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Synthesis of di-, tri-, tetra- and pentacyclic arene complexes of ruthenium(II):[Ru(η^6-polycyclic arene)-(1-5-η^5-cyclooctadienyl)]PF_6 and their reactions with $NaBH_4$

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Abstract

The phenanthrene complex of ruthenium(II), [Ru(η^6-phenanthrene)(1,5-η^5-cyclooctadienyl)]PF_6 (**2c**), is prepared by the reaction of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) with phenanthrene and HPF_6 in 65% yield. Similar treatments with di- tri-, tetra- and pentacyclic arenes give corresponding polycyclic arene complexes, [Ru(η^6-polycyclic arene)(1-5-η^5-cyclooctadienyl)]PF_6 [polycyclic arene = naphthalene (**2b**), anthracene (**2d**), triphenylene (**2e**), pyrene (**2f**) and perylene (**2g**)] in 46–90% yields. The molecular structure of the perylene complex **2g** is characterized by X-ray crystallography. Reaction of **2c** with $NaBH_4$ gives a mixture of the 1,5- and 1,4-COD complexes of ruthenium(0), Ru(η^6-phenanthrene)(η^4-1,5-COD) (**3c**) and Ru(η^6-phenanthrene)(η^4-1,4-COD) (**4c**) in 76% in 1:8 molar ratio. The arene exchange reactions among cationic complexes [Ru(η^6-arene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2**) showed the coordination ability of arenes in the following order: benzene ~ triphenylene > phenanthrene > naphthalene > perylene ~ pyrene > anthracene, suggesting the benzo fused rings, particularly those of acenes, decreasing thermal stability of the arene complex.

Keywords: Ruthenium; Polycyclic arene complex; Protonation; Coordination ability of polycyclic arenes; Hydride reagent

1. Introduction

Much attention has been paid to the arene complexes of ruthenium as starting compounds of various organoruthenium complexes [1], catalysts [2] and organometallic materials [3]. On the other hand, among arene ligands, polycyclic arenes currently attract a great deal of interest in material properties since they would permit introduction of two or more transition metals on the discrete aromatic rings [4]. Such alignment of transition metal fragments is expected to give low-dimensional molecular wires exhibiting semi-conductivity [5], conductivity and ferromagnetism [6]. The arene complexes of ruthenium are generally prepared by (*a*) reaction of arene with [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ [7,8], (*b*) 2e reduction of Ru(acac)$_2$(η^4-1,5-COD) [9] or [$RuCl_2(\eta^4$-1,5-COD)]$_n$ [10], (*c*) ligand exchange reaction with arene by use of Ru(η^6-naphthalene)(η^4-1,5-COD) in MeCN [11], or (*d*) ligand exchange reaction with arene by use of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) under hydrogen atmosphere [12]. Among these methodologies, Porter has reported the synthesis of polycyclic arene complexes of ruthenium(II) by method *a* and we have shown the synthesis of polycyclic arene complexes of ruthenium (0) by methods *b* [13], *c* and *d* [4]. However, these conventional methods commonly result in low yields owing to difficulty in purification process. As a much better preparation method, Vitulli and his coworkers reported that protonation of **1** with HPF_6 in aromatic solvents afforded [Ru(η^6-arene)(η^5-cyclooctadienyl)]PF_6 (arene = benzene, *p*-xylene, mesitylene and chlorobenzene) in almost quantitative yield [14]. Chaudret, Tkatchenko and their

Abbreviations: COD, cyclooctadiene (C_8H_{12}); COT, cyclooctatriene (C_8H_{10}); acac, acetylacetonato (2,4-pentanedionato, $C_5H_7O_2$).

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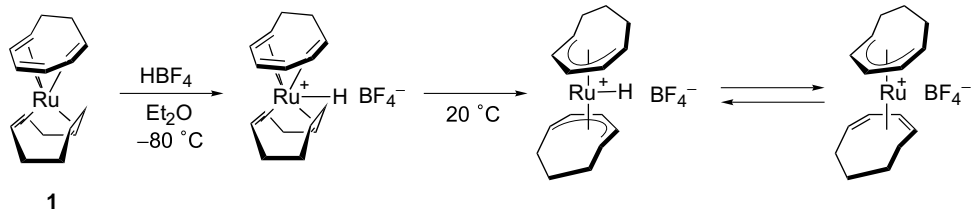


1

Scheme 1.

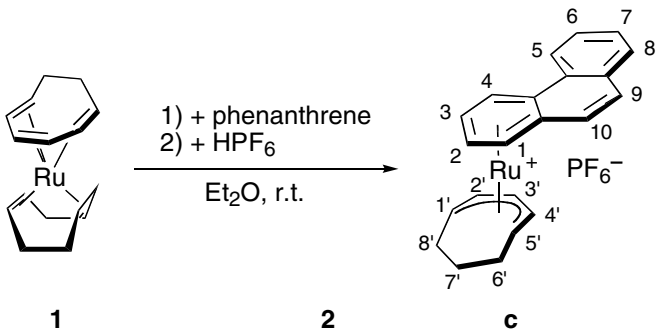
coworkers elucidated the protonation mechanism of **1** with HBF_4 by low temperature NMR studies and X-ray analysis, where the system initially produced [RuH(η^4-1,5-COD)(η^6-1,3,5-COT)]BF_4 which isomerized to an equilibrium mixture of [RuH(1-5-η^5-cyclooctadienyl)$_2$]BF_4 and [Ru(η^5-cyclooctadienyl)(η^4-1,3-COD)]BF_4 (Scheme 1) [15].

They also reported formation of [Ru(η^6-benzene)(1-5-η^5-cyclooctadienyl)]BF_4 and [Ru(η^6-hexamethylbenzene)-(1-5-η^5- cyclooctadienyl)]BF_4 in high yield by the treatment of the cationic complexes in Scheme 1 with benzene and hexamethylbenzene, respectively. Though only monocyclic arenes have been employed as the ligand in this procedure, this methodology would potentially provide an efficient preparation route for polycyclic arene complexes. We thus focused on this methodology to prepare a variety of polycyclic arene complexes of ruthenium(II). Herein we wish to report synthesis of di-, tri-, tetra- and pentacyclic arene complexes of ruthenium(II) with an η^5-cyclooctadienyl ligand, [Ru(η^6-arene)(1-5-η^5-cyclooctadienyl)]PF_6 and their reduction with hydride reagents giving Ru(η^6-arene)(η^4-COD). The relative coordination ability among polycyclic arene compounds is also described.

2. Results and discussion

2.1. Synthesis of cationic cyclooctadienyl complexes having a polycyclic arene ligand

Protonation of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) by HPF_6 in the presence of phenanthrene in Et_2O at room temperature resulted in immediate precipitation of orange powder of [Ru(η^6-phenanthrene)(1-5-η^5- cyclooctadienyl)]PF_6 (**2c**) [Eq. (1)].



1 **2** **c**

(1)

Recrystallization of the precipitate from cold CH_2Cl_2/Et_2O gave yellow micro crystals of **2c** in 65% yield. Complex **2c** was characterized by ^1H and $^{31}P\{^1H\}$ NMR, and the elemental analysis. The ^1H NMR spectrum shows no resonance in the hydride region and characteristically correlated signals at δ 6.41 (t, 1H), 6.54 (t, 1H), 6.74 (d, 1H) and 7.47 (d, 1H) due to the coordinated aromatic protons. The uncoordinated aromatic protons appear at δ 7.48 (d, 1H), 7.87 (dd, 1H), 7.90 (dd, 1H), 8.0 (m, 2H), and 8.49 (m, 1H). These data indicates an asymmetric structure of the phenanthrene ring due to coordination to the ruthenium fragment. Correlated resonances at δ −0.25 (qt, 1H), 0.83 (m, 1H) 1.00 (m, 2H), 1.61 (m, 2H), 3.82 (dt, 1H), 3.90 (dt, 1H), 4.22 (ddd, 1H), 4.44 (ddd, 1H) and 6.24 (t, 1H) are assigned for the η^5-cyclooctadienyl ligand attached to the asymmetric (η^6-phenanthrene)ruthenium moiety.

