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FULL PAPER

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Microwave-Assisted Synthesis and Transformations of Cationic CpRu(II)(naphthalene) and CpRu(II)(naphthoquinone) Complexes

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Dedicated to *François Diederich* on the occasion of his retirement

Details of the direct synthesis of cationic Ru(II)(η^5-Cp)(η^6-arene) complexes from ruthenocene using microwave heating are reported. Developed for the important catalyst precursor [Ru(II)(η^5-Cp)(η^6-1-4,4a,8a-naphthalene)][PF_6] reaction time could be shortened from three days to 15 min. The method was extended to [Ru(II)(η^6-benzene)(η^5-Cp)][PF_6], [Ru(II)(η^5-Cp)(η^6-toluene)][PF_6], [Ru(II)(η^5-Cp)(η^6-mesitylene)][PF_6], [Ru(II)(η^5-Cp)(η^6-hexamethylbenzene)][PF_6], [Ru(II)(η^5Cp)(η^6-indane)][PF_6], [Ru(II)(η^5-Cp)(η^6-2,6-dimethylnaphthalene)][PF_6], and [Ru(II)(η^5-Cp)(η^6-pyrene)][PF_6]. 1-methylnaphthalene and 2,3-dimethylnaphthalene afforded mixtures of regioisomeric complexes. [Ru(Cp)(CH_3CN)$_3$][PF_6], derived from the naphthalene precursor provided access to the cationic RuCp complexes of naphthoquinone, tetralindione, 1,4-dihydroxynaphthalene, and 1,4-dimethoxynaphthalene. Reduction of the tetralindione complex afforded selectively the *endo,endo* diol derivative. X-Ray structures of five complexes are reported.

Keywords: ruthenium, microwave chemistry, naphthoquinones, tetralindiones, naphthalene.

Introduction

Ru(0) and Ru(II) catalysts figure very prominently in organic synthesis.[1–4] An important class of the latter contain η^5-cyclopentadienyl (Cp) as stabilizing spectator ligand with the ruthenium complex **1** (*Figure 1*)

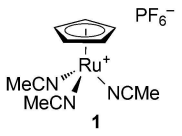

Figure 1. [Ru(II)Cp(CH_3CN)$_3$][PF_6], an excellent precursor for catalysts and mixed sandwich complexes.

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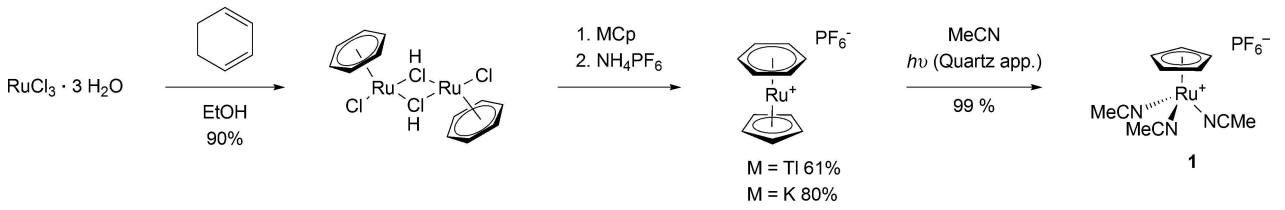
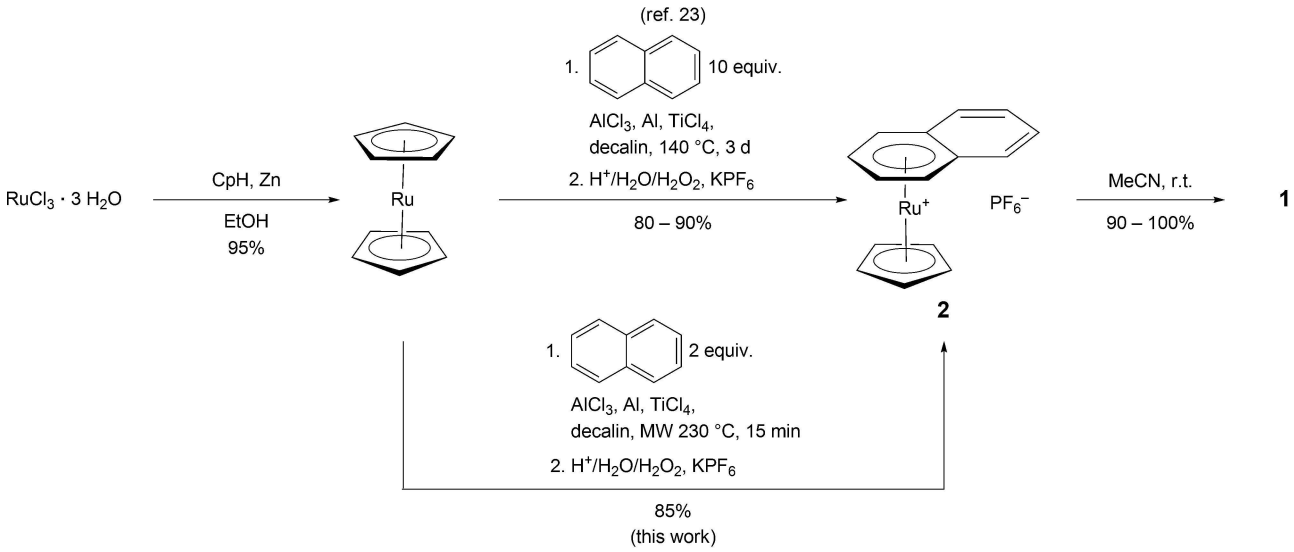
being a key source of a large group of powerful homogeneous catalysts. The catalytic activity of **1** derives from the lability of the three acetonitrile ligands which can be readily substituted for a wide variety of mono-and bidentate ligands as well as alkene- and alkyne-substrates.[5] Ru-complex **1** and derived catalysts were used primarily by *Trost* and coworkers for C–C coupling reactions.[6,7] His group as well as others applied these efficient catalysts in natural product syntheses.[8–14] *Lacour* and coworkers used **1** in asymmetric *Caroll* rearrangements and related reactions as well as in catalytic carbene C–H insertion and condensation reactions.[15–19]

The main drawback of the use of **1** was its synthetic access. The *Gill* and *Mann* 1982 procedure involves the toxic reagent TlCp and an inconvenient photolysis in quartz glassware.[20] *Trost* and *Older* followed up in 2002 with a report showing that TlCp can be replaced by KCp. The photolysis step remained, however



Scheme 1. *Gill* and *Mann* (M = Tl)[20] and *Trost* and *Older* (M = K)[21] syntheses of $[Ru(II)(\eta^5\text{-}C_5H_5)(CH_3CN)_3][PF_6]$ (**1**).



