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Article

Reactivity of [TpRuCl(PTA)(PPh_3)] with Alkynes and Propargylic Alcohols: Occurrence of Structurally Related Cationic vs Neutral Allenylidene Complexes with the Ruthenium Hydrotris(pyrazolyl)borate Moiety

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[TpRuCl(PTA)(PPh_3)] (**1**; PTA = 1,3,5-triaza-7-phosphaadamantane) reacts with phenylacetylene, yielding the alkynyl complex [TpRu(C≡CPh)(PTA)(PPh_3)] (**2**) or the neutral vinylidene complex [TpRuCl{C=C(H)Ph}(PTA)] (**4**), depending on the solvent and the reaction conditions (Tp = hydrotris(pyrazolyl)borate). Protonation of **2** with HOTf (OTf = OSO_2CF_3) in CH_2Cl_2 yields the dicationic vinylidene compound [TpRu{C=C(H)Ph}{PTAH}(PPh_3)](OTf)$_2$ (**3**), bearing a N-protonated PTA ligand. Reaction of **1** with 1,1-diphenyl-2-propyn-1-ol affords the new cationic compound [TpRu(C=C=CPh_2)(PTA)(PPh_3)]PF_6 (**5**) or neutral allenylidene compound [TpRuCl(C=C=CPh_2)(PTA)] (**6**), depending on the reaction solvent (MeOH or toluene, respectively). The reactivity of complexes **5** and **6** toward tertiary phosphines (PTA and PPh_2Me) has been investigated. Remarkably, both the cationic and the neutral allenylidene compounds undergo regioselective nucleophilic attack at the allenylidene C_α position to give the σ-allenyl-phosphonium complexes [TpRu{C(L)=C=CPh_2}(PTA)(PPh_3)]PF_6 (L = PPh_2Me (**8**), PTA (**9**)) and [TpRuCl{C(L)=C=CPh_2}(PTA)] (L = PTA (**10**), PPh_2Me (**11**)), respectively. Noticeably, the reaction goes to completion in the case of the neutral allenylidene complex **6**, whereas an equilibrium between the phosphonioallenyl adduct and the educt species is observed in the case of the cationic allenylidene compound **5**. The thermodynamic parameters for such an equilibrium have been determined by NMR methods at different temperatures. Finally, the hydrolysis of the neutral allenylidene **6** has been briefly considered, showing the formation of the carbonyl compound [TpRuCl(CO)(PTA)] (**7**).

Introduction

The investigation of the chemistry of complexes bearing the {TpRu} moiety (Tp = hydrotris(pyrazolyl)borate) has dramatically accelerated in the past decade, the formal similarity of the Tp ligand to the most widely employed Cp ligand being one of the most important motivations for most of these studies.[1] Although the topology of both ligands predisposes their complexes toward pseudo-octahedral geometry, Tp exhibits a significantly greater steric profile than Cp (cone angles of 183° for Tp and 100° for Cp).[2] In addition, and as far as ruthenium is concerned, the Tp ligand, generally conforming to a facial disposition in octahedral complexes, disfavors higher coordination numbers of the metal center, so that processes involving an increase of the coordination number (oxidative additions, associative substitutions, etc.) are very rare. On the other hand and in spite of the many similarities, there are also significant differences of the frontier orbitals dictating the stereochemistry of the final complexes. Thus, Cp is essentially a π-donor, whereas Tp also behaves as a good σ-donor. In the case of Tp, the π-bonding properties of the ligand may come into play in the presence of π-accepting coligands, such as CO.[3]

Following the recent increased interest in the chemistry of CpRu complexes supported by water-soluble phosphines

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such as 1,3,5-triaza-7-phosphaadamantane (PTA),[4] we have recently reported the first example of TpRu complexes bearing PTA as ancillary ligand, either alone or in combination with other hydrosoluble, {*N*-*B*-PTA(BH_3)}, or hydrophobic, PPh_3, phosphines.[5]

We decided therefore to start an in-depth study of the chemistry of the intriguing [TpRu(PTA)] fragment. Here, we report our first results in this area, describing the behavior of such a moiety as a versatile precursor for the synthesis of ruthenium unsaturated carbenes such as vinylidenes and allenylidenes. A rationale for this investigation comes from the observation that [TpRuCl(PTA)(PPh_3)] (**1**) fulfills a priori all the requisites necessary for achieving metallacumulene complexes. These call for metal precursors capable of generating (normally in a preliminary step) a 16-electron species still endowed with reactivity toward the organic molecule from which the unsaturated carbenes may be generated.

Among the results here presented is the remarkable synthesis, following Selegue's protocol,[6] from the common precursor **1** of the pair of related allenylidene species [TpRu(C═C═CPh_2)(PTA)(PPh_3)]PF_6 (**5**) and [TpRuCl(C═C═CPh_2)(PTA)] (**6**), depending on the polarity of the reaction solvent (MeOH vs toluene). The two complexes represent rare examples of structurally related cationic and neutral Ru(II) allenylidenes showing a controllable and partially diverging reactivity toward nucleophiles. In particular, addition of tertiary phosphines (PTA or PPh_2Me) to either **5** or **6** results in the formation of α-phosphonioallenyl species upon delivery of the added phosphine to the C_α allenylidene carbon atom. Although such regioselectivity is not unusual,[7,8] the reaction does not go to completion in the case of **5**, allowing us to calculate for the first time the thermodynamic parameters of the equilibrium **5** ↔ **1** + PR_3. In contrast, the neutral allenylidene complex [TpRuCl(C═C═CPh_2)(PTA)] (**6**) displays an enhanced electrophilic behavior, reacting *irreversibly and instantaneously* with tertiary phosphines, to yield [TpRuCl{C(PTA)═C═CPh_2}(PTA)] (**10**) and [TpRuCl{C(PPh_2Me)═C═CPh_2}(PTA)] (**11**), which represent rare examples of neutral α-phosphonioallenyl compounds.

The crystal structure of the cationic ruthenium(II) α-phosphonioallenyl compound [TpRu{C(PTA)═C═CPh_2}(PTA)(PPh_3)](PF_6) (**9**) has been also determined to supplement the scarce crystallographic library of this kind of ruthenium complex studied by X-ray difraction analysis.[9]

Results and Discussion

1. Reaction of [TpRuCl(PTA)(PPh_3)] (1) with Phenylacetylene. Complex **1** reacts with phenylacetylene, giving different products depending on the solvent and the reaction conditions as well (Scheme 1).

2. Reaction of 1 in MeOH: Synthesis of the Alkynyl Complex [TpRu(C≡CPh)(PTA)(PPh_3)] (2). [TpRuCl(PTA)(PPh_3)][5] (**1**) reacts with HC≡CPh in MeOH at 60 °C, affording the neutral alkynyl complex [TpRu(C≡Ph)(PTA)(PPh_3)] (**2**) as a yellow solid in high yield. In contrast with previous findings,[10] the reaction with phenylacetylene proceeds directly to give the neutral alkynyl complex, without traversing the cationic vinylidene species, which in a subsequent deprotonation step may afford the alkynyl **2**. $^{31}P\{^1H\}$ NMR monitoring of the reaction at room temperature and near the reflux temperature of MeOH does not show any intermediate compound. Complex **2** is not soluble in water and does not react with it. Thus, a suspension of **2** in water may be heated at 100 °C for 24 h without decomposition. The IR spectrum (KBr) shows a strong band at 2076 cm^{-1} characteristic for ν(C≡C), as found for other neutral TpRu(II) alkynyl complexes.[10,11] A weak-intensity ν_{BH} vibration is found at 2472 cm^{-1} which is characteristic of the B−H stretching in hydrotris(pyrazolyl)borate bonded to a metal center.[12] Compound **2** was fully characterized in solution by multinuclear (^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$) and multidimensional (^1H,^1H) COSY and (^1H,^{13}C) HSQC) NMR experiments. Both ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** in CD_2Cl_2 show the expected signals and do not deserve any particular comment, apart from the presence of two distinct resonances in the ^{13}C NMR spectrum ascribable to the C_α (126.8 ppm, collapsed double doublet, $^2J_{CP}$ = 19.1 Hz) and C_β (111.2 ppm, singlet) alkynyl carbons. In keeping with the proposed formula, the $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ −31.8 and 53.8 ppm ($^2J_{PP}$ = 3.7 Hz) assignable to PTA and PPh_3 phosphine ligands, respectively. The X-ray crystal structure of **2** was determined, and an ORTEP view of the molecule is shown in Figure 1. Relevant bond lengths and angles are given in Table 1.