Similar treatments of complex **1** with monocyclic benzene, bicyclic naphthalene, tricyclic anthracene, tetracyclic triphenylene and pyrene, and pentacyclic perylene also gave corresponding cationic arene complexes **2a**–**g** (Chart 1) of which the molecular structure of [Ru(η^6-perylene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2g**) was determined by single-crystal X-ray diffraction (Fig. 1).

As shown in Fig. 1, the molecular structure of **2g** is regarded as (η^6-perylene)(1-5-η^5-cyclooctadienyl)ruthenium(II), which has a basically similar structure to the related complex Ru(η^6-*p*-tosylate)(1-5-η^5-cyclooctadienyl) derived from the reaction of [Ru(H_2O)$_6$][*p*-tosylate]$_2$ with 1,3-COD [16]. The X-ray analysis of **2g** shows incorporation of 0.5 equiv. of free perylene per **2g**. Consistently, the ^1H NMR spectrum of **2g** contains broad signals at δ 8.1 and 7.5, which are assignable to 0.5 equiv. of free perylene.

It is notable that all cationic complexes **2a**–**g** were isolated as η^5-cyclooctadienyl complexes and no contribution as hydride complexes were observed both in solid and solution states. The η^5-cyclooctadienyl and the alternative hydrido(η^6-1,3,5-COT) fragments formally act as 5e and 7e donors, respectively. This feature may reflect arene ligands having a great propensity to act as 6π donors to form coordinatively saturated complexes. In fact, Bergens and Rautenstrauch reported formation of [RuH(1,3,5-COT)(diphosphine)]BF_4 by the treatment of **1** with a 4e donor such as Me-DUPHOS in the presence of HBF_4 [17].

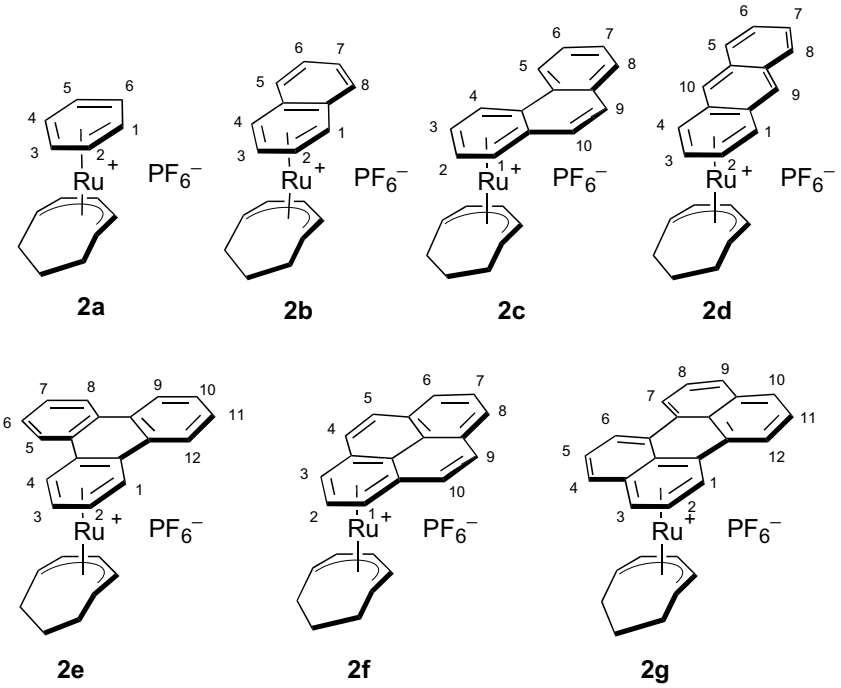


Chart 1.

2.2. Treatment of [Ru(η⁶-phenanthrene)(1-5-η⁵-cyclooctadienyl)]PF₆ (2c) with NaBH₄

As we have previously shown, protonation of a COD (C_8H_{12}) complex Ru(η⁶-phenanthrene)(η⁴-1,5-COD) (**3c**) by HPF_6 affords a cationic hydride complex [RuH(η⁶-phenanthrene)(η⁴-1,5-COD)]PF_6, which constitutes an equilibrium with a cyclooctenyl (C_8H_{13}) complex [Ru(η⁶-phenanthrene)(1-3-η³-cyclooctenyl)]PF_6 having an agostic interaction between the Ru and *endo*-methylene protons in cyclooctenyl ligand, and the resulting cationic complex can be deprotonated to **3c** by the treatment with base such as NaOH (Scheme 2) [13].

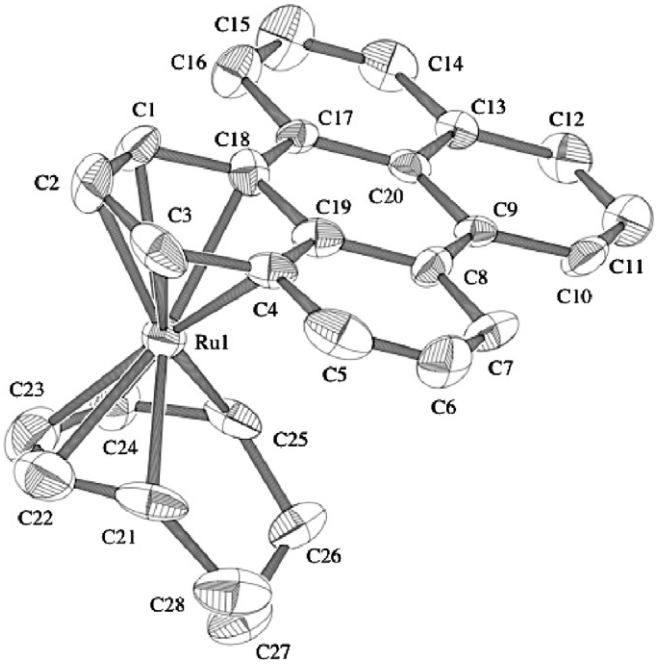
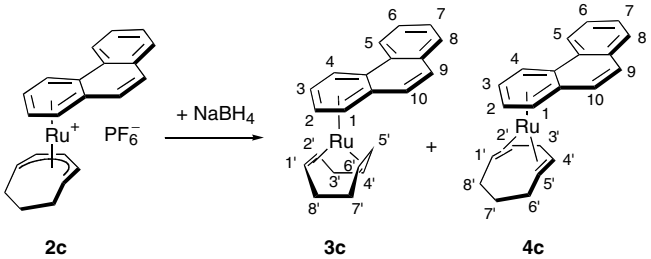


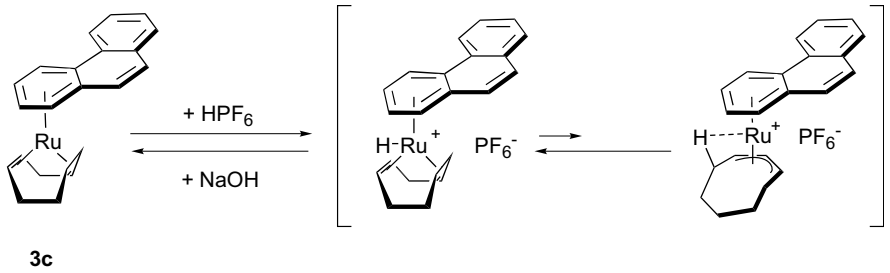
Fig. 1. Molecular structure of [Ru(η⁶-perylene)(1-5-η⁵-cyclooctadienyl)]PF_6 [**2g**] · CH_2Cl_2 · 0.5perylene together with atom-labeling scheme. All hydrogen atoms, PF_6^- anion, incorporated CH_2Cl_2 and free perylene are omitted for clarity. Ellipsoids represent 50% probability.

