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Reaction of the RuTp(PR$_3$)Cl fragment with alkynols: Formation of carbene, vinylidene, allenylidene, and carbyne complexes

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Abstract

The reaction of RuTp(COD)Cl (**1**) with PR$_3$ (PR$_3$ = PPh$_2$^{i}Pr, P^{i}Pr$_3$, PPh$_3$) and propargylic alcohols HC≡CCPh$_2$OH, HC≡CCFc$_2$OH (Fc = ferrocenyl), and HC≡CC(Ph)MeOH has been studied.In the case of PR$_3$ = PPh$_2$^{i}Pr, P^{i}Pr$_3$ and HC≡CCPh$_2$OH, the 3-hydroxyvinylidene complexes RuTp(PPh$_2$^{i}Pr)(=C=CHC(Ph)$_2$OH)Cl (**2a**) and RuTp(P^{i}Pr$_3$)(=C=CHC(Ph)$_2$OH)Cl (**2b**) were isolated.With PR$_3$ = PPh$_2$^{i}Pr and HC≡CCFc$_2$OH as well as with PR$_3$ = PPh$_3$ and HC≡CCPh$_2$OH dehydration takes place affording the allenylidene complexes RuTp(PPh$_2$^{i}Pr)(=C=C=CFc$_2$)Cl (**3b**) and RuTp(PPh$_3$)(=C=C=CPh$_2$)Cl (**3c**).Similarly, with PPh$_2$^{i}Pr and HC≡CC(Ph)MeOH rapid elimination of water results in the formation of the vinylvinylidene complex RuTp(PPh$_2$^{i}Pr)(=C=CHC(Ph)=CH$_2$)Cl (**4**).In contrast to the reactions of the RuTp(PR$_3$)Cl fragment with propargylic alcohols, with HC≡C(CH$_2$)$_n$OH (n = 2, 3, 4, 5) six-, and seven-membered cyclic oxycarbene complexes RuTp(PR$_3$)(=C$_4$H$_6$O)Cl (**5**), RuTp(PR$_3$)(=C$_5$H$_8$O)Cl (**6**), and RuTp(PR$_3$)(=C$_6$H$_{10}$O)Cl (**7**) are obtained. On the other hand, with 1-ethynylcyclohexanol the vinylvinylidene complex RuTp(PPh$_2$^{i}Pr)(=C=CHC$_6$H$_9$)Cl (**8**) is formed. The reaction of the allenylidene complexes **3a**–**c** with acid has been investigated. Addition of CF$_3$COOH to a solution of **3a**–**c** resulted in the reversible formation of the novel RuTp vinylcarbyne complexes [RuTp(PPh$_2$^{i}Pr)(≡C–CH=CPh$_2$)Cl]$^+$ (**9a**), [RuTp(PPh$_2$^{i}Pr)(≡C–CH=CFc$_2$)Cl]$^+$ (**9b**), and [RuTp(PPh$_3$)(≡C–CH=CPh$_2$)Cl]$^+$ (**9c**). The structures of **3a**, **3b**, and **5b** have been determined by X-ray crystallography.

Keywords: Carbenes; Vinylidenes; Allenylidenes

1. Introduction

Ruthenium vinylidene and allenylidene complexes play an important role in organometallic chemistry as emphasized in several recent reviews [1]. Interest in these compounds stems from the fact that they are key intermediates in stoichiometric and catalytic transformations of organic molecules. Moreover, they are readily prepared from terminal alkynes and propargylic alcohols. Representative examples involving vinylidene complexes as catalysts have been reported for the cyclization of dienylalkynes [2], the dimerization of HCC-^{t}Bu [3], the tandem cyclization-reconstructive addition of propargyl alcohols with allyl alcohols [4], and the reconstitute condensation of acetylenes and allyl alcohols [5]. Allenylidene complexes, for instance, have been shown to be active catalysts in the ring closing metathesis reaction of α,ω-diolefins [6].

In developing the chemistry of the tris(pyrazolyl)borate (Tp) ligand, we have recently shown [7] that also the neutral vinylidene complex RuTp(PPh$_3$)(=C=CHPh)Cl is an efficient catalyst precursor in the

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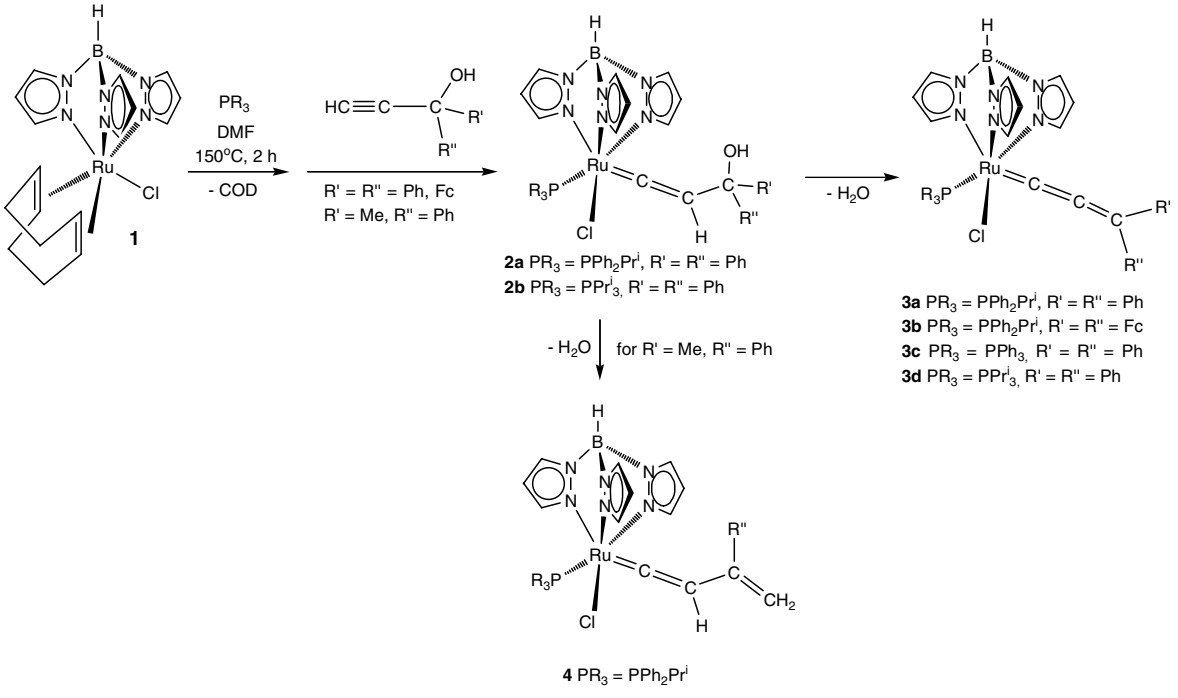
dimerization of terminal acetylenes to yield enynes. In the present contribution we extend our studies on the chemistry of RuTp complexes and report on the reaction of the RuTp(PR_3)Cl fragment with alkynols. The synthesis and characterization of a variety of neutral RuTp carbene, vinylidene, allenylidene, and carbyne complexes is described and X-ray structures of representative complexes are presented.

2. Results and discussion

Treatment of a refluxing solution of RuTp(COD)Cl (**1**) with 1 equiv of PR_3 (PR_3 = $PPh_2{}^iPr$, P^iPr_3, PPh_3) in DMF for 2h affords, after removal of the solvent, the highly reactive intermediate RuTp(PR_3)(Cl)(DMF). This complex has not been isolated [8] but is reacted in situ with the propargylic alcohols HC≡CCPh_2OH, HC≡CCFc_2OH (Fc = ferrocenyl) and HC≡ CC(Ph)-MeOH in boiling CH_2Cl_2 for 24h. In the case of PR_3 = $PPh_2{}^iPr$, P^iPr_3 and HC≡CCPh_2OH, on workup, the 3-hydroxyvinylidene complexes RuTp($PPh_2{}^iPr$)-(=C=CHC$(Ph)_2$OH)Cl (**2a**) and RuTp(P^iPr_3) (=C= CHC(Ph_2)OH)Cl (**2b**) are obtained (Scheme 1). With PR_3 = $PPh_2{}^iPr$ and HC≡CCFc_2OH as well as with PR_3 = PPh_3 and HC≡CCPh_2OH spontaneous dehydration takes place affording directly the allenylidene complexes RuTp($PPh_2{}^iPr$)(=C=C=CFc_2)Cl (**3b**) and RuTp(PPh_3)(=C=C=CPh_2)Cl (**3c**). It has to be noted that **3c** has been already prepared by Hill and co-workers [9] by reacting RuTp$(PPh_3)_2$Cl with the respective propargylic alcohol. Similarly, with $PPh_2{}^iPr$ and HC≡CC(Ph)MeOH rapid elimination of water leads to formation of the vinylvinylidene complex RuTp-($PPh_2{}^iPr$)(=C=CHC(Ph)=CH_2)Cl (**4**). However, the 3-hydroxyvinylidene complexes **2a** and **2b** can be easily dehydrated to give the respective allenylidene complexes **3a** and **3d** by passing a solution of these complexes in CH_2Cl_2 through an acidic alumina column. All complexes are thermally robust orange to purple solids which are stable to air in the solid state and in solution. They were characterized by a combination of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy as well as by elemental analysis. In the ^1H and $^{13}C\{^1H\}$ solution NMR spectra, all complexes exhibit three distinct sets of pyrazol-1-yl resonances in a 1:1:1 ratio due to three distinct pyrazol-1-yl rings differing by their *trans* ligand atoms.

