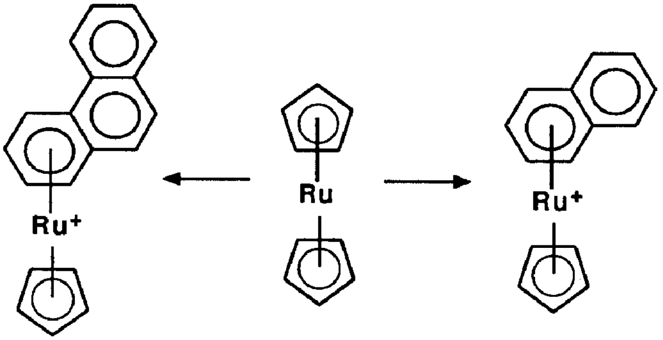
2.4. Synthesis using ruthenocene and derivatives

Aluminum chloride catalyzed ligand exchange reaction between one cyclopentadienyl (Cp) ring of ruthenocene and arenes has been used for the synthesis of mixed (η^6-arene) (Cp) ruthenium(II) complexes (eq. 7). Ruthenocene exchanges its Cp ring for an arene with more difficulty than does ferrocene. Nesmeyanov et al. [7] and Astruc et al. [8] independently reported low yields (3-10%) of products resulting from exchange reactions of ruthenocene with an arene to yield (η^6-arene)(Cp)ruthenium(II) complexes. An



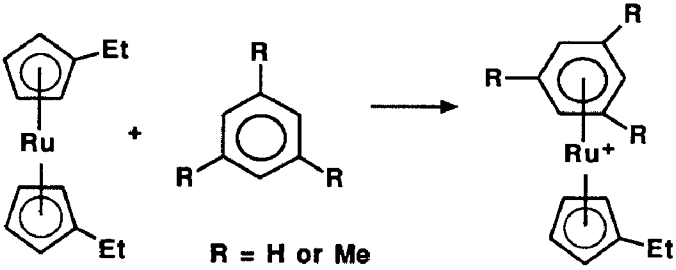
(eq. 7)

important factor in raising the yield of these complexes (up to 66% in some cases) is the presence of a few drops of water [8,9]. The stoichiometry of the reactants generally is $Cp_2Ru/AlCl_3/H_2O$/Arene: 1/3/1/1-5 drops/excess. The reaction times and temperatures reported range from 4-16 h and 100-190°C, respectively. In the case of solid arenes the reaction is carried out in an inert solvent such as heptane, octane, nonane or decalin [9]. Complexation of halobenzenes (C_6H_5Cl and C_6H_5F) was carried out with Al dust to avoid dehalogenation. Demethylation problems are encountered in this method with ethylbenzene and hexamethylbenzene [8,9]. However, (η^6-hexamethylbenzene)(Cp)ruthenium complex can be obtained in pure form if the exchange reaction is carried out at 130°C in octane with the hexamethylbenzene/Cp_2Ru ratio 2/1. It is possible to complex naphthalene or phenanthrene selectively with one $[CpRu(II)]^+$ group using suitable conditions (eq. 8).

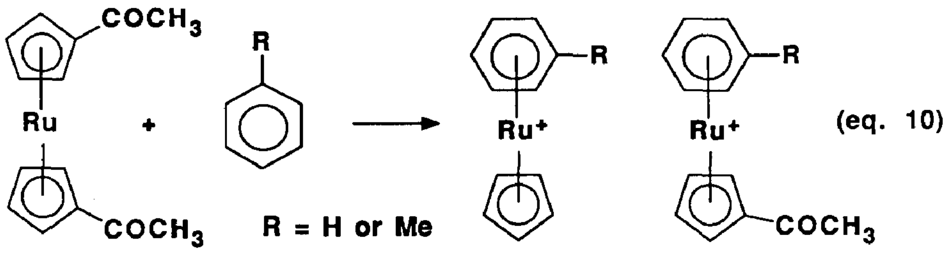


(eq. 8)

Complexes prepared via ligand exchange reaction are given in Table 2. The ligand exchange reaction between 1,1'-diethylruthenocene and benzene or mesitylene gave low yields [10] of corresponding mixed sandwich complexes (Eq. 9). Similarly, reaction between 1,1'-diacetylruthenocene and benzene or toluene gave mixed π-complexes with substituted and unsubstituted cyclopentadienyl ligands in very low yields (eq. 10) [10]. However, the



(eq. 9)



(eq. 10)

Table 2

[(η^6-Arene)(η^5-cyclopentadienyl)ruthenium]X Complexes via Cp/Arene Exchange of Cp_2Ru with an Arene in the Presence of $AlCl_3$

Arene[a]	MP(°C)	X	Yield%	References
Benzene	-	BF_4	66	9
	-	PF_6	7	7b
	248	BPh_4	-	7b
Toluene	260	BF_4	6	7b
Ethylbenzene	251~252	PF_6	25	9
Biphenyl	129~131	PF_6	3	9
Hexamethylbenzene[b,e]	-	BF_4	25	9
	-	PF_6	10	8
Phenanthrene[b]	132~140	BF_4	0.4	9
Naphthalene[b]	125~130	BF_4	13	9
Chlorobenzene[c]	209~212	PF_6	40	9
Fluorobenzene[d]	-	BF_4	13	9
Anisole[b]	126~132	BF_4	1.1	9
Mesitylene[f]	195	PF_6	50	8

a. $Cp_2Ru/AlCl_3/Al$ (1/3/1); H_2O (1~5 drops) except for ethylbenzene: arene was in excess.

b. Solvent used: hexamethylbenzene (octane); phenanthrene and naphthalene (heptane) and anisole (nonane).

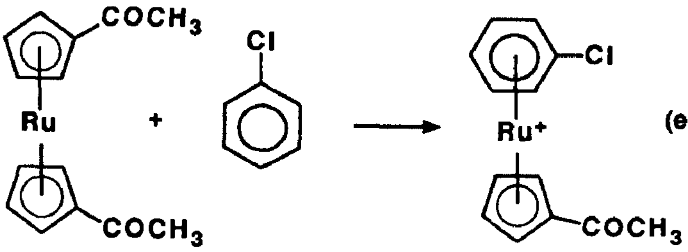
c. $Cp_2Ru/AlCl_3/Al$ (1/3/0.3).

d. $Cp_2Ru/AlCl_3/Al$(1/4/0) yield 13%; 1/3/0 yield 23%.

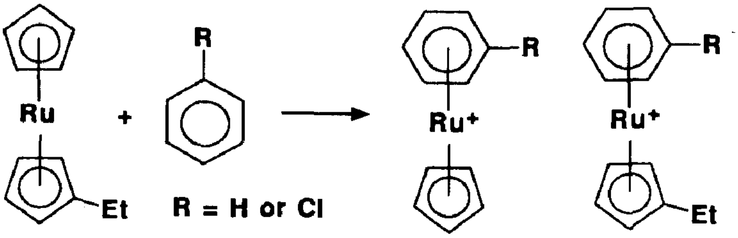
e. $Cp_2Ru/AlCl_3/H_2O$ (1/2/0)

f. $Cp_2Ru/AlCl_3/H_2O$ (1/3/1)

exchange reaction between chlorobenzene and 1,1'-diacetylruthenocene is reported to yield one product (eq.11). The ligand exchange reactions of ethylruthenocene with benzene or chlorobenzene are reported to give sandwich complexes bearing substituted and unsubstituted Cp ligands (eq. 12) [10]. The product ratio varies from experiment to experiment. On the other hand, the exchange reaction between acetylruthenocene and benzene or toluene gave complexes having an unsubstituted cyclopentadienyl ligand (eq. 13). Table 3 lists the mixed sandwich complexes which have been obtained via ligand exchange reaction from di- and monosubstituted ruthenocenes.



(eq. 11)



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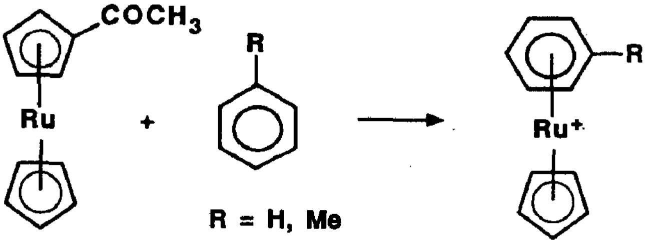


(eq. 13)

Table 3

[(η^6-Arene)(η^5-C_5H_4R)ruthenium]PF_6 Complexes from Substituted Ruthenocenes

Ruthenocene	Arene	R	References
$(C_2H_5C_5H_4)Ru$	Benzene	C_2H_5	10
	Mesitylene	C_2H_5	10
$(CH_3COC_5H_4)_2Ru$	Benzene	mixture	10
	Toluene	mixture	10
	Chlorobenzene	CH_3CO	10
$(C_2H_5C_5H_4)(C_5H_5)Ru$	Benzene	C_2H_5(H)	10
	Chlorobenzene	mixture	10
$(CH_3COC_5H_4)(C_5H_5)Ru$	Benzene	H	10
	Toluene	H	10

a. Nonane used as a diluent.

b. Al dust was not used.

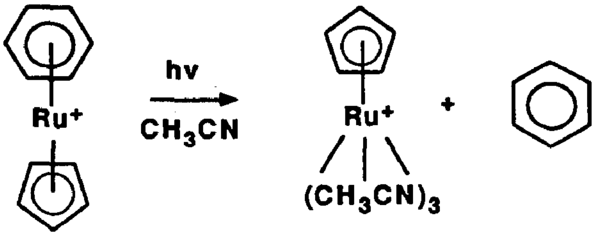
c. Mixture of [arene(C_5H_5)Ru]PF_6 and [arene($C_5H_4COCH_3$)Ru]PF_6

d. Mixture of [C_6H_5Cl(C_5H_5)Ru]PF_6 and [C_6H_5Cl($C_5H_4C_2H_5$)Ru]PF_6

f. No H_2O added.