Complex **2** consists of an octahedral coordinated ruthenium atom. Ligands are a N,N′,N″-tridentate tris(pyrazolyl)borate (Tp), a P-coordinated 1,3,5-triaza-7-phosphaadamantane (PTA), a triphenylphosphine (PPh_3), and a *κC*-phenylethynyl ligand. The resulting core is RuN_3P_2C. There is some distortion in the octahedron, mainly due to both the chelate angle of the Tp ligand, with N−Ru−N

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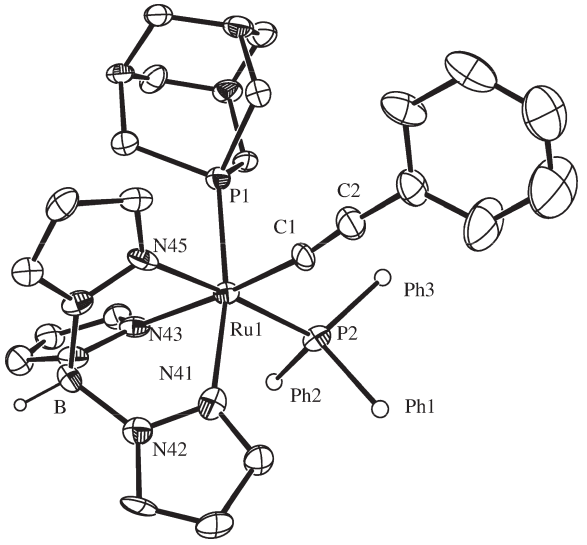
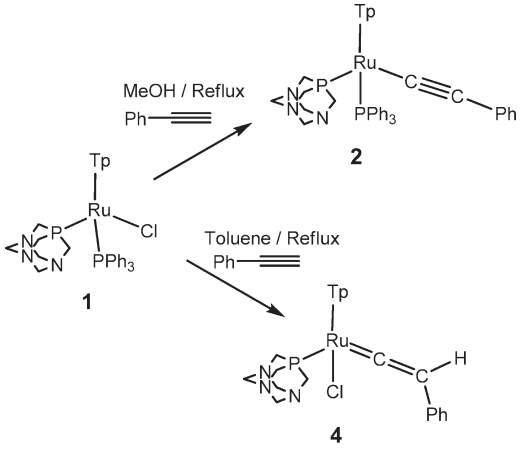


Figure 1. ORTEP representation of complex **2**. Thermal ellipsoids are drawn at the 20% probability level. The phenyl groups of the PPh_3 are not shown, their positions being indicated by the three ipso carbons of the aromatic rings. All of the hydrogen atoms, except for that of the hydroborate, are omitted for the sake of clarity.

Scheme 1



angles ranging from 80.6(4) to 87.0(4)°, and the steric requirement of the bulky PPh_3 ligand. In fact, if the octahedron is defined with the PPh_3 ligand in an axial position, the resulting equatorial plane is significantly bent out of the PPh_3 ligand with all the cis angles around the PPh_3 ligand greater than 90°.

The Ru−N bond distances range from 2.10(1) Å (trans to the PPh_3 phosphorus atom) to 2.19(1) Å, which refers to the Ru−N bond length trans to the phenylalkynyl ligand and reflects the stronger trans influence of this ligand.

The Ru−P bond distances, 2.320(4) Å (Ru−PPh_3) and 2.276(3) Å (Ru−PTA), are similar to those found in other Ru(II) complexes containing the same ligands disposed trans to a Tp nitrogen atom.[5] Inspection of the Ru−C−C backbone shows that the Ru−C bond distance (1.95(1) Å) is relatively shorter with respect to the known ruthenium(II) alkynyl complexes ($d_{Ru-C(sp)}$(av) = 2.02 Å),[13] while the C(1)−C(2) bond distance (1.25(2) Å) is relatively longer than those reported in the literature. The bond lengths found in the Ru(II)−alkynyl moiety of **2** suggest an important contribution of the zwitterionic vinylidene resonance form $[Ru]^{-}=C=C^{+}-Ph$ to represent the bond situation exhibited by the alkynyl ligand. Finally, the angles Ru−C(1)−C(2) of 172.2(13)° and C(1)−C(2)−C(3) of 175.7(18)° are almost linear.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [TpRu(C≡CPh)(PTA)(PPh_3)] (2)

Ru(1)−C(1)	1.949(14)	Ru(1)−N(45)	2.102(12)
Ru(1)−N(41)	2.171(12)	Ru(1)−N(43)	2.193(11)
Ru(1)−P(1)	2.276(3)	Ru(1)−P(2)	2.320(4)
C(1)−C(2)	1.246(19)	C(2)−C(3)	1.45(2)
C(1)−Ru(1)−N(45)	85.6(5)	C(1)−Ru(1)−N(41)	92.2(5)
N(45)−Ru(1)−N(41)	80.6(4)	N(45)−Ru(1)−N(43)	87.0(4)
N(41)−Ru(1)−N(43)	86.9(4)	C(1)−Ru(1)−P(1)	91.2(4)
N(45)−Ru(1)−P(1)	88.9(3)	N(43)−Ru(1)−P(1)	88.3(3)
C(1)−Ru(1)−P(2)	91.2(4)	N(41)−Ru(1)−P(2)	93.2(3)
N(43)−Ru(1)−P(2)	96.2(3)	P(1)−Ru(1)−P(2)	97.46(13)
N(41)−Ru(1)−P(1)	168.7(3)	C(1)−Ru(1)−N(43)	172.6(5)
N(45)−Ru(1)−P(2)	172.9(3)	C(2)−C(1)−Ru(1)	172.2(13)
C(1)−C(2)−C(3)	175.7(18)		

3. Reaction of the Alkynyl Compound 2 with HOTf. Synthesis of the Dicationic Vinylidene Complex [TpRu{C=C(H)-Ph}{PTAH}(PPh_3)]($OTf)_2$ (3). The addition of strong protic acids to a terminal alkynyl ligand is a straightforward method to achieve vinylidene compounds. In the case of **2**, the three nitrogen donors of the PTA ligand may, however, represent a competitive target for electrophiles. Thus, it seemed of interest to study the reactivity of **2** toward protic substrates to see which between the vinylidene or the protonated PTA ligand is the preferred product of the protonation reaction. A sample of compound **2** dissolved in a NMR tube test (CD_2Cl_2) was therefore treated sequentially with incremental aliquots of HOTf, and the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see Figure 2).

