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Ruthenium complexes of sterically-hindered pentaarylcyclopentadienyl ligands†

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The synthesis of ruthenium complexes incorporating an overcrowded pentaarylcyclopentadienyl ligand has been investigated, and higher efficiency has been reached using chlorine-functionalised precursors when compared with their brominated counterparts. A new methodology for the preparation of chlorocyclopentadienes has been developed which is well adapted for highly sterically hindered compounds and works with either electron rich or poor systems.

Introduction

A molecular-level machine can be defined as a molecule or an assembly of molecular components designed to perform precise functions in response to controlled stimulation. Driven by the seminal works of Sauvage, Stoddart and Feringa, the field of artificial molecular machines[1] has developed significantly over the last few decades with the many types of machines prepared revolutionising the way chemists think about motional molecular systems. Remarkable synthetic masterpieces have opened the door to new dimensions of chemistry with the control of motion at the molecular level moving from a static to a dynamic view where animated objects take the place of immobile structures.

Coordination chemistry is a very versatile and efficient way to assemble mechanical subunits, allowing for the production of a large and diverse range of molecular machines. Many ligands are available and a vast number of metal centres can be chosen to vary and complexify molecular architectures.[2] In this field the pentaphenylcyclopentadienyl anion is a common and useful ligand, with functionalised analogues already applied as rotors in various molecular machines[3] including molecular motors[4] and gears.[5] Interest in this ligand started as a result of the availability of pentaphenylcyclopentadiene precursors which can be readily synthesised in large quantities and are air stable. Such hindered ligands are also more electron-withdrawing than their cyclopentadienyl and pentamethylcyclopentadienyl anionic analogues and their large volume is reported to confer enhanced kinetic stability towards organometallic derivatives.[6] Interestingly, the reactivity pathways of pentaarylcyclopenta-dienyl ligands (Cp^{5Ar}) seems to vary significantly when compared to cyclopentadiene (Cp) and pentamethylcyclopentadiene, due to both differences in the steric hindrance at the Cp ring and the electronic contributions from the metal-Cp coordination. These propeller shaped ligands are capable of conferring novel steric and electronic properties to metal centres[7] and can also be deposited on metal surfaces chirally, with both left- and right-handed propeller chirality being represented and recognised.[4c] In such case, a pentaphenylcyclopentadienyl ligand functionalised with bromine atoms in the five *para* positions is exploited both as an anchoring subunit and as a chiral surface, contributing to the unidirectionality in the movement of the upper rotating units. Unique properties also arise from a combination of electronic effects and the steric hindrance provided by the five phenyl substituents, including protection of the metallic centre and influence on the electron releasing ability of the complex. It has also been shown that coordination of the peripheral phenyl rings can occur in place of the central cyclopentadienyl one,[8] giving rise to highly dissymmetric compounds.

Among the available metals, ruthenium offers a very interesting target for preparing stable and inert heteroleptic complexes, however the coordination of ruthenium to highly sterically constrained ligands is not an easy task. Many previous attempts to directly coordinate pentaarylcyclopentadienyl (Cp^{5Ar}) ligands from $RuCl_3$ (ref. 9) or $[Ru(p\text{-cymene})Cl_2]_2$ (ref. 10) failed, mainly due to the steric hindrance of the phenyl groups on the Cp ligand. As an alternative, the triruthenium dodecacarbonyl cluster $Ru_3(CO)_{12}$ is recognised as a reliable source of ruthenium(0) for the preparation of halogenodicarbonyl(η^5-1,2,3,4,5-pentaaryl)cyclopentadienyl ruthenium(II) complexes $Cp^{5Ar}Ru(CO)_2X$. Indeed, in 1989 Manners reported the synthesis of $Cp^{5Ph}Ru(CO)_2Br$ starting from $Ru_3(CO)_{12}$ and 5-bromo-1,2,3,4,5-pentaphenylcyclopenta-1,3-diene in refluxing toluene

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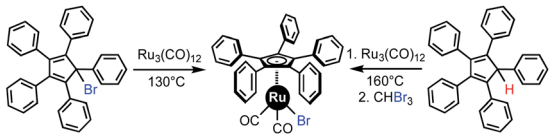


Scheme 1 Coordination of ruthenium to the pentaphenylcyclopentadiene ligand by previously published procedures.[11,14]

(Scheme 1, left).[11] This reaction proceeds *via* the formal oxidative addition of the brominated cyclopentadiene precursor onto ruthenium(0) and involves a transient cyclopentadienyl radical intermediate. In the last decades, the scope of this reaction has been expanded to include a variety of *para*-substituted pentaphenylcyclopentadienes, as precursors of ruthenium-based molecular machines.[12] In addition, the analogous chlororuthenium complex $Cp^{5Ph}Ru(CO)_2Cl$ has been successfully prepared from the corresponding chlorocyclopentadiene and exploited as a catalyst for the dynamic kinetic resolution of secondary alcohols.[13] To avoid preparation of potentially unstable halogenocyclopentadienes, new conditions for the synthesis of this family of complexes were developed by Martin-Matute *et al.*, involving the direct oxidative addition of bare pentaphenylcyclopentadiene $Cp^{5Ph}H$ onto $Ru_3(CO)_{12}$.[14a] However this reaction only proceeds under very harsh conditions (160 °C for several days in a decane/toluene mixture) giving the corresponding ruthenium hydride intermediate, which finally yields $Cp^{5Ph}Ru(CO)_2X$ (X = I, Br, Cl) after treatment with the appropriate haloform (Scheme 1, right). Even though some variations in aryl groups have been achieved,[14] the relatively high temperatures required has limited the use of this process when cyclopentadienyl ligands bearing sensitive substituents are involved.

In our efforts towards the development of photo-controlled molecular machines, we aimed to introduce a terarylene photochrome on the cyclopentadienyl rotating subunit of a ruthenium complex.[15] Given the synthetic cost and sensitivity of the terarylene moiety, the direct oxidative addition of the cyclopentadiene precursor $Cp^{5Ar}H$ was ruled out and we instead turned our attention to Manners' method, starting from the bromocyclopentadiene carrying four phenyl groups and a terarylene fragment (Scheme 2). Strikingly, its reaction with $Ru_3(CO)_{12}$ was inoperative due to decomposition of the bromine precursor *via* radical side-reactions, preventing formation of the desired ruthenium complex. To understand the influence of the substituents located on the cyclopentadiene ring on this complexation reaction, we decided to investigate the reactivity of a series of brominated tetraphenylcyclopentadienes bearing one aryl group with particular electronic and/or steric properties. As an alternative, the chlorinated analogues were also prepared and their reactivity studied.