2.5. Synthesis using (CpRu(MeCN)$_3$]PF_6 complex

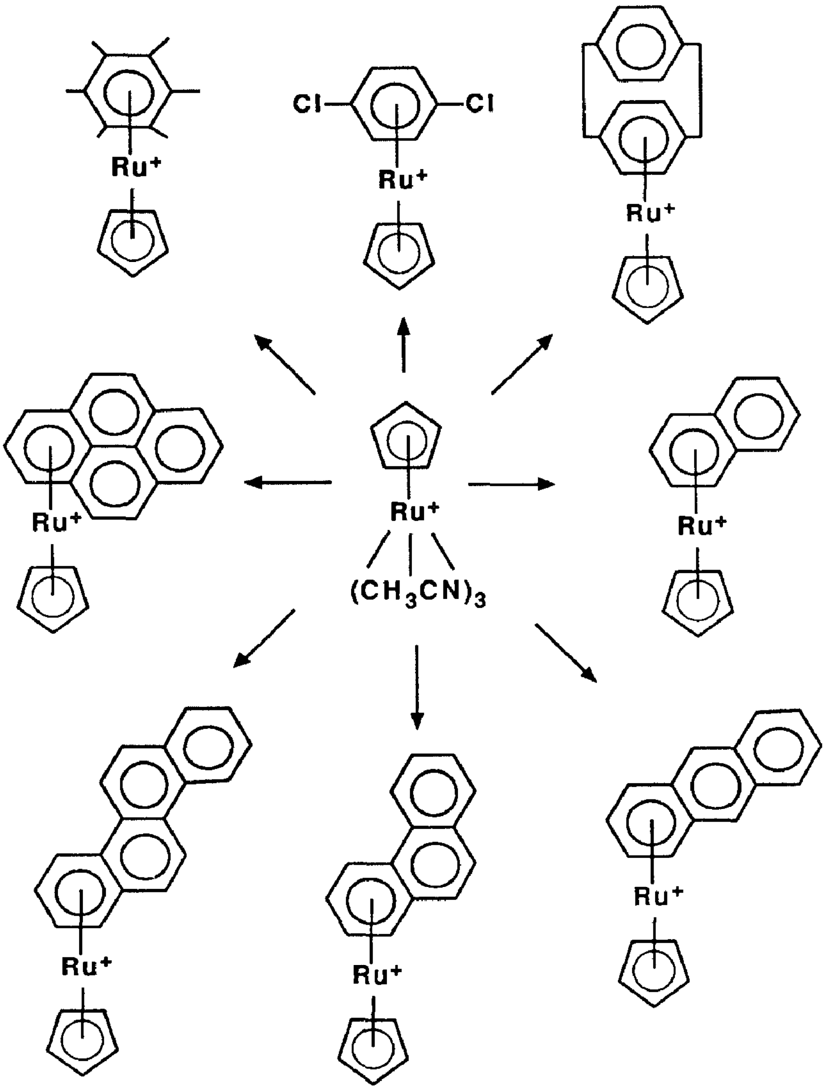
Irradiation of (η^6-benzene)(Cp)ruthenium (II) hexafluorophosphate in MeCN gave *tris*acetonitrile species containing the CpRu(II) group (eq. 14). This complex is air stable



(eq.14)

at room temperature in the solid state and in acetonitrile solution but decomposes in other solvents. These *tris*acetonitrile ruthenium(II) complexes are very useful precursors for a variety of (η^6-arene)(Cp)ruthenium(II) complexes, examples of which are summarized in Scheme II. For example, the reaction between hexamethylbenzene and *tris*acetonitrile

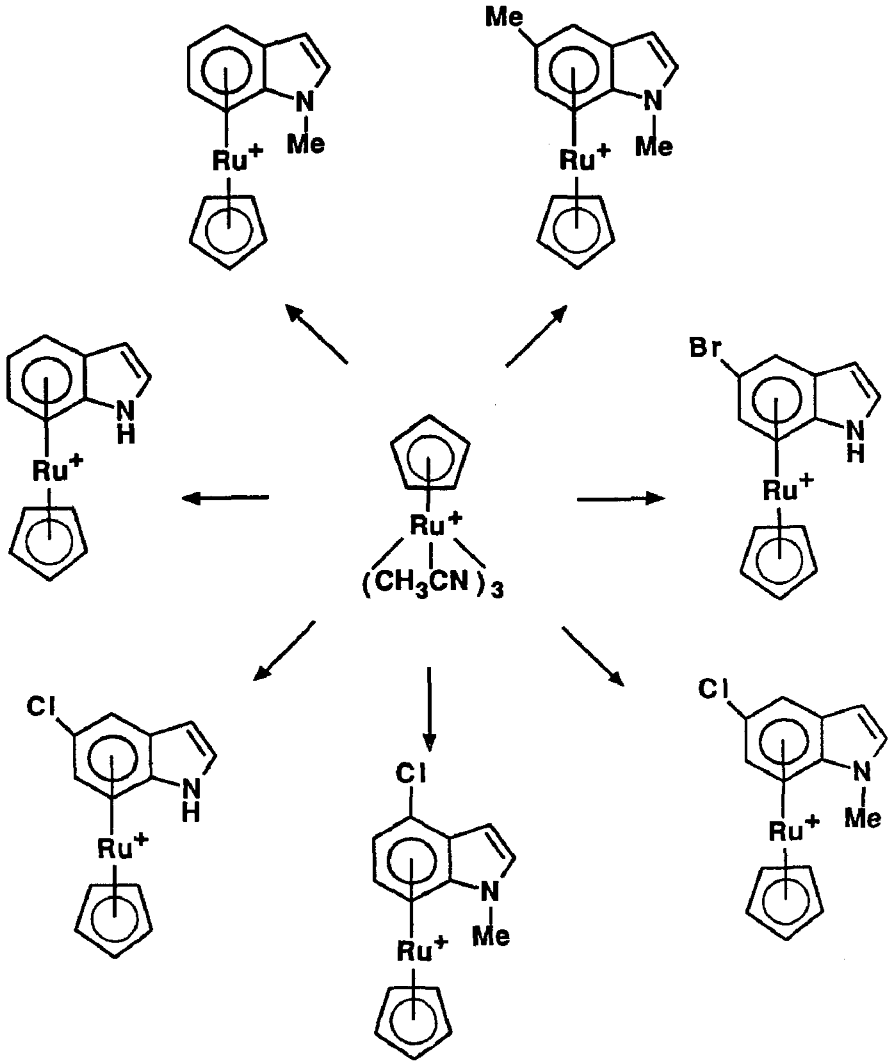
Scheme II



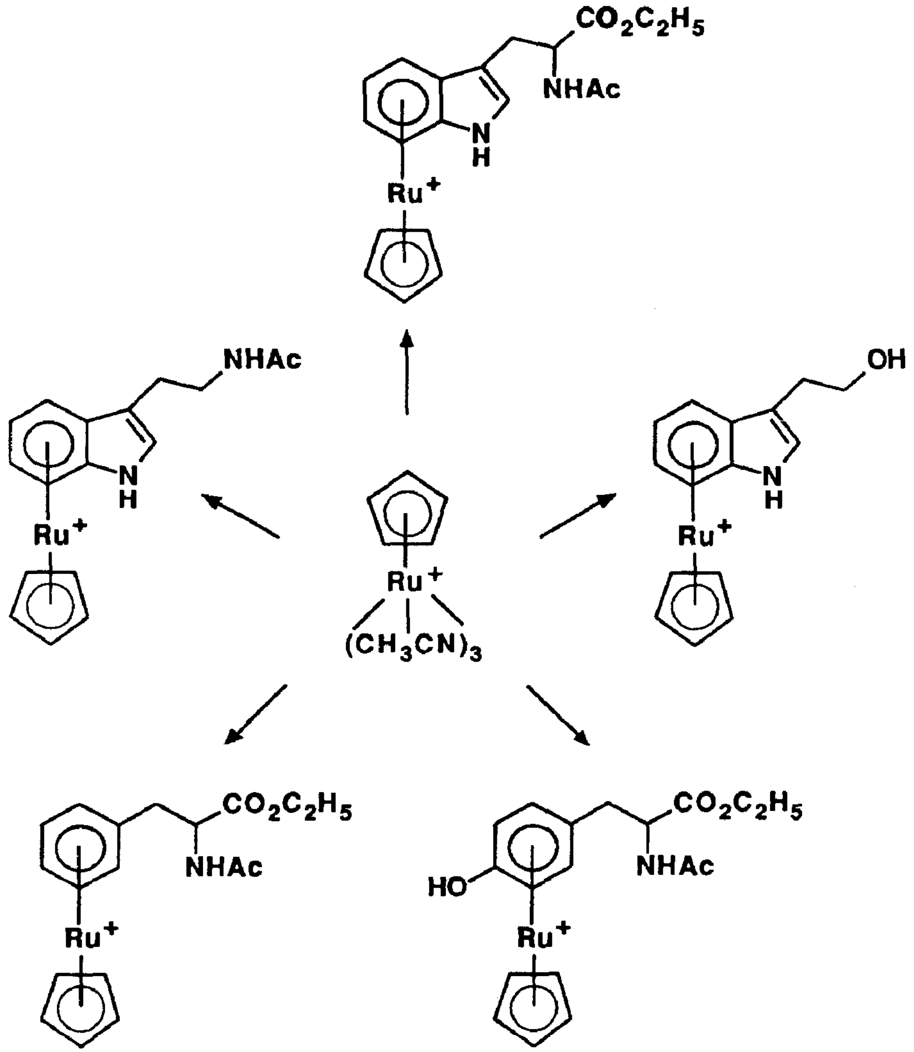
(Cp)ruthenium(II) hexafluorophosphate in refluxing 1,2-dichloroethane produces (η^6-hexamethylbenzene)(Cp)ruthenium(II) hexafluorophosphate in excellent yield [11]. With condensed polyaromatics, complexation occurs at the more nucleophilic outer aromatic ring [12].

