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Synthesis, molecular structure, substitution and C–C coupling reactions of ruthenium complexes containing $(\eta^5\text{-}C_9H_7)Ru(PPh_3)$ as a molecular unit

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Dedicated to Professor F. Gordon A. Stone in recognition of his inspiring work in organometallic chemistry

Abstract

The 2-methallyl complex $[(\eta^5\text{-}C_9H_7)Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (**3**), prepared from $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ (**2**) and $2\text{-}MeC_3H_4MgCl$, reacts with HX (X = Cl, CF_3CO_2) in the presence of ethene to give the chiral-at-metal compounds $[(\eta^5\text{-}C_9H_7)Ru(C_2H_4)(PPh_3)X]$ (**4**, **5**) in nearly quantitative yields. Treatment of **2** with $AgPF_6$ and ethene affords $[(\eta^5\text{-}C_9H_7)Ru(C_2H_4)(PPh_3)_2]PF_6$ (**6**), which reacts with acetone to give the substitution product $[(\eta^5\text{-}C_9H_7)Ru(OCMe_2)(PPh_3)_2]PF_6$ (**7**). The molecular structure of **7** has been determined crystallographically. Whereas treatment of **4** with $CH(CO_2Et)N_2$ yields the olefin complex $[(\eta^5\text{-}C_9H_7)Ru\{\eta^2\text{-}(Z)\text{-}C_2H_2(CO_2Et)_2\}(PPh_3)Cl]$ (**8**), the reactions of **4** and **5** with Ph_2CN_2, $PhCHN_2$ and $(Me_3Si)CHN_2$ lead to the formation of the carbeneruthenium(II) derivatives $[(\eta^5\text{-}C_9H_7)Ru(=CRR')(PPh_3)Cl]$ (**9**–**11**) and $[(\eta^5\text{-}C_9H_7)Ru(=CRR')(PPh_3)(\kappa^1\text{-}O_2CCF_3)]$ (**12**–**14**), respectively. Treatment of **9** (R = R′ = Ph), **10** (R = H, R′ = Ph) and **11** (R = H, R′ = $SiMe_3$) with MeLi produces the hydrido(olefin) complexes $[(\eta^5\text{–}C_9H_7)RuH(\eta^2\text{-}CH_2{=}CPh_2)(PPh_3)]$ (**15**), $[(\eta^5\text{-}C_9H_7)RuH(\eta^2\text{-}CH_2{=}CHPh)(PPh_3)]$ (**18a**,**b**) and $[(\eta^5\text{-}C_9H_7)RuH(\eta^2\text{-}CH_2{=}CHSiMe_3)(PPh_3)]$ (**19**) via C–C coupling and β-hydride shift. The analogous reactions of **11** with PhLi gives the η^3-benzyl compound $[(\eta^5\text{-}C_9H_7)Ru\{\eta^3\text{-}(Me_3Si)CHC_6H_5\}(PPh_3)]$ (**20**). The η^3-allyl complex $[(\eta^5\text{-}C_9H_7)Ru(\eta^3\text{-}1\text{-}PhC_3H_4)(PPh_3)]$ (**17**) was prepared from **10** and $CH_2{=}CHMgBr$ by nucleophilic attack.

Keywords: Ruthenium; Ethene complexes; Carbene complexes; Allyl complexes; C–C coupling reactions

1. Introduction

Carbeneruthenium(I) complexes of the general composition $[RuCl_2(=CHR)(L)_2]$ with L = tertiary phosphines, which were first prepared by Grubbs and his group [1], belong to the most frequently used organometallic compounds both in organic synthesis and homogeneous catalysis [2]. The best known representative $[RuCl_2(=CHPh)(PCy_3)_2]$, being honoured in 1998 as "the compound of the year", is accessible in two steps from $[RuCl_2(PPh_3)_3]$ and phenyldiazomethane as the carbene source [3]. Prior to the early 1990s, this "diazoalkane route", mainly introduced by Herrmann [4] and Roper [5], had only rarely been applied, most notably for the preparation of metal carbenes with d^6 and d^8 metal centers.

In the context of our studies on the chemistry of cyclopentadienyl and pentamethylcyclopentadienyl ruthenium complexes with vinylidene and allenylidene ligands [6], we recently described a synthetic protocol that is also applicable to the corresponding carbene

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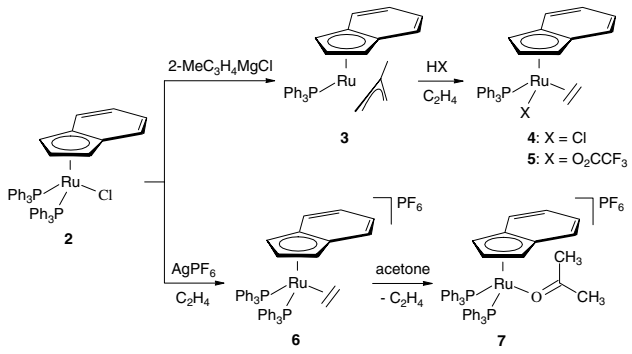
derivatives $[(\eta^5\text{-}C_5H_5)Ru(=CRR')(PPh_3)X]$ and $[(\eta^5\text{-}C_5Me_5)Ru(=CRR')(PPh_3)X]$ (X = Cl, CF_3CO_2) [7]. Although these compounds are highly reactive toward C-nucleophiles such as methyllithium, phenyllithium and vinyl Grignard reagents, in contrast to the Grubbs-type ruthenium carbenes they are inactive in olefin metathesis.

By considering these results and taking into account that η^5-indenyl transition-metal complexes are sometimes more reactive toward nucleophiles than their η^5-cyclopentadienyl counterparts [8–10], we set out to prepare ruthenium compounds of the general composition $[(\eta^5\text{-}C_9H_7)Ru(=CRR')(PPh_3)X]$. In this paper, we describe the synthesis of corresponding derivatives with X = Cl and CF_3CO_2 and report on the reactivity of these complexes toward organolithium and Grignard reagents. The preparation of some halfsandwich-type ethene ruthenium(II) compounds will also be described.

2. Results and discussion

Following previous work by Lehmkuhl et al. [11] on the chemistry of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (**1**), the analogous η^5-indenyl complex **3** was prepared by treatment of the starting material **2** with the Grignard reagent $2\text{-}MeC_3H_4MgCl$ (Scheme 1). Compound **3** is a yellow, only moderately air-sensitive solid, which in contrast to **1** is inert toward water and methanol. This is an advantage for the work-up procedure since excess of the Grignard reagent can be easily removed. The ^1H NMR spectrum of **3** displays the expected two signals for the allylic-CH_2 protons in *syn* and *anti* position of which that for H_{anti} at 0.38 ppm is split into a doublet due to ^1H–^{31}P coupling. While for the related carbonyl compounds $[(\eta^5\text{-}C_5R_5)Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(CO)]$ (R = H, Me) a mixture of exo/endo conformational isomers was observed in solution [12,13], the ^1H and ^{13}C NMR spectra of **3** indicate that in this case only the exo isomer exists.



Scheme 1.

The 2-methallyl complex **3** reacts with HCl and CF_3CO_2H in toluene at −40 °C under an ethene atmosphere to give orange, air-sensitive solids of the general composition $[(\eta^5\text{-}C_9H_7)Ru(C_2H_4)(PPh_3)X]$ (**4**, **5**). Both compounds (in particular **5**) are rather labile but can be stored at −60 °C under argon for days. Typical spectroscopic features are the two multiplets at 3.04 and 2.42 ppm (for **4**) and 3.00 and 2.91 ppm (for **5**) due to the ethene protons in the ^1H NMR spectra, and the singlet at 53.3 ppm (for **4**) and 56.0 ppm (for **5**) due to the olefinic carbon atoms in the ^{13}C NMR spectra. The signals for the quarterary carbon atoms C^1 and C^5 of the C_9H_7 unit (for assignment, see Fig. 1) appear at ca. 107–109 ppm, indicating that the indenyl ligand, similarly as in **2** and the precursor **3**, is mainly coordinated in a η^5 fashion. For indenyl complexes, in which a η^3 bonding mode predominates, the corresponding resonances are usually observed at somewhat lower fields [14].

The preparation of the cationic ethene complex **6** has been achieved by treatment of the neutral compound **2** with $AgPF_6$ in the presence of C_2H_4 (see Scheme 1). The yellow microcrystalline solid could be isolated in 95% yield. We note that the synthesis of the corresponding perchlorate $[(\eta^5\text{-}C_9H_7)Ru(C_2H_4)(PPh_3)_2]ClO_4$ has already been described, though in this case the yield was only moderate [15].

