One-Step Preparation of [RuCp*(η⁶-arene)]⁺ Sandwich Complexes

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Keywords: Ruthenium / Sandwich complexes / NMR spectroscopy / Synthetic methods

In a single step, several variously functionalized [RuCp*(η⁶-arene)]⁺ sandwich complexes have been prepared starting from $RuCl_3 \cdot xH_2O$ in yields ranging from 35 to 80%, referring to ruthenium. The protocol covers the preparation of valuable [RuCp*]⁺-complexed amino acids. In comparative experiments starting from the oligomer $[RuCp^*Cl_2]_n$ and using methanol/methanolate as the reducing agent, the formation of undesired side products was observed, resulting from nucleophilic substitution at the *o*-chloroanisole complex and from methoxylation of the Cp* ligand.

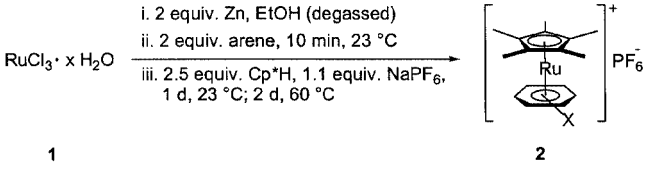
Introduction

Our program on the synthesis of oligomeric Ru-labelled diaryl ether peptoids[1] requires the availability of large quantities of various ruthenium sandwich complexes by a facile synthetic procedure. Radioactive labelling of peptoids[2] holds the promise to selectively bind and destroy tumour cells by combining the biological activity of biooligomers with the physical properties of metals. Ruthenium appears to be especially suitable because its radioactive isotopes cover half-lives ranging from three days to one year.[3] In this paper, we report a one-step procedure that provides large quantities of several [RuCp*]⁺ complexes, including some with amino acid ligands, to be used in bioorganometallic chemistry.

Pearson et al., Rich et al., and Matassa et al. have published pioneering work in the field of [RuCp]⁺-labelled peptoid diaryl ethers.[4] The [RuCp]⁺ complexation of the chloroarene precursors of the diaryl ethers follows a procedure based on the work of Gill and Mann.[5] Recently, the protocol was improved by Trost and Older,[6] but still needs four subsequent steps, starting from $RuCl_3 \cdot xH_2O$ (**1**). The situation may be simplified if [RuCp*]⁺ complexes are pursued instead (Cp* = pentamethylcyclopentadienyl). Kudinov et al. have obtained [RuCp*(η⁶-arene)]⁺ sandwich complexes from the reaction of $RuCl_3 \cdot xH_2O$ (**1**) with Cp*H and the three robust arenes benzene, toluene, and mesitylene in boiling alcohols as reducing agents.[7] The use of Zn — a milder reductant of the oligomer $[RuCp^*Cl_2]_n$ — in an overall two-step procedure was first reported by Chaudret et al.[8] In this paper we report a practically useful one-step procedure to [RuCp*(η⁶-arene)]⁺ sandwich complexes merging both approaches.

Results

Scheme 1 gives the reaction conditions we have developed. Upon addition of Zn (2 equiv.) to the ethanol solution of $RuCl_3 \cdot xH_2O$, a rapid colour change of the ethanolic solution from cherry red to dark blue occurred. Subsequently, the arene and Cp*H were added. The chosen stoichiometry gave the best yields. Table 1 gives 15 examples, 13 of which have been synthesised by the reported method. For comparison, only complexes **4**, **14** and **15** were obtained using methanol/methoxide as reducing agent, starting from the oligomer $[RuCp^*Cl_2]_n$.[14]



Scheme 1. One-step preparation of [RuCp*(η⁶-arene)]⁺ sandwich complexes

It was observed that the yield of the sandwich complexes **2** increased substantially with prolonged reaction times. While, for example, the reaction with acetophenone had proceeded to about 36% (referring to a Ru content of 37% in $RuCl_3 \cdot xH_2O$) after 10 minutes, a yield of 51% of the sandwich complex **11** was isolated after three days at 60 °C. Facile workup of the reaction mixture (Scheme 2) is very

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important for practical applications and had to include the separation of non-polar by-products. The most convenient way was by partitioning of the column-filtered residue between water/methanol and *iso*-octane. Removal of inorganic salts was secured by exhaustive extraction of the crude product with dichloromethane. As reported by us for $[RuCp]^+$-complexed diaryl ether peptoids, aminopropyl-functionalised silica proved to be suitable for further purification of the cationic sandwich complexes by HPLC.[1]

Two new diastereomeric sandwich complexes (**13a**, **13b**) were obtained from (*E*)-ethyl cinnamate (entry 11), resulting from Diels–Alder cycloadditions of Cp*H to the olefinic double bond.[9] 2D NMR spectroscopic analysis (COSY, HSQC, HMBC) allowed the complete assignment of all chemical shifts to the diastereomers **13a** and **13b**. Since it was not possible to separate these diastereomers, even by HPLC, a NOESY spectrum of the mixture had to be the basis for the decision on which set of NMR signals belonged to which diastereomer. Complex **13a**, with the sandwich complex in the axial position of the norbornene system, shows a correlation between 7-H and 17-H while for the diastereomer **13b** a cross-peak between 8-H and 17-H is observed. For **13a** an X-ray analysis (Figure 1) confirmed its stereochemistry.

Figure 2 gives the crystal structure of the Cp*-monomethoxylated sandwich complex of ethyl benzene (**14**). Complex **14** was only formed by the oligomer route, and not in the direct preparation (entry 2).

We also prepared $[RuCp^*]^+$ complexes of amino acid esters (entries 14 and 15). The $[RuCp^*]^+$-complexed ethyl

Table 1. $[RuCp^*(\eta^6\text{-arene})]^+$ sandwich complexes obtained via the one-step procedure (Scheme 1, for entries 1–11, 14, 15) and via the oligomer route (entries 12, 13); the counterion is always hexafluorophosphate

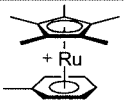
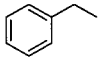
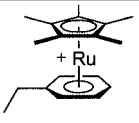
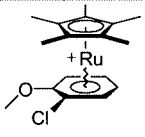
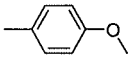
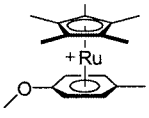
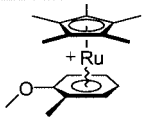
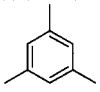
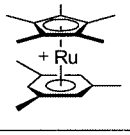
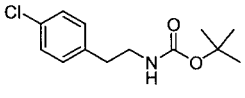
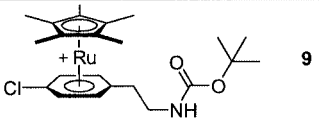
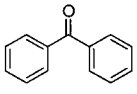
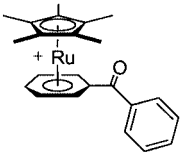
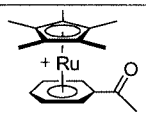
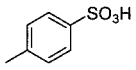
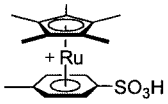
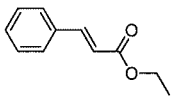
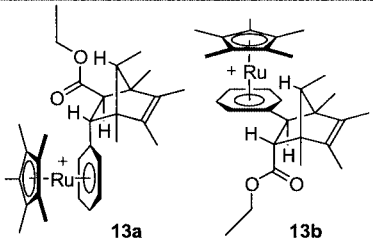
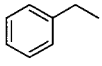
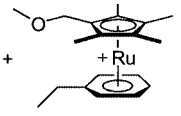
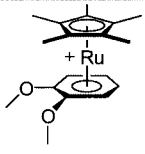
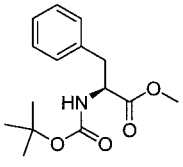
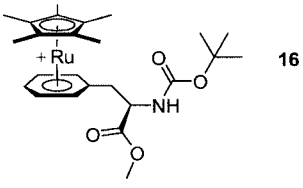
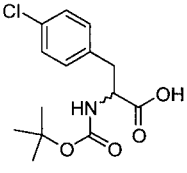
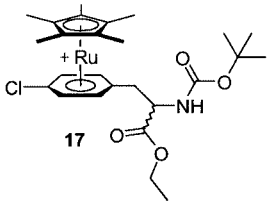
Entry	Arene	Sandwich complex	Yield [%]
1		 **3**	54
2		 **4**	67
3		 **5**	35
4		 **6**	69
5		 **7**	67
6		 **8**	80
7		 **9**	44
8		 **10**	35