We postulated that treatment of present cyclooctadienyl complex [Ru(η⁶-phenanthrene)(1-5-η⁵-cyclooctadienyl)]PF_6 (**2c**) with some hydride (H^-) reagent enabled the divalent cyclooctadienyl (C_8H_{11}) complex to become a zerovalent COD (C_8H_{12}) complex, Ru(η⁶-phenanthrene)(η⁴-COD). In fact, treatment of **2c** with 5 equiv. of $NaBH_4$ in THF at 0 °C gave an orange solid containing two neutral species, Ru(η⁶-phenanthrene)(η⁴-1,5-COD) (**3c**) and Ru(η⁶-phenanthrene)(η⁴-1,4-COD) (**4c**) [Eq. (2)].



(2)

The total yield of the products was 76% and the ratio of **3c** to **4c** in CD_2Cl_2 at 19.5 °C was 1:8 from the ^1H NMR spectra. In CD_2Cl_2 solution, **4c** gradually decomposed at room temperature while **3c** remained intact. ^1H NMR spectrum of the predominant species **4c** resembles **3c**, which has been reported by us [13], with characteristic signals of the 1,4-COD fragment. Complex **4c** contains coordinated aromatic



Scheme 2.

protons at δ 4.81 (d, 1H), 5.43 (d,1H), 5.91 (t, 1H) and 6.00 (t, 1H), and the ^{1}H–^{1}H COSY revealed characteristic spin correlations for the 1,4-COD fragment, where the resonance contains a broad quartet at δ -0.21 (1H) due to the *endo*-7′ methylene proton and two multiplets at δ 0.3 (2H) and 1.1 (1H) due to the *exo*-7′, *endo*-6′ and -8′ methylene protons, overlapped resonances at δ 1.2, 1.5, and 1.7 assigned to *exo*-8′, -6′, and *endo*-3′ methylene protons, a doublet of triplets at δ 2.16 (1H) due to the *exo*-3′ methylene proton, and signals at δ 2.38 (dt, 1H), 2.53 (td, 1H), and 2.7 (m, 2H) due to the four olefinic protons.

In order to optimize amount of the reducing reagent in this reaction, the amounts of $NaBH_4$ were varied. Treatments of **2c** with 1.5, 3.0, 5.0 and 10.0 equiv. of $NaBH_4$ at 0 °C for 20 h in THF produced the zerovalent COD complexes in 22% (**3c**:**4c** = 1:0), 32% (**3c**:**4c** = 1:4), 76% (**3c**:**4c** = 1:8) and 52% (**3c**:**4c** = 1:12) yields respectively. On the other hand, treatment of **2e** with 1.5, 3.0, 5.0 and 10.0 equiv. of $NaBH_4$ under the same conditions gave the zerovalent COD complexes in 64% (**3e**:**4e** = 1:6), 72% (**3e**:**4e** = 1:7), 76% (**3e**:**4e** = 1:2) and 54% (**3e**:**4e** = 1:7). In both reactions, the best product yield was accomplished when 5.0 equiv. of $NaBH_4$ was employed.

Similar treatments of benzene, naphthalene, triphenylene and pyrene complexes **2a**, **2b**, **2e** and **2f** with $NaBH_4$ also gave corresponding zerovalent COD complexes **3** and **4** (Table 1). For anthracene and perylene complexes, **2d** and **2g**, the reductions were failed and free arenes were liberated [18].

These results show exclusive formation of the 1,5-COD complex **3** (for naphthalene) or the 1,4-COD complex **4** (for benzene, pyrene), or formation of mixtures of **3** and **4** (for phenanthrene, triphenylene). Since isomerization between **3** and **4** was not observed under these conditions (at 20 °C), complexes **3** and **4** were probably formed by independent mechanisms [19]. Attempts for the reduction of **2c** with more powerful hydride reagents such as NaH or $LiBH_4$ failed to give **3c** and **4c** but gave black precipitate probably due to ruthenium metal.

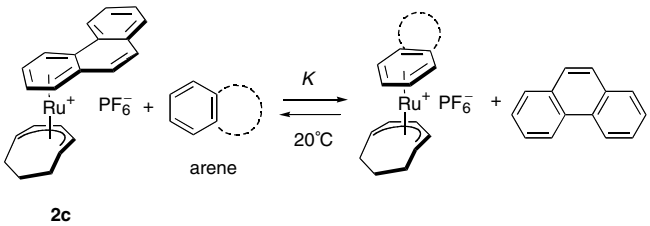
Table 1
Reduction of [Ru(η^6-arene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2**) with $NaBH_4$ giving Ru(η^6-arene)(η^4-1,5-COD) (**3**) and Ru(η^6-arene)(η^4-1,4-COD) (**4**)

Entry	Complex	Arene	**3**/%	**4**/%
1	**2a**	Benzene	0	64
2	**2b**	Naphthalene	22	0
3	**2c**	Phenanthrene	8	68
4	**2d**	Anthracene	0	0
5	**2e**	Triphenylene	23	53
6	**2f**	Pyrene	0	58
7	**2g**	Perylene	0	0

Conditions: **2**: $NaBH_4$ = 1:5, solvent = THF, temp. = 0 °C, time = 20 h. Yields were calculated on the basis of the ^{1}H NMR spectra.

2.3. Arene exchange reactions

According to a pioneering study concerning reactions of (η^6-naphthalene)ruthenium(0), it is generally believed that Ru(η^6-naphthalene)(η^4-1,5-COD) (**3b**) is more labile than the corresponding monocyclic arene complex [9,20]. However, such tendency in arene ligand exchange among polycyclic arenes is unexplored to date. Therefore we studied arene ligand exchange reactions among polycyclic arene complexes [Eq. (3) and Table 2]. When the cationic anthracene complex **2d** was treated with 3.0 equiv. of phenanthrene in CD_2Cl_2 at room temperature, slow but quantitative arene exchange reaction took place in the absence of MeCN [21,22] to give the phenanthrene complex **2c** and free anthracene (entry 10). On the other hand, treatment of **2c** with 2.6 equiv. of free anthracene under the same conditions did not take place at all (entry 6). These facts clearly suggest that the cationic Ru moiety favors phenanthrene than anthracene. Complex **2c** also did not react with perylene at all (entry 9). Similarly addition of 3 equiv. of benzene, naphthalene, triphenylene and pyrene to a CD_2Cl_2 solution of the phenanthrene complex **2c** at 20 °C, gave benzene complex **2a** (86%), naphthalene complex **2b** (25%), triphenylene complex **2e** (59%) and pyrene complex **2f** (6%) for 24 h, in 90%, 30%, 100% and 47% conversions, respectively (entries 4, 5, 7 and 8).