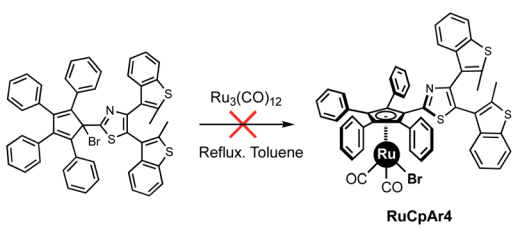
Here we report the preparation of a series of ruthenium pentaarylcyclopentadienyl complexes *via* halogen containing intermediates, in good to excellent yields even with very crowded Cp ligands such as mesityl or terarylenyl substituents.

Results and discussion

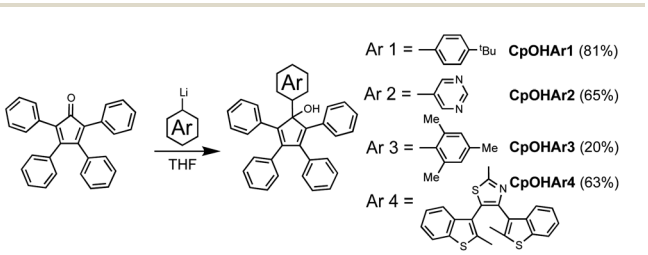
For this study, we selected four aryl-functionalised tetraphenyl Cp ligands (Scheme 3). The first two to serve as representative model compounds, without significant steric hindrance, but instead having opposite electronic effects to each other. Here, the electron donating 4-*tert*-butylphenyl (**Ar1**) and the electron accepting 5-pyrimidyl (**Ar2**) aryl moieties were chosen as they have similar steric volume to the phenyl groups already present on the Cp. Two further aryl fragments were selected to study more sterically overcrowded substituents; a mesityl model (**Ar3**) offering a similar electronic effect to the 4-*tert*-butylphenyl group, and the sterically demanding terarylene already discussed (**Ar4**), which acts as a strong electron acceptor due to the thiazole ring at the point of connection to the Cp ring. This group has previously been used by our group as a photoactive brake subunit to hinder the rotation of a molecular motor with the rotational braking observed using both NMR and UV/Visible analysis.[15]

Synthesis of the aryl-functionalised cyclopentadienol precursors

Reaction of 2,3,4,5-tetraphenylcyclopentadienone with organolithium or organomagnesium aryl derivatives, is known to be a very efficient route to pentaarylcyclopentadienols.[7c,7d,16] In a typical reaction, the 2,3,4,5-tetraphenylcyclopentadienone was treated with the appropriate aryllithium reagent in tetrahydrofuran at −78 °C (Scheme 3). The corresponding pentaarylcyclopentadienols **CpOHAr1**,[16b] **CpOHAr2**, **CpOHAr3**,[7d] and **CpOHAr4** (ref. 15) were isolated in moderate to good yields, from 20% in the case of the mesityl derivative (**CpOHAr3**) to 81% for the *tert*-butyl precursor (**CpOHAr1**). As expected, this step is strongly affected by the steric hindrance close to the lithium centre. For reactants of similar steric effect (**CpOHAr1**



Scheme 2 Photochrome-functionalised tetraphenylcyclopentadiene brominated precursor unable to coordinate to ruthenium *via* reaction with $Ru_3(CO)_{12}$.



Scheme 3 Synthetic pathway to form the functionalised cyclopentadienol precursors.

or **CpOHAr2**), the more electron-rich derivative gave better addition yield.

Activation of the Cp ring by halogenation

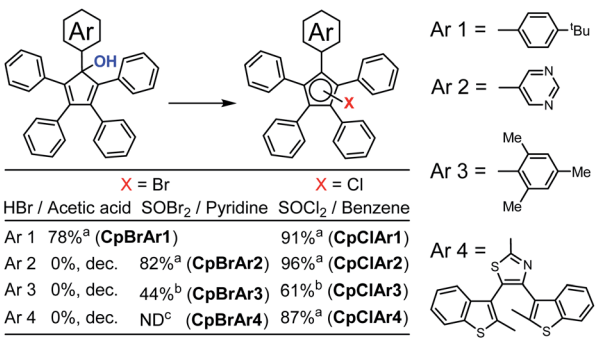
For pentaphenycyclopentadienols, it is well known[11,12] that conversion to the halogen derivative is required prior to ruthenium coordination.[17] The cyclopentadienol is generally converted to its brominated analogue by reaction with HBr in acetic acid.[18] In the case of our electron rich model compound functionalised with a 4-*tert*-butylphenyl fragment, the brominated Cp ring (**CpBrAr1**) was obtained using HBr in 78% yield (Scheme 4).[16b] This reaction is highly sensitive to electronic effects with the electron poor 5-pyrimidyl precursor giving no brominated product. This can be explained by protonation of the nitrogen centres of the heterocycle under acidic conditions, making this fragment highly electron poor and dramatically impacting on the reactivity of the cyclopentadienol.

The same reaction conditions applied to the two sterically-hindered Cp ring containing molecules **CpOHAr3** and **CpOHAr4** were also found to be ineffective. We noticed that using HBr in acetic acid, led to the decomposition of the compounds with no starting material detected. This may be due to the instability of the brominated Cp's generated and/or because an electron accepting group destabilises the cation, not allowing for the elimination of the oxonium ion generated under acidic conditions.

To overcome this lack of reactivity towards acidic bromination, J.-Y. Thépot and Lapinte reported the conversion of cyclopentadienol derivatives to their brominated analogues using a $SOBr_2$–pyridine mixture instead of HBr in acetic acid.[7d] Since the mechanism of halogenation is different in the case of SOX_2 compared to HX (X = Cl or Br), different results could be expected, especially as the sulfur-containing by-products further decompose to volatile SO_2 gas rendering the process irreversible (Scheme 5). As shown on Scheme 4, the $SOBr_2$–pyridine reagents allowed the conversion of the electron deficient cyclopentadienol **CpOHAr2** to its bromo derivative in 82% yield and the sterically-hindered bromocyclopentadiene carrying a mesityl substituent **CpBrAr3** was prepared in 44% yield. Interestingly for the attempted reaction of **CpOHAr4** with thionyl bromide, the desired **CpBrAr4** product was obtained as an inseparable mixture with its chlorinated counterpart **CpClAr4** and the hydrogenated analogue **CpHAr4**. This side-reactivity likely results from the washing of the reaction mixture during workup with dilute aqueous HCl,[7d] and highlights the increased stability of the chlorinated cyclopentadiene **CpClAr4** as compared to its brominated analogue.