Scheme 2. Ruthenocene route to **2** with conventional heating[22] (top) and microwave heating in a *Biotage* reactor (bottom, this study).

(*Scheme 1*).[21] A further drawback of the use of **1** is its rapid oxidative degradation in air. A new route of access developed in this laboratory in 2004 solved both the above shortcomings. It described an efficient synthesis of the air-stable mixed sandwich complex [Ru(II)Cp(naphthalene)][PF_6] (**2**)[22,23] from which the more labile acetonitrile complex **1** is readily obtained under mild conditions. The only problem with this ruthenocene method is the use of a large excess of naphthalene (10 equiv.) and a long reaction time (three days) under harsh conditions (*Scheme 2*, top).

In the first part of this article, we disclose details of the same route but using microwave heating.[24] This dramatically shortens the reaction time while keeping the yield high (*Scheme 2*, bottom). We also show that a range of simple cationic Ru(II)(arene)Cp complexes are accessible through this procedure. In the second part we report the results of our study of new cationic Ru(II)Cp(naphthoquinone) complexes and their reactions.

Results and Discussion

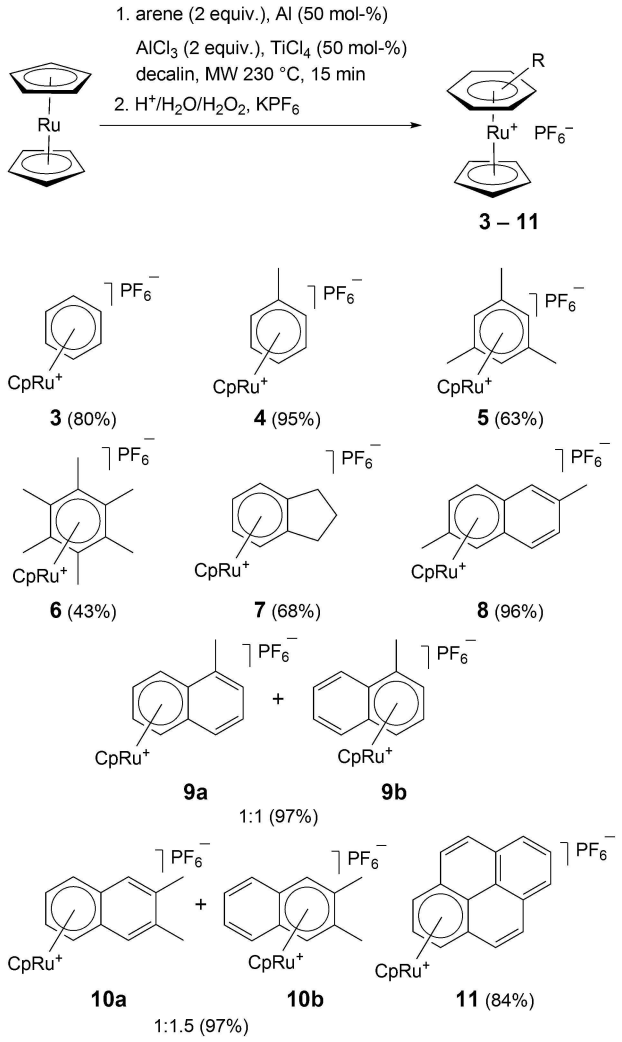
Optimization of the microwave synthesis of **2** included variation of the quantities of added naphthalene, aluminum, aluminum trichloride, temperature, and reaction time. $TiCl_4$ was held constant to 50 mol-% since it serves to trap Cp to yield titanocene dichloride. Aluminum powder (0.5 mol-equiv.) proved best (85% yield of **2**), yield dropping to 78% with 0.7 or 0.3 equiv., respectively. Two equiv. of naphthalene and two equiv. of $AlCl_3$ were best, yields with four to ten equivalents of naphthalene lowered yields of **2** by 5–9%. **Attention**: When filling the microwave vial care was taken to have no Al dust on the glass wall above the solvent level. With this precaution, vial cracking was avoided, and five sets of experiments were run in the same 20 mL microwave vial in succession. Multigram quantities of **2** were thus readily synthesized. The straightforward access to the naphthalene complex **2** has made it a preferred direct precursor for a large variety of complexes incorporating the $RuCp^+$ fragment. Thus, naphthalene substitution in **2** by arenes, phosphines, acetonitrile, amines takes place

under mild conditions and can be accelerated by visible light.[20,22,25–32]

The microwave-mediated substitution of Cp for an arene ligand was extended to the preparation of a number of CpRu(arene)$^+$ complexes (*Scheme 3*).

Standard conditions were applied for all reactions in *Scheme 3*. While this is a very direct route to cationic CpRu(II)(arene) complexes, foregoing the intermediacy of either **1** or **2**, due to the harsh conditions alkoxy substituted arenes and halo-arenes are not tolerated in this procedure. We note, however, that heteroatom-substituted CpRu(arene)$^+$ complexes are readily synthesized through acetonitrile exchange in **1**.[33]

We have reported the application of **1** prepared through the ruthenocene microwave route for the syntheses of the RuCp(dibromonaphthalene) complex **12** and of the RuCp(dibromoindenyl) complex **13**.



Scheme 3. Ru(II)Cp(arene) complexes through *Lewis* acid- and microwave-assisted Cp/arene exchange.

