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Ruthenium Complexes Bearing Bulky Pentasubstituted Cyclopentadienyl Ligands and Evaluation of $[Ru(\eta^5\text{-}C_5Me_4R)(MeCN)_3][PF_6]$ Precatalysts in Nucleophilic Allylic Substitution Reactions

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$[Ru(\eta^5\text{-}C_5Me_4R)(MeCN)_3][PF_6]$ (R = CH_2tBu, *i*Pr, *t*Bu, and CF_3; **2**–**5**) complexes were synthesized in two steps starting from the appropriate cyclopentadienes and $RuCl_3{\cdot}3H_2O$. The fully substituted ruthenocenes $[Ru(C_5Me_5)(C_5Me_4R^*)]$, $[Ru(C_5Me_5)(C_5nPr_4R^*)]$ {R* = (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl} and $[Ru(C_5Me_5)(C_5nPr_5)]$ were obtained by treating $[Ru(C_5Me_5)Cl]_4$ with the corresponding cyclopentadienyllithium salts. Complexes **2**–**5** were evaluated as catalyst precursors for nucleophilic allylic substitution reactions, and the results were compared to those obtained with the $[Ru(C_5Me_5)(MeCN)_3][PF_6]$ (**1**) precatalyst. The etherification of *p*-methoxyphenol with the typical aliphatic chlorohexene allylic substrate shows that the introduction of the bulky *tert*-butyl and trifluoromethyl groups into the tetramethylcyclopentadienyl ring results in a valuable enhancement in regioselectivity in favour of the branched allyl aryl ether.

Introduction

As a result of the lability of their acetonitrile ligands, the cyclopentadienyltris(acetonitrile)ruthenium cations continue to provide a popular entry to a rich coordination chemistry. To hinder the undesired formation of ruthenocene, their access was based on the removal, under UV-irradiation conditions in acetonitrile, of the benzene ligand from $[Ru(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-benzene})]^+$ intermediates.[1–3] Such a procedure has also been successful for cyclopentadienyl ligands bearing a coordinating phosphane or pyridine side arm.[4] Depending on the nature of the cyclopentadiene, the synthesis of the intermediates requires the treatment of $[(\eta^6\text{-benzene})RuCl_2]_2$ with cyclopentadienylthallium derivatives,[1,2,4] although a "one-pot" procedure starting from $RuCl_3{\cdot}3H_2O$, cyclopentadiene, benzene and zinc as a reducing reagent was efficient in the cases of trifluoromethyltetramethylcyclopentadiene and pentamethylcyclopentadiene.[3,5] For the simple $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ cation, efforts have been made to prepare the corresponding $[Ru(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-benzene})]^+$ intermediate without the involvement of toxic thallium.[6] Recently, the synthesis of the $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-naphthalene})][PF_6]$ alternate intermediate allowed the UV-irradiation step to be avoided and thus provided a more efficient procedure.[7] This required, however, the sacrifice of one cyclopentadienyl ligand from ruthenocene, under drastic conditions.

Furthermore, the selective coordination of only one cyclopentadienyl ring was easily reached when pentamethylcyclopentadiene was treated with $RuCl_3{\cdot}3H_2O$.[8–10] The subsequent reduction of the resulting $[Ru(\eta^5\text{-}C_5Me_5)Cl_2]_2$ ruthenium(III) dimer with $Li[BHEt_3]$ or zinc and coordination of acetonitrile afforded the desired cation, which was conveniently isolated as its $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)_3][PF_6]$ (**1**) salt.[10–12] We report herein the synthesis of the analogous $[Ru(\eta^5\text{-}C_5Me_4R)(MeCN)_3][PF_6]$ (R = CH_2tBu, *i*Pr, *t*Bu or CF_3) complexes and of the new ruthenocene-type complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5nPr_5)]$ and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5R_4R^*)]$ {R = Me or *n*Pr, R* = (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl} arising from very bulky substituted cyclopentadienes. The $[Ru(\eta^5\text{-}C_5Me_4R)(MeCN)_3][PF_6]$ cationic ruthenium derivatives were subsequently evaluated as new catalyst precursors for allylation reactions favouring the formation of branched products. Thus, the influence of the steric and electronic modifications at the cyclopentadienyl ring on regioselectivity was specified.