Characteristic features of the 3-hydroxyvinylidene complexes **2a** and **2b** comprise, in the $^{13}C\{^1H\}$ NMR spectrum, a marked low-field resonance at 358.2 and 358.5 ppm with J_{CP} = 18.4 and 17.6 Hz, respectively, assignable to the α-carbon of the vinylidene moiety. The C_β atoms display a resonance at 119.4 and 121.7 ppm, with a carbon–phosphorus coupling constants of 1.5 Hz. Further, the C_β hydrogen atoms show a doublet centered at 5.20 (J_{HP} = 3.8 Hz) and 4.89 ppm (J_{HP} = 3.7 Hz). The $^{31}P\{^1H\}$ NMR resonances are observed at 40.5 and 40.3 ppm. Finally, the ^1H and $^{13}C\{^1H\}$ NMR resonances of Tp and the phosphine ligands are in the expected ranges.

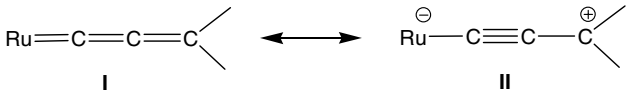
The $^{13}C\{^1H\}$ NMR spectrum of the allenylidene complexes **3a**, **b** displays two singlets in the range of



Scheme 1.

199.5–241.1 and 146.1–158.7 ppm attributable, respectively, to the C_β and C_γ atoms of the allenylidene unit, whereas one weak doublet between 290.1 and 317.3 ppm corresponds to the C_α atom directly attached to ruthenium and coupled to phosphorus (J_{CP} = 19–22 Hz).

Structural views of **3a** and **3b** are depicted in Figs. 1 and 2 with selected bond distances and angles given in the figure captions. The coordination geometry of both complexes is approximately octahedral with all angles at ruthenium between 83° and 97° and 168° and 178°. There are no structural features pointing to unusual deviations or distortions. The two Ru–N(Tp) bond lengths *cis* to the allenylidene unit are slightly shorter than the one *trans* to allenylidene. Clearly, allenylidene is a strongly π-accepting ligand giving rise to an appreciable *trans* influence. The Ru–C(25) bond distances in **3a** and **3b** are 1.862(2) and 1.889(2) Å, respectively, comparable to other ruthenium allenylidene complexes. The Ru=C=C=C group is slightly bent with Ru–C(25)–C(26) angles of 163.6(2)° and 168.8(2)°. The C(25)–C(26) bond distances are 1.259(3) and 1.254(2) Å, while the C(26)–C(27) bond lengths are significantly longer being 1.349(3) and 1.365(2) Å. This is consistent with a substantial contribution from the alkynyl mesomer **II** as is usually the case for complexes of that type.



The overall structural data compare well with those reported for other ruthenium allenylidene complexes such as $[Cp^*Ru(=C=C=CMePh)(dippe)]^+$ (dippe = 1,2-bis-(diisopropylphosphanyl)ethane), (1.884(5), 1.257(6), and 1.338(7) Å) [10], $[(\eta^5\text{-}C_9H_7)Ru\{=C=C=C(C_{13}H_{20})\}(PPh_3)_2]^+$ (1.889(5), 1.256(7), and 1.339(7) Å) [11], $[Cp^*Ru\text{-}(=C=C=CPh_2)(PEt_3)_2]^+$, (1.876(5), 1.245(7), and 1.352(8) Å) [12], or $[CpRu(=C=C=CPh_2)(PMe_3)_2]^+$ (1.884(5), 1.255(8), and 1.329(9) Å) [13]. The Ru–P bond lengths in **3a** and **3b** are very similar being 2.328(1) and 2.321(4) Å, while the Ru–Cl distances are slightly different being 2.377(2) and 2.417(4) Å, respectively.

The structural identity of the vinylvinylidene **4** is readily apparent from ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Diagnostic is the low-field resonance at 362.0 ppm (d, J_{CP} = 19.2 Hz) assignable to the C_α carbon atom of the vinylidene unit as well as the resonances at 137.4, 112.1, and 109.8 ppm which are assigned to the internal vinylic carbon atom, the C_β carbon atom of the vinylidene moiety, and the terminal vinyl carbon atom, respectively. Characteristic signals of the ^1H NMR spectrum include two doublets centered at 5.22 and 5.12 ppm assignable to the C_β hydrogen atom of the vinylidene unit and the two olefinic hydrogen atoms of the vinyl moiety, respectively.

In contrast to the reactions of $RuTp(PR_3)(DMF)Cl$ (prepared in situ) with propargylic alcohols, the reaction with 3-butyn-1-ol, 4-pentyn-1-ol, and 5-hexyn-1-ol yields the five-, six-, and seven-membered cyclic oxy-carbene complexes $RuTp(PR_3)(=C_4H_6O)Cl$ (**5**), $RuTp(PR_3)(=C_5H_8O)Cl$ (**6**), and $RuTp(PR_3)(=C_6H_{10}O)Cl$ (**7**) as

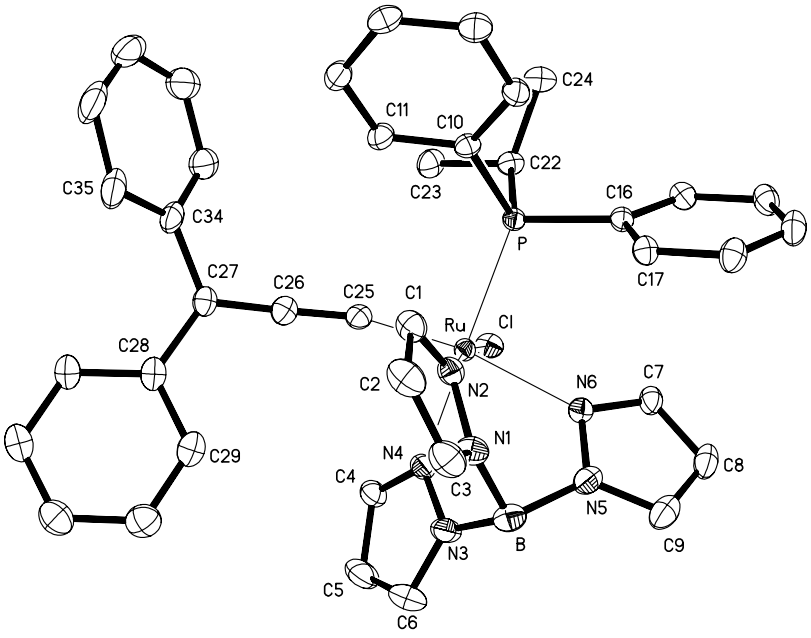


Fig. 1. Structural view of $RuTp(PPh_2{}^iPr)(=C=C=CPh_2)Cl$ (**3a**) showing 50% thermal ellipsoids (H atoms and second independent complex omitted for clarity). Selected bond lengths (Å) and bond angles (°): Ru–N(2) 2.092(1), Ru–N(4) 2.112(2), Ru–N(6) 2.181(2), Ru–C(25) 1.862(2), Ru–P 2.328(1), Ru–Cl 2.377(1), C(25)–C(26) 1.259(3), C(26)–C(27) 1.349(3), Ru–C(25)–C(26) 163.6(2), C(25)–C(26)–C(27) 171.9(2).

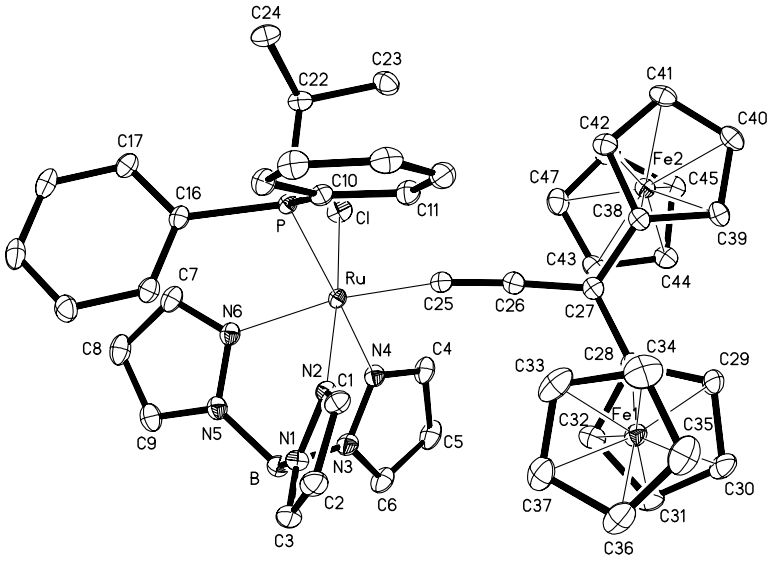
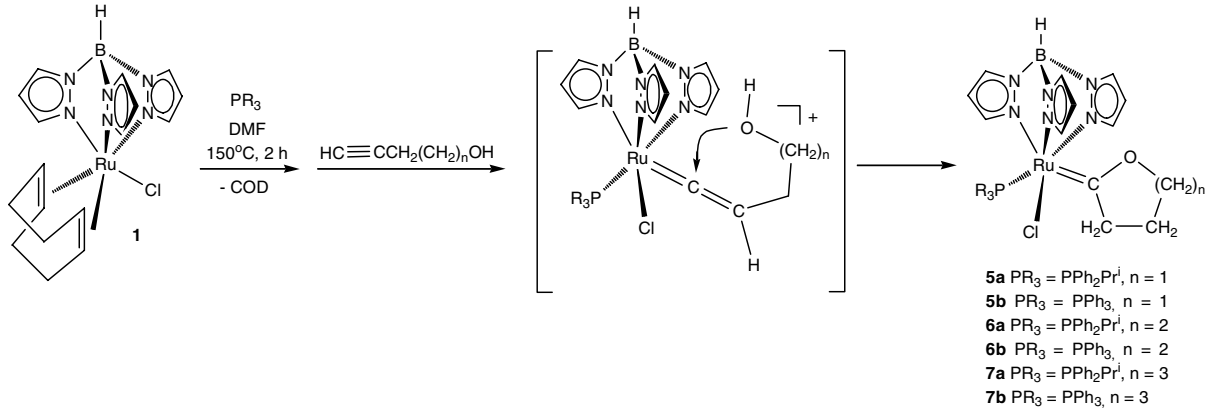