Since the ethene-to-metal bond in **6** is rather weak, the olefinic ligand is easily displaced by acetone. Stirring a solution of **6** in acetone at 50 °C for 10 min gave the substitution product **7** as a yellow air-stable solid in almost quantitative yield. Conductivity measurements in nitromethane confirm for both **6** and **7** the existence of 1:1 electrolytes. The IR spectrum of **7** shows a strong

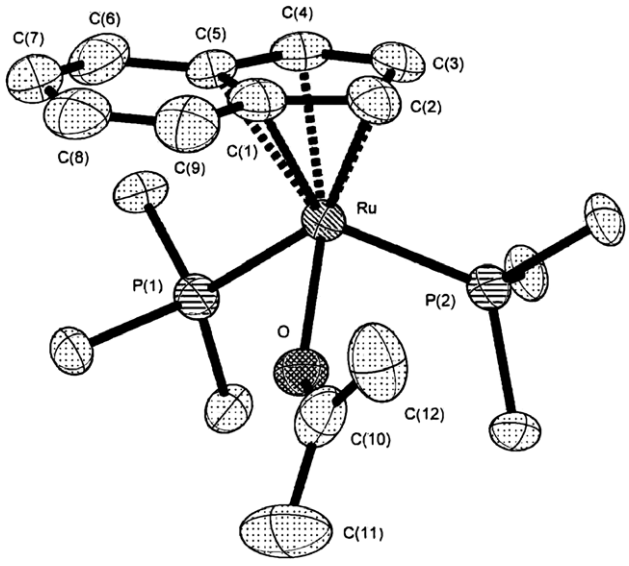


Fig. 1. Molecular structure of the cation of compound **7**. Hydrogen atoms are omitted for clarity; only the *ipso*-carbon atoms of the phenyl rings are shown.

band at 1720 cm^{-1}, which is assigned to the ν(C=O) stretching mode of the O=CMe_2 molecule. The ^{13}C NMR spectrum of **7** displays a singlet at 206.0 ppm for the carbonyl carbon atom and another singlet at 30.4 ppm for the methyl carbon atoms of coordinated acetone. These data are in good agreement with those reported by Esteruelas et al. [16] and Valerga and his group [17] for the cationic complexes $[(\eta^5\text{-}C_5H_5)Ru(O{=}CMe_2)(CO)(P\textit{i}Pr_3)]^+$ and $[(\eta^5\text{-}C_5Me_5)Ru(O{=}CMe_2)(CO)(PMe\textit{i}Pr_2)]^+$, respectively.

The molecular structure of **7** was established by X-ray crystallography. As shown in Fig. 1, the cation possesses the expected three-legged piano-stool configuration with a Ru–O distance of 2.167(5) Å (Table 1). This distance differs only slightly from the bond lengths found in other ruthenium(II) compounds with a Ru–O link [6a,18]. The slip-fold parameter Δ [19], which results from the difference between the distances Ru–C(1), Ru–C(5) and Ru–C(2), Ru–C(4) is 0.160(7) Å and thus similar to that in $[(\eta^5\text{-}C_9H_7)Ru(=C=CMe_2)(PPh_3)_2]^+$ (0.197(7) Å) [20] and $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ (0.161 Å) [21]. The parameter, together with the hinge angle HA (6.9(7)°) and the fold angle FA (8.4(7)°) [19,22], indicates that in **7** a considerable slippage of the indenyl moiety from a η^5 to a η^3 bond mode had occurred.

The reaction of complex **4** with ethyl diazoacetate also leads to the displacement of the ethene ligand but affords instead of the anticipated ruthenium carbene $[(\eta^5\text{-}C_9H_7)Ru(=CHCO_2Et)(PPh_3)Cl]$ the diethyl maleate complex **8** in excellent yield (Scheme 2). Diagnostic of the chiral-at-metal compound **8** is the observation of two ^1H NMR resonances due to the olefinic CH protons (which remain unchanged between 273 and 343 K) and of two sets of signals due to the ^{13}C carbon nuclei of the $CHCO_2Et$ units. The chemical shifts of these signals are in good agreement with those for some cyclopentadienylruthenium(II) complexes with diethyl maleate as ligand [7b,23]. With regard to the mechanism of the reaction of **4** with ethyl diazoacetate we assume that in the initial step the expected carbene derivative $[(\eta^5\text{-}C_9H_7)Ru(=CHCO_2Et)(PPh_3)Cl]$ is generated, which rapidly reacts with a second molecule of $CH(CO_2Et)N_2$, possibly through a [3 + 2] cycloaddition of the diazoalkane to the Ru=C bond followed by elimination of N_2, to yield the product.

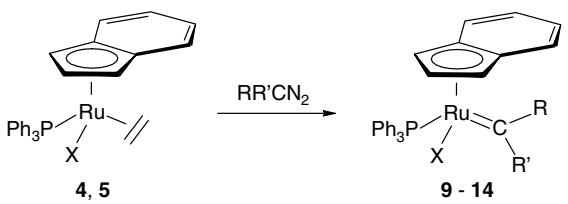
Table 1
Selected bond distances (Å) and bond angles (°) with estimated S.D. for the cation of compound **7**

Bond distances (Å)			
Ru–C(1)	2.337(6)	Ru–C(5)	2.342(6)
Ru–C(2)	2.186(7)	Ru–P(1)	2.424(2)
Ru–C(3)	2.157(7)	Ru–P(2)	2.302(2)
Ru–C(4)	2.173(6)	Ru–O	2.167(5)
Bond angles (°)			
Ru–O–C(10)	142.1(6)	P(1)–Ru–O	84.4(2)
P(1)–Ru–P(2)	103.39(6)	P(2)–Ru–O	87.2(1)

4 **8**

Scheme 2.

In contrast to $CH(CO_2Et)N_2$ other diazoalkanes such as Ph_2CN_2, $PhCHN_2$ and $(Me_3Si)CHN_2$ react with both **4** and **5** in toluene or toluene/hexane at room temperature to give the halfsandwich-type ruthenium carbenes **9**–**14** in 66–85% yield (Scheme 3). An alternative procedure for the preparation of **14** consists in treatment of the η^3-allyl complex **3** with an equimolar amount of CF_3CO_2H to generate as an intermediate the chelate compound $[(\eta^5\text{-}C_9H_7)Ru(\kappa^2\text{-}O_2CCF_3)(PPh_3)]$ [^{19}F NMR (376.5 MHz, C_6D_6): δ −75.0 (br s); ^{31}P NMR (162.0 MHz, C_6D_6): δ 56.3 (br s)], which reacts with $(Me_3Si)CHN_2$ by partial opening of the four-membered chelate ring to give **14**. The carbene complexes **9**–**14** are green moderately air-stable solids which can be stored under argon for weeks without decomposition. Regarding the spectroscopic data of **9**–**14**, the most characteristic feature is the low-field signal due to the carbene carbon atom at δ 302.6–358.6 ppm in the ^{13}C NMR spectra, which is split into a doublet due to ^1C–^{31}P coupling. The signals for the bridging carbon atoms ^{13}C and C^5 of the C_9H_7 unit (for assignment, see Fig. 1) appear at δ 117.8–131.5 ppm indicating that the bonding mode of the indenyl ligand is best described as lying between η^5 and η^3 [19,24]. The ^1H NMR spectra of **10**, **11** and **13**, **14** display a resonance for the carbene CH proton with a chemical shift at around δ 17.2 ppm (**10**, **13**) and δ 20.6 ppm (**11**, **14**), which is the same region as that observed for $[(\eta^5\text{-}C_5H_5)Ru(=CHR)(PPh_3)X]$ (R = Ph, $SiMe_3$; X = Cl, CF_3CO_2) [7b] and for the Grubbs-type catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$ [3].



4, 5 **9 - 14**

X = Cl	R	R'	X = CF_3CO_2	R	R'
9	Ph	Ph	**12**	Ph	Ph
10	Ph	H	**13**	Ph	H
11	$SiMe_3$	H	**14**	$SiMe_3$	H

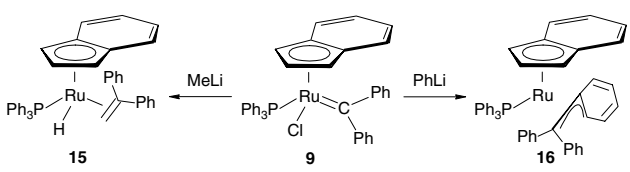
Scheme 3.

Taking the results obtained with the cyclopentadienyl complexes [(η^5-C_5H_5)Ru(=CRR′)(PPh_3)X] into consideration [7b], we also became interested in ascertaining the behavior of the indenylruthenium counterparts toward organolithium compounds and Grignard reagents. Treatment of a solution of **9** in toluene with a solution of methyllithium in diethyl ether at room temperature, followed by addition of acetone, gave a yellow-brown reaction mixture from which after evaporation of the solvent and extraction with pentane a yellow solid analyzing as [(η^5-C_9H_7)RuH(CH_2=CPh_2)(PPh_3)] (**15**) could be isolated in 80% yield. The ^{1}H NMR spectrum of **15** displays (in C_6D_6) a high-field resonance at δ −12.56 ppm due to the metal-bonded hydride as well as two well-separated signals at δ 3.18 and 1.75 ppm due to the olefinic protons. These data, together with those from the ^{13}C NMR spectrum, leave no doubt that the proposed structure of **15** shown in Scheme 4 is correct. With regard to the course of formation of **15**, it seems conceivable that the initial product of the reaction is the carbene(methyl)ruthenium(II) compound [(η^5-C_9H_7)RuCH_3(=CPh_2)(PPh_3)], which by migratory insertion gives the 16-electron alkylmetal intermediate [(η^5-C_9H_7)Ru(CPh_2CH_3)(PPh_3)] and then, by β-hydride shift, the (hydrido)olefin complex **15**.