Results and Discussion

Synthetic work stimulated by an increasing need for pentamethylcyclopentadiene has also provided two conve-

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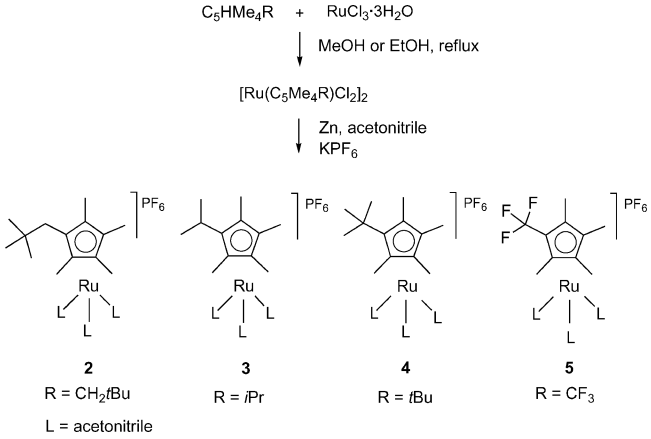
nient routes to 1-alkyl-2,3,4,5-tetramethylcyclopentadienes on the basis of (i) the reaction between two molecules of 2-lithio-2-butene with an ethyl ester RCO_2Et and (ii) the addition of an alkyllithium RLi to 2,3,4,5-tetramethylcyclopent-2-en-1-one.[13,14] Thus, trifluoromethyl-,[15] isopropyl-[16] and *tert*-butyl-tetramethylcyclopentadienes[17] were readily available. We have similarly prepared neopentyltetramethylcyclopentadiene as a yellow oil obtained in a 60% yield by treating neopentyllithium with 2,3,4,5-tetramethylcyclopent-2-en-1-one. Available according to a distinct procedure allowing the introduction of the R alkyl substituent from the aldehyde RCHO,[18] (1*R*,5*S*)-2-(2,3,4,5-tetramethylcyclopentadien-1-yl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene, (1*R*,5*S*)-2-(2,3,4,5-tetra-*n*-propylcyclopentadien-1-yl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene and 1,2,3,4,5-penta-*n*-propylcyclopentadiene were also involved in this study. The (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl group was conveniently introduced from commercially available (–)-myrtenal as the aldehyde.

The reaction of 1-alkyl-2,3,4,5-tetramethylcyclopentadienes bearing a neopentyl, isopropyl or *tert*-butyl group with $RuCl_3·3H_2O$ in ethanol (R = CH_2tBu) or methanol (R = *i*Pr, *t*Bu) at reflux yielded purple-brown crystalline precipitates reasonably assumed to be $[Ru(C_5Me_4R)Cl_2]_2$ dimers, as such a structure was determined when R = Me,[19] Et[20] and for the similarly prepared $[Ru(C_5Me_4CF_3)Cl_2]_2$ dimer.[21] Such chlorine-bridged ruthenium dimers might exhibit a bond-stretch isomerism,[22] as shown by previous structural, EPR and variable-temperature NMR spectroscopic studies.[20,23c] These ruthenium(III) intermediates were subsequently reduced with zinc in acetonitrile to generate the $[Ru(C_5Me_4R)(MeCN)_3]^+$ cations. The addition of KPF_6 to supply the $[PF_6]^-$ anion afforded $[Ru(C_5Me_4R)(MeCN)_3][PF_6]$ complexes **2**–**5** (Scheme 1).

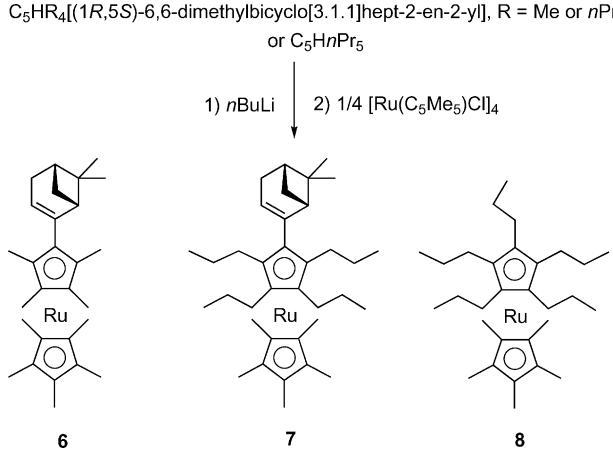


Scheme 1. Synthesis of $[Ru(\eta^5\text{-}C_5Me_4R)(MeCN)_3][PF_6]$ complexes **2**–**5**.

Complexes **2**–**5** were obtained in good yields (58–69% after recrystallization) as orange to orange-brown crystals, and they were moderately sensitive to air in the solid state. Complex **5** was previously synthesized by UV irradiation of the $[Ru(C_5Me_4CF_3)(C_6H_6)][PF_6]$ intermediate in acetonitrile as solvent.[3] New complexes **2**–**4** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H NMR spectra exhibited two resonances corresponding to the methyl groups, besides the resonances arising from the protons of the alkyl substituent. The ^{13}C NMR spectra were also in agreement with the proposed structure.

Highly sterically demanding and electron-donating cyclopentadienyl-type ligands continue to stimulate interest to modify the reactivity of metal centres.[22,23] Under similar conditions, attempts to obtain ruthenium(III) intermediates starting from cyclopentadienes featuring *n*-propyl and (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl groups failed.

