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Synthesis of various (pentamethylcyclopentadienyl) Ru(η^6-arene) complexes of phenalene derivatives

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Summary — The η^6-(pentamethylcyclopentadienyl)ruthenium complexes of phenalenone **9**, phenalenes **10** and **11**, phenalane **12** and phenalanone **13** have been prepared from the corresponding phenalenic derivatives, following Chaudret's procedure. The electron-donating pentamethylcyclopentadienyl ligand modifies the reactivity of phenalene in the corresponding ruthenium complexes, which become unreactive towards dioxygen. Phenalenone, which reacts readily with 2-methylindole in presence of *para*-toluenesulfonic acid, becomes unreactive when complexed to ruthenium (complex **9**).

(pentamethylcyclopentadienyl)ruthenium(η^6-arene) / phenalenone / phenalene / phenalane / phenalanone

Résumé — Synthèse de divers complexes (pentaméthylcyclopentadiényl(η^6-arène))Ru dérivés du phénalène. *Les complexes η^6-(pentaméthylcyclopentadiényl)ruthénium dérivés de la phénalénone* **9**, *du phénalène* **10** *et* **11**, *du phénalane* **12** *et de la phénalanone* **13** *ont été préparés à partir des dérivés phénaléniques correspondants en mettant en œuvre le protocole expérimental décrit par Chaudret. Le ligand pentaméthylcyclopentadiényle, donneur d'électrons, modifie la réactivité du phénalène, dans les complexes correspondants du ruthénium. Ces derniers ne sont plus sensibles à l'oxydation par le dioxygène. La phénalénone qui se condense facilement avec le 2-méthylindole en présence d'acide* para-*toluènesulfonique est inerte lorsqu'elle est complexée (complexe* **9***).*

(pentaméthylcyclopentadiényl)ruthénium(η^6-arène) / phénalénone / phénalène / phénalane / phénalanone

Introduction

Phenalene derivatives have recently attracted attention because of their peculiar properties [1] and reactivity [2] which result from their odd alternant hydrocarbon structure [1c,d]. For instance, phenalenone **3** is easily formed from phenalene **1** by oxidation with dioxygen via the intermediacy of the delocalized phenalenyl radical [1e,f, 4] **2** (fig 1).

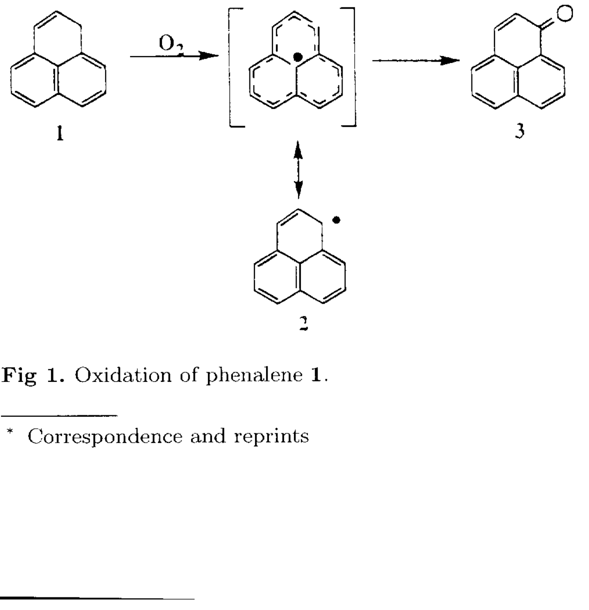

Fig 1. Oxidation of phenalene **1**.

The reactivity of phenalenone and more particularly the acid-catalyzed condensation with 2-methylindole (which essentially acts as a nucleophile [6a]) has been studied from the structural point of view [5], because such derivatives have been identified as being at the origin of the instability of liquid fuels [4c, 6].

It was therefore of interest from both the theoretical and the practical points of view to modify the reactivity of phenalenone towards 2-methylindole. The strategy we adopted was to increase the electron density of the entire system, in the hope that the electrophilic character of the carbonyl carbon, or of the dienone structure taken as a whole, would be strongly decreased. Since phenalene **1** features the possibility of producing various σ- and π-complexes [3, 7], we wondered if the reactivity and chemical behavior of phenalene would be altered, when involved in such complexes. The lifetimes of the η^2-iron carbonyl derivatives **4** and **5**, and even of η^6-chromium carbonyl complex **6**, are too short (between 30 min and 2 days); as a consequence such complexes cannot be used for reactivity studies (fig 2).

However, it was known that the neutral (methylcyclopentadienyldicarbonyl)Mn(η^2-phenalene) complex

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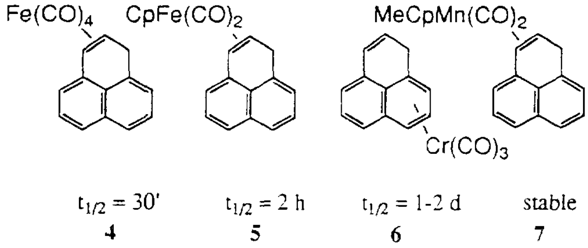
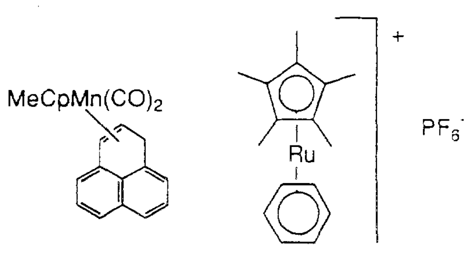


Fig 2. Structures and lifetimes of (phenalene)Fe(CO)$_4$, **4**, [(phenalene)Fe(cyclopentadienyl)(CO)$_2$]$_2$, **5**, (phenalene)Cr(CO)$_3$, **6**, and (phenalene)Mn(methylcyclopentadienyl)(CO)$_2$, **7**.