These were used in catalytic asymmetric hydrogenolysis to access planar chiral complexes thus opening a new route of access to this family of compounds (*Figure 2*).[24,34–36]

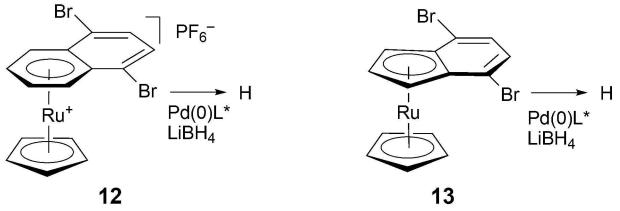
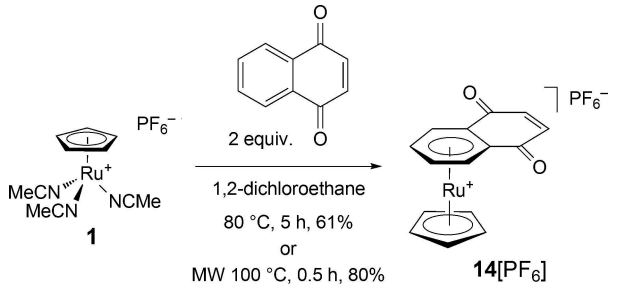


Figure 2. Cationic Ru(II)Cp(dibromonaphthalene) and neutral Ru(II)Cp(dibromoindenyl) complexes and their catalytic highly enantioselective C–Br hydrogenolysis.

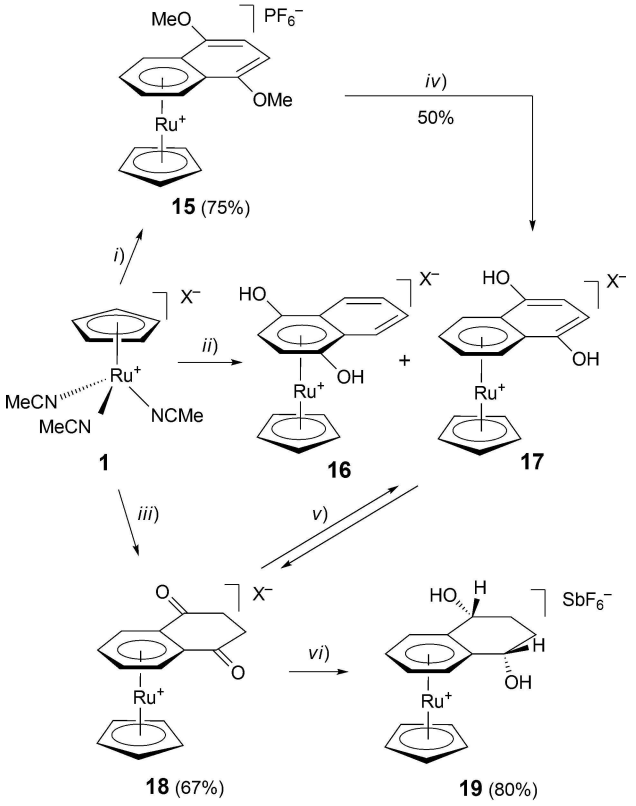
Our earlier findings in the study of $Cr(CO)_3$ complexes of 1,4-naphthoquinone, 1,4-dihydroxynaphthalene, and 1,4-tetralindione[37–40] prompted us to next investigate analogous organometallics containing the isolobal CpRu$^+$ fragment (*Scheme 4*).

Complexation of 1,4-naphthoquinone by substitution of the acetonitrile ligands in **1** was straightforward. We remind the readers that direct complexation was not a viable route in the $Cr(CO)_3$ analogue as naphthoquinone oxidizes Cr(0) precursors. $Cr(CO)_3$(5,8-naphthoquinone) was obtained by selective ligand oxidation in $Cr(CO)_3$((η^6-1-4,4a,8a)-5,8-dihydroxynaphthalene). The use of a microwave reactor in the transformation of **1** to **14** strongly shortened reaction time and increased yields. The analogous complex with the counter ion SbF_6^- was also prepared using the same procedure. Its increased solubility enabled crystals suitable for X-ray analysis to be obtained from an acetone solution (*Figure 3*).[1]



Scheme 4. Synthesis of [Ru(II)Cp(5,8-naphthoquinone)][PF_6].

[1]CCDC 1900013–1900017 contain the supplementary crystallographic data for **14–19**. These data can be



Scheme 5. $X^- = PF_6^-$ or SbF_6^-, *i*) X = PF_6, 1,4-dimethoxynaphthalene, 1,2-dichloroethane, 80 °C, 16 h, 75% or MW, 80 °C, 5 min, 81%. *ii*) X = PF_6, 1,4-dihydroxynaphthalene, 1,2-dichloroethane, 80 °C, 16 h, 70%, **16**[PF_6]:**17**[PF_6] = 65:35 or MW, 80 °C, 5 min, 75%, **16**[PF_6]:**17**[PF_6] = 60:40; X = SbF_6, 1,4-dihydroxynaphthalene, 1,2-dichloroethane, 80 °C, 24 h, 60%, **16**[SbF_6]:**17**[SbF_6] = 57:43 or MW, 80 °C, 10 min, 65%, **16**[SbF_6]:**17**[SbF_6] = 50:50. *iii*) X = PF_6,1,4-tetralindione, 1,2-dichloroethane, 80 °C, 5 h, 67%; X = SbF_6, 1,4-tetralindione, 1,2-dichloroethane, 80 °C, 5 h, 73%. *iv*) 1. BBr_3, CH_2Cl_2, −78 °C to r.t. 2. KPF_6, MeOH, 1 h, 50%. *v*) Tautomerization, see text; *vi*) $NaBH_4$, MeOH, 0 °C.

In transition-metal complexes containing fused arene ring ligands a slippage away from bridgehead carbons is generally observed. This is well documented and it arises from the high energy barrier for moving the metal atom towards the bridgehead on a direct path for haptotropic rearrangement. Conversely, in Cr(CO)$_3$(η^6-5,8-naphthoquinone), and also here in **14**[SbF_6], the shift is opposite, and M–C distances to bridgehead carbons (C(3),C(3′)) are shorter than to carbons C(1) and C(1′).

obtained free of charge from *The Cambridge Crystallographic Data Centre* through www.ccdc.cam.ac.uk/data_request/cif.

Transformations of **14** by either alkene or ketone reductions were rendered difficult by the lack of solubility of the complex and by the difficulty of isolation of the cationic products. We therefore turned to different approaches for their syntheses (*Scheme 5*).