(3)

Table 2
Reaction of [Ru(η^6-arene)(η^5-cyclooctadienyl)]PF_6 (**2**) with 3 equiv. of arenes at 20 °C in CD_2Cl_2

Entry	Starting complex	Added arene	0 h (%)		24 h (%)	
1	**2a**	Triphenylene[a]	**2a** (100)	**2e** (0)	**2a** (100)	**2e** (0)
2	**2b**	Phenanthrene	**2b** (63)	**2c** (35)	**2b** (0)	**2c** (86)
3	**2b**	Pyrene	**2b** (88)	**2f** (trace)	**2b** (57)	**2f** (19)
4	**2c**	Benzene	**2a** (10)	**2c** (87)	**2a** (86)	**2c** (10)
5	**2c**	Naphthalene	**2b** (27)	**2c** (88)	**2b** (25)	**2c** (70)
6	**2c**	Anthracene	**2c** (100)	**2d** (0)	**2c** (100)	**2d** (0)
7	**2c**	Triphenylene[b]	**2c** (55)	**2e** (21)	**2c** (0)	**2e** (59)
8	**2c**	Pyrene	**2c** (94)	**2f** (trace)	**2c** (53)	**2f** (6)
9	**2c**	Perylene[c]	**2c** (>99)	**2g** (<1)	**2c** (>99)	**2g** (<1)
10	**2d**	Phenanthrene	**2c** (<1)	**2d** (>99)	**2c** (100)	**2d** (0)
11	**2d**	Perylene[c]	**2d** (45)	**2g** (57)	**2d** (14)[d]	**2g** (91)[d]
12	**2e**	Benzene	**2a** (0)	**2e** (100)	**2a** (0)	**2e** (100)
13	**2f**	Naphthalene	**2b** (23)	**2f** (85)	**2b** (85)	**2f** (8)
14	**2f**	Phenanthrene	**2c** (0)	**2f** (100)	**2c** (20)	**2f** (29)
15	**2f**	Anthracene	**2d** (19)	**2f** (80)	**2d** (30)	**2f** (43)
16	**2f**	Perylene	**2f** (43)	**2g** (17)	**2f** (14)	**2g** (63)
17	**2g**	Anthracene	**2d** (0)	**2g** (69)	**2d** (8)[d]	**2g** (54)[d]

[a] 4.1 equiv.
[b] 1.1 equiv.
[c] Part of perylene remained unsolved because of poor solubility.
[d] 58 h.

Pyrene complex **2f** is less stable than naphthalene complex **2b** (entry 13). Treatments of **2f** with 3 equiv. of anthracene and perylene gave a mixture of **2f** and anthracene complex **2d** (**2f**: 43%, **2d**: 30%), and a mixture of **2f** and perylene complex **2g** (**2f**: 14%, **2g**: 63%), respectively (entries 15 and 16). Though decomposition during the reaction in an NMR tube was not negligible for entries 2, 3, 7, 8 and 14-17, these reactions were basically reversible. It is notable that the arene exchange reactions between benzene and triphenylene did not proceed even in the presence of MeCN at 20 °C. Since MeCN is believed to act as an auxiliary ligand to assist in the ring-slippage to promote the arene exchange reaction [22], these findings in benzene and triphenylene complexes reflect tight binding to the ruthenium center, probably owing to a great barrier to the η^4-arene intermediate, under these conditions.

Inspite of these ambiguous arene exchange reactions, stability of these complexes: **2a** ~ **2e** > **2c** > **2b** > **2g** ~ **2f** > **2d**. In other words, the order of coordination ability of arenes toward [Ru(1-5-η^5-cyclooctadienyl)]$^+$ fragment is as follows: benzene ~ triphenylene > phenanthrene > naphthalene > perylene ~ pyrene > anthracene. This tendency can be correlated with a loss of aromaticity in the uncoordinated part of the aromatic compounds, since coordination of arenes to the ruthenium center leads to the increase of bond localizations in the uncoordinated part [13,23]. We can therefore conclude by these observations that the benzo fused rings, particularly those of acenes, decrease the thermal stability.

3. Concluding remarks

Present results show a preparation method of polycyclic arene complexes [Ru(η^6-arene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2**) in moderate to high yield. The arene exchange reactions revealed coordination ability of arenes toward [Ru(1-5-η^5-cyclooctadienyl)]$^+$ fragment being in the

following order; benzene, triphenylene > phenanthrene > naphthalene > perylene ~ pyrene > anthracene. This is the first example to show the difference in coordination ability among these polycyclic arene ligands.

4. Experimental

4.1. General procedures

All manipulations and reactions were performed under dry nitrogen with use of standard Schlenk and vacuum line techniques. Diethyl ether, THF, benzene and hexane were distilled over benzophenone ketyl, and dichloromethane was distilled from Drierite; these solvents were stored under nitrogen atmosphere. The compound Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) was prepared according to literature procedure but magnetic stirring was used instead of sonication [24]. All other reagents were obtained from commercial suppliers (Wako Pure Chemical Industries, Aldrich). ^{1}H NMR spectra were recorded on JEOL LA300 (300.4 MHz for ^{1}H). Dichloromethane-d_2 and chloroform-d_1 were distilled over P_4O_{10} and stored under nitrogen. Chemical shifts (δ) are given in ppm, relative to tetramethylsilane for ^{1}H and external 85% H_3PO_4 in D_2O for ^{31}P. All coupling constants are given in Hz. Elemental analyses were carried out on a Perkin-Elmer 2400 series II CHN analyzer.

4.2. Prepartion of [Ru(η^6-benzene)(1-5-η^5-cyclooctadiernyl)]PF_6 (**2a**)

To an Et_2O solution (6 ml) of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) (220 mg, 0.70 mmol), excess HPF_6 (6 drops) was added to give orange precipitate. After removal of the solution layer, the resulting precipitate was washed with Et_2O (5 ml × 2) and hexane (5 ml × 2) to give gray powder of [Ru(η^6-benzene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2a**) in 34% yield (103 mg, 0.24 mmol). ^{1}H NMR (CD_2Cl_2): δ 0.07 (qt, $J = 14.0$, 2.4 Hz, 1H, *endo*-7′-CH_2), 1.25 (m, 1H, *exo*-7′-CH_2), 1.44 (m, 2H, *endo*-6′- and -8′-CH_2), 1.96 (m, 2H, *exo*-6′- and -8′-CH_2), 4.47 (dt, $J = 8.7$, 4.2 Hz, 2H, 1′- and 5′-CH), 4.83 (br. t, 2H, 2′- and 4′-CH), 6.20 (s, 6H, C_6H_6), 6.61 (t, $J = 6.9$ Hz, 1H, 3′-CH). ^{31}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 296 K): −143.6 (sep, $J = 711$ Hz, PF_6^-).

4.3. Prepartion of [Ru(η^6-naphthalene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2b**)

To an Et_2O solution (6 ml) of **1** (103 mg, 0.33 mmol) with naphthalene (53.2 mg, 0.45 mmol) excess HPF_6 (6 drops) was added to give orange precipitate. After removal of the solution layer, the resulting precipitate was recrystallized from cold CH_2Cl_2/Et_2O (2 ml/6 ml) at −30 °C to give yellow powder of [Ru(η^6-naphthalene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2b**) in 65% yield (103 mg, 0.21 mmol). ^{1}H NMR (CD_2Cl_2): δ −0.26 (qt, $J = 13.7$, 2.7 Hz, 1H, *endo*-7′-CH_2), 1.00 (m, 3H, *exo*-7′-CH_2 and *endo*-6′- and -8′-CH_2), 1.67 (m, 2H, *exo*-6′- and -8′-CH_2), 4.08 (dt, $J = 8.7$, 4.2 Hz, 2H, 1′- and 5′-CH), 4.39 (br t, $J = 8$ Hz, 2H, 2′- and 4′-CH), 6.27 (t, $J = 6.9$ Hz, 1H, 3′-CH), 6.35 (AA′BB′, 2H, 1- and 4-CH or 2- and 3-CH), 6.72 (AA′BB′, 2H, 2- and 3-CH or 1- and 4-CH), 7.76 (m, 4H, 5-, 6-, 7- and 8-CH). ^{1}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 296K):δ −143.3 (sept, $J = 713$ Hz, PF_6^-). m.p. = 129–131 °C (decomp.). Anal. Calc. for $C_{18}H_{19}F_6PRu$: C, 44.91; H, 3.98 %. Found: C, 44.71; H, 4.25%.