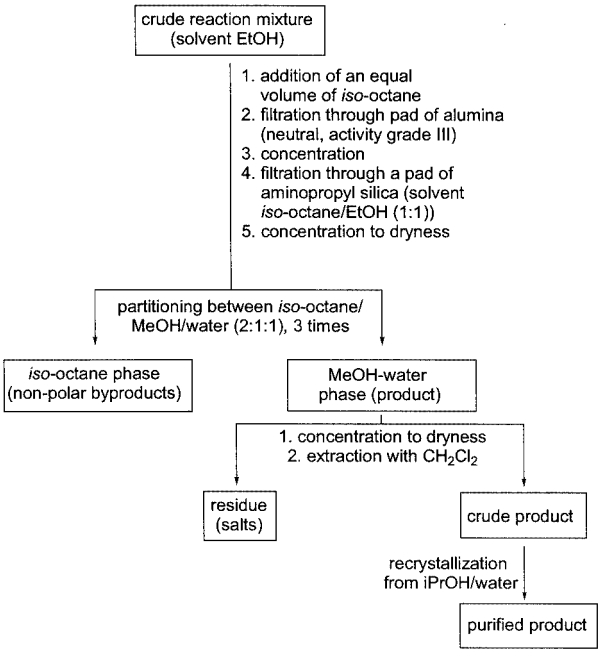
Table 1. *(continued)*

9		 **11**	51
10		 **12**	66
11		 **13a** **13b**	51
12		 **4** + **14**	44 + 12
13		 **15**	20
14		 **16**	55
15		 **17**	45

ester **17** was formed directly from the acid (entry 15) when the reaction was carried out in ethanol. The esterification can be prevented if *tert*-butanol is used as a solvent instead.

Discussion

There are several multi-step routes to [RuCp*(η⁶-arene)]⁺ sandwich complexes. For the Cp analogues, a popular approach uses the reaction of $[RuCp(CH_3CN)_3]^+$ half-sandwich complexes with various arenes. The tris-acetonitrile complexes are air-sensitive and should be freshly prepared before use.[10] The availability[11] of the oligomer $[RuCp^*Cl_2]_n$ has opened several synthetic routes to [RuCp*(η⁶-arene)]⁺ sandwich complexes using $LiBEt_3H$,[12] Zn,[8,13] methanol/methoxide,[14] or various alcohols/K_2CO_3 [15] as reducing agents. However, the purity of the oligomer $[RuCp^*Cl_2]_n$ may vary and therefore have an unpredictable influence on the yields (55 to 80%) of the desired [RuCp*(η⁶-arene)]⁺ sandwich complexes.[11,16] The only characterised complex was obtained for $n = 2$ in a benchmark procedure, but this complex should not be stored for long periods.[17] As a by-product of the synthesis of the oligomer, decamethylruthenocene is formed in about 10−30% yield.[18] In addition, it has been reported that on prolonged standing the oligomer may transform into an entity with lower solubility which is less available for further conversion.[16b] As a consequence, it is desirable to avoid



Scheme 2. Flow chart outlining the workup of the charged ruthenium complexes

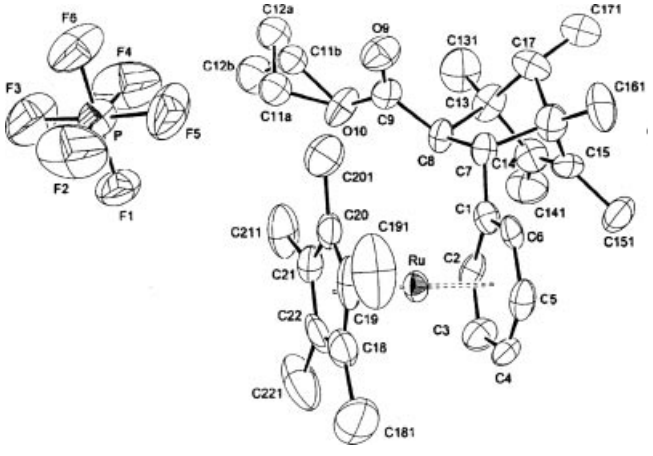


Figure 1. ORTEP plot of the Diels–Alder adduct **13a**; the atoms $C11_a$ and $C12_a$ (ethyl group) are disordered

the oligomer $[RuCp^*Cl_2]_n$ in the synthetic sequence. Koelle et al. circumvented that problem and synthesised alkoxoruthenium(II) complexes from the oligomer under mild conditions in quantitative yields. $[RuCp^*(Oalkyl)]_2$ is then reacted with two equivalents of arene to form the sandwich complex in yields ranging from 36% to 72%.[15,19] A pathway to $[RuCp^*(\eta^6\text{-arene})]^+$ sandwich complexes that does not begin with $RuCl_3 \cdot xH_2O$ (**1**) was pursued by Salzer and Ludi.[20] Ru^{II} triflate is reacted with a mixture of Cp*H and arene. The synthesis of $[Ru(H_2O)_6](OTf)_2$ is itself a three-step procedure including the distillation of the toxic RuO_4.[21]

The isolated yields obtained by our one-step procedure are similar to the more complicated protocols and vary from 35% (**5**, **10**) to 80% (**8**), relative to ruthenium (Table 1). At least partial reduction of $RuCl_3 \cdot xH_2O$ (**1**) prior to the addition of arene or Cp*H is indicated by the rapid colour change of the ethanolic solution from cherry red to dark blue. The excessive Zn may also act as a quencher of HCl after the subsequent reduction of the η^6-arene, Cp*H, and $NaPF_6$, as suggested by Salzer et al.[22] The $[RuCp^*]^+$ sandwich complexes of the electron-rich arenes **3**–**8** (entries 1–6) were prepared in order to establish the synthetic route. Compounds **3**, **6**, **8**, **10**, and **12** have been prepared before by other protocols.[23] The $[RuCp^*]^+$ sandwich complex **9** of *N*-Boc-protected *p*-chlorophenylethylamine (entry 7) is important for the synthesis of metal-complexed diaryl ether peptoids.[1] As for the correspondingly Boc-protected compounds **16** and **17**, the yield of compound **9** is very much improved if two equivalents of $NaHCO_3$ are added as a buffer before the addition of the arene. The Boc protecting groups would otherwise be cleaved off under the acidic conditions.