7

8

Fig 3. Stable complexes **7** and **8**.

7 and cationic Ru(η^6-arene) η^5-Cp* complex **8** (Cp* = pentamethylcyclopentadienyl) are stable (fig 3) [7c, 8, 9].

The strong electron-donating character of the Cp* ligand fulfils the requirement mentioned above, as it is likely to decrease the electrophilic character of the phenalenone **3**, even if the corresponding complex **9** is cationic.

Furthermore, it could be imagined, for similar reasons, that the reactivity of phenalene towards dioxygen could be modified in the corresponding complexes **10** or **11** (see below). Finally, because the experimental procedure to prepare such Cp*Ru complexes is mild and fairly general, we decided to prepare complexes **9**–**13** for comparison purposes (fig 4).

Results and discussion

Preparation of the complexes

Several experimental procedures are available to prepare Cp*Ru(arene) complexes [3, 9, 10, 12]. The one reported by Chaudret et al [10c] is characterized by its simplicity; it requires only two steps and reactive intermediate **15** does not need to be isolated. This is not the case with other procedures [9, 12]. The reactive intermediate **14** (fig 5), "known as a dimer", was prepared according to Oshima [13] from the ruthenium trichloride trihydrate (reaction (1), fig 5). Complex **14** is immediately reduced with zinc powder in tetrahydrofuran to form the air-sensitive key intermediate **15** upon precipitation of zinc chloride (reaction (2), fig 5). After filtration, potassium hexafluoride and the appropriate phenalene derivative (Phe) were added to the corresponding solution of **15**, to yield a complex with the general formula **A**, where Phe depends on the structure of the derivative used in reaction (3) (fig 5).

Phenalenone **3** gives a single complex **9** isolated with a 50% yield, as an air-stable amorphous yellow powder soluble in dichloromethane and acetone. As in the case of chromium complexes of phenalene [7], the complexation occurs preferentially on the most electron-rich aromatic ring, which can be considered as the one that features the highest aromatic character. The metal binds to the aromatic ring that is the most distant from the carbonyl group acting as an electron-withdrawing group. This situation reflects in the ^{1}H and ^{13}C NMR spectra. For instance, it is possible to observe an upfield shift of the aromatic protons of the ring complexed to the metal, in the range of 1 to 1.15 ppm relative to uncomplexed phenalenone. This can be compared with the 0.13 ppm upfield shift of the methylenic proton in complex **6**. Similarly, the shielding

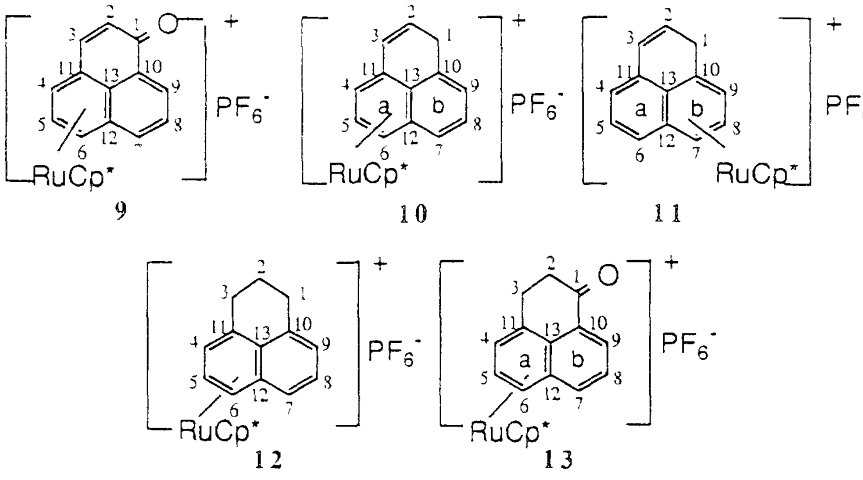
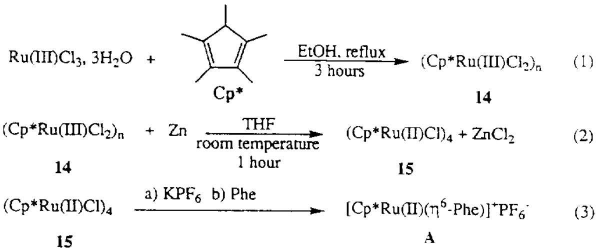


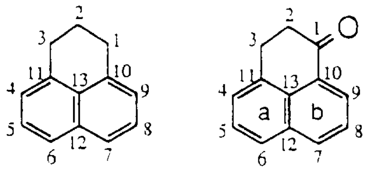
Fig 4. Representative structures of the Cp*Ru(η^6-arene) complexes of phenalene derivatives **9**–**13**.