Complexes **15**–**18** were readily obtained from **1**. The use of microwave heating again significantly reduced reaction times. The reaction with 1,4-dimethoxynaphthalene afforded **15** (*Figure 4*) as single isomer. Metal complexation is thus regiospecific to the unsubstituted ring. This is analogous to the corresponding Cr(CO)$_3$ complex.[41]

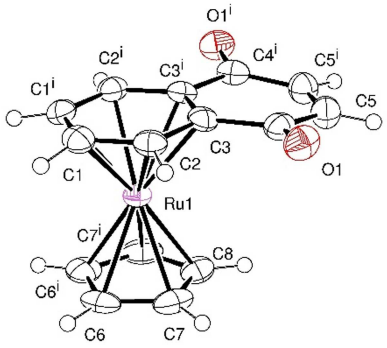


Figure 3. ORTEP View of the crystal structure of [Ru(η^5-Cp)(η^6-naphthoquinone)][SbF_6] (**14**[SbF_6]). The SbF_6 anion is omitted for clarity. Ellipsoids are represented with 50% probability. Selected bond distances [Å]: Ru(1)–C(1^i) 2.220(4), Ru(1)–C(1) 2.221(4), Ru(1)–C(2^i) 2.217(4), Ru(1)–C(2) 2.217(4), Ru(1)–C(3) 2.214(3), Ru(1)–C(3^i) 2.214(3), C(1)–C(1^i) 1.414(9), C(1)–C(2) 1.406(6), C(2)–C(3) 1.420(5), C(3)–C(3^i) 1.432(8), C(3)–C(4) 1.497(5), C(4)–C(5) 1.473(6), C(5)–C(5^i) 1.327(9).

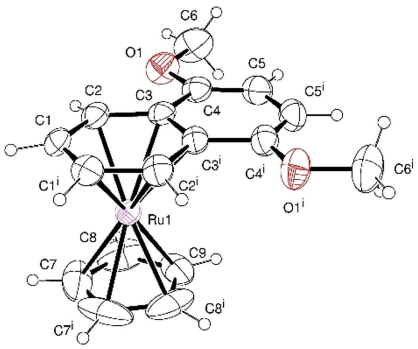


Figure 4. ORTEP View of the crystal structure of [Ru(η^5-Cp)(η^6-5,8-dimethoxynaphthalene)][PF_6] (**15**[PF_6]). The PF_6 anion is omitted for clarity. Ellipsoids are represented with 50% probability. Selected bond distances: Ru(1)–C(1) and Ru(1)–C(1^i) 2.218(3), Ru(1)–C(2) and Ru(1)–C(2)^i 2.214(4), Ru(1)–C(3)and Ru(1)–C(3)^i 2.257(3), C(1)–C(1^i) 1.419(8), C(1)–C(2) 1.410(5), C(2)–C(3) 1.433(5), C(3)–C(3^i) 1.439(7), C(3)–C(4) 1.443(5), C(4)–C(5) 1.341(5), C(5)–C(5^i) 1.429(8).

1,4-Dihydroxynaphthalene yielded an inseparable mixture of the two regioisomers **16** and **17**. The use of microwave heating significantly reduces reaction time again but did not significantly alter the ratio of the two isomers. There was no interconversion of the two regioisomers on heating in THF at 70 °C. Increasing the temperature to 130 °C led to partial decomposition. More polar solvents (MeOH) did alter the ratio, but this may well be due to the intermediacy of a cationic $RuCp(solvent)_3$ complex. These observations are in keeping with precedent reports of high activation barriers for interring haptotropic migration in RuCp (polyarene) complexes.[42] Repeated partial dissolution of the [SbF_6] salt mixture with 1,2-dichloroethane afforded a sample highly enriched in **17**[SbF_6] (95:5). This allowed crystals of **17**[SbF_6] for X-ray analysis to be obtained (*Figures 5* and *6*).

First reactions of **1** with tetralindione[39] gave mixtures of **18**[PF_6] (*Figure 7*) and **17**[PF_6], indicating tautomerization to have occurred, presumably by the presence of OH groups on the glass wall. This problem was overcome by carrying out the reaction in silylated glassware. The crystal structure of **17**[SbF_6], like that of **14**[SbF_6] shows a displacement of the vertical projection of the metal onto the arene plane towards the ring junction. The Ru–C(12) bonds are 0.04 A shorter than the Ru–C(11) bonds.

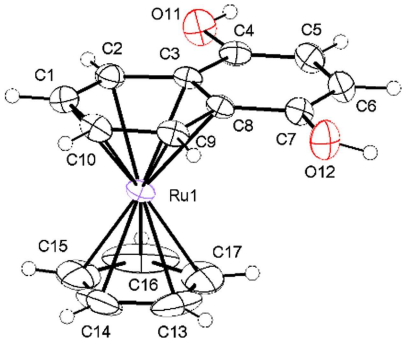


Figure 5. ORTEP View of the crystal structure of [Ru(η^5-Cp)(η^6-dihydroxynaphthalene)][SbF_6] (**17**[SbF_6]). The SbF_6 anion is omitted for clarity. Ellipsoids are represented with 50% probability. Selected bond distances: Ru(1)–C(1) 2.230(5), Ru(1)–C(2) 2.214(5), Ru(1)–C(3) 2.270(5), Ru(1)–C(8) 2.267(5), Ru(1)–C(9) 2.207(5), Ru(1)–C(10) 2.224(5), C(1)–C(10) 1.418(8), C(1)–C(2) 1.411(8), C(2)–C(3) 1.424(8), C(3)–C(4) 1.431(7), C(3)–C(8) 1.454(7), C(4)–C(5) 1.359(8), C(5)–C(6) 1.425(8), C(6)–C(7) 1.365(8), C(7)–C(8) 1.436(7), C(8)–C(9) 1.439(7), C(9)–C(10) 1.408(8).

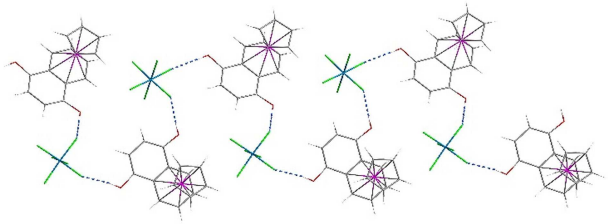


Figure 6. Representation of the hydrogen bonds between cation and anion in **17**[SbF_6]. Distances O–H: 0.84 Å and 0.86 Å, H···F: 1.84 Å and 1.90 Å.

