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Formation of Oxaphosphacarbenes by Reaction of [RuTpCl(PPh_3)(thp)] with Terminal Alkynes and a Propargylic Alcohol

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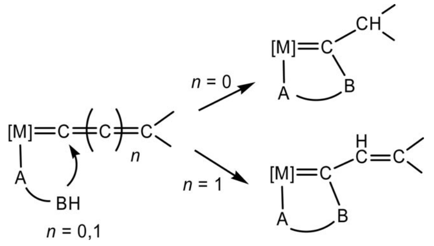
The reaction of [TpRuCl(PPh_3)$_2$] [Tp = hydrotris(pyrazolyl)borate] with $P(CH_2OH)_3$ (thp) afforded [TpRuCl(PPh_3)(thp)] (**1**). Compound **1** heated at reflux in NCMe yielded the cationic compound [TpRu(NCMe)(PPh_3)(thp)]Cl (**2**). The reaction of **1** with terminal alkynes R–C≡CH [R = Ph, *p*-C_6H_4Me, $Si(Me)_3$, EtC(O)O] and with the propargylic alcohol [Ph_2(OH)C–C≡CH] in methanol gave the new metallacyclic cationic carbenes [TpRu{κ^2-(*C*,*P*)=C(CH_2R')$OCH_2P(CH_2OH)_2$}(PPh_3)]Cl [R′ = Ph (**3a**), *p*-C_6H_4Me (**4a**), H (**5a**), MeC(O)O (**6a**)] and [TpRu{κ^2-(*C*,*P*)=C(CH=CPh_2)$OCH_2P(CH_2OH)_2$}(PPh_3)]Cl (**7a**), respectively. When methanolic solutions of compounds **3a**–**5a** were heated at reflux for several hours, the compounds eliminate formaldehyde to afford the new carbene complexes [RuTp{κ^2-(*C*,*P*)=C(R′′)$OCH_2PH(CH_2OH)$}(PPh_3)]Cl [R′′ = CH_2Ph (**3b**), $CH_2C_6H_4Me$ (**4b**), CH_3 (**5b**), respectively]. Compound **7a** showed a very high tendency to eliminate formaldehyde. As a result, the carbene [RuTp{κ^2-(*C*,*P*)=C(HC=CPh_2)$OCH_2PH(CH_2OH)$}(PPh_3)]Cl (**7b**) formed is always present during the synthesis of **7a**. When heating at reflux in methanol was sufficiently prolonged, pure **7b** was obtained. When the reaction of **1** with R–C≡CH [R = Ph, *p*-C_6H_4Me, $(Me)_3Si$] and with Ph_2(OH)CC≡CH was performed in refluxing toluene, the neutral oxaphosphacarbene complexes [TpRuCl{κ^2-(*C*,*P*)=C(CH_2R)$OCH_2P(CH_2OH)_2$}] [R = Ph (**8**), *p*-C_6H_4Me (**9**), $(Me)_3Si$ (**10**)] and [TpRuCl{κ^2-(*C*,*P*)=C(CH=CPh_2)$OCH_2P(CH_2OH)_2$}] (**11**) were obtained. Compound **9** was structurally characterised by X-ray diffraction analysis.

Introduction

The interest in vinylidene- and allenylidene-metal complexes has enormously increased in recent decades, mostly because of their role in many catalytic and stoichiometric transformations of organic molecules. A recently edited book by C. Bruneau and P. H. Dixneuf[1] nicely gathers all aspects of these complexes, with emphasis on their applications in selective transformations of functional terminal alkynes.

A key characteristic of vinylidene- and allenylidene-metal complexes is the electrophilicity of the α-carbon atom, which allows the simple production of heteroatom-stabilised carbene complexes by the addition of different nucleophiles as phosphanes, amines, alcohols, etc.[2] The use of bifunctional ligands in the precursor complex (as diamine, amidoamine, phosphanylamine, etc.) may induce intramolecular attack on the unsaturated carbon chain to afford new series of metal complexes in which the carbene moiety is part of a chelate ligand[3] (Scheme 1).

Continuing our studies on {TpRu} moieties,[4] we report on the reactions of TpRu complexes [Tp = hydrotris(pyrazolyl)borate], containing the tris(hydroxymethyl)phosphane (thp) ligand, with terminal alkynes and 1,1-diphenyl-2-propyn-1-ol. This yields cyclic oxaphosphacarbenes presumably by intramolecular addition of one of the thp hydroxy groups to the corresponding intermediate vinylidene or allenylidene complexes.



Scheme 1. Intramolecular nucleophilic attack of a bifunctional ligand on the α-carbon atom of a vinylidene or allenylidene ligand.

Results and Discussion

Synthesis of [TpRuCl(PPh_3)(thp)] (1) and [TpRu($NCCH_3$)(PPh_3)(thp)]Cl (2)

When a thf solution of [TpRuCl(PPh_3)$_2$] is heated at reflux for 1 h with 1 equiv. $P(CH_2OH)_3$ (thp), [TpRuCl(PPh_3)(thp)] (**1**) is obtained in high yield (Scheme 2). Complex **1** is a yellow solid, stable under inert atmosphere, and it was characterised by elemental analysis and NMR spec-

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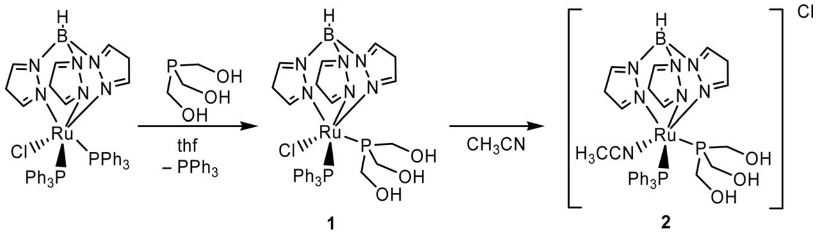


Scheme 2. Syntheses of **1** and **2**.

troscopy. In the ^{1}H NMR spectrum in CD_2Cl_2, the hydroxy groups of the thp ligand display a broad singlet at δ = 3.58 ppm, whereas the CH_2 resonance appears as a multiplet (the AB part of an ABX system, X = P) at δ = 4.10 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the CH_2 resonance is observed as a doublet at δ = 59.9 ppm with a C–P coupling constant of 23.9 Hz, which indicates the magnetic equivalence of the three hydroxymethyl groups of the thp ligand. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets at 45.3 (thp) and 37.8 ppm (PPh_3) with a P–P coupling constant of 30.9 Hz. It is worth noting that the HRMS(ESI) spectrum shows a peak at 701 amu, in agreement with the loss of the chlorido ligand, which is probably assisted by the conditions of the ionisation chamber of the spectrometer (samples dissolved in polar solvents).

In accordance with this behaviour (and supporting the labilisation of the chlorido ligand in **1** after its dissolution in polar solvents), it has been observed that when **1** is heated at reflux for 30 min. in CH_3CN, [TpRu($NCCH_3$)(PPh_3)(thp)]Cl (**2**) is obtained in a 92% yield by the replacement of the chlorido ligand by the CH_3CN group (Scheme 2). Compound **2** is a yellow solid, stable in air, and it was also characterised by the usual techniques. The signal for the hydroxy groups of the thp ligand is not observed in its ^{1}H NMR spectrum in CD_2Cl_2, and the methyl group of the CH_3CN ligand appears as a singlet at δ = 2.10 ppm. Analogous to the observation in the spectrum of compound **1**, the CH_2 resonance appears as a multiplet at δ = 3.95 ppm, which indicates the magnetic equivalence of the three hydroxymethyl groups of the thp ligand. In the $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, the CH_3 resonance of the CH_3CN ligand appears as a singlet at 4.6 ppm and the CH_2 resonance is observed as a doublet at δ = 56.9 ppm with a C–P coupling constant of 26.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets at 43.2 (thp) and 26.6 ppm (PPh_3) with a P–P coupling constant of 29.1 Hz.

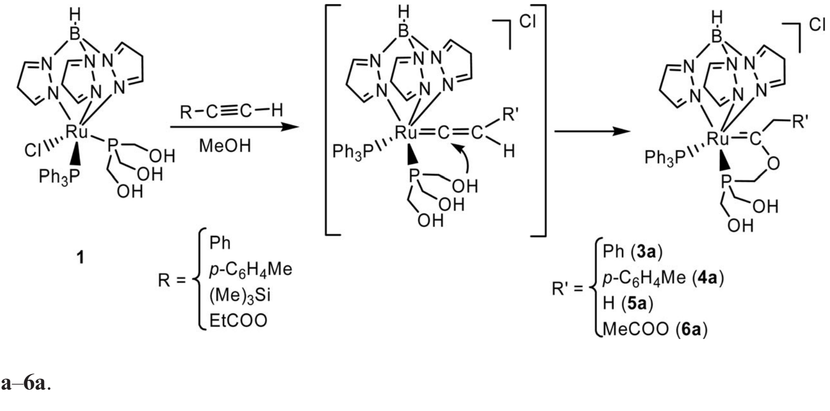
Reactions of 1 with Terminal Alkynes in MeOH

The easy substitution of the chlorido ligand of **1**, when dissolved in polar solvents, prompted us to explore the reactions of **1** with terminal alkynes and 1,1-diphenyl-2-propyn-1-ol in methanol with the aim of obtaining new vinylidene and allenylidene complexes, respectively.

Instead, the reaction of a suspension of **1** in methanol with an excess of the terminal alkynes R–C≡CH [R = Ph, p-C_6H_4Me, $Si(Me)_3$, EtC(O)O] gave the new metallacyclic cationic carbenes [TpRu{κ^2-(C,P)=C(CH_2R')OCH_2P($CH_2OH)_2$}(PPh_3)]Cl [R′ = Ph (**3a**), p-C_6H_4Me (**4a**), H (**5a**), and MeC(O)O (**6a**)] in high yields (Scheme 3).

In the case of **5a**, the reaction is accompanied by a desilylation process. On the other hand, the synthesis of **6a** indicates a transesterification process with the solvent (MeOH).

As far as we know, five-membered oxaphosphacarbene complexes have not been described in the literature before. Despite the fact that no vinylidene intermediates could be observed, such species are most likely to be key intermediates during the process of transformation into oxaphosphacyclic carbene complexes.[3,5] The reaction probably proceeds by nucleophilic addition of one of the thp hydroxy groups to the α-carbon atom of the cationic intermediates, as sketched in Scheme 3. A cyclation reaction is probably favoured by the proximity of the nucleophilic OH group to the vinylidene moiety and the chelate effect of the linked thp ligand. It should be noted that deprotonation of the thp ligand to give metal alkoxide complexes have already been reported.[6]



Scheme 3. Syntheses of **3a**–**6a**.