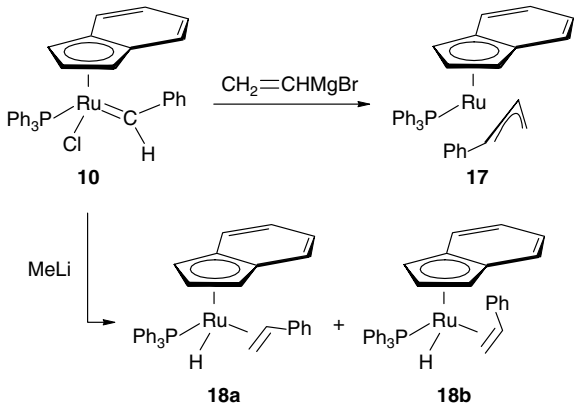
The reaction of **10** with the vinyl Grignard reagent CH_2=CHMgBr in toluene/THF also leads to the displacement of the chloro ligand and affords the η^3-allyl compound **17** (Scheme 5). It is a yellow microcrystalline, slightly air-sensitive solid that was isolated in 76% yield. The ^{1}H NMR spectrum of **17** displays the signal for the terminal C*H*Ph proton of the allylic ligand at δ 2.55 ppm as a doublet-of-doublets with a small *J*(PH) and a larger *J*(HH) coupling constant. The corresponding resonance for the *C*HPh carbon atom appears in the ^{13}C NMR spectrum at δ 54.0 ppm as a doublet. By comparison of these data with those of [Rh(η^3-1-PhC_3H_4)(P*i*Pr_3)$_2$] [25], we assume that the phenyl group of the CHPh moiety is in *syn* and the proton in *anti* position. We note that compound **16**, even after stirring for 15 h in C_6D_6, does not rearrange to the *syn* isomer, which is supposed to be thermodynamically more stable [26].

The indenyl complexes **10** and **11**, containing a secondary metal-bonded carbene, behave analogously to **9** toward methyllithium and afford in toluene/diethyl ether the hydrido(olefin) derivatives **18** and **19** in good yields (Schemes 5 and 6). Owing to the NMR spectroscopic data, in the case of the hydrido(styrene) compound a mixture of two isomers **18a** and **18b** is obtained in which the phenyl substituent at the C=C double bond is either pointing away (exo) or toward (endo) the indenyl ligand. Diagnostic for the exo isomer is a multiplet for the =C*H*Ph proton at δ 3.53 ppm and both a doublet at δ 3.05 ppm and a doublet-of-doublets at δ 1.10 ppm for the magnetically and stereochemically different =CH_2 protons in the ^{1}H NMR spectrum. For the endo isomer, the corresponding resonances appear at δ 2.81 (triplet), 1.81 (doublet-of-doublets) and 0.86 (triplet) ppm. For the hydrido(vinylsilane) complex **19**, the ^{1}H NMR spectrum displays two singlets for the =CH_2 protons at δ 1.80 and 1.24 ppm and also a singlet for the =C*H*$SiMe_3$ proton up-field at δ 0.43 ppm. The hydride signal for **18a**, **18b** and **19** is observed at around δ −12.0 to −13.0 ppm.

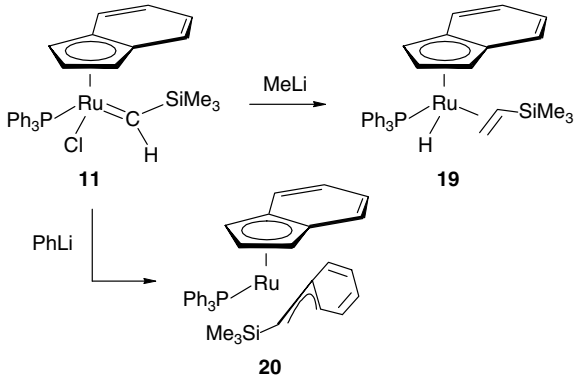
In contrast to the cyclopentadienyl compound [(η^5-C_5H_5)Ru(=CPh_2)(PPh_3)Cl], which upon treatment with PhLi affords a mixture of products with [(η^5-C_5H_5)Ru(η^3-$Ph_2CC_6H_5$)(PPh_3)] as the dominating species [7b], the reaction of **11** with phenyllithium proceeds cleanly and gives, after recrystallization of the crude product from pentane, the η^3-benzyl complex **20** as a



Scheme 4.



Scheme 5.



Scheme 6.

light yellow solid in 85% yield (see Scheme 2). The most characteristic feature in the ^{13}C NMR spectrum of **19** are the three signals for the metal-bonded benzylic carbon atoms at δ 95.5, 65.9 and 32.4 ppm, of which two are split into doublets due to ^{13}C–^{31}P coupling. The observed chemical shifts are similar to those of related η^3-benzyl compounds such as $[(\eta^5\text{-}C_5H_5)Mo\{\eta^3\text{-}(Ph_3Sn)CHC_6H_5\}(CO)_2]$ [27] and $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}PhCHC_6H_5)(PPh_3)]$ [7b], respectively. The ^1H NMR spectrum of **20** shows the resonances for the benzylic protons at δ 2.98 ppm (CH of the ring) and −0.81 ppm ($CHSiMe_3$). The relative large $^3J(PH)$ coupling constants of both signals (11.4 and 13.6 Hz) support the assumption that not only the CH-ring proton but also the C*H*$SiMe_3$ proton is in an *anti* position with respect to the substituent at the central allylic carbon atom.

In summarizing, the present work has shown that not only cyclopentadienyl- but also indenylruthenium(II) complexes with CPh_2, CHPh and $CHSiMe_3$ as carbene ligands can be prepared in high yields using the "diazoalkane route". Although they seem to be, despite the relatively weak indenyl-to-metal linkage, poor catalysts for olefin metathesis, they are potentially useful starting materials for making C–C bonds with the carbene ligand as one building block and organolithium or Grignard compounds as coupling reagents. Whether the hydrido(olefin) complexes **15**, **18** and **19**, similarly to analogous cationic rhodium derivatives [28], can be employed as catalysts for the oligomerization or polymerization of alkenes is the topic of ongoing research in our group.

3. Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting material **2** was prepared as described in the literature [15]. IR spectra were recorded on a Perkin–Elmer 1420 Infrared spectrometer and NMR spectra at room temperature (r.t.) on Bruker AC 200 and AMX 400 instruments. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal. Mass spectra were measured on a Finnigan 90 MAT instrument. Conductivity measurements were carried out with a Schott Konduktometer CG 851. Melting points were determined by Differential Thermal Analysis (DTA).

3.1. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (**3**)

A suspension of 1.00 g (1.22 mmol) of $\mathbf{2}\cdot 1/2CH_2Cl_2$ in 20 ml of toluene was treated with 5.0 ml of a 0.60 M solution of $2\text{-}MeC_3H_4MgCl$ (3.00 mmol) in THF and stirred for 45 min at 80 °C. After the reaction mixture was cooled to r.t., 20 ml of degassed water was added and the suspension was stirred for 10 min. The aqueous phase was separated and the organic phase was brought to dryness in vacuo. The remaining yellow solid was washed three times with 20-ml portions of methanol and dried; yield 561 mg (86%), m.p. (decomposition) 114 °C. *Anal.* Calc. for $C_{31}H_{29}PRu$: C, 69.78; H, 5.48; Ru, 18.94. Found: C, 69.49; H, 5.60; Ru, 19.46%. MS (70 eV): *m/z* 534 (M^+), 479 ($M^+ - MeC_3H_4$), 272 ($M^+ - PPh_3$). ^1H NMR (C_6D_6, 200 MHz): δ 7.38–6.89 (br m, 19H, C_6H_5 and C_6H_4 part of C_9H_7), 5.13 [t, 1H, $^3J(HH) = 2.6$ Hz, H^2 of C_3H_3 part of C_9H_7], 4.21 [d, 2H, $^3J(HH) = 2.6$ Hz, H^1 and H^3 of C_3H_3 part of C_9H_7], 2.62 (s, 2H, H_{syn} of MeC_3H_4), 2.08 (s, 3H, CH_3 of MeC_3H_4), 0.38 [d, 2H, $^3J(PH) = 16.1$ Hz, H_{anti} of MeC_3H_4]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 136.9 [d, $^1J(PC) = 37.0$ Hz, *ipso*-C of C_6H_5], 134.9 [d, $^2J(PC) = 10.2$ Hz, *ortho*-C of C_6H_5], 128.9 [d, $^4J(PC) = 1.8$ Hz, *para*-C of C_6H_5], 127.6 [d, $^3J(PC) = 9.2$ Hz, *meta*-C of C_6H_5], 123.6, 123.3 (both s, $C^{6,9}$ and $C^{7,8}$ of C_9H_7), 100.7 (s, $C^{1,5}$ of C_9H_7), 84.0 (s, C^3 of C_9H_7), 82.3 [d, $^2J(PC) = 1.8$ Hz, CCH_3 of MeC_3H_4], 77.1 [d, $^2J(PC) = 4.6$ Hz, $C^{2,4}$ of C_9H_7], 35.4 [d, $^2J(PC) = 4.6$ Hz, CH_2 of MeC_3H_4], 28.6 (s, CCH_3 of MeC_3H_4); for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (C_6D_6, 81.0 MHz): δ 67.0 (s).