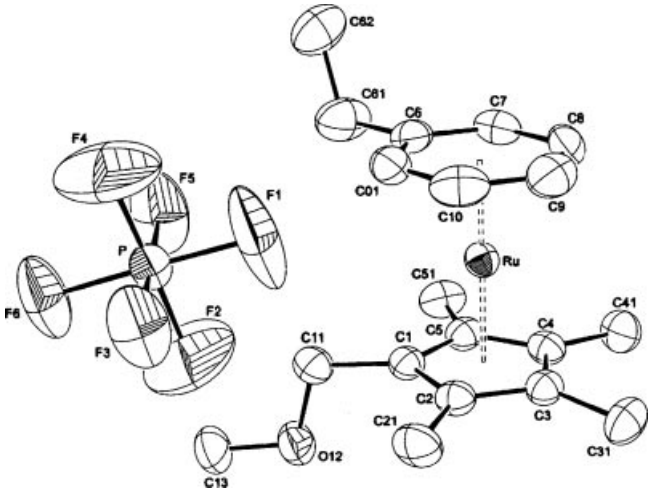
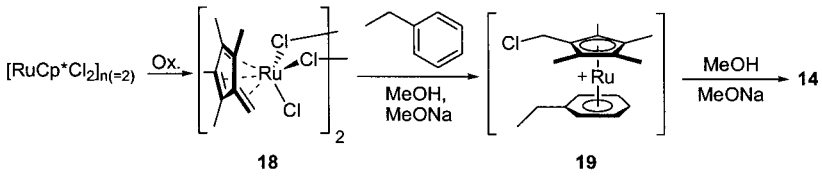


Figure 2. ORTEP plot of the methoxylated sandwich complex **14**

It was unclear if benzophenone (entry 8) would be complexed once or twice. Thus far, the doubly complexed sandwich complex of benzophenone has been obtained as by far the major product.[19] Our procedure provides the mono product **10** exclusively. The decrease in electron density in the uncomplexed phenyl group may prevent a second reaction. *p*-Toluenesulfonic acid (entry 10) cleanly gives the corresponding sandwich complex **12**.

Compared with our protocol (entries 2 and 3), difficulties were encountered when using methanol/methanolate as reducing agent of the oligomer $[RuCp^*Cl_2]_n$ ($n = 2$) (entries 12 and 13). Complexation of *o*-chloroanisole (entry 13) led to the dimethoxy sandwich complex **15** as the major product, with the desired chlorinated product formed in yields below 5%. Obviously, nucleophilic substitution is not suppressed under the reaction conditions. On the other hand, entry 3 demonstrates that the one-step procedure provides the desired *o*-chloroanisole complex **5**.

We discovered the monomethoxy sandwich **14** to be a side product (12%) when reacting ethylbenzene via the oligomer route (Scheme 3; Table 1, entry 12). An explanation could be the oxidation of the two Cp* ligands of the oligomer $[RuCp^*Cl_2]_n$ ($n = 2$) to two η^6-tetramethylfulvene li-



Scheme 3. Possible mechanism leading to the formation of the methoxylated sandwich complex **14** in methanol (explanation see text)

gands (Scheme 3). Upon treatment of **18** with carbon monoxide, Maitlis et al. have observed monochlorination of the Cp* ring.[24] In our case, ethylbenzene may take the role of carbon monoxide leading to the formation of the Cp*-chlorinated sandwich complex **19**. It has been reported that nucleophilic substitution by methoxide occurs readily.[24b]

In summary, this contribution presents, for the first time, a detailed study of the one-step preparation of [RuCp*(η⁶-arene)]⁺ sandwich complexes. Compounds **4**, **5**, **7**, **9**, **11**, **13a**, **13b**, **14**, **15**, **16**, and **17** have been prepared for the first time. The sandwich complexes **9**, **16** and **17** are used by us for applications in bioinorganic chemistry.[1] Very recently, Mann et al. used a similar protocol for the preparation of the trifluoromethylated complex [RuCp′(η⁶-benzene)]⁺PF_6^-, which was used as a starting point of the synthesis of other [RuCp′(η⁶-arene)]⁺ sandwich complexes.[25]

Experimental Section

General: All reactions were carried out under an argon atmosphere with distilled, non-anhydrous solvents. Yields refer to purified compounds. Reagents, of high commercial quality, were purchased from Aldrich, Acros, Merck and Fluka and were used without further purification. Reactions were controlled by thin-layer chromatography (0.25 mm E. Merck alumina plates NH_2 $F_{254}S$). TLCs were analysed under UV light (λ = 254 nm), followed by heating after treatment with 1,10-phenanthroline (2 M dipping solution in EtOH). E. Merck Al_2O_3 90 standardised (activity grade III, particle size 63−200 μm), E. Merck aminopropyl silica LiChroprep NH_2 (particle size 40−63 μm), and E. Merck silica 60 (particle size 40−63 μm) were used for preparative column chromatography. NMR spectra were recorded on a Varian VRX 400S spectrometer. The NMR shifts were calibrated using the solvent peak as internal reference and assigned on the basis of HSQC and HMBC experiments. All infrared spectra were recorded on an IFS 45 Bruker spectrometer. The UV/Vis spectra were recorded using a Omega 20 Bruins Instruments UV-spectrophotometer. High resolution fast atom bombardment (FAB) and electrospray ionization (ESI) mass spectra were recorded on a Finnigan MAT 95Q mass spectrometer. Only the three predominant isotopes are listed. Melting points were determined with a Electrothermal IA 9000 Series melting point microscope and are uncorrected.

General Procedure for the Preparation of the Ruthenium Sandwich Complexes: Zinc dust (2 equiv.) was added to a solution of $RuCl_3 \cdot xH_2O$ (35−40% Ru) in degassed EtOH (15 mL per mmol). After the solution had turned blue the arene (2 equiv.) was added and the mixture stirred for 10 min. In the case of the Boc-protected compounds **9**, **16**, and **17**, $NaHCO_3$ (2 equiv.) was added to the blue solution before the arene was added. 1,2,3,4,5-Pentamethylcyclopentadiene (2.5 equiv.) and $NaPF_6$ (1.1 equiv.) were added and the reaction mixture was stirred for 1 day at room temperature and for 2 days at 60 °C. *iso*-Octane (15 mL per mmol) was added and the mixture filtered through a pad of aluminium oxide. The filtrate was concentrated and filtered through a pad of aminopropyl silica [*iso*-octane/EtOH (1:1) as eluent]. After concentration of the filtrate to dryness, water (50 mL per mmol), *iso*-octane (100 mL per mmol) and MeOH (50 mL per mmol) were added. Further MeOH was added until the solution became clear. The *iso*-octane phase was separated and the polar phase was extracted with *iso*-octane (twice). The combined *iso*-octane phases were extracted with water/MeOH (1:1) and the polar phases were combined and concentrated to dryness. The product was extracted from the residue with dichloromethane (15 mL, three times) and recrystallised from water/isopropanol (addition of isopropanol to a boiling aqueous suspension).

(η⁶-Methylbenzene)(η⁵-pentamethylcyclopentadienyl)ruthenium Hexafluorophosphate (3): Yellowish powder (142 mg, 54%); m.p. 332 °C (decomp.). ^{1}H NMR (400 MHz [D$_4$]methanol): δ = 1.98 (s, 15 H, η⁵-CCH_3), 2.19 (s, 3 H, η⁶-$C_{ar}CH_3$), 5.82 (m, 5 H, η⁶-CH_{ar}) ppm. ^{13}C NMR (100 MHz, [D$_4$]methanol): δ = 10.52 (η⁵-CCH_3), 18.54 (η⁶-$C_{ar}CH_3$), 87.75 (η⁶-C_{ar}H), 88.44 (η⁶-C_{ar}H), 89.49 (η⁶-C_{ar}H), 97.42 (η⁵-CCH$_3$), 101.81 (η⁶-C_{ar}CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (m), 3095 (w), 2921 (m), 1637 (vw), 1528 (w), 1476 (m), 1457 (m), 1388 (s), 1075 (vw), 1036 (m), 836 (vs), 779 (vw), 585 (vs), 458 (vw), 409 (w). UV/Vis (MeOH): λ_{max} (ε) = 206 nm (46734 mol^{-1}dm^{3}cm^{-1}). MS (FAB+, NBA): *m*/*z* (%) = 328/329/331 (67/100/54) [M$^+$]. HRMS (ESI+): calcd. for $C_{17}H_{23}{}^{102}$Ru: 329.0837; found 329.0842.