The compounds are yellow solids, stable if stored under inert atmosphere (a sample exposed to air for 5–6 d displays new signals of unidentified products in its $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2), and they have been characterised by microanalysis and IR and NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 show two pairs of doublets corresponding to the two different phosphorus atoms present in the molecule in all cases. A careful examination of the ^1H, $^{13}C\{^1H\}$, $^1H,^1H$-COSY and $^1H,^{13}C$-HSQC NMR spectra in CD_2Cl_2 allows us to assign all signals, which are in agreement with the proposed structures. The ^1H NMR spectra of **3a**–**6a** confirm the presence of the Tp ligand, as the characteristic signals of the pyrazolyl protons in the range δ = 5.99–8.41 ppm are present. Similarly, the $^{13}C\{^1H\}$ NMR spectra indicates the presence of PPh_3 and Tp ligands (signals in the range 106.3–149.7 ppm). In addition, resonances corresponding to four different methylenic groups can be observed for **3a**, **4a** and **6a**: three doublets for each compound between 50.5 and 70.6 ppm with coupling constants between 22 and 41 Hz, which correspond to the three different PCH_2 groups, and a singlet for each compound between δ = 59.3 and 59.8 ppm for the CH_2R group. In the case of **5a**, a singlet at δ = 40.9 ppm corresponds to the resonance of the CH_3 group. The three doublets corresponding to the three different methylenic PCH_2 groups appear at δ = 51.4, 34.9 and 69.8 ppm with coupling constants between 23 and 40 Hz. In the ^1H NMR spectra of the complexes, most of the resonances of each proton from each CH_2P group appear far apart and constitute the AM part of an AMX (X = P) spin system (with $^2J_{HP}$ values spanning from close to zero to 10.6 Hz) (See Experimental Section). This behaviour is illustrated in Figure 1, which shows the methylenic region of the $^1H,^{13}C$-HSQC spectrum of **4a** and the molecule with the methylenic groups highlighted. Doublets at 52.0 ($^1J_{CP}$ = 38.6 Hz), 54.8 ($^1J_{CP}$ = 24.5 Hz) and 70.4 ppm ($^1J_{CP}$ = 23.2 Hz) in the vertical axis correspond to the methylenic carbon atoms directly bonded to the phosphorus atom, and the singlet at δ = 59.3 ppm corresponds to the methylenic carbon atoms bonded to the R′ (*p*-tolyl) group. The quartet at about 3.4 ppm corresponds to ethyl ether, which is used for the isolation of the product.

The formation of a carbene ligand in **3a**–**6a** is indicated by a downfield doublet of doublets in the $^{13}C\{^1H\}$ NMR spectra[7] [**3a**: 327.1 ppm ($^2J_{C,P}$ = 11.7, 7.8 Hz), **4a**: 327.6 ppm ($^2J_{C,P}$ = 11.6, 7.7 Hz), **5a**: 331.9 ppm ($^2J_{C,P}$ = 12.9, 7.6 Hz) and **6a**: 319.4 ppm ($^2J_{C,P}$ = 12.9, 7.7 Hz)].

As already mentioned, in the case of **5a**, the reaction is accompanied by a desilylation process. In the ^1H NMR spectrum, the methyl group directly bonded to the carbenic carbon atom displays a singlet resonance at δ = 1.98 ppm. There are precedents for the cleavage of the Si–C bond in related processes,[8] which supports the participation of a vinylidene species as the key intermediate.[9] Compounds **3a**–**6a** are not very stable in methanolic solution, slowly decomposing when they are left aside for several days at room temperature. In the mixture of different products that were obtained for **3**–**5**, we were only able to identify the product that appears in greater proportion (**3b**–**5b**). Therefore, when methanol solutions of these compounds were heated at reflux for several hours (see Experimental Section for details) and monitored by $^{31}P\{^1H\}$ NMR spectroscopy, a progressive substitution of the initial pair of doublets by a new pair was observed [**3b**: 43.0 (PPh_3), 71.3 ppm (cyclic *P*) ($^2J_{P,P}$ = 32.0 Hz); **4b**: 43.2 (PPh_3), 71.6 ppm (cyclic *P*) ($^2J_{P,P}$ = 32.0 Hz); **5b**: 43.4 (PPh_3), 71.5 ppm (cyclic *P*) ($^2J_{P,P}$ = 32.4 Hz)].

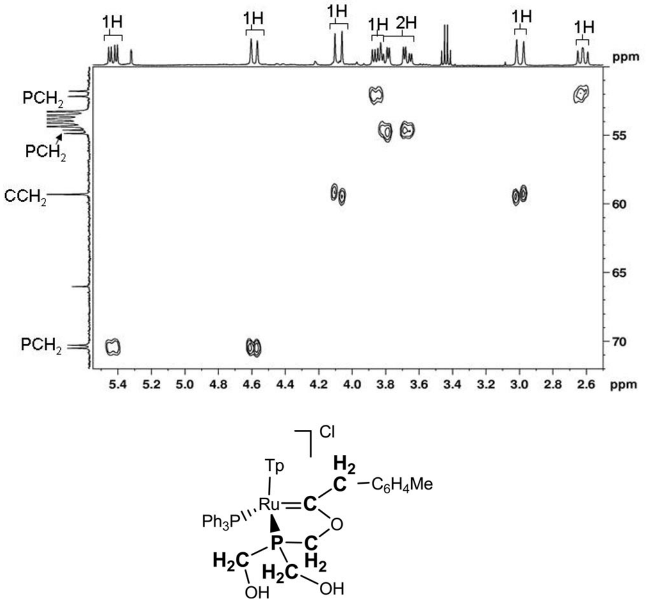
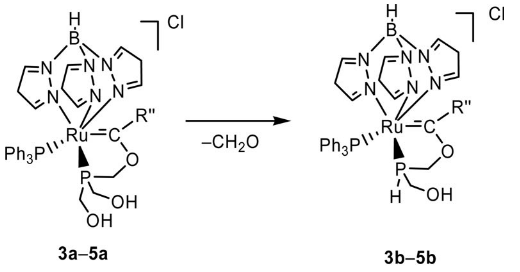


Figure 1. $^1H,^{13}C$-HSQC spectrum of **4a** (methylenic region).

Unfortunately, when this conversion approaches 60–80%, new signals for the unidentified products begin to emerge, thus preventing us from obtaining the new product as a pure substance. Further attempts to separate both products by means of crystallisation and column chromatography on silica, as well as on neutral or basic Al_2O_3 failed. Nevertheless, a careful perusal of the ^1H, $^{13}C\{^1H\}$, $^1H,^1H$-COSY and HSQC NMR experiments of the final mixture allowed us to characterise the new compounds. Thus, compounds $[RuTp\{\kappa^2\text{-}(C,P)\text{=}C(R'')OCH_2PH(CH_2OH)\}(PPh_3)]Cl$ [R′′ = CH_2Ph (**3b**), $CH_2C_6H_4Me$ (**4b**), CH_3 (**5b**)] were obtained from **3a**–**5a**, respectively, by elimination of formaldehyde from one of the two hydroxymethyl groups bonded to the phosphorus atom (Scheme 4). Elimination of a formaldehyde unit from coordinated hydroxymethyl ligands has already been reported.[10] This reaction is, in fact, the reverse of the synthesis of thp from PH_3 and formaldehyde.[11]

The corresponding compound obtained by elimination of formaldehyde from **6a** could not be identified, although it is probably present in the complex mixture of unidentified products obtained on heating at reflux for a sufficiently prolonged period.

Besides the expected resonances corresponding to the Tp, PPh_3 and R′′ groups, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3b**–**5b** display other resonances, in agreement with the proposed structures. Therefore, in the ^1H NMR spectra,



R'' = CH_2Ph (**3a**,**b**); $CH_2–C_6H_4Me$ (**4a**,**b**); CH_3 (**5a**,**b**)

Scheme 4. Syntheses of **3b**–**5b**.

a doublet centred at δ = 4.87 ppm for **3b**, at δ = 4.85 ppm for **4b** and at δ = 4.87 ppm for **5b**, with coupling constants $^1J_{H,P}$ of 389.9, 391.3 and 386.0 Hz, respectively, account for the proton directly bonded to the phosphorus atom. The signals for the protons of the two remaining PCH_2 groups appear in the region 3.51–6.23 ppm. In the $^{13}C\{^1H\}$ NMR spectra of the compounds, the characteristic low field resonance of the carbenic carbon atom[7] appears as a multiplet at 326.9, 327.3 and 331.7 for **3b**–**5b**, respectively.

Reaction of 1 with 1,1-Diphenyl-2-propyn-1-ol in MeOH

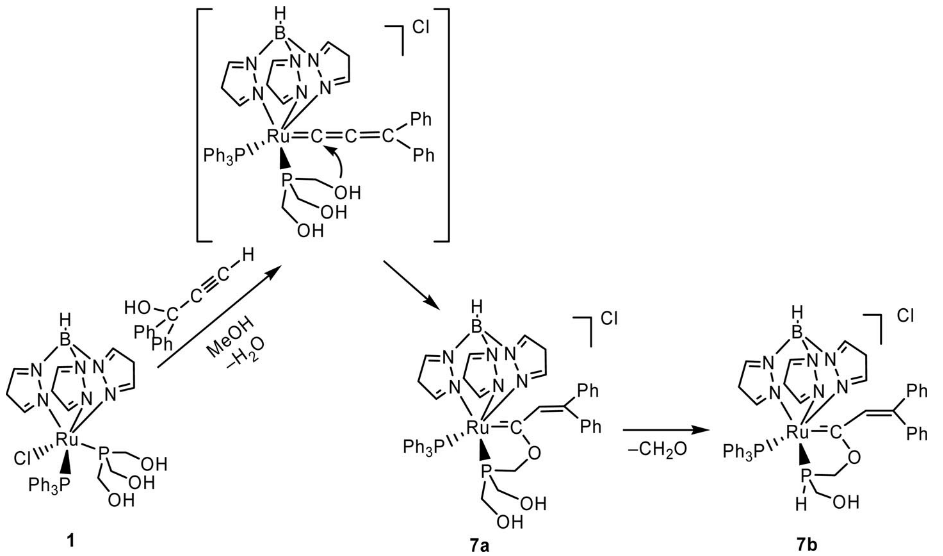
When the reaction of a suspension of **1** in methanol was carried out with 1,1-diphenyl-2-propyn-1-ol at room temperature for 24 h, a mixture of the cyclic vinyl carbenes [TpRu{κ²-(*C,P*)=C(CH=CPh₂)OCH₂P(CH₂OH)₂}(PPh₃)]Cl (**7a**) and [TpRu{κ²-(*C,P*)=C(CH=CPh₂)OCH₂PH(CH₂OH)}(PPh₃)]Cl (**7b**) was obtained (Scheme 5).

Similarly as mentioned in the previous paragraph, the reaction probably proceeds by nucleophilic addition of one of the thp hydroxy groups to the α-carbon atom of the cationic allenylidene intermediate to give **7a**. Other nucleophilic additions as a result of the presence in the reaction media of MeOH (solvent) or H_2O (eliminated in Selegue's reaction to give the allenylidene group[12]) were not observed.[13] Compound **7a** easily eliminates a formaldehyde unit from one of the two hydroxymethyl groups bonded to the phosphorus atom to yield **7b**. When the reaction mixture was heated at reflux for 6 h, the conversion of **7a** to **7b** is total, which allows us to completely characterise both compounds by means of an in-depth NMR study of both the final product and the reaction mixture.

The $^{31}P\{^1H\}$ NMR spectrum of the mixture in CD_2Cl_2 displays two sets of two doublets each at δ = 38.4 ($^2J_{P,P}$ = 31.6 Hz) and 69.9 ($^2J_{P,P}$ = 31.6 Hz) ppm, which can be assigned to **7a**, and at δ = 43.3 ($^2J_{P,P}$ = 33.2 Hz) and 71.0 ($^2J_{P,P}$ = 33.2 Hz) ppm, assigned to **7b**.