3.2. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(C_2H_4)(PPh_3)Cl]$ (**4**)

A slow stream of ethene was passed through a solution of 100 mg (0.19 mmol) of **3** in 10 ml of toluene at −40 °C. After 2 min, 1.6 ml of a 0.30 M solution of HCl (0.48 mmol) in toluene was added. The solution was slowly warmed to r.t. and stirred for 5 min. The solvent was evaporated in vacuo, the remaining orange solid was washed twice with 2-ml portions of pentane and dried; yield 100 mg (97%), m.p. (decomposition) 60 °C. *Anal.* Calc. for $C_{29}H_{26}ClPRu$: C, 64.26; H, 4.84. Found: C, 64.01; H, 4.71.%. ^1H NMR (C_6D_6, 400 MHz): δ 8.34–6.55 (br m, 19H, C_6H_5 and C_6H_4 part of C_9H_7), 5.65 (s, 1H, H^1 or H^3 of C_3H_3 part of C_9H_7), 4.93 [t, 1H, $^3J(HH) = 2.6$ Hz, H^2 of C_3H_3 part of C_9H_7], 4.05 (s, 1H, H^1 or H^3 of C_3H_3 part of C_9H_7), 3.04, 2.42 (both m, 2H each, C_2H_4). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 137.9 [d, $^1J(PC) = 40.6$ Hz, *ipso*-C of C_6H_5], 130.0 [d, $^4J(PC) = 1.9$ Hz, *para*-C of C_6H_5], 128.2 [d, $^2J(PC) = 12.4$ Hz, *ortho*-C of C_6H_5], 127.8 [d, $^3J(PC) = 10.0$ Hz, *meta*-C of C_6H_5], 126.4, 124.9, 121.3, 119.6 (all s, C^{6-9} of C_9H_7), 109.3 [d, $^2J(PC) = 5.1$ Hz, C^1 or C^5 of C_9H_7], 107.2 [d, $^2J(PC) = 6.1$ Hz, C^1 or C^5 of C_9H_7], 92.3 (s, C^3 of C_9H_7), 79.8, 65.8 (both s, $C^{2,4}$ of C_9H_7), 53.3 (s,C_2H_4); for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 63.2 (s).

3.3. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(C_2H_4)(PPh_3)(\kappa^1\text{-}O_2CCF_3)]$ (5)

A slow stream of ethene was passed through a solution of 99 mg (0.19 mmol) of **3** in 10 ml of toluene at −40 °C. After 2 min, 15 μl (0.19 mmol) of trifluoroacetic acid was added. The solution was slowly warmed to r.t. and stirred for 5 min. The solvent was evaporated in vacuo, the remaining yellow solid was washed twice with 5-ml portions of pentane and dried; yield 112 mg (95%), m.p. (decomposition) 121 °C. IR (C_6H_6): ν(C=O) 1691 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 7.54–6.77 (br m, 19H, C_6H_5 and C_6H_4 part of C_9H_7), 5.65 (br s, 1H, H^2 of C_3H_3 part of C_9H_7), 4.26, 4.03 (both br s, 1H each, H^1 and H^3 of C_3H_3 part of C_9H_7), 3.00, 2.91 (both m, 2H each, C_2H_4). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 163.2 [q, ^2J(FC) = 36.1 Hz, *C*CF_3], 136.7 [d, ^1J(PC) = 40.7 Hz, *ipso*-C of C_6H_5], 133.6 [d, ^3J(PC) = 9.2 Hz, *meta*-C of C_6H_5], 130.3 [d, ^4J(PC) = 1.9 Hz, *para*-C of C_6H_5], 129.3, 127.7, 127.0, 122.3 (all s, C^{6-9} of C_9H_7), 128.4 [d, ^2J(PC) = 10.2 Hz, *ortho*-C of C_6H_5], 115.4 [q, ^1J(FC) = 293.1 Hz, CF_3], 109.0 [d, ^2J(PC) = 2.8 Hz, C^1 or C^5 of C_9H_7], 107.0 [d, ^2J(PC) = 3.7 Hz, C^1 or C^5 of C_9H_7], 89.2 (s, C^3 of C_9H_7), 72.2, 64.9 (both s, $C^{2,4}$ of C_9H_7), 56.0 (s, C_2H_4); for assignment of indenyl carbon atoms see Fig. 1. ^{19}F NMR (C_6D_6, 188.3 MHz): δ −74.5 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 60.2 (s).

3.4. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(C_2H_4)(PPh_3)_2]PF_6$ (6)

A slow stream of ethene was passed through a solution of 106 mg (0.13 mmol) of **2** · 1/2CH_2Cl_2 in 10 ml of dichloromethane at r.t. for 2 min. After 33 mg (0.13 mmol) of $AgPF_6$ was added to the solution, the reaction mixture was stirred for 5 min. The off-white precipitate (AgCl) was filtered and the filtrate was evaporated in vacuo. The remaining yellow solid was washed three times with 5-ml portions of pentane and dried; yield 113 mg (95%), m.p. (decomposition) 136 °C. Conductivity: Λ (CH_3NO_2) 89 $cm^2 \cdot \Omega^{-1} \cdot mol^{-1}$. ^1H NMR (acetone-d_6, 200 MHz): δ 7.62–6.80 (br m, 34H, C_6H_5 and C_6H_4 part of C_9H_7), 5.73 (m, 2H, H^1 and H^3 of C_3H_3 part of C_9H_7), 5.04 (m, 1H, H^2 of C_3H_3 part of C_9H_7), 2.45 [t, 4 H, ^2J(PH) = 3.1 Hz, C_2H_4]. ^{13}C NMR (acetone-d_6, 50.3 MHz): δ 135.7 [d, ^1J(PC) = 40.0 Hz, *ipso*-C of C_6H_5], 134.5, 129.5 (both m, *ortho*- and *meta*-C of C_6H_5), 131.8 (s, *para*-C of C_6H_5), 132.7, 124.0 (both s, $C^{6,9}$ and $C^{7,8}$ of C_9H_7), 106.8 (s, C^1 and C^5 of C_9H_7), 90.9 (s, C^3 of C_9H_7), 82.2 (s, $C^{2,4}$ of C_9H_7), 50.8 (s, C_2H_4); for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (acetone-d_6, 81.0 MHz): δ 45.4 (s, PPh_3), 142.6 [sept, ^1J(PF) = 707.6 Hz, PF_6^-].

3.5. Preparation of $[(\eta^5\text{-}C_9H_7)Ru\{O{=}C(CH_3)_2\}(PPh_3)_2]PF_6$ (7)

A solution of 100 mg (0.11 mmol) of **6** in 5 ml of acetone was stirred for 10 min at 50 °C. After the solution was cooled to r.t., the solvent was evaporated in vacuo and the remaining yellow solid washed three times with 3-ml portions of diethyl ether; yield 98 mg (94%), m.p. (decomposition) 140 °C. *Anal.* Calc. for $C_{48}H_{43}F_6OP_3Ru$: C, 61.08; H, 4.59. Found: C, 60.85; H, 4.41%. Conductivity: Λ (CH_3NO_2) 75 $cm^2 \cdot \Omega^{-1} \cdot mol^{-1}$. IR (KBr): ν(C=O) 1720 cm^{-1}. ^1H NMR (acetone-d_6, 400 MHz): δ 7.68–6.80 (br m, 34H, C_6H_5 and C_6H_4 part of C_9H_7), 5.70 (m, 2H, H^1 and H^3 of C_3H_3 part of C_9H_7), 4.73 (m, 1H, H^2 of C_3H_3 part of C_9H_7), 2.43 (s, 6H, CH_3). ^{13}C NMR (acetone-d_6, 100.6 MHz): δ 206.0 (s, CH_3CO), 135.3 (br s, *ipso*-C of C_6H_5), 134.3, 129.3 (both br s, *ortho*- and *meta*-C of C_6H_5), 132.5 (s, *para*-C of C_6H_5), 130.7, 125.6 (both s, $C^{6,9}$ and $C^{7,8}$ of C_9H_7), 106.7 (s, C^1 and C^5 of C_9H_7), 90.7 (s, C^3 of C_9H_7), 81.9 (s, $C^{2,4}$ of C_9H_7), 30.4 (s, CH_3); for assignment of indenyl carbon atoms see Fig. 1. ^{31}P NMR (acetone-d_6, 162.0 MHz): δ 46.3 (s, PPh_3), −144.0 [sept, ^1J(PF) = 704.7 Hz, PF_6^-].