The first addition broadens both doublets of the starting product (−31.8 and 53.8 ppm) in the $^{31}P\{^1H\}$ NMR spectrum and transforms the ^1H NMR singlet at 3.8 ppm, due to the PCH_2N PTA protons, into an AB system, indicating that protonation of the PTA ligand has occurred.[4a] By addition of further aliquots of triflic acid, a new pair of doublets in the $^{31}P\{^1H\}$ NMR spectrum appears (−34.05 and 34.16 ppm) which progressively replaces the original one. At the same time, the two PTA proton multiplets in the ^1H NMR spectrum broaden significantly, suggesting that extensive proton exchanging processes likely involving both PTA and protonated alkynyl ligands takes place. Finally, addition of a slight excess of acid sharpens both ^{31}P and ^1H NMR resonances with a pair of doublets at δ −30.67, 33.34 appearing in the $^{31}P\{^1H\}$ NMR spectrum. Similarly, the ^1H NMR spectrum shows sharper signals, indicating that the fast equilibriums occurring at lower acid concentrations are no longer present. The final reaction product was spectroscopically characterized by ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H,^1H-COSY, and ^1H,^{13}C-HSQC NMR experiments. All the NMR data indicate that the protonation of the alkynyl compound **2** initially takes place at one of the N-donor atoms of the PTA ligand with significant scrambling between the possible protonation sites. Subsequent acid addition generates the vinylidene complex, which eventually converts **2** into the

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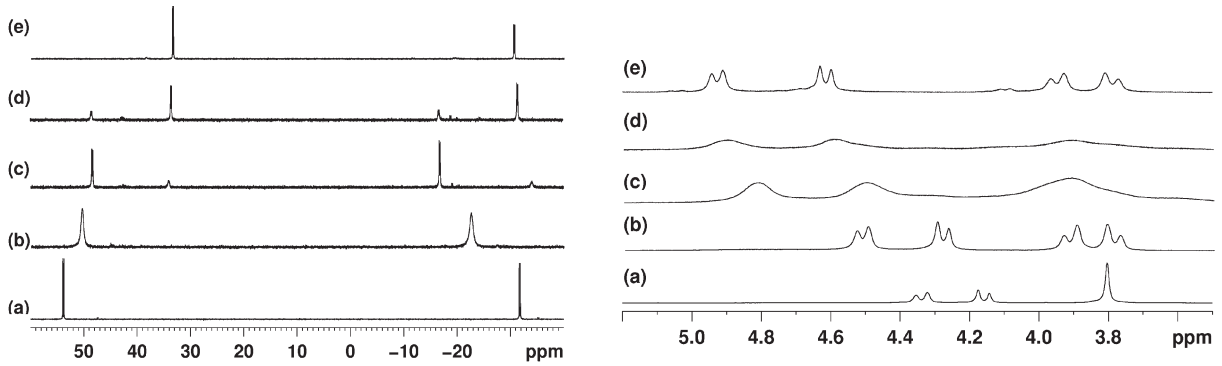
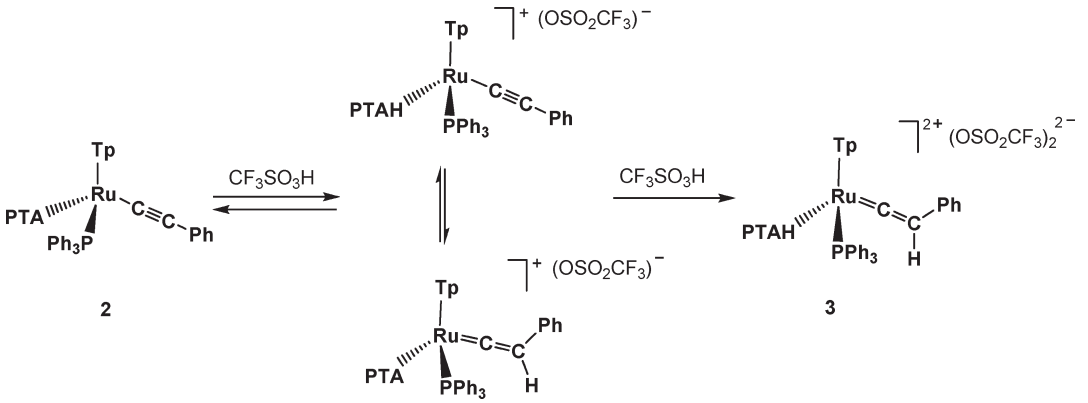


Figure 2. $^{31}P\{^1H\}$ (left) and ^1H (3.5−5.2 ppm) (right) NMR spectra in CD_2Cl_2 of the reaction of compound **2** with (a) 0, (b) 1.0, (c) 1.5, (d) 2.0, and (e) 2.5 equiv of HOTf.

Scheme 2



dicationic PTA-protonated vinylidene complex [TpRu{C=C(H)Ph}{PTAH}(PPh$_3$)](OTf)$_2$ (**3**), as shown in Scheme 2.

The $^{13}C\{^1H\}$ NMR spectrum of **3** displays a low-field pseudotriplet at 378.0 ppm characteristic of the vinylidene α-carbon atom with degenerate coupling ($^2J_{CP}$ = 16.0 Hz) with either of the phosphorus donors.

4. Reaction of 1 in Toluene. Synthesis of the Neutral Vinylidene Complex [TpRuCl{C=C(H)Ph}(PTA)] (4). When the reaction of [TpRuCl(PTA)(PPh$_3$)] with HC≡CPh is carried out in refluxing toluene instead of MeOH, labilization of the Ru−PPh$_3$ bond occurs, affording in high yield the neutral vinylidene complex [TpRuCl{C=C(H)Ph}(PTA)] (**4**) as a pink solid. Apart from the absorption due to the Tp ancillary ligand at 2473 cm^{-1}, the IR spectrum of **4** displays a strong band at 1631 cm^{-1} assignable to the vinylidene ν(C=C) stretch. The NMR spectral parameters of the vinylidene ligand in **4** are very similar to those exhibited by the related [TpRuCl{C=C(H)Ph}(PPh$_3$)][14] complex (see the Experimental Section). Two ^{13}C resonances at 111.4 (C_β) and 366.3 (C_α) ppm confirm the presence of a vinylidene ligand. Finally, the $^{31}P\{^1H\}$ spectrum displays a singlet at −39.9 ppm assignable to the PTA ligand.

Complex **4** is produced selectively, as no trace of [TpRuCl{C=C(H)Ph}(PPh$_3$)], which should be generated following PTA dissociation from **1**, is observed by NMR monitoring of the reaction. In agreement with this finding, formation of free PPh$_3$ during the reaction converting **1** into **4** is observed. Remarkably, NMR monitoring of the reaction does not allow us to intercept any putative intermediate along the path leading to the vinylidene product, which is not surprising due to the forced reaction conditions and the facility of π-coordinated terminal alkyne ruthenium(II) complexes to quickly tautomerize to the vinylidene species.[15]

5. Reaction of [TpRuCl(PTA)(PPh$_3$)] (1) with 1,1-Diphenyl-2-propyn-1-ol. Like the reaction described above between **1** and phenylacetylene, the reaction of **1** with 1-diphenyl-2-propyn-1-ol also gives different products depending on the solvent used (Scheme 3).