Phe = Phenalene **1**	A = **10** or **11**
Phe = Phenalenone **3**	A = **9**
Phe = Phenalane **16**	A = **12**
Phe = Phenalanone **17**	A = **13**

Fig 5. General procedure to prepare Cp*Ru(arene) complexes **9**–**13**.

ranges from 37 to 40 ppm for the corresponding carbons in the ^{13}C NMR spectrum. A 22 ppm upfield shift was observed for the benzene carbons in the [Cp*Ru (η^6-benzene)]$^+$PF$_6^-$ complex prepared by Chaudret [10c]. Two air-stable isomers **10** and **11** could be isolated after column chromatography on silica of the amorphous yellow powder obtained in 50% yield as the crude product of reaction (3) (fig 5) with phenalene **1**. As mentioned above, evidence for the complexation of the metal with either aromatic ring a or b of phenalene, results from the upfield shift of the proton or carbon signals observed of the ^{1}H or ^{13}C NMR spectra of either **10** or **11**. Complexes **12** and **13** could be prepared from the corresponding phenalane **16** and phenalanone **17** (fig 6) in 90 and 80% yields respectively.



16 **17**

Fig 6. Structure of phenalane **16** and phenalanone **17**.

Because of the symmetry of phenalane **16**, it is clear that compound **12** is formed as the unique product of the reaction. For complex **13**, the analysis of the ^{1}H and ^{13}C NMR spectra show that the ring a is complexed with ruthenium. There was no evidence for another isomer, in which ring b was complexed. This selective complexation of ring a in complex **13** can be compared with a similar situation observed for complex **9**. When the carbonyl group is not present, the complexation can occur on either ring a or b as in **10** and **11**.

Reactivity

As mentioned above, we prepared complexes **12** and **13** in order to compare the site of complexation of the metal with that in complexes **9**–**11**. For complex **9**, it was most interesting to investigate its reaction with 2-methylindole in the presence of stoichiometric amounts of *para*-toluenesulfonic acid. We have reported previously [4c, 5a, 6a] that under such conditions phenalenone **3** yields a complex mixture of products. The structure of the various derivatives thus obtained has been thoroughly and extensively analysed. When complex **9** is reacted with 2-methylindole and *para*-toluenesulfonic acid for 24 h in dichloromethane at room temperature, an orange compound **18** was formed (R_f = 0.24 on silica with CH$_2$Cl$_2$/methanol (90:10) as the eluent) (fig 7).

The ^{1}H and ^{13}C NMR spectra clearly show that the exchange of the counterions is the only reaction which has occurred. This is emphasized by the disappearance of the sharp IR band at 850 cm^{-1} characteristic of the PF$_6^-$ anion, and the appearance of bands at 1 180, 1 025 and 1 005 cm^{-1} characteristic of the *para*-toluenesulfonic anion.

These observations show that, although the phenalenone ligand is involved in a cationic complex, it has now become totally unreactive towards 2-methylindole. The steric hindrance of the Cp* ligand cannot be used to explain the lack of reactivity, because one of the faces of the phenalenone is necessarily uncomplexed. The most probable explanation is that the enone system at the origin of the condensation with 2-methylindole [4c, 5, 6a] is no longer reactive, because it is electronically enriched by the Cp* ligand via the ruthenium core. Another possible reason could be that *para*-toluenesulfonic acid can no longer play its catalytic role because it is now exclusively involved as a counteranion.

The air stability of complexes **10** and **11** has already been mentioned. The UV-vis spectrum (200–900 nm) of a degassed solution of any of these complexes in CH$_2$Cl$_2$ (concentration 10^{-4} M), is not altered by exposure to daylight or to UV radiation at 254 nm for 5 h or more.

This observation is in serious contrast with the behavior of phenalene, which is stable at low temperature in the dark in the absence of dioxygen, but reacts rapidly in its presence to yield quantitatively the phenalenyl radical **2** (fig 1), which is further oxidized into phenalenone **3** [4]. Similarly, 3-(2-methylindolyl)phenalene **19** also gives rise to the corresponding radical in a few minutes [4c, 6a] and is later transformed into the corresponding substituted phenalenone **20** (fig 8).

We thus conclude that when phenalenes are complexed as in **10** or **11**, they no longer undergo oxidation into phenalenone. The intimate nature of this mechanism is not known with certainty. If it involves a radical, the occurrence of an initiation step, which could be an allylic/benzylic hydrogen abstraction by triplet dioxygen, has not been demonstrated [1c, 4, 14]. Another mechanism could involve an 'ene' reaction of singlet dioxygen with phenalene [4b], because phenalenone **3** is known to be an excellent sensitizer [15]. Whatever the mechanism, it necessarily involves the reactivity of the allylic benzylic hydrogens of phenalene **1**. The absence of reactivity of complex **9** towards a nucleophile such as 2-methylindole, and of complexes **10** and **11** towards dioxygen are in strong contrast with the chemical behavior of the corresponding species which are not complexed with Cp*Ru. Uncomplexed phenalenone **3** reacts readily with 2-methylindole [5a, 6]

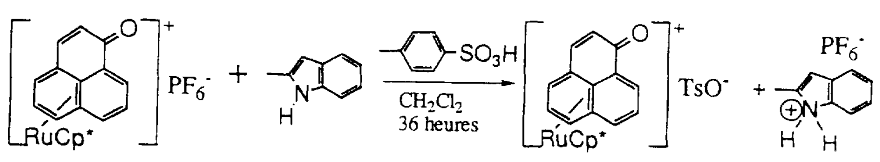


Fig 7. Synthetic scheme for the exchange of the counterion in complex **9** and the absence of reaction of the phenalenone ligand with 2-methylindole.