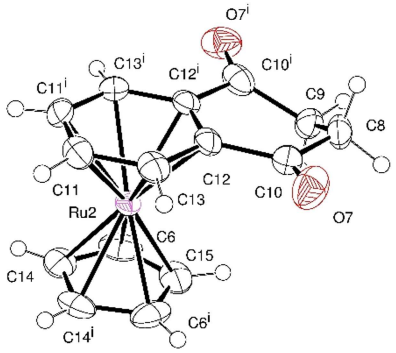


Figure 7. ORTEP View of the crystal structure of [Ru(η^5-Cp)(η^6-tetralinedione)][SbF_6] (**18**[SbF_6]). Ellipsoids are represented with 50% probability. The SbF_6 anion is omitted for clarity. Selected bond distances: Ru(2)–C(12^i) 2.212(2), Ru(2)–C(12) 2.212(2), Ru(2)–C(11) 2.216(2), Ru(2)–C(11^i) 2.216(2), Ru(2)–C(13) 2.217(2), Ru(2)–C(13^i) 2.217(2), C(11)–C(13) 1.405(3), C(12)–C(13) 1.417(3), C(10)–C(12) 1.501(3), C(8)–C(10) 1.402(6), C(8)–C(9) 1.517(8), C(9)–C(10^i) 1.617(6).

Complexes **15** and **18** offer the possibility of selective syntheses of **17**, the regioisomer having Ru coordinated to the unsubstituted ring of the condensed aromatic system (*Scheme 5*). Sequential treatment of **15** with BBr_3 and KPF_6 affords **17**[PF_6]. More convenient, dissolving **18**[SbF_6] in trifluoroacetic acid results in tautomerization and an equilibrium between **18**[SbF_6] and **17**[SbF_6]. The latter is much less soluble, precipitates on solvent removal and was isolated in 80% yield.[38]

Finally, it is shown that the carbonyl functions in the tetralindione complex can be reduced by $NaBH_4$. As one face is blocked by the RuCp fragment, hydride addition occurred stereoselectively to the *exo*-face of the complex yielding the *endo,endo* 1,4-dihydroxytetralin complex **19** (*Figure 8*).

Conclusions

Microwave heating shortens the time of synthesis of [Ru(II)Cp(naphthalene)][PF_6] (**2**) from ruthenocene from three days to 15 minutes. This complex serves as an excellent air-stable precursor for the widely used

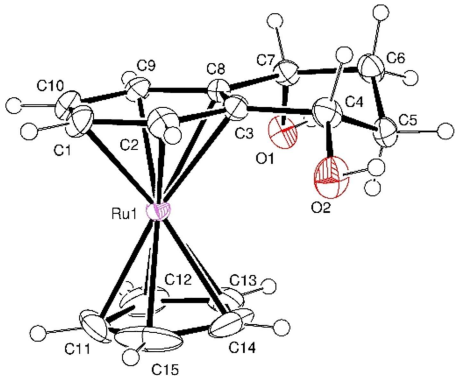


Figure 8. ORTEP View of the crystal structure of [Ru(η^5-Cp)(η^6-*endo*,*endo*-dihydroxy tetraline)][SbF_6] (**19**[SbF_6]). Ellipsoids are represented with 50% probability. The SbF_6 anion is omitted for clarity. Bond-distances and -angles see *Supporting Information*.

catalyst [Ru(II)Cp(CH_3CN)$_3$][PF_6] (**1**). It is shown here that this direct method can also be applied to a range of other simple cationic Ru(arene)Cp complexes. The functionalities present in 1,4-naphthoquinone, 1,4-tetralindione, 1,4-dihydroxynaphthalene, and 1,4-dimethoxynaphthalene require Ru arene complexation through the acetonitrile complex **1**. Here too, microwave heating renders the complexation more efficient. The series of complexes of naphthoquinone derivatives were all structurally characterized by X-ray diffraction.

Experimental Section

General

All reactions and manipulations were carried out under an inert atmosphere of nitrogen using an inert gas/vacuum double manifold line and standard *Schlenk* techniques, unless otherwise noted. Dichloromethane, acetonitrile, tetrahydrofuran, hexane, diethyl ether, and toluene were dried by passing through activated Al_2O_3 using a *Solvtek*® purification system. Dichloroethane was purified by distillation over calcium hydride under nitrogen. When required, the solvents were degassed by three successive freeze-thaw-pump cycles or by bubbling nitrogen through for 10 min. Naphthoquinone was crystallized before use from cyclohexanol/methylcyclohexane. Commercially available chemicals were purchased from *Fluka*, *Aldrich*, and *Acros* and used as received.

Microwave reactions were performed in a *Biotage Initiator SW* apparatus operating at a frequency of 2450 MHz and using either 10 mL or 20 mL glass microwave vials. Melting points were measured in open capillary tubes on a *Büchi 540* apparatus and are uncorrected. Elemental analyses were carried out by *K. L. Buchwalder* from the University of Geneva. Infrared spectra were recorded on a *Perkin-Elmer 1650* FT-IR spectrometer using diamond *ATR Golden Gate* sampling. NMR Spectra were recorded on 500, 400, or 300 MHz *Bruker Avance* spectrometers in the solvent indicated. Electron impact (EI) HR-MS mass spectra were obtained using a *Finnigan MAT 95* operating at 70 eV. Electrospray ionization (ESI) HR-MS analyses were measured on a *VG analytical 7070E* instrument. X-Ray structure determinations were performed using a *STOE IPDS 2* image-plate diffractometer with a graphite-monochromatic MoK_α radiation ($\lambda =$ 0.71069 Å).