6. Reaction of 1 and HCCCPh$_2$OH in MeOH. Synthesis of the Cationic Allenylidene Complex [TpRu(C=C=CPh$_2$)(PTA)(PPh$_3$)](PF$_6$) (5). The reaction of **1** with an excess of 1,1-diphenyl-2-propyn-1-ol in refluxing methanol (ca. 24 h) in the presence of NaPF$_6$, which favors the removal of the coordinated halide, affords the cationic allenylidene complex [TpRu(C=C=CPh$_2$)(PTA)(PPh$_3$)](PF$_6$) (**5**), which may be isolated as an air-stable purple solid. Monitoring the reaction by ^{31}P NMR spectroscopy does not show any intermediate species preceding the formation of **5**. This suggests that the preliminary π-alkyne coordination and the following tautomerization to γ-hydroxyvinylidene species are fast with respect to the water elimination step, completing the Selegue scheme leading to the final allenylidene complex.[6] Compound **5** is not soluble in water but easily dissolves in chlorinated solvents. It has been characterized by microanalysis and IR and NMR ($^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$, ^1H,^1H-COSY, and ^1H,^{13}C-HSQC) spectroscopy. The IR

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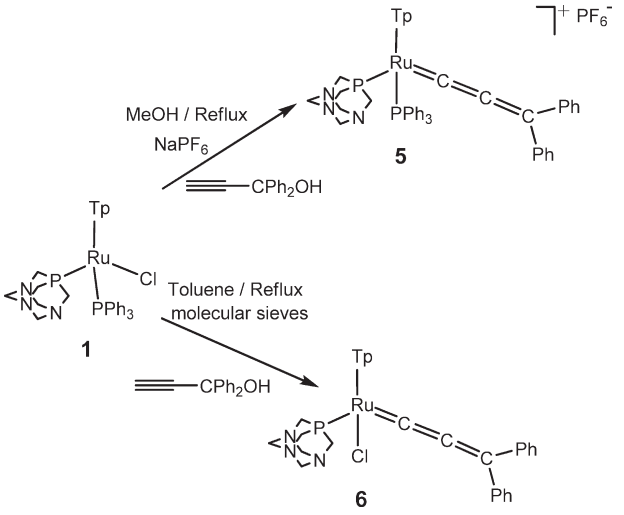
Scheme 3



spectrum exhibits, in addition to the strong P−F hexafluorophosphate stretching (841 cm^{-1}) and the absorptions due to the Tp ancillary ligand (2482 cm^{-1}), a strong band at 1937 cm^{-1} ascribable to an asymmetric ν(C=C=C) stretching vibration. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra also support the formation of the allenylidene complex, showing (i) the typical carbene Ru=C_α low-field resonance, which appears as a broad triplet at δ 309.33 ppm ($^2J_{CP}$ = 18.4 Hz), (ii) two singlet resonances for the C_β and C_γ carbons at δ 204.06 and 163.13 ppm, and (iii) two doublets in the $^{31}P\{^1H\}$ NMR spectrum at δ −46.55 ppm (PTA) and 40.42 ppm (PPh_3) ($^2J_{PP}$ = 31.5 Hz).

7. Reaction of 1 in Toluene. Synthesis of the Neutral Allenylidene Complex [TpRuCl(C=C=CPh$_2$)(PTA)] (6). When the reaction of **1** with an excess of 1,1-diphenyl-2-propyn-1-ol, is carried out in refluxing toluene (ca. 24 h) and in the presence of molecular sieves, the chloride ligand is retained into the coordination polyhedron while the Ru−PPh_3 bond is labilized and the neutral allenylidene [TpRuCl(C=C=CPh_2)(PTA)] (**6**) is obtained. $^{31}P\{^1H\}$ NMR analysis of the solution confirms the loss of PPh_3 (δ −5.7), but does not disclose any intermediate species preceding the formation of **6**. Compound **6** is an air-stable purple solid, quite soluble in both chlorinated solvents and toluene. Confirmatory evidence for the presence of the allenylidene moiety comes from both the IR spectrum (ν(C=C=C) band at 1931 cm^{-1} (s)) and the $^{13}C\{^1H\}$ NMR spectrum with resonances at 307.83 (d, J_{CP} = 24.5 Hz, C_α), 226.81 (s, C_β), and 147.89 (s, C_γ) ppm. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at δ −40.37 ppm (PTA).

Noticeably, when the reaction is carried out in the absence of any drying agent (molecular sieves etc.), the carbonyl complex [TpRuCl(CO)(PTA)] (**7**) becomes the principal product. Complex **7** likely forms from the reaction of the allenylidene ligand in **6** with the water (1 equiv) released along the Selegue reaction which assembles the metallacumulene species[6] (Scheme 4). The carbonyl compound **7** can also be obtained by directly replacing the PPh_3 ligand of **1** with CO in a carbonylation test. Different evidence confirmed the formation of the carbonyl compound by hydrolysis of the allenylidene complex. Particularly, monitoring by $^{31}P\{^1H\}$ NMR spectroscopy a sample containing both **6** and **7** (7:3 molar ratio) with several drops of water at ambient temperature shows a progressive increase of the signal due to the carbonyl compound until it becomes the only ruthenium-containing species (Scheme 4).

Similar addition reactions of water have been already described for other cationic ruthenium(II) allenylidene complexes[16] but only in one case for a neutral ruthenium(II) allenylidene complex.[17] In the latter case the formation of 1,1-diphenylethylene accompanies the generation of the carbonyl derivative.

8. Reactivity of the Cationic Allenylidene Compound 5 with Tertiary Phosphines. Synthesis of the α-Phosphonioallenyl Complexes [TpRu{C(PR$_3$)=C=CPh$_2$}(PTA)(PPh$_3$)]PF$_6$ (PR$_3$ = PPh$_2$Me (8), PTA (9)). Cationic allenylidene complexes regioselectively add phosphines to C_α or C_γ as a function of both electronic and steric properties of the ancillary ligands on the metal atom and the substituents of the γ-carbon.[8a,18] An in-depth investigation of the reaction mechanism carried out on the rhenium(I) allenylidene $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2\{C=C=CPh_2\}]^+$[19] and backed up by a computational analysis[20] has confirmed that the kinetic attack takes place at C_γ to give γ-phosphonioalkynyl species which thermally isomerize to the thermodynamic α-phosphioallenyl derivatives (Scheme 5).

Steric reasons may, however, hamper any reactivity of the phosphine.[19] Thus, PPh_3 reacts neither with $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2\{C=C=CPh_2\}]^+$ (CH_2Cl_2, reflux) nor with **5** (room temperature, NMR tube test in MeOD), probably due to the steric hindrance of PPh_3 which hampers access to either the diphenylsubstituted C_γ atom or the metallic fragment. In contrast, PPh_2Me and PTA, with fewer steric requirements (θ_{PPh_3} = 145°, θ_{PPh_2Me} = 136°, θ_{PTA} = 103°), add regioselectively to the C_α atom of the allenylidene **5**, giving the two novel derivatives **8** and **9**, respectively (see Scheme 6). Monitoring the reaction of **5** with PTA or PPh_2Me at low temperature does not allow us to intercept any intermediate before the formation of **8** or **9** (the formation of these compounds is immediate) which do not clarify whether these α-phosphonioallenyl species are directly formed or derive from their putative γ-phosphonioalkynyl tautomers via C_γ to C_α PR_3 shift.

Remarkably, the reactions of **5** with both the sterically undemanding phosphines PTA and PPh_2Me do not go to completion but afford solution equilibria, with phosphine uptake and release, whose thermodynamic parameters may be figured out by variable-temperature NMR experiments (Figure 3) using relaxation delays as longer as 10 s in order to collect reliable integral data of the ^{31}P NMR resonances. The addition of PPh_2Me to a deep purple solution of **5** in MeOD does not cause any significant color change likely due to the moderate formation of the adduct species whose color (probably yellow) is completely masked by the very intense purple color of the allenylidene precursor (always present in the reaction mixture). In contrast, the reaction with the more basic and less encumbering phosphine PTA results in an

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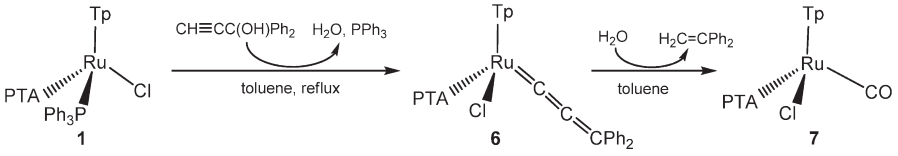
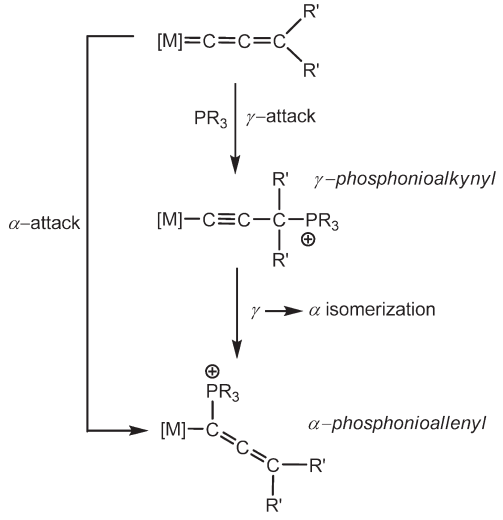
(20) Peruzzini, M.; Re, N. Manuscript in preparation.