(η⁶-Ethylbenzene)(η⁵-pentamethylcyclopentadienyl)ruthenium Hexafluorophosphate (4): Colourless powder (194 mg, 67%); m.p. 290 °C (decomp.). ^{1}H NMR (400 MHz, [D$_4$]methanol): δ = 1.17 (t, ^3J = 7.7 Hz, 3 H, η⁶-$C_{ar}CH_2CH_3$), 1.92 (s, 15 H, η⁵-CCH_3), 2.36 (q, ^3J = 7.7 Hz, 2 H, η⁶-$C_{ar}CH_2CH_3$), 5.91 (m, 5 H, η⁶-$C_{ar}H$) ppm. ^{13}C NMR (100 MHz, [D$_4$]methanol): δ = 10.57 (η⁵-CCH_3), 15.88 (η⁶-$C_{ar}CH_2CH_3$), 27.40 (η⁶-$C_{ar}CH_2CH_3$), 87.92 (η⁶-C_{ar}H), 88.49 (η⁶-C_{ar}H), 88.66 (η⁶-C_{ar}H), 97.48 (η⁵-CCH$_3$), 107.30 (η⁶-$C_{ar}CH_2CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (s), 2975 (m), 2918 (m), 1629 (m), 1525 (w), 1477 (m), 1458 (m), 1417 (w), 1389 (m), 1074 (w), 1035 (m), 837 (vs), 767 (w), 558 (s), 493 (w), 461 (w). MS (ESI+): *m*/*z* (%) = 342/343/345 (57/100/55) [M$^+$]. HRMS (ESI+): calcd. for $C_{18}H_{25}{}^{102}$Ru: 343.0993; found 343.0997.

(η⁶-1-Chloro-2-methoxybenzene)(η⁵-pentamethylcyclopentadienyl)-ruthenium Hexafluorophosphate (5): Colourless powder (101 mg, 35%); m.p. 335 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.02 (s, 15 H, η⁵-CCH_3), 4.02 (s, 3 H, η⁶-$C_{ar}OCH_3$), 5.96 (ddd, ^3J = 6.4, ^3J = 4.9, ^4J = 1.0 Hz, 1 H, η⁶-$C_{ar}H$), 6.12 (ddd, ^3J = 5.4, ^3J = 4.9, ^4J = 1.0 Hz, 1 H, η⁶-$C_{ar}H$), 6.38 (dd, ^3J = 5.4, ^4J = 1.0 Hz, 1 H, η⁶-$C_{ar}H$), 6.54 (dd, ^3J = 6.4, ^5J = 0.5 Hz, 1 H, η⁶-$C_{ar}H$) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 10.13 (η⁵-CCH_3), 58.38 (η⁶-$C_{ar}OCH_3$), 74.95 (η⁶-C_{ar}H), 86.18 (η⁶-C_{ar}H), 87.21 (η⁶-C_{ar}H), 89.02 (η⁶-C_{ar}H), 95.67 (η⁶-C_{ar}Cl), 97.69 (η⁵-CCH$_3$), 130.93 (η⁶-C_{ar}OCH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (m), 3104 (w), 2919 (vw), 1636 (w), 1514 (m), 1460 (m), 1429 (m), 1407

(vw), 1391 (m), 1266 (s), 1224 (w), 1179 (vw), 1111 (vw), 1062 (w), 1029 (w), 1005 (m), 838 (vs), 794 (vw), 740 (vw), 685 (m), 660 (vw), 581 (vw), 559 (s), 514 (vw), 457 (vw), 424 (vw). UV/Vis (MeOH): λ_{max} (ε) = 214 nm (29363 $mol^{-1}dm^3cm^{-1}$). MS (ESI+): *m/z* (%) = 378/379/381 (43/100/76) [M^+]. HRMS (ESI+): calcd. for $C_{17}H_{22}{}^{35}ClO^{102}Ru$: 379.0396; found 379.0415.

(η⁶-1-Methoxy-4-methylbenzene)(η⁵-pentamethylcyclopentadienyl)-ruthenium Hexafluorophosphate (6): Colourless powder (195 mg, 69%); m.p. 324 °C (decomp.). ^{1}H NMR (400 MHz, [D$_4$]methanol): δ = 1.95/1.97 (2s, 15 H, η⁵-CCH_3), 2.13/2.14 (2s, 3 H, η⁶-C$_{ar}$CH_3), 3.77/3.78 (2s, 3 H, η⁶-C$_{ar}$OCH_3), 5.70/5.78 (2ddd, ^3J = 6.5, ^4J = 1.8, ^4J = 1.5 Hz, 2 H, η⁶-CH_{ar}), 5.84/5.91 (2ddd, ^3J = 6.5, ^4J = 1.8, ^4J = 1.5 Hz, 2 H, η⁶-CH_{ar}) ppm. ^{13}C NMR (100 MHz, [D$_4$]methanol): δ = 10.14/10.31/10.37 (η⁵-C*C*H$_3$), 17.64/17.84 (η⁶-C$_{ar}$*C*H$_3$), 57.32/57.35 (η⁶-C$_{ar}$O*C*H$_3$), 76. 75/76. 78 (η⁶-*C*$_{ar}$H), 88.20/88.32 (η⁶-*C*$_{ar}$H), 96.64/97.25/97.65 (η⁵-*C*CH$_3$), 99.05/99.72 (η⁶-*C*$_{ar}$CH$_3$), 133.36/133.92 (η⁶-*C*$_{ar}$OCH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (vs), 2920 (w), 1632 (w), 1539 (m), 1486 (s), 1442 (w), 1390 (m), 1255 (s), 1183 (vw), 1102 (w), 1030 (w), 1010 (w), 840 (vs), 715 (w), 667 (w), 558 (s), 434 (w). UV/Vis (MeOH): λ_{max} (ε) = 211 nm (38686 $mol^{-1}dm^3cm^{-1}$). MS (ESI+): *m/z* (%) = 358/359/361 (57/100/55) [M^+]. HRMS (ESI+): calcd. for $C_{18}H_{25}O^{102}Ru$: 359.0943; found 359.0960.

(η⁶-1-Methoxy-2-methylbenzene)(η⁵-pentamethylcyclopentadienyl)-ruthenium Hexafluorophosphate (7): Colourless powder (188 mg, 67%); m.p. 323 °C (decomp.). ^{1}H NMR (400 MHz, [D$_4$]methanol): δ = 1.94/1.96 (2s, 15 H, η⁵-CCH_3), 2.08/2.10 (2s, 3 H, η⁶-C$_{ar}$CH_3), 3.82/3.83 (2s, 3 H, η⁶-C$_{ar}$OCH_3), 5.55/5.61 (2ddd, ^3J = 5.8, ^3J = 5.5, ^4J = 1.1 Hz, 1 H, η⁶-C$_{ar}$*H*), 5.73/5.79 (2ddd, ^3J = 6.2, ^3J = 5.5, ^4J = 1.1 Hz, 1 H, η⁶-C$_{ar}$*H*), 5.77/5.85 (2dd, ^3J = 5.8, ^5J = 0.4 Hz, 1 H, η⁶-C$_{ar}$*H*), 6.04/6.11 (2dd, ^3J = 6.2, ^5J = 0.4 Hz, 1 H, η⁶-C$_{ar}$*H*) ppm. ^{13}C NMR (100 MHz, [D$_4$]methanol): δ = 10.19/10.22/10.37 (η⁵-C*C*H$_3$), 13.89/14.12 (η⁶-C$_{ar}$*C*H$_3$), 57.37/57.41 (η⁶-C$_{ar}$O*C*H$_3$), 74.41/74.48 (η⁶-*C*$_{ar}$H), 85.85/85.92 (η⁶-*C*$_{ar}$H), 86.65/86.66 (η⁶-*C*$_{ar}$H), 89.63/89.79 (η⁶-*C*$_{ar}$H), 91.63/92.32 (η⁶-*C*$_{ar}$CH$_3$), 96.40/96.99/97.06/97.35 (η⁵-*C*CH$_3$), 132.54/133.20 (η⁶-*C*$_{ar}$OCH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (s), 2919 (w), 1629 (w), 1530 (w), 1508 (w), 1473 (m), 1437 (w), 1412 (w), 1389 (w), 1260 (m), 1182 (w), 1104 (w), 1032 (w), 840 (vs), 742 (w), 673 (w), 558 (s). UV/Vis (MeOH): λ_{max} (ε) = 212 nm (37200 $mol^{-1}dm^3cm^{-1}$). MS (ESI+): *m/z* (%) = 358/359/361 (56/100/55) [M^+]. HRMS (ESI+): calcd. for $C_{18}H_{25}O^{102}Ru$: 359.0943; found 359.0935.