3.6. Preparation of $[(\eta^5\text{-}C_9H_7)Ru\{\eta^2\text{-}(Z)\text{-}C_2H_2\text{-}(CO_2Et)_2\}(PPh_3)Cl]$ (8)

A solution of 100 mg (0.18 mmol) of **4** in 10 ml of toluene was treated with a solution of 37 μl (0.36 mmol) of $CH(CO_2Et)N_2$ in 2 ml of toluene at r.t. After the reaction mixture was stirred for 5 min, the solvent was evaporated, the remaining brown solid was washed twice with 5-ml portions of diethyl ether and dried; yield 105 mg (85%), m.p. 32 °C. *Anal.* Calc. for $C_{35}H_{34}ClO_4PRu$: C, 61.27; H, 5.00. Found: C, 61.10; H, 4.97%. IR (C_6H_6): ν(C=O) 1729, 1689 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 7.65–6.40 (br m, 19H, C_6H_5 and C_6H_4 part of C_9H_7), 5.90 (m, 1H, H^2 of C_3H_3 part of C_9H_7), 5.15, 4.64 (both m, 1H each, H^1 and H^3 of C_3H_3 part of C_9H_7), 4.06, 4.01 [both q, 2H each, ^3J(HH) = 4.7 Hz, CH_2CH_3], 3.80, 3.55 (both m, 1H each, =CH), 1.00, 0.95 [both t, 3H each, ^3J(HH) = 4.7 Hz, CH_2CH_3]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 173.8, 173.5 (both s, CO_2Et), 138.7 (br s, *ipso*-C of C_6H_5), 135.8 [d, ^2J(PC) = 10.1 Hz, *ortho*-C of C_6H_5], 130.0 (s, *para*-C of C_6H_5), 132.3 [d, ^3J(PC) = 9.3 Hz, *meta*-C of C_6H_5], 130.3, 129.0, 128.4, 125.4 (all s, C^{6-9} of C_9H_7), 113.6, 113.0 (both s, C^1 and C^5 of C_9H_7), 95.6 [d, ^2J(PC) = 3.0 Hz, C^3 of C_9H_7], 83.8 [d, ^2J(PC) = 10.0 Hz, C^2 or C^4 of C_9H_7], 72.2 (s, C^2 or C^4 of C_9H_7), 60.7, 60.3 (both s, CH_2CH_3), 54.2, 53.9 (both s, =CH), 14.4, 14.2 (both s, CH_2CH_3); for assignment of indenyl carbon atoms see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 47.0 (s).

3.7. Preparation of [(η^5-C_9H_7)Ru(=CPh_2)(PPh_3)Cl] (**9**)

A solution of 108 mg (0.20 mmol) of **4** in 10 ml of toluene was treated with a solution of 39 mg (0.20 mmol) of Ph_2CN_2 in 2 ml of toluene at r.t. After the reaction mixture was stirred for 5 min, the solvent was evaporated. The residue was dissolved in 3 ml of dichloromethane and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With CH_2Cl_2 a green fraction was eluted and brought to dryness in vacuo. The remaining green solid was washed twice with 5-ml portions of pentane and dried; yield 113 mg (83%), m.p. (decomposition) 116 °C. *Anal*. Calc. for $C_{40}H_{32}ClPRu$: C, 70.63; H, 4.74; Ru, 14.86. Found: C, 70.37; H, 4.56; Ru, 14.99%. MS (FAB, 2-nitrophenyloctylether): *m/z* 680 (M^+), 645 ($M^+ - Cl$), 565 ($M^+ - C_9H_7$). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.40–6.45 (br m, 29H, C_6H_5 and C_6H_4 part of C_9H_7), 5.32, 5.09 (both br s, 1H each, H^1 and H^3 of C_3H_3 part of C_9H_7), 4.73 [t, 1H, ^3J(HH) = 3.0 Hz, H^2 of C_3H_3 part of C_9H_7]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 316.5 [d, ^2J(PC) = 14.6 Hz, Ru=C], 162.9 [d, ^3J(PC) = 4.5 Hz, *ipso*-C of CC_6H_5], 135.2 [d, ^1J(PC) = 43.3 Hz, *ipso*-C of PC_6H_5], 134.6 [d, ^2J(PC) = 10.3 Hz, *ortho*-C of PC_6H_5], 129.1 [d, ^3J(PC) = 2.4 Hz, *para*-C of PC_6H_5], 127.9, 127.6, 123.1, 122.4 (all s, C^{6-9} of C_9H_7), 127.8 [d, ^3J(PC) = 9.6 Hz, *meta*-C of PC_6H_5], 127.5 (s, *para*-C of CC_6H_5), 127.0, 125.6 (both s, *ortho*- and *meta*-C of CC_6H_5), 124.6 (s, C^1 or C^5 of C_9H_7), 117.8 [d, ^2J(PC) = 2.5 Hz, C^1 or C^5 of C_9H_7], 105.0 [d, ^2J(PC) = 1.9 Hz, C^3 of C_9H_7], 71.1 [d, ^2J(PC) = 11.4 Hz, C^2 or C^4 of C_9H_7], 69.3 (s, C^2 or C^4 of C_9H_7); for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 52.3 (s).

3.8. Preparation of [(η^5-C_9H_7)Ru(=CHPh)(PPh_3)Cl] (**10**)

This compound was prepared analogously as described for **9**, with 103 mg (0.19 mmol) of **4** and 22 mg (0.19 mmol) of $PhCHN_2$ as starting materials. The isolated green solid still contained some impurities which could not be completely removed either by column chromatography or fractional crystallization; yield 98 mg. Data for **10**: MS (FAB, 2-nitrophenyloctylether): *m/z* 604 (M^+), 568 ($M^+ - HCl$). ^{1}H NMR (C_6D_6, 400 MHz): δ 17.28 [d, 1H, ^3J(PH) = 22.8 Hz, =C*H*Ph], 7.80–6.68 (br m, 24H, C_6H_5 and C_6H_4 part of C_9H_7), 6.12, 5.61 (both br s, 1H each, H^1 and H^3 of C_3H_3 part of C_9H_7), 4.90 [t, 1H, ^3J(HH) = 3.0 Hz, H^2 of C_3H_3 part of C_9H_7]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 302.6 [d, ^2J(PC) = 15.3 Hz, Ru=C], 157.6 (s, *ipso*-C of CC_6H_5), 134.5 [d, ^2J(PC) = 10.2 Hz, *ortho*-C of PC_6H_5], 133.6 [d, ^1J(PC) = 51.3 Hz, *ipso*-C of PC_6H_5], 130.0 [d, ^3J(PC) = 2.6 Hz, *para*-C of PC_6H_5], 128.6 (s, *para*-C of CC_6H_5), 128.5, 128.0, 124.0, 123.0 (all s, C^{6-9} of C_9H_7), 128.3, 127.2 (both s, *ortho*- and *meta*-C of CC_6H_5), 128.2 [d, ^3J(PC) = 9.0 Hz, *meta*-C of PC_6H_5], 124.9 [d, ^2J(PC) = 6.3 Hz, C^1 or C^5 of C_9H_7], 119.5 [d, ^2J(PC) = 2.6 Hz, C^1 or C^5 of C_9H_7], 106.5 [d, ^2J(PC) = 2.5 Hz, C^3 of C_9H_7], 81.0 [d, ^2J(PC) = 15.3 Hz, C^2 or C^4 of C_9H_7], 64.4 [d, ^2J(PC) = 7.6 Hz, C^2 or C^4 of C_9H_7]; for assignment of indenyl carbon atoms see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 55.0 (s).

3.9. Preparation of [(η^5-C_9H_7)Ru(=$CHSiMe_3$)(PPh_3)Cl] (**11**)

A solution of 94 mg (0.17 mmol) of **4** in 10 ml of toluene was treated with 100 μl of a 2.0 M solution of Me_3SiCHN_2 (0.20 mmol) in hexane and then stirred for 5 min at r.t. The solvent was evaporated in vacuo and the residue extracted with 10 ml of pentane. The extract was brought to dryness in vacuo, the residue was dissolved in 5 ml of acetone and the solution was filtered. After the solvent was removed from the filtrate, an olive-green solid was obtained which was washed with small amounts of acetone (0 °C) and dried; yield 80 mg (78%), m.p. (decomposition) 48 °C. *Anal*. Calc. for $C_{31}H_{32}ClPRuSi$: C, 61.99; H, 5.37. Found: C, 61.68; H, 5.33%. ^{1}H NMR (C_6D_6, 400 MHz): δ 20.74 [d, 1H, ^3J(PH) = 21.2 Hz, =C*H*Ph], 7.93–6.74 (br m, 19H, C_6H_5 and C_6H_4 part of C_9H_7), 6.48, 6.20, 3.66 (all br s, 1H each, H^{1-3} of C_3H_3 part of C_9H_7), 0.33 (s, 9H, $SiCH_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 352.7 [d, ^2J(PC) = 11.0 Hz, Ru=C], 134.6 [d, ^2J(PC) = 10.2 Hz, *ortho*-C of C_6H_5], 134.1 [d, ^1J(PC) = 45.8 Hz, *ipso*-C of C_6H_5], 131.5 [d, ^2J(PC) = 2.5 Hz, C^1 or C^5 of C_9H_7], 129.9 [d, ^3J(PC) = 2.5 Hz, *para*-C of C_6H_5], 128.3, 127.2, 124.2, 122.9 (all s, C^{6-9} of C_9H_7), 128.0 [d, ^3J(PC) = 9.0 Hz, *meta*-C of C_6H_5], 121.1 [d, ^2J(PC) = 2.5 Hz, C^1 or C^5 of C_9H_7], 103.2 [d, ^2J(PC) = 3.0 Hz, C^3 of C_9H_7], 84.7 [d, ^2J(PC) = 15.1 Hz, C^2 or C^4 of C_9H_7], 65.9 (s, C^2 or C^4 of C_9H_7), −1.2 (s, $SiCH_3$); for assignment of indenyl carbon atoms, see Fig. 1. ^{29}Si NMR (C_6D_6, 39.8 MHz): δ −21.4 (s). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 52.3 (s).