Scheme 4



Scheme 5



equilibrium more shifted toward the phosphonio adduct also because of its low solubility in MeOH. In fact, **9** precipitates from a MeOH solution of **5** and excess PTA, giving **9** as a yellow solid. When **9** is redissolved in CH_2Cl_2, the solution immediately turns to deep violet as soon as **9** equilibrates back to **5**, releasing free PTA (NMR detected). Although both reactions are slightly endoergonic, that with PTA is more favored than that with PPh_2Me, in accord with their respective steric requirements and nucleophilic properties (see Table 2).

The solution characterization of each phosphonium adduct is largely complicated by the occurrence of the equilibrium giving back the allenylidene species. Thus, the NMR spectra of **8** (MeOD solution) or **9** (CD_2Cl_2 solution) always display signals of both allenylidene educt and free phosphine. Typical NMR experiments were conducted at low temperature (0 to −5 °C) where the equilibrium is more shifted toward the formation of the phosphonium complexes (see the largely entropic factors in Table 2).

To discriminate between the two possible phosphonium isomers resulting from the nucleophilic attack preferred site, C_γ vs C_α of the phosphine, we investigated by X-ray diffraction analysis the yellow crystals obtained by slow evaporation of **9** from a dilute MeOH solution. The crystallographic analysis confirmed that the adduct is a genuine α-phosphonioallenyl species with the PTA phosphine is selectively bound to the α-carbon of a ruthenium coordinated allenyl ligand (see Figure 4).

The geometry around the ruthenium center in **9** is close to octahedral, with the Tp ligand occupying three sites of a face. The Ru−C(1) distance (2.137(3) Å) is that expected for a Ru−C(sp^2) single bond and is comparable to the related distance in other ruthenium allenyl complexes.[9] The C(1)−C(2) (1.318(4) Å) and C(2)−C(3) (1.320(4) Å) bond lengths, as well as the C(1)−C(2)−C(3) angle (177.1(3)°), which are in agreement with those reported for compounds of this type,[9] strongly support the allenyl formulation (Table 3).

The phosphonioallenyl complex **9** is air-stable in the solid state at atmospheric pressure, while in solution it equilibrates with the parent allenylidene and free PTA (vide supra). The IR spectrum (KBr pellet) shows the typical allenyl ν(C=C=C) absorption band at 1840 cm^{-1} slightly moved to low frequencies, in line with the presence of an unbalanced positive charge on the *P*-phosphonium atom. Remarkably, grinding of **9** during the preparation of the solid KBr pellet for the IR analysis results in fading of the yellow color, which becomes pale reddish, suggesting that also in the solid state external effects such as an applied physical pressure may result in the C−P bond cleavage of the α-phosphonioallenyl derivative. The $^{31}P\{^1H\}$ spectrum run at −5 °C in CD_2Cl_2 shows three signals at 49.22 (d, $^2J_{PP}$ = 32.4 Hz, PPh_3), −44.10 (d, $^2J_{PP}$ = 32.4 Hz, Ru−P_{PTA}), and −46.78 (s, C_α−P_{PTA}) ppm, the latter assignable to the α-phosphonioallenyl P-atom. Noticeably, this phosphorus nucleus does not show any appreciable coupling with the metal-coordinated P-phosphorus phosphine atoms ($^3J_{PP}$), which has precedents in the sparse literature.[9a,9d,9e] The $^{13}C\{^1H\}$ NMR spectrum agrees with the proposed formulation showing a doublet at 102.68 ppm ($^1J_{CP}$ = 26 Hz) and a broad singlet at 209.75 ppm, attributable to the C_γ and C_β of the allenylphosphonio ligand, respectively.[18b] Unfortunately, the signal of C_α cannot be safely located, probably being obscured by the signals of the PTA ligand around 70 ppm (it is not unusual that the signal of the metal-bonded carbon appears at higher field than the signals of C_β and C_γ).[16a,21] Although the electrophilicity of C_γ is greater than that of C_α (23% of the LUMO centered on C_α and 31% on C_γ for Esteruelas' model cation complex $[CpRu(CO)(PH_3)(C{=}C{=}CH_2)]^+$),[22] it seems that the presence of the phenyl groups at the C_γ and the relatively low steric crowding at the ruthenium center (PTA is not sterically demanding) facilitate the nucleophilic attack at the C_α, giving the allenylphosphonio complex, in contrast with what observed for the indenyl derivative $[(C_9H_7)Ru(=C=C=CPh_2)(PPh_3)_2]^+$, in which the indenyl ligand and the two bulky triphenylphosphine ligands protect this atom and direct the nucleophile to attack the C_γ position, thus yielding the γ-phosphonioalkynyl complex.[18b]

In the case of PPh_2Me a similar behavior was observed, but the existence of an equilibrium poorly shifted toward the addition product does not permit us to clearly establish the nature of the phosphonium adduct by NMR studies. Reasoning similar to the PTA case would imply that a similar product was obtained, but the attack at C_γ cannot be completely disregarded. The $^{31}P\{^1H\}$ spectrum of the reaction mixture in CD_3OD shows, apart from the signals of both **5** and PPh_2Me (−27.4 ppm), three new slightly broadened

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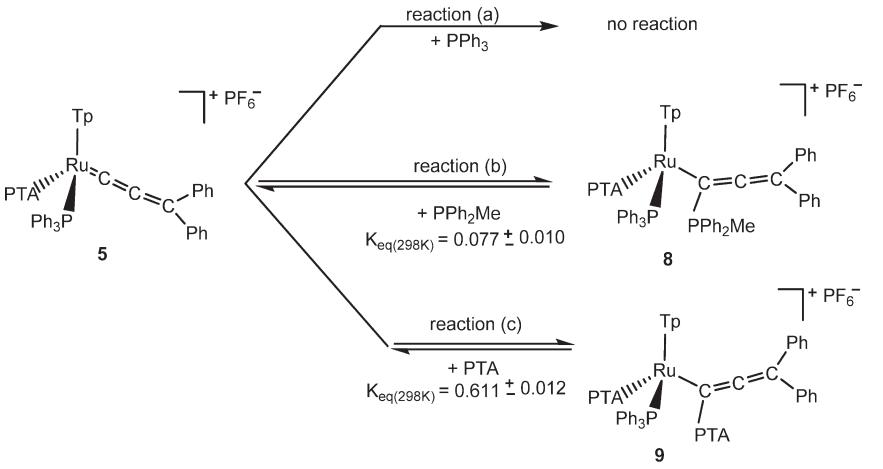
Scheme 6



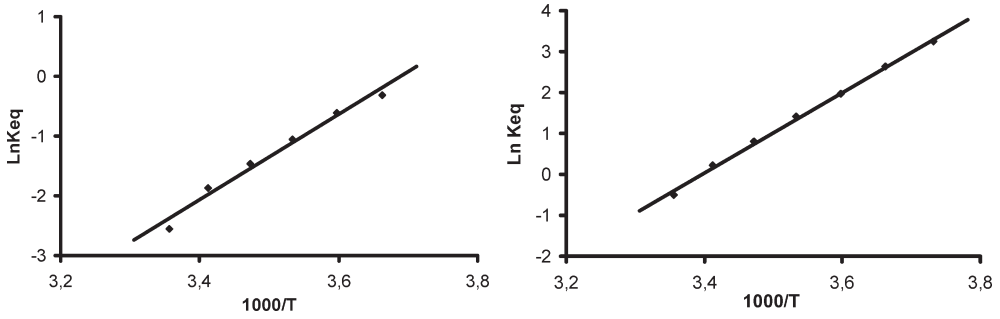


Figure 3. Plots of ln K_{eq} vs $1000/T$ (K^{-1}) for the equilibrium reactions of compound **5** with PPh_2Me (left) and with PTA (right).