4.4. Preparation of [Ru(η^6-phenathrene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2c**)

To an Et_2O solution (6 ml) of **1** (104 mg, 0.33 mmol) with phenanthrene (72.5 mg, 0.41 mmol) excess HPF_6 (6 drops) was added to give orange precipitate. After removal of the solution layer, the resulting precipitate was recrystallized from cold CH_2Cl_2/Et_2O (2 ml/f143 6 ml) at −30 °C to give orange powder of [Ru(η^6-phenanthrene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2c**) in 65% yield (114 mg, 0.22 mmol). ^{1}H NMR (CD_2Cl_2): δ −0.25 (qt, $J = 14.0$, 2.4 Hz, 1H, *endo*-7′-CH_2), 0.83 (ddt, $J = 16.5$, 14.0, 3.0 Hz, 1H, *exo*-7′-CH_2), 1.00 (m, 2H, *endo*-6′- and -8′-CH_2), 1.61 (m, 2H, *exo*-6′- and -8′-CH_2), 3.82 (dt, $J = 9.0$, 3.6 Hz, 1H, 1′- or 5′-CH), 3.90 (dt, $J = 9.0$, 3.6 Hz, 1H, 5′- or 1′-CH), 4.22 (ddd, $J = 9.0$, 6.9, 1.2 Hz, 1H, 2′- or 4′-CH), 4.44 (ddd, $J = 9.0$, 6.9, 1.2 Hz, 1H, 4′- or 2′-CH), 6.24 (t, $J = 6.9$ Hz, 1H, 3′-CH), 6.41 (t, $J = 5.7$ Hz, 1H, 2- or 3-CH), 6.54 (t, $J = 5.7$ Hz, 1H, 3- or 2-CH), 6.74 (d, $J = 6.0$ Hz, 1H, 1- or 4-CH), 7.47 (d, $J = 6.0$ Hz, 1H, 4- or 1-CH), 7.47 (d, $J = 9.3$ Hz, 1H, 5- or 8-CH), 7.87 (dd, $J = 9.3$, 5.4 Hz, 1H, 6- or 7-CH), 7.90 (dd, $J = 9.3$, 5.4 Hz, 1H, 7- or 6-CH), 8.0 (m, 8- or 5-CH and 9- or 10-CH), 8.49 (m, 10- or 9-CH). ^{31}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 296K):−143.5 (sep, $J = 711$ Hz, PF_6^-). m.p. = 110–120 °C (decomp.). Anal. Calc. for $C_{22}H_{21}F_6PRu$: C, 49.72; H, 3.98%. Found: C, 49.23; H, 4.42%.

4.5. Preparation of [Ru(η^6-anthracene)(1-5-η^5-cyclooctadienyl)]PF_6 (**2d**)

To an Et_2O solution (6 ml) of **1** (106 mg, 0.33 mmol) with anthracene (70.2 mg, 0.39 mmol) excess HPF_6 (6 drops) was added to give orange precipitate. After removal of the solution layer, the resulting precipitate was recrystallized from cold CH_2Cl_2/Et_2O (2 ml / 6 ml) at −30 °C to give yellow powder of [Ru(η^6-anthracene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2d**) · 0.3 anthracene in 46% yield (107 mg, 0.15 mmol). ^{1}H NMR (CD_2Cl_2): δ −0.38 (qt, $J = 13.5$, 2.4 Hz, 1H, *endo*-7′-CH_2), 0.74 (ddt, $J = 16.5$, 13.5, 3.0 Hz, 2H, *endo*-6′- and -8′-CH_2), 0.88 (m, 1H, *exo*-7′-CH_2), 1.56 (ddqui, $J = 16.5$, 2.0, 1.8 Hz, 2H, *exo*-6′- and 8′-CH_2), 4.22 (br.dt, $J = 8$, 4 Hz, 2H, 1′- and 5′-CH), 4.40 (br.t, $J = 8$ Hz, 2H, 2′- and 4′-

C*H*), 6.12 (t, $J = 6.9$ Hz, 1H, 3′-C*H*), 6.37 (AA′BB′, 2H, 1- and 4-C*H* or 2- and 3-C*H*), 6.92 (AA′BB′, 2H, 2- and 3-C*H* or 1- and 4-C*H*). 7.58 (AA′BB′, 2H, 5- and 8-C*H* or 6- and 7-C*H*), 7.99 (AA′BB′, 6- and 7-C*H* or 5- and 8-C*H*), 8.43 (s, 2H, 9- and 10-C*H*). $^{31}P\{^1H\}$ NMR (121.6 MHz, CD_2Cl_2, 296 K):δ −143.5 (sept, $J = 711$ Hz, PF_6^-). m.p. = 134–137 °C. Anal. Calc. for $C_{22}H_{21}F_6PRu \cdot 0.3$ anthracene: C, 54.21; H, 4.15%. Found: C, 54.65; H, 4.48%.

4.6. Preparation of [Ru(η⁶-triphenylene)(1-5-η⁵-cyclooctadienyl)]PF₆ (2e)

To an Et_2O solution (6 ml) of **1** (106 mg, 0.34 mmol) with triphenylene (88.3 mg, 0.38 mmol) excess HPF_6 (6 drops) was added to give orange precipitate. After removal of the solution layer, the resulting precipitate was recrystallized from cold CH_2Cl_2/Et_2O (2 ml/4 ml) at −30 °C to give yellow crystal of [Ru(η⁶-triphenylene)(1-5-η⁵-cycloocatadienyl)]PF_6 (**2e**) in 90% yield (178 mg, 0.31 mmol). ^1H NMR ($CDCl_3$): δ −0.31 (qt, $J = 13.8$, 2.4 Hz, 1H, *endo*-7′-CH_2), 0.65 (ddt, $J = 16.8$, 13.5, 3.0 Hz, 2H, *endo*-6′- and -8′-CH_2), 0.88 (m, 1H, *exo*-7′-CH_2), 1.5 (dm, $J = 16.8$ Hz, 2H, *exo*-6′- and 8′-CH_2), 3.64 (dt, $J = 9.0$, 3.6 Hz, 2H, 1′- and 5′-C*H*), 4.32 (tm, $J = 7$ Hz, 2H, 2′- and 4′-C*H*), 6.14 (t, $J = 6.9$ Hz, 1H, 3′-C*H*), 6.51 (AA′BB′, 2H, 2- and 3-C*H*), 7.30 (AA′BB′, 2H, 1- and 4-C*H*), 7.78 (td, $J = 7.2$, 1.2 Hz, 2H, 6- and 11-C*H* or 7- and 10-C*H*), 7.86 (td, $J = 7.2$, 1.2 Hz, 2H, 7- and 10-C*H* or 6- and 11-C*H*), 8.34 (dd, $J = 7.2$, 1.2 Hz, 2H, 5- and 12-C*H* or 8- and 9-C*H*), 8.64 (dd, $J = 7.2$, 1.2 Hz, 2H, 8- and 9-C*H* or 5- and 12-C*H*).$^1P\{^1H\}$ NMR (121.6 MHz, CD_2Cl_2, 296 K):δ −143.2 (sept, $J = 713$ Hz, PF_6^-). m.p. = 160–162 °C (decomp.). Anal. Calc. for $C_{26}H_{23}F_6PRu$: C, 53.70; H, 3.99%. Found: C, 53.43; H, 4.23%.