3.10. Preparation of [(η^5-C_9H_7)Ru(=CPh_2)(PPh_3)(κ^1-O_2CCF_3)] (**12**)

This compound was prepared analogously as described for **9**, with 108 mg (0.17 mmol) of **5** and 33 mg (0.17 mmol) of Ph_2CN_2 as starting materials. Light green solid; yield 109 mg (85%), m.p. (decomposition) 104 °C. *Anal*. Calc. for $C_{42}H_{32}F_3O_2PRu$: C, 66.57; H, 4.26; Ru, 13.34. Found: C, 66.32; H, 4.31; Ru, 13.48%. IR (C_6H_6): ν(C=O) 1688 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.38–6.85 (br m, 29H, C_6H_5 and C_6H_4 part of C_9H_7), 6.66, 4.53, 4.48 (all br s, 1H each, H^{1-3} of C_3H_3 part of C_9H_7). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 321.3 [d, ^2J(PC) = 9.0 Hz, Ru=C], 162.8 (s, *ipso*-C of

CC_6H_5), 133.6 [d, ^2J(PC) = 10.8 Hz, *ortho*-C of PC_6H_5], 132.2 [d, ^1J(PC) = 31.7 Hz, *ipso*-C of PC_6H_5], 129.8 [d, ^3J(PC) = 1.9 Hz, *para*-C of PC_6H_5], 129.2, 127.5, 126.7, 121.6 (all s, C^{6-9} of C_9H_7), 128.3 (s, *para*-C of CC_6H_5), 128.2 [d, ^3J(PC) = 9.6 Hz, *meta*-C of PC_6H_5], 127.3, 125.0 (both s, *ortho*- and *meta*-C of CC_6H_5), 122.2 [d, ^2J(PC) = 1.2 Hz, C^1 or C^5 of C_9H_7], 118.6 [d, ^2J(PC) = 3.1 Hz, C^1 or C^5 of C_9H_7], 115.7 [q, ^1J(FC) = 291.2 Hz, CF_3], 102.6 (s, C^3 of C_9H_7), 68.9 [d, ^2J(PC) = 10.2 Hz, C^2 or C^4 of C_9H_7], 63.6 (s, C^2 or C^4 of C_9H_7); for assignment of indenyl carbon atoms, see Fig. 1; signal for $COCF_3$ carbon atom not exactly located. ^{19}F NMR (C_6D_6, 376.5 MHz): δ −74.6 (s). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 37.2 (s).

3.11. Preparation of [(η^5-C_9H_7)Ru(=CHPh)(PPh_3)(κ^1-O_2CCF_3)] (**13**)

This compound was prepared analogously as described for **9**, with 100 mg (0.16 mmol) of **5** and 19 mg (0.16 mmol) of $PhCHN_2$ as starting materials. Olive-green solid; yield 76 mg (69%); m.p. (decomposition) 92 °C. *Anal*. Calc. for $C_{36}H_{28}F_3O_2PRu$: C, 63.43; H, 4.14; Ru, 14.83. Found: C, 66.32; H, 4.31; Ru, 13.48%. MS (FAB, 2-nitrophenyloctylether): *m*/*z* 682 (M^+), 568 ($M^+ - CF_3CO_2H$). IR (C_6H_6): (C=O) 1707 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 17.21 [d, 1H, ^3J(PH) = 15.2 Hz, =C*H*Ph], 7.78–6.61 (br m, 24H, C_6H_5 and C_6H_4 part of C_9H_7), 6.40 [d, 1H, ^3J (HH) = 7.6 Hz, H^1 or H^3 of C_3H_3 part of C_9H_7], 4.96 (br s, 1H, H^2 of C_3H_3 part of C_9H_7), 3.71 (br s, 1H, H^1 or H^3 of C_3H_3 part of C_9H_7). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 304.8 [d, ^2J(PC) = 12.8 Hz, Ru=;C], 163.6 [dq, ^3J (FC) = 35.3, ^5J(PC) = 1.9 Hz, $COCF_3$], 156.7 (s, *ipso*-C of CC_6H_5), 133.7 [d, ^2J(PC) = 10.2 Hz, *ortho*-C of PC_6H_5], 133.3 [d, ^1J(PC) = 43.9 Hz, *ipso*-C of PC_6H_5], 130.2 [d, ^3J(PC) = 2.6 Hz, *para*-C of PC_6H_5], 129.5, 127.6 (both s, *ortho*- and *meta*-C of CC_6H_5), 129.3 (s, *para*-C of CC_6H_5), 128.6, 128.1, 124.5, 122.8 (all s, C^{6-9} of C_9H_7), 128.3 [d, ^3J(PC) = 10.0 Hz, *meta*-C of PC_6H_5], 123.1 [d, ^2J(PC) = 3.2 Hz, C^1 or C^5 of C_9H_7], 119.8 [d, ^2J(PC) = 1.3 Hz, C^1 or C^5 of C_9H_7], 115.9 [q, ^1J(FC) = 292.4 Hz, CF_3], 103.1 [d, ^2J(PC) = 2.1 Hz, C^3 of C_9H_7], 76.9 [d, ^2J(PC) = 12.7 Hz, C^2 or C^4 of C_9H_7], 63.8 [d, ^2J(PC) = 3.1 Hz, C^2 or C^4 of C_9H_7]; for assignment of indenyl carbon atoms, see Fig. 1. ^{19}F NMR (C_6D_6, 376.5 MHz): δ −74.1 (s). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 46.6 (s).

3.12. Preparation of [(η^5-C_9H_7)Ru(=CHSiMe$_3$)(PPh_3)(κ^1-O_2CCF_3)] (**14**)

3.12.1. Method a

The procedure was the same as that described for **11**, with 100 mg (0.16 mmol) of **5** and 100 μl of a 2.0 M solution of Me_3SiCHN_2 (0.20 mmol) in hexane as starting materials. Green solid; yield 72 mg (66%).

3.12.2. Method b

A solution of 95 mg (0.18 mmol) of **3** in 5 ml of toluene was treated at −40 °C with 14 μl (0.18 mmol) of trifluoracetic acid. The solution was slowly warmed to 0 °C and then 90 μl of a 2.0 M solution of Me_3SiCHN_2 (0.18 mmol) in hexane was added. After the evolution of gas (N_2) was finished, the solvent was evaporated in vacuo. The residue was extracted with 10 ml of pentane, the extract was concentrated to ca. 1 ml in vacuo and the solution was stored for 12 h at −60 °C. Green crystals precipitated, which were separated from the mother liquor, washed twice with small amounts of pentane (0 °C) and dried; yield 90 mg (75%), m.p. (decomposition) 96 °C. *Anal*. Calc. for $C_{33}H_{32}F_3O_2PRuSi$: C, 58.48; H, 4.76; Ru, 14.91. Found: C, 58.52; H, 4.97; Ru, 15.04%. MS (FAB, 2-nitrophenyloctylether): *m*/*z* 678 (M^+), 592 ($M^+ - CHSiMe_3$), 564 ($M^+ - CF_3CO_2H$). ^{1}H NMR (C_6D_6, 400 MHz): δ 20.45 [d, 1H, ^3J(PH) = 17.3 Hz, =C*H*Ph], 7.47–6.51 (br m, 19H, C_6H_5 and C_6H_4 part of C_9H_7), 6.39, 5.88, 3.66 (all br s, 1H each, H^{1-3} of C_3H_3 part of C_9H_7), 0.18 (s, 9H, $SiCH_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 358.6 [d, ^2J(PC) = 10.2 Hz, Ru=C], 162.8 [q, ^3J(FC) = 35.2 Hz, $COCF_3$], 133.9 [d, ^2J(PC) = 10.5 Hz, *ortho*-C of C_6H_5], 132.9 [d, ^1J(PC) = 45.8 Hz, *ipso*-C of C_6H_5], 130.2 [d, ^3J(PC) = 1.9 Hz, *para*-C of C_6H_5], 129.3, 128.6, 123.7, 123.2 (all s, C^{6-9} of C_9H_7), 128.3 [d, ^3J(PC) = 10.5 Hz, *meta*-C of C_6H_5], 126.1 [d, ^2J(PC) = 2.5 Hz, C^1 or C^5 of C_9H_7], 121.1 [d, ^2J(PC) = 3.8 Hz, C^1 or C^5 of C_9H_7], 115.4 [q, ^1J(FC) = 291.6 Hz, CF_3], 100.5 [d, ^2J(PC) = 3.8 Hz, C^3 of C_9H_7], 80.5 [d, ^2J(PC) = 12.4 Hz, C^2 or C^4 of C_9H_7], 66.0 (s, C^2 or C^4 of C_9H_7), −1.1 (s, $SiCH_3$); for assignment of indenyl carbon atoms see Fig. 1. ^{19}F NMR (C_6D_6, 376.5 MHz): δ −74.0 (s). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −21.0 (s). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 48.2 (s).