The presence of the Tp ligand in **7a** is confirmed by the characteristic signals of the pyrazolyl protons in the ^1H NMR spectrum in the range δ = 6.09–8.29 ppm. Similarly, the $^{13}C\{^1H\}$ NMR spectrum indicates the presence of PPh_3 and Tp ligands (signals in the range δ = 106.4–149.4 ppm). The signal corresponding to the vinyl α-carbon atom (H*C*=CPh₂) for **7a** could not be detected as it is probably masked by the signals of the Ph groups at about 130 ppm. The PCH_2 methylenic groups are observed at δ = 50.6, 54.7 and 68.6 ppm with coupling constants between 39 and 25 Hz. The formation of a carbene ligand in **7a** is indicated by a downfield doublet of doublets at δ = 307.8 ppm ($^2J_{C,P}$ = 13.0, 9.1 Hz) in the $^{13}C\{^1H\}$ NMR spectrum.[7]

On the other hand, **7b** is a red solid, stable if stored under inert atmosphere. Besides the expected resonances corresponding to the Tp, PPh_3 and the vinyl groups, **7b** shows other resonances, in accordance with the proposed structure. Thus, the ^1H NMR spectrum displays a doublet at δ = 5.08 ppm, with a coupling constant $^1J_{H,P}$ = 387.3 Hz, assignable to the proton directly bonded to the phosphorus atom. In the $^{13}C\{^1H\}$ NMR spectrum, a low field multiplet at δ = 307.4 ppm accounts for the carbenic carbon atom.[7]



Scheme 5. Syntheses of **7a** and **7b**.

Reaction of 1 with Terminal Alkynes and 1,1-Diphenyl-2-propyn-1-ol in Toluene

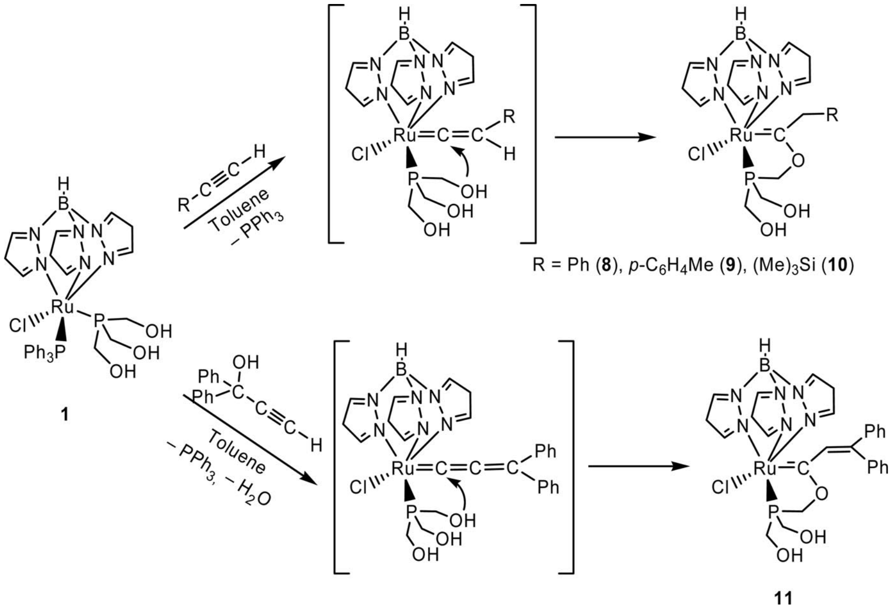
With the aim of comparing the reactivity of complex **1** with that of the same compounds described in the previous paragraph but in a nonpolar media, we have used toluene as the reaction medium. Thus, the reaction of **1** with HC≡CR [R = Ph, *p*-C_6H_4Me, $(Me)_3Si$] in refluxing toluene for 1–4 h results in the formation of the neutral oxaphosphacarbene complexes [TpRuCl{κ^2-(*C*,*P*)=C(CH_2R)OCH_2-P(CH_2OH)$_2$}] [R = Ph (**8**), *p*-C_6H_4Me (**9**), $(Me)_3Si$ (**10**)] in high yields (Scheme 6).[14] Substitution of the PPh_3 ligand is confirmed by the presence of a singlet at δ = –5.30 ppm in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixture and also by the $^{31}P\{^1H\}$ NMR spectra of the complexes in CD_2Cl_2, all of which present only one singlet at 81.5 (**8**), 81.6 (**9**) and 85.5 ppm (**10**) attributable to the cyclic oxaphosphacarbene ligand. Complexes **8–10** are yellow solids, stable under argon atmosphere, which slowly decompose in solution (alcoholic, chlorinated and toluene solvents). A careful inspection of the ^1H, $^{13}C\{^1H\}$, $^1H,^1H$-COSY and $^1H,^{13}C$-HSQC NMR spectra in CD_2Cl_2 confirms the presence of the five-membered oxaphosphacarbene cyclic ligand. In the ^1H NMR spectra of the complexes **8–10**, each PCH_2 group displays a distinct multiplet resonance corresponding to the AB part of an ABX (X = P) spin system, as the simulation[15] performed for **8** demonstrates (see Experimental Section). The fourth methylenic group, the one directly bonded to the carbenic carbon atom, displays a singlet resonance at δ = 4.33 ppm for **8** and multiplets at δ = 4.28 and 3.14 ppm for **9** and **10**, respectively.

In the $^{13}C\{^1H\}$ NMR spectra in CD_2Cl_2, **8–10** show three doublets each between δ = 57.4 and 68.9 ppm with coupling constants between 22 and 32 Hz, which correspond to the three different CH_2P groups. In contrast, the fourth CH_2R group appears as a singlet at δ = 58.5 ppm for **8**, at δ = 58.2 ppm for **9** and at δ = 49.9 ppm for **10**. The carbenic carbon atom[7] appears as a doublet at low field at δ = 323.3 ppm ($^2J_{C,P}$ = 10.3 Hz) for **8**, at 323.7 ppm ($^2J_{C,P}$ = 11.6 Hz) for **9** and at δ = 327.6 ppm ($^2J_{C,P}$ = 10.4 Hz) for **10**.

In the case of complex **9**, we were able to obtain X-ray quality crystals. A structural view of **9** is shown in Figure 2 with selected bond lengths and angles given in Table 1. As expected from the spectroscopic studies, the crystallographic analysis reveals that one of the hydroxymethyl groups of the thp ligand is implicated in the formation of a five-membered oxaphosphacyclic carbene ligand, presumably by intramolecular nucleophilic addition to the α-carbon atom of an intermediate vinylidene ligand. The compound consists of a ruthenium(II) atom coordinated by a κ^3-*N*,*N*′,*N*′′ tris(pyrazolyl)borate ligand, one chlorido ligand, together with a phosphorus and a carbon atom from a five-membered oxaphosphacyclic bidentate carbene ligand.

The environment around the ruthenium metal centre corresponds to a slightly distorted octahedron, and the bite angle of the Tp ligand produces N–Ru–N angles of 83.4(6), 84.2(6) and 86.6(5)°, only slightly distorted from 90°. The three Ru–N(Tp) bond lengths span from 2.052(14) Å (*trans* to the chlorido ligand) to 2.204(12) Å (*trans* to the carbene carbon atom, which reflects its strong *trans* influence) and are similar to those found in other TpRu carbene complexes.[16] The Ru–P bond length 2.226(4) Å is shorter than that found in other ruthenium complexes with the thp ligand,[10c] and the Ru–C bond length 1.92(2) Å is similar to those found in other TpRuClP carbene complexes.[17]

The supramolecular structure contains one H bond between one of the hydroxy groups of the ligand and the chlorine atom of a neighbouring molecule, which results in a zig-zag chain along the *b* axis. This is in contrast with the



Scheme 6. Syntheses of **8–11**.

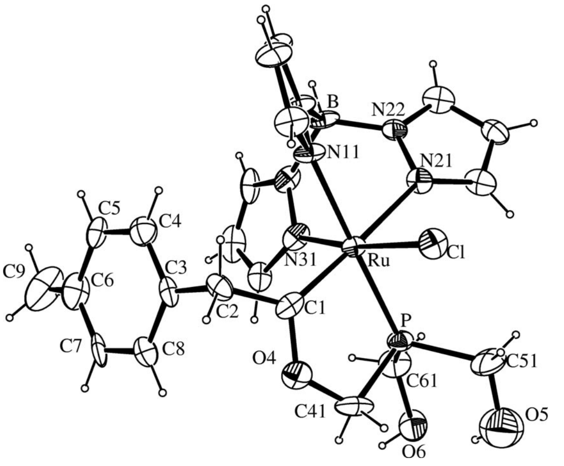


Figure 2. Structural view of [RuTpCl{κ^2-(C,P)=C($CH_2C_6H_4CH_3$)-$OCH_2P(CH_2OH)_2$}] (**9**), showing 30% thermal ellipsoids.

Table 1. Selected bond lengths [Å] and angles [°] for **9**.[a]

Bonds			
Ru–N11	2.152(14)	Ru–N21	2.204(12)
Ru–N31	2.052(14)	Ru–C1	1.918(19)
Ru–P	2.226(4)	Ru–Cl	2.406(4)
Angles			
N31–Ru–N11	86.6(5)	N11–Ru–N21	83.4(6)
N31–Ru–N21	84.2(6)	C1–Ru–N21	177.1(7)
C1–Ru–N31	93.0(6)	C1–Ru–N11	95.5(6)
C1–Ru–P	83.9(5)	N31–Ru–P	96.0(4)
N11–Ru–P	177.3(4)	N21–Ru–P	97.3(4)
C1–Ru–Cl	93.1(5)	N31–Ru–Cl	172.6(5)
N11–Ru–Cl	88.6(4)	N21–Ru–Cl	89.6(4)
P–Ru–Cl	88.75(17)		

[a] Symmetry transformations used to generate equivalent atoms: (i) $-x$, $y + 0.5$, $1 - z$.

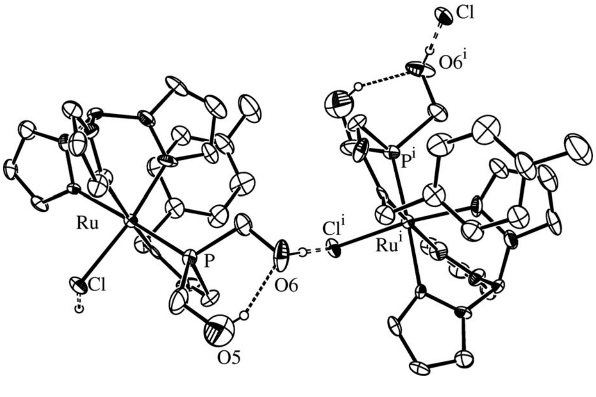


Figure 3. Hydrogen-bond network of complex **9**.

general observation for complexes bearing the thp ligand, which usually present an extensive H-bond network.[10c,18] The second hydroxy group is implicated in an intramolecular H-bond between both hydroxy groups (Figure 3). Furthermore, the *p*-tolyl group is situated in such a way that it allows a π–π stacking interaction[19] between the phenyl ring and one of the pyrazolic rings (containing N31 and N32 atoms) of the Tp ligand, with a distance between the centroids of 3.770(1) Å and dihedral angles between the best planes of 15.1(8)°.