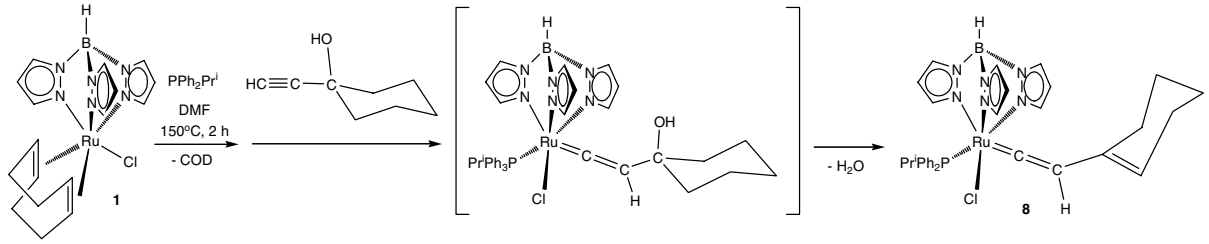
Fig. 2. Structural view of RuTp($PPh_2{}^iPr$)(=C=C=CFc_2)Cl (**3b**) showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°): Ru–N(2) 2.089(2), Ru–N(4) 2.108(2), Ru–N(6) 2.177(2), Ru–C(25) 1.889(2), Ru–P 2.3214(4), Ru–Cl 2.4166(4), C(25)–C(26) 1.254(2), C(26)–C(27) 1.365(2), Ru–C(25)–C(26) 168.8(2), C(25)–C(26)–C(27) 175.0(2).

air-stable yellow solids in high isolated yields (Scheme 2) [14]. On the other hand, with 1-ethynylcyclohexanol, the vinylvinylidene complex RuTp($PPh_2{}^iPr$)(=C=CHC_6H_9)Cl (**8**) is obtained through elimination of H_2O as shown in Scheme 3.

The cyclic oxycarbenes are evidenced by resonances in the range of 313.2–325.0 ppm (d, J_{PC} = 13–15 Hz) for the carbene carbon atom in the $^{13}C\{^1H\}$ NMR spectrum. The chemical shifts are similar to those reported for other oxycyclic carbene ruthenium complexes [15].



Scheme 2.



Scheme 3.

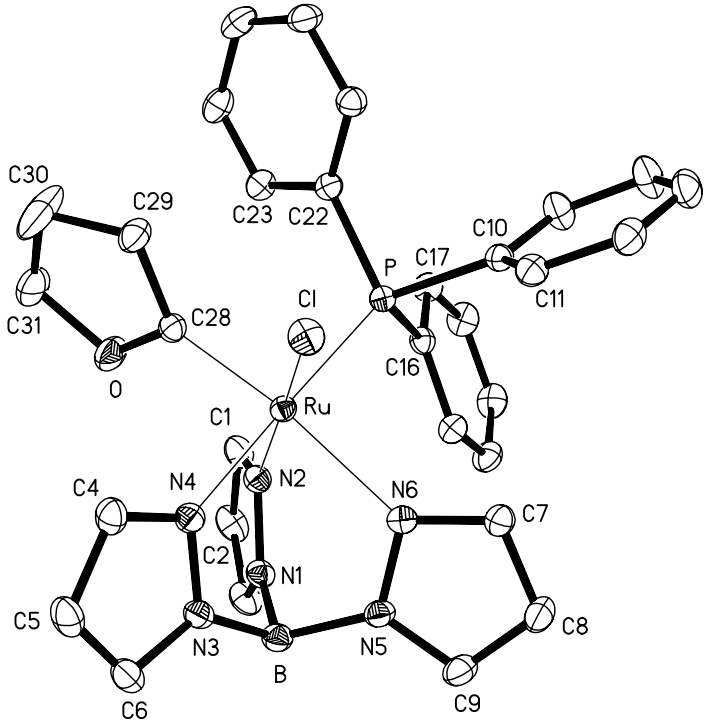
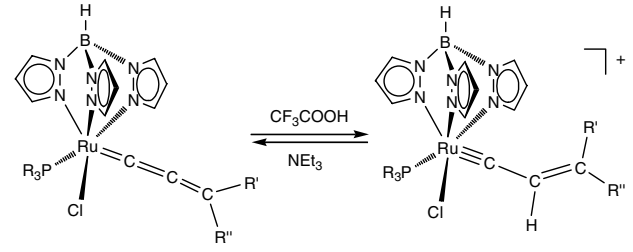


Fig. 3. Structural view of $RuTp(PPh_3)(=C_4H_6O)Cl$ (**5b**) showing 30% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å): Ru–N(2) 2.087(2), Ru–N(4) 2.107(2), Ru–N(6) 2.233(2), Ru–C(28) 1.921(2), Ru–P 2.3345(4), Ru–Cl 2.4370(4).

In addition, complex **5b** is characterized by X-ray crystallography. A structural view is shown in Fig. 3 with selected bond distances given in the figure caption. The overall octahedral structure of **5b** is very similar to **3a** and **3b**. The two Ru–N(Tp) bond lengths *cis* to the carbene moiety are significantly shorter (Ru–N(2) = 2.087(2) Å, Ru–N(4) = 2.107(2) Å) than that *trans* to the carbene unit (Ru–N(6) = 2.233(2) Å) due to the strong *trans* influence of the strong π-accepting carbene. The Ru–C(28) bond distance is 1.921(2) Å and comparable to other oxacycloalkylidene ruthenium complexes. For instance, the Ru=C bond distances in $[RuCp(dppe)(=C_4H_6O)]^+$ and $[RuCp(dppe)(=C_5H_8O)]^+$ featuring five- and six-membered oxacyclocarbene ligands are 1.92(1) and 1.938(4) Å, respectively [15f]. The Ru–P and Ru–Cl bond lengths are 2.332(2) and 2.437(1) Å.

While many allenylidene complexes, especially if they are cationic, add nucleophiles either at the C_α or C_γ carbon atom, electron-rich allenylidene complexes, particularly neutral ones, are capable of adding electrophiles at the C_β carbon atom thereby forming vinylcarbyne complxes [16]. Accordingly, we investigated the reaction of the allenylidene complexes **3a**–**c** with CF_3COOH. Addition of CF_3COOH to a solution of **3a**–**c** in CD_2Cl_2 resulted in an immediate color change from either purple to yellow or blue to green affording quantitatively the novel RuTp vinylcarbyne complexes $[RuTp(PPh_2{}^iPr)(\equiv C–CH=CPh_2)Cl]^+$ (**9a**), $[RuTp(PPh_2{}^iPr)(\equiv C–CH=CFc_2)Cl]^+$ (**9b**), and $[RuTp(PPh_3)(\equiv C–CH=CPh_2)Cl]^+$ (**9c**) as monitored by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 4). The $^{13}C\{^1H\}$ NMR spectra show the resonance corresponding to the α-carbon atom of the carbyne ligand for **9a**–**c** at 324.4, 328.5, and 326.4 ppm as doublets with coupling constants of 15.2, 18.0, and 14.2 Hz, respectively. The β-carbon signals are singlets at 129.5, 131.1, and 129.9 ppm, whereas the more electrophilic γ-carbons appear at 181.1, 185.4, and 181.2 ppm, respectively. The vinylic C_β-hydrogen atom could not be observed due to peak overlap. The hydrogen β-carbon of these complexes is relatively acidic and the formation of **9** is reversible. In fact, addition of NEt_3 leads to a clean back-transformation to **3**.



3a PR_3 = PPh_2Pr^i, R' = R'' = Ph
3b PR_3 = PPh_2Pr^i, R' = R'' = Fc
3c PR_3 = PPh_3, R' = R'' = Ph

9a PR_3 = PPh_2Pr^i, R' = R'' = Ph
9b PR_3 = PPh_2Pr^i, R' = R'' = Fc
9c PR_3 = PPh_3, R' = R'' = Ph

Scheme 4.

In summary, we have shown that the $RuTp(PR_3)Cl$ fragment reacts readily with a variety of propargylic alcohols and $HC{\equiv}C(CH_2)_nOH$ ($n = 2$, 3, 4) to afford neutral electron-rich vinylvinylidene, allenylidene, and five-, six, and seven-membered oxyalkylidene complexes. We have further demonstrated that neutral allenylidene complexes can be easily protonated at the C_β carbon atom to afford vinylcarbyne complexes of the type $[RuTp(PR_3)(\equiv C{-}CH{=}CR'_2)Cl]^+$.

3. Experimental

3.1. General methods

Manipulation were performed under an inert atmosphere of purified argon by using Schlenk techniques and/or a glove box. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [17]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. RuTp(COD)Cl (**1**) was prepared according to the literature [18]. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance-250 and 300 spectrometers and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively. ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, DEPT-135, and ^1H-^{13}C-HSQC experiments. Infrared spectra were recorded on a Bruker Vector 22 spectrometer.