3.13. Preparation of [(η^5-C_9H_7)RuH(CH_2=CPh_2)(PPh_3)] (**15**)

A solution of 105 mg (0.15 mmol) of **9** in 5 ml of toluene was treated with 0.19 ml of a 1.60 M solution of methyllithium (0.30 mmol) in diethyl ether at r.t. After the solution was stirred for 30 min, 5 ml of acetone was added, and the solution was again stirred for 15 min. The solvent was evaporated in vacuo and the residue was extracted four times with 10-ml portions of pentane. The combined extracts were concentrated to ca. 5 ml and the solution was then stored for 12 h at −60 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed twice with small amounts of pentane (0 °C) and dried; yield 79 mg (80%); m.p. (decomposition) 58 °C. *Anal*. Calc. for $C_{41}H_{35}PRu$: C, 74.64; H, 5.35. Found:

C, 74.22; H, 5.07%. MS (FAB, 2-nitrophenyloctylether): *m/z* 660 (M^+), 544 ($M^+ - C_9H_8$), 479 ($M^+ - H-CH_2{=}CPh_2$). ^1H NMR (C_6D_6, 400 MHz): δ 7.64–6.72 (br m, 29H, C_6H_5 and C_6H_4 part of C_9H_7), 5.83 [t, 1H, ^3J(HH) = 2.6 Hz, H^2 of C_3H_3 part of C_9H_7], 4.41, 3.55 (both br s, 1H each, H^1 and H^3 of C_3H_3 part of C_9H_7), 3.18 (br s, 1H, one H of $=CH_2$), 1.75 [dd, 1H, ^3J(PH) = 13.2, ^3J(HH) = 1.6 Hz, one H of $=CH_2$], – 12.56 [d, 1H, ^2J(PH) = 36.0 Hz, RuH]. C^{13} NMR (C_6D_6, 100.6 MHz): δ 153.5, 149.8 (both s, *ipso*-C of CC_6H_5), 137.6 [d, ^1J(PC) = 43.0 Hz, *ipso*-C of PC_6H_5], 133.8 [d, ^2J(PC) = 10.6 Hz, *ortho*-C of PC_6H_5], 132.8, 128.8, 127.8, 127.2 (all s, *ortho*- and *meta*-C of CC_6H_5), 128.7 [d, ^3J(PC) = 2.9 Hz, *para*-C of PC_6H_5], 127.5 [d, ^3J(PC) = 9.6 Hz, *meta*-C of PC_6H_5], 125.1, 125.0 (both s, *para*-C of CC_6H_5), 124.4, 123.9, 123.0, 122.4 (all s, C^{6-9} of C_9H_7), 110.6, 107.5 (both s, C^1 and C^5 of C_9H_7), 88.5 [d, ^2J(PC) = 2.9 Hz, C^3 of C_9H_7], 88.3 [d, ^2J(PC) = 9.6 Hz, C^2 or C^4 of C_9H_7], 74.0 (s, C^2 or C^4 of C_9H_7), 34.4 (s, $=CH_2$); for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 67.7 (s).

3.14. Preparation of [(η^5-C_9H_7)Ru(η^3-1-PhC_3H_4)(PPh_3)] (**17**)

A solution of 107 mg (0.18 mmol) of **10** in 5 ml of toluene was treated with 0.55 ml of a 0.65 M solution of $CH_2{=}CHMgBr$ (0.36 mmol) in THF and stirred for 45 min at r.t. The reaction mixture was worked up as described for **3**. Yellow microcrystalline solid; yield 81 mg (76%); m.p. (decomposition) 172 °C. *Anal.* Calc. for $C_{36}H_{31}PRu$: C, 72.58; H, 5.26. Found: C, 72.28; H, 5.29%. MS (FAB, 2-nitrophenyloctylether): *m/z* 596 (M^+), 479 ($M^+ - PhC_3H_4$), 334 ($M^+ - PPh_3$). ^1H NMR (C_6D_6, 400 MHz): δ 7.74–6.62 (br m, 24H, C_6H_5 and C_6H_4 part of C_9H_7), 4.80 [dddd, 1H, ^3J(PH) = 1.5, ^3J(HH) = 9.4, 9.2 and 6.9 Hz, CHC*H*CH_2], 4.45, 4.40 (both br s, 1H each, H^1 and $H^3$of C_3H_3 part of C_9H_7), 4.32 [t, 1H, ^3J(HH) = 2.9 Hz, H^2 of C_3H_3 part of C_9H_7], 2.55 [dd, 1H, ^3J(PH) = 1.2, ^3J(HH) = 6.9 Hz, C*H* $CHCH_2$], 1.98 [dd, 1H, ^3J(PH) = 12.6, ^3J(HH) = 9.4 Hz, H_{syn} of allyl-CH_2], 0.52 [dd, 1H, ^3J(PH) = 15.1, ^3J(HH) = 9.2 Hz, H_{anti} of allyl-CH_2]. C^{13} NMR (C_6D_6, 100.6 MHz): δ 148.3 (s, *ipso*-C of CC_6H_5), 136.8 [d, ^1J(PC) = 38.2 Hz, *ipso*-C of PC_6H_5], 134.9 [d, ^2J(PC) = 10.2 Hz, *ortho*-C of PC_6H_5], 129.1 (s, *para*-C of PC_6H_5), 128.4, 125.4 (both s, *ortho*- and *meta*-C of CC_6H_5), 127.7 [d, ^3J(PC) = 8.9 Hz, *meta*-C of PC_6H_5], 124.5, 124.4, 123.8, 123.7 (all s, C^{6-9} of C_9H_7), 122.9 (s, *para*-C of CC_6H_5), 101.4, 100.2 (both s, C^1 and C^5 of C_9H_7), 89.2 (s, C^3 of C_9H_7), 73.6, 72.8 [both d, ^2J(PC) = 3.8 Hz, C^2 and C^4 of C_9H_7], 65.9 (s, CH*C*HCH$_2$), 54.0 [d, ^2J(PC) = 2.5 Hz, *C*HCHCH$_2$], 36.0 [d, ^2J(PC) = 6.4 Hz, CH_2]; for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 64.8 (s).

3.15. Preparation of exo/endo- [(η^5-C_9H_7)RuH($CH_2{=}$CHPh)(PPh_3)] (**18a,18b**)

This compound was prepared analogously as described for **15**, with 104 mg (0.17 mmol) of **10** and 0.22 ml of a 1.60 M solution of methyllithium (0.34 mmol) in diethyl ether. Yellow microcrystalline solid; yield 64 mg (64%); m.p. (decomposition) 79 °C. *Anal.* Calc. for $C_{35}H_{31}PRu$: C, 72.01; H, 5.36. Found: C, 71.50; H, 5.81%. Owing to the NMR spectroscopic data a mixture of exo/endo isomers **18a**,**18b** in the ratio of 4:3 was obtained. Data for **18a**: ^1H NMR (C_6D_6, 400 MHz): δ 7.48–6.55 (br m, C_6H_5 and C_6H_4 part of C_9H_7), 5.29 [dt, 1H, ^2J(PH) = 1.6, ^3J(HH) = 2.6 Hz, H^2 of C_3H_3 part of C_9H_7], 4.75, 4.56 (both br s, 1H each, H^1 and $H^3$of C_3H_3 part of C_9H_7), 3.53 (m, 1H, $=CHPh$), 3.05 [d, 1H, ^3J(HH) = 10.1 Hz, one H of $=CH_2$], 1.10 [dd, 1H, ^3J(PH) = 10.7, ^3J(HH) = 10.1 Hz, one H of $=CH_2$], – 12.21 [d, 1H, ^2J(PH) = 39.1 Hz, RuH]. C^{13} NMR (C_6D_6, 100.6 MHz): δ 150.0 (s, *ipso*-C of CC_6H_5), 136.6 [d, ^1J(PC) = 42.9 Hz, *ipso*-C of PC_6H_5], 133.6 [d, ^2J(PC) = 10.5 Hz, *ortho*-C of PC_6H_5], 129.2 [d, ^3J(PC) = 1.9 Hz, *para*-C of PC_6H_5], 128.1, 124.3 (both s, *ortho*- and *meta*-C of CC_6H_5), 127.9 [d, ^3J(PC) = 9.5 Hz, *meta*-C of PC_6H_5], 126.2 (s, *para*-C of CC_6H_5), 125.2, 124.3, 123.6, 123.2 (all s, C^{6-9} of C_9H_7), 110.0 (s, C^1 or C^5 of C_9H_7), 109.5 [d, ^2J(PC) = 1.9 Hz, C^1 or C^5 of C_9H_7], 87.0 [d, ^2J(PC) = 2.9 Hz, C^3 of C_9H_7], 86.0 [d, ^2J(PC) = 10.5 Hz, C^2 or C^4 of C_9H_7], 71.8 (s, C^2 or C^4 of C_9H_7), 48.9 (s, $=CHPh$), 26.9 [d, ^2J(PC) = 4.8 Hz, $=CH_2$]; for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 71.3 (s). – Data for **18b**: ^1H NMR (C_6D_6, 400 MHz): δ 7.48–6.55 (br m, C_6H_5 and C_6H_4 part of C_9H_7), 5.77 [d, 1H, ^3J (HH) = 2.6 Hz, H^1 or H^3 of C_3H_3 part of C_9H_7], 5.74 [dt, 1H, ^2J (PH) = 1.6, ^3J(HH) = 2.6 Hz, H^2 of C_3H_3 part of C_9H_7], 4.34 (br s, 1H, H^1 or $H^3$of C_3H_3 part of C_9H_7), 2.81 [t, 1H, ^3J(HH) = 8.1 Hz, = C*H*Ph], 1.81 [dd, 1H, ^2J(PH) = 2.4, ^3J(HH) = 8.1 Hz, one H of $=CH_2$], 0.86 [t, 1H, ^3J(HH) = 8.1 Hz, one H of $=CH_2$], – 13.06 [d, 1H, ^2J(PH) = 39.9 Hz, RuH]. C^{13} NMR (C_6D_6, 100.6 MHz): δ 148.9 (s, *ipso*-C of CC_6H_5), 136.9 [d, ^1J(PC) = 42.9 Hz, *ipso*-C of PC_6H_5], 133.7 [d, ^2J(PC) = 10.5 Hz, *ortho*-C of PC_6H_5], 129.3 [d, ^3J(PC) = 2.9 Hz, *para*-C of PC_6H_5], 128.2, 126.2 (both s, *ortho*- and *meta*-C of CC_6H_5), 127.8 [d, ^3J(PC) = 9.5 Hz, *meta*-C of PC_6H_5], 126.9 (s, *para*-C of CC_6H_5), 124.1, 123.8, 123.7, 121.8 (all s, C^{6-9} of C_9H_7), 110.5 [d, ^2J(PC) = 2.9 Hz, C^1 or C^5 of C_9H_7], 109.6 [s, C^1 or C^5 of C_9H_7], 87.1 [d, ^2J(PC) = 1.9 Hz, C^3 of C_9H_7], 79.3 [d, ^2J(PC) = 10.5 Hz, C^2 or C^4 of C_9H_7], 69.3 [d, ^2J(PC) = 1.9 Hz, C^2 or C^4 of C_9H_7], 47.2 [d, ^2J(PC) = 1.9 Hz, = *C*HPh], 27.0 [s, $=CH_2$]; for assignment of indenyl carbon atoms, see Fig. 1. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 67.9 (s).