As can be seen in Scheme 6, the reaction of **1** with the propargylic alcohol $Ph_2(OH)CC{\equiv}CH$ under the same conditions gives the α,β-unsaturated oxaphosphacarbene [TpRuCl{κ^2-(C,P)=C(CH=CPh_2)$OCH_2P(CH_2OH)_2$}] (**11**) as a red solid. This reaction probably occurs through a neutral allenylidene intermediate formed by Selegue's reaction[12] with concomitant water elimination. The α-carbon atom of this intermediate is susceptible to nucleophilic attack by one of the hydroxy groups of thp, and hence the cyclic carbene **11** is produced. Although the allenylidene intermediate was not observed, a small singlet appearing at δ = 84.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum when the reaction is performed in the absence of any drying agent (molecular sieves, etc) can be considered as evidence for this hypothesis. Such a small singlet may be attributable to the carbonyl compound [RuTpCl(CO)(thp)],[20] presumably produced by reaction of the allenylidene with water released from Selegue's reaction. Similar addition reactions of water have already been described for other cationic[21] and neutral[22] ruthenium(II) allenylidene complexes.

Compound **11** was characterised by NMR spectroscopy. Analogously to the spectra of **8**–**10**, the $^{13}C\{^1H\}$ NMR spectrum of **11** displays three different doublets at δ = 57.7, 58.1 and 67.5 ppm ($^1J_{C,P}$ = 23–31 Hz), which can be attributed to the three CH_2P groups. The vinyl α- and β-carbon atoms display singlets at δ = 136.9 and 106.6 ppm, and the signal for the carbenic carbon atom appears as a doublet at lower field (δ =310.9 ppm, $^2J_{C,P}$ = 12.9 Hz).

Conclusions

Compound [TpRuCl(PPh_3)(thp)] (**1**), obtained through substitution of one PPh_3 ligand by thp in [TpRuCl-$(PPh_3)_2$], reacted with terminal alkynes and with 1,1-diphenyl-2-propyn-1-ol to yield five-membered cyclic oxaphosphacarbenes. The type of compounds obtained depends on the polarity of the solvent employed in the reaction. When methanol was used, the chlorido ligand was labilised, and cationic carbenes were obtained. When the less polar toluene was employed, the triphenylphosphane ligand was displaced to afford neutral carbenes. In the case of compounds [TpRu{κ^2-(C,P)=C(CH_2R')$OCH_2P(CH_2OH)_2$}(PPh_3)]Cl [R′ = Ph (**3a**), *p*-C_6H_4Me (**4a**), H (**5a**), MeC(O)O (**6a**)] and [TpRuCl{κ^2-(C,P)=C(CH_2R)$OCH_2P(CH_2OH)_2$}] [R = Ph (**8**), *p*-C_6H_4Me (**9**), $(Me)_3Si$ (**10**)], which were obtained by reaction of **1** with terminal alkynes, the mechanism probably includes a vinylidene intermediate that undergoes intramolecular nucleophilic addition to the α-carbon atom by one of the hydroxymethyl groups of the thp ligand. A similar mechanism could be proposed for the synthesis of compounds [TpRu{κ^2-(C,P)=C(CH=CPh_2)$OCH_2P(CH_2OH)_2$}-(PPh_3)]Cl (**7a**) and [TpRuCl{κ^2-(C,P)=C(CH=CPh_2)-$OCH_2P(CH_2OH)_2$}] (**11**), which were obtained by means of reaction of **1** with $Ph_2(OH)CC{\equiv}CH$, but, in these cases, an allenylidene intermediate must be responsible for the process. Compounds **3a**–**5a** and **7a** undergo elimination of formaldehyde from one of the hydroxymethyl groups to yield the new cyclic oxaphosphacarbenes [TpRu{κ^2-(*C*,*P*)=C(R′′)OCH$_2$PH(CH$_2$OH)}(PPh$_3$)]Cl [R′′ = CH$_2$Ph (**3b**), CH$_2$C$_6$H$_4$Me (**4b**), CH$_3$ (**5b**)] and [TpRu{κ^2-(*C*,*P*)=C(CH=CPh$_2$)OCH$_2$PH(CH$_2$OH)}(PPh$_3$)]Cl (**7b**).

Experimental Section

General Methods: All synthetic operations were performed under a dry argon atmosphere by following conventional Schlenk techniques. Solvents were purified through distillation from the appropriate drying agents[23] and degassed before use. The ligands thp[24] and KTp[25] and the complex [TpRuCl(PPh$_3$)$_2$][26] were prepared according to published methods. Other reagents were purchased from commercial sources in the highest purity available and used as received. IR spectra were recorded in KBr pellets on a Jasco FT/IR-6100 spectrophotometer. Mass spectrometry was performed on a microTOF(focus) mass spectrometer (Bruker Daltonics, Bremen, Germany). Ions were generated by using an Apollo (ESI) source. Ionization was achieved by electrospray, with a voltage of 4500 V applied to the needle and a counter voltage between 100 and 150 V applied to the capillary. Data acquisition was performed with the microTOF Control software, version 2.1, and data processing was carried out with the Data Analysis software, version 3.4, both from Bruker Daltonics. NMR spectra were taken on a Bruker AMX 400 instrument. Chemical shifts are given in parts per million with reference to SiMe$_4$ [^{1}H and ^{13}C(^{1}H)] or 85% H$_3$PO$_4$ [^{31}P(^{1}H)]. The ^{1}H and ^{13}C{1H} NMR signal assignments were confirmed by ^{1}H-COSY and HSQC(^{1}H-^{13}C) experiments. Elemental analyses were performed on a Fisons EA-1108 apparatus.

Synthesis of [TpRuCl(PPh$_3$)(thp)] (1): The ligand thp (71.0 mg, 0.57 mmol) was added to a yellow solution of [TpRuCl(PPh$_3$)$_2$] (500 mg, 0.57 mmol) in thf (40 mL). The mixture was stirred and heated at reflux for 1 h. The resultant yellow solution was filtered through Celite to remove the decomposition products. The yellow filtrate was reduced under vacuum to about 3 mL, and a yellow solid precipitated upon addition of a mixture of hexane (5 mL) and diethyl ether (1 mL). This precipitate was vacuum filtered, washed with hexane and diethyl ether and dried in vacuo. Yield: 364.4 mg (86.9%). C$_{30}$H$_{34}$BClN$_6$O$_3$P$_2$Ru (735.92 g/mol): calcd. C 48.91, H 4.66, N 11.41; found C 48.96, H 4.17, N 11.67. MS: 701 [M$^+$ – Cl]. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2478 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 3.58 (br. s, 3 H, O*H*), 3.95–4.28 (m, 6 H, C*H*$_2$P), 5.66 [t, $^3J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 5.81 [br. td, $^3J_{\mathrm{H,H}}$ = 2.3, $^5J_{\mathrm{H,P}}$ = 0.7 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.19 [br. td, $^3J_{\mathrm{H,H}}$ = 2.1, $^5J_{\mathrm{H,P}}$ = 0.9 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.26 [d, $^3J_{\mathrm{H,H}}$ = 1.9 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.63 [d, $^3J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.21–7.28 (m, 6 H, *Ph*), 7.29–7.33 (m, 3 H, *Ph*), 7.47–7.53 (m, 6 H, *Ph*), 7.61 [br. d, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.64 [br. d, $^3J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.68 [br. d $^3J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 8.32 [br. d, $^3J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 59.9 (d, $^1J_{\mathrm{C,P}}$ = 23.9 Hz, P*C*H$_2$), 105.2 [br. d, $^4J_{\mathrm{C,P}}$ = 2.6 Hz, HB(*C*$_3$H$_3$N$_2$)$_3$], 105.8 [d, $^4J_{\mathrm{C,P}}$ = 2.4 Hz, HB(*C*$_3$H$_3$N$_2$)$_3$], 106.3 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 128.1 (d, $^2J_{\mathrm{C,P}}$ = 8.7 Hz, C_{meta} PPh$_3$), 129.5 (d, $^4J_{\mathrm{C,P}}$ = 2.6 Hz, C_{para} PPh$_3$), 134.4 (d, $^3J_{\mathrm{C,P}}$ = 9.1 Hz, C_{ortho} PPh$_3$), 135.2 (d, $^1J_{\mathrm{C,P}}$ = 43.2 Hz, C_{ipso} PPh$_3$), 135.7 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 136.1 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 136.3 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.4 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 145.0 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 148.1 [s, HB(*C*$_3$H$_3$N$_2$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 45.3 (d, $^2J_{\mathrm{P,P}}$ = 30.9 Hz, P_{thp}), 37.8 (d, $^2J_{\mathrm{P,P}}$ = 30.9 Hz, *P*Ph$_3$) ppm.

Synthesis of [TpRu(NCCH$_3$)(PPh$_3$)(thp)]Cl (2): A yellow suspension of **1** (200 mg, 0.27 mmol) in acetonitrile (15 mL) was heated at reflux for 30 min. The resultant yellow solution was filtered through Celite to remove the decomposition products. The yellow filtrate was concentrated under vacuum, and the residue obtained was treated with diethyl ether (5 mL). The yellow precipitate obtained was washed with hexane and diethyl ether and dried in vacuo. Yield: 192.5 mg (91.8%). C$_{32}$H$_{37}$BClN$_7$O$_3$P$_2$Ru (776.97 g/mol): calcd. C 49.47, H 4.80, N 12.62; found C 49.12, H 5.02, N 12.95. MS: 742 [M$^+$], 712 [M$^+$ – CH$_2$O]. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2530 (w), ν_{CN} = 2279 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.10 (s, 3 H, C*H*$_3$), 3.89–4.01 (m, 6 H, C*H*$_2$P), 5.97 [br. t, $^3J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.22 [br. t, $^3J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.28 [br. t, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.78 [br. d, $^3J_{\mathrm{H,H}}$ = 1.7 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.15–7.24 (m, 6 H, *Ph*), 7.27–7.34 (m, 6 H, *Ph*), 7.36–7.43 (m, 3 H, *Ph*), 7.57 [br. d, $^3J_{\mathrm{H,H}}$ = 1.76 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.74 [br. d, $^3J_{\mathrm{H,H}}$ = 2.20 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.81 [br. d, $^3J_{\mathrm{H,H}}$ = 2.4 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.95 [d, $^3J_{\mathrm{H,H}}$ = 2.4 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 8.13 [br., 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 4.6 (s, *C*H$_3$), 56.9 (d, $^1J_{\mathrm{C,P}}$ = 26.0 Hz, P*C*H$_2$), 106.6 [br. d, $^4J_{\mathrm{C,P}}$ = 2.6 Hz, HB(*C*$_3$H$_3$N$_2$)$_3$], 106.7 [br. d, $^4J_{\mathrm{C,P}}$ = 2.6 Hz, HB(*C*$_3$H$_3$N$_2$)$_3$], 107.0 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 124.6 (s, N≡*C*), 128.5 (d, $^2J_{\mathrm{C,P}}$ = 9.1 Hz, C_{meta} PPh$_3$), 130.2 (s, C_{para} PPh$_3$), 134.5 (d, $^3J_{\mathrm{C,P}}$ = 10.4 Hz, C_{ortho} PPh$_3$), 134.9 (d, $^1J_{\mathrm{C,P}}$ = 40.6 Hz, C_{ipso} PPh$_3$), 136.3 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 136.5 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 138.0 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 143.1 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.7 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 148.4 [s, HB(*C*$_3$H$_3$N$_2$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 43.2 (d, $^2J_{\mathrm{P,P}}$ = 29.1 Hz, P_{thp}), 26.6 (d, $^2J_{\mathrm{P,P}}$ = 29.1 Hz, *P*Ph$_3$) ppm.