3.1.1. Synthesis of $RuTp(PPh_2{}^iPr)(=C{=}CHCPh_2OH)Cl$ (**2a**)

A suspension of **1** (150 mg, 0.33 mmol) and $PPh_2{}^iPr$ (75.3 mg, 0.33 mmol) in dmf (5 mL) was heated for 2 h at reflux temperature. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 (5 mL) and 1,1-diphenyl-2-propyn-1-ol (81.9 mg, 0.40 mmol) was added and stirred overnight at room temperature. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et_2O and petroleum ether. The purple residue was collected on a glass-frit, washed with petroleum ether, and dried under vacuum. Yield: 163 mg (63%). Anal. Calc. for $C_{39}H_{39}BClN_6OPRu$ (MG: 786.1 g/mol): C, 59.59; H, 5.00; N, 10.69. Found: C, 59.62; H, 5.12; N, 10.66%. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.31–6.79 (m, 25H, Ph, Tp), 6.37 (d, $J_{HH} = 2.0$ Hz, 1H, Tp), 6.10 (s, 1H, Tp), 5.85 (dd, $J_{HH} = J_{HH} = 2.3$ Hz, 1H, Tp), 5.83 (dd, $J_{HH} = J_{HH} = 2.3$ Hz, 1H, Tp), 5.20 (d, $^4J_{HP} = 3.8$ Hz, 1H, Ru=C=C*H*CPh$_2$OH), 4.36 (s, 1H, OH), 3.38–3.21 (m, 1H, CH), 1.30 (dd, $^3J_{HP} = 16.6$ Hz, $^3J_{HH} = 6.9$ Hz, 3H, CH_3), 0.97 (dd, $^3J_{HP} = 13.8$ Hz, $^3J_{HH} = 6.8$ Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 358.2 (d, $^2J_{CP} = 18.4$ Hz, Ru=*C*=CHCPh$_2$OH), 149.5–125.8 (Ph, Tp), 119.4 (d, $^3J_{CP} = 1.5$ Hz, Ru=C=*C*HCPh$_2$OH), 105.9 (Tp), 105.3 (d, $J_{CP} = 3.1$ Hz, Tp), 105.2 (Tp), 75.4 (d, $^4J_{CP} = 2.3$ Hz, Ru=C=CH*C*(Ph)$_2$OH), 24.2 (d, $J_{CP} = 27.6$ Hz, CH), 18.9 (d, $J_{CP} = 3.0$ Hz, CH_3), 18.4 (d, $J_{CP} = 4.6$ Hz,CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 40.5.

3.1.2. Synthesis of $RuTp(P^iPr_3)(=C{=}CHCPh_2OH)Cl$ (**2b**)

This complex has been prepared analogously to **2a** using **1** (100 mg, 0.22 mmol), P^iPr_3 (50 μL, 0.26 mmol) and 1,1-diphenyl-2-propyn-1-ol (54.5 mg, 0.26 mmol) as starting materials. Yield: 93 mg (59%). Anal. Calc. for $C_{33}H_{43}BClN_6OPRu$ (MG: 718.1 g/mol): C, 55.20; H, 6.04; N, 11.70. Found: C, 55.19; H, 6.09; N, 11.56%. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.28–7.05 (m, 16H, Ph, Tp), 6.32 (dd, $J_{HH} = J_{HH} = 2.1$ Hz, 1H, Tp), 6.16 (dd, $J_{HH} = J_{HH} = 2.2$ Hz, 1H, Tp), 5.97–5.90 (m, 1H, Tp), 4.89 (d, $^4J_{HP} = 3.7$ Hz, 1H, Ru=C=C*H*CPh$_2$OH), 2.57–2.22 (m, 3H, CH), 1.16 (dd, $^3J_{HP} = 12.3$ Hz, $^3J_{HH} = 7.0$ Hz, 9H, CH_3), 1.02 (dd, $^3J_{HP} = 13.5$ Hz, $^3J_{HH} = 7.1$ Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 358.5 (d, $^2J_{CP} = 17.6$ Hz, Ru=*C*=CHCPh$_2$OH), 149.8 (Ph^1), 148.2 (Ph$^{1'}$), 145.8 (Tp), 144.6 (Tp), 143.6 (d, $J_{CP} = 1.5$ Hz, Tp), 137.5 (Tp), 136.0 (Tp), 134.0 (d, $J_{CP} = 2.3$ Hz, Tp), 128.3–126.0 (Ph), 121.7 (Ru=C=*C*HCPh$_2$OH), 106.4 (Tp), 106.1 (Tp), 105.3 (d, $J_{CP} = 2.3$ Hz, Tp), 75.7 (d, $^4J_{CP} = 1.5$ Hz, Ru=C=CH*C*Ph$_2$OH), 24.8 (d, $J_{CP} = 20.7$ Hz, *C*H), 19.5 (*C*H$_3$), 19.4 (d, $J_{CP} = 2.3$ Hz, *C*H$_3$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 40.3.

3.1.3. Synthesis of $RuTp(PPh_2{}^iPr)(=C{=}C{=}CPh_2)Cl$ (**3a**)

A solution of **2a** (140 mg, 0.18 mmol) in CH_2Cl_2 was passed through a column charged with acidic Al_2O_3. The product was eluated with acetone, evaporated to dryness, and dried in vacuo. Yield: 115 mg (83%). Anal. Calc. for $C_{39}H_{37}BClN_6PRu$ (MG: 768.1 g/mol): C, 60.99; H, 4.86; N, 10.94. Found: C, 61.10; H, 4.81; N, 10.89%. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.98–6.84 (m, 25H, Ph, Tp), 6.40 (d, $J_{HH} = 1.7$ Hz, 1H, Tp), 6.01 (s, 1H, Tp), 5.91 (dd, $J_{HH} = J_{HH} = 2.0$ Hz, 1H, Tp), 5.75 (dd, $J_{HH} = J_{HH} = 2.1$ Hz, 1H, Tp), 3.46–3.31 (m, 1H, CH), 1.67 (dd, $^3J_{HP} = 16.7$ Hz, $^3J_{HH} = 6.8$ Hz, 3H, CH_3), 0.93 (dd, $^3J_{HP} = 13.0$ Hz, $^3J_{HH} = 6.7$ Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 313.3 (d, $J_{CP} = 21.5$ Hz, Ru=*C*=C=CPh$_2$), 233.7 (d, $J_{CP} = 1.5$ Hz, Ru=C=*C*=CPh$_2$), 146.8 (d, $J_{CP} = 1.5$ Hz, Ru=C=C=*C*Ph$_2$), 146.0-127.6 (Ph, Tp), 105.6 (Tp), 105.4 (Tp), 105.3 (d, $J_{CP} = 3.1$ Hz, Tp), 23.4 (d, $J_{CP} = 27.6$ Hz, *C*H), 19.4 (d, $J_{CP} = 3.1$ Hz, CH_3), 18.3 (d, $J_{CP} = 5.4$ Hz, CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 42.5.

*3.1.4. Synthesis of RuTp(PPh$_2$^{i}Pr)(=C=C=CFc$_2$)Cl (**3b**)*

A suspension of **1** (150 mg, 0.33 mmol) and PPh$_2$^{i}Pr (75.3 mg, 0.33 mmol) in dmf (5 mL) was heated for 2 h at reflux temperature. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 (5 mL) and 1,1-diferrocenyl-2-propyn-1-ol (75.7 mg, 0.36 mmol) was added and stirred overnight at room temperature. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et_2O and petroleum ether. The residue was collected on a glass-frit, washed with petroleum ether, and dried in vacuo. Yield: 248 mg (76%). Anal. Calc. for $C_{47}H_{45}BClFe_2N_6PRu$ (MG: 983.9 g/mol): C, 59.57; H, 4.78; N, 8.86. Found: C, 59.59; H, 4.69; N, 8.92%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.79–6.85 (m, 15H, Ph, Tp), 6.63–6.57 (m, 1H, Tp), 6.10–6.05 (m, 1H, Tp), 5.86–5.82 (m, 1H, Tp), 5.82–5.77 (m, 1H, Tp), 5.19–5.11 (m, 2H, Fc), 5.11–5.05 (m, 2H, Fc), 4.66–4.57 (m, 4H, Fc), 4.13 (s, 10H, Fc), 3.74–3.29 (m, 1H, CH), 1.71 (dd, $^3J_{HP}$ = 16.9 Hz, $^3J_{HH}$ = 6.3 Hz, 3H, CH_3), 0.99 (dd, 3H, $^3J_{HP}$ = 12.5 Hz, $^3J_{HH}$ = 6.3 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 290.1 (d, J_{CP} = 19.9 Hz, Ru=*C*=C=CFc$_2$), 199.5 (Ru=C=*C*=CFc$_2$), 158.7 (d, J_{CP} = 2.3 Hz, Ru=C=C=*C*Fc$_2$), 144.9 (Tp), 143.3 (Tp), 142.6 (Tp), 135.6 (Tp), 134.1 (d, $^2J_{CP}$ = 8.4 Hz, Ph^{2,6}), 133.9 (Tp), 133.8 (d, J_{CP} = 2.3 Hz, Tp), 133.2 (d, $^2J_{CP}$ = 7.7 Hz, Ph$^{2',6'}$), 132.8 (d, $^1J_{CP}$ = 31.4 Hz, Ph^1), 132.2 (d, $^1J_{CP}$ = 32.2 Hz, Ph$^{1'}$), 129.4 (d, $^4J_{CP}$ = 1.5 Hz, Ph^4), 128.8 (d, $^4J_{CP}$ = 1.5 Hz, Ph$^{4'}$), 127.5 (d, $^3J_{CP}$ = 8.4 Hz, Ph^{3,5}), 127.3 (d, $^3J_{CP}$ = 8.4 Hz, Ph$^{3',5'}$), 105.1 (Tp), 90.4 (Fc), 72.7 (Fc), 72.6 (Fc), 72.0 (Fc), 71.7 (Fc), 71.5 (Fc), 71.1 (Fc), 69,1 (Fc), 67.9 (Fc), 67.8 (Fc), 67.6 (Fc), 65.4 (Fc), 24.3 (d, $^1J_{CP}$ = 26.8 Hz, CH), 19.3 (d, $^2J_{CP}$ = 3.1 Hz, CH_3), 18.4 (d, $^2J_{CP}$ = 4.6 Hz, CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 52.7.