However, the reaction of the cyclopentadienyllithium salts with $[Ru(\eta^5\text{-}C_5Me_5)Cl]_4$ afforded the corresponding neutral ruthenocenes (Scheme 2) and provided evidence for the ability of these bulky ligands to coordinate a ruthenium centre. New ruthenocenes **6**–**8** were obtained in good yields (53–69%) as colourless crystallized solids, and they were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H and ^{13}C NMR spectra of **6** showed both singlet resonances indicating the presence of five equivalent Me groups from the C_5Me_5 ring. Concerning the second ring, the observation of four distinct methyl groups resulted from the presence of the optically pure (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl group. The ^1H and ^{13}C NMR spectra of **7** led to similar observations, whereas the ^1H and ^{13}C NMR spectra of **8** were both consistent with the presence of five equivalent *n*-propyl groups besides the five equivalent methyl groups from the pentamethylcyclopentadienyl ring.



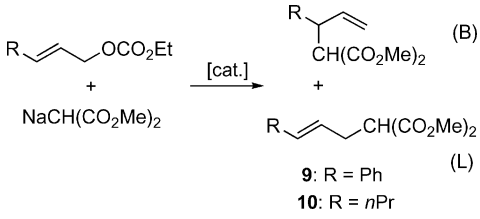
Scheme 2. Synthesis of the new fully substituted ruthenocenes **6**–**8**.

Starting from cyclopentadienes involving *n*-propyl groups, a minor product arose from the presence of *n*PrCH=C(*n*Pr)–C(*n*Pr)=CH*n*Pr as an impurity coming with the cyclopentadienes since identified and characterized as the diene–ruthenium derivative $[Ru(C_5Me_5)\{\eta^4\text{-}$*n*PrCH=C(*n*Pr)–C(*n*Pr)=CH*n*Pr$\}Cl]$ (see Experimental Section).

The easy formation of ruthenocenes **6**–**8** contrasts with the failure to obtain ruthenium(III) dimers when the reaction of the corresponding cyclopentadienes with $RuCl_3·3H_2O$ in alcohols was attempted.

Ruthenium-Catalyzed Allylic Substitution Reactions

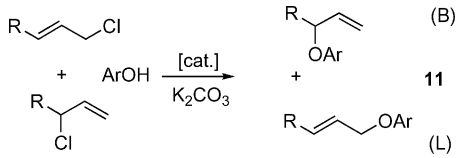
The pentamethylcyclopentadienyl complex $[Ru(C_5Me_5)(MeCN)_3][PF_6]$ (**1**) and the related $Ru(C_5Me_5)$ cationic derivatives have received considerable attention as catalyst precursors for regioselective allylation reactions favouring the formation of branched products.[24] However, little is known concerning the influence of the cyclopentadienyl ligand itself on the fate of the catalytic process. Therefore, complexes **2**–**5** were involved in selected allylic substitution reactions. As a classical test, the reaction between allylic carbonates and sodiodimethylmalonate [Equation (1)] allowed the catalytic activity of complexes **2**–**5** to be compared with that of **1**.



(1)

Thus, the addition of sodiodimethylmalonate (1.2 equiv.) to a solution of ethyl cinnamyl carbonate (0.5 mmol) in THF (4.0 mL) in the presence of **2**–**5** (3 mol-%) at ambient temperature for 18 h to ensure complete conversion led to monosubstituted dimethyl malonates **9** as a mixture of branched (B) and linear (L) isomers, the ratio of which was determined by ^1H NMR spectroscopy. Excellent regioselectivities in favour of the branched product (94:6 B/L ratio) were reached by using **2**–**4** as catalyst precursors, that is, a similar regioselectivity as observed when **1** was used as catalyst precursor.[24c] The involvement of **5** in this catalytic process was less satisfactory, as a moderate 82:18 B/L ratio was obtained. On the contrary, starting from ethyl 2-(*E*)-hexen-1-yl carbonate as the allylic substrate leading to monosubstituted dimethyl malonates **10** [Equation (1)], the linear (L) allylic derivative was produced as the major compound under similar conditions. A modest 26:74 B/L ratio was reached when **1**, **2** and **5** were used as catalyst precursors, whereas the use of **3** and **4** resulted in a B/L ratio of 35:65. These results mainly emphasized again that the favoured formation of branched products remains a challenging problem with ruthenium catalysts when starting from aliphatic allylic substrates.[25]

Recently, we reported the synthesis of allyl aryl ethers from allylic chlorides and phenols in the presence of K_2CO_3 and complex **1** as catalyst precursor.[26] Only modest regioselectivities in favour of the branched products were obtained when starting from aliphatic allylic substrates, and a further enhancement in the regioselectivity is needed. As a typical reaction, the etherification of *p*-methoxyphenol with chlorohexene, as a 4:1 mixture of 1-chloro-2-hexene and 3-chloro-1-hexene arising from the reaction of PCl_3 with commercial 3-(*E*)-hexen-1-ol,[27] allowed complexes **2**–**5** to be compared to **1** as catalyst precursors [Equation (2)].