Synthesis of [TpRu{κ^2-(*C*,*P*)=C(CH$_2$Ph)OCH$_2$P(CH$_2$OH)$_2$}(PPh$_3$)]Cl (3a): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and phenylacetylene (30.5 µL, 0.27 mmol) in methanol (15 mL) was heated at 60 °C for 2 h to give a yellow solution. The resulting solution was filtered through Celite to remove the decomposition products. The solvent was vacuum removed, and the residue obtained was treated with hexane to yield a yellow solid. This solid was washed with a mixture of hexane/diethyl ether (5:1 v/v, 3 × 10 mL) and dried in vacuo. Yield: 85.3 mg (74.8%). C$_{38}$H$_{40}$BClN$_6$O$_3$P$_2$Ru (838.05 g/mol): calcd. C 54.46, H 4.81, N 10.03; found C 54.51, H 4.87, N 10.11. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2483 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.63 (collapsed dd, $^2J_{\mathrm{H,H}}$ = 11.9 Hz, 1 H, C*H*$_2$P), 3.02 (d, $^2J_{\mathrm{H,H}}$ = 16.7 Hz, 1 H, C*H*$_2$Ph), 3.63–3.83 (m, 2 H, C*H*$_2$P), 3.86 (dd, $^2J_{\mathrm{H,H}}$ = 13.1, $^2J_{\mathrm{H,P}}$ = 6.6 Hz, 1 H, C*H*$_2$P), 4.13 (d, $^2J_{\mathrm{H,H}}$ = 16.7 Hz, 1 H, C*H*$_2$Ph), 4.59 (d, $^2J_{\mathrm{H,H}}$ = 14.9 Hz, 1 H, C*H*$_2$P), 5.44 (dd, $^2J_{\mathrm{H,H}}$ = 14.8, $^2J_{\mathrm{H,P}}$ = 6.3 Hz, 1 H, C*H*$_2$P), 5.99 [br. t, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.13 [br. t, $^3J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.31 [br. t, $^3J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.49–6.54 (m, 2 H, *Ph*), 6.72 [br. d, $^3J_{\mathrm{H,H}}$ = 1.8 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.93–7.05 (m, 6 H, *Ph*), 7.06–7.14 (m, 3 H, *Ph*), 7.28–7.38 (m, 6 H, *Ph*), 7.39–7.47 (m, 3 H, *Ph*), 7.31 [br. s, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.66 [br. d, $^3J_{\mathrm{H,H}}$ = 1.7 Hz, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.99 [br. t, $^3J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 8.38 [d, $^3J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 51.9 (d, $^1J_{\mathrm{C,P}}$ = 39.0 Hz, P*C*H$_2$), 54.7 (d, $^1J_{\mathrm{C,P}}$ = 24.7 Hz, P*C*H$_2$), 59.6 (s, *C*H$_2$), 70.4 (d, $^1J_{\mathrm{C,P}}$ = 22.1 Hz, P*C*H$_2$), 106.3 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 106.8 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 107.4 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 126.9 (s, *C* Ph), 128.5 (s, *C* Ph), 129.0 (d, $^2J_{\mathrm{C,P}}$ = 10.4 Hz, *C* Ph), 129.7 (s, *C* Ph), 130.9 (s, *C* Ph), 134.0 (d, $^3J_{\mathrm{C,P}}$ = 9.1 Hz, *C* Ph), 134.0 (d, $^1J_{\mathrm{C,P}}$ = 32.5 Hz, *C* Ph), 134.4 (d, $^1J_{\mathrm{C,P}}$ = 42.9 Hz, *C* Ph), 136.8 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 137.2 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 137.3 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.1 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 145.0 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 149.3 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 327.1 (dd, $^{2}J_{C,P}$ = 11.7, $^{2}J_{C,P}$ = 7.80 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 36.3 (d, $^{2}J_{P,P}$ = 31.2 Hz, *P*Ph$_3$), 69.8 (d, $^{2}J_{P,P}$ = 31.2 Hz, P_{thp}) ppm.

Synthesis of [TpRu{κ^2-(*C,P*)=C(CH$_2$Ph)OCH$_2$PH(CH$_2$OH)}(PPh$_3$)]Cl (3b): Complex **3a** (50 mg) was heated at reflux in methanol (15 mL) for 3 h to give a yellow solution. This solution was filtered through Celite to remove the decomposition products. The solvent was vacuum removed, and the oily yellowish-green residue obtained was treated with a mixture of diethyl ether/hexane to yield a yellowish-green solid. This solid was washed with a mixture of hexane/diethyl ether (5:1 v/v, 3 × 10 mL) and dried in vacuo. Yield: 24.10 mg. A mixture of **3a**/**3b** (1:4 molar ratio, estimated by ^{31}P{^{1}H} NMR) was obtained. C$_{37}$H$_{38}$BO$_2$N$_6$P$_2$ClRu (808.03 g/mol). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 3.51–3.63 (m, 1 H, CH_2P), 3.98–4.07 (m, 1 H, CH_2P), 3.94–4.19 (m, 2 H, CH_2Ph), 4.45 (br. d, $^{2}J_{H,H}$ = 15.0 Hz, 1 H, CH_2P), 4.87 (d, $^{1}J_{H,P}$ = 389.9 Hz, 1 H, P*H*), 6.00 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.10 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.11 (br., 1 H, CH_2P), 6.17 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.78 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.79–6.90 (m, 5 H, *Ph*), 6.97 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.15–7.50 (m, 15 H, *Ph*), 7.57 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.64 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.89 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 8.02 [br. s, 1 H HB(C$_3H_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 55.6 (d, $^{1}J_{C,P}$ = 27.3 Hz, PCH_2), 60.1 (s, *C*H$_2$Ph), 70.1 (d, $^{1}J_{C,P}$ = 28.6 Hz, PCH_2), 106.5 [br. s, HB(C_3H$_3$N$_2$)$_3$], 106.8 [br. s, HB(C_3H$_3$N$_2$)$_3$], 107.1 [br. s, HB(C_3H$_3$N$_2$)$_3$], 127.1 (s, *C* Ph), 128.7 (s, *C* Ph), 129.0 (d, $^{2}J_{C,P}$ = 10.4 Hz, *C* Ph), 129.8 (s, *C* Ph), 131.3 (s, *C* Ph), 134.9 (d, $^{3}J_{C,P}$ = 9.1 Hz, *C* Ph), 134.4 (d, $^{1}J_{C,P}$ = 42.9 Hz, *C* Ph), 134.0 (d, $^{1}J_{C,P}$ = 32.5 Hz, *C* Ph), 133.8 [two overlapped doublets, $J \approx 40$ Hz, *C* Ph], 136.3 [s, HB(C_3H$_3$N$_2$)$_3$], 136.8 [s, HB(C_3H$_3$N$_2$)$_3$], 137.1 [s, HB(C_3H$_3$N$_2$)$_3$], 144.4 [s, 2 HB(C_3H$_3$N$_2$)$_3$], 146.9 [s, HB(C_3H$_3$N$_2$)$_3$], 326.9 (m, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 43.0 (d, $^{2}J_{P,P}$ = 32.0 Hz, *P*Ph$_3$), 71.33 (d, $^{2}J_{P,P}$ = 32.0 Hz, P_{thp}) ppm.

Synthesis of [TpRu{κ^2-(*C,P*)=C(CH$_2$C$_6$H$_4$Me)OCH$_2$P(CH$_2$OH)$_2$}(PPh$_3$)]Cl (4a): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and *p*-tolylacetylene (35.3 µL, 0.27 mmol) in methanol (15 mL) was heated at 60 °C for 3 h to give a yellow solution. The resultant solution was filtered through Celite to remove the decomposition products. The yellow filtrate was reduced to dryness under vacuum and then treated with hexane/diethyl ether (5:1, 3 × 10 mL). The yellow solid was dried in vacuo. Yield: 87.0 mg (75.1 %). C$_{39}$H$_{42}$BClN$_6$O$_3$P$_2$Ru (852.08 g/mol): calcd. C 54.97, H 4.97, N 9.86; found C 55.03, H 5.13, N 9.92. IR (KBr pellet): $\nu_{BH(Tp)}$ = 2484 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.24 (s, 3 H, CH_3), 2.62 (collapsed dd, $^{2}J_{H,H}$ = 11.9 Hz, 1 H, CH_2P), 2.99 (d, $^{2}J_{H,H}$ = 16.7 Hz, 1 H, CH_2), 3.62–3.84 (m, 2 H, CH_2P), 3.85 (dd, $^{2}J_{H,H}$ = 13.0, $^{2}J_{H,P}$ = 6.5 Hz, 1 H, CH_2P), 4.08 (d, $^{2}J_{H,H}$ = 16.8 Hz, 1 H, CH_2), 4.59 (d, $^{2}J_{H,H}$ = 14.8 Hz, 1 H, CH_2P), 5.43 (dd, $^{2}J_{H,H}$ = 14.8, $^{2}J_{H,P}$ = 6.4 Hz, 1 H, CH_2P), 5.99 [br. t, $^{3}J_{H,H}$ = 2.3 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.12 [br. t, $^{3}J_{H,H}$ = 2.3 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.31 [br. t, $^{3}J_{H,H}$ = 2.2 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.39 (d, $^{3}J_{H,H}$ = 7.7 Hz, 2 H, C$_6H_4$), 6.71 [br. d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.91 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2 H, C$_6H_4$), 6.95–7.04 (m, 6 H, *Ph*), 7.28–7.36 (m, 6 H, *Ph*), 7.31 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$],7.40–7.47 (m, 3 H, *Ph*), 7.66 [br. d, HB(C$_3H_3$N$_2$)$_3$, $^{3}J_{H,H}$ = 2.3 Hz, 1 H], 7.97–8.01 [m, 2 H, HB(C$_3H_3$N$_2$)$_3$], 8.38 [d, $^{3}J_{H,H}$ = 1.9 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 21.0 (s, *C*H$_3$), 52.0 (d, $^{1}J_{C,P}$ = 38.6 Hz, PCH_2), 54.8 (d, $^{1}J_{C,P}$ = 24.5 Hz, PCH_2), 59.3 (s, *C*H$_2$), 70.4 (d, $^{1}J_{C,P}$ = 23.2 Hz, PCH_2), 106.3 [br. s, HB(C_3H$_3$N$_2$)$_3$], 106.8 [br. s, HB(C_3H$_3$N$_2$)$_3$], 107.4 [br. s, HB(C_3H$_3$N$_2$)$_3$], 129.2 (s, *C* C$_6$H$_4$), 129.6 (s, *C* C$_6$H$_4$), 129.0 (d, $^{2}J_{C,P}$ = 10.3 Hz, *C* Ph), 130.9 (s, *C* Ph), 131.1 (s, *C* Ph), 134.0 (d, $^{3}J_{C,P}$ = 9.0 Hz, *C* Ph), 134.5 (d, $^{1}J_{C,P}$ = 43.8 Hz, *C* Ph), 136.7 [br. s, HB(C_3H$_3$N$_2$)$_3$], 136.8 (s, *C* Ph), 137.2 [br. s, HB(C_3H$_3$N$_2$)$_3$], 137.2 [s, HB(C_3H$_3$N$_2$)$_3$], 144.1 [s, HB(C_3H$_3$N$_2$)$_3$], 145.1 [s, HB(C_3H$_3$N$_2$)$_3$], 149.3 [s, HB(C_3H$_3$N$_2$)$_3$], 327.6 (dd, $^{2}J_{C,P}$ = 11.6, $^{2}J_{C,P}$ = 7.73 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 36.8 (d, $^{2}J_{P,P}$ = 31.2 Hz, *P*Ph$_3$), 70.1 (d, $^{2}J_{P,P}$ = 31.2 Hz, P_{thp}) ppm.