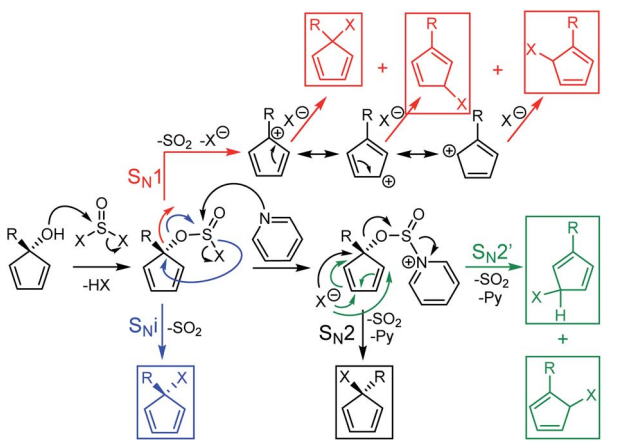
In the case of SOX_2 with or without pyridine, the envisioned mechanisms will be a competitive mixture of S_N1, S_Ni, S_N2 and S_N2' processes depending on the substrate, the solvent and the presence of pyridine (Scheme 5). As with the HBr reaction, the S_N1 mechanism gives a mixture of three regioisomers (in red) while the S_Ni pathway (in blue) gives only one and the S_N2 gives one direct compound (in black) along with two others *via* a S_N2' variation (in green). In consequence a 66 : 30 : 4 ratio of regioisomers was obtained for **CpBrAr2**, as determined by integrating the three sets of pyrimidyl protons signals on the ^1H NMR spectrum (Fig. S3†). In the case of the mesityl-containing **CpBrAr3**, only one regioisomer has been obtained with or without pyridine, in agreement with the results obtained by Thépot and Lapinte.[7d] In this case, the bromine atom is located at the 3-position of the Cp ring related to the mesityl moiety, *i.e.* on the less sterically hindered position. This indicates that the S_N1 mechanism might not be followed for this substrate.

Given the higher stability of chloro- *vs.* bromocyclopentadiene observed with **CpBrAr4**, we next explored the possibility of selectively forming the chlorinated derivatives of the sterically-hindered cyclopentadienol rings using a $SOCl_2$–pyridine system in diethyl ether.[19] The reaction proceeded smoothly with the chloride derivative of the terarylene (**CpClAr4**) obtained with a yield of 74%. The pyridine is generally used with thionyl



HBr / Acetic acid	$SOBr_2$ / Pyridine	$SOCl_2$ / Benzene
Ar 1 78%[a] (**CpBrAr1**)		91%[a] (**CpClAr1**)
Ar 2 0%, dec.	82%[a] (**CpBrAr2**)	96%[a] (**CpClAr2**)
Ar 3 0%, dec.	44%[b] (**CpBrAr3**)	61%[b] (**CpClAr3**)
Ar 4 0%, dec.	ND[c] (**CpBrAr4**)	87%[a] (**CpClAr4**)

Scheme 4 Synthetic pathway to form the brominated and chlorinated derivatives. [a]The product is obtained as a mixture of three regioisomers, with the halogen (X) in Cp position 1, 2 or 3 relative to the Ar moiety. [b]The product is obtained as a single regioisomer, with the halogen (X) in Cp position 3 relative to the Ar moiety. [c]The yield could not be determined as the product was obtained as an inseparable mixture of chlorinated and hydrogenated analogues.



Scheme 5 Mechanisms involved in the halogenation of secondary alcohols by SOX_2 (X = Cl or Br) with and without pyridine. S_N1 mechanism gives access to three regioisomers (in red) while S_Ni gives only one (in blue). When pyridine is used, a S_N2 pathway is followed, giving access to one regioisomer (in black) plus two others *via* S_N2' variations (in green). A monosubstituted cyclopentadienol instead of a pentasubstituted one has been considered for clarity.

chloride or bromide for the halogenation of secondary alcohols *via* a S_N2-type mechanism, whereas if pyridine is not used, an intramolecular S_Ni mechanism can also take place. In the case of the sterically constrained precursors, the S_N2 mechanism is kinetically difficult because of the low access available to the carbon atom. This is the reason why we next tested the reaction without pyridine. Reaction of the cyclopentadienol derivatives with $SOCl_2$ in benzene proceeded well in all cases, presumably *via* a S_N1 or S_Ni nucleophilic substitution mechanisms,[20] with yields from 61% for the highly sterically constrained mesityl derivative (**CpClAr3**) to 87, 91 and 96% for compounds **CpClAr4**,[15] **CpClAr1** and **CpClAr2** respectively. This method is very well adapted for highly sterically hindered compounds and is working very well for both electron rich and poor systems.

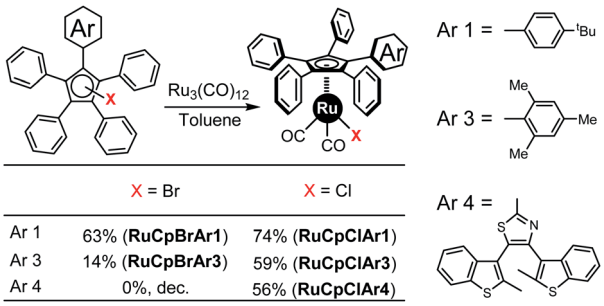
CpClAr1 was obtained as a mixture of three regioisomers with the chlorine atom at three possible positions of the Cp ring due to the S_N1 mechanism (Scheme 5, red products). Their respective proportion can be quantified by ^{1}H-NMR, using the equivalent methyl groups of the *tert*-butyl substituent as a probe. Three singlets were obtained (Fig. S5†), corresponding to the three regioisomers, with a 46 : 34 : 20 ratio which slightly differs from the statistical mixture of 40 : 40 : 20 expected from a S_N1 mechanism, due to the varying stabilities of the carbocations involved as a result of the presence of the *tert*-butylphenyl donor substituent. A 57 : 37 : 6 ratio of regioisomers has been obtained for **CpClAr2** (Fig. S7†). In the case of **CpClAr4**, it has not been possible to determine a ratio as the methyl signals are usually very broad in such terarylene fragments and no other region of the spectrum could be exploited for this purpose. However, the presence of these mixtures of regioisomers is not an issue as in the next step the aromatisation of the Cp ring through η^5-coordination to the ruthenium centre leads to the same single cyclopentadienide complex in all cases.

In the case of the sterically crowded, electron donating, mesityl substituent **CpClAr3** (Fig. S9†) one single regioisomer is obtained as for the brominated analogue. The ^{1}H NMR spectrum also shows that rotation of the mesityl moiety is blocked, as evidenced by the non-equivalence of the aromatic and methyl protons located on this bulky group.