*3.1.5. Synthesis of RuTp(PPh$_3$)(=C=C=CPh$_2$)Cl (**3c**)*

A suspension of **1** (150 mg, 0.33 mmol) and PPh_3 (90.3 mg, 0.35 mmol) in dmf (5 mL) was heated for 2 h at reflux temperature. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 (5 mL) and 1,1-diphenyl-2-propyn-1-ol (82 mg, 0,40 mmol) was added and heated overnight at reflux temperature. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et_2O and petroleum ether. The residue was collected on a glass-frit, washed with petroleum ether, and dried under vacuum. Yield: 164 mg (62%). Anal. Calc. for $C_{42}H_{35}BClN_6PRu$ (MG: 802.1 g/mol): C, 62.89; H, 4.40; N, 10.48. Found: C, 62.97; H, 4.50; N, 10.39%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.96–6.78 (m, 30H, Ph, Tp), 6.18–6.90 (m, 2H, Tp), 5.82–5.53 (m, 2H, Tp). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 313.7 (d, J_{CP} = 22.2 Hz, Ru=*C*=C=CPh$_2$), 230.5 (d, J_{CP} = 3.1 Hz, Ru=C=*C*=CPh$_2$), 146.3 (d, J_{CP} = 1.5 Hz, (=C(Ph$^1_2$))), 146.1 (d, J_{CP} = 3.1 Hz, Ru=C=C=*C*Ph$_2$), 144.5 (Tp), 143.5 (Tp), 143.1 (Tp), 136.1 (Tp), 134.7 (d, $^2J_{CP}$ = 9.2 Hz, Ph^{2,6}), 133.9 (Tp), 133.6 (Tp), 133.2 (d, $^1J_{CP}$ = 43.7 Hz, Ph^1), 129.4 (=C(Ph$^{3,5}_2$)), 129.1 (=C(Ph$^4_2$)), 128.9 (=C(Ph$^{2,6}_2$)), 128.3 (Ph^4), 127.7 (d, $^3J_{CP}$ = 9.2 Hz, Ph^{3,5}), 105.8 (Tp), 105.3 (d, J_{CP} = 3.1 Hz, Tp), 105.1 (Tp). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 38.9. IR (KBr pellet, cm^{-1}): 2464 ν(B–H), 1911 ν(C=C).

*3.1.6. Synthesis of RuTp(P^{i}Pr$_3$)(=C=C=CPh$_2$)Cl (**3d**)*

Complex **2b** (70 mg, 0.10 mmol) was dissolved in CH_2Cl_2 and passed through a column charged with acidic Al_2O_3. The product was eluated with acetone, evaporated to dryness, and dried under vacuum. Yield: 53 mg (76%). Anal. Calc. for $C_{33}H_{41}BClN_6PRu$ (MG: 700.0 g/mol): C, 56.62; H, 5.06; N, 12.01. Found: C, 56.58; H, 5.00; N, 12.11%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.57–7.15 (m, 16H, Ph, Tp), 6.45 (dd, J_{HH} = J_{HH} = 2.1 Hz, 1H, Tp), 6.07 (dd, J_{HH} = J_{HH} = 2.2 Hz, 1H, Tp), 5.92–5.86 (m, 1H, Tp), 2.68–2.44 (m, 3H, CH), 1.20–1.02 (m, 18H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 317.3 (d, J_{CP} = 19.2 Hz, Ru=*C*=C=CPh$_2$), 241.1 (d, J_{CP} = 1.5 Hz, Ru=C=*C*=CPh$_2$), 147.0 (=C(Ph$^{1,1'}_2$)), 146.9 (Ru=C=C=*C*Ph$_2$), 145.6 (Tp), 154.1 (Tp), 142.5 (d, J_{CP} = 1.5 Hz, Tp), 136.7 (Tp), 136.4 (Tp), 133.5 (d, J_{CP} = 2.3 Hz, Tp), 129.2 (=C(Ph$^{3,3',5,5'}_2$)), 128.9 (=C(Ph$^{2,2',6,6'}_2$)), 126.0 (=C(Ph$^{4,4'}_2$)), 106.2 (Tp), 105.9 (Tp), 105.3 (d, J_{CP} = 2.3 Hz, Tp), 24.4 (d, J_{CP} = 20.0 Hz, CH), 19.3 (*C*H$_3$), 19.4 (d, J_{CP} = 1.5 Hz, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 41.8. IR (KBr pellet, cm^{-1}): 2469 ν(B–H), 1907 ν(C=C).

*3.1.7. Synthesis of RuTp(PPh$_2$^{i}Pr)(=C=CHC(Ph)=CH$_2$)Cl (**4**)*

A suspension of **1** (250 mg, 0.55 mmol) and PPh$_2$^{i}Pr (125.5 mg, 0.55 mmol) in dmf (5 mL) was heated for 2 h at reflux temperature. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 (5 mL) and 2-phenyl-3-butyn-2-ol (95.8 mg, 0.66 mmol) was added and stirred overnight at room temperature. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et_2O and petroleum ether. The dark red residue was collected on a glass-frit, washed with petroleum ether, and dried under vacuum. Yield: 253 mg (65%). Anal. Calc. for $C_{34}H_{35}BClN_6PRu$ (MG: 706.0 g/mol): C, 57.87; H, 5.00; N, 11.90. Found: C, 57.80; H, 4.96; N, 11.89%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 8.05–6.63 (m, 20H, Ph, Tp), 6.26–6.21 (m, 1H, Tp), 6.19–6.15 (m, 1H, Tp), 5.79 (dd, J_{HH} = J_{HH} = 2.1 Hz, 1H, Tp), 5.66 (dd, J_{HH} = J_{HH} = 2.3 Hz, 1H, Tp), 5.22 (d, $^4J_{HP}$ = 3.8 Hz, 1H, Ru=C=C*H* C(Ph)=CH$_2$), 5.12 (d, $^2J_{HH}$ = 1.1 Hz, 1H, =C*H*$_2$), 4.89 (d, $^2J_{HH}$ = 1.1 Hz, 1H, =C*H*$_2$), 3.50–3.32 (m, 1H, CH), 1.64 (dd, $^3J_{HP}$ = 17.0 Hz,

$^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.00 (dd, $^3J_{HP}$ = 13.3 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 362.0 (d, J_{CP} = 19.2 Hz, Ru=*C*=CHCPh=CH_2), 144.7 (Tp), 142.5 (Tp), 137.4 (Ru=C=CH*C*(Ph)=CH_2), 137.3 (C(Ph^1)=CH_2), 136.2 (Tp), 134.1 (d, $^2J_{CP}$ = 8.4 Hz, $Ph^{2,6}$), 133.6 (d, J_{CP} = 3.1 Hz, Tp), 133.3 (Tp), 132.9 (d, $^2J_{CP}$ = 7.7 Hz, $Ph^{2',6'}$), 130.8 (d, $^1J_{CP}$ = 37.6 Hz, Ph^1), 130.5 (d, $^1J_{CP}$ = 38.3 Hz, $Ph^{1'}$), 130.1 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 129.4 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 128.9 (d, $^3J_{CP}$ = 9.2 Hz, $Ph^{3,5}$), 127.9 (C($Ph^{3,5}$)=CH_2), 127.8 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3',5'}$), 127.6 (C(Ph^4)=CH_2), 126.5 (C($Ph^{2,6}$)=CH_2), 112.1 (d, $^3J_{CP}$ = 1.5 Hz, Ru=C=*C*HC(Ph)=CH_2), 109.8 (Ru=C=CHC(Ph)=*C*H_2), 105.7 (Tp), 105.6 (d, J_{CP} = 2.3 Hz, Tp), 104.7 (Tp), 23.8 (d, $^1J_{CP}$ = 29.1 Hz, CH), 18.7 (d, $^2J_{CP}$ = 1.5 Hz, CH_3) 18.3 (d, $^2J_{CP}$ = 5.4 Hz, CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 43.3.