Synthesis of [TpRu{κ^2-(*C,P*)=C(CH$_2$C$_6$H$_4$Me)OCH$_2$PH(CH$_2$OH)}(PPh$_3$)]Cl (4b): Complex **4a** (50 mg) was heated at reflux in methanol (15 mL) for 24 h to give a yellow solution. The solution was filtered through Celite to remove the decomposition products. The filtrate was reduced to dryness under vacuum to obtain an oil, which was treated with a mixture of hexane/diethyl ether (5:1, 3 × 10 mL). The yellowish-green solid formed was filtered and dried in vacuo. Yield: 36.7 mg. A mixture of **4a**/**4b** (1:4 molar ratio, estimated by ^{31}P{^{1}H} NMR) was obtained. C$_{38}$H$_{40}$BClN$_6$O$_2$P$_2$Ru (822.06 g/mol). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.28 (s, 3 H, CH_3), 3.51–3.61 (m, 1 H, CH_2P), 3.91–3.98 (m, 1 H, CH_2), 3.98–4.04 (m, 1 H, CH_2P), 4.06–4.13 (m, 1 H, CH_2), 4.44 (br. dd, $^{2}J_{H,H}$ = 14.5, $^{2}J_{H,P}$ = 3.6 Hz, 1 H, CH_2P), 4.85 (d, $^{1}J_{H,P}$ = 391.3 Hz, 1 H, P*H*), 6.01 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.11 [br. t, $^{3}J_{H,H}$ = 2.1 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.12 [br. t, $^{3}J_{H,H}$ = 2.2 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.13 (br., 1 H, CH_2P), 6.66 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2 H, C$_6H_4$), 6.77 [br. d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.81–6.89 (m, 6 H, Ph), 6.95 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.00 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2 H, C$_6H_4$), 7.28–7.37 (m, 4 H, *Ph*), 7.47 (br., 2 H, *Ph*), 7.56 [br. d, HB(C$_3H_3$N$_2$)$_3$, $^{3}J_{H,H}$ = 1.7 Hz, 1 H], 7.63 [br. s, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.67–7.71 (m, 2 H, Ph), 7.69 (s, 1 H, *Ph*), 7.88 [d, $^{3}J_{H,H}$ = 2.5 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 8.00 [d, $^{3}J_{H,H}$ = 2.4 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 21.1 (s, *C*H$_3$), 55.9 (d, $^{1}J_{C,P}$ = 26.0 Hz, PCH_2), 59.8 (s, *C*H$_2$), 70.8 (d, $^{1}J_{C,P}$ = 28.1 Hz, PCH_2), 106.5 [br. s, HB(C_3H$_3$N$_2$)$_3$], 106.8 [br. s, HB(C_3H$_3$N$_2$)$_3$], 107.1 [br. s, HB(C_3H$_3$N$_2$)$_3$], 129.1 (d, $^{2}J_{C,P}$ = 9.1 Hz, *C* Ph), 129.4 (s, *C* C$_6$H$_4$), 129.6 (s, *C* C$_6$H$_4$), 131.0 (s, *C* C$_6$H$_4$), 136.9 (s, *C* C$_6$H$_4$), 129.0–134.2 (*C* Ph), 136.3 [br. s, HB(C_3H$_3$N$_2$)$_3$], 136.9 [br. s, HB(C_3H$_3$N$_2$)$_3$], 137.1 [br. s, HB(C_3H$_3$N$_2$)$_3$], 144.4 [br. s, HB(C_3H$_3$N$_2$)$_3$], 144.5 [br. s, HB(C_3H$_3$N$_2$)$_3$], 146.9 [br. s, HB(C_3H$_3$N$_2$)$_3$], 327.3 (m, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 43.2 (d, $^{2}J_{P,P}$ = 32.0 Hz, *P*Ph$_3$), 71.6 (d, $^{2}J_{P,P}$ = 32.0 Hz, P_{thp}) ppm.

Synthesis of [TpRu{κ^2-(*C,P*)=C(CH$_3$)OCH$_2$P(CH$_2$OH)$_2$}(PPh$_3$)]Cl (5a): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and (trimethylsilyl)acetylene (92.1 µL, 0.68 mmol) in methanol (15 mL) was stirred at room temperature for 24 h to give a yellow solution, which was filtered through Celite to remove the decomposition products. The yellow filtrate was reduced to dryness under vacuum and then treated with a mixture of hexane/diethyl ether (5:1, 3 × 10 mL). The yellow solid obtained was dried in vacuo. Yield: 60.1 mg (58.0 %). C$_{32}$H$_{36}$BClN$_6$O$_3$P$_2$Ru (761.96 g/mol): calcd. C 50.44, H 4.76, N 11.03; found C 50.36, H 4.71, N 11.11. IR (KBr pellet): $\nu_{BH(Tp)}$ = 2465 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 1.98 (s, 3 H, CH_3), 2.53 (dd, $^{2}J_{H,H}$ = 12.8, $^{2}J_{H,P}$ = 10.6 Hz, 1 H, CH_2P), 3.70–3.84 (m, 2 H, CH_2P), 3.88 (dd, $^{2}J_{H,H}$ = 13.0, $^{2}J_{H,P}$ = 6.7 Hz, 1 H, CH_2), 4.52 (br. d, $^{2}J_{H,H}$ = 14.5 Hz, 1 H, CH_2), 5.57 (dd, $^{2}J_{H,H}$ = 14.3, $^{2}J_{H,P}$ = 7.1 Hz, 1 H, CH_2P), 6.04 [br. t, $^{3}J_{H,H}$ = 2.2 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.15 [br. t, $^{3}J_{H,H}$ = 2.1 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.30 [br. t, $^{3}J_{H,H}$ = 2.2 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 6.88–6.98 (m, 6 H, *Ph*), 7.00 [br. d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.02 [br. d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.24–7.32 (m, 6 H, *Ph*), 7.37–7.45 (m, 3 H, *Ph*), 7.69 [br. d, $^{3}J_{H,H}$ = 2.6 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.91 [br. d, $^{3}J_{H,H}$ = 2.3 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 7.99 [br. d, $^{3}J_{H,H}$ = 2.5 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$], 8.38 [br. d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, HB(C$_3H_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 40.9 (s, *C*H$_3$), 51.4 (d, $^{1}J_{C,P}$ =

39.9 Hz, P*C*H$_2$), 54.9 (d, $^{1}J_{\mathrm{C,P}}$ = 23.6 Hz, P*C*H$_2$), 69.8 (d, $^{1}J_{\mathrm{C,P}}$ = 22.8 Hz, P*C*H$_2$), 106.5 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 106.6 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 107.4 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 128.9 (d, $^{3}J_{\mathrm{C,P}}$ = 9.3 Hz, *C* Ph), 130.9 (s, *C* Ph), 134.0 (d, $^{2}J_{\mathrm{C,P}}$ = 9.6 Hz, *C* Ph), 134.3 (d, $^{1}J_{\mathrm{C,P}}$ = 46.1 Hz, *C* Ph), 137.0 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 137.1 (s, *C* Ph), 137.2 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 143.7 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.8 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 149.4 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 331.9 (dd, $^{2}J_{\mathrm{C,P}}$ = 12.9, $^{2}J_{\mathrm{C,P}}$ = 7.60 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 37.2 (d, $^{2}J_{\mathrm{P,P}}$ = 31.1 Hz, *P*Ph$_3$), 70.0 (d, $^{2}J_{\mathrm{P,P}}$ = 31.1 Hz, *P*$_{\mathrm{thp}}$) ppm.

Synthesis of [TpRu{κ^2-(*C,P*)=C(CH$_3$)OCH$_2$PH(CH$_2$OH)}-(PPh$_3$)]Cl (5b): Complex **5a** (50 mg) was heated at reflux in methanol (15 mL) for 5 h to give a yellow solution, which was filtered through Celite to remove the decomposition products. The yellow filtrate was reduced to dryness under vacuum and then treated with a mixture of hexane/diethyl ether (5:1, 3 × 10 mL). The pale yellow solid was dried in vacuo. Yield: 25.2 mg. A mixture of **5a**/**5b** (2:5 molar ratio, estimated by ^{31}P{^{1}H} NMR) was obtained. C$_{31}$H$_{34}$BClN$_6$O$_2$P$_2$Ru (731.93 g/mol). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.39 (s, 3 H, C*H*$_3$), 3.57 (dd, $^{2}J_{\mathrm{H,H}}$ = 15.0, $^{2}J_{\mathrm{H,P}}$ = 7.8 Hz, 1 H, C*H*$_2$P), 4.05–4.15 (m, 1 H, C*H*$_2$P), 4.28–4.37 (m, 1 H, C*H*$_2$P), 4.87 (d, $^{1}J_{\mathrm{H,P}}$ = 386.0 Hz, 1 H, P*H*), 6.16–6.23 (m, 1 H, C*H*$_2$P), 6.06 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.11 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.2 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.16 [br., 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.47 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.77–6.85 (m, 6 H, *Ph*), 7.25 [br. d, $^{3}J_{\mathrm{H,H}}$ = 1.9 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.31–7.36 (m, 6 H, *Ph*), 7.45–7.49 (m, 3 H, *Ph*), 7.56 [br. d, $^{3}J_{\mathrm{H,H}}$ = 1.9 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.67 [br. s, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.88 [d, $^{3}J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.93 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 41.2 (s, *C*H$_3$), 55.9 (d, $^{1}J_{\mathrm{C,P}}$ = 27.0 Hz, P*C*H$_2$), 70.0 (d, $^{1}J_{\mathrm{C,P}}$ = 29.6 Hz, P*C*H$_2$), 106.6 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 106.6 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 107.2 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 129.0 (d, $^{3}J_{\mathrm{C,P}}$ = 9.0 Hz, *C* Ph), 133.8 (d, $^{2}J_{\mathrm{C,P}}$ = 9.0 Hz, *C* Ph), 136.6 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 137.0 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 136.9 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.4 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.4 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 331.7 (m, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 43.4 (d, $^{2}J_{\mathrm{P,P}}$ = 32.4 Hz, *P*Ph$_3$), 71.5 (d, $^{2}J_{\mathrm{P,P}}$ = 32.4 Hz, *P*$_{\mathrm{thp}}$) ppm.