Recently, we have prepared a number of (η^6-indole)(Cp)ruthenium(II) complexes by thermal ligand exchange reactions of trisacetonitrile(Cp)ruthenium(II) hexafluorophosphate with indole substrates [13]. Typical examples are presented in Scheme III. Particularly interesting is the successful incorporation of $[CpRu(II)]^+$ moiety into the arene ring of suitable protected aromatic amino acids (Scheme IV) under mild conditions [14]. In a related study we have transferred $[CpRu(II)]^+$ group from the

Scheme III

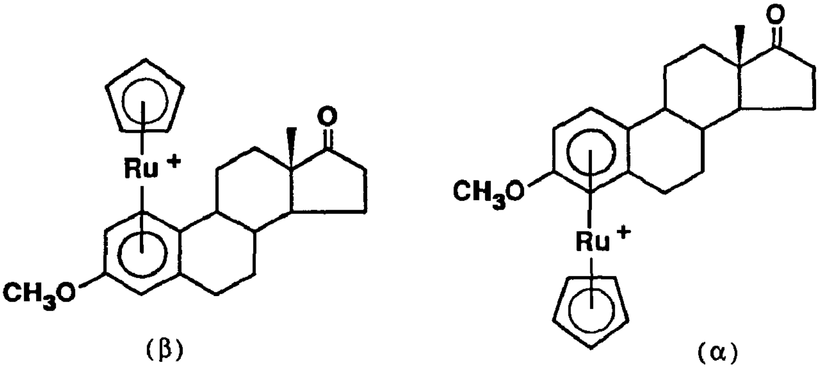


Scheme IV



[CpRu(MeCN)3]PF6 complex to the aromatic ring of estrone 3-methyl ether to give mixed cationic complexes (Scheme V). The complexation from the α and β faces of estrone 3-methyl ether occurred to give the two complexes in the ratio 7:3 [15]. Various complexes obtained from thermal ligand exchange reactions of trisacetonitrile(Cp)ruthenium(II) hexafluorophosphate are collected in Table 4.

Scheme V



(β) (α)

Table 4

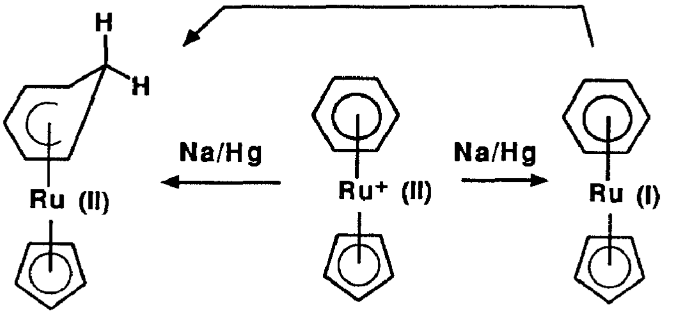
(η^6-Arene)(Cp)ruthenium(II) Hexafluorophosphates Obtained via Thermal Ligand Exchange Reaction Between $(MeCN)_3(Cp)$ruthenium Hexafluorophosphate and Arenes

Arene	Yield%	MP(°C)	References
Benzene-d_6	-	325~326	20
Hexamethylbenzene	-	295~296	11
Toluene			20
p-Dichlorobenzene	66	248~250	11
Pentamethylbenzene	-	322~325	20
[2,2]-p-Cyclophane	85	266~267	11
1,3,5-Tri-*t*-butylbenzene		289~290	20
Naphthalene	88	224~226	12
Anthracene	82	208~213	12
Pyrene	94	-	12
Chrysene	93	200~202	12
Azulene	80	-	12
Indole	85	245~247	13
N-methylindole	89	192~194	13
5-Methyl N-methylindole	88	223~225	13
5-Bromoindole	80	146~148	13
5-Chloro N-methylindole	83	211~213	13
4-Chloro N-methylindole	85	185~187	13
5-Chloroindole	80	156~158	13

3. Chemical Reactivity

3.1. Reducing Metals

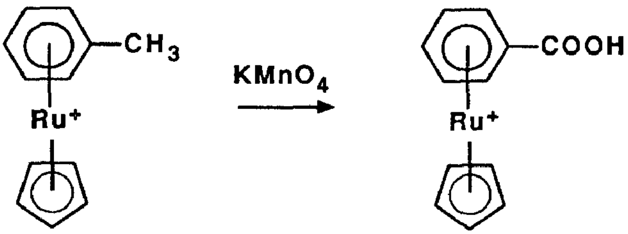
Sodium/mercury amalgam (Na/Hg) was shown to reduce the (η^6-benzene)(Cp) ruthenium(II) complex in THF at -20°C to give the neutral (η^5-cyclohexadienyl) (Cp)ruthenium complex as the only product (eq. 15) [16]. The structure of this neutral complex was based on IR (presence of band at 2780 cm^{-1}, endo C-H stretch) and mass spectra. The initial reduced species, i.e. the (η^6-benzene)(Cp)Ru(I) complex is very reactive toward the solvent and abstracts a hydrogen atom to yield the (η^5-cyclohexadienyl) (Cp)ruthenium complex (eq. 15). However, reduction (Na/Hg) in pentane/water provided the same neutral complex [16]. The formation of the neutral complex was explained in terms of initial two electron reduction of the cationic species followed by protonation to yield the (η^5-cyclohexadienyl)(Cp)ruthenium complex.



(eq.15)

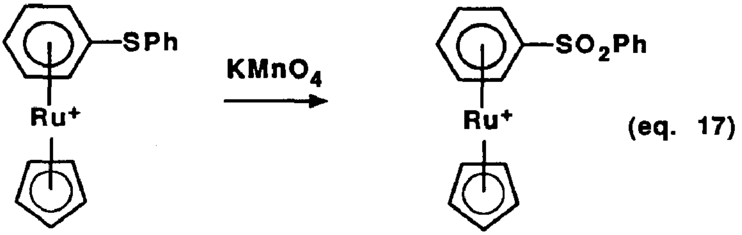
3.2. Oxidation

(η ^{6}-Arene)(Cp)ruthenium(II) salts are stable towards strong oxidizing agents [16]. These salts are not converted into doubly-charged (η^6-arene)(Cp)ruthenium(III) salts by KMnO4. Instead, the ligand substituents are oxidized. For example, KMnO4 oxidation of (η^6-toluene)(Cp)ruthenium(II) tetrafluoroborate gives the corresponding complex of benzoic acid in 80% yield (Eq. 16) [16]. Similar KMnO4 oxidation of (η^6-diphenylsulfide)(Cp)



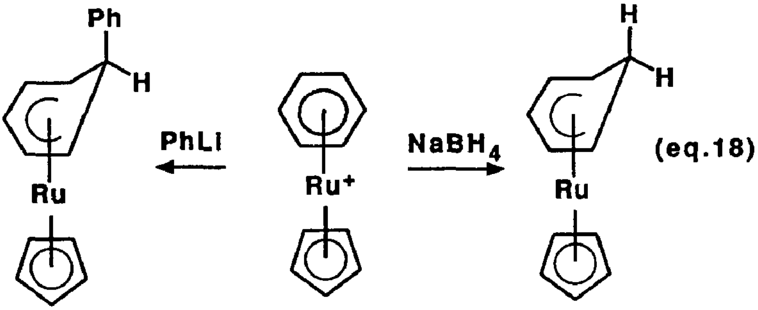
(eq. 16)

ruthenium(II) hexafluorophosphate produced the corresponding sulfone complex (eq. 17) [16].

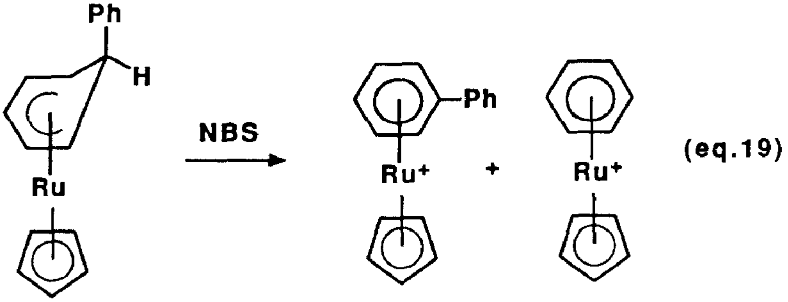


3.3. Nucleophilic addition

Reaction of hydrides and other nucleophiles with arene-metal complexes has been rationalized in terms of charge control. Thus, Davies et al. formulated simple rules which . point out the fact that nucleophilic attack occurs at an even closed cyclic (arene) rather than at an odd one, in a kinetically controlled reaction [17]. A few reactions of (η^6-arene) (Cp)ruthenium(II) complexes with nucleophiles have been investigated. Hydride addition to the (η^6-benzene)(Cp)ruthenium complex using sodium borohydride in DME was reported to yield only 5% of the neutral (η^5-cyclohexadienyl)(Cp)ruthenium complex [6]. The yield of neutral complex can be increased to 55% by conducting the reaction in THF rather than DME (eq. 18). Similar reaction of phenyllithium [16] with the (η^6-C_6H_6)(Cp)ruthenium complex was reported to give the (η^5-<u>exo</u>-phenylcyclohexadienyl) (Cp)ruthenium (eq. 18). Hydride abstraction from the (η^5-cyclohexadienyl)(Cp)ruthenium complex with N-bromosuccinimide (NBS) in methanol regenerated the (benzene)(Cp) ruthenium complex [16]. However, similar reaction of (η^5-<u>exo</u>-phenylcyclohexadienyl)(Cp)ruthenium complex with NBS proceeded with <u>exo</u>-phenyl abstraction to give (η^6-C_6H_6)(Cp)



ruthenium complex as well as endo hydride abstraction to yield (η^6-PhC$_6$H$_5$)(Cp) ruthenium(II) complex (eq. 19). The latter endo-hydride abstraction was the major reaction path. Attempted addition reaction of PR$_3$, $^-$CN and $^-$OH nucleophiles to (η^6-benzene)(Cp)ruthenium complex resulted in extensive decomposition involving displacement of both carbocyclic rings [6].