Coordination to the ruthenium

Next, coordination to ruthenium using the triruthenium dodecacarbonyl cluster in toluene was attempted for each of the halogenated derivatives. For **CpBrAr2** and **CpClAr2** this led apparently to the formation of polynuclear metal complexes through the nitrogens on the 5-pyrimidyl ring, so they were discounted. For the other six systems this was found to yield, after purification by column chromatography, the corresponding cyclopentadienylruthenium(II) complexes **[RuCpArBr(CO)$_2$]** or **[RuCpArCl(CO)$_2$]** (Scheme 6, complexes are named as **RuCpXAr**).

In the case of precursors **CpXAr1**, the reaction yields are similar whichever halogen derivative is present (63 and 74% for Br and Cl respectively) but surprisingly for the sterically overcrowded Cp systems the chlorinated precursors gave



	X = Br	X = Cl
Ar 1	63% (**RuCpBrAr1**)	74% (**RuCpClAr1**)
Ar 3	14% (**RuCpBrAr3**)	59% (**RuCpClAr3**)
Ar 4	0%, dec.	56% (**RuCpClAr4**)

Scheme 6 Formation of the ruthenium complexes from bromo or chloro precursors (**Ar2** is not suitable for ruthenium complexation due to multiple coordination sites available which might give many polynuclear complexes as well as coordination polymers of various size).

significantly improved yields over the brominated ones, with 59% obtained in the case of the mesityl-functionalised tetraphenylcyclopentadiene **CpClAr3** compared to 14% for **CpBrAr3**. In the case of the electron poor terarylene-functionalised cyclopentadienyl ligand, the ruthenium complex has been obtained with a yield of 56% (ref. 15) from the chlorinated precursor **CpClAr4**, while it is inaccessible using its brominated analogue. Despite both the changes in halogen atom present and the varying steric effects of the Ar groups the electronic character of these complexes remains largely the same as reflected in the similar CO stretches in their IR spectra. It appears that the use of a chloride instead of a bromide offers a new pathway for the preparation of novel cyclopentadienylruthenium complexes in cases where the steric hindrance around the Cp ligand is large. The use of chlorine-functionalised pentaarylcyclopentadienyl precursors, similar to those developed here opens up a new synthetic route for the preparation of molecular motors containing sterically hindered pentaarylcyclopentadienyl ligands.

As a representative example of this pathway, exploiting this new synthetic methodology we recently reported the use of these chlorinated derivatives in the preparation of a photochromic molecular motor containing the terarylene unit **Ar4**. This was achieved using **CpClAr4** and $Ru_3(CO)_{12}$ in conjunction with our previously reported tris[(ethylsulfanyl)methyl]indazolylborate surface anchor to give a new ruthenium based molecular motor.[15]

Conclusions

In this work investigations into the preparation of halogen pentaarylcyclopentadienyl ligands as intermediates for ruthenium containing molecular motors have been carried out. The effect of changes in sterics and electronics on one of the five rings on the cyclopentadiene ligand have been investigated for a series of four model compounds. A new methodology for the preparation of chlorine functionalised intermediates has been developed which is well adapted for highly sterically hindered compounds and works with either electron rich or poor systems. It has been used for the preparation of new functionalised tetraphenyl cyclopentadiene complexes in yields well beyond those previously reported for similar highly sterically

hindered molecular motors. This methodology has already been used successfully for the synthesis of a photo-controlled molecular motor functionalized with a terarylene photochrome on the cyclopentadienyl rotating subunit.[15]

Experimental

Materials and methods

All commercially available chemicals were of reagent grade and were used without further purification. Anhydrous tetrahydrofuran, anhydrous toluene, anhydrous diethyl ether, magnesium sulfate, HCl, ammonium chloride, *n*-butyllithium (2.5 M in hexanes), 5-bromopyrimidine and 2,3,4,5-tetraphenylcyclopenta-2,4-dienone were purchased from Aldrich. Triruthenium dodecacarbonyl was purchased from Acros or Fluorochem. Benzene was purchased from Fluka. Thionyl chloride and thionyl bromide were purchased from Wako or Aldrich. **CpOHAr1**,[16b] **CpBrAr1**,[16b] **CpOHAr3**,[7d] **CpBrAr3**,[7d] **CpOHAr4**,[15] **CpClAr4**,[15] **RuCpClAr4** (ref. 15) were prepared according to the corresponding published procedures. Reactions were carried out using standard Schlenk techniques under an argon atmosphere. Thin layer chromatography (TLC) was performed on pre-coated aluminium-backed silica gel 60 UV_{254} plates (Macherey-Nagel) with visualisation effected with ultraviolet irradiation (λ = 254, 366 nm). Flash column chromatography was carried out on 230–400 mesh silica gel (Aldrich) unless otherwise stated. NMR spectra were recorded with a Bruker Avance 300, a Bruker Avance 500 or a JEOL JNM-ECA600 spectrometer and assignments were made with the assistance of COSY, HMBC and HSQC spectra when necessary. ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in ppm relative to the signal of tetramethylsilane (TMS). Residual solvent signals were used as an internal reference. Coupling constants (J) are given in Hz and the following abbreviations have been used to describe the signals: singlet (s); doublet (d); triplet (t); multiplet (m). The numbering system used for the assignment of signals in some compounds is provided in the ESI,† along with the spectra of new compounds. IR spectra were recorded with a Jasco 4200 FTIR-ATR. Only selected characteristic peaks are listed. High-resolution mass spectra (HRMS) were performed with a Waters GCT Premier spectrometer (DCI), with a Waters Xevo G2 QTof spectrometer (ESI) and a JEOL JMS-Q1000TD spectrometer with JMS-700 Mstation (MALDI). Elemental analyses have been measured on a Perkin Elmer 2400 Series II CHNS/O system. Melting points were measured using a Krüss M5000 melting point meter or a MEL-TEMP capillary melting point apparatus. Melting points were not reported for compounds obtained as a mixture of regioisomers.

2,3,4,5-Tetraphenyl-1-(pyrimidin-5′-yl)-cyclopenta-2,4-dien-1-ol (CpOHAr2)

5-Bromopyrimidine (620 mg, 3.9 mmol, 1.5 eq.) was placed in a Schlenk flask with a stir bar, and anhydrous tetrahydrofuran (10 mL) was added. The solution was quickly degassed by bubbling argon and cooled down to −78 °C. Then, a 2.5 M solution of *n*-butyllithium in hexanes (2 mL, 5.2 mmol, 2 eq.) was added dropwise while carefully maintaining the temperature. The suspension was stirred for 30 minutes at this temperature and a degassed solution of 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (1 g, 2.6 mmol, 1 eq.) in 30 mL of anhydrous tetrahydrofuran was added dropwise *via* a cannula. The reaction was stirred for two hours at −78 °C before being neutralised by pouring it slowly into 20 mL of a saturated aqueous ammonium chloride solution. The crude product was then extracted with diethyl ether, washed three times with water and once with brine. The organic layer was dried over magnesium sulfate and the solvents were removed under vacuum. The crude product was adsorbed onto SiO_2 and purified by a quick column chromatography on SiO_2, eluting impurities with dichloromethane followed by pure ethyl acetate to collect the product. Solvents were evaporated to afford a yellow solid, still contaminated with impurities. This solid was then recrystallised from a minimal amount of boiling chloroform, to give **CpOHAr2** as a clear white solid in a 65% yield (780 mg, 1.7 mmol).