(η⁵-Pentamethylcyclopentadienyl)(η⁶-1,3,5-trimethylbenzene)-ruthenium Hexafluorophosphate (8): Colourless powder (224 mg, 80%); m.p. 325 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.95 (s, 15 H, η⁵-CCH_3), 2.24 (s, 9 H, η⁶-C$_{ar}$CH_3), 5.84 (s, 3 H, η⁶-C$_{ar}$*H*) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 9.96 (η⁵-C*C*H$_3$), 18.28 (η⁶-C$_{ar}$*C*H$_3$), 89.55 (η⁶-*C*$_{ar}$H), 95.47 (η⁵-*C*CH$_3$), 101.22 (η⁶-*C*$_{ar}$CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (s), 2969 (vw), 2921 (w), 1636 (m), 1534 (w), 1475 (vw), 1458 (w), 1389 (m), 1074 (vw), 1031 (m), 838 (vs), 558 (s), 455 (vw). UV/Vis (MeOH): λ_{max} (ε) = 210 nm (33051 $mol^{-1}dm^3cm^{-1}$). MS (ESI+): *m/z* (%) = 356/357/359 (57/100/55) [M^+]. HRMS (ESI+): calcd. for $C_{19}H_{27}{}^{102}Ru$: 357.1150; found 357.1146.

(η⁵-Pentamethylcyclopentadienyl)[η⁶-1-{2-(*tert*-butoxycarbonyl-amino)ethyl}-4-chlorobenzene]ruthenium Hexafluorophosphate (9): Yellowish powder (157 mg, 44%); m.p. 117 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.35 [s, 9 H, (CH_3)$_3$CO], 2.01 (s, 15 H, η⁵-CCH_3), 2.63 (t, ^3J = 6.4 Hz, 2 H, η⁶-C$_{ar}$CH_2CH$_2$), 3.40 (td, ^3J = 6.7, ^3J = 6.4 Hz, 2 H, η⁶-C$_{ar}$CH$_2$CH_2), 6.10 (d, ^3J = 6.1 Hz, 2 H, η⁶-C$_{ar}$*H*C$_{ar}$HC$_{ar}$Cl), 6.18 (br. s, 1 H, CH$_2$CH$_2$N*H*), 6.36 (d, ^3J = 6.1 Hz, 2 H, η⁶-C$_{ar}$HC$_{ar}$*H*C$_{ar}$Cl) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 11.02 (η⁵-C*C*H$_3$), 29.57 ((*C*H$_3$)$_3$CO], 34.71 (η⁶-C$_{ar}$*C*H$_2$CH$_2$), 42.88 (η⁶-C$_{ar}$CH$_2$*C*H$_2$), 79.99 [(CH$_3$)$_3$*C*O], 90.33 (η⁶-C$_{ar}$H*C*$_{ar}$HC$_{ar}$Cl), 90.60 (η⁶-*C*$_{ar}$HC$_{ar}$HC$_{ar}$Cl), 99.21 (η⁵-*C*CH$_3$), 104.10 (η⁶-*C*$_{ar}$CH$_2$), 105.50 (η⁶-*C*$_{ar}$Cl), 157.51 (NH*C*O) ppm. IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (m), 3091 (w), 2980 (m), 2931 (w), 1706 (s), 1513 (m), 1477 (w), 1454 (m), 1390 (m), 1367 (m), 1339 (w), 1271 (m), 1251 (m), 1170 (s), 1088 (m), 1033 (m), 984 (w), 840 (vs), 780 (w), 739 (w), 623 (w), 558 (s), 454 (w), 412 (w). UV/Vis (MeOH): λ_{max} (ε) = 213 nm (37200 $mol^{-1}dm^3cm^{-1}$). MS (FAB+, NBA): *m/z* (%) = 491/492/494 (60/100/75) [M^+]. HRMS (ESI+): calcd. for $C_{23}H_{33}{}^{35}ClNO_2{}^{102}Ru$: 492.1243; found 492.1224.

(η⁶-Benzoylbenzene)(η⁵-pentamethylcyclopentadienyl)ruthenium Hexafluorophosphate (10): Yellowish powder (109 mg, 35%); m.p. 192 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.95 (s, 15 H, η⁵-CCH_3), 6.31 (m, 3 H, η⁶-C$_{ar}$*H*), 6.49 (m, 2 H, η⁶-C$_{ar}$*H*CCO), 7.63 (dd, ^3J = 8.0, ^3J = 1.5 Hz, 2 H, C$_{ar}$*H*C$_{ar}$HCCO), 7.77 (m, 1 H, C$_{ar}$*H*C$_{ar}$HC$_{ar}$HCCO), 7.95 (dd, ^3J = 8.0, ^3J = 1.5 Hz, 2 H, C$_{ar}$*H*CCO) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 11.31 (η⁵-C*C*H$_3$), 89.57 (η⁶-*C*$_{ar}$H), 89.92 (η⁶-*C*$_{ar}$H), 91.19 (η⁶-*C*$_{ar}$H), 97.74 (η⁶-*C*$_{ar}$CO), 99.82 (η⁵-*C*CH$_3$), 130.28 (*C*$_{ar}$H), 131.58 (*C*$_{ar}$H), 135.83 (*C*$_{ar}$H), 138.12 (*C*$_{ar}$CO), 194.73 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3429 cm^{-1} (s), 3094 (w), 2970 (s), 2925 (m), 1665 (s), 1598 (m), 1511 (w), 1477 (w), 1381 (m), 1294 (m), 1266 (m), 1161 (w), 1125 (m), 1083 (s), 1036 (w), 952 (m), 919 (w), 861 (m), 840 (vs), 738 (m), 717 (w), 697 (w), 637 (w), 558 (m), 447 (w), 409 (w). UV/Vis (MeOH): λ_{max} (ε) = 210 nm (10812 $mol^{-1}dm^3cm^{-1}$). MS (ESI+): *m/z* (%) = 418/419/421 (57/100/54) [M^+]. HRMS (ESI+): calcd. for $C_{23}H_{25}O^{102}Ru$: 419.0949; found 419.0939.