3.4. Nucleophilic substitution

3.4.1. Halobenzenes

Halogen substituents (Cl of F) on the six-membered ring in (η^6-halobenzene) (Cp)ruthenium complexes are reactive towards nucleophilic substitution. Reaction of (η^6-chlorobenzene)(Cp)ruthenium complex with sodium carbonate (MeOH), sodium cyanide (DMF), sodium hydroxide (H$_2$O and acetone), liquid ammonia, piperidine (acetone), or sodium thiophenoxide (acetone) resulted in substitution of the chloro group to give the corresponding (η^6-C$_6$H$_5$X)(Cp)ruthenium complexes (Scheme VI) [9, 18]. (η^6-Arene) (Cp)ruthenium complexes obtained via nucleophilic substitution reaction upon (η^6-chlorobenzene)(Cp)ruthenium are tabulated in Table 5.

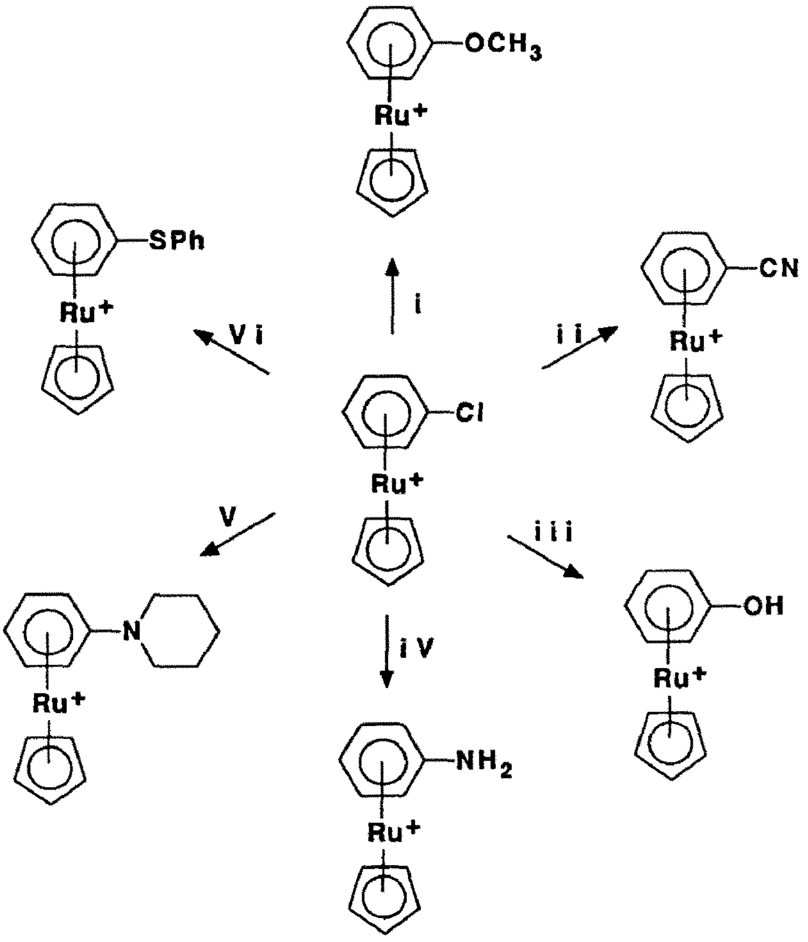
Table 5

η^6-Arene(Cp)ruthenium Complexes Obtained via Halogen Displacement from [η^6-C$_6$H$_5$Cl(Cp)Ru]X

Nucleophile	X	Reference
OCH$_3$	BF$_4$	18,9
OH	PF$_6$	16
SC$_6$H$_5$	PF$_6$	16
CN	BPh$_4$	16
NC$_5$H$_{10}$	BF$_4$	18,9
NH$_2$	BF$_4$	9

Similar nucleophilic substitution reactions upon (η^6-fluorobenzene)(Cp)ruthenium complex with sodium carbonate (MeOH) and piperidine (acetone) are reported to yield (η^6-anisole)(Cp)ruthenium and (η^6-phenylpiperidine)(Cp)ruthenium complexes,

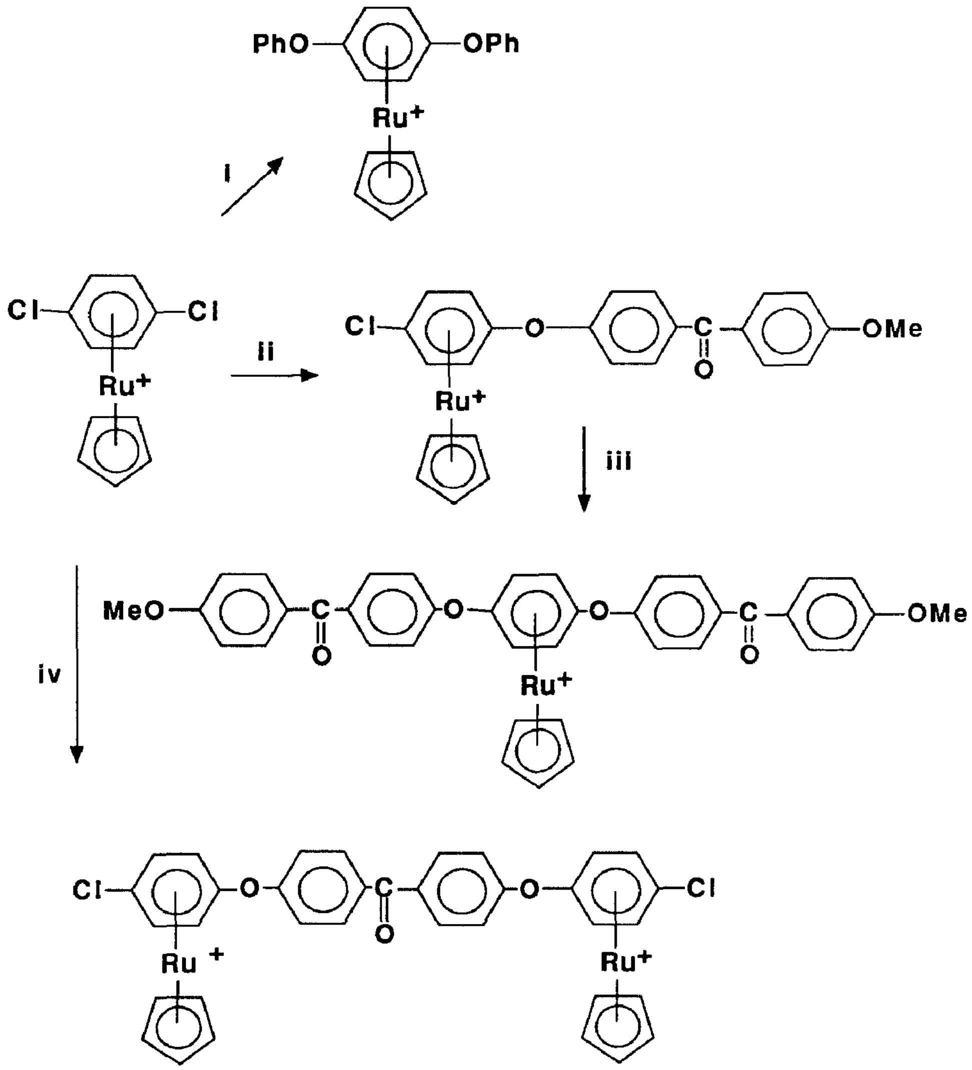
Scheme VI



i)Na_2CO_3(MeOH); ii)NaCN(DMF); iii)KOH(H_2O and Me_2CO); iv)NH_3; v)HNC_5H_{10}(Me_2CO); vi)NaSPh(Me_2CO)

respectively [9]. As one may expect, the (η^6-fluorobenzene)(Cp)ruthenium complex is more reactive to substitution than the corresponding chlorobenzene analogue. (η^6-p-Dichlorobenzene)(Cp)ruthenium complex [19] undergoes a mono and double aromatic nucleophilic substitution reaction with phenol derivatives, exchanging one or both chloro groups depending upon the ratio of nucleophile to dichlorocomplex. Such nucleophilic substitution reactions with phenol, 4,4'-dihydroxybenzophenone and 4-hydroxy-4'-methoxylbenzophenone are summarized in Scheme VII. Furthermore, reaction of the