Synthesis of [TpRu{κ^2-(*C,P*)=C(CH$_2$OOCMe)OCH$_2$P(CH$_2$OH)$_2$}-(PPh$_3$)]Cl (6a): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and ethyl propiolate (55.7 µL, 0.54 mmol) in methanol (15 mL) was heated at reflux for 4 h to give an orange solution, which was filtered through Celite to remove the decomposition products. The filtrate was reduced to dryness under vacuum and then was treated with a mixture of hexane/diethyl ether (5:1, 3 × 10 mL). The orange solid was dried in vacuo. Yield: 40.3 mg. (35.1 %). C$_{34}$H$_{38}$BClN$_6$O$_5$P$_2$Ru (819.99 g/mol): calcd. C 49.80, H 4.67, N 10.25; found C 49.58, H 4.73, N 10.11. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2484 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.37 (br. collapsed dd, $^{2}J_{\mathrm{H,H}}$ = 13.5 Hz, 1 H, C*H*$_2$P), 2.88 (d, $^{2}J_{\mathrm{H,H}}$ = 18.0 Hz, 1 H, C*H*$_2$), 3.57 (d, $^{2}J_{\mathrm{H,H}}$ = 17.8 Hz, 1 H, C*H*$_2$), 3.63 (s, 3 H, C*H*$_3$), 3.78 (br., 2 H, C*H*$_2$P), 3.94 (br., 1 H, C*H*$_2$P), 4.50 (d, $^{3}J_{\mathrm{H,H}}$ = 14.1 Hz, 1 H, C*H*$_2$P), 5.57 (dd, $^{2}J_{\mathrm{H,H}}$ = 14.1, $^{2}J_{\mathrm{H,P}}$ = 7.4 Hz, 1 H, C*H*$_2$P), 6.03 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.20 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.29 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.80 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.88–6.97 (m, 6 H, *Ph*), 7.19 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.28–7.36 (m, 6 H, *Ph*), 7.41–7.47 (m, 3 H, *Ph*), 7.72 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.92 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 8.00 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.3 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 8.41 [d, $^{3}J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 50.5 (d, $^{1}J_{\mathrm{C,P}}$ = 41.2 Hz, P*C*H$_2$), 52.38 (s, *C*H$_3$), 54.5 (d, partially obscured by the solvent signal, P*C*H$_2$), 59.8 (s, *C*H$_2$), 70.6 (d, $^{1}J_{\mathrm{C,P}}$ = 23.2 Hz, P*C*H$_2$), 106.6 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 106.8 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 107.5 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 129.1 (d, $^{2}J_{\mathrm{C,P}}$ = 9.01 Hz, *C* Ph), 131.2 (s, *C* Ph), 135.5 (d, $^{1}J_{\mathrm{C,P}}$ = 43.8 Hz, *C* Ph), 134.0 (d, $^{2}J_{\mathrm{C,P}}$ = 9.10 Hz, *C* Ph), 137.3 [br. s, 2 HB(*C*$_3$H$_3$N$_2$)$_3$], 137.4 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.4 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.7 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 149.7 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 167.6 [s, *C*(O)O–], 319.4 (dd, $^{2}J_{\mathrm{C,P}}$ = 12.9, $^{2}J_{\mathrm{C,P}}$ = 7.73 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 36.4 (d, $^{2}J_{\mathrm{P,P}}$ = 30.5 Hz, *P*Ph$_3$), 60.4 (d, $^{2}J_{\mathrm{P,P}}$ = 30.5 Hz, *P*$_{\mathrm{thp}}$) ppm.

NMR Characterisation of [TpRu{κ^2-(*C,P*)=C(CH=CPh$_2$)-OCH$_2$P(CH$_2$OH)$_2$}(PPh$_3$)]Cl (7a): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and 1,1-diphenyl-2-propyn-1-ol (56.80 µL, 0.27 mmol) in methanol (15 mL) was stirred for 4 d at room temperature to give a red solution, which was filtered through Celite to remove the decomposition products. The red filtrate was reduced to dryness under vacuum, and the oil obtained was then treated with hexane/diethyl ether (5:1, 3 × 10 mL). The red solid obtained was filtered out and dried in vacuo. A mixture of **7a**/**7b** (1:1 molar ratio estimated by ^{31}P{^{1}H} NMR spectroscopy) was obtained. A careful perusal of the ^{1}H, ^{13}C{^{1}H}, ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-HSQC NMR spectra of the mixture allowed us to assign all signals for **7a**: ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 2.31–2.42 (m, 1 H, C*H*$_2$P), 3.64–3.77 (m, 2 H, C*H*$_2$P), 3.78–3.86 (m, 1 H, C*H*$_2$P), 4.10 (br. d, $^{2}J_{\mathrm{H,H}}$ = 14.3 Hz, 1 H, C*H*$_2$P), 4.93 (dd, $^{2}J_{\mathrm{H,H}}$ = 14.5, $^{2}J_{\mathrm{H,P}}$ = 6.7 Hz, 1 H, C*H*$_2$P), 6.09 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.16 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.24 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.62–6.68 (m, 2 H, *Ph*), 6.93–7.00 (m, 6 H, *Ph*), 7.05–7.12 (m, 2 H, *Ph*), 7.09 [br. s, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.13 [br. s, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.17–7.37 (m, 15 H, Ph), 7.71 [br. s, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.94 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.99 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.7 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 8.29 [d, $^{3}J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$] ppm, the signal for C*H* is masked by other signals. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz): δ = 50.6 (d, $^{1}J_{\mathrm{C,P}}$ = 39.0 Hz, P*C*H$_2$), 54.7 (d, $^{1}J_{\mathrm{C,P}}$ = 24.7 Hz, P*C*H$_2$), 68.6 (d, $^{1}J_{\mathrm{C,P}}$ = 22.1 Hz, P*C*H$_2$), 106.4 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 106.6 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 107.3 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 128.1–134.8 (*C* Ph + *C*H), 137.0 [br. s, HB(*C*$_3$H$_3$N$_2$)$_3$], 137.1 [br. s, 2 HB(*C*$_3$H$_3$N$_2$)$_3$], 144.2 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 144.3 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 149.4 [s, HB(*C*$_3$H$_3$N$_2$)$_3$], 307.8 (dd, $^{2}J_{\mathrm{C,P}}$ = 13.0, $^{2}J_{\mathrm{C,P}}$ = 9.10 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161 MHz): δ = 38.4 (d, $^{2}J_{\mathrm{P,P}}$ = 31.6 Hz, *P*Ph$_3$), 69.9 (d, $^{2}J_{\mathrm{P,P}}$ = 31.6 Hz, *P*$_{\mathrm{thp}}$) ppm.

Synthesis of [TpRu{κ^2-(*C,P*)=C(CH=CPh$_2$)OCH$_2$PH(CH$_2$OH)}-(PPh$_3$)]Cl (7b): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and 1,1-diphenyl-2-propyn-1-ol (56.80 µL, 0.27 mmol) in methanol (15 mL) was heated at reflux for 6 h to give a red solution, which was filtered through Celite to remove the decomposition products. The red filtrate was reduced to dryness under vacuum and then treated with hexane/diethyl ether (5:1, 3 × 10 mL). The red solid obtained was filtered out and dried in vacuo. Yield: 45.9 mg. (36.6 %). C$_{44}$H$_{42}$BClN$_6$O$_2$P$_2$Ru (896.14 g/mol): calcd. C 58.97, H 4.72, N 9.38; found C 59.10, H 4.65, N 9.26. IR (KBr pellet): $\nu_{\mathrm{BH(Tp)}}$ = 2482 cm^{-1}. (w) ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 3.55 (br. dd, $^{2}J_{\mathrm{H,H}}$ = 13.9, $^{2}J_{\mathrm{H,P}}$ = 6.7 Hz, 1 H, C*H*$_2$P), 3.92–4.00 (m, 1 H, C*H*$_2$P), 3.89 (dd, $^{2}J_{\mathrm{H,H}}$ = 13.8, $^{2}J_{\mathrm{H,P}}$ = 3.4 Hz, 1 H, C*H*$_2$P), 5.36 (dd, $^{2}J_{\mathrm{H,H}}$ = 14.1, $^{2}J_{\mathrm{H,P}}$ = 7.2 Hz, 1 H, C*H*$_2$P), 5.08 (d, $^{1}J_{\mathrm{H,P}}$ = 387.3 Hz, 1 H, P*H*), 6.10 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.1 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.12 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.14 [br. t, $^{3}J_{\mathrm{H,H}}$ = 2.5 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.70 [br. d, $^{3}J_{\mathrm{H,H}}$ = 2.0 Hz, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 6.79–6.87 (m, 6 H, *Ph*), 7.10–7.35 (m, 15 H, *Ph*), 7.28 [br. s, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.56 [br. s, 1 H, HB(C$_3$*H*$_3$N$_2$)$_3$], 7.60–7.65 (m, 4 H, *Ph*), 7.68 [br. d, $^3J_{H,H}$ = 2.1 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.89 [br. d, $^3J_{H,H}$ = 2.4 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.97 [d, $^3J_{H,H}$ = 2.2 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$] ppm, the signal for C*H* is masked by phenyl signals. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ = 55.9 (d, $^1J_{C,P}$ = 24.7 Hz, P*C*H_2), 68.9 (d, $^1J_{C,P}$ = 28.6 Hz, P*C*H_2), 106.5 [br. s, 2 $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.6 (s, =*C*Ph$_2$), 107.2 [br. s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 126.1–134.0 (*C* Ph + *C*H), 136.6 [br. s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 136.8 [br. s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 137.1 [br. s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 144.3 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 144.2 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 149.4 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 307.4 (dd, $^2J_{C,P}$ = 12.0, $^2J_{C,P}$ = 8.9 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ = 43.3 (d, $^2J_{P,P}$ = 33.2 Hz, *P*Ph$_3$), 71.0 (d, $^2J_{P,P}$ = 33.2 Hz, P_{thp}) ppm.

Synthesis of [TpRuCl{κ^2-(*C*,*P*)=C(CH$_2$Ph)OCH$_2$P(CH$_2$OH)$_2$}] (8): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and phenylacetylene (30.5 µL, 0.27 mmol) in toluene (20 mL) was heated at reflux for 4 h to give a yellow solution, which was filtered through Celite to remove the decomposition products. The solvent was removed by vacuum to a volume of about 1 mL, and the residue was treated with hexane to yield a yellow solid. This solid was washed with a mixture of hexane/diethyl ether (5:1, 3 × 10 mL) and dried in vacuo. Yield: 65.0 mg (83.0%). $C_{20}H_{25}BClN_6O_3PRu$ (575.76 g/mol): calcd. C 41.72, H 4.38, N 14.60; found C 41.37, H 4.22, N 14.94. IR (KBr pellet): $\nu_{BH(Tp)}$ = 2478 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 3.63 (br., 2 H, O*H*), 3.83, 3.88 (ABX system, $J_{A,B}$ = 13.6, $J_{A,X}$ = 2.9, $J_{B,X}$ = –0.2 Hz, 2 H, C*H*$_2$P), 4.33 (s, 2 H, C*H*$_2$Ph), 4.66, 4.74 (ABX system, $J_{A,B}$ = 13.1, $J_{A,X}$ = 5.0, $J_{B,X}$ = 4.2 Hz, 2 H, C*H*$_2$P), 5.10, 5.16 (ABX system, $J_{A,B}$ = 13.4, $J_{A,X}$ = 4.9, $J_{B,X}$ = –2.4 Hz, 2 H, C*H*$_2$P), 5.94 [br. t, $^3J_{H,H}$ = 2.3 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.28 [br. t, $^3J_{H,H}$ = 2.1 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.32 [br. td, $^3J_{H,H}$ = 2.1, $^5J_{H,P}$ = 1.0 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.48 [d, $^3J_{H,H}$ = 2.0 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.80–6.86 (m, 2 H, *Ph*), 7.09–7.17 (m, 3 H, *Ph*), 7.68 [br. d, $^3J_{H,H}$ = 2.5, $^4J_{H,H}$ = 0.6 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.77 [br. d, $^3J_{H,H}$ = 2.2, $^4J_{H,H}$ = 0.6 Hz, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.82 [br., 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.89 [d, $^3J_{H,H}$ = 1.8 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.96 [d, $^3J_{H,H}$ = 2.0 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ = 57.8 (d, $^1J_{C,P}$ = 23.2 Hz, P*C*H_2), 58.3 (d, $^1J_{C,P}$ = 30.9 Hz, P*C*H_2), 58.5 (s, *C*H_2Ph), 68.7 (d, $^1J_{C,P}$ = 25.7 Hz, P*C*H_2), 106.0 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.1 [br. d, $^3J_{C,P}$ = 2.6 Hz, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.4 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 126.4 (s, *C* Ph), 128.6 (s, 2 *C* Ph), 129.8 (s, 2 *C* Ph), 135.8 (s, *C* Ph), 135.2 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 135.3 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 137.0 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 143.0 [br. s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 144.0 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 144.9 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 323.3 (d, $^2J_{C,P}$ = 10.3 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ = 81.5 (s, P_{thp}) ppm.