R_f = 0.4 (SiO_2, ethyl acetate/hexane 3 : 7); mp 233 °C; ^{1}H NMR (300 MHz, $(CD_3)_2SO$, 25 °C): δ 8.98 (s, 1H, H_a), 8.81 (s, 2H, H_b), 7.22–7.14 (m, 6H, H_{Ph}), 7.12–6.95 (m, 14H, H_{Ph}), 6.87 (s, 1H, OH); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25 °C): δ 168.4 (C_a), 168.4 (C_b), 161.3 (C_{quat}), 157.0 (C_{quat}), 149.3 (C_{quat}), 149.2 (C_{quat}), 148.0 (C_{quat}), 143.8 (C_{Ph}–H), 143.3 (C_{Ph}–H), 142.4 (C_{Ph}–H), 142.1 (C_{Ph}–H), 141.7 (C_{Ph}–H), 141.4 (C_{Ph}–H), 101.5 (C_{quat}–OH); HR-MS (DCI-CH_4): calcd for $C_{34}H_{24}N_2O$ $[MH]^+$: 465.1940, found 465.1960; and calcd for $C_{33}H_{23}N_2O$ $[M]^+$: 464.1889, found 464.1881.

5-Bromo-1,2,3,4-tetraphenyl-5-(pyrimidin-5′-yl)cyclopenta-1,3-diene (CpBrAr2)

Obtained as a 66 : 30 : 4 mixture of 3 regioisomers.

2,3,4,5-Tetraphenyl-1-(pyrimidin-5′-yl)cyclopenta-2,4-dien-1-ol **CpOHAr2** (200 mg, 0.43 mmol, 1 eq.) was placed in a Schlenk tube containing a magnetic stir bar and anhydrous diethyl ether (10 mL) and freshly distilled pyridine (44 μL, 0.54 mmol, 1.25 eq.) were added. The mixture was cooled down to −10 °C and thionyl bromide (42 μL, 0.54 mmol, 1.25 eq.) was added. The medium was then allowed to warm up to room temperature over one hour, under stirring. It was then neutralised by adding it slowly to 20 mL of a 1 M aqueous hydrochloric acid solution. The product was extracted with ethyl acetate (150 mL) and washed three times with water (3 × 150 mL). The organic layer was dried over magnesium sulfate and the solvents were removed by rotary evaporation. The crude product was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane 1 : 9) to afford the desired brominated product. Nevertheless, traces of impurities were still observed in some batches, so the product was further recrystallised from boiling heptane and rinsed with ice-cold pentane to give **CpBrAr2** in 82% yield (187 mg, 0.36 mmol) as a yellow solid composed of a 66 : 30 : 4 mixture of regioisomers.

R_f = 0.41 (SiO_2, ethyl acetate/hexane 3 : 7); elemental analysis: found: C, 75.0; H, 4.18; N, 5.26. Calc. for $C_{33}H_{23}BrN_2$: C, 75.14; H, 4.40; N, 5.31; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C,

66 : 30 : 4 mixture of regioisomers): δ 9.05 (s, 0.04H, Ha_{regio3}), 8.91 (s, 0.30H, Ha_{regio2}), 8.86 (s, 0.66H, Ha_{regio1}), 8.78 (s, 0.08H, Hb_{regio3}), 8.27 (s, 1.32H, Hb_{regio1}), 8.24 (s, 0.60H, Hb_{regio2}), 7.55–7.46 (m, 2H, H_{Ph}), 7.36–6.84 (m, 18H, H_{Ph}); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C, 66 : 30 : 4 mixture of regioisomers): δ 157.6 (C_{pyr}–H), 157.3 (C_{pyr}–H), 157.2 (C_{pyr}–H), 156.4 (C_{pyr}–H), 150.2 (C_{quat}), 145.5 (C_{quat}), 142.4 (C_{quat}), 142.2 (C_{quat}), 134.9 (C_{quat}), 134.8 (C_{quat}), 134.5 (C_{quat}), 134.4 (C_{quat}), 134.0 (C_{quat}), 133.9 (C_{quat}), 133.5 (C_{quat}), 131.1 (C_{Ph}–H), 130.9 (C_{Ph}–H), 130.7 (C_{Ph}–H), 130.6 (C_{Ph}–H), 130.3 (C_{Ph}–H), 130.1 (C_{Ph}–H), 129.3 (C_{Ph}–H), 129.0 (C_{Ph}–H), 128.9 (C_{Ph}–H), 128.7 (C_{Ph}–H), 128.5 (C_{Ph}–H), 128.4 (C_{Ph}–H), 128.3 (C_{Ph}–H), 128.1 (C_{Ph}–H), 128.0 (C_{Ph}–H), 127.9 (C_{Ph}–H), 127.7 (C_{Ph}–H), 75.9 (C_{quat}–Br); HR-MS (ESI^+): calcd for $C_{33}H_{24}BrN_2$ $[MH]^+$: 529.1108, found 529.1114.

2-(1-Bromo-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-yl)-4,5-bis(2-methylbenzo[*b*]thiophen-3-yl)thiazole (CpBrAr4)

1-(4,5-Bis(2-methylbenzo[*b*]thiophen-3-yl)thiazol-2-yl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol **CpOHAr4** (100 mg, 0.13 mmol, 1 eq.) was placed in a Schlenk tube containing a magnetic stir bar and anhydrous diethyl ether (10 mL) and freshly distilled pyridine (61 µL, 0.79 mmol, 6.0 eq.) were added. The mixture was cooled down to −10 °C and thionyl bromide (64 µL, 0.79 mmol, 6.0 eq.) was added. The medium was then allowed to warm up to room temperature over two hours, under stirring. It was then neutralised by adding it slowly to 1 mL of a 1 M aqueous hydrochloric acid solution. The product was extracted with diethyl ether (100 mL) and washed with three times water (3 × 100 mL). The organic layer was dried over magnesium sulfate and the solvents were removed by rotary evaporation. The crude mixture was purified by column chromatography (SiO_2, dichloromethane/hexane 1 : 4) to give the brominated product **CpBrAr4** along with its chlorinated counterpart **CpClAr4** (ref. 15) and the hydrogenated product **CpHAr4** as an inseparable mixture (40 mg). Each of these products is present as a mixture three regioisomers and the structures of all products are very similar, therefore it was not possible to provide a proper NMR characterization of **CpBrAr4**.