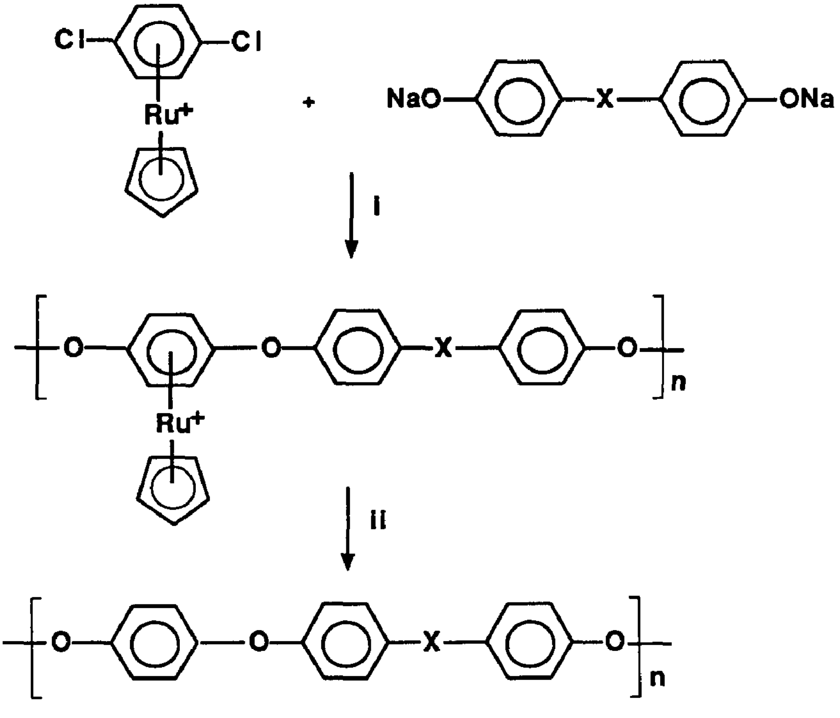
Scheme VII



i)NaOPh in acetone, 40°C; ii) $NaOC_6H_4COC_6H_4OMe$, 1:1 ratio with ruthenium complex, DMF, 50°C, 10 min; iii), $NaOC_6H_4COC_6H_4OMe$, 2:1 ratio with ruthenium complex, DMF, 85°C, 20 min; V) $NaOC_6H_4COC_6H_4ONa$,1:2 ratio with ruthenium complex,DMF,70°C, 1h.

disodium salt of 4,4'-dihydroxybenzophenone with an equimolar quantity of the p-dichlorobenzene(Cp)ruthenium complex in DMF or DMSO at 85-90°C (Scheme VIII) yielded the soluble organometallic polymer, which was isolated as a solid [19]. Subsequent decomplexation reactions (photolysis in MeCN or better thermal reaction in DMSO at 160°C) provided an excellent route to the poly(ether-ether-ketone) polymer. Similar double S_NAr reaction upon the p-dichlorobenzene(Cp)ruthenium complex was accomplished using 4,4'-isopropylidenediphenol in DMF to yield the soluble organometallic polymer [19] which upon decomplexation gave the corresponding metal free polymer (Scheme VIII).

Scheme VIII



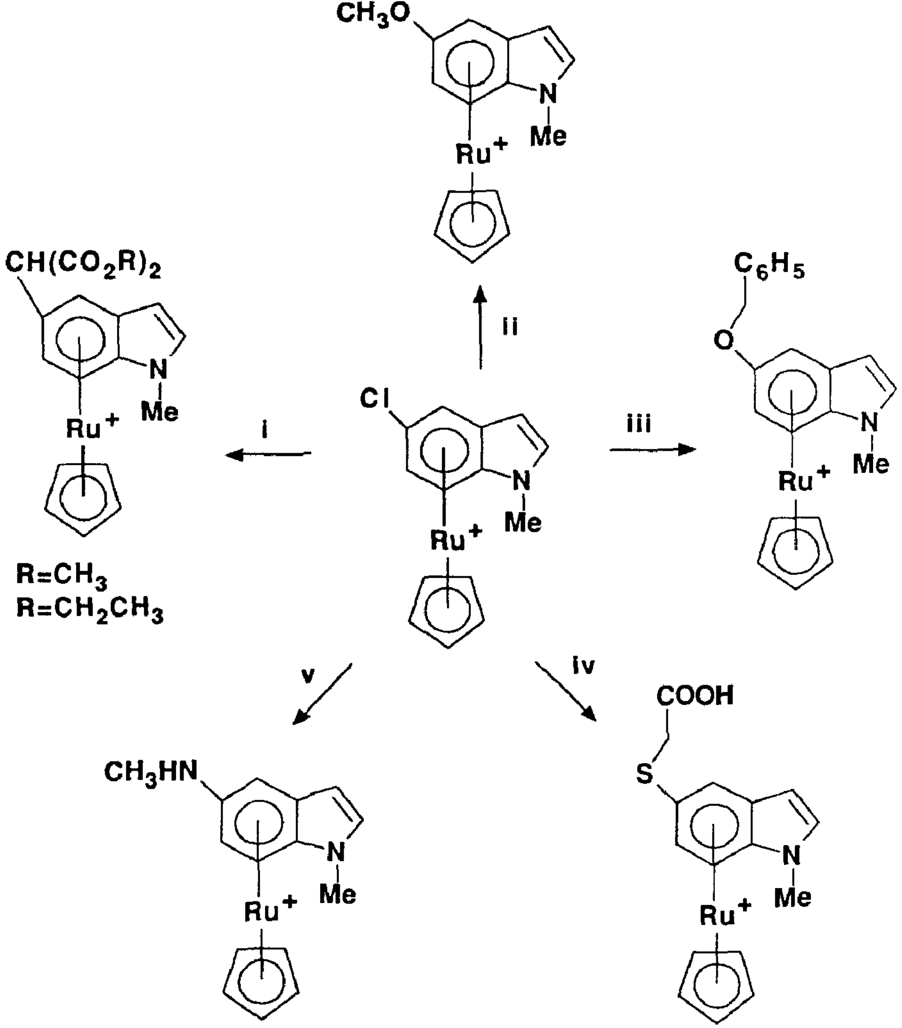
$X{=}CO, CMe_2$

i) Na or K bis-phenate, 1:1 ratio with p-dichlorobenzene(Cp) ruthenium complex, DMSO, 85-90°C, 1.5h; ii) DMSO, 160°C, 1.5h or $h\nu(CH_3CN)$.

3.4.2. Chloroindoles

Nucleophilic displacement of the chloro groups from [CpRu(II)]$^+$ complexed 5-chloro-N-methylindole and 4-chloro-N-methylindole with various oxygen, nitrogen,

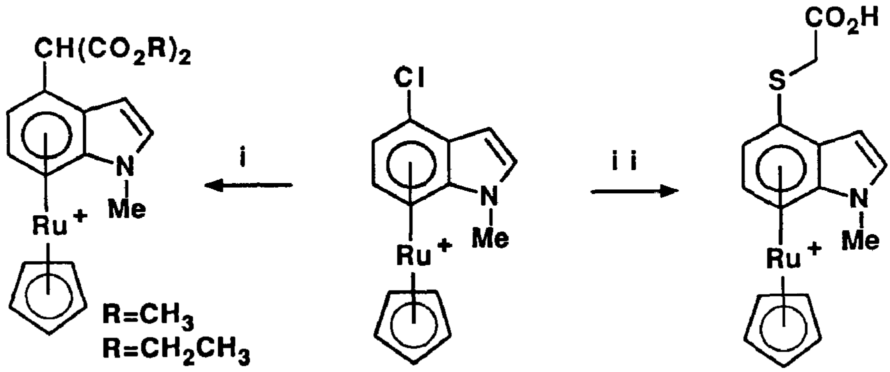
Scheme IX



i) $H_2C(CO_2R)_2$ (2eq), NaH (2eq), THF, 40~50°C, 10h; HPF6; ii) NaOH (20eq), CH_3OH, 50°C, 14h, HPF_6. iii) $HOCH_2C_6H_5$ (4eq), NaH (4eq), THF, 40~50°C, 10h; HPF_6. iv) $HSCH_2CO_2H$ (10eq), NaH (10eq), THF, RT, 36h; HPF_6. v) H_2NCH_3 (40eq), CH_2Cl_2, RT, 2days; HPF_6.

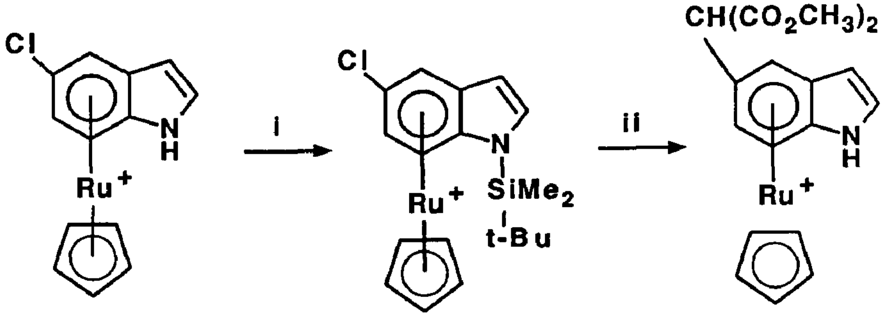
sulfur and carbon nucleophiles has provided a new method for controlled functionalization of the aryl ring of the indole nucleus (Scheme IX and X). In the case of the (η^6 - 5 - chloroindole)(Cp)ruthenium(II) complex, *t*-butyldimethylsilane has been used as an N-protecting group during nucleophilic displacement of the chloro group with the carbanion derived from diethylmalonate to yield the (η^6-5-substituted-indole)(Cp)ruthenium complex (Scheme XI).