(η⁶-Acetylbenzene)(η⁵-pentamethylcyclopentadienyl)ruthenium Hexafluorophosphate (11): Yellowish powder (144 mg, 51%); m.p. 208 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.00 (s, 15 H, η⁵-CCH_3), 2.62 (s, 3 H, CH_3CO), 6.29 (m, 2 H, η⁶-C$_{ar}$*H*CHCCO), 6.32 (m, 1 H, η⁶-C$_{ar}$*H*CHCHCCO), 6.61 (dd, ^3J = 6.1, ^3J = 1.2 Hz, 2 H, η⁶-C$_{ar}$*H*CCO) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 11.33 (η⁵-C*C*H$_3$), 28.39 (*C*H$_3$CO), 88.35 (η⁶-*C*$_{ar}$H), 90.40 (η⁶-*C*$_{ar}$H), 91.23 (η⁶-*C*$_{ar}$H), 94.30 (η⁶-*C*$_{ar}$CO), 99.61 (η⁵-*C*CH$_3$), 198.07 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (s), 3098 (m), 2967 (m), 2926 (m), 1694 (s), 1636 (m), 1515 (w), 1497 (w), 1473 (m), 1455 (m), 1406 (w), 1390 (m), 1363 (w), 1292 (w), 1254 (s), 1079 (w), 1035 (m), 959 (w), 839 (vs), 741 (w), 584 (w), 559 (s), 465 (w), 416 (w). UV/Vis (MeOH): λ_{max} (ε) = 215 nm (27454 $mol^{-1}dm^3cm^{-1}$). MS (ESI+): *m/z* (%) = 356/357/359 (56/100/55) [M^+]. HRMS (ESI+): calcd. for $C_{18}H_{23}O^{102}Ru$: 357.0792; found 357.0776.

(η⁶-4-Methylbenzenesulfonic acid)(η⁵-pentamethylcyclopentadienyl)-ruthenium Hexafluorophosphate (12): Yellowish powder (203 mg, 66%); m.p. 258 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.98 (s, 15 H, η⁵-CCH_3), 2.26 (s, 3 H, η⁶-C$_{ar}$CH_3), 5.82 (d, ^3J = 6.1 Hz, 2 H, η⁶-C*H*C$_{ar}$CH$_3$), 6.14 (d, ^3J = 6.1 Hz, 2 H, η⁶-C*H*C$_{ar}$SO$_3$H), 10.17 (br. s, 1 H, SO$_3$*H*) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 11.13 (η⁵-C*C*H$_3$), 19.20 (η⁶-C$_{ar}$*C*H$_3$), 86.77 (η⁶-*C*$_{ar}$H), 89.21 (η⁶-*C*$_{ar}$H), 97. 85 (η⁵-*C*CH$_3$), 130.37 (η⁶-*C*$_{ar}$CH$_3$), 131.22 (η⁶-*C*$_{ar}$SO$_3$H) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (vs), 3060 (w), 2962 (w), 2919 (m), 2854 (w), 1631 (s), 1522 (w), 1476 (m), 1454 (m), 1388 (s), 1349 (w), 1234 (vs), 1223 (vs), 1107 (s), 1031 (vs), 1005 (vw), 875 (w), 797 (w), 671 (vs), 574 (s), 565 (s), 505 (w), 458 (w), 426 (s). UV/Vis (MeOH): λ_{max} (ε) = 212 nm (262744 $mol^{-1}dm^3cm^{-1}$). MS (ESI+): *m/z* (%) = 408/409/411 (57/100/59) [M^+]. HRMS (ESI+): calcd. for $C_{17}H_{23}O_3S^{102}Ru$: 409.0411; found 409.0437.

Diels−Alder Adducts *rac*-13a and *rac*-13b: Yellowish powder (199 mg, 51%); m.p. 240 °C (decomp.). **13a:** ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 0.60 (d, ^3J = 6.7 Hz, 3 H, 171-H), 0.95 (dd, ^4J = 1.2, ^4J = 2.7 Hz, 3 H, 131-H), 1.05 (s, 3 H, 151-H), 1.11 (s, 3 H, 141-H), 1.34 (t, ^3J = 7.0 Hz, 3 H, C*H*$_3$CH$_2$O), 1.66 (d, ^4J = 1.2 Hz, 3 H, 161-H), 1.98 (s, 15 H, η⁵-CC*H*$_3$), 2.15 (q, ^3J = 6.7 Hz, 1 H, 17-H), 2.54 (d, ^3J = 4.6 Hz, 1 H, 8-H), 3.27 (d, ^3J = 4.6 Hz, 1 H, 7-H), 4.16−4.30 (q, ^3J = 7.0 Hz, 2 H, CH$_3$C*H*$_2$O), 5.60 (m, 1 H, η⁶-4-H), 5.89−6.03 (m, 4 H, η⁶-C$_{ar}$*H*) ppm; **13b:** δ = 0.55 [d, ^3J = 6.4 Hz, 3 H, C*H*$_3$C$_q$(C$_q$)(C$_q$)H], 0.65 [s, 3 H, (C=O)CH(C$_q$)C(C*H*$_3$)=C(CH$_3$)], 1.34 [s, 3 H, (C=O)CH(C$_q$)C(CH$_3$)=C(C*H*$_3$)], 1.34 (t, ^3J = 7.0 Hz, 3 H, C*H*$_3$CH$_2$O), 1.45 [dd, ^4J = 1.2, ^4J = 2.4 Hz, 3 H, (C=O)CHC$_q$(C*H*$_3$)], 1.59 [d, ^4J = 1.2 Hz, 3 H, (η⁶-C$_{ar}$)CHC$_q$(C*H*$_3$)], 1.82 [q, ^3J = 6.4 Hz, 1 H, CH$_3$C$_q$(C$_q$)(C$_q$)*H*], 2.04 (s, 15 H, η⁵-CC*H*$_3$), 2.94 [d, ^3J = 4.6 Hz, 1 H, (η⁶-C$_{ar}$)C*H*], 2.98 [d, ^3J = 4.6 Hz, 1 H, (C=O)C*H*], 4.16−4.30 (q, ^3J = 7.0 Hz, 2 H, CH$_3$C*H*$_2$O), 5.96−6.09 (m, 4 H, η⁶-C$_{ar}$*H*), 6.32 (m, 1 H, η⁶-C$_{ar}$*H*) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): **13a:** δ = 9.60 (C-171), 10.80 (C-161), 11.68 (η⁵-C*C*H$_3$), 13.6 (C-131), 14.6 (C-141), 14.8 (C-151), 15.6 (*C*H$_3$CH$_2$O), 53.78 (C-8), 56.47 (C-7), 58.49 (C-17), 60.63 (C-16), 61.92 (C-13), 62.50 (O*C*H$_2$CH$_3$), 85.87 (C-4), 88.86 (C-2/6), 89.11 (C-3/5), 98.20 (η⁵-*C*CH$_3$), 108.34 (C-1), 136.55 (C-15), 137.74 (C-14), 175.87 (C=O) ppm; **13b:** δ = 9.20 [*C*H$_3$C$_q$(C$_q$)(C$_q$)H], 10.70 [(η⁶-C$_{ar}$)CHC$_q$(*C*H$_3$)], 11.48 (η⁵-C*C*H$_3$), 12.40 [(C=O)CHC$_q$(*C*H$_3$)], 14.90 [(C=O)CH(C$_q$)C(*C*H$_3$)=C(CH$_3$)], 15.50 [(C=O)CH(C$_q$)C(CH$_3$)=C(*C*H$_3$)], 15.60 (*C*H$_3$CH$_2$O), 52.11 [(η⁶-C$_{ar}$)*C*H], 56.56 [(C=O)*C*H], 57.90 [CH$_3$*C*$_q$(C$_q$)(C$_q$)H], 60.57 [(C=O)CH*C*$_q$(CH$_3$)], 60.75 [(η⁶-C$_{ar}$)CH*C*$_q$(CH$_3$)], 62.50 (O*C*H$_2$CH$_3$), 85.77 (η⁶-*C*$_{ar}$H), 88.92 (η⁶-*C*$_{ar}$H), 89.65 (η⁶-*C*$_{ar}$H), 98.23 (η⁵-*C*CH$_3$), 109.73 [(η⁶-*C*$_{ar}$)CH], 135.52 [(C=O)CH(C$_q$)C(CH$_3$)=*C*(CH$_3$)], 137.83 [(C=O)CH(C$_q$)*C*(CH$_3$)=C(CH$_3$)], 174.73 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (m), 3101 (vw), 2963 (m), 2929 (m), 2873 (w), 1720 (vs), 1628 (vw), 1522 (vw), 1477 (m), 1455 (m), 1416 (vw), 1386 (m), 1312 (m), 1275 (w), 1239 (vw), 1183 (s), 1154 (w), 1138 (vw), 1079 (w), 1035 (m), 841 (vs), 739 (vw), 698 (vw), 558 (s), 460 (vw), 405 (m). MS (ESI+): *m*/*z* (%) = 548/549/551 (58/100/54) [M$^+$]. HRMS (ESI+): calcd. for C$_{31}$H$_{43}$O$_2$^{102}Ru: 549.2307; found 549.2299.