$R_f = 0.8$ (SiO_2, dichloromethane/hexane 1 : 4); MS (DCI-NH_3) of the mixture of products: *m/z* 826 (**CpBrAr4**, $[M + H]^+$, 9%), 780 (**CpClAr4**, $[M + H]^+$, 100), 746 (**CpHAr4**, $[M + H]^+$, 52).

5-[4-(*tert*-Butyl)phenyl]-5-chloro-1,2,3,4-tetraphenylcyclopenta-1,3-diene (CpClAr1)

Obtained as a 46 : 34 : 20 mixture of 3 regioisomers.

1-(4-(*tert*-Butyl)phenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol **CpOHAr1** (100 mg, 0.19 mmol, 1 eq.) was placed in a Schlenk tube containing a magnetic stir bar. Benzene (2 mL) and thionyl chloride (84 µL, 1.16 mmol, 6 eq.) were added and the suspension was refluxed using a preheated oil bath for 30 minutes. The reaction medium was then cooled down, diluted with diethyl ether (20 mL) and washed with a saturated aqueous solution of sodium hydrogen carbonate (20 mL) followed by distilled water (2 × 20 mL). The organic layer was dried with magnesium sulfate and the solvent was then removed using rotary evaporation. The crude product was purified by column chromatography (SiO_2, dichloromethane/hexane 1 : 1) to give pure product **CpClAr1** in 91% yield (94 mg, 0.18 mmol) as a pale-orange solid composed of a 46 : 34 : 20 mixture of regioisomers.

$R_f = 0.8$ (SiO_2, dichloromethane/hexane 1 : 1); ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, 46 : 34 : 20 mixture of regioisomers) δ 7.48–7.34 (m, 2H, H_{Ar}), 7.25–6.78 (m, 22H, H_{Ar}), 1.22 (s, 1.84H, $H_{tBu,regio3}$), 1.15 (s, 2.97H, $H_{tBu,regio2}$), 1.11 (s, 4.04H, $H_{tBu,regio1}$); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C, 46 : 34 : 20 mixture of regioisomers) δ 151.5 (C_{quat}–*t*Bu), 150.8 (C_{quat}–*t*Bu), 150.5 (C_{quat}–*t*Bu), 148.4 (C_{quat}), 148.3 (C_{quat}), 147.9 (C_{quat}), 147.6 (C_{quat}), 143.4 (C_{quat}), 143.2 (C_{quat}), 143.1 (C_{quat}), 143.0 (C_{quat}), 136.8 (C_{quat}), 136.5 (C_{quat}), 135.5 (C_{quat}), 135.1 (C_{quat}), 135.0 (C_{quat}), 134.5 (C_{quat}), 134.3 (C_{quat}), 133.1 (C_{quat}), 131.8 (C_{quat}), 130.9 (C_{quat}), 130.6 (C_{Ph}–H), 130.5 (C_{Ph}–H), 130.3 (C_{Ph}–H), 130.2 (C_{Ph}–H), 129.9 (C_{Ph}–H), 129.8 (C_{Ph}–H), 128.9 (C_{Ph}–H), 128.3 (C_{Ph}–H), 128.1 (C_{Ph}–H), 128.0 (C_{Ph}–H), 127.8 (C_{Ph}–H), 127.6 (C_{Ph}–H), 127.5 (C_{Ph}–H), 126.7 (C_{Ph}–H), 126.6 (C_{Ph}–H), 126.4 (C_{Ph}–H), 125.8 (C_{Ph}–H), 125.0 (C_{Ph}–H), 124.8 (C_{Ph}–H), 82.4 (C_{quat}–Cl), 82.3 (C_{quat}–Cl), 82.2 (C_{quat}–Cl), 34.8 (C_{tBu}), 34.7 (C_{tBu}), 31.4 (C_{tBu}), 31.3 (C_{tBu}), 31.2 (C_{tBu}).; HR-MS (spiral-TOF) signal: calcd for $C_{39}H_{33}Cl$ $[M]^+$: 536.2265, found. 536.2266.

5-Chloro-1,2,3,4-tetraphenyl-5-(pyrimidin-5′-yl)cyclopenta-1,3-diene (CpClAr2)

Obtained as a 57 : 37 : 6 mixture of 3 regioisomers.

2,3,4,5-Tetraphenyl-1-(pyrimidin-5′-yl)cyclopenta-2,4-dien-1-ol **CpOHAr2** (100 mg, 0.22 mmol, 1 eq.) was placed in a round-bottom flask equipped with a magnetic stirring bar. Benzene (2.5 mL) was added and the suspension was heated to reflux using a preheated oil bath. Thionyl chloride (94 µL, 1.29 mmol, 6 eq.) was then added, and the mixture was refluxed for 30 minutes. The reaction medium was then cooled down, diluted with ethyl acetate (20 mL) and washed with a saturated aqueous solution of sodium hydrogen carbonate (20 mL) followed by distilled water (2 × 20 mL). The organic layer was then dried with magnesium sulfate and the solvents were evaporated to dryness. TLC of the crude (SiO_2, ethyl acetate/hexane 3 : 7) showed only one spot resulting from a quantitative conversion of the starting material. The crude product was dissolved in ethyl acetate and filtered through a silica plug, using the same solvent for elution, to remove eventual impurities or salts. The solvent was then removed using rotary evaporation to give pure product **CpClAr2** in 96% yield (99.3 mg, 0.21 mmol) as a pale-yellow solid composed of a 57 : 37 : 6 mixture of regioisomers.

$R_f = 0.5$ (SiO_2, ethyl acetate:hexane 3 : 7); ^1H NMR (500 MHz, CD_2Cl_2, 25 °C, 57 : 37 : 6 mixture of regioisomers): δ 9.06 (s, 0.06H, Ha_{regio3}), 8.91 (s, 0.57H, Ha_{regio2}), 8.85 (s, 0.37H, Ha_{regio1}), 8.80 (s, 0.12H, Hb_{regio3}), 8.25 (s, 0.75H, Hb_{regio1}), 8.23 (s, 1.15H, Hb_{regio2}), 7.59–7.46 (m, 2H, H_{Ph}), 7.41–6.83 (m, 18H, H_{Ph}); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C, 57 : 37 : 6 mixture of regioisomers): δ 157.5 (C_{pyr}–H), 157.4 (C_{pyr}–H), 157.3 (C_{pyr}–H), 157.2 (C_{pyr}–H), 155.5 (C_{quat}), 152.3 (C_{quat}), 149.7 (C_{quat}), 148.7 (C_{quat}), 146.4 (C_{quat}), 143.0 (C_{quat}), 141.9 (C_{quat}), 136.3 (C_{quat}), 135.4 (C_{quat}), 135.3 (C_{quat}), 134.4 (C_{quat}), 134.3 (C_{quat}), 133.7 (C_{quat}), 133.6 (C_{quat}), 133.2 (C_{quat}), 130.7 (C_{Ph}–H), 130.6