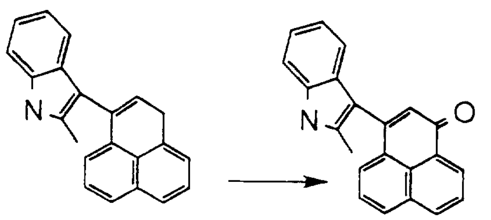


Fig 8. Oxidation of 3-(2-methylindolyl)phenalene **19** into 3-(2-methylindolyl)phenalenone **20**.

and uncomplexed phenalene **1** is easily oxidized into phenalenone **3** [1c, 1f, 4].

This absence of reactivity of **9** towards 2-methylindole seems to show that the enone system is no longer electrophilic, even though the complex is cationic. This could be the result of an electron enrichment by the Cp* ligand (Cp*Ru) via the ruthenium. This should be compared with the activation role of Cp*Ru relative to the nucleophilic substitution of chlorinated by fluorinated arenes [17]. However, in this case the leaving groups (chlorine or fluorine) are directly bound to a single aromatic ring. The situation is obviously different with phenalenone where the enonic system is deactivated.

A similar situation is likely to arise with the two methylene hydrogens of phenalene **1**, which are both benzylic and allylic and are no longer reactive towards dioxygen, when **1** is complexed with Cp*Ru as in **10** and **11** whatever mechanism is involved . Either the C-H bond are strengthened in such a way that the C-H abstraction by dioxygen can no longer occur, or the intermediate radical (if it is formed) is now destabilized by the complexation of the phenalenyl radical with Cp*Ru. In the present state of our knowledge it is not reasonable to make any further assumptions, but this topic definitely deserves further research. The stability of complexes **10** and **11** towards dioxygen is therefore an indication of the modification of the reactivity of these allylic and benzylic hydrogens in Cp*Ru complexes of phenalene.

As a conclusion, we have been able to prepare five new stable Cp*Ru complexes of phenalene (complexes **10** and **11**), phenalenone (complex **9**), phenalane (complex **12**) and phenalanone (complex **13**). The complexation of phenalene modifies its reactivity towards dioxygen, because complexes **10** and **11** remain unchanged in presence of air or dioxygen. Finally, phenalenone, when involved in complex **9**, no longer reacts with 2-methylindole in presence of *para*-toluenesulfonic acid.

Experimental section

General

All reagents were commercially available. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey. Phenalenone (perinaphthenone), lithium aluminum hydride ($LiAlH_4$), diisobutylaluminum hydride (DIBAL-H) 1.0 M in hexanes/1.5 M in toluene, and potassium hexafluoride phosphate (KPF_6) were purchased from Aldrich. Palladium on charcoal (5%) and 1,1,3,3-tetramethyldisiloxane were purchased from Janssen Chimica. Tetrahydrofuran was refluxed and distilled over sodium and benzophenone under an argon atmosphere. Toluene was distilled from sodium under argon. Zinc was activated using hydrochloric acid (10%), filtered, washed with water and acetone, dried in the drying oven. Methanol was distilled from activated magnesium and iodine.

Thin layer chromatography (TLC) was carried out on Merck silica-gel 60 F_{254} plates. Column chromatography (Flash) was performed on Merck silica-gel 60, 230-400 mesh. The ultraviolet spectrophotometer used was a Philips PU 8720 UV/vis scanning spectrophotometer, the infrared (IR) was a Philips PU 9706 infrared spectrophotometer. ^1H and ^{13}C NMR spectra were obtained using one of the following machines: Bruker AC 200 and 400 MHz, Varian 200 MHz for protons (respectively 50.3 or 100 MHz for carbon). The chemical shifts are given in reference to the deuterated solvent as indicated. The letters s, d, t and m used to describe the NMR proton spectra are related to a singlet, doublet, triplet or multiplet respectively. IR spectra were recorded either as solid potassium bromide (KBr) pellets or solution samples. Melting points were taken with a Reichert apparatus and have not been corrected. Elemental analysis have been carried out by the Service de microanalyse de la faculté des sciences de Marseille-Saint-Jérôme on the new compounds isolated. For the other known compounds, the literature reference is reported for comparison.

Phenalenone 3 *(perinaphthenone commercial from Aldrich)*

We report here the NMR spectra recorded in CD_2Cl_2 for a matter of comparison with complex **9**.

^1H NMR (CD_2Cl_2, 200 MHz): δ 6.60 (d, $J_{H_2H_3} = 9.89$ Hz, 1H, H_2), 7.54 (dd, $J_{H_5H_4} = 7.25$ and $J_{H_5H_6} = 8.28$ Hz, 1H, H_5), 7.73 (m, 3H, H_3, H_4 and H_8), 8.00 (d, $J_{H_6H_5} = 8.28$ Hz, 1H, H_6), 8.16 (d, $J_{H_7H_8} = 7.32$ Hz, 1H, H_7), 8.50 (d, $J_{H_9H_8} = 7.33$ Hz, 1H, H_9).