3.1.8. Synthesis of $RuTp(PPh_2{}^iPr)(=C_4H_6O)Cl$ (**5a**)

A suspension of **1** (150 mg, 0.33 mmol) and $PPh_2{}^iPr$ (100 mg, 0.38 mmol) in dmf (5 mL) was heated for 2 h at reflux temperature. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 (5 mL) and 3-butyn-1-ol (33.5 μL, 0,44 mmol) was added and stirred overnight at room temperature. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et_2O and petroleum ether. The pale yellow residue was collected on a glass-frit, washed with petroleum ether, and dried under vacuum. Yield: 158 mg (74%). Anal. Calc. for $C_{28}H_{33}BClN_6OPRu$ (MG: 647.9 g/mol): C, 51.91; H, 5.13; N, 12.97. Found: C, 51.87; H, 5.18; N, 12.88%. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.08–6.93 (m, 15H, Ph, Tp), 6.71–6.63 (m, 1H, Tp), 6.16–6.06 (m, 1H, Tp), 5.94 (dd, J_{HH} = J_{HH} = 1.9 Hz, 1H, Tp), 5.62 (dd, J_{HH} = J_{HH} = 2.1 Hz, 1H, Tp), 4.90–4.69 (m, 1H), 4.63–4.46 (m, 1H), 3.97–3.73 (m, 1H), 3.36–2.96 (m, 2H), 2.15–1.85 (m, 2H), 1.18 (dd, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.07 (dd, $^3J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 313.2 (d, J_{CP} = 14.6 Hz, Ru=C_4H_6O), 145.3 (Tp), 143.6 (Tp), 141.7 (d, J_{CP} = 1.5 Hz, Tp), 135.2 (Tp), 134.4 (Tp), 134.3 (Tp), 133.8 (d, $^2J_{CP}$ = 8.4 Hz, $Ph^{2,6}$), 133.4 (d, $^1J_{CP}$ = 36.8 Hz, Ph^1), 133.2 (d, $^2J_{CP}$ = 8.4 Hz, $Ph^{2',6'}$), 132.5 (d, $^1J_{CP}$ = 34.5 Hz, $Ph^{1'}$), 128.8 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 128.7 (d, $^4J_{CP}$ = 1.5 Hz, $Ph^{4'}$), 127.4 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3,5}$), 127.2 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3',5'}$), 105.2 (d, J_{CP} = 2.3 Hz, Tp), 105.0 (Tp), 104.6 (Tp), 80.0 (*C*H_2), 52.9 (*C*H_2), 24.6 (d, J_{CP} = 23.8 Hz, *C*H), 22.6 (*C*H_2), 18.8 (*C*H_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 53.4.

3.1.9. Synthesis of $RuTp(PPh_3)(=C_4H_6O)Cl$ (**5b**)

This complex has been prepared analogously to **5a** using **1** (100 mg, 0.22 mmol), PPh_3 (65.9 mg, 0.25 mmol) and 3-butyn-1-ol (22.3 μL, 0.29 mmol) as starting materials. Yield: 115 mg (77%). Anal. Calc. for $C_{31}H_{31}BClN_6OPRu$ (MG: 681.9 g/mol): C, 54.60; H, 4.58; N, 12.32. Found: C, 54.64; H, 4.62; N, 12.36%. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.84–6.92 (m, 20H, Ph, Tp), 6.56–6.47 (m, 1H, Tp), 6.12–6.03 (m, 1H, Tp), 5.94 (dd, J_{HH} = J_{HH} = 2.1 Hz, 1H, Tp), 5.69 (dd, J_{HH} = J_{HH} = 2.2 Hz, 1H, Tp), 4.84–4.71 (m, 1H), 4.55–4.39 (m, 1H), 3.54–3.33 (m, 1H), 3.20–3.02 (m, 1H), 2.06–1.85 (m, 1H), 1.81–1.63 (m, 1H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 314.4 (d, J_{CP} = 13.8 Hz, Ru=C_4H_6O), 146.4 (Tp), 144.3 (Tp), 141.9 (Tp), 135.5 (Tp), 134.8 (Tp), 134.2 (d, J_{CP} = 2.3 Hz, Tp), 134.2 (d, $^1J_{CP}$ = 39.9 Hz, Ph^1), 134.1 (d, $^2J_{CP}$ = 10.0 Hz, $Ph^{2,6}$), 129.3 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 127.7 (d, $^3J_{CP}$ = 9.2 Hz, $Ph^{3,5}$), 105.5 (Tp), 105.3 (d, J_{CP} = 3.1 Hz, Tp), 105.0 (Tp), 80.8 (CH_2), 54.3 (CH_2), 22.7 (CH_2). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 48.2.

3.1.10. Synthesis of $RuTp(PPh_2{}^iPr)(=C_5H_8O)Cl$ (**6a**)

This complex has been prepared analogously to **5a** using **1** (150 mg, 0.33 mmol), $PPh_2{}^iPr$ (100 mg, 0.38 mmol) and 4-pentyn-1-ol (46.1 μL, 0.50 mmol) as starting materials. Yield: 171 mg (78%). Anal. Calc. for $C_{29}H_{35}BClN_6OPRu$ (MG: 661.9 g/mol): C, 55.62; H, 5.33; N, 12.70. Found: C, 55.67; H, 5.23; N, 12.65%. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.99–6.90 (m, 15H, Ph, Tp), 6.54–6.41 (m, 1H, Tp), 6.15–6.02 (m, 1H, Tp), 5.98–5.81 (m, 1H, Tp), 5.73–5.59 (m, 1H, Tp), 4.64–4.35 (m, 2H), 3.70–3.46 (m, 1H), 3.37–3.12 (m, 1H), 3.08–2.83 (m, 1H), 2.05–1.53 (m, 4H), 1.31 (dd, $^3J_{HP}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 1.09 (dd, $^3J_{HP}$ = 13.3 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 318.3 (d, J_{CP} = 15.3 Hz, Ru=C_5H_8O), 144.9 (Tp), 143.8 (Tp), 142.0 (d, J_{CP} = 1.5 Hz, Tp), 135.5 (Tp), 134.4 (d, J_{CP} = 2.3 Hz, Tp), 134.2 (Tp), 133.7 (d, $^2J_{CP}$ = 8.4 Hz, $Ph^{2,6}$), 133.6 (d, $^1J_{CP}$ = 29.1 Hz, Ph^1), 133.5 (d, $^2J_{CP}$ = 8.4 Hz, $Ph^{2',6'}$), 133.1 (d, $^1J_{CP}$ = 28.4 Hz, $Ph^{1'}$), 128.9 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 128.5 (d, $^4J_{CP}$ = 1.5 Hz, $Ph^{4'}$), 127.4 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3,5}$), 127.2 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3',5'}$), 105.1 (d, J_{CP} = 2.3 Hz, Tp), 105.0 (Tp), 104.8 (Tp), 71.7 (CH_2), 47.3 (CH_2), 24.8 (d, J_{CP} = 23.8 Hz, CH), 21.9 (CH_2), 19.2 (d, J_{CP} = 1.5 Hz, CH_3), 18.9 (CH_3), 16.8 (*C*H_2). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 53.4.

3.1.11. Synthesis of $RuTp(PPh_3)(=C_5H_8O)Cl$ (**6b**)

This complex has been prepared analogously to **5a** using **1** (150 mg, 0.33 mmol), PPh_3 (98.8 mg, 0.38 mmol) and 4-pentyn-1-ol (33.5 μL, 0.36 mmol) as starting materials. Yield: 178 mg (78%). Anal. Calc. for $C_{32}H_{33}BClN_6OPRu$ (MG: 696.0 g/mol): C, 55.23; H, 4.78; N, 12.08. Found: C, 55.18; H, 4.69; N, 12.29%. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.79–7.02 (m, 20H, Ph, Tp), 6.50–6.38 (m, 1H, Tp), 6.15–6.05 (m, 1H, Tp), 5.90 (dd, J_{HH} = J_{HH} = 2.1 Hz, 1H, Tp), 5.71 (dd, J_{HH} = J_{HH} = 2.2 Hz, 1H, Tp), 4.50–4.17 (m, 2H),

3.75–3.38 (m, 1H), 2.78–2.55 (m, 1H), 1.90–1.44 (m, 4H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 320.2 (d, J_{CP} = 13.8 Hz, Ru=C_5H_8O), 146.1 (Tp), 144.4 (Tp), 142.2 (d, J_{CP} = 1.5 Hz, Tp), 135.6 (Tp), 134.6 (d, $^1J_{CP}$ = 39.1 Hz, Ph^1), 134.5 (Tp), 134.2 (d, $^2J_{CP}$ = 9.2 Hz, $Ph^{2,6}$), 134.0 (Tp), 129.2 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 127.6 (d, $^3J_{CP}$ = 9.2 Hz, $Ph^{3,5}$), 105.5 (Tp), 105.2 (d, J_{CP} = 2.3 Hz, Tp), 105.0 (Tp), 71.7 (CH_2), 48.2 (d, J_{CP} = 1.5 Hz, CH_2), 22.0 (CH_2), 16.7 (CH_2). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 49.1.