Scheme X



i) $H_2C(CO_2R)_2$ (2eq), NaH (2eq), THF, 40~50°C, 10h; HPF_6;
ii) $HSCH_2CO_2H$ (10eq), NaH (10eq), THF, RT, 36h; HPF_6.

Scheme XI



I: NaH/THF/*t*-BuSiMe2Cl
II: NaH/THF/$CH_2(CO_2CH_3)_2$; HCl/H_2O

4. Photochemistry

Photolysis [11] of (η^6-benzene)(Cp)ruthenium(II) complex in acetonitrile affords the trisacetonitrile(Cp)ruthenium(II) complex quantitatively with a quantum yield (ϕ) at 315 nm of 0.4. On the other hand, photolysis under the same conditions but in dichloromethane and in the absence of other ligands gives no net reaction. Addition of $P(OMe)_3$ or $P(OEt)_3$ yields trisphosphite products [11]. The photoactive state in various (η^6-arene)(Cp)ruthenium complexes is reported as a non-dissociated but distorted excited state relative to the ground state [12,20,21]. A linear correlation between $\log[\phi(1 - \phi)]$ and the Hammett parameter (σ_p) for chloro- and methylarene-substituted complexes has been observed [20]. Permethylation of Cp ligands is reported to decrease the quantum yields (ϕ) of arene release as compared to the analogus unsubstituted Cp compounds [21]. The increase in the Hammett parameter (σ_p) from +1.38 to +2.05 upon Cp permethylation suggests a slight increase in negative charge at the arene in the excited state of (Me_5C_5) complexes relative to Cp complexes. Kinetic studies on arene displacement [12] in (η^6-arene)(Cp)ruthenium and (η^6-arene)(Me_5C_5)ruthenium complexes (arene = naphthalene, anthracene, pyrene, chrysene or azulene) support an associative mechanism. The pseudo-first-order rate constants measured with [MeCN] = 2.73M are between 1.3×10^{-2} and $4.6\times10^{-6}/s^{-1}$ in the order anthracene > naphthalene > pyrene > chrysene. The k_{obsd} measured for the (η^6-anthracene)(Cp)ruthenium complex (2.7×10^{-3} s^{-1}) is approximately a factor of 5 smaller than that measured for the (η^6-anthracene)(Me_5C_5)ruthenium(II) complex (1.3×10^{-2} s^{-1}). A study of the effects of varying concentration of acetonitrile as well as temperature on the rate of arene release from (η^6-anthracene)(Me_5C_5)ruthenium(II) complex has been reported [12]. Plots of k_{obsd} vs [MeCN] yield a straight line. The similar plots of log k vs 1/T also yield a straight line. The $\Delta S^{\neq}$ of -13.3(9) eu and $\Delta H^{\neq}$ = +14.9(3) kcal/mol for arene release further confirm the associative mechanism. Two mechanisms for photochemical arene release by MeCN are proposed [12]. The first involves preequilibrium between the parent and η^4-bound complex which precedes MeCN attack at the metal center (i.e. arene slippage $\eta^6 \rightleftharpoons \eta^4$). The second involves direct attack of MeCN at the η^6-complex which produces [(η^4-arene)(Cp)(MeCN)ruthenium] complex via a purely associative mechanism. The negative $\Delta S^{\neq}$ derived from temperature dependence data is also consistent with either mechanism [12]. Photolysis in acetonitrile has been reported as an efficient route to generate free polyether polymers from corresponding $[CpRu(II)]^+$ group complexed polymers [19].

5. Physical and Spectroscopic Properties

(η^6-Arene)(Cp)ruthenium complexes are thermally stable, diamagnetic solids. Their thermal stability also permits the use of a wide variety of purification techniques. Most of these complexes are soluble in dichloromethane, acetone, and acetonitrile and can be crystallized from either dichloromethane/ether or acetone/ether.

The electronic absorption spectra of these complexes have been examined in acetonitrile in the ligand field (LF) spectral region [12, 20]. These complexes generally exhibit a single absorption peak or a shoulder on the low-energy side of an intense UV absorption (Table 6). The low energy feature is attributed to a^1E_1-$^1A_1$ d-d transitions in all cases. Schlenk et al. [21] studied the effect of permethylation of ligands (Cp and benzene) on the electronic absorption spectra. They have observed that both peak positions and

Table 6

Electronic Absorption Spectra of η^6-Arene(Cp)Ruthenium(II) and η^6-Arene(Cp*)ruthenium(II) Hexafluorophosphates[a]

	λmax(Emax)[b]		
Arene	Cp	Cp*	Reference
Benzene	325(144)	321(221)	20,12
Toluene	323(157)	------	20
Mesitylene	327(166)	326(195)	20,12
p-Dichlorobenzene	330(186)[c]	------	20
Pentamethylbenzene	328(183)[c]	------	20
Hexamethylbenzene	328(170)[c]	324(251)	20,12
1,3,5-Tri-t-butylbenzene	330(133)[c]	------	20
Naphthalene	364(780)[c]	365(760)[c]	21
Anthracene	480(1320)	480(2400)	21
Pyrene	355(7470)	360(3150)[c]	21
Chrysene	380(2066)	370(2450)[c]	21
Azulene	515(1296)	505(1349)	21

a. Determined at 25°C in MeCN.

b. Wavelength (λ) in nm and extinction coefficient (e) in M^{-1} cm^{-1} (±10%).

c. Shoulder

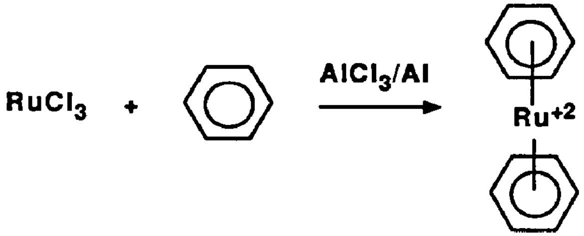
extinction coefficients of the Me_5C_5 and Cp ruthenium complexes of a given arene are nearly identical. For mixed sandwich complexes having polycyclic arene ligands [12], the molar extinction coefficients for the absorption bands are rather large for d-d transitions and are attributed to a moderate degree of metal-ligand orbital mixing.

Multinuclear NMR spectroscopy has provided valuable insights into the effects on arenes of metal coordination. A characteristic feature of the ^1H NMR spectra of (η^6-arene)(Cp)ruthenium(II) complexes is that arene protons resonate at significantly higher (ca 1.07 ppm) fields than in the free ligands [7a,9]. The downfield shift (0.85 ppm) of the Cp hydrogens relative to the signal of the Cp hydrogens in ruthenocene is considered to be due to delocalization of positive charge on the ligands [9]. The ^{19}F NMR spectra of (η^6-fluorobenezene)(Cp)ruthenium complex [9] showed an upfield shift of the fluorine signal by 23.18 ppm as compared to the free fluorobenzene. This shift has been interpreted in terms of the arene being a strong acceptor. High resolution ^1H and ^{13}C NMR spectral data for substituted indole(Cp)ruthenium complexed as well as for the corresponding CpRu(II) complexes of protected aromatic amino acids have been utilized for determination of their structures [13,14]. Polarographic and cyclic voltametric studies showed that (η^6-arene)(Cp)ruthenium(II) complexes are not reduced before the solvents [6]. However, (η^6-hexamethylbenzene)(Cp)ruthenium and (η^6-p-isopropyl-toluene)(Cp)ruthenium tetraphenylborates undergo irreversible oxidation at modest potentials. Moreover, these processes remained irreversible even at low temperature (-40°C) and high scan rates ($100VS^{-1}$). These results are rationalized in the terms of greater π-back bonding ability of ruthenium(II) complexes.

6. Bis(arene)ruthenium(II) complexes

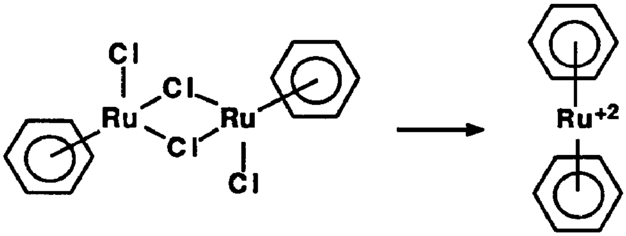
6.1. Synthesis

The Fischer-Hafner [22] synthesis provides a convenient route to a variety of symmetrical bis(η^6-arene)ruthenium(II) complexes [23,24]. This method involves the reaction of $RuCl_3$ with excess arene in the presence of $AlCl_3$ and Al dust (eq. 20). It cannot be applied to arenes bearing functional groups (e.g Cl, Br, I, NH_2, OCH_3, CO_2R etc.) which are reactive under Friedel-Crafts conditions. Another complication arises with alkylbenzenes where dealkylation [23,24,25] often occurs. Several modifications of the original synthesis have been described, including the use of Me_2AlCl as a reducing agent instead of Al dust [26]. This method involves shorter reaction times and lower temperature and the rearrangement and fission of alkylsubstituents in alkylbenzenes is less important.