4.7. Preparation of [Ru(η⁶-pyrene)(1-5-η⁵-cyclooctadienyl)]PF₆ (2f)

To an Et_2O solution (6 ml) of **1** (107 mg, 0.34 mmol) with pyrene (82.3 mg, 0.41 mmol) excess HPF_6 (6 drops) was added to give orange precipitate. After removal of the solution layer, the resulting precipitate was recrystallized from cold CH_2Cl_2/Et_2O (2 ml/4 ml) at −30 °C to give orange powder of [Ru(η⁶-pyrene)(1-5-η⁵-cycloocatadienyl)]PF_6 (**2f**) in 62% yield (117 mg, 0.21 mmol). ^1H NMR (CD_2Cl_2): δ −0.4 (qt, 1H, *endo*-7′-CH_2), 1.0 (m, 3H, *exo*-7′-, *endo*-6′- and -8′-CH_2), 1.5 (m, 1H, *exo*-6′- or -8′-CH_2), 1.6 (m, 1H, *exo*-8′- or -6′-CH_2), 3.7 (m, 2H, 1′- and 5′-C*H*), 3.87 (br.t, 2H, 2′- and 4′-CH_2), 5.71 (t, $J = 6.7$ Hz, 3′-C*H*), 6.76 (t, $J = 6.3$ Hz, 1H, 2-C*H*), 6.98 (d, $J = 6.3$ Hz, 2H, 1- and 3-C*H*), 7.76 (d, $J = 9.3$ Hz, 2H, 4- and 10-C*H*), 8.2 (m, 3H, 6-, 7- and 8-C*H*), 8.24 (d, $J = 9.3$ Hz, 2H, 5- and 9-C*H*).$^1P\{^1H\}$ NMR (121.6 MHz, CD_2Cl_2, 296 K):δ −143.3 (sept, $J = 713$ Hz, PF_6^-). m.p. = 164–168 °C (decomp.). Anal. Calc. for $C_{24}H_{21}F_6PRu$: C, 51.90; H, 3.81%. Found: C, 52.50; H, 4.22%.

4.8. Preparation of [Ru(η⁶-perylene)(1-5-η⁵-cyclooctadienyl)]PF₆ (2g)

To an Et_2O solution (6 ml) of **1** (107 mg, 0.34 mmol) with perylene (98.1 mg, 0.39 mmol) excess HPF_6 (6 drops) was added to give orange precipitate. After removal of the solution layer, the resulting precipitate was recrystallized from cold CH_2Cl_2/Et_2O (2 ml/4 ml) at −30 °C to give yellow powder of [Ru(η⁶-perylene)(1-5-η⁵-cycloocatadienyl)]PF_6 (**2g**) in 64% yield (158 mg, 0.22 mmol). ^1H NMR (CD_2Cl_2): δ −0.35 (br.q, $J = 14$ Hz, 1H, *endo*-7′-CH_2), 0.9 (m, 3H, *exo*-7′-, *endo*-6′- and -8′-CH_2), 1.5 (m, 2H, *exo*-6′- and -8′-CH_2), 3.66 (br.dt, $J = 8$, 4 Hz, 1H, 1′- or 5′-C*H*), 3.73 (br.dt, $J = 8$, 4 Hz, 1H, 5′- or 1′-C*H*), 3.98 (br.q, $J = 7$ Hz, 2H, 2′- and 4′-C*H*), 5.88 (t, $J = 6.6$ Hz, 1H, 3′-C*H*), 6.5 (m, 2H, 1- and 3-C*H*), 6.93 (m, 1H, 3-C*H*), 7.49 (d, $J = 8.1$ Hz, 1H, 12-C*H*), 7.57 (t, $J = 7.8$ Hz, 1H, 8-C*H*), 7.58 (t, $J = 7.6$ Hz, 1H, 11-C*H*), 7.82 (d, $J = 8.1$ Hz, 1H, 7-C*H*), 7.9 (m, 2H, 5- and 6-C*H*), 7.92 (d, $J = 7.2$ Hz, 1H, 4-C*H*), 8.16 (d, $J = 8.1$ Hz, 1H, 9-C*H*), 8.22 (d, $J = 7.5$ Hz, 1H, 10-C*H*).$^{31}P\{^1H\}$ NMR (121.6 MHz, CD_2Cl_2, 296K):δ −143.5 (sept, $J = 711$ Hz, PF_6^-). m.p. = 162–164 °C (decomp). Anal. Calc. for $C_{38}H_{29}F_6PRu \cdot 0.5$perylene: C, 62.38; H, 4.00%. Found: C, 61.91; H, 4.20%.

4.9. Reduction of 2a with NaBH₄

A THF solution (6 ml) of a mixture of [Ru(η⁶-benzene)-(1-5-η⁵-cycloocatadienyl)]PF_6 (**2a**) (75 mg, 0.17 mmol) and 5 equiv. of $NaBH_4$ (32.0 mg, 0.85 mmol) at 0 °C for 20 h. The resulting solution was evaporated to dryness and then the residue was extracted with hexane (10 ml × 3) to give an orange solution, which was concentrated to give orange powder. After removal of the solution by cannular tube, the collected powder was dried under reduced pressure to give orange powder of **4a** in 64% yield (32.0 mg, 0.11 mmol). **4a**: ^1H NMR (CD_2Cl_2): δ 0.54 (m, 2H, *endo*-3′- and -7′-CH_2), 1.1 (m, 1H, *exo*-7′-CH_2), 1.6-2.2 (m, 4H, 6′- and 8′-CH_2), 2.41 (td, $J = 13.2$, 7.8 Hz, 1H, *exo*-3′-CH_2), 2.67 (td, $J = 7.8$, 4.5 Hz, 2H, 1′- and 5′-C*H* or 2′- and 4′-C*H*), 2.79 (td, $J = 7.8$, 4.2 Hz, 2H, 2′- and 4′-C*H* or 1′- and 5′-C*H*), 5.29 (s, 6H, C_6H_6). m.p. = 64–68 °C (decomp.).

4.10. Reduction of 2b with NaBH₄

Complex **2b** was treated with $NaBH_4$ by similar workup described for **2a**. [Ru(η⁶-naphthalene)(1-5-η⁵-cycloocatadienyl)]PF_6 (**2b**) (91.1 mg, 0.19 mmol), $NaBH_4$ (36.4 mg, 0.96 mmol) at 0 °C for 20 h. The NMR analysis of this the product (orange powder, 17.7 mg) by use of 1,4-dioxane as an internal standard showed formation of complex **3b** (22%) with unidentified species. **3b**: ^1H NMR (CD_2Cl_2): δ 1.71 (m, 8H, 3′-, 4′- 7′- and 8′-CH_2), 4.39 (br s, 4H, 1′-, 2′-, 5′- and 6′-C*H*), 4.75 (AA′BB′, 2H, 1- and 4-C*H* or 2- and 3-C*H*), 6.05 (AA′BB′, 2H, 2- and 3-C*H* or 1- and 4-

C*H*), 7.40 (m, 4H, 5-, 6-, 7- and 8-C*H*). m.p. = 187–190 °C (decomp.).