Table 2. Thermodynamic Parameters for the Formation of Complexes 8 (MeOD) and 9 (CD_2Cl_2)

complex	$\Delta H°$ (kcal)	$\Delta S°$ (cal)	$\Delta G°$ (kcal)	K_{eq}(298 K)
8	-14.13 ± 0.27	-52.13 ± 0.06	$+1.41 \pm 0.27$	0.077 ± 0.010
9	-19.46 ± 0.31	-66.08 ± 0.07	$+0.23 \pm 0.31$	0.611 ± 0.012

resonances attributable to the phosphonium compound (δ 54.0 ($RuPPh_3$), 22.8 ($C-P_{PPh_2Me}$), and −31.1 (RuPTA)).

9. Reactivity of the Neutral Allenylidene Compound 6 with Tertiary Phosphines. Synthesis of the α-Phosphonioallenyl Complexes [TpRuCl{C(PR_3)=C=CPh_2}(PTA)] (PR_3 = PPh_2Me (10), PTA (11)). Neutral allenylidene compounds are not as abundant as cationic ones and do not exhibit the typical electrophilic behavior proper of the much more represented cationic derivatives.[23] The lack of any positive charge on the metallocumulene assembly depresses the electrophilic behavior generally observed at the C_α and C_γ sites while emphasizing the nucleophilic behavior at the β-carbon.[24] In spite of this general tendency, compound **6** reacts quickly and completely with nucleophiles such as phosphines (PPh_2Me or PTA), sharply contrasting with the uncompleted reactivity shown by the cationic allenylidene **5** discussed above (see Scheme 7). Thus, adding phosphine (PPh_2Me or PTA) in small portions to a solution of [TpRuCl{C=C=CPh_2}(PTA)] in CD_2Cl_2 (NMR tube test) and monitoring the reaction course by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy confirm the immediate replacement of the allenylidene signals by a new set of resonances, ascribable to the

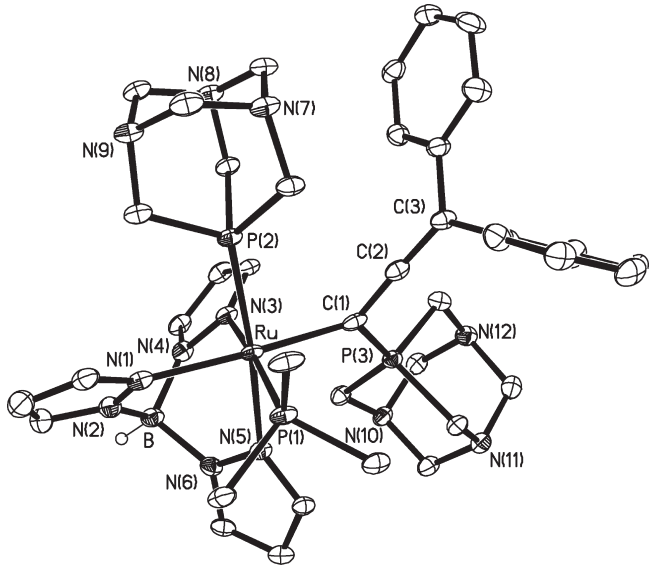


Figure 4. ORTEP representation of the cation of **9**. Thermal ellipsoids are drawn at 50% probability level. All of the hydrogen atoms, except for that of the hydroborate, are omitted for the sake of clarity.

(23) (a) Werner, H.; Wiedemann, R.; Laubender, M.; Windmüller, B.; Steinert, P.; Gevert, O.; Wolf, J. *J. Am. Chem. Soc.* **2002**, *124*, 6966. (b) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *265*, 271. (c) Berke, H.; Härter, P.; Huttner, G., Zsolnai, L. Z. Naturforsch. B **1981**, *36*, 929. (d) Bianchini, C.; Peruzzini, M.; Zanobini, F.; López, C.; de los Rios, I.; Romerosa, A. *Chem. Commun.* **1999**, 443.

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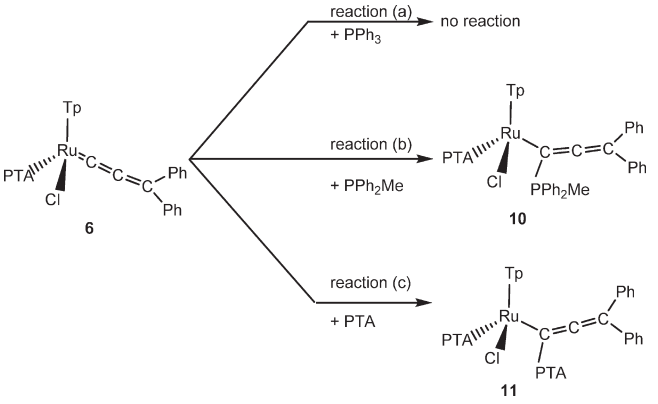
Table 3. Selected Bond Distances (Å) and Angles (deg) for [TpRu{C(PTA)=C=CPh$_2$}(PTA)(PPh$_3$)]PF$_6$ (9)

Ru−P(2)	2.3337(8)	Ru−C(1)	2.137(3)
Ru−P(1)	2.3338(8)	P(3)−C(1)	1.812(3)
Ru−N(1)	2.151(3)	C(1)−C(2)	1.318(4)
Ru−N(3)	2.150(2)	C(2)−C(3)	1.320(4)
Ru−N(5)	2.138(2)	C(3)−C(10)	1.496(4)
P(1)−C(49)	1.836(3)	C(3)−C(4)	1.508(4)
P(1)−C(37)	1.848(3)	P(1)−C(43)	1.852(3)
C(1)−Ru−P(2)	91.56(8)	C(2)−C(1)−P(3)	105.2(2)
C(1)−Ru−P(1)	98.66(8)	C(2)−C(1)−Ru	131.9(2)
P(2)−Ru−P(1)	97.83(3)	P(3)−C(1)−Ru	122.56(16)
C(1)−C(2)−C(3)	177.1(3)		

Scheme 7



α-phosphonioallenyl species **10** and **11**, respectively. The reaction is also accompanied by a color change of the solution from deep purple to brown. The replacement of the typical allenylidene asymmetric stretching vibration at 1931 cm^{-1} by weak bands at 1853 and 1851 cm^{-1} for compounds **10** and **11**, respectively, ascribable to the stretching vibration of the allenyl group,[9d] also supports the allenylphosphonio formulation of the adduct species.