(η⁵-Pentamethylcyclopentadienyl)[η⁶-1-{2*S*-(*tert*-butoxycarbonylamino)-2*S*-(methoxycarbonyl)ethyl}benzene]ruthenium Hexafluorophosphate (16): Yellowish powder (195 mg, 55%); m.p. 90 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.33 [s, 9 H, (C*H*$_3$)$_3$CO], 2.02 (s, 15 H, η⁵-CC*H*$_3$), 2.78 [dd, ^2J = 13.6 Hz, ^3J = 9.2 Hz, 1 H, η⁶-C$_{ar}$C*H*HCH(CO)NH], 2.96 [dd, ^2J = 13.6 Hz, ^3J = 5.2 Hz, 1 H, η⁶-C$_{ar}$CH*H*CH(CO)NH], 3.69 (s, 3 H, OC*H*$_3$), 4.42 [ddd, ^3J = 5.2, ^3J = 8.8, ^3J = 9.2 Hz, 1 H, CH$_2$C*H*(CO)NH], 5.96 (d, ^3J = 5.5 Hz, 1 H, η⁶-C$_{ar}$*H*), 6.02 (d, ^3J = 5.2 Hz, 2 H, η⁶-C$_{ar}$*H*), 6.04 (dd, ^3J = 5.2, ^3J = 5.5 Hz, 2 H, η⁶-C$_{ar}$*H*), 6.45 (d, ^3J = 8.8 Hz, 1 H, N*H*) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 10.51 (η⁵-C*C*H$_3$), 28.45 [(*C*H$_3$)$_3$CO], 36.08 [η⁶-C$_{ar}$*C*H$_2$CH(CO)NH], 52.64 (O*C*H$_3$), 55.46 [CH$_2$*C*H(CO)NH], 79.84 [(CH$_3$)$_3$*C*O], 88.47 (η⁶-*C*$_{ar}$H), 89.18 (η⁶-*C*$_{ar}$H), 89.53 (η⁶-*C*$_{ar}$H), 97.29 (η⁵-*C*CH$_3$), 100.51 (η⁶-*C*$_{ar}$CH$_2$), 156.15 (NH*C*O), 172.03 (*C*OOCH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3427 cm^{-1} (m), 2978 (m), 1743 (m), 1704 (s), 1514 (w), 1477 (w), 1455 (w), 1368 (m), 1254 (m), 1167 (m), 1033 (s), 984 (w), 843 (vs), 740 (vw), 558 (m). UV/Vis (MeOH): λ_{max} (ε) = 210 nm (206655 mol^{-1}dm^{3}cm^{-1}). MS (FAB+, NBA): *m*/*z* (%) = 515/516/518 (60/100/54) [M$^+$]. HRMS (FAB+): calcd. for C$_{25}$H$_{36}$NO$_4$^{102}Ru: 516.1688; found 516.1697.

(η⁵-Pentamethylcyclopentadienyl)[η⁶-1-{2-(*tert*-butoxycarbonylamino)-2-(ethoxycarbonyl)ethyl}-4-chlorobenzene]ruthenium Hexafluorophosphate (17): Yellowish powder (160 mg, 45%); m.p. 97 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.21 (t, ^3J = 7.3 Hz, 3 H, CH$_2$C*H*$_3$), 1.34 [s, 9 H, (C*H*$_3$)$_3$CO], 2.00 (s, 15 H, η⁵-CC*H*$_3$), 2.80 [dd, ^2J = 13.6 Hz, ^3J = 9.5 Hz, 1 H, η⁶-C$_{ar}$C*H*HCH(-CO)NH], 2.98 [dd, ^2J = 13.6 Hz, ^3J = 5.1 Hz, 1 H, η⁶-C$_{ar}$CH*H*CH(CO)NH], 4.15 (q, ^3J = 7.3 Hz, 2 H, C*H*$_2$CH$_3$), 4.41 [ddd, ^3J = 5.1 Hz, ^3J = 8.8, ^3J = 9.5 Hz, 1 H, CH$_2$C*H*(CO)NH], 6.08 (d, ^3J = 5.9 Hz, 1 H, η⁶-C$_{ar}$*H*CCH), 6.19 (d, ^3J = 5.9 Hz, 1 H, η⁶-C$_{ar}$*H*CCH$_2$), 6.37 (d, ^3J = 5.9 Hz, 1 H, η⁶-C$_{ar}$*H*CCl) 6.39 (d, ^3J = 5.9 Hz, 1 H, η⁶-C$_{ar}$*H*CCl) 6.48 (d, ^3J = 8.8 Hz, 1 H, N*H*). ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 10.94 (η⁵-C*C*H$_3$), 15.40 (OCH$_2$*C*H$_3$), 29.41 [(*C*H$_3$)$_3$CO], 36.23 [η⁶-C$_{ar}$*C*H$_2$CH(CO)NH], 56.39 [CH$_2$*C*H(CO)NH], 63.00 (O*C*H$_2$CH$_3$), 80.83 [(CH$_3$)$_3$*C*O], 90.40 (η⁶-*C*$_{ar}$HCCH$_2$), 90.53 (η⁶-*C*$_{ar}$HCCl), 90.55 (η⁶-*C*$_{ar}$HCCl), 90.70 (η⁶-*C*$_{ar}$HCCH$_2$), 99.39 (η⁵-*C*CH$_3$), 101.84 (η⁶-*C*$_{ar}$CH$_2$), 105.64 (η⁶-*C*$_{ar}$Cl), 157.16 (NH*C*O), 172.30 (*C*OOCH$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3351 cm^{-1} (s), 3089 (w), 2983 (m), 2931 (s), 2852 (m), 2495 (w), 1740 (s), 1703 (vs), 1627 (m), 1609 (w), 1575 (w), 1527 (w), 1479 (m), 1453 (m), 1421 (w), 1392 (m), 1369 (m), 1344 (m), 1257 (m), 1218 (vw), 1164 (s), 1089 (m), 1032 (vs), 980 (w), 842 (vs), 558 (s), 442 (vw), 412 (m). UV/Vis (MeOH): λ_{max} (ε) = 213 nm (193339 mol^{-1}dm^{3}cm^{-1}). MS (FAB+, NBA): *m*/*z* (%) = 562/564/566 (43/100/41) [M$^+$]. HRMS (FAB+): calcd. for C$_{26}$H$_{37}$^{35}ClNO$_4$^{102}Ru: 564.1455; found 564.1459.