3.1.12. Synthesis of $RuTp(PPh_2{}^iPr)(=C_6H_{10}O)Cl$ (7a)

This complex has been prepared analogously to **5a** using **1** (150 mg, 0.33 mmol), $PPh_2{}^iPr$ (100 mg, 0.38 mmol) and 5-hexyn-1-ol (54.6 μL, 0.50 mmol) as starting materials. The solution was heated at 50 °C for 3 days. Yield: 151 mg (68%). Anal. Calc. for $C_{30}H_{37}BClN_6OPRu$ (MG: 676.0 g/mol): C, 53.31; H, 5.52; N, 12.43. Found: C, 53.11; H, 5.48; N, 12.39%. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.13–6.90 (m, 15H, Ph, Tp), 6.66–6.53 (m, 1H, Tp), 6.21–6.06 (m, 1H, Tp), 6.00–5.90 (m, 1H, Tp), 5.66–5.55 (m, 1H, Tp), 4.93–4.40 (m, 3H), 3.22–3.03 (m, 1H), 2.77–2.59 (m, 1H), 2.00–1.40 (m, 6H), 1.18 (dd, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.07 (dd, $^3J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 323.7 (d, J_{CP} = 13.8 Hz, Ru=$C_6H_{10}O$), 144.5 (Tp), 143.5 (Tp), 142.1 (d, J_{CP} = 2.3 Hz, Tp), 135.3 (Tp), 134.5 (d, J_{CP} = 2.3 Hz, Tp), 134.3 (Tp), 133.9 (d, $^2J_{CP}$ = 8.4 Hz, $Ph^{2,6}$), 133.5 (d, $^1J_{CP}$ = 28.4 Hz, Ph^1), 133.4 (d, $^2J_{CP}$ = 7.7 Hz, $Ph^{2',6'}$), 132.9 (d, $^1J_{CP}$ = 28.4 Hz, $Ph^{1'}$), 128.9 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 128.5 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 127.1 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3,5}$), 127.1 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3',5'}$), 105.0 (Tp), 104.9 (Tp), 104.6 (Tp), 74.4 (CH_2), 50.7 (CH_2), 29.3 (CH_2), 28.9 (CH_2), 26.6 (d, J_{CP} = 24.5 Hz, CH), 22.3 (CH_2), 19.0 (d, J_{CP} = 1.5 Hz, CH_3), 18.9 (CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 53.0.

3.1.13. Synthesis of $RuTp(PPh_3)(=C_6H_{10}O)Cl$ (7b)

This complex has been prepared analogously to **5a** using **1** (150 mg, 0.33 mmol), PPh_3 (98.8 mg, 0.38 mmol) and 5-hexyn-1-ol (40.0 μL, 0.36 mmol) as starting materials. The reaction mixture was heated at 50° for 3 days. Yield: 196 mg (84%). Anal. Calc. for $C_{33}H_{35}BClN_6OPRu$ (MG: 710.0 g/mol): C, 55.83; H, 4.97; N, 11.84. Found: C, 55.90; H, 5.01; N, 11.81%. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.83–6.83 (m, 20H, Ph, Tp), 6.53–6.46 (m, 1H, Tp), 6.12–6.05 (m, 1H, Tp), 5.91 (dd, J_{HH} = J_{HH} = 2.1 Hz, 1H, Tp), 5.68 (dd, J_{HH} = J_{HH} = 2.3 Hz, 1H, Tp), 4.74–4.39 (m, 3H), 2.17–2.00 (m, 1H), 1.93–1.39 (m, 6H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 325.0 (d, J_{CP} = 14.6 Hz, Ru=C_5H_8O), 146.0 (Tp), 144.5 (Tp), 142.5 (d, J_{CP} = 1.5 Hz, Tp), 135.4 (Tp), 134.6 (Tp), 134.5 (d, $^1J_{CP}$ = 39.1 Hz, Ph^1), 134.1 (d, $^2J_{CP}$ = 10 Hz, $Ph^{2,6}$), 134.0 (d, J_{CP} = 2.3 Hz, Tp), 129.2 (d, $^4J_{CP}$ = 1.5 Hz, Ph^4), 127.6 (d, $^3J_{CP}$ = 9.2 Hz, $Ph^{3,5}$), 105.5 (Tp), 105.1 (d, J_{CP} = 2.3 Hz, Tp), 105.0 (Tp), 71.5 (CH_2), 52.5 (d, J_{CP} = 3.1 Hz, CH_2), 29.3 (CH_2), 28.8 (CH_2), 21.3 (CH_2). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 47.9.

3.1.14. Synthesis of $RuTp(PPh_2{}^iPr)(=C=CHC_6H_9)Cl$ (8)

This complex has been prepared analogously to **2a** using **1** (150 mg, 0.33 mmol), $PPh_2{}^iPr$ (75.3 mg, 0.33 mmol) and 1-ethynylcyclohexanol (0.40 mmol, 49.2 mg) as starting materials. Yield: 120 mg (53%). Anal. Calc. for $C_{32}H_{37}BClN_6PRu$ (MG: 684.0 g/mol): C, 56.19; H, 5.45; N, 12.29. Found: C, 56.23; H, 5.50; N, 12.33%. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.05–6.89 (m, 15H, Ph, Tp), 6.52–6.36 (m, 1H, Tp), 6.31–6.10 (m, 1H, Tp), 5.96–5.73 (m, 2H, Tp), 5.26–5.16 (m, 1H, =CH), 4.77 (d, $^4J_{HP}$ = 3.2 Hz, 1H, Ru=C=C*H*C_6H_9), 3.54–3.29 (m, 1H), 2.36–2.16 (m, 2H), 2.10–1.82 (m, 2H), 1.74–1.56 (m, 4H), 1.50 (dd, $^3J_{HP}$ = 16.1 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.11 (dd, $^3J_{HP}$ = 13.9 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 369.2 (d, J_{CP} = 19.2 Hz, Ru=*C*=CHC_6H_9), 144.5 (Tp), 142.7 (Tp), 142.5 (d, J_{CP} = 1.5 Hz, Tp), 136.3 (Tp), 134.3 (d, J_{CP} = 3.1 Hz, Tp), 134.0 (Tp), 133.9 (d, $^2J_{CP}$ = 7.7 Hz, $Ph^{2,6}$), 133.3 (d, $^2J_{CP}$ = 7.7 Hz, $Ph^{2',6'}$), 131.4 (d, $^1J_{CP}$ = 37.6 Hz, Ph^1), 130.5 (d, $^1J_{CP}$ = 37.6 Hz, $Ph^{1'}$), 129.9 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 129.5 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 128.0 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3,5}$), 127.8 (d, $^3J_{CP}$ = 8.4 Hz, $Ph^{3',5'}$), 126.1 (C_6H_9), 116.8 (C_6H_9), 115.0 (d, $^3J_{CP}$ = 1.5 Hz, Ru=C=*C*HC_6H_9), 105.5 (Tp), 105.3 (d, J_{CP} = 3.1 Hz, Tp), 104.9 (Tp), 29.7 (C_6H_9), 25.6 (C_6H_9), 23.9 (d, J_{CP} = 28.4 Hz, –CH), 23.1 (C_6H_9), 22.4 (C_6H_9), 18.7 (CH_3), 18.4 (d, J_{CP} = 3.8 Hz, CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 40.7.

3.1.15. Reaction of $RuTp(PPh_2{}^iPr)(=C=C=CPh_2)Cl$ (3a) with CF_3COOH. Formation of $[RuTp(PPh_2{}^iPr)(\equiv C–CH=CPh_2)Cl]CF_3COO$ (9a)

A 5 mm NMR tube was charged with **3a** (50 mg, 0.07 mmol) in CD_2Cl_2 (0.5 mL). Upon addition of CF_3COOH (15 μL, 0.2 mmol) the color of the solution changed from purple to yellow. The reaction was monitored by ^1H and ^{13}C NMR spectroscopy and quantitative formation of **9a** was observed. ^1H NMR (δ, CD_2Cl_2): 8.25–6.55 (m, 26H, Ph, Tp, –C*H*=CPh_2), 6.48–6.25 (m, 1H, Tp), 6.07–5.58 (m, 3H, Tp), 3.84–3.43 (m, 1H, CH), 1.99–1.57 (m, 3H, CH_3), 1.09–0.65 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 324.4 (d, J_{CP} = 15.2 Hz, Ru≡C–CH=CPh_2), 181.1 (Ru≡C–CH=*C*Ph_2), 143.8 (Tp), 142.7 (Tp), 142.3 (Tp), 138.6–130.1 (Tp, Ph), 129.5 (Ru≡C–CH=CPh_2), 129.3–124.5 (Ph), 108.1 (Tp), 107.7 (Tp), 105.9 (Tp), 23.9 (d, J_{CP} = 31.8 Hz, CH), 18.6 (CH_3), 18.3 (CH_3). ^{31}P NMR (δ, CD_2Cl_2): 43.9.

3.1.16. Reaction of $RuTp(PPh_2{}^iPr)(=C=C=CFc_2)Cl$ (**3b**) with CF_3COOH: formation of $[RuTp(PPh_2{}^iPr)(\equiv C–CH=CFc_2)Cl]CF_3COO$ (**9b**)

A 5 mm NMR tube was charged with **3a** (50 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL). Upon addition of CF_3COOH (15 μL, 0.2 mmol) the color of the solution changed from blue to dark-green. The reaction was monitored by ^1H and ^{13}C NMR spectroscopy and quantitative formation of **9b** was observed. ^1H NMR (δ, CD_2Cl_2): 8.09–7.71 (m, 4H), 7.67–7.42 (m, 4H), 7.41–7.09 (m, 4H), 6.99–6.82 (m, 1H), 6.55–6.26 (m, 3H), 6.22–6.00 (m, 1H), 5.87–5.70 (m, 1H), 5.69–5.50 (m, 1H), 5.32–5.15 (m, 1H, Fc), 5.10–4.93 (m, 1H, Fc), 4.76–3.94 (m, 16H, Fc), 3.78–3.45 (m, 1H, CH), 1.86–1.49 (m, 3H, CH_3), 1.16–0.76 (m, 3H, CH_3). ^{13}C {^1H} NMR (δ, CD_2Cl_2): 328.5 (d, J_{PC} = 18.0 Hz, Ru≡C–CH=CFc_2), 185.4 (Ru≡C–CH=CFc_2), 144.7–132.3 (Tp, Ph), 131.0 (Ru≡C–CH=CFc_2), 128.8–121.9 (Ph), 106.9 (Tp), 106.7 (Tp), 105.6 (Tp), 84.2 (Fc), 80.6 (Fc), 80.3 (Fc), 79.8 (Fc), 79.6 (Fc), 78.3 (Fc), 77.9 (Fc), 77.4 (Fc), 77.0 (Fc), 75.4 (Fc), 73.3 (Fc), 73.0 (Fc), 23.9 (d, $^1J_{CP}$ = 30.9 Hz, CH), 18.4 (CH_3). ^{31}P NMR (δ, CD_2Cl_2): 54.8.