(C_{Ph}–H), 130.4 (C_{Ph}–H), 130.3 (C_{Ph}–H), 130.1 (C_{Ph}–H), 129.4 (C_{Ph}–H), 129.1 (C_{Ph}–H), 129.0 (C_{Ph}–H), 128.9 (C_{Ph}–H), 128.8 (C_{quat}), 128.7 (C_{Ph}–H), 128.6 (C_{Ph}–H and C_{quat}), 128.5 (C_{Ph}–H), 128.4 (C_{Ph}–H), 128.3 (C_{Ph}–H), 126.7 (C_{Ph}–H), 126.5 (C_{Ph}–H), 82.1 (C_{quat}–Cl), 81.9 (C_{quat}–Cl); HRMS (DCI-CH_4): calcd for $C_{33}H_{24}N_2Cl$ $[MH]^+$: 483.1628, found 483.1642.

5-Chloro-2-mesityl-1,3,4,5-tetraphenylcyclopenta-1,3-diene (CpClAr3)

1-Mesityl-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol **CpOHAr3** (50 mg, 0.10 mmol, 1 eq.) was placed in a Schlenk tube containing a magnetic stir bar. Benzene (2 mL) and thionyl chloride (43 μL, 0.60 mmol, 6 eq.) were added and the suspension was refluxed using a preheated oil bath for 30 minutes. The reaction medium was then cooled down, diluted with diethyl ether (20 mL) and washed with a saturated aqueous solution of sodium hydrogen carbonate (20 mL) followed by distilled water (2 × 20 mL). The organic layer was dried with magnesium sulfate and the solvent was then removed using rotary evaporation. The crude product was purified by column chromatography (SiO_2, dichloromethane/hexane 1 : 1) to give **CpClAr3** as a yellowish-orange solid in 61% yield (32 mg, 0.061 mmol).

R_f = 0.8 (SiO_2, dichloromethane/hexane 1 : 1); mp 93–95 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$, 25 °C): δ 7.59–7.58 (m, 2H, H_{Ph}), 7.36–7.25 (m, 3H, H_{Ph}), 7.11–7.01 (m, 11H, H_{Ph}), 6.97–6.93 (m, 4H, H_{Ph}), 6.81 (s, 1H, H_{Mes}), 6.79 (s, 1H, H_{Mes}), 2.20 (s, 6H, H_{Me}), 2.15 (s, 3H, H_{Me}); $^{13}C\{^1H\}$ NMR (151 MHz, $(CD_3)_2CO$, 25 °C) δ 148.7 (C_{quat}), 146.7 (C_{quat}), 143.1 (C_{quat}), 142.5 (C_{quat}), 137.2 (C_{quat}), 136.7 (C_{quat}), 136.1 (C_{quat}), 135.8 (C_{quat}), 134.6 (C_{quat}), 134.0 (C_{quat}), 133.7 (C_{quat}), 131.8 (C_{quat}), 130.3 (C_{Ph}–H), 129.3 (C_{Ph}–H), 128.7 (C_{Ph}–H), 128.4 (C_{Mes}–H), 128.3 (C_{Mes}–H), 128.3 (C_{Ph}–H), 128.0 (C_{Ph}–H), 127.7 (C_{Ph}–H), 127.6 (C_{Ph}–H), 127.5 (C_{Ph}–H), 127.4 (C_{Ph}–H), 127.3 (C_{Ph}–H), 126.4 (C_{Ph}–H), 81.8 (C_{quat}–Cl), 20.3 (C_{Me}), 20.3 (C_{Me}), 19.5 (C_{Me}); HR-MS (MALDI): calcd for $C_{38}H_{31}Cl$ $[M]^+$: 522.2109, found 522.2106.

Bromodicarbonyl-η^5-5-[4-(*tert*-butyl)phenyl]-1,2,3,4-tetraphenylcyclopentadienylruthenium(II) (RuCpBrAr1)

5-(4-(*tert*-Butyl)phenyl)-5-bromo-1,2,3,4-tetraphenylcyclopenta-1,3-diene **CpBrAr1** (50 mg, 0.086 mmol, 1 eq.) and triruthenium dodecacarbonyl $Ru_3(CO)_{12}$ (32 mg, 0.052 mmol, 0.6 eq.) were placed in a Schlenk tube containing a magnetic stir bar under argon. Anhydrous and degassed toluene (3 mL) was then added, and the mixture was refluxed for 2 hours. The colour of suspension changed from orange to brown. The reaction mixture was allowed to reach rt and the solvent was then removed using rotary evaporation. The crude product was purified by column chromatography (SiO_2, dichloromethane/hexane 1 : 2 to 2 : 1) to give **RuCpBrAr1** as a yellow solid in 63% yield (40 mg, 0.0.54 mmol).

R_f = 0.2 (SiO_2, dichloromethane/hexane 1 : 1); mp 206–208 °C (dec.); IR: ν_{max}/cm^{-1} 2037 (CO) and 1988 (CO); ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ 7.24–7.21 (m, 4H, H_{Ar}), 7.13–7.04 (m, 18H, H_{Ar}), 6.95 (d, ^3J = 8.9 Hz, 2H, H_{Ar}), 1.24 (s, 9H, H_{tBu}); $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 25 °C): δ 197.4 (CO), 152.2 (C_{quat}–*t*Bu), 132.8 (C_{Ar}), 132.8 (C_{Ar}), 132.4 (C_{Ar}), 130.3 (C_{Ar}), 130.2 (C_{Ar}), 128.7 (C_{Ar}), 128.1 (C_{Ar}), 125.1 (C_{Ar}), 107.6 (C_{Cp}), 107.3 (C_{Cp}), 106.6 (C_{Cp}), 34.9 (C_{tBu}), 31.3 (C_{tBu}); HR-MS (ESI$^+$): calcd for $C_{41}H_{33}BrNaO_2Ru$ $[M + Na]^+$: 763.0607, found. 763.0619.