In agreement with the formation of the α-phosphonio adduct, the $^{13}C\{^1H\}$ spectra show the disappearance of the allenylidene resonances (307.83 (d, J = 24.5 Hz, C$_\alpha$), 226.81 (s, C$_\beta$), and 147.89 (s, C$_\gamma$) ppm) and the appearance of a new set of signals at 214.9 ppm (C$_\beta$) and 100.7 ppm (d, J = 24.1 Hz, C$_\gamma$) for the reaction with PPh$_2$Me and at 210.7 ppm (s, C$_\beta$) and 102.8 ppm (d, J = 25.8 Hz, C$_\gamma$) in the case of the reaction with PTA. The signal corresponding to C$_\alpha$ could not be safely localized in the spectra of both compounds, likely due to superimposition with PTA backbone signals around 70 ppm. In the case of the bulkier PPh$_3$, no reaction was again observed, which is also consistent with the synthesis of **6**, where PPh$_3$ is liberated during the reaction.

As a final consideration, it is worth mentioning that alkyl (R = Me, Et, Bz, Cy) or aryl (Ph) phosphonium salts of PTA cannot be generated by direct electrophilic attack on PTA, the nitrogen atoms being much more electrophilic.[25] In this respect, it is intriguing that the α-phosphonioallenyl species **10** and **11**, representing a rare example of PTA phosphonium derivatives, may be formed by direct nucleophilic attack of PTA at an electrophilic carbon center such as C$_\alpha$.

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Conclusions

The reactivity of [TpRuCl(PTA)(PPh$_3$)] (**1**) with phenylacetylene and 1,1-diphenyl-2-propyn-1-ol was found to be strongly dependent on the polarity of the reaction medium, and different reaction pathways were followed in polar (MeOH) and apolar (toluene) solvents. Indeed, while the reaction in the polar solvent proceeded with easy substitution of the chloride ligand to yield the neutral alkynyl complex [TpRu(C≡CPh)(PTA)(PPh$_3$)] (**2**) and the cationic allenylidene species [TpRu(C=C=CPh$_2$)(PTA)(PPh$_3$)]PF$_6$ (**5**), respectively, the reaction in toluene afforded the neutral vinylidene complex [TpRuCl{C=C(H)Ph}(PTA)] (**4**) and allenylidene species [TpRuCl(C=C=CPh$_2$)(PTA)] (**6**), respectively, following the substitution of the PPh$_3$ ligand. The reactivity of these species with selected electrophiles and nucleophiles was then investigated with the aim of shedding light on the possible different reactivities exhibited by related neutral versus cationic pair of unsaturated carbenes (exemplified by **5** and **6**). In keeping with our expectations, while the protonation of **2** with HOTf gave the expected dicationic vinylidene [TpRu(C=CHPh)(PTAH)(PPh$_3$)](OTf)$_2$ (**3**), which bears a protonated PTA ligand, the systematic study of the nucleophilic additions of different phosphines (PPh$_3$, PPh$_2$Me, PTA) to both allenylidene complexes **5** and **6** was of much interest. In particular, in the case of the cationic allenylidene complex **5**, the reaction with PPh$_2$Me or PTA (the bulkier PPh$_3$ did not react at all) gave the corresponding α-phosphonioallenyl complexes [TpRu{C(PPh$_2$Me)=C=CPh$_2$}(PTA)(PPh$_3$)]PF$_6$ (**8**) and [TpRu{C(PTA)=C=CPh$_2$}(PTA)(PPh$_3$)]PF$_6$ (**9**), respectively, which exhibit an interesting solution equilibrium featuring phosphine uptake and release. These equilibria could be followed by NMR methods, and the thermodynamic parameters for the formation of **8** and **9** have been reported. Even more remarkable was the reaction of the neutral allenylidene **6** with both PTA and PPh$_2$Me that, in spite of the general reluctance observed by neutral allenylidenes to react with nucleophiles, regioselectively afforded the α-phosphonioallenyl complexes [TpRuCl{C(PPh$_2$Me)=C=CPh$_2$}(PTA)] (**10**) and [TpRuCl{C(PTA)=C=CPh$_2$}(PTA)] (**11**). As a final consideration, the solid-state structure of compound **9**, a rare example of an α-phosphonioallenyl derivative, was determined by X-ray methods, which confirmed the presence of the P-alkylated water-soluble PTA phosphine as the pendant group of the phosphonioallenyl moiety.

Experimental Section

All synthetic operations were performed under a dry argon atmosphere by following conventional Schlenk techniques. Solvents were purified by distillation from the appropriate drying agents[26] and degassed before use. 1-Phenyl-2-propyn-1-ol, phenylacetylene, and triflic acid were Aldrich products and were used without further purification. The starting material [TpRuCl(PTA)(PPh$_3$)] (**1**) was prepared by the published method.[5] IR spectra were recorded in KBr pellets on a Bruker Vector IFS28 FTIR spectrophotometer. NMR spectra were recorded on a Bruker AMX 400 instrument. Chemical shifts are given in parts per million from SiMe$_4$ (^{1}H and $^{13}C\{^1H\}$) or 85% H$_3$PO$_4$ ($^{31}P\{^1H\}$). ^{1}H and $^{13}C\{^1H\}$ NMR signal assignments were

(26) *Purification of Laboratory Chemicals*, 3rd ed.; Perrin, D. D., Armarego W. L. F., Eds.; Butterworth and Heinemann: Oxford, U.K., 1988.

confirmed by ^{1}H-COSY and HSQC (^{1}H−^{13}C) experiments. Elemental analyses were performed on a Fisons EA-1108 apparatus.

Preparation of [TpRu(C≡CPh)(PTA)(PPh$_3$)] (2). An excess of HC≡CPh (0.4 mL) was added to a solution of [TpRuCl-(PTA)(PPh$_3$)] (**1**; 100.0 mg, 0.13 mmol) in 20 mL of methanol. The mixture was heated to reflux and stirred gently for several minutes, and then it was cooled to room temperature. A yellow microcrystalline precipitate was formed that was filtered off and washed with MeOH and Et$_2$O before being dried under a stream of nitrogen. Yield: 83.55 mg (77.0%). Anal. Calcd for $C_{41}H_{42}BN_9P_2Ru$ (834.67 g/mol): C, 59.00; H, 5.07; N 15.10. Found: C, 59.12; H, 5.14; N, 15.07. IR (KBr pellet): $\nu_{BH(Tp)}$ 2472 (w), $\nu_{C\equiv C}$ 2075 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.80 (s, 6H, PCH_2N), 4.00−4.40 (AB system, 6H, NCH_2N), 5.75 (br, 1H, HB($C_3H_3N_2$)$_3$), 5.82 (t, $^3J_{H,H}$ = 2.1 Hz, 1H, HB-($C_3H_3N_2$)$_3$), 6.20 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.21 (br, 1H, HB-($C_3H_3N_2$)$_3$), 6.64 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.03 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, *Ph*), 7.18−7.39 (m, 13H, *Ph*), 7.58 (br, 1H, HB-($C_3H_3N_2$)$_3$), 7.62 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.65 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, HB($C_3H_3N_2$)$_3$), 7.69−7.77 (m, 6H, *Ph*), 8.27 (br, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 52.8 (d, $^1J_{C,P}$ = 14.6 Hz, P*C*H$_2$N), 73.4 (d, $^3J_{C,P}$ = 5.4 Hz, N*C*H$_2$N), 104.7 (d, $^4J_{C,P}$ = 1.6 Hz, HB($C_3H_3N_2$)$_3$), 105.3 (s, HB(C_3H_3-N_2)$_3$), 105.5 (d, $^4J_{C,P}$ = 2.3 Hz, HB($C_3H_3N_2$)$_3$), 111.2 (s, C≡*C*Ph), 123.1−131.2 (*C* PPh$_3$), 126.8 (collapsed double doublet, $^2J_{C,P}$ = 19.1 Hz, *C*≡CPh), 133.8−138.0 (*C* PPh$_3$), 134.9 (s, HB($C_3H_3N_2$)$_3$), 135.3 (s, HB($C_3H_3N_2$)$_3$), 135.6 (s, HB($C_3H_3N_2$)$_3$), 144.1 (s, HB($C_3H_3N_2$)$_3$), 144.4 (s, HB-($C_3H_3N_2$)$_3$), 144.5 (s, HB($C_3H_3N_2$)$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ −31.8 (d, $^2J_{P,P}$ = 33.7 Hz, *P*PTA), 53.8 (d, $^2J_{P,P}$ = 33.7 Hz, *P*Ph$_3$) ppm.