(eq.20)

Recently, Bennett et al. [27] have provided a straightforward general method for the preparation of symmetrical as well as unsymmetrical bis(η^6-arene)ruthenium(II) complexes. For example, the treatment of $[(\eta^6\text{-arene})RuCl_2]_2$ in acetone successively with $AgBF_4$ or $AgPF_6$, acid (CF_3CO_2H, HBF_4 or HPF_6) and arene yields (arene)(arene′) ruthenium(II) complex (eq. 21). The initially formed thermally labile $[(\eta^6\text{-arene})Ru(OCMe_2)_3]^{+2}$ complex undergoes rapid isomerization or partial solvolysis



(eq.21)

depending on the nature of the counter-anion (BF_4^- or PF_6^-) to yield the new diacetonealcohol complex $[(\eta^6\text{-arene})Ru(OCMe_2)(Me_2C(OH)CH_2COMe)](BF_4)_2$ and the *tri*-μ-difluorophosphato complex, $[(\eta^6\text{-arene})Ru(MePO_2F)_3]PF_6$. Both diacetonealcohol and *tri*-μ-difluorophosphato complexes undergo the thermal acid catalyzed ligand exchange reactions with arenes′, yields range from 20% to quantitative and being dependent upon the arene in dimer in the order hexamethylbenzene> mesitylene > benzene. This method failed to yield (η^6-arene)(η^6-arene′)ruthenium(II) complexes for arene′ = hexafluorobenzene, nitrobenzene, s-collidine, aniline or thiophene. Maitlis et al [28] have reported the synthesis of the (η^6-p-cymene)(η^6-tetramethylthiophene)ruthenium(II) complex from reaction of dimer $[(\eta^6\text{-p-cymene})RuCl_2]_2$ and tetramethylthiophene in the presence of $AgPF_6$. Rybinskaya et al. [29] have modified Bennett's procedure using water as a solvent and a readily available silver salt ($AgNO_3$). A new synthesis of (η^6-arene)(η^6-arene′)ruthenium(II) complexes involves direct exchange of arenes(arene′) for chlorides on $[(\eta^6\text{-arene})RuCl_2]_2$ in refluxing CF_3CO_2H (eq. 22) [30]. The reaction is considerably. accelerated by $(CF_3CO)_2O$ and this method has been successfully employed for arenes bearing the carboxylic acid function. Recently, Hull and Gladfelter [31] have synthesized various (η^6-arene)(η^6-octamethylnaphthalene)ruthenium(II) complexes using Bennett's method. Table 7 lists (η^6-arene)(η^6-arene′)ruthenium(II) complexes prepared according to the above methods.

$$[(\eta^6\text{-arene})RuCl_2]_2 \xrightarrow[CF_3CO_2H]{\text{arene}'} [(\eta^6\text{-arene})(\eta^6\text{-arene}')Ru]^{+2} \qquad \text{(eq. 22)}$$

Table 7

(η^6-Arene)(η^6-arene′)(II) Salts (BF_4^-, PF_6^- or BPh_4^-)

Arene	Arene′	Method	Reference
Benzene	Benzene	A,C	27,29
	Toluene	B,C	29,30
	Mesitylene	A,B	27,30
	p-Xylene	B,C	29,30
	Hexamethylbenzene	A,C	27,30
	Biphenyl	A	27
	Anisol	A	27
	Chlorobenzene	A	27
	Acetophenone	A	27
	Methylbenzoate	A	27
	Naphthalene	B	29
	Aniline	B,C	29,30
	1,3,5-Trimethylphenyl-butanoic acid	B,C	29,30
	Phenylpentane	B	29
	Phenylethyl ether	B,C	29,30
	Octamethylnaphthalene	A,D	27,31
Mesitylene	Benzene	A	27
	Mesitylene	A,C	27,30
	Hexamethylbenzene	A	27
	Naphthalene	A	27
	Anthracene	A	27
	Biphenyl	A	27

continue Table 7

Arene	Arene′	Method	Reference
	Anisol	A	27
	Chlorobenzene	A	27
	N,N-Dimethylaniline	A	27
	Phenol	A	27
	Acetophenone	A	27
	Benzoicacid	A	27
	Methylbenzoate	A	27
	Phenyltrifluoromethane	A	27
	Octamethylnaphthalene	A,D	27,31
Hexamethylbenzene	Benzene	A	27
	Mesitylene	A	27
	Hexamethylbenzene	A	27
	Anisol	A	27
	Naphthalene	A	27
	Chlorobenzene	A	27
	N,N-Dimethylaniline	A	27
	Acetophenone	A	27
	Methylbenzoate	A	27
	Octamethylnaphthalene	A,D	27,31
p-Cymene	Tetramethlnaphthalene	A,	27,31
	Tetramethylnaphthalene	A	27
	Octamethylnaphthalene	A,D	27,31
Pentamethylbenzene	Octamethylnaphthalene	A,D	27,31
1,3,5-Triethybenzene	Octamethylnaphthalene	A,D	27,31
1,3,5-Triisopropylbenzene	Octamethylnaphthalene	A,D	27,31

General synthetic methods of preparation are as follow:

$$\text{A.}(\eta^6\text{-areneRuCl}_2) \xrightarrow[\text{2.CF}_3\text{CO}_2\text{H, arene}']{\text{1.AgBF}_4\text{/acetone}} [\eta^6\text{-arene}(\eta^6\text{-arene}')\text{Ru}]^{+2}(\text{BF}_4^-)_2$$

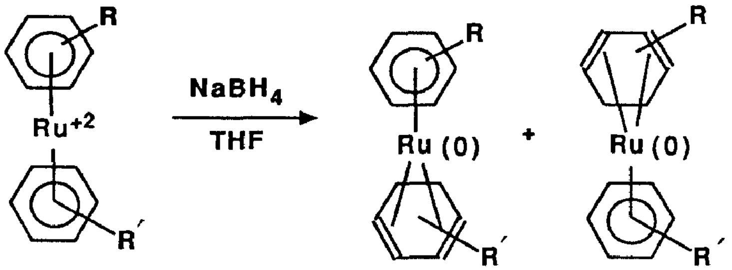
$$\text{B. }(\eta^6\text{-areneRuCl2})2 \xrightarrow[\text{2. arene}']{\text{1. H}_2\text{O/AgNO}_3} [\eta^6\text{-arene}(\eta^6\text{-arene}')\text{Ru}]^{+2}$$

$$\text{C. }(\eta^6\text{-areneRuCl2})2 \xrightarrow[\text{2. arene}',\text{ NH4PF6}]{\text{1.CF}_3\text{CO}_2\text{H}} [\eta^6\text{-arene}(\eta^6\text{-arene}')\text{Ru}]^{+2}$$

$$\text{D. }(\eta^6\text{-areneRuCl2})2 \xrightarrow[\text{arene}']{\text{AlCl}_3} [\eta^6\text{-arene}(\eta^6\text{-arene}')\text{Ru}]^{+2}$$

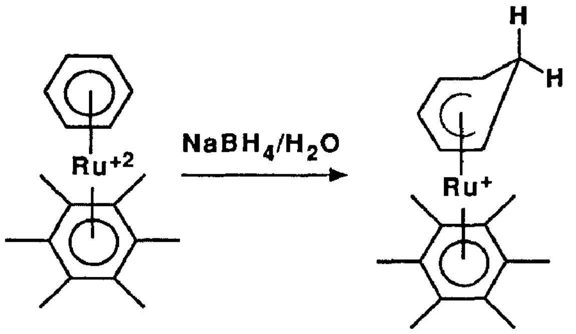
6.2. Chemical and electrochemical studies

Some reactions of bis(η^6-arene)ruthenium(II) complexes with various nucleophiles have been investigated. Hydride additions using $NaBH_4$ or $LiAlH_4$ in tetrahydrofuran (THF) or a similar solvent have been reported with symmetrical as well as unsymmetrical bis(η^6-arene)ruthenium(II) complexes [24,29]. Addition occurs preferentially to the less akylated arene ring [29] to yield new zerovalent (η^6-arene)(η^4-cyclohexadiene) ruthenium(0) complexes (eq. 23). When water is used as a solvent medium in $NaBH_4$ reductions of dicationic complexes, an intermediate monocationic (η^6-arene)(η^5-cyclohexadienyl)ruthenium(II) can be obtained [29]. For example $NaBH_4$ reduction of the (η^6-benzene)(η^6-hexamethylbenzene)ruthenium(II) complex in water gives the intermediate (η^5-cyclohexadienyl)(η^6-hexamethylbenzene)ruthenium(II) complex. (eq. 24). A second hydride can be added to this under forced conditions to yield (η^4-cyclohexadiene) (η^6-hexamethylbenzene)ruthenium(0) complex [32]. Further reaction of



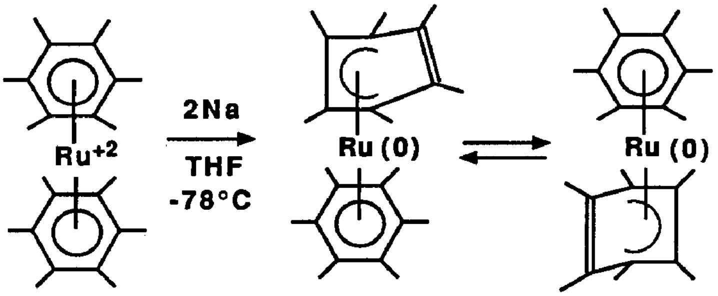
(eq. 23)

R=R′=H
R=R′=1,3,5-Me3
R=1,3,5-Me3; R′=H
R=Me; R′=H



(eq.24)

this cyclohexadiene complex with HCl liberates cyclohexene (>92%) [32]. Jones et al. [34] have reported the addition of phenyllithium to bis(η^6-benzene)ruthenium(II) perchlorate to yield an air-stable yellow crystalline complex. This new complex is mistakenly formulated as bis(1-*endo*-phenyl-η^5-cyclohexadienyl)ruthenium(II) instead of bis(1-*exo*-phenyl-η^5-cyclohexadienyl)ruthenium(II) [7a and references therein]. Kinetic studies [33] have been reported on reversible additions of phosphines and phosphites to a benzene ligand of $(\eta^6\text{-benzene})_2M^{+2}$ (M = Fe, Ru, Os); reactivity towards addition decreases through the series M = Fe > Ru > Os. (η^6-Chlorobenzene)(η^6-benzene) ruthenium(II) undergoes nucleophilic substitution of the chloro group in methanol at room temperature to yield the corresponding (η^6-anisol)(η^6-benzene)ruthenium(II) complex [27]. Fischer and Elschenbroich [26] reported that two-electron reduction of bis(η^6-hexamethylbenzene)ruthenium(II) complex by sodium-ammonia yielded (η^6-hexamethylbenzene)(η^4-hexamethylbenzene)ruthenium(0) (eq. 25).