Procedure for the Preparation of the Ruthenium Sandwich Complexes 4, 14, and 15 via the Methanol/Methoxide Route: The arene (2 equiv.) was added to a solution of [Cp*RuCl$_2$]$_2$ (1 equiv.) in MeOH (6.5 mL per mmol) and NaOMe (1 equiv.). The solution was stirred for 3 h under reflux. After addition of $NaPF_6$ (1.1 equiv.) and MeOH (15 mL per mmol) the mixture was filtered through a pad of aluminium oxide. The filtrate was concentrated and filtered through a pad of aminopropyl silica [*iso*-octane/EtOH (1:1) as eluent]. After concentration of the filtrate to dryness, water (50 mL per mmol), *iso*-octane (100 mL per mmol) and MeOH (50 mL per mmol) were added. Further MeOH was added until the solution became clear. The *iso*-octane phase was separated and the polar phase extracted with *iso*-octane (twice). The combined *iso*-octane phases were extracted with water/MeOH (1:1) and the polar phases were combined and concentrated to dryness. The product was extracted from the residue with dichloromethane (15 mL, three times) and recrystallised from water/*iso*-propanol (addition of *iso*-propanol to a boiling aqueous suspension).

(η⁶-1,2-Dimethoxybenzene)(η⁵-pentamethylcyclopentadienyl)-ruthenium Hexafluorophosphate (15). Colourless powder (66 mg, 20%); m.p. 342 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.01 (s, 15 H, η⁵-CC*H*$_3$), 3.93 (s, 6 H, η⁶-C$_{ar}$OC*H*$_3$), 5.75 (m, 2 H, η⁶-C$_{ar}$*H*), 6.33 (m, 2 H, η⁶-C$_{ar}$*H*) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 10.52 (η⁵-C*C*H$_3$), 57.68 (η⁶-C$_{ar}$O*C*H$_3$), 75.36 (η⁶-*C*$_{ar}$H), 83.86 (η⁶-*C*$_{ar}$H), 95.86 (η⁵-*C*CH$_3$), 124.44 (η⁶-*C*$_{ar}$OCH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (s), 3104 (w), 2920 (w), 1629 (w), 1526 (m), 1516 (m), 1485 (s), 1437 (m), 1417 (w), 1390 (m), 1267 (s), 1216 (m), 1177 (w), 1106 (m), 1031 (w), 1011 (s), 840 (vs), 748 (m), 584 (m), 558 (s), 524 (w), 458 (w). UV/Vis (MeOH): λ_{max} (ε) = 214 nm (32491 mol^{-1}dm^{3}cm^{-1}). MS (FAB+, NBA): *m*/*z* (%) = 374/375/377 (59/100/56) [M$^+$]. HRMS (ESI+): calcd. for C$_{18}$H$_{25}$O$_2$^{102}Ru: 375.0892; found 375.0905.

(η⁶-Ethylbenzene)[η⁵-(1-methoxymethyl-2,3,4,5-tetramethyl)cyclopentadienyl]ruthenium Hexafluorophosphate (14) and (η⁶-Ethylbenzene)(η⁵-pentamethylcyclopentadienyl)ruthenium Hexafluorophosphate (4): Colourless powder (1.62 g, 56%); m.p. 277 °C (decomp.). **14:** ^{1}H NMR (400 MHz, [D$_4$]methanol): δ = 1.17 (t, ^3J = 7.7 Hz, 3 H, η⁶-C$_{ar}$CH$_2$C*H*$_3$), 1.92 (s, 12 H, η⁵-CC*H*$_3$), 2.36 (q, ^3J = 7.7 Hz, 2 H, η⁶-C$_{ar}$C*H*$_2$CH$_3$), 3.40 (s, 3 H, η⁵-CCH$_2$OC*H*$_3$), 4.19

(s, 2 H, η^5-CCH_2O), 5.91 (m, 5 H, η^6-C$_{ar}H$) ppm. ^{13}C NMR (100 MHz, [D$_4$]methanol): δ = 10.57 (η^5-CCH_3), 15.88 (η^6-C$_{ar}$CH_2CH_3), 27.40 (η^6-C$_{ar}$CH_2CH$_3$), 59.03 (η^5-CCH$_2$OCH_3), 66.04 (η^5-CCH_2O), 87.92 (η^6-C$_{ar}$H), 88.49 (η^6-C$_{ar}$H), 88.66 (η^6-C$_{ar}$H), 97.29 (η^5-CCH$_2$O), 97.48 (η^5-CCH$_3$), 107.30 (η^6-C$_{ar}$CH$_2$CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (s), 2975 (m), 2918 (m), 1629 (m), 1525 (w), 1477 (m), 1458 (m), 1417 (w), 1389 (m), 1074 (w), 1035 (m), 837 (vs), 767 (w), 558 (s), 493 (w), 461 (w). UV/Vis (MeOH): λ_{max} (ε) = 209 nm (36330 mol^{-1}dm^{3}cm^{-1}). MS (ESI+): *m*/*z* (%) = 372/373/375 (56/100/54) [M$^+$]. HRMS (ESI+): calcd. for $C_{19}H_{27}O^{102}Ru$: 373.1105; found 373.1117. For spectroscopic data of **4** see above.

Crystallographic Analysis: Single-crystal intensity data were collected from colourless crystals with a Stoe Imaging Plate Diffraction System **(13a)** or by use of an Enraf−Nonius Kappa CCD equipped with a rotating anode **(14)**. In both cases, graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) was used and the measurement temperature was 200(2) K. A numerical absorption correction (XRed[26]) was applied to the data. All relevant information concerning the data collection are listed in Table 3. The structures were solved by direct methods (SIR97[27]) and refined using SHELXL-97 (full-matrix least-squares on F^2).[27,28] The hydrogen atoms were considered with a riding model. All other atoms were refined with anisotropic atomic displacement parameters, except a disordered ethyl group in **13a** which was refined isotropically.

Table 3. Data collection and structural refinement parameters for compounds **13a** and **14**

	13a	**14**
Formula	$C_{31}H_{42}F_6O_2PRu$	$C_{19}H_{27}F_6OPRu$
M_r	693.71	517.45
Crystal system	orthorhombic	monoclinic
Space group	$Pca2_1$	$P2_1/c$
Crystal size [mm^3]	0.02 × 0.30 × 0.32	0.02 × 0.08 × 0.10
a [pm]	2007.8(2)	1104.67(2)
b [pm]	914.78(4)	1237.41(2)
c [pm]	1739.88(9)	1597.03(2)
α [°]	90.0	90.0
β [°]	90.0	106.472(1)
γ [°]	90.0	90.0
V (Å^3)	3195.6(3)	2093.43(6)
Z	4	4
ρ calcd. [Mg·m^{-3}]	1.442	1.642
μ [mm^{-1}]	0.602	0.884
Transmission (min/max)	0.8619/0.9876	0.9360/0.9785
F(000)	1432	1048
Range in *hkl*	±22, ±10, ±19	±12, ±14, ±18
Reflections collected	17452	22699
Independent refl. ($R_{int.}$)	4886 (0.0631)	3269 (0.0872)
Data/restraints/parameters	4886/1/381	3269/0/259
Goodness-of-fit on F^2	0.885	1.033
*R*1 [$I > 2\sigma(I)$]	0.0412	0.0389
*R*1 (all data)	0.0715	0.0579
*wR*2 [$I > 2\sigma(I)$]	0.0761	0.0863
*wR*2 (all data)	0.0822	0.0919
Flack parameter	−0.05(4)	−
Largest diff. peak/hole	0.394/−0.338	0.548/−0.606

CCDC-189008 (**13a**) and CCDC-189009 (**14**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Supporting Information Available: Spectra of selected compounds (see footnote on the first page of this article).

Acknowledgments

Petra Böhrer is thanked for technical assistance in the preparation of selected model compounds. Special thanks go to Degussa AG for a generous donation of $RuCl_3 \cdot xH_2O$.

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Received October 20, 2002