General Procedure for the Preparation of [Ru(η^5-Cp)(η^6-arene)][PF_6] Complexes from Ruthenocene

A 20 mL microwave vial equipped with a magnetic stirring bar was charged with ruthenocene, the arene (2 mol equiv), Al (fine powder, 0.5 mol equiv.), and $AlCl_3$ (2 mol-equiv.). After purging with nitrogen, degassed decalin (1.5 mL per mmol of ruthenocene) and $TiCl_4$ (0.5 mol equiv) were added through syringe. The mixture was stirred for 5 min and then subjected to microwave irradiation for 15 min at 230 °C. After cooling to room temperature (r.t.), the mixture was poured into a mixture of ice and water (80 mL), 32% HCl (20 mL), and 30% H_2O_2 (20 mL) and stirred vigorously for 10 min. The mixture was extracted with pentane (3×200 mL). KPF_6 (1.5 mol-equiv.) was then added to the aqueous phase causing the precipitation of a light yellow solid. After stirring for 10 min, the aqueous phase was extracted with four portions of CH_2Cl_2, and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum to afford the crude product. This was taken up in CH_2Cl_2 and filtered through a short plug of *Celite*. The *Celite* was washed with CH_2Cl_2 until washings become colorless. The CH_2Cl_2 solution was concentrated to *ca.* 10 mL and then poured into vigorously stirred diethyl ether (100 mL) to yield a pale yellow precipitate which was filtered of on a *Büchner* filter and washed with pentane (3×20 mL). After drying under reduced pressure, the complex was stored in dark glass vials.

[Ru(η^5-Cp)(η^6-naphthalene)][PF_6] (**2**).[20–22] 10 mmol scale, yield 3.700 g, 85%. M.p. 155–160 °C (decomp.). FT-IR: 3122, 1630, 1530, 1412, 818, 554.^{1}H-

NMR (400 MHz, (D_6)acetone): 5.15 (*s*, 5 H); 6.47–6.48 (*m*, 2 H); 7.24–725 (*m*, 2 H); 7.70–7.73 (*m*, 2 H); 7.89–7.92 (*m*, 2 H). ^{13}C-NMR (100 MHz, (D_6)acetone): 79.7; 83.9; 85.9; 97.2; 129.3; 131.5. ^{31}P-NMR (162 MHz, (D_6)acetone): −144.1 (*sept.*, J = 708). ESI-MS: 295 (100, $[M+H]^+$). Anal. calc. for $C_{15}H_{13}F_6PRu$ (439.30): C 41.01, h 2.98; found: C 41.66, h 3.35.

[Ru(η^6-benzene)(η^5-Cp)][PF_6] (**3**).[28,43,44] 1 mmol scale, yield 0.310 g, 80%. ^{1}H-NMR (400 MHz, CD_2Cl_2): 5.39 (*s*, 5 H); 6.13 (*s*, 6 H). ^{13}C-NMR (100 MHz, CD_2Cl_2): 81.0, 86.4. ^{31}P-NMR (121 MHz, CD_2Cl_2): −144.5 (*sept.*). ^{19}F-NMR (282 MHz, CD_2Cl_2): −72.9 (*d*).

[Ru(η^5-Cp)(η^6-toluene)][PF_6] (**4**). [44] 1 mmol scale, yield 0.385 g, 92%. ^{1}H-NMR (400 MHz, CD_2Cl_2): 2.35 (*s*, 3 H); 5.32 (*s*, 5 H); 6.01–6.11 (*m*, 5 H).

[Ru(η^5-Cp)(η^6-mesitylene)][PF_6] (**5**).[29,44] 1 mmol scale, yield 0.293 g, 68%. ^{1}H-NMR (400 MHz, (D_6)acetone): 2.37 (*s*, 9 H); 5.38 (*s*, 5 H); 6.28 (*s*, 3 H). ^{13}C-NMR (100.5 MHz, (D_6)acetone): 19.4; 81.0; 87.3; 101.2.

[Ru(η^5-Cp)(η^6-hexamethylbenezene)][PF_6] (**6**).[20,28,44] 1 mmol scale, yield 0.203 g, 43%. ^{1}H-NMR (400 MHz, CD_2Cl_2): 2.39 (*s*, 18 H); 4.90 (*s*, 5 H). ^{13}C-NMR (100 MHz, CD_2Cl_2): 81.7; 84.6.

[Ru(η^5-Cp)(η^6-indane)][PF_6] (**7**). 1 mmol scale, yield 0.270 g, 63%. ^{1}H-NMR (400 MHz, (D_6)acetone): 2.05 (*m*, 2 H); 2.82 (*m*, 2 H); 2.95 (*m*, 2 H); 5.47 (*s*, 5 H); 6.14 (*s*, 2 H); 6.44 (*s*, 2 H). ^{13}C-NMR (100.5 MHz, (D_6)acetone): 24.0; 30.9; 80.5; 82.5; 84.1; 108.9.

[Ru(η^5-Cp)(η^6-2,6-Dimethylnaphthalene)][PF_6] (**8**). 1 mmol scale, yield 0.449 g, 96%. ^{1}H-NMR (400 MHz, CD_2Cl_2): 2.43 (*s*, 3 H); 2.46 (*s*, 3 H); 4.90 (*s*, 5 H); 6.16 (*d*, J = 6.0, 1 H); 6.81 (*d*, J = 6.0, 1 H); 6.87 (*s*, 1 H); 7.38 (*s*, 1 H); 7.44 (*d*, J = 8.8, 1 H); 7.61 (*d*, J = 8.8, 1 H). ^{13}C-NMR (100 MHz, CD_2Cl_2): 20.9; 22.4; 80.2; 83.0; 85.0; 87.3; 95.3; 98.0; 100.5; 102.1; 125.9; 129.4; 135.3; 143.2. ^{31}P-NMR (121 MHz, CD_2Cl_2): −144.2 (*sept.*). ^{19}F-NMR (282 MHz, CD_2Cl_2): −72.5 (*d*).

[Ru(η^5-Cp)(η^6-5-methylnaphthalene)][PF_6] (**9a**) *and* **[Ru(η^5-Cp)(η^6-1-methylnaphthalene)][PF_6]** (**9b**). 1 mmol scale, yield 0.440 g, 97% of a 1:1 mixture of regioisomers **9a** and **9b**. Complex **9a**: ^{1}H-NMR (400 MHz, CD_2Cl_2): 2.62 (*s*, 3 H); 4.89 (*s*, 5 H); 6.17–7.75 (*m*, 6 H); 7.90 (*d*, J = 8.8, 1 H). ^{31}P-NMR (162 MHz, CD_2Cl_2): M- > 144.4 (*sept.*). Complex **9b**: ^{1}H-NMR: 2.82 (*s*, 3 H); 4.96 (*s*, 5 H); 6.17–7.75 (*m*, 7 H). ^{31}P-NMR (162 MHz, CD_2Cl_2): −144.4 (*sept.*).