Synthesis of [TpRuCl{κ^2-(*C*,*P*)=C(CH$_2$C$_6$H$_4$Me)OCH$_2$P(CH$_2$OH)$_2$}] (9): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and *p*-tolylacetylene (34.0 mg, 0.27 mmol) in toluene (20 mL) was heated at reflux for 1 h to give a yellow solution, which was filtered through Celite to remove the decomposition products. The solvent was removed by vacuum to a volume of about 1 mL, and the residue was then treated with hexane to yield a yellow solid. This solid was washed with hexane/diethyl ether (5:1 v/v, 3 × 10 mL) after it was dried in vacuo. Yield: 65.0 mg (81.0%). $C_{21}H_{27}BClN_6O_3PRu$ (589.79 g/mol): calcd. C 42.77, H 4.61, N 14.25; found C 42.95, H 4.89, N 12.79. IR (KBr pellet): $\nu_{BH(Tp)}$ = 2468 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 2.26 (s, 3 H, C*H*$_3$), 3.67–3.76 (m, 1 H, C*H*$_2$P), 3.76–3.85 (m, 1 H, C*H*$_2$P), 4.22–4.34 [m, 2 H, C*H*$_2$(C$_6$H$_4$)], 4.59–4.77 (m, 2 H, C*H*$_2$P), 5.07–5.14 (m, 2 H, C*H*$_2$P), 5.94 [t, $^3J_{H,H}$ = 2.2 Hz, 1 H, $\mathrm{HB(C_3H_3N_2)_3}$], 6.26 [t, $^3J_{H,H}$ = 2.08 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.28 [br. t, $^3J_{H,H}$ = 2.2 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.47 [d, $^3J_{H,H}$ = 1.9 Hz, 1 H, $\mathrm{HB(C_3H_3N_2)_3}$], 6.72 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, C$_6$*H*$_4$), 6.95 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, C$_6$*H*$_4$), 7.68 [br. d, $^3J_{H,H}$ = 2.5 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.76 [br. d, $^3J_{H,H}$ = 2.2 Hz, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.80 [br., 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.86 [br. d, $^3J_{H,H}$ = 1.6 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.93 [br. d, $^3J_{H,H}$ = 1.6 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ = 21.1 (s, *C*H$_3$), 57.6 (d, $^1J_{C,P}$ = 21.9 Hz, P*C*H_2), 58.2 (d, $^1J_{C,P}$ = 30.9 Hz, P*C*H_2), 58.2 [s, *C*H$_2$(C$_6$H$_4$)], 68.9 (d, $^1J_{C,P}$ = 25.7 Hz, P*C*H_2), 106.1 [s, 2 $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.3 [br., $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 129.2 [s, C_{meta} C$_6H_4$], 129.6 [s, C_{ortho} C$_6H_4$], 132.6 (s, C_{ipso} C$_6H_4$), 135.1 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 135.3 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 136.08 (s, C_{ipso} C$_6H_4$), 136.9 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 143.1 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 144.0 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 145.0 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 323.7 (d, $^2J_{C,P}$ = 11.6 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ = 81.6 (s) ppm.

Synthesis of [TpRuCl{κ^2-(*C*,*P*)=C(CH$_2$SiMe$_3$)OCH$_2$P(CH$_2$OH)$_2$}] (10): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and (trimethylsilyl)acetylene (36.5 µL, 0.27 mmol) in toluene (20 mL) was heated at reflux for 4 h to give a yellow solution, which was filtered through Celite to remove the decomposition products. The solvent was removed by vacuum to a volume of about 1 mL, and the residue was treated with hexane to afford a yellow solid. This solid was washed with a mixture of hexane/diethyl ether (5:1 v/v, 3 × 10 mL) and dried in vacuo. Yield: 65.2 mg (83.8%). $C_{17}H_{29}BClN_6O_3PRuSi$ (571.85 g/mol): calcd. C 35.71, H 5.11, N 14.70; found C 35.81, H 5.06, N 14.38. IR (KBr pellet): $\nu_{BH(Tp)}$ = 2474 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = –0.14 (s, 9 H, C*H*$_3$), 1.73 (br., 1 H, O*H*), 3.01–3.27 (m, 2 H, C*H*$_2$Si), 3.88 (s, 2 H, C*H*$_2$P), 4.30 (br., 1 H, O*H*), 4.48–4.69 (m, 2 H, C*H*$_2$P), 4.96–5.09 (m, 2 H, C*H*$_2$P), 6.08 [t, $^3J_{H,H}$ = 2.2 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.25 [t, $^3J_{H,H}$ = 2.0 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.34 [br. t, $^3J_{H,H}$ = 2.2 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.79 [d, $^3J_{H,H}$ = 2.1 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.69 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$), 7.74 [br. d, $^3J_{H,H}$ = 2.2 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.77 [br., 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.87 [d, $^3J_{H,H}$ = 1.7 Hz, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 8.01 [br. s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ = –0.24 (s, *C*H$_3$), 49.9 (s, *C*H$_2$Si), 57.4 (d, $^1J_{C,P}$ = 23.0 Hz, P*C*H_2), 58.6 (d, $^1J_{C,P}$ = 32.4 Hz, P*C*H_2), 67.3 (d, $^1J_{C,P}$ = 24.5 Hz, P*C*H_2), 105.9 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.0 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.4 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 135.2 [s, 2 $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 137.2 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 142.9 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 143.7 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 144.7 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 327.6 (d, $^2J_{C,P}$ = 10.4 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ = 85.5 (s) ppm.

Synthesis of [TpRuCl{κ^2-(*C*,*P*)=C(CH=CPh$_2$)OCH$_2$P(CH$_2$OH)$_2$}] (11): A yellow suspension of complex **1** (100 mg, 0.14 mmol) and 1,1-diphenyl-2-propyn-1-ol (56.8 mg, 0.27 mmol) in toluene (20 mL) was heated at reflux for 2 h with molecular sieves; a red solution, which was filtered through Celite to remove the decomposition products and the molecular sieves, was obtained. The solvent was removed by vacuum to a volume of about 1 mL, and the residue was treated with hexane to yield a red solid. This solid was vacuum filtered, washed with a mixture of hexane/diethyl ether (5:1 v/v, 3 × 5 mL) and dried in vacuo. Yield: 45.2 mg (50.1%). $C_{27}H_{29}BClN_6O_3PRu$ (663.87 g/mol): calcd. C 48.85, H 4.40, N 12.66; found C 49.12, H 4.64, N 12.91. IR (KBr pellet): $\nu_{BH(Tp)}$ = 2474 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 3.74–3.92 (m, 2 H, C*H*$_2$P), 4.53–4.76 (m, 3 H, C*H*$_2$P), 4.82–4.92 (m, 1 H, C*H*$_2$P), 6.12 [br., 2 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.31 [s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 6.76 [s, 1 H, C*H*=], 6.87 [s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.08–7.42 (m, 10 H, *Ph*), 7.71 [s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.73 (s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$), 7.76 [s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 7.80 [s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$], 8.00 [s, 1 H, $\mathrm{HB(C_3\mathit{H}_3N_2)_3}$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ = 57.7 (d, $^1J_{C,P}$ = 23.2 Hz, P*C*H_2), 58.1 (d, $^1J_{C,P}$ = 30.9 Hz, P*C*H_2), 67.5 (d, $^1J_{C,P}$ = 25.7 Hz, P*C*H_2), 105.7 [s, 2 $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.2 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 106.6 (s, =*C*Ph$_2$), 125.9–134.6 (*C* Ph), 135.0 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 135.3 [s, $\mathrm{HB(\mathit{C}_3H_3N_2)_3}$], 136.9 (s, *C*(H)=), 137.4 [s, HB($C_3H_3N_2$)$_3$], 143.2 [s, HB($C_3H_3N_2$)$_3$], 144.2 [s, HB($C_3H_3N_2$)$_3$], 144.5 [s, HB($C_3H_3N_2$)$_3$], 310.9 (d, $^2J_{C,P}$ = 12.9 Hz, Ru=C) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161 MHz): δ = 79.9 (s) ppm.

X-ray Structure Determination: The crystal was mounted on a glass fiber and was encapsulated with glue to prevent its damage during exposure. Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at 20 °C by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarisation effects. All crystals of **9** under investigation were non-merohedral twins, and two components were identified with the CELL_NOW[27] program. SAINT-PLUS[28] (version 6.29) was used for integration and the data were merged and corrected for absorption by using TWINABS.[29] 5315 data (4073 unique) involve domain 1 only, (mean I/σ 7.4), 5114 data (3876 unique) involve domain 2 only, (mean I/σ 5.0), and 2609 data (2284 unique) involve both domains, (mean I/σ 5.1). By using the Oscail program,[30] the structure was solved with only the reflections of component 1 by direct methods and refined by a full-matrix least-squares based on F^2.[31] The Squeeze program was used to correct the reflection data for the diffuse scattering resulting from disordered CH_2Cl_2 solvent found in the asymmetric unit.[32] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Some restraints to the model were used in order to keep the toluene group within accepted chemical parameters, which include displacement parameters and planarity of the group. Details of the crystal data and structural refinement are presented in Table 2. CCDC-746341 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement for **9**.

Empirical formula	$C_{21}H_{27}BClN_6O_3PRu$
Formula weight	589.79
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a [Å]	10.403(2)
b [Å]	12.712(3)
c [Å]	10.422(2)
β [°]	93.20(3)
Volume [Å^3]	1376.0(5)
Z	2
Density (calculated) [Mg/m^3]	1.423
Absorption coefficient [mm^{-1}]	0.757
F(000)	600
Crystal size [mm]	0.30 × 0.15 × 0.13
θ range for data collection [°]	1.96–28.28
Index ranges	$-13 \leq h \leq 13$; $0 \leq k \leq 16$; $0 \leq l \leq 13$
Independent reflections	3259 [R(int) = 0.33]
Reflections observed (>2σ)	2283
Data Completeness	0.915
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.7459 and 0.5530
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3259/9/293
Goodness-of-fit on F^2	1.120
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0908, wR_2 = 0.2246
R indices (all data)	R_1 = 0.1217, wR_2 = 0.2432
Absolute structure parameter	0.09(13)
Largest diff. peak and hole [e Å^{-3}]	1.818 and –1.945

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