^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 127.3 (C_5), 127.6 (C_8), 128.1 (C_{12}), 128.4 (C_{11}), 129.7 (C_2), 130.1 (C_{10}), 130.4 (C_9), 131.9 (C_4), 132.4 (C_6), 132.8 (C_{13}), 135.4 (C_7), 142.2 (C_3), 185.8 (C_1).

IR ($CHCl_3$): 3 020, 1 650, 1 595, 1 585, 1 355, 1 295 cm^{-1}.

Preparation of phenalene, **1** *[16]*

Phenalene **1** was prepared according to the procedure of Boudjouk et al [16]. Phenalenone **3** (1.0 g, 5.5 mM) was dissolved in toluene (30 mL) in a 100 mL three-necked round-bottomed flask fitted with a reflux condenser under argon. DIBAL-H (11.2 mL, 1.0 M in hexane) was added slowly to the swirling mixture over a 30 min period. Afterwards, the red mixture was heated overnight. The solution was cooled, and saturated ammonium chloride (8 mL) was added. Pentane (60 mL) was added, and the resulting solution was filtered through a celite pad. The organic layer was washed with saturated NH_4Cl (75 mL) and the aqueous layer was washed with pentane (60 mL). The pentane extract were combined, dried with anhydrous magnesium sulfate, and evaporated to yield a red oil. The latter was dissolved in dichloromethane and chromatographed on a silica column; phenalene was eluted with pentane. Overall yield: 40% (0.40 g, 2.41 mM).

^{1}H NMR (CD_2Cl_2, 200 MHz) δ 4.01 (bs, 2H, H_1), 6.00 (dt, $J_{H_2H_1}$ = 4.15 and $J_{H_2H_3}$ = 9.8 Hz, 1H, H_2), 6.58 (dt, $J_{H_3H_1}$ = 2.2 and $J_{H_3H_2}$ = 9.8 Hz, 1H, H_3), 6.93 (d, $J_{H_9H_8}$ = 6.82 Hz, 1H, H_9), 7.1–7.2 (m, 3H, H_4, H_5 and H_8), 7.40 (m, 2H, H_6 and H_7).

^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 32.50, 122.57, 125.51, 125.85 (2C), 126.81, 127.15, 127.95, 128.59, 130.00, 132.61, 134.16, 134.90.

IR (solution, $CHCl_3$): 3 020, 3 000, 2 920, 2 850, 2 790, 1 925, 1 860, 1 780, 1 580, 1 500, 1 410, 1 390, 1 350, 1 370, 1 165, 935, 820 cm^{-1}.

Preparation of phenalane (2,3-dihydrophenalene) **16** *[1a, 4c]*

Phenalene **1** (166 mg, 1 mmol), platinum dioxide (10 mg) and anhydrous methanol (10 mL) were mixed in a 20 mL one-necked round-bottomed flask. The system was placed under an atmosphere of hydrogen and stirred for 48 h. The resulting solution was filtered through a celite pad (which was rinsed with diethyl ether (2 × 10 mL)) and evaporated to yield the phenalane with yields ranging from 55 to 90%.

^{1}H NMR (CD_2Cl_2, 200 MHz) [22]: δ 2.14 (2H, H_{2ax} and H_{2eq} (these two protons appear as a quintuplet, but are not equivalent and give rise to what is a double doublet of doublets of doublets; first order analysis is difficult; $J_{H2axH3ax} = J_{H2axH1ax}$ = 6.31 and $J_{H2axH3eq} = J_{H2axH1eq}$ = 5.96. $J_{H1axH1eq}$ cannot be estimated)), 3.18 (4H, H_1 and H_3 (these four protons appear as a triplet but give rise to what is a doublet of doublets of doublets; $J_{H1axH2ax} = J_{H3axH2ax}$ = 6.15 and $J_{H3axH2eq} = J_{H2eqH1ax}$ = 5.94)), 7.30 (d, $J_{H_4H_5} = J_{H_9H_8}$ = 6.96 Hz, 2H, H_4 and H_9), 7.46 (dd, $J_{H_5H_4}$ = 6.96 Hz and $J_{H_8H_7}$ = 8.10 Hz, 2H, H_5 and H_8), 7.75 (d, $J_{H_7H_8} = J_{H_6H_5}$ = 8.10 Hz, 2H, H_6 and H_7).

^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 23.90, 31.91 (2C), 124.47 (2C), 126.03 (2C), 126.40 (2C), 130.77, 134.45, 137.18 (2C).

Preparation of phenalanone (2,3-dihydrophenalenone) **17** *[16]*

Phenalanone was prepared according to the procedure of Boudjouk et al [16]. Phenalenone **3** (1.0 g, 5.5 mmol), concentrated hydrochloric acid (6 drops) and ethanol (45 mL, 95%) were mixed in a 100 mL three-necked round-bottomed flask, and heated to reflux. 1,1,3,3-Tetramethyldisiloxane (TMDS) (2.2 mL, 12.5 mmol) was added by syringe at a rate so as to maintain reflux. The mixture was heated for 1.5 h, cooled and filtered through a celite pad, and evaporated to yield a red-brown oil. The oil was dissolved in ether (50 mL) and washed with water (3 × 75 mL). The water layers were extracted with ether. The ether layers were combined, washed with saturated sodium chloride solution, dried with anhydrous sodium sulfate and evaporated. The resulting oil was dissolved in dichloromethane, and chromatographed on a silica column and eluted with dichloromethane. The corresponding residue, which contains **17**, was again chromatographed on a silica column; phenalanone **17** was eluted with pentane/ether (60:40). Overall yield: 29% (0.29 g, 1.57 mmol).