4.11. Reduction of *2c* with $NaBH_4$

Complex **2c** was treated with $NaBH_4$ by similar workup described for **2a**. [Ru(η^6-phenanthrene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2c**) (201 mg, 0.38 mmol), $NaBH_4$ (71.5 mg, 1.9 mmol) at 0 °C for 20 h. Orange powder of a mixture of **3c** and **4c** (1.0:8.3 in CD_2Cl_2 at 19.5 °C) in 76% yield (111 mg, 0.28 mmol). **3c**: ^{1}H NMR (CD_2Cl_2): δ 1.6 (m, 2H, *endo*-3′- and -7′-CH_2 (or *endo*-4′- and -8′-CH_2)), 1.7 (m, 6H, *exo*-3′-, -4′-, -7′- and -8′-CH_2 and *endo*-4′- and -8′-CH_2 (or *endo*-3′- and 7′-CH_2)), 3.0 (m, 2H, 1′- and 5′-C*H* (or 2′- and 6′-C*H*)), 3.3 (m, 2H, 2′- and 6′-C*H* (or 1′- and 5′-C*H*)), 4.91 (d, $J = 5.4$ Hz, 1H, 1-C*H*), 5.48 (d, $J = 5.4$ Hz, 1H, 4-C*H*), 6.07 (t, $J = 5.4$ Hz, 1H, 2- or 3-C*H*), 6.11 (t, $J = 5.4$ Hz, 1H, 3- or 2-C*H*), 7.33 (d, $J = 9.0$ Hz, 1H, 10-C*H*), 7.59 (m, 2H, 6- and 7-C*H*), 7.64 (d, $J = 9.0$ Hz, 1H, 9-C*H*), 7.86 (m, 1H, 5- or 8-C*H*), 8.13 (m, 1H, 8- and 5-C*H*). **4c**: ^{1}H NMR (CD_2Cl_2): δ −0.21 (br.q, $J = 12$ Hz, 1H, *endo*-7′-CH_2), 0.3 (m, 2H, *exo*-7′-CH_2 and *endo*-6′- or -8′-CH_2), 1.1 (m, 1H, *exo*-8′- or -6′-CH_2), 1.2 (overlapped with incorporated hexane, *exo*-6′- or -8′-CH_2), 1.5 (overlapped with signals due to **3c**, *exo*-8′- or -6′-CH_2), 1.7 (overlapped with signals due to **3c**, *endo*-3′-CH_2), 2.16 (dt, $J = 13.5$, 7.5 Hz, 1H, *exo*-3′-CH_2), 2.38 (td, $J = 8.3$, 4.5 Hz, 1H, 1′- or 5′-C*H*), 2.53 (td, $J = 8.1$, 4.5 Hz, 1H, 4′- or 2′-C*H*), 2.7 (m, 2H, 2′- or 4′-C*H* and 5′- or 1′-C*H*), 4.81 (d, $J = 5.4$ Hz, 1H, 1- or 4-C*H*), 5.43 (d, $J = 5.4$ Hz, 1H, 4- or 1-C*H*), 5.91 (t, $J = 5.4$ Hz, 1H, 2- or 3-C*H*), 6.00 (t, $J = 5.4$ Hz, 1H, 3- or 2-C*H*), 7.39 (d, $J = 8.4$ Hz, 1H, 9- or 10-C*H*), 7.56 (d, J = 8.4 Hz, 1H, 10- or 9-C*H*), 7.6 (m, 2H, 6- and 7-C*H*), 7.86 (m, 1H, 5- or 8-C*H*), 8.23 (m, 1H, 8- or 5-C*H*). m.p. = 122–124 °C (decomp.). Anal. Calc. for $C_{22}H_{22}Ru$: C, 68.19; H, 5.72%. Found: C, 68.38; H, 5.29%.

4.12. Reduction of *2d* with $NaBH_4$

Complex **2d** was treated with $NaBH_4$ by similar workup described for **2a**. [Ru(η^6-anthracene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2d**) · 0.3 anthracene (111.2 mg, 0.19 mmol), $NaBH_4$ (42.6 mg, 1.13 mmol) at 0 °C for 20 h. Pale yellow powder (33.3 mg), which was characterized as a crude free anthracene was obtained.

4.13. Reduction of *2e* with $NaBH_4$

A THF solution (6 ml) of a mixture of [Ru(η^6-triphenylene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2e**) (86.0 mg, 0.15 mmol) and 5 equiv. of $NaBH_4$ (42.0 mg, 1.10 mmol) was stirred at 0 °C for 20 h. The resulting solution was evaporated to dryness and then the residue was extracted with benzene (5 ml × 3) to give an orange solution, which was concentrated to give orange powder. After removal of the solution by cannular tube, the collected powder was under reduced pressure to give orange powder (57.1 mg). The NMR analysis of the powder showed formation of **3e** in 23% yield and **4e** in 53% yield. **3e**: ^{1}H NMR (CD_2Cl_2): δ −0.02 (m, 1H, *endo*-7′-CH_2), 0.3 (m, 2H, *exo*-7′-CH_2 and *endo*-6′- or -8′-CH_2), 1.1 (m, 1H, *exo*-8′- or -6′-CH_2), 1.2 (overlapped with incorporated hexane, *exo*-6′- or -8′-CH_2), 1.5 (overlapped with signals due to **3c**, *exo*-8′- or -6′-CH_2), 1.7 (overlapped with signals due to **3e**, *endo*-3′-CH_2), 2.05 (dt, $J = 12.9$, 7.8 Hz, 1H, *exo*-3′-CH_2), 2.29 (td, $J = 8.4$, 4.2 Hz, 2H, 1′- and 5′-C*H*), 2.43 (td, $J = 8.4$, 4.5 Hz, 2H, 4′- and 2′-C*H*), 5.58 (AA′BB′, 2H, 2- and 3-C*H*), 6.01 (AA′BB′, 2H, 1- and 4-C*H*), 7.78 (td, $J = 7.2$, 1.5 Hz, 2H, 6- and 11-C*H* or 7- and 10-C*H*), 7.60 (td, $J = 7.2$, 1.5 Hz, 4H, 7- , 10-C*H* and 6-, 11-C*H*), 8.17 (dd, $J = 7.2$, 1.5 Hz, 2H, 5- and 12-C*H* or 8- and 9-C*H*), 8.60 (dd, $J = 7.2$, 1.5 Hz, 2H, 8- and 9-C*H* or 5- and 12-C*H*). **4e**: ^{1}H NMR (CD_2Cl_2): δ 1.62 (m, 8H, 3′-, 4′- 7′- and 8′-CH_2), 3.0 (br.s, 4H, 1′-, 2′-, 5′- and 6′-C*H*), 5.64 (AA′BB′, 2H, 2- and 3-C*H*), 6.15 (AA′BB′, 2H, 1- and 4-C*H*), 7.64 (m, 4H, 7- , 10-C*H* and 6-, 11-C*H*), 8.11 (dd, $J = 7.8$, 1.5 Hz, 2H, 5- and 12-C*H* or 8- and 9-C*H*), 8.59 (dd, $J = 7.8$, 1.5 Hz, 2H, 8- and 9-C*H* or 5- and 12-C*H*). Similar treatment of **2e** (89.9 mg, 0.15 mmol) with 1.6 equiv. of $NaBH_4$ (9.1 mg, 0.24 mmol) gave **3e** (9%) and **4e** (55%). Treatment of **2e** (77.4 mg, 0.13 mmol) with 3.4 equiv. of $NaBH_4$ (16.7 mg, 0.44 mmol) gave **3e** (9%) and **4e** (63%). Treatment of **2e** (35.1 mg, 0.087 mmol) with 11 equiv. of $NaBH_4$ (35.1 mg, 0.92 mmol) gave **3e** (7%) and **4e** (47%). m.p. = 168–170 °C (decomp.).