(2)

The results given in Table 1 show the favoured formation of the branched isomer of allylic ethers **11**. A reaction time of 18 h largely ensured completion of the reaction: the conversion of the substrate (as determined by GC analysis) reached 82 and 92% after reaction times of 1 and 2 h, respectively, when complex **3** was used as catalyst precursor (Table 1, Entries 3, 4). No isomerization took place, as the observed regioselectivities were the same after 1, 2 and 18 h of reaction (Table 1, Entries 3–5). Furthermore, the regioselectivity was significantly improved by using **4** and **5** instead of **1** as catalyst precursor. Thus, the substitution of one Me group in the C_5Me_5 ligand by a bulkier *t*Bu or CF_3 group resulted in a significant enhancement in the B/L ratio from 61:39 (Table 1, Entry 1) to 72:28 (Table 1, Entries 6, 7).

Table 1. Ruthenium-catalyzed formation of allyl aryl ethers **11**.[a]

Entry	Catalyst	Reaction time [h]	Conversion[b] [%]	B/L[b]
1	**1**	18	100	61:39
2	**2**	18	100	66:34
3	**3**	1	82	68:32
4	**3**	2	92	68:32
5	**3**	18	100	68:32
6	**4**	18	100	72:28
7	**5**	18	100	72:28

[a] Experimental conditions: Catalyst (3 mol-%), MeCN as solvent, room temperature. [b] Conversion and B/L ratio as determined by ^1H NMR spectroscopy and GC analysis.

These regioselectivities compete with the best results obtained from the same substrates in the presence of $[Ru(C_5Me_5)(Ph_2POMe)(MeCN)_2][PF_6]$ as catalyst precursor.[25] However, although the substitution of one methyl group in the pentamethylcyclopentadienyl ligand by a *tert*-butyl group preserves the high reactivity of cyclopentadienyltris(acetonitrile)ruthenium cations, the substitution of one acetonitrile ligand in **1** by the bulky methyl diphenylphosphinite resulted in markedly reduced reactivity.[25] Moreover, there is no additional constraint to prepare complex **4** relative to **1**, as the syntheses of the corresponding cyclopentadienes are very similar.

The $C_5Me_4CF_3$ ligand was described as equivalent to a C_5H_5 one at the electronic point of view and to a C_5Me_5 one at the steric point of view.[15,21b] In contrast, recent studies have shown that complex **1** is a much more reactive and selective catalyst for allylic substitution than the cyclopentadienyl $[Ru(C_5H_5)(MeCN)_3][PF_6]$ complex.[24c,28] Our results provide straightforward evidence of the main influence of steric effects resulting from the modification of the cyclopentadienyl ring with respect to regioselectivity, as the

catalytic behaviour of complex **5** is much more connected to that of complexes **1**–**4** than to that of $[Ru(C_5H_5)(MeCN)_3][PF_6]$.

Conclusions

The cationic $[Ru(\eta^5\text{-}C_5Me_4R)(MeCN)_3][PF_6]$ (R = CH_2tBu, *i*Pr, *t*Bu, and CF_3) complexes bearing three labile acetonitrile ligands were conveniently prepared like the parent $[Ru(C_5Me_5)(MeCN)_3][PF_6]$ ruthenium derivative. Cyclopentadienes featuring one (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl or several *n*-propyl groups were appropriate for the synthesis of fully substituted bulky ruthenocenes. The involvement of the cationic $[Ru(\eta^5\text{-}C_5Me_4R)(MeCN)_3][PF_6]$ complexes, wherein R is a *tert*-butyl or a trifluoromethyl group, as catalyst precursors for regioselective allylation reactions allowed a significant enhancement in the regioselectivity in favour of branched allyl aryl ethers.

Experimental Section

General Considerations: The reactions were carried out under an inert atmosphere of argon according to Schlenk techniques. THF, diethyl ether and dichloromethane were distilled after drying according to conventional methods, whereas HPLC-grade acetonitrile, methanol and ethanol were straightforwardly used. ^1H and ^{13}C NMR spectra were recorded at 297 K with AC 200 FT Bruker instrument and referenced internally to the solvent peak. Elemental analyses were performed at the "Service Central de Microanalyse du CNRS" (Vernaison) or at the "Centre Régional de Mesures Physiques de l'Ouest" (Rennes).