^{1}H NMR (CD_2Cl_2, 200 MHz): δ 2.88 (2H, H_2, (although not rigorously non-equivalent, both protons on carbon 2 give pratically a triplet signal; the $J_{H2axH2eq}$ cannot be read on the spectrum; what appears as a triplet is in fact a double doublet of doublets which has merged; J_{H2H3ax} = 7.51 Hz and J_{H2H3eq} = 6.77 Hz)), 3.36 (2H, H_3 (the signal appears as a triplet, but is in fact a double doublet of doublets which has merged; $J_{H3axH3eq}$ cannot be read on the spectrum; J_{H3H2ax} = 7.51 Hz and J_{H3H2eq} = 6.77 Hz)), 7.39–7.60 (m, 3H, H_4, H_5 and H_8), 7.75 (dd, $J_{H_6H_4}$ = 2.01, $J_{H_6H_5}$ = 6.74 Hz, 1H, H_6), 8.04 (bd, $J_{H_7H_8}$ = 8.24 Hz, 1H, H_7), 8.07 (dd, $J_{H_8H_9}$ = 7.23, $J_{H_7H_9}$ = 2.0 Hz, 1H, H_9).

^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 29.06, 39.04, 125.23, 126.07, 126.17, 126.69, 126.85, 130.45, 132.15, 133.98, 134.05, 134.44, 198.67.

IR ($CHCl_3$): 3 000, 1 675, 1 615, 1 580, 1 500, 1 455, 1 430, 1 410, 1 135, 1 270, 1 220, 1 170, 1 120, 1 075, 1 010, 820 cm^{-1}.

Preparation of [dichloro(pentamethylcyclopentadienyl)-Ru III]$_n$, **14** *[13]*

Ruthenium trichloride (510.9 mg, 2.0 mmol), pentamethylcyclopentadiene (0.63 mL, 4.0 mmol), and 10 mL of ethanol were mixed in a one-necked round-bottomed flask and heated to reflux with stirring. After 3 h, the brown solid is filtered, washed twice with ethanol (6 mL, absolute) and ether (6 mL), and dried under vacuum. The Cp^*RuCl_2 **14** was obtained with 80% yield.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.2 (s).

IR (solution, $CHCl_3$): 2 960, 2 900, 1 720, 1 600, 1 450, 1 370, 1 025 cm^{-1}.

Preparation of [Cp Ru(η^6-phenalene)]PF$_6$* **10** *and* **11** *[10c]*

The $(Cp^*RuCl_2)_n$ complex (612 mg, 2 mmol) and tetrahydrofuran (40 mL) were introduced in a Schlenk tube. The solution underwent three successive freeze-thaw cycles and was placed under argon. Solid zinc (4 g, 61.2 mmol) was then added rapidly. The resulting solution was stirred for 1 h whereupon its color changed to green as expected from the formation of the $(Cp^*RuCl)_4$. After a 1 h reaction time, the solution was filtered. The precipitate was washed with degassed THF (10 mL). The filtrate was always stored under an argon atmosphere. The filtrate, which is the air-sensitive complex $(Cp^*RuCl)_4$, was treated with phenalene **1** (332 mg, 2 mmol) and potassium pentafluoride (1.35 equiv per mmol of phenalene). After 12 h of stirring, the tetrahydrofuran was evaporated under reduced pressure yielding a brown residue. The solid was dissolved in 40 mL dichloromethane, which was washed with 40 mL water. The organic phase was collected, dried with anhydrous magnesium sulfate, and filtered through a celite pad. After evaporation, the crude product was purified using column chromatography on silica with CH_2Cl_2/methanol 99:1 as the eluent. The overall yield of the two isomers **10** and **11** was 50%.

- *Identification of* **10**

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 1.57 (s, 15H), 4.15 (dm, J = 25 Hz, 2H), 5.70 (d, J = 5.9 Hz, 1H), 5.93 (t, J = 5.9 Hz, 1H), 6.31 (d, J = 5.9 Hz, 1H), 6.36 (dt, J = 9.9 and 2.3 Hz, 1H), 6.52 (dt, J = 9.9 and 4.0 Hz, 1H, H_2), 7.29 (dq, J = 8.7 and 1.1 Hz, 1H), 7.48 (dm, J = 6.9 and 0.9 Hz, 1H), 7.60 (dd, J = 8.7 and 6.9 Hz, 1H).

^{13}C NMR (CD_2Cl_2, 100 MHz): δ 9.5, 29.6, 84.8, 86.6, 87.9, 92.4, 93.8, 96.2, 97.2, 125.4, 125.7, 126.5, 128.9, 132.0, 132.6.

IR (solution, CH_2Cl_2): 2 900, 1 465, 1 380, 1 020, 840 cm^{-1}.