[Ru(η^5-Cp)(η^6-6,7-dimethylnaphthalene)][PF_6] (**10a**) *and* **[Ru(η^5-Cp)(η^6-2,3-dimethylnaphthalene)][PF_6]** (**10b**) 1 mmol scale, yield 0.439 g, 94% of a 1:1.5 mixture of regioisomers **10a** and **10b**. Complex **10a**: ^{1}H-NMR (400 MHz, CD_2Cl_2): 2.40 (*s*, 6 H); 4.94 (*s*, 5 H); 6.12–6.14 (*m*, 2 H); 6.81–6.83 (*m*, 2 H); 7.41 (*s*, 2 H). Complex **10b**: ^{1}H-NMR: 2.45 (*s*, 6 H); 4.83 (*s*, 5 H); 6.92 (*s*, 2 H); 7.55–7.57 (*m*, 2 H); 7.65–7.67 (*m*, 2 H).

[Ru(η^5-Cp)(η^6-pyrene)][PF_6] (**11**)[45]: 1 mmol scale, yield 0.429 g, 84%. ^{1}H-NMR (400 MHz, CD_2Cl_2): 4.67 (*s*, 5 H); 6.39 (*t*, J = 5.80, 1 H); 6.88 (*d*, J = 5.8, 2 H); 7.77 (*d*, J = 9.0, 2 H); 8.07–8.18 (*m*, 5 H). ^{13}C-NMR (100 MHz, CD_2Cl_2): 80.1; 83.3; 85.3; 94.8; 100.5; 124.9; 126.1; 129.8; 130.6; 131.9; 133.8.

[Ru(η^5-Cp)(η^6-5,8-naphthoquinone)][PF_6] (**14**[PF_6]). *Method 1*: In a glove box, [Ru(η^5-Cp)$(NCMe)_3$][PF_6] (**1**[PF_6]), naphthoquinone (0.370 g, 2 mmol, 2 equiv.) were placed in a *Carius* tube. 1,2-Dichloroethane (15 mL) was added and the mixture was stirred at 80 °C for 5 h. Cooling to r.t., filtration through cannula over *Celite*, removal of volatiles *in vacuo*, and washing of the residue with 1.2-dichloroethane afforded **14**[PF_6] as pale cream colored solid (0.267 g, 61%).

Method 2: A microwave vial was charged with **1**[PF_6] (0.430 g, 1 mmol), naphthoquinone (0.370 g, 2 equiv.), and 1,2-dichloroethane (15 mL). The tube was sealed and subjected to microwave irradiation at 100 °C for 30 min (normal absorption level). Workup as described above afforded **14**[PF_6] (0.350 g, 80%). Pale brown solid. M.p. 230 °C (dec.). IR (neat): 3117, 2164, 1675, 1610, 1525, 1417, 1307, 1150, 1094, 1046, 1004, 978, 821, 628, 554. ^{1}H-NMR (400 MHz, DMSO): 7.20 (*s*, 2 H); 6.95 (*dd*, J = 2.4, 4.2, 2 H); 6.72 (*dd*, J = 2.4, 4.2, 2 H); 5.63 (*s*, 5 H). ^{13}C-NMR (100 MHz, DMSO): 184.2; 138.8; 88.3; 87.4; 83.5; 83.1. ^{31}P-NMR (162 MHz, (D_6)acetone): −144.2 (*sept.*, PF_6). HR-ESI-MS: 324.9797 ($C_{15}H_{11}O_2Ru^+$, $[M-PF_6]^+$; calc. 324.9802).

Complex **14**[SbF_6] was obtained from **1**[SbF_6] by the same procedures.

[Ru(η^5-Cp)(η^6-5,8-dimethoxynaphthalene)][PF_6] (**15**): *Method 1*: In a glove box, a *Carius* tube was charged with **1**[PF_6] (0.434 g, 1 mmol) and 1,4-dime-

thoxynaphthalene (0.134 g, 1.4 mmol). 1,2-Dichloroethane (85 mL) was added next, and the mixture was stirred for 16 h at 80 °C, then cooled to r.t. Filtration over *Celite* under nitrogen, concentration, and precipitation by addition of Et_2O afforded **15** as yellow solid. Yield: 0.375 g, 75 %.

Method 2. A 20 mL microwave vial equipped with a magnetic stirring bar was charged in the glove box with **1**[PF_6] (1.33 g, 3.06 mmol) and 1,4-dimethoxynaphthalene (0.66 g, 3.51 mmol, 1.5 equiv.). Dry 1,2-dichloroethane (15 mL) degassed by three freeze-pump-thaw cycles was added, the tube was sealed and subjected to microwave irradiation at 80 °C for 5 min (normal absorption level). After completion of reaction, cooling to r.t., filtration under nitrogen over *Celite* through a cannula, and removal of volatiles *in vacuo* afforded crude **15**. Crystallization from CH_2Cl_2/Et_2O gave **15** as yellow solid (1.24 g, 81 %). M.p. 188–190 °C (dec.). IR (neat): 1623, 1522, 1469, 1446, 1413, 1370, 1267, 125, 1133, 1083, 1028, 998, 952, 870, 830, 809, 714, 555. ^{1}H-NMR (400 MHz, (D_6)acetone): 7.29 (*dd*, *J* = 4.6, 2.4, 2 H); 6.95 (*s*, 2 H); 6.47 (*dd*, *J* = 4.6, 2.4, 2 H); 5.17 (*s*, 5 H); 4.02 (*s*, 6 H). ^{13}C-NMR (100 MHz, (D_6)acetone): 150.4; 107.9; 93.0; 87.3; 81.7; 80.3; 58.0. ^{31}P-NMR (162 MHz, (D_6)acetone): −144.3 (*sept.*, PF_6). ^{19}F-NMR (282 MHz, (D_6)acetone) −72.6 (*d*, *J* = 707.8). HR-ESI-MS: 355.0267 ($C_{17}H_{17}O_2Ru^+$, [*M*−PF_6]$^+$; calc. 355.0272).