4.14. Reduction of *2f* with $NaBH_4$

Complex **2f** was treated with $NaBH_4$ by similar workup described for **2a**. [Ru(η^6-pyrene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2f**) (167 mg, 0.30 mmol), $NaBH_4$ (57.1 mg, 1.51 mmol) at 0 °C for 20 h. Orange powder of **4f** in 58% yield (72.0 mg, 0.17 mmol). **4f**: ^{1}H NMR (CD_2Cl_2): δ 0.09 (br.t, $J = 12$ Hz, 2H, *endo*-6′ and -8′-CH_2), 0.25 (qt, $J = 12$, 2 Hz, 1H, *endo*-7′-CH_2), 1.2 (m, 1H, *exo*-7′-CH_2), 1.4 (m, 2H, *exo*-6′- and 8′-C*H*), 1.6 (br, *endo*-3′-CH_2), 1.95 (dt, $J = 12.9$, 7.5 Hz, 1H, *exo*-3′-C*H*), 2.05 (td, $J = 8.7$, 4.5 Hz, 2H, 1′- and 5′-C*H* or 2′- and 4′-C*H*) 2.18 (td, $J = 8.1$, 6.0 Hz, 1H, 2′- and 4′-C*H* or 1′- and 5′-C*H*), 5.75 (d, $J = 6$ Hz, 2H, 1- and 3-C*H*), 5.87 (t, $J = 6$ Hz, 1H, 2-C*H*), 7.36 (d, $J = 9$ Hz, 2H, 4- and 10-C*H* or 5- and 9-C*H*), 7.67 (d, $J = 9$ Hz, 2H, 5- and 9-C*H* or 4- and 10-C*H*), 7.73 (dd, $J = 7.5$, 6.3 Hz, 1H, 7-C*H*), 7.5 (br,t, $J = 7.5$ Hz, 2H, 6- and 8-C*H*), and incorporated 0.5 equiv. of pyrene was observed at 8.03 (dd, $J = 7.2$, 0.9 Hz, 2H), 8.11 (s, 4 H), 8.21 (d, $J = 7.2$ Hz, 4H). m.p. = 138–140 °C (decomp.).

4.15. Reduction of *2g* with $NaBH_4$

Complex **2g** was treated with $NaBH_4$ by similar workup described for **2a**. [Ru(η^6-perylene)(1-5-η^5-cycloocatadienyl)]PF_6 (**2d**) · 0.5 perylene (70.8 mg, 0.10 mmol), $NaBH_4$

(22.9 mg, 0.60 mmol) at 0 °C for 20 h. Pale yellow powder (38.6 mg), which was characterized as crude free perylene with trace amount of perylene complexes, was obtained.

4.16. Ligand exchange reaction of arenes

Complex **2a** (7.3 mg, 0.012 mmol) and 4.1 equiv. of triphenylene (11.5 mg, 0.050 mmol) were placed in an NMR tube under vacuum into which dry CD_2Cl_2 (0.60 ml) was introduced by valve-to-valve distillation. The reaction system was placed at 20 °C for 20 h. The product was confirmed by the ^1H NMR spectrum on the basis of 1,4-dioxane as an internal standard (Table 2 entry 1). Similarly, following reactions were also monitored by the ^1H NMR spectroscopy. Although part of ruthenium complexes decomposed during the reaction and the integration of signals may involve unavoidable errors, the results were shown in Table 2. entry 2: **2b** (13.9 mg, 0.029 mmol) with 3.0 equiv. of phenanthrene (15.4 mg, 0.086 mmol). entry 3: **2b** (24.9 mg, 0.052 mmol) with 3.1 equiv. of pyrene (33.6 mg, 0.16 mmol). entry 4: **2c** (12.4 mg, 0.023 mmol) with 3.0 equiv. of benzene (6.2 μl, 0.069 mmol). entry 5: **2c** (9.9 mg, 0.018 mmol) with 3.1 equiv. of naphthalene (7.3 mg, 0.056 mmol). entry 6: **2c** (15.8 mg, 0.029 mmol) with 2.6 equiv. of anthracene (13.2 mg, 0.074 mmol). entry 7: **2c** (14.7 mg, 0.027 mmol) with 1.1 equiv. of triphenylene (6.8 mg, 0.029 mmol). entry 8: **2c** (20.3 mg, 0.038 mmol) with 2.9 equiv. of pyrene (23.1 mg, 0.11 mmol). entry 9: **2c** (15.4 mg, 0.029 mmol) with 3.0 equiv. of perylene (21.8 mg, 0.086 mmol). entry 10: **2d**(20.3 mg, 0.034 mmol) with 3.0 equiv. of phenanthrene (18.1 mg, 0.010 mmol). entry 11: **2d** (15.7 mg, 0.026 mmol) with 3.1 equiv. of perylene (20.1 mg, 0.080 mmol). entry 12: **2e** (19.5 mg, 0.033 mmol) with 3.0 equiv. of benzene (8.9 μl, 0.10 mmol). entry 13: **2f** (12.8 mg, 0.023 mmol) with 2.8 equiv. of naphthalene (8.4 mg, 0.065 mmol). entry 14: **2f** (13.5 mg, 0.024 mmol) with 3.1 equiv. of phenanthrene (13.4 mg, 0.075 mmol). entry 15: **2f** (14.9 mg, 0.027 mmol) with 2.9 equiv. of anthracene (14.2 mg, 0.079 mmol). entry 16: **2f** (14.6 mg, 0.026 mmol) with 3.1 equiv. of perylene (20.1 mg, 0.080 mmol). entry 17: **2g** (13.9 mg, 0.018 mmol) with 3.1 equiv. of anthracene (10.1 mg, 0.056 mmol).

4.17. X-ray structure analysis of complex *2g*

Single crystals of **2g** suitable for X-ray analysis were obtained from a mixture of CH_2Cl_2 and Et_2O. A single crystal was selected by using monochromated microscope and mounted on the top of capillary using Paraton-N oil. Diffraction experiments were performed on a Rigaku RASA-7R diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å). The crystallographic data and details associated with data collection for **2g** are given in Table 3. The data were processed using the teXsan crystal solution package operating on a SGI O2 workstation. The structure was solved by Patterson Methods (SAPI). An absorption correction was applied with the program PSI-scan. All non-hydrogen atoms were found on difference maps and were refined anisotropically. All hydrogen atoms were located in the calculated positions. Crystallographic thermal parameters are given in Table 3.

Table 3
Crystallographic data for complex **2g** · CH_2Cl_2 · 0.5perylene

Formula	$C_{28}H_{22}Cl_2F_6PRu$
Formula weight	675.42
Crystal system	Triclinic
Lattice type	Primitive
a (Å)	11.514(5)
b (Å)	15.544(7)
c (Å)	11.038(5)
α (°)	108.57(4)
β (°)	116.50(3)
γ (°)	79.97(4)
V (Å^3)	1674(1)
Space group	$P-1$ (No.2)
Z value	2
D_{calc} (g cm^{-3})	1.339
$F(000)$	674.00
μ (Mo Kα) (cm^{-1})	7.22
Temp. (K)	200
Scan-type	ω–2θ
$2\theta_{max}$ (°)	55.0
Number of reflections measured	Total: 8051, unique: 7671
Structure solution	Patterson methods (SAPI)
Number of observations ($I > 3.00\ \sigma(I)$)	3578
Number of variables	443
Reflection/parameter ratio	8.08
R	0.0936
R_w	0.133
GOF	1.216

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Appendix A. Supplementary material

CCDC 627199 contains the supplementary crystallographic data for **2g**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.023.

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[19] Although the reaction mechanism for this reduction reaction is not clear to date, the selectivity in the reduction giving **3** and **4** would be due to independent reaction mechanisms: one is the hydride attack on the ruthenium center followed by migration of the Ru–H to the cycloocatdienyl fragment, and the other is a direct attack of hydride ion on the cyclooctadienyl fragment.

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