3.1.17. Reaction of $RuTp(PPh_3)(=C=C=CPh_2)Cl$ (**3c**) with CF_3COOH: formation of $[RuTp(PPh_3)(\equiv C–CH=CPh_2)Cl]CF_3COO$ (**9c**)

A 5 mm NMR tube was charged with **3a** (50 mg, 0.06 mmol) in CD_2Cl_2 (0.5 mL). Upon addition of CF_3COOH (15 μL, 0.2 mmol) the color of the solution changed from purple to yellow. The reaction was monitored by ^1H and ^{13}C NMR spectroscopy and quantitative formation of **9c** was observed. ^1H NMR (δ, CD_2Cl_2): 8.07–6.80 (m, 30H, Ph, Tp, –C*H*=CPh_2), 6.61–6.26 (m, 2H), 6.14–5.85 (m, 2H), 5.82–5.64 (m, 1H). ^{13}C {^1H} NMR (δ, CD_2Cl_2): 326.4 (d, J_{CP} = 14.2 Hz, Ru≡C–CH=CPh_2), 181.2 (Ru≡C–CH=CPh_2), 144.0 (Tp), 144.3 (Tp), 143.2 (Tp), 137.7–131.1 (Tp, Ph), 129.9 (Ru≡C–CH=CPh_2), 129.3–125.5 (Ph), 108.1 (Tp), 107.6 (Tp), 106.8 (Tp). ^{31}P NMR (δ, CD_2Cl_2): 42.2.

3.2. X-ray structure determination

Crystals of $RuTp(PPh_2{}^iPr)(=C=C=CPh_2)Cl$ (**3a**), $RuTp(PPh_2{}^iPr)(=C=C=CFc_2)Cl$ (**3b**), and $RuTp(PPh_3)(=C_4H_6O)Cl$ (**5b**) were obtained by diffusion of diethyl ether (**3b**, **5b**) or pentane into CH_2Cl_2 solutions of these complexes. X-ray data were collected on a Bruker Smart APEX CCD area detector diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å, 0.3° ω-scan frames covering complete spheres of the reciprocal space) [19]. Corrections for crystal decay and for absorption were applied. The structure were solved with direct methods using the program SHELXS-97 [16]. Structure refinements on F^2 were carried out with program SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Salient crystal data are: **3a**: $C_{39}H_{37}BClN_6PRu$, M_r = 768.05, orthorhombic, space group $P2_12_12_1$ (No. 19), T = 100(2) K, a = 10.8159(4) Å, b = 18.2406(6) Å, c = 37.3744(13) Å, V = 737.5(4) Å^3, Z = 8, μ = 0.578 mm^{-1}. Of 110 701 reflections collected up to θ = 30°, 21 390 were independent, R_{int} = 0.024; final R indices: R_1 = 0.031 (all data), wR_2 = 0.076 (all data); the structure contains two independent Ru complexes. **3b**: $C_{47}H_{45}BClFe_2N_6PRu$, M_r = 983.89, monoclinic, space group $P2_1/c$ (No. 14), T = 100(2) K, a = 11.5834(6) Å, b = 18.6367(10) Å, c = 19.5379(10) Å, β = 94.697(1)°, V = 4203.6(4) Å^3, Z = 4, μ = 1.180 mm^{-1}. Of 61 775 reflections collected up to θ = 30°, 12218 were independent, R_{int} = 0.029; final R indices: R_1 = 0.039 (all data), wR_2 = 0.087 (all data); **5b**: $C_{31}H_{31}BClN_6OPRu$, M_r = 681.92, orthorhombic, space group *Pbca* (No. 61), T = 173(2) K, a = 18.1069(8) Å, b = 16.7217(7) Å, c = 19.3929(8) Å, V = 5871.7(4) Å^3, Z = 8, μ = 0.717 mm^{-1}. Of 63 810 reflections collected up to θ = 30°, 8533 were independent, R_{int} = 0.040; final R indices: R_1 = 0.039 (all data), wR_2 = 0.066 (all data).

4. Supplementary material

Crystallographic data (excluding structure factors) for the crystal structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 267089–267091. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] (a) V. Cadierno, M.P. Gamasa, J. Gimeno, Coord. Chem. Rev. 248 (2004) 1627;
(b) S. Rigaut, D. Touchard, P.H. Dixneuf, Coord. Chem. Rev. 248 (2004) 1585;
(c) V. Guerchais, Eur. J. Inorg. Chem. (2002) 783;
(d) V. Cadierno, M.P. Gamasa, J. Gimeno, Eur. J. Inorg. Chem. (2001) 571;
(e) C. Bruneau, P.H. Dixneuf, Acc. Chem. Res. 32 (1999) 311;

(f) M.C. Puerta, P. Valerga, Coord. Chem. Rev. 193–195 (1999) 977;
(g) V. Cadierno, J. Diez, M.P. Gamasa, J. Gimeno, E. Lastra, Coord. Chem. Rev. 193–195 (1999) 147;
(h) M.I. Bruce, Chem. Rev. 98 (1998) 2797;
(i) D. Touchard, P.H. Dixneuf, Coord. Chem. Rev. 178–180 (1998) 409;
(j) H. Werner, Chem. Commun. (1997) 903;
(k) M.I. Bruce, Chem. Rev. 91 (1991) 197.

[2] C.A. Merlic, M.E. Pauly, J. Am. Chem. Soc. 118 (1996) 11319.

[3] Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J.Y. Satoh, J. Am. Chem. Soc. 113 (1991) 9604.

[4] B.M. Trost, J.A. Flygare, J. Am. Chem. Soc. 114 (1992) 5476.

[5] B.M. Trost, G. Dyker, R. Kulawiec, J. Am. Chem. Soc. 112 (1990) 7809.

[6] (a) A. Fürstner, M. Liebl, C.W. Lehmann, M. Piquet, R. Kunz, C. Bruneau, D. Touchard, P.H. Dixneuf, Chem. Eur. J. 6 (2000) 1847;
(b) A. Fürstner, M. Piquet, C. Bruneau, P.H. Dixneuf, Chem. Commun. (1998) 1315.

[7] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275.

[8] The PPh_3 analog $RuTp(PPh_3)(Cl)(DMF)$ has recently been isolated and crystallographically characterized C. Slugovc, V.N. Sapunov, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, J. Chem Soc., Dalton Trans. (1997) 4209.

[9] B. Buriez, I.D. Burns, A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, Organometallics 18 (1999) 1504.

[10] I. de los Rios, M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, J. Organomet. Chem. 549 (1997) 221.

[11] V. Cadierno, M.P. Gamasa, J. Gimeno, E. Lastra, J. Borge, S. Garcia-Granda, Organometallics 13 (1994) 745.

[12] E. Bustelo, M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 18 (1999) 4563.

[13] J.P. Selegue, Organometallics 1 (1982) 217.

[14] For oxyalkylidenes, see: B. Weyershausen, K.H. Dötz, Eur. J. Inorg. Chem. (1999) 1057.

[15] (a) A. Keller, B. Jasionka, T. Glowiak, A. Ershov, R. Matusiak, Inorg. Chim. Acta 344 (2003) 49;
(b) M.P. Gamasa, J. Gimeno, B.M. Martin-Vaca, R. Isea, A. Vegas, J. Organomet. Chem. 651 (2002) 22;
(c) H.D. Hansen, J.H. Nelson, Organometallics 19 (2000) 4740;
(d) L.P. Barthel-Rosa, K. Maitra, J.H. Nelson, Inorg. Chem. 37 (1998) 633;
(e) W.H. Leung, E.Y.Y. Chan, I.D. Williams, W.T. Wong, Organometallics 16 (1997) 3234;
(f) R.L. Beddoes, R.W. Grime, Z.I. Hussain, M.W. Whiteley, J. Organomet. Chem. 526 (1996) 371;
(g) P. Nombel, N. Lugan, R. Mathieu, J. Organomet. Chem. 503 (1995) C22;
(h) M.I. Bruce, A.G. Swincer, B.J. Thomson, R.C. Wallis, Aust. J. Chem. 33 (1980) 2605.

[16] (a) S. Rigaut, D. Touchard, P.H. Dixneuf, Organometallics 22 (2003) 3980;
(b) R. Castarlenas, P.H. Dixneuf, Angew. Chem. Int. Ed. 42 (2003) 4524;
(c) E. Bustelo, M. Jimenez-Tenorio, K. Mereiter, M.C. Puerta, P. Valerga, Organometallics 21 (2002) 1903;
(d) S. Jung, C.D. Brandt, H. Werner, New J. Chem. 25 (2001) 1101.

[17] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon Press, New York, 1988.

[18] C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 15 (1996) 3998.

[19] Bruker, Programs SMART, version 5.054; SAINT, version 6.2.9; SADABS version 2.03; XPREP, version 5.1; SHELXTL, version 5.1. Bruker AXS Inc., Madison, WI, USA, 2001.

[20] G.M. Sheldrick, SHELX-97: Program System for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1997.