[Ru(η^5-Cp)(η^6-1,4-dihydroxynaphthalene)][SbF_6] (**16**[SbF_6]) *and* **[Ru(η^5-Cp)(η^6-5,8-dihydroxynaphthalene)][SbF_6]** (**17**[SbF_6]). *Method 1*: In a glove box, **1**[SbF_6] (0.500 g, 0.95 mmol) and 1,4-dihydroxynaphthalene (0.300 g, 1.9 mmol) were placed in a *Carius* tube. N_2-sat. 1,2-dichloroethane (30 mL) was added, and the mixture was stirred for 24 h at 80 °C, then cooled to r.t. Filtration over *Celite* under nitrogen, concentration, and recrystallization from THF/hexane afforded a 1.3 : 1 mixture of **16** and **17** as pale yellow solid. Yield: 0.320 g, 60 %.

Method 2: A 10 mL microwave vial equipped with a magnetic stirring bar was charged in the glove box with **1**[SbF_6] (0.100 g, 0.19 mmol) and 1,4-dihydroxynaphthalene (0.060 g,0.41 mmol). Dry 1,2-dichloroethane (7 mL) degassed by three freeze-pump-thaw cycles was added, the tube was sealed and subjected to microwave irradiation at 80 °C for 10 min (normal absorption level). After completion of reaction, filtration under nitrogen over *Celite* through cannula and removal of volatiles *in vacuo* and washing with three portions of 1,2-dichloromethane afforded a 1 : 1 mixture of **16** and **17**. Yield: 0.069 g, 65 %. The major isomer **16** is more soluble in 1,2-dichloroethane than **17**. Repeated washing of the mixtures afforded a 5 : 95 mixture of **16**[SbF_6]:**17**[SbF_6]. Analogous procedures for the [PF_6] complexes. Complex **16**[PF_6]: ^{1}H-NMR (300 MHz, (D_6)acetone): 8.08 (*dd*, *J* = 7.0, 3.0, 2 H); 7.63 (*dd*, *J* = 7.0, 3.0, 2 H); 6.35 (*s*, 2 H); 4.81 (*s*, 5 H). Complex **17**[SbF_6]: IR (neat): 3494, 1636, 1531, 1412, 1286, 1254, 1124, 1058, 830, 751, 740, 665, 636, 520. ^{1}H-NMR (400 MHz, MeOD): 7.23 (*dd*, *J* = 4.4, 2.4, 2 H); 6.70 (*s*, 2 H); 6.31 (*dd*, *J* = 4.4, 2.4, 2 H); 5.05 (*s*, 5 H). ^{13}C-NMR (100 MHz, MeOD): 147.0; 110.8; 92.7; 85.9; 80.3; 30.0.

[Ru(η^5-Cp)(η^6-5,8-tetralindione)][PF_6] (**18**[PF_6]). A *Carius* tube was silylated by filling with a 5 % (*v*/*v*) solution of *N*,*O*-bis(trimethylsilyl)acetamide in Et_2O. After 10 min, the glassware was rinsed with Et_2O and the tube was dried under vacuum for 30 min before transferring to a glove box and charging with **1**[PF_6] (0.400 g, 0.92 mmol) and 1,4-tetralindione (0.24 g, 1.84 mmol, 2 equiv.). Then, dry 1,2-dichloroethane (8 mL) was added and the mixture was stirred for 5 h at 80 °C. Filtration over *Celite*, removal of volatiles *in vacuo* and washing with 1,2-dichloroethane afforded **18**[PF_6] as colorless solid (0.290 g, 67 %). IR (neat): 3099, 1702, 1519, 1420, 1304, 1280, 1200, 971, 829, 555, 524, 503. ^{1}H-NMR (400 MHz, (D_6)acetone): 6.97 (*dd*, *J* = 4.4, 2.5, 2 H); 6.83 (*dd*, *J* = 2.4, 4.4, 2 H); 5.77 (*s*, 5 H, cp); 3.25–3.34 (*m*, 4 H). ^{13}C NMR (100 MHz, (D_6) acetone): 37.2; 84.5; 84.6; 89.6; 92.1; 195.3.

Complex **18**[SbF_6] was prepared analogously from **1**[SbF_6].

1 mmol scale, yield: 0.410 g, 73 %. HR-ESI-MS: 326.9956 ($C_{15}H_{13}O_2Ru^+$, [*M*−SbF_6]$^+$; calc. 326.9959).

[Ru(η^5-Cp)(η^6-5,8-*endo*,*endo*-tetralindiol)][SbF_6] (**19**[SbF_6]). [Ru(η^5-Cp)(η^6-5,8-tetralinedione)][SbF_6] (**18**[SbF_6]) (0.1 g, 0.17 mmol) and dry MeOH (4 mL) were placed in a *Schlenk* tube. $NaBH_4$ (20 mg, 0.52 mmol, 3 equiv.) was added. Gas evolution was observed, and the white suspension changed to red. Volatiles were evaporated and the crude mixture was washed with dry acetone (3 × 2 mL) under nitrogen to obtain **19**[SbF_6] as colorless solid (0.077 g, 80 %). Yield: 80 %. ^{1}H-NMR (400 MHz, (D_6)acetone): 6.23 (*dd*, *J* = 4.3, 2.5, 2 H); 6.16 (*dd*, *J* = 4.4, 2.4, 2 H); 4.47 (*s*, 5 H); 4.53–4.50 (*m*, 2 H); 2.04–1.97 (*m*, 2 H); 1.87–1.78 (*m*, 2 H). ^{13}C-NMR (100 MHz, (D_6)acetone): 110.5; 85.3; 84.3; 81.8; 65.2; 29.6.

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Author Contribution Statement

Eva Bocekova-Gajdošíkova (PostDoc): syntheses and crystal preparation of complexes **16–19**. *Bugra Epik* (intern): initial experiments of microwave synthesis of **2**. *Jingyu Chou* (PostDoc): microwave synthesis of **2–11**. *Katsuhiro Akiyama* and *Nobuaki Fukui* (interns): syntheses of **15–17** and attempts of haptotropic rearrangements. *Laure Guénée* (crystallographer): X-Ray structure determinations. *E. P. K.*: project director.

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