Bromodicarbonyl-η^5-5-mesityl-1,2,3,4-tetraphenylcyclopentadienylruthenium(II) (RuCpBrAr3)

5-Bromo-2-mesityl-1,3,4,5-tetraphenylcyclopenta-1,3-diene **CpBrAr3** (48 mg, 0.085 mmol, 1 eq.) and triruthenium dodecacarbonyl $Ru_3(CO)_{12}$ (33 mg, 0.053 mmol, 0.6 eq.) were placed in a Schlenk tube containing a magnetic stir bar under argon. Anhydrous and degassed toluene (2 mL) was then added and the mixture was refluxed for 2 hours. The colour of suspension changed from orange to brown. The reaction mixture was allowed to reach rt and the solvent was then removed using rotary evaporation. The crude product was purified by column chromatography (SiO_2, dichloromethane/hexane 1 : 1 to 2 : 1) to give **RuCpBrAr3** as a yellow solid in 14% yield (8.6 mg, 0.012 mmol).

R_f = 0.2 (SiO_2, dichloromethane/hexane 1 : 1); mp 203–205 °C (dec.); IR: ν_{max}/cm^{-1} 2040 (CO) and 1989 (CO); ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 25 °C): δ 7.32–7.23 (m, 10H, H_{Ph}), 7.16–7.13 (m, 2H, H_{Ph}), 7.02–6.99 (m, 4H, H_{Ph}), 6.94–6.93 (m, 5H, H_{Ph} and H_{Mes}), 6.77 (s, 1H, H_{Mes}), 2.57 (s, 3H, H_{Me}), 2.22 (s, 3H, H_{Me}), 1.99 (s, 3H, H_{Me}); $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, 25 °C): δ 198.0 (CO), 138.9 (C_{quat}–Me), 138.0 (C_{quat}–Me), 137.2 (C_{quat}–Me), 132.6 (C_{Ar}), 131.2 (C_{Ar}), 130.5 (C_{Ar}), 129.6 (C_{Ar}), 129.0 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 128.2 (C_{Ar}), 127.7 (C_{Ar}), 127.2 (C_{Ar}), 113.9 (C_{Cp}), 103.2 (C_{Cp}), 22.9 (C_{Me}), 21.1 (C_{Me}), 20.1 (C_{Me}); HR-MS (ESI$^+$): calcd for $C_{40}H_{31}BrNaO_2Ru$ $[M + Na]^+$: 747.0450, found 747.0451.

Chlorodicarbonyl-η^5-5-[4-(*tert*-butyl)phenyl]-1,2,3,4-tetraphenylcyclopentadienylruthenium(II) (RuCpClAr1)

5-(4-(*tert*-Butyl)phenyl)-5-chloro-1,2,3,4-tetraphenylcyclopenta-1,3-diene **CpClAr1** (50 mg, 0.093 mmol, 1 eq.) and triruthenium dodecacarbonyl $Ru_3(CO)_{12}$ (36 mg, 0.056 mmol, 0.6 eq.) were placed in a Schlenk tube containing a magnetic stir bar under argon. Anhydrous and degassed toluene (3 mL) was then added and the mixture was refluxed for 2 hours. The colour of suspension changed from orange to brown. The reaction mixture was allowed to reach rt and the solvent was then removed using rotary evaporation. The crude product was purified by column chromatography (SiO_2, dichloromethane/hexane 1 : 1 to 2 : 1) to give **RuCpClAr1** as a yellow solid in 74% yield (48 mg, 0.069 mmol).

R_f = 0.2 (SiO_2, dichloromethane/hexane 1 : 1); mp 197–199 °C (dec.); IR: ν_{max}/cm^{-1} 2038 (CO) and 1985 (CO); ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C):δ 7.24–7.20 (m, 4H, H_{Ar}), 7.13–7.04 (m, 18H, H_{Ar}), 6.96–6.95 (m, 2H, H_{Ar}), 1.24 (s, 9H, H_{tBu}); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 197.8 (CO), 152.1 (C_{quat}–*t*Bu), 132.7 (C_{Ar}), 132.6 (C_{Ar}), 132.2 (C_{Ar}), 130.3 (C_{Ar}), 130.2 (C_{Ar}), 128.7 (C_{Ar}), 128.2 (C_{Ar}), 128.1 (C_{Ar}), 125.1 (C_{Ar}), 107.8 (C_{Cp}), 107.4 (C_{Cp}), 106.6 (C_{Cp}), 34.9 (C_{tBu}), 31.3 (C_{tBu}); HR-MS (ESI$^+$): calcd for $C_{41}H_{33}ClNaO_2Ru$ $[MNa]^+$: 717.1110, found 717.1097.

Chlorodicarbonyl-η^5-5-mesityl-1,2,3,4-tetraphenylcyclopentadienylruthenium(II) (RuCpClAr3)

5-Chloro-2-mesityl-1,3,4,5-tetraphenylcyclopenta-1,3-diene **CpClAr3** (17 mg, 0.032 mmol, 1 eq.) and triruthenium dodecacarbonyl $Ru_3(CO)_{12}$ (12 mg, 0.019 mmol, 0.6 eq.) were placed in a Schlenk tube containing a magnetic stir bar under argon. Anhydrous and degassed toluene (2 mL) was then added and the mixture was refluxed for 2 hours. The colour of suspension changed from orange to brown. The reaction mixture was allowed to reach rt and the solvent was then removed using rotary evaporation. The crude product was purified by column chromatography (SiO_2, dichloromethane/hexane 1 : 1 to 2 : 1) to give the ruthenium complex **RuCpClAr3** as a yellow solid in 59% yield (13 mg, 0.019 mmol).

R_f = 0.2 (SiO_2, dichloromethane/hexane 1 : 1); mp 189–191 °C (dec.); IR: ν_{max}/cm^{-1} 2045 (CO) and 1996 (CO); ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 25 °C): δ 7.32–7.23 (m, 10H, H_{Ph}), 7.15 (t, ^3J = 7.4 Hz, 2H, H_{Ph}), 7.03–6.99 (m, 4H, H_{Ph}), 6.94–6.92 (m, 5H, H_{Ph} and H_{Mes}), 6.77 (s, 1H, H_{Mes}), 2.57 (s, 3H, H_{Me}), 2.21 (s, 3H, H_{Me}), 1.99 (s, 3H, H_{Me}); $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, 25 °C): δ 198.0 (CO), 138.9 (C_{quat}–Me), 138.0 (C_{quat}–Me), 137.2 (C_{quat}–Me), 132.6 (C_{Ar}), 131.2 (C_{Ar}), 130.5 (C_{Ar}), 129.6 (C_{Ar}), 129.6 (C_{Ar}), 129.0 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 128.2 (C_{Ar}), 127.2 (C_{Ar}), 113.9 (C_{Cp}), 103.2 (C_{Cp}), 22.9 (C_{Me}), 21.1 (C_{Me}), 20.1 (C_{Me}); HR-MS (ESI$^+$): calcd for $C_{40}H_{31}ClNaO_2Ru$ $[MNa]^+$: 703.0954, found 703.0976.

Conflicts of interest

There are no conflicts to declare.

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