3.16. Preparation of [(η^5-C_9H_7)RuH(CH_2=CHSiMe_3)(PPh_3)] (**19**)

This compound was prepared analogously as described for **15**, with 120 mg (0.20 mmol) of **11** and 0.25 ml of a 1.60 M solution of methyllithium (0.40 mmol) in diethyl ether. Light yellow microcrystalline solid; yield 95 mg (82%); m.p. (decomposition) 68 °C. *Anal*. Calc. for $C_{32}H_{35}PRuSi$: C, 66.30; H, 6.09; Ru, 17.43. Found: C, 66.61; H, 6.28; Ru, 17.88%. MS (70 eV): *m/z* 580 (M^+), 507 ($M^+ - SiMe_3$), 478 ($M^+ - H-CH_2$=CHSiMe_3). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.34–6.69 (br m, 19H, C_6H_5 and C_6H_4 part of C_9H_7), 5.72 (br s, 1H, H^2 of C_3H_3 part of C_9H_7), 4.88, 4.71 (both br s, 1H each, H^1 and $H^3$of C_3H_3 part of C_9H_7), 1.80, 1.24 (both s, 1H each, =CH_2), 0.43 (s, 1H, =C*H*SiMe_3], 0.24 (s, 9H, $SiCH_3$), − 12.86 [d, 1H, ^2J(PH) = 37.5 Hz, RuH]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 136.3 [d, ^1J(PC) = 44.8 Hz, *ipso*-C of C_6H_5], 133.8 [d, ^2J(PC) = 10.5 Hz, *ortho*-C of C_6H_5], 129.1 [d, ^3J(PC) = 1.9 Hz, *para*-C of C_6H_5], 127.7 [d, ^3J(PC) = 8.6 Hz, *meta*-C of C_6H_5], 125.2, 125.1, 122.5, 122.3 (all s, C^{6-9} of C_9H_7), 108.3 [d, ^2J(PC) = 3.8 Hz, C^1 or C^5 of C_9H_7], 104.7 [d, ^2J(PC) = 4.8 Hz, C^1 or C^5 of C_9H_7], 86.6 [d, ^2J(PC) = 2.9 Hz, C^3 of C_9H_7], 79.6 [d, ^2J(PC) = 6.7 Hz, C^2 or C^4 of C_9H_7], 74.4 [d, ^2J(PC) = 11.4 Hz, C^2 or C^4 of C_9H_7), 36.3 [d, ^2J(PC) = 1.9 Hz, =CH_2], 8.7 (s, =C*H*SiMe_3), 1.4 (s, $SiCH_3$); for assignment of indenyl carbon atoms see Fig. 1. ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 24.7 [d, ^3J(PSi) = 16.6 Hz]. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 71.3 (s).

3.17. Preparation of [(η^5-C_9H_7)Ru(η^3-$Me_3SiCHC_6H_5$)(PPh_3)] (**20**)

A solution of 96 mg (0.16 mmol) of **11** in 5 ml of toluene was treated with 0.18 ml of a 1.80 M solution of phenyllithium (0.32 mmol) in cyclohexane/diethyl ether (7:3). The reaction mixture was worked up as described for **15**. Light yellow microcrystalline solid; yield 87 mg (85%); m.p. (decomposition) 111 °C. *Anal*. Calc. for $C_{37}H_{37}PRuSi$: C, 69.24; H, 5.81; Ru, 15.75. Found: C, 68.93; H, 5.83; Ru, 15.57%. MS (FAB, 2-nitrophenyloctylether): *m/z* 642 (M^+), 479 ($M^+ - PhCHSiMe_3$), 380 ($M^+ - PPh_3$). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.58 [d, 1H, ^3J(HH) = 8.4 Hz, one H of uncoordinated part of CC_6H_5], 7.45–6.37 (br m, 22H, PC_6H_5, C_6H_4 part of C_9H_7, and 3H of uncoordinated part of CC_6H_5), 5.37 [t, 1H, ^3J (HH) = 2.6 Hz, H^2 of C_3H_3 part of C_9H_7], 4.37, 3.94 (both br s, 1H each, H^1 and H^3 of C_3H_3 part of C_9H_7), 2.98 [dd, 1H, ^3J(PH) = 11.4, ^4J(HH) = 5.6 Hz, CH of coordinated part of CC_6H_5], 0.38 (s, 9H, $SiCH_3$), − 0.81 [d, ^3J(PH) = 13.6 Hz, C*H*SiMe_3]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 139.4, 132.3, 126.2, 125.0, 124.2, 124.0, 122.5, 120.1 (all s, C^{6-9} of C_9H_7 and 4C of uncoordinated part of CC_6H_5), 136.5 [d, ^1J(PC) = 35.2 Hz, *ipso*-C of PC_6H_5], 135.1 [d, ^2J(PC) = 10.5 Hz, *ortho*-C of PC_6H_5], 129.2 [d, ^4J(PC) = 1.9 Hz, *para*-C of PC_6H_5], 127.7 [d, ^3J(PC) = 8.6 Hz, *meta*-C of PC_6H_5], 102.8, 98.7 (both s, C^1 and C^5 of C_9H_7), 95.5 [d, ^2J(PC) = 1.9 Hz, *C*CHSiMe_3], 82.4 [d, ^2J (PC) = 1.9 Hz, C^2 or C^4 of C_9H_7], 79.1 [d, ^2J(PC) = 11.5 Hz, C^3 of C_9H_7], 71.5 (s, C^2 or C^4 of C_9H_7), 65.9 (s, CH of coordinated part of CC_6H_5), 32.4 [d, ^2J (PC) = 2.8 Hz, *C*HSiMe_3], 2.5 (s, $SiCH_3$); for assignment of indenyl carbon atoms, see Fig. 1. ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 0.6 (s). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 61.8 (s).

3.18. Crystal structure analysis of 7

Crystals were obtained from acetone upon cooling a saturated solution from 50 to 20 °C. Crystal structure determination of **7**: $C_{48}H_{43}F_6OP_3Ru$, M_r = 949.85; monoclinic, space group $P2_1$ (no. 4), Z = 2, a = 10.539(7) Å, b = 17.621(2) Å, c = 11.520(2) Å, β = 96.987(9)°, V = 2124(2) Å^3, D_{calc} = 1.486 g cm^{-3}, λ = 0.71073 Å, T = 293(2) K, μ(Mo Kα) = 0.540 mm^{-1}. Crystal size 0.20 × 0.22 × 0.46 mm^3; $2\Theta_{max}$ = 60°; 6685 reflections were measured, 5433 of these were independent (R_{int} = 0.0315) and employed in the structure refinement (534 parameters). The R values are R_1 = 0.0476 and wR_2 = 0.0763 [$I > 2\sigma(I)$] and R_1 = 0.1048 and wR_2 = 0.0916 (all data); reflex/parameter ratio = 10.17; min/max residual electron density: 0.379/−0.406 e Å^{-3}. Data were collected on a Enraf-Nonius CAD 4 diffractometer. A semi-empirical absorption correction was applied. The structure was solved by direct methods (SHELXS-86) [29] and refined against F^2 by least-squares (SHELXL-93) [30]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å) and used only in structure factor calculations.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 243763 for compound **7**. Copies of this information may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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