Synthesis of Cyclopentadienes: The C_5HMe_4R 1-alkyl-2,3,4,5-tetramethylcyclopentadienes, R = CF_3,[15] *i*Pr,[16] *t*Bu,[17] were prepared as reported previously. The $C_5HMe_4CH_2tBu$ neopentyl cyclopentadiene was prepared as detailed for the *tert*-butyl one[17] by using $tBuCH_2Li$[29] instead of a commercial solution of *t*BuLi. The resulting crude yellow oil (b.p. 48 °C/<1 Torr), which was expected to consist of several isomers, was used without further characterization. The synthesis of (1*R*,5*S*)-2-(2,3,4,5-tetramethylcyclopentadien-1-yl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene, (1*R*,5*S*)-2-(2,3,4,5-tetra-*n*-propylcyclopentadien-1-yl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene, and 1,2,3,4,5-penta-*n*-propylcyclopentadiene transiently involved the in situ formation of a zirconacyclopentadiene $[ZrC_4R_4(\eta^5\text{-}C_5H_5)_2]$ from 2-butyne (R = Me) or 4-octyne (R = *n*Pr) followed by the addition of the appropriate myrtenal or butyraldehyde and $AlCl_3$. A detailed procedure is given elsewhere.[18] The crude oils isolated after hydrolysis and chromatographic workup were used without further characterization. The subsequent synthesis of ruthenium complexes accounts for the nature of the desired cyclopentadienes. The products involving *n*-propyl groups retained a variable amount of *n*PrCH=C(*n*Pr)–C(*n*Pr)=CH*n*Pr arising from hydrolysis of the $[ZrC_4nPr_4(\eta^5\text{-}C_5H_5)_2]$ intermediate. This was detected by the formation of the $[Ru(C_5Me_5)\{\eta^4\text{-}n\text{PrCH=C}(n\text{Pr})\text{C}(n\text{Pr})\text{=CH}n\text{Pr}\}\text{Cl}]$ diene–ruthenium complex as a byproduct.

Synthesis of $[Ru(C_5Me_4R)Cl_2]_2$ Intermediates: As a typical procedure, the cyclopentadiene $C_5HMe_4CH_2tBu$ (5.90 g, 30.7 mmol) and ethanol (50 mL, ethanol was required because this cyclopentadiene was not soluble in methanol) were added whilst stirring to $RuCl_3{\cdot}3H_2O$ (4.03 g, 15.4 mmol), and the mixture was heated at reflux for 2.5 h to afford a dark-brown solution that was then cooled in a refrigerator. The resulting crystalline purple-brown precipitate of $[Ru(C_5Me_4CH_2tBu)Cl_2]_2$ was collected by filtration, washed with cold ethanol (20 mL) and dried under vacuum. Yield: 3.78 g, 67%. $C_{28}H_{46}Cl_4Ru_2$ (728.64): calcd. C 46.28, H 6.38; found C 45.97, H 6.45. The intermediates $[Ru(C_5Me_4iPr)Cl_2]_2$ and $[Ru(C_5Me_4tBu)Cl_2]_2$ were conveniently obtained by using methanol instead of ethanol in 52 and 67% yield, respectively. For $[Ru(C_5Me_4tBu)Cl_2]_2$, $C_{26}H_{42}Cl_4Ru_2$ (700.59): calcd. C 44.70, H 6.06; found C 45.36, H 6.18. The $[Ru(C_5Me_4CF_3)Cl_2]_2$ intermediate was prepared as reported in the literature.[21]

Synthesis of $[Ru(C_5Me_4R)(MeCN)_3][PF_6]$ Complexes 2–5

2: As a typical procedure, a mixture consisting of $[Ru(C_5Me_4CH_2tBu)Cl_2]_2$ (1.05 g, 1.44 mmol), granular zinc (0.9 g, excess) and acetonitrile (30 mL) was stirred for 2 h. KPF_6 (0.53 g, 2.88 mmol) was then added, and the mixture was stirred overnight. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (30 mL). The solution was filtered, and the orange filtrate was evaporated to leave the crude product, which was recrystallized from hot methanol (20 mL) containing acetonitrile (0.5 mL) to afford orange-brown crystals of **2**. Yield: 1.04 g, 64%. ^1H NMR (200 MHz, CD_2Cl_2): δ = 0.93 (s, 9 H, *t*Bu), 1.66 (s, 6 H, 2 Me), 1.67 (s, 6 H, 2 Me), 2.08 (s, 2 H, *t*BuCH_2), 2.32 (br., 9 H, MeCN) ppm. ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 4.0 (*Me*CN), 9.8 (2 Me), 11.9 (2 Me), 30.2 (C*Me*$_3$), 34.0 (*C*Me$_3$), 39.1 (*t*Bu*C*), 80.4 (2 *C*Me), 84.2 (*C*CH_2), 82.7 (2 *C*Me) ppm; no Me*C*N resonance was detected due to coalescence. $C_{20}H_{32}F_6N_3PRu$ (560.53): calcd. C 42.86, H 5.75, N 7.50; found C 42.63, H 5.75, N 7.30.

3: Prepared as above. Orange crystals, 58% yield. ^1H NMR (200 MHz, CD_3CN): δ = 1.26 (d, ^3J = 7.2 Hz, 6 H, CH*Me*$_2$), 1.62 (s, 6 H, 2 Me), 1.65 (s, 6 H, 2 Me), 1.99 (s, 9 H, free MeCN), 2.53 (sept, ^3J = 7.1 Hz, 1 H, C*H*Me$_2$) ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 9.1 (2 Me), 10.0 (2 Me), 22.3 (CH*Me*$_2$), 25.6 (*C*HMe$_2$), 78.7 (2 *C*Me), 83.2 (*i*Pr*C*), 84.9 (2 *C*Me) ppm. $C_{18}H_{28}F_6N_3PRu$ (532.47): calcd. C 40.60, H 5.30, N 7.89; found C 39.41, H 5.08, N 7.12; the low carbon and nitrogen values likely resulted from a residual presence of mineral salt.