Anal calc for $C_{23}H_{23}RuPF_6$ (M = 545.47): C, 50.64; H, 4.25. Found: C, 50.37; H, 4.64.

- *Identification of* **11**

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 1.60 (s, 15H), 3.78 (dd, J = 25.1 and 4.3 Hz, 2H), 5.78 (d, J = 5.7 Hz, 1H), 5.87 (t, J = 5.7 Hz, 1H), 6.22 (m, 2H), 6.67 (dt, J = 10 and 2.1 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.54 (dd, J = 6.8, 8.6 Hz, 1H).

^{13}C NMR (CD_2Cl_2, 100 MHz): δ 9.5, 29.6, 84.8, 86.6, 87.9, 92.4, 93.8, 96.2, 97.2, 125.4, 125.7, 126.5, 128.9, 132.0, 132.6.

IR (solution, CH_2Cl_2): 2 900, 1 465, 1 380, 1 020, 840 cm^{-1}.

Anal calc for $C_{23}H_{23}RuPF_6$ (M = 545.47): C, 50.64; H, 4.25. Found: C, 50.36; H, 4.66.

Preparation of [Cp*Ru(η^6-phenalenone)]PF_6 **9** [10c]

The procedure was the same as that used for the preparation of **10** and **11**, but using the phenalenone **3** (540 mg, 3 mmol). The crude product was purified using column chromatography on silica 230–460 nm with CH_2Cl_2/methanol 90:10 as the eluent. The yield of **9** was 56%.

^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.56 (s, 15H, CH_3), 6.6 (dd, $J_{H_5H_4}$ = 6.0 Hz, $J_{H_5H_6}$ = 6.1 Hz, 1H, H_5), 6.75 (d, $J_{H_4H_5}$ = 6.0 Hz, 1H, H_4), 6.78 (d, $J_{H_2H_3}$ = 10.0 Hz, 1H, H_2), 7.16 (d, $J_{H_6H_5}$ = 6.1 Hz, 1H, H_6), 8.0 (dd, $J_{H_8H_9}$ = 7.0 Hz, $J_{H_8H_7}$ = 8.0 Hz, 1H, H_8), 8.13 (d, $J_{H_7H_8}$ = 8.0 Hz, 1H, H_7), 8.16 (d, $J_{H_3H_2}$ = 10.0 Hz, 1H, H_3), 8.28 (d, $J_{H_9H_8}$ = 7.0 Hz, 1H, H_9).

^{13}C NMR (CD_2Cl_2, 50.3 Mz): δ 9.05 ($5CH_3$), 84.95, 86.58, 88.28, 89.31, 91.47, 94.16, 96.51, 129.41, 129.85, 132.43, 132.84, 135.44, 142.97, 185.35.

IR (solution, CH_2Cl_2): 3 050, 2 900, 1 690, 1 630, 1 375, 1 230, 1 015, 835 cm^{-1}.

Anal calc for $C_{23}H_{23}ORuPF_6$ (M = 561): C, 49.19; H, 4.09; Ru, 18. Found: C, 49.10; H, 4.18; Ru, 22.

Preparation of [Cp*Ru(η^6-phenalane)]PF_6 **12** [10c]

The procedure was the same as that used for the preparation of **10** and **11**, but using the phenalane **16** (168 mg, 1 mmol). The crude product was purified by dissolving the complex in CH_2Cl_2 (4 mL) followed by precipitation with diethyl ether (4 mL). Based on the amount of product precipated the yield of **12** was 80%.

^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.62 (s, 15H, CH_3), 1.95 (dtd, J_{H2axH2eq} = 13.5 Hz, J_{H2axH1ax} = J_{H2axH3ax} = 9.7 Hz, J_{H2axH1eq} = 5 Hz, J_{H2axH3eq} = 4.8 Hz, 1H, H_{2ax}), 2.17 (dtt, J_{H2eqH2ax} = 13.5 Hz, J_{H2eqH3eq} = J_{H2eqH1eq} = 5.5 Hz, J_{H2eqH3ax} = J_{H2eqH1ax} = 4.8 Hz, 1H, H_{2eq}), 2.84 (ddd, J_{H3eqH2ax} = 16.6 Hz, J_{H3eqH2eq} = 5.5 Hz, J_{H3eqH2ax} = 4.8 Hz, 1H, H_{3eq}), 3.01 (dt, J_{H1eqH1ax} = 9.6 Hz, J_{H1eqH2ax} = J_{H1eqH2eq} = 5 Hz, 1H, H_{1eq}), 3.02 (ddd, J_{H1axH1eq} = 9.6 Hz, J_{H1axH2ax} = 9.7 Hz, J_{H1axH2eq} = 4.8 Hz, 1H, H_{1ax}), 3.11 (ddd, J_{H3axH3eq} = 16.6 Hz, J_{H3axH2ax} = 9.7 Hz, J_{H3axH2eq} = 4.8 Hz, 1H, H_{3ax}), 5.81 (d, J = 5.8 Hz, 1H, H_4 or H_6), 5.84 (dd, J = 5.9 and 5.8 Hz, 1H, H_5), 6.24 (d, J = 5.9 Hz, 1H, H_4 or H_6), 7.32 (d, J = 8.7 Hz, 1H, H_7 or H_9), 7.43 (d, J = 6.7 Hz, 1H, H_7 or H_9), 7.59 (dd, J = 8.7 and 6.7 Hz, 1H, H_8).