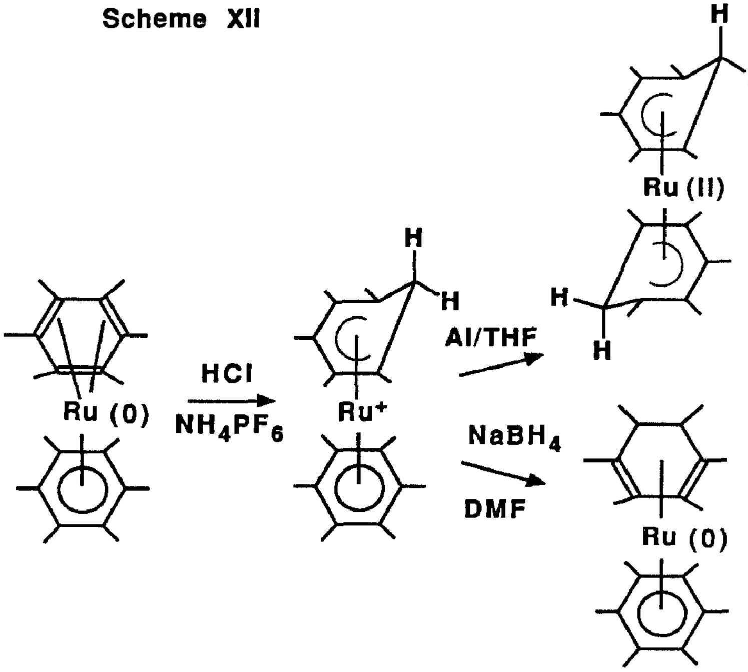


(eq.25)

Variable temperature studies have shown that this zerovalent complex is highly fluxional. Recently, Darensbourg and Muetterties [34] measured the kinetic of this valence tautomerization (activation energy = 16.6 kcal/mol with $\Delta H^{\neq}$ = 15.6 ± 1.3 kcal/mol and $\Delta S^{\neq}$ = -3 ± 5 eu). The analogus reduction of bis(η^6-benzene)ruthenium(II) yields the thermally unstable (η^6-benzene)(η^4-benzene)ruthenium(0) complex [26]. An alternative preparation of zerovalent bis(η^6-benzene)ruthenium(0) has been reported from a reaction between ruthenium metal vapor and benzene [35]. Two-electron reduction (with Na/Hg) of various (η^6-arene)(η^6-octamethylnaphthalene) ruthenium(II) complexes (arene = benzene, p-cymene, mesitylene, 1,2,3,4-tetramethylbenzene and hexamethylbenzene) produces zerovalent (η^6-arene)(η^4-octamethylnaphthalene) ruthenium(0) complexes [31]. However, the attempts to prepare zerovalent (η^6-

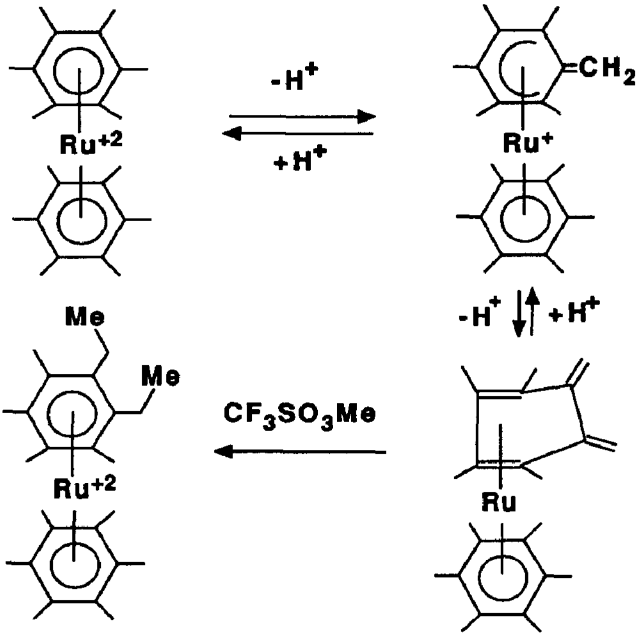
hexamethylbenzene)(η^4-naphthalene)ruthenium(0) failed [31]. Boekelheide et al. [36,37] reported the protonation reaction of (η^6-hexamethylbenzene)(η^4-hexamethylbenzene)ruthenium(0) complex with conc. HCl in acetone to produce (η^6-hexamethylbenzene)(η^5-hexamethylcyclohexadienyl)ruthenium(II) complex. Further reduction of this complex with Al at 0°C produced bis(η^6-hexamethylcyclohexadienyl) ruthenium(II) species (Scheme XII). But reduction with $NaBH_4$ in boiling 1,2-DME gave an alternative diene complex (Scheme XII).

Scheme XII



Deprotonation of bis(η^6-hexamethylbenzene)ruthenium(II) complex with two equivalent of potassium t-butoxide in THF gives (η^6-C_6Me_6)(η^5-$C_6Me_4(CH_2)_2Ru$(II) in 87% yield (Scheme XIII) [40]. The crystal structure of which shows that the metal is attached to the endocyclic diene system of the o-xylylene ligand. The reaction is reversed with acid. The intermediate (η^6-C_6Me_6)($C_6Me_5CH_2$)Ru(I) can be isolated as BPh_4 salt. Methylation with trifluoro methylsulfonate yields (η^6-C_6Me_6)($C_6Me_4Et_2$) Ru(II) as SO_3CF_3 salt (Scheme XIII).

Scheme XIII



Cyclic voltametric and coulometric studies on dicationic complexes are reported [37,39]. A two-electron, partially reversible reduction wave converts bis(η^6-hexamethylbenzene)ruthenium(II) complex to the neutral (η^6-hexamethylbenzene) (η^4-hexamethylbenzene)ruthenium(0) complex (Eq. 25). The mechanism for reductions is proposed to be EEC, where the geometry of the radical cation intermediate is closer to that of the starting Ru(II) complex than to that of the product Ru(0) complex.

6.3. Physical and spectroscopic properties

6.3.1. Bis(η^6-arene)ruthenium(II) complexes

Both symmetrical and unsymmetrical (η^6-arene)(η^6-arene)ruthenium(II) complexes are generally colorless or pale yellow, air stable solids and form salts of low water solubility with anions such as BPh_4^-, BF_4^-, ClO_4^- and PF_6^-. These salts behave as 2/1 electrolytes in nitromethane, and are highly soluble in dimethyl sulphoxide, the solutions being stable for long periods. The arene ring protons in all bis(η^6-arene) ruthenium(II) complexes experience a characteristic upfield shift (^1H NMR) from the uncomplexed arene protons. These complexes possess somewhat more robust ruthenium-arene bonds as compared to the isoelectronic cations $[(\eta^5\text{-}C_5Me_5)(\eta^6\text{-arene})M]^{+2}$ (M

=Rh, Ir) [28], the coordinated arenes are not readily replaced by other ligands. Nevertheless, the (η^6-mesitylene)(η^6-anthracene)ruthenium(II) complex is exceptional since it rapidly yields [(η^6-mesitylene)Ru(DMSO)$_3$]$^{+2}$ and free anthracene in DMSO [27]. The analysis of the IR spectroscopic data for bis(η^6-arene)ruthenium(II) complexes has not proven very revealing. There is a reduction in ν(C=C) for the arene ligand upon complexation. For example ν(C=C) for bis(η^6-hexamethylbenzene)ruthenium(II) complex is 1445cm^{-1} [26].

6.3.2. Bis(η^6-arene)ruthenium(0) complexes

The majority of these zerovalent bis(η^6-arene)ruthenium(0) complexes are very air sensitive [26]. However, as might be expected, permethylation of the arene rings enhances their stability [26]. They are highly fluxional [26, 34]. The ^{1}H NMR methyl resonances for the bis(η^6-hexamethylbenzene)ruthenium(0) complex at -10°C in solution are consistent with the (η^6-hexamethylbenzene)(η^4-hexamethylbenzene)ruthenium(0) (section 6.2.) structure whereas at ~50°C all the methyl ^{1}H resonances are equivalent on the NMR scale. A line-shape analysis [26,34] of ^{1}H DNMR spectra showed that the permutational character of the dynamic process is consistent with an (η^6-hexamethylbenzene)Ru(η^4-hexamethylbenzene) = (η^4-hexamethylbenzene)Ru(η^6-hexamethylbenzene) rearrangement. The mass spectra of various zerovalent bis(arene)ruthenium(0) complexes [26, 31] exhibit an intense parent ion peak followed by loss of methyl from the parent ion. X-ray crystal structures are reported for (η^6-hexamethylbenzene)(η^4-hexamethybenzene) ruthenium(0) [41] and (η^6-hexamethylbenzene)(η^4-octamethylnaphthalene) ruthenium(0) complex [31].

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