4: Prepared as above. Orange-brown crystals, 60% yield. ^1H NMR (200 MHz, CD_2Cl_2): δ = 1.34 (s, 9 H, *t*Bu), 1.63 (s, 6 H, 2 Me), 1.75 (s, 6 H, 2 Me), 2.37 (s, 9 H, MeCN) ppm. ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 4.3 (*Me*CN), 10.4 (2 Me), 13.8 (2 Me), 32.7 (C*Me*$_3$), 33.7 (*C*Me$_3$), 80.3 (2 *C*Me), 84.2 (*t*Bu*C*), 86.7 (2 *C*Me), 123.9 (Me*C*N) ppm. $C_{19}H_{30}F_6N_3PRu$ (546.50): calcd. C 41.76, H 5.53, N 7.69; found C 41.37, H 5.50, N 7.27.

5: Prepared as above. Orange crystals, 69% yield. ^1H NMR spectroscopic data as reported previously.[3]

Synthesis of Ruthenocenes 6–8

$[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4R^*)]$ {R* = (1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl} (6): To a solution of C_5HMe_4\{(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl\} (0.24 g, 1.00 mmol) in THF (10 mL) was added *n*BuLi (1.6 M in hexane, 0.63 mL, 1.01 mmol). The solution was stirred at room temperature for 0.5 h and $[Ru(C_5Me_5)Cl]_4$[10b] (0.27 g, 0.25 mmol) was added. The mixture was heated at reflux overnight and then evaporated under vacuum. The residue was extracted with hot heptane (20 mL), and the solution was chromatographed on an alumina column (10 cm, heptane). A yellow fraction was collected, and removal of the solvent

under reduced pressure followed by addition of ethanol and cooling in a refrigerator afforded **6** as a white microcrystalline solid. Yield: 0.28 g, 59%. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 0.99 (s, 3 H, 1 Me, CMe_2), 1.29 (m, 1 H, from R*), 1.34 (s, 3 H, 1 Me, CMe_2), 1.66 (s, 6 H, 2 Me, C_5Me_4), 1.68 (s, 3 H, Me, C_5Me_4), 1.70 (s, 15 H, C_5Me_5), 1.71 (s, 3 H, Me, C_5Me_4), 2.13 (m, 1 H, CH in R), 2.36–2.50 (m, 4 H, R*), 5.42 (s, 1 H, CH=) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 10.4 (C_5Me_4R*), 10.4 (C_5Me_4R*), 10.8 (C_5Me_5), 11.5 (C_5Me_4R*), 11.8 (C_5Me_4R*), 22.1 (Me, R*), 26.76 (Me, R*), 32.4 (CH_2, R*), 33.0 (CH_2, R*), 38.3 (CMe_2, R*), 40.9 (CH, R*), 48.2 (CH, R*), 82.1 (C_5Me_4R*), 82.2 (C_5Me_4R*), 83.7 (C_5Me_4R*), 83.8 (C_5Me_4R*), 83.8 (C_5Me_5), 93.6 (C_5 Me_4R*), 122.1 (CH=, R*), 143.7 (C=, R*) ppm. $C_{28}H_{40}Ru$ (477.70): calcd. C 70.40, H 8.44; found C 70.60, H 8.50.

[Ru(η^5-C_5Me_5)(η^5-C_5nPr$_4$R*)] {R* = (1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl} (7): According to a similar procedure, ruthenocene **7** was isolated as colourless crystals starting from C_5HnPr$_4${(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl}. Yield: 53%. A red-brown fraction was subsequently obtained by eluting the column with diethyl ether to afford [Ru(η^5-C_5Me_5)(η^4-C_4H_2nPr$_4$)Cl] as an orange brown solid. Yield 11%. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ = 0.92 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, 2 Me, *n*Pr), 1.00 (t, $^3J_{H,H}$ = 7.8 Hz, 6 H, 2 Me, *n*Pr), 1.03 (s, 3 H, 1 Me, CMe_2), 1.27 (m, 1 H, R*), 1.35 (s, 3 H, 1 Me, CMe_2), 1.25–1.53 (m, 8 H, CH_2Me), 1.69 (s, 15 H, C_5Me_5), 1.83–2.10 (m, 8 H, CH_2CH_2Me), 2.10 (m, 1 H, R*), 2.34–2.52 (m, 4 H, R*), 5.51 (s, 1 H, CH=) ppm. ^{13}C{^{1}H} NMR (50.32 MHz, CD_2Cl_2): δ = 10.8 (C_5Me_5), 15.0 (Me, *n*Pr), 15.1 (Me, *n*Pr), 15.3 (2 Me, *n*Pr), 21.7 (Me, R*), 25.9 (CH_2, *n*Pr), 26.3 (CH_2, *n*Pr), 26.4 (CH_2, *n*Pr), 26.5 (Me, R*, and CH_2, *n*Pr), 29.3 (2 CH_2, *n*Pr), 29.4 (CH_2, *n*Pr), 29.6 (CH_2, *n*Pr), 32.2 (CH_2, R*), 32.8 (CH_2, R*), 38.3 (CMe_2, R*), 41.0 (CH, R*), 49.4 (CH, R*), 83.7 (C_5Me_5), 87.2 (C_5nPr$_4$), 87.4 (C_5nPr$_4$), 87.6 (C_5nPr$_4$), 88.1 (C_5nPr$_4$), 95.7 (C_5R*), 123.5 (CH=, R*), 143.5 (C=, R*) ppm. $C_{36}H_{56}Ru$ (589.91): calcd. C 73.30, H 9.57; found C 73.20, H 9.64.