^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 9.65 (CH_3), 21.56, 28.06, 30.49, 84.87, 87.32, 88.05, 93.56, 95.91, 96.91, 99.13, 125.5, 127.93, 131.26, 137.17.

IR (solid, KBr): 3 439, 3 401, 2 914, 1 620, 1 385, 1 029, 880, 833, 558 cm^{-1}.

Anal calc for $C_{23}H_{27}RuPF_6$ (M = 549.53): C, 50.26; H, 4.95. Found: C, 50.23; H, 4.98.

Preparation of [Cp*Ru(η^6-phenalanone)]PF_6 **13** [10c]

The procedure was the same as that used for the preparation of **10** and **11**, but using the phenalanone **17** (182 mg, 1 mmol). The crude product was purified by dissolving the complex in CH_2Cl_2 (4 mL) followed by precipitation with diethyl ether (4 mL). Based on the amount of product precipitated, the yield of **13** was 90%.

^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.62 (s, 15H, CH_3), 2.81 (ddd, J_{H2aH2b} = 16.2 Hz, J_{H2aH3b} = 9.5 Hz, J_{H2aH3a} = 6.3 Hz, 1H, H_{2a}), 3.06 (ddd, J_{H2bH2a} = 16.2 Hz, J_{H2bH3b} = 6.35 Hz, J_{H2bH3a} = 6.25 Hz, 1H, H_{2b}), 3.2 (ddd, J_{H3aH3b} = 16.8 Hz, J_{H3aH2a} = 6.35 Hz, J_{H3aH2b} = 6.25 Hz, 1H, H_{3a}), 3.46 (ddd, J_{H3bH3a} = 16.8 Hz, J_{H3bH2a} = 9.5 Hz, J_{H3bH2b} = 6.3 Hz, 1H, H_{3b}), 6.02 (d, 2H), 6.46 (d, J = 5 Hz, 1H), 7.81 (d, $J_{H_9H_8}$ = $J_{H_9H_7}$ = 4 Hz, 2H, H_9, H_7), 8.32 (dd, $J_{H_8H_7}$ = $J_{H_8H_9}$ = 4 Hz, 1H, H_8).

^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 9.81 (CH_3), 25.62 (C_2), 37.34 (C_3), 85.33, 88.17, 88.49, 94.69, 95.6, 96.03, 96.46, 130.03, 130.75, 131.13, 134.68, 193.73 (C_1).

IR (solid, KBr): 1 696, 1 616, 1 525, 1 447, 1 441, 1 422, 1 367, 1 280, 1 256, 1 250, 1 222, 1 127, 1 629, 893, 554 cm^{-1}.

Anal calc for $C_{23}H_{25}ORuPF_6$ (M = 563.474): C, 49.02; H, 4.47; Ru, 18. Found: C, 49.01; H, 4.45; Ru, 22.

Reactivity of [Cp*Ru(η^6-phenalene)]PF_6 **10**

A solution containing **10** (10^{-4} M) in CH_2Cl_2 was placed in a quartz cuvette. The solution was irradiated using a ultraviolet lamp (λ = 254 nm). The ultraviolet spectrum was run from 200–900 nm every 5 min for 1 h and remained unchanged.

Reactivity of [Cp*Ru(η^6-phenalenone)]PF_6 **9**, *with 2-methylindole*

[Cp*Ru(η^6-phenalenone)]PF_6 **9** (561 mg, 1 mmol), 2-methylindole (131 mg, 1 mmol), *para*-toluenesulfonic acid (172 mg, 1 mmol) and methylene chloride (30 mL) were mixed in a one-necked round-bottomed flask and reacted for 36 h without any precautions to protect the reaction from daylight. The reaction was quenched with a saturated solution of $NaHCO_3$ (30 mL), followed by a saturated solution of NaCl (30 mL). The aqueous phase was extracted with methylene chloride (3 × 20 mL). The organic phases were collected, dried with anhydrous sodium sulfate, filtered through a celite pad and evaporated under reduced pressure to yield an oil (800 mg). The crude product was purified using column chromatography on silica with CH_2Cl_2/MeOH 95:5 as the eluent (yield of 42% (230 mg, 0.417 mmol)). The spectral data show that the phenalenone ligand remains unchanged.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.50 (s, 15H), 2.34 (s, 3H), 6.55 (bs, 2H), 6.70 (d, $J = 10$ Hz, 1H), 7.12 (d, $J = 9.0$ Hz, 2H), 7.45 (s, 1H), 7.78 (d, $J = 9.0$ Hz, 2H), 7.82 (d, $J = 8.5$, 7.5 Hz, 1H), 7.95 (d, $J = 9.5$ Hz, 1H), 8.10 (d, $J = 7.1$ Hz, 1H), 8.18 (d, $J = 8.5$ Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 9.6, 21.4, 83.7, 85.0 , 91.8, 92.8, 95.7, 98.2, 126.4, 127.8, 128.2, 128.6, 131.4, 133.2, 135.0, 139.3, 142.1, 144.3, 185.0.

IR (solution, CH_2Cl_2): 3 340, 1 635, 1 380, 1 185, 1 110, 1 025, 1 010 cm^{-1}.

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