[Ru(η^5-C_5Me_5)(η^5-C_5nPr$_5$)] (8): Starting from C_5HnPr$_5$, a similar procedure led to ruthenocene **8** as colourless crystals and to [RuCl(η^5-C_5Me_5)(η^4-C_4H_2nPr$_4$)] as a minor product. Yields: 69 and 15%, respectively. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ = 0.99 (t, $^3J_{H,H}$ = 7.2 Hz, 15 H, Me, *n*Pr), 1.35–1.45 (m, 10 H, CH_2Me), 1.65 (s, 15 H, C_5Me_5), 1.91–1.99 (m, 10 H, CH_2CH_2Me) ppm. ^{13}C NMR (50.32 MHz, CD_2Cl_2): δ = 10.8 (C_5Me_5), 15.6 (Me, *n*Pr), 26.8 (CH_2), 29.8 (CH_2), 83.5 (C_5Me_5), 88.4 (C_5nPr$_5$) ppm. $C_{30}H_{50}Ru$ (511.80): calcd. C 70.40, H 9.85; found C 70.06, H 9.76.

Characterization of [Ru(η^5-C_5Me_5)(η^4-C_4H_2nPr$_4$)Cl]: Orange-brown crystals of [Ru(η^5-C_5Me_5)(η^4-C_4H_2nPr$_4$)Cl] were obtained upon cooling a saturated solution in diethyl ether. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 0.93 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, 2 Me, *n*Pr), 1.07 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2 Me, *n*Pr), 1.44–2.25 (m, 18 H, CH_2CH_2Me and RuCH), 1.55 (s, 15 H, C_5Me_5) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 10.3 (C_5Me_5), 15.6 (Me, *n*Pr), 16.0 (Me, *n*Pr), 24.6 (CH_2), 25.6 (CH_2), 31.5 (CH_2), 33.0 (CH_2), 72.1 (*n*PrCH), 94.8 (C_5Me_5), 101.4 (*n*PrC) ppm. $C_{26}H_{45}ClRu$ (494.17): calcd. C 63.19, H 9.18; found C 63.17, H 9.26.

Catalytic Experiments: In a typical catalytic experiment, a sample of *p*-methoxyphenol (0.5 mmol, 1 equiv.) was added to a stirred mixture consisting of hexenyl chloride (0.5 mmol, 1 equiv.), catalyst precursor (0.015 mmol, 3 mol-%), K_2CO_3 (1 equiv.) and acetonitrile (4.0 mL). After stirring for 18 h at room temperature, the slurry was filtered (for GC analysis) then concentrated under vacuum (for ^{1}H NMR spectroscopy analysis).

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[1] T. P. Gill, K. R. Mann, *Organometallics* **1982**, *1*, 485–488.
[2] a) Y. Matsushima, H. Kikuchi, M. Uno, S. Takahashi, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2475–2482; b) G. P. McGlacken, C. T. O'Brien, A. C. Whitwood, I. J. S. Fairlamb, *Organometallics* **2007**, *26*, 3722–3728.
[3] J. K. Evju, K. R. Mann, *Organometallics* **2002**, *21*, 993–996.
[4] N. Dodo, Y. Matsushima, M. Uno, K. Onitsuka, S. Takahashi, *J. Chem. Soc., Dalton Trans.* **2000**, 35–41.
[5] A. Schmid, H. Piotrowski, T. Lindel, *Eur. J. Inorg. Chem.* **2003**, 2255–2263, and references cited therein.
[6] B. M. Trost, C. M. Older, *Organometallics* **2002**, *21*, 2544–2546.
[7] E. P. Kündig, F. R. Monnier, *Adv. Synth. Catal.* **2004**, *346*, 901–904.
[8] N. Oshima, H. Suzuki, Y. Moro-oka, *Chem. Lett.* **1984**, 1161–1164.
[9] T. D. Tilley, R. H. Grubbs, J. E. Bercaw, *Organometallics* **1984**, *3*, 274–278.
[10] a) P. J. Fagan, M. D. Ward, J. V. Caspar, J. C. Calabrese, P. J. Krusic, *J. Am. Chem. Soc.* **1988**, *110*, 2981–2983; b) P. J. Fagan, M. D. Ward, J. C. Calabrese, *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719; c) P. G. Gassman, C. H. Winter, *J. Am. Chem. Soc.* **1988**, *110*, 6130–6135.
[11] a) W.-K. Wong, Y. Chen, W.-T. Wong, *Polyhedron* **1996**, *15*, 1575–1577; b) W.-K. Wong, Y. Chen, W.-T. Wong, *Polyhedron* **1997**, *16*, 433–439.
[12] a) B. Steinmetz, W. A. Schenk, *Organometallics* **1999**, *18*, 943–946; b) J. L. Schrenk, A. M. McNair, F. B. McCormick, K. R. Mann, *Inorg. Chem.* **1986**, *25*, 3501–3504.
[13] R. S. Threlkel, J. E. Bercaw, *J. Organomet. Chem.* **1977**, *136*, 1–5.
[14] a) C. M. Fendrick, L. D. Schertz, V. W. Day, T. J. Marks, *Organometallics* **1988**, *7*, 1828–1838; b) F. X. Kohl, P. Jutzi, *J. Organomet. Chem.* **1983**, *243*, 119–121.
[15] P. G. Gassman, J. W. Mickelson, J. R. Sowa, *J. Am. Chem. Soc.* **1992**, *114*, 6942–6944.
[16] H. Schumann, M. R. Keitsch, J. Winterfeld, S. Mühle, G. A. Molander, *J. Organomet. Chem.* **1998**, *559*, 181–190.
[17] H. Schumann, K. Zietzke, F. Erbstein, R. Weimann, *J. Organomet. Chem.* **1996**, *520*, 265–268.
[18] C. Zhao, P. Li, X. Cao, Z. Xi, *Chem. Eur. J.* **2002**, *8*, 4292–4298.
[19] U. Kœlle, J. Kossakowski, N. Klaff, L. Wesemann, U. Englert, G. E. Herberich, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 690–691.
[20] U. Kœlle, H. Lueken, K. Handrick, H. Schilder, J. K. Burdett, S. Balleza, *Inorg. Chem.* **1995**, *34*, 6273–6278.
[21] a) O. V. Gusev, M. A. Ievlev, K. A. Lyssenko, P. V. Petrovskii, N. A. Ustynyuk, P. M. Maitlis, *Inorg. Chim. Acta* **1998**, *280*, 249–256; b) O. V. Gusev, M. A. Ievlev, T. A. Peganova, M. G. Peterleitner, P. V. Petrovskii, Y. F. Oprunenko, N. A. Ustynyuk, *J. Organomet. Chem.* **1998**, *551*, 93–100.
[22] J. E. McGrady, *Angew. Chem. Int. Ed.* **2000**, *39*, 3077–3079.
[23] a) P. Bazinet, K. A. Tupper, T. Don Tilley, *Organometallics* **2006**, *25*, 4286–4291; b) S. Gauthier, E. Solari, R. Scopelliti, B. Dutta, K. Severin, *Chem. Commun.* **2007**, 1837–1839; c) B. Dutta, E. Solari, S. Gauthier, R. Scopelliti, K. Severin, *Organometallics* **2007**, *26*, 4791–4799; d) B. Dutta, R. Scopelliti, K. Severin, *Organometallics* **2008**, *27*, 423–429.
[24] a) C. Bruneau, J.-L. Renaud, B. Demerseman, *Chem. Eur. J.* **2006**, *12*, 5178–5187; b) J.-L. Renaud, B. Demerseman, M. D. Mbaye, C. Bruneau, *Curr. Org. Chem.* **2006**, *10*, 115–133; c) B. M. Trost, P. L. Fraisse, Z. T. Ball, *Angew. Chem. Int. Ed.*

2002, *41*, 1059–1061; d) T. Kondo, T. Mitsudo, *Curr. Org. Chem.* **2002**, *6*, 1163–1179.
[25] B. Demerseman, J.-L. Renaud, L. Toupet, C. Hubert, C. Bruneau, *Eur. J. Inorg. Chem.* **2006**, 1371–1380.
[26] M. D. Mbaye, B. Demerseman, J.-L. Renaud, L. Toupet, C. Bruneau, *Adv. Synth. Catal.* **2004**, *346*, 835–841.
[27] C. D. Hurd, R. W. McNamee, *J. Am. Chem. Soc.* **1932**, *54*, 1648–1651.
[28] R. Hermatschweiler, I. Fernández, P. S. Pregosin, F. Breher, *Organometallics* **2006**, *25*, 1440–1447.
[29] R. R. Schrock, J. D. Fellmann, *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.

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