In Situ NMR Formation of [TpRu(C=CHPh)(PTAH)-(PPh$_3$)](OTf)$_2$ (3). A solution of **2** (16.7 mg, 0.02 mmol) in 0.5 mL of CD_2Cl_2 was placed in a NMR tube. Different portions of HOTf were sequentially added through the serum cap via a microsyringe at room temperature. The progress of the reaction was monitored by ^{1}H and ^{31}P{^{1}H}, and the acid addition was finished (4.50 μL, 0.05 mmol) when the NMR analysis revealed the reaction completeness. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.68−4.05 (AB system, 6H, PCH_2N), 4.51−5.01 (AB system, 7H, NCH_2N), 6.00 (t, br, $^3J_{H,H}$ = 2.1, 1H, HB($C_3H_3N_2$)$_3$), 6.24 (t, br, $^3J_{H,H}$ = 2.1 Hz, 1H, HB($C_3H_3N_2$)$_3$), 6.33 (t, br, $^3J_{H,P}$ = 3.0 Hz, 1H, =C(*H*)Ph), 6.35 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.38 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.64 (m, 2H, *Ph*), 6.75 (br, 1H, HB-($C_3H_3N_2$)$_3$), 7.07 (m, 3H, *Ph*), 7.29−7.52 (m, 15H, *Ph*), 7.83 (br, 2H, HB($C_3H_3N_2$)$_3$), 7.98 (br, 1H, HB($C_3H_3N_2$)$_3$), 8.33 (br, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 48.7 (d, $^1J_{C,P}$ = 17.3 Hz, P*C*H$_2$N), 72.1 (br, N*C*H$_2$N), 106.8 (s, HB($C_3H_3N_2$)$_3$), 108.2 (s, HB($C_3H_3N_2$)$_3$), 108.3 (s, HB-($C_3H_3N_2$)$_3$), 115.2 (s, HB($C_3H_3N_2$)$_3$), 119.3 (s, =*C*(H)Ph), 122.0−135.1 (s, *C* PPh$_3$), 126.2 (*C* PPh$_3$), 138.2 (s, HB-($C_3H_3N_2$)$_3$), 138.5 (s, HB($C_3H_3N_2$)$_3$), 144.3 (s, HB($C_3H_3N_2$)$_3$), 144.7 (s, HB($C_3H_3N_2$)$_3$), 145.4 (s, HB($C_3H_3N_2$)$_3$), 378.0 (m, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ −30.7 (d, $^2J_{P,P}$ = 28.2 Hz, *P*PTA), 33.3 (d, $^2J_{P,P}$ = 28.2 Hz, *P*Ph$_3$) ppm.

Preparation of [TpRuCl{C=C(H)Ph}(PTA)] (4). A yellow suspension of **1** (100.0 mg, 0.13 mmol) and phenylacetylene (245.7 μL) was refluxed for 24 h in toluene (15 mL), giving an orange solution. The solvent was removed under vacuum, and the residue was treated with Et$_2$O (3 × 3 mL), giving a pink solid. Yield: 50.2 mg (63.4%). Anal. Calcd for $C_{23}H_{28}BN_9PClRu$ (608.84 g/mol): C, 45.37; H, 4.64; N, 20.70. Found: C, 46.03; H, 4.80; N, 20.58. IR (KBr pellet): $\nu_{BH(Tp)}$ 2473 (w), $\nu_{C=C}$ 1631 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.37 (s, 6H, PCH_2N), 4.00−4.60 (AB system, 6H, NCH_2N), 4.97 (d, $^4J_{H,P}$ = 4.40 Hz, 1H, =C(*H*)Ph), 6.14 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.24 (t, $^3J_{H,H}$ = 2.3 Hz, 1H, HB($C_3H_3N_2$)$_3$), 6.38 (t, $^3J_{H,H}$ = 2.4 Hz, 1H, HB($C_3H_3N_2$)$_3$), 7.05 (q, $^3J_{H,H}$ = 4.3 Hz, 1H, *Ph*), 7.15 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.27 (d, $^3J_{H,H}$ = 4.3 Hz, 4H, *Ph*), 7.59 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.63 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.74 (d, $^3J_{H,H}$ = 2.4 Hz, 1H, HB($C_3H_3N_2$)$_3$), 7.81 (d, 1H, $^3J_{H,H}$ = 2.1 Hz, HB($C_3H_3N_2$)$_3$), 8.01 (br, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 52.0 (d, $^1J_{C,P}$ = 16.0 Hz, P*C*H$_2$N), 73.7 (d, $^3J_{C,P}$ = 7.4 Hz, N*C*H$_2$N), 106.2 (s, HB($C_3H_3N_2$)$_3$), 106.3 (s, HB($C_3H_3N_2$)$_3$), 106.9 (s, HB($C_3H_3N_2$)$_3$), 111.4 (d, $^3J_{C,P}$ = 2.1 Hz, =*C*(H)Ph), 125.7 (s, *C* PPh$_3$), 126.2 (s, *C* PPh$_3$), 129.2 (s, *C* PPh$_3$), 134.9 (s, HB($C_3H_3N_2$)$_3$), 135.8 (s, HB-($C_3H_3N_2$)$_3$), 137.2 (s, HB($C_3H_3N_2$)$_3$), 143.4 (s, HB($C_3H_3N_2$)$_3$), 143.9 (s, HB($C_3H_3N_2$)$_3$), 145.6 (s, HB($C_3H_3N_2$)$_3$), 366.3 (d, $^2J_{C,P}$ = 22.2 Hz, Ru=*C*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ −34.9 (s, *P*PTA) ppm.

Preparation of [TpRu(C=C=CPh$_2$)(PTA)(PPh$_3$)]PF$_6$ (5). A 100 mg portion (0.13 mmol) of **1** was dissolved in MeOH (30 mL), and 136.8 mg (0.65 mmol) of 1-phenyl-2-propyn-1-ol was added. The mixture was stirred for 1 min, and 22.3 mg (0.13 mmol) of $NaPF_6$ was added. This solution was refluxed for 24 h, during which time the color changed from yellow to purple. The mixture was filtered, and the solvent was removed in vacuo. The residue was then treated with diethyl ether (3 × 3 mL) and *n*-hexane (5 mL), and a purple solid precipitated. Yield: 136.16 mg (98.0%). Anal. Calcd for $C_{48}H_{47}BN_9P_3F_6Ru$ (1068.75 g/mol): C, 53.94; H, 4.43; N, 11.80. Found: C, 53.89; H, 4.48; N, 11.73. IR (KBr pellet): $\nu_{BH(Tp)}$ 2482 (w), $\nu_{C=C=C}$ 1937 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.65−3.85 (AB system, 6H, PCH_2N), 4.10−4.40 (AB system, 6H, NCH_2N), 5.82 (t, $^3J_{H,H}$ = 1.9, 1H, HB($C_3H_3N_2$)$_3$), 5.97 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, HB($C_3H_3N_2$)$_3$), 6.16 (td, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 0.6 Hz, 1H, HB($C_3H_3N_2$)$_3$), 6.22 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.64 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, HB($C_3H_3N_2$)$_3$), 7.22−7.48 (m, 19H, *Ph*), 7.59 (br, 2H, HB($C_3H_3N_2$)$_3$), 7.72−7.77 (m, 6 + 1H, *Ph* + HB-($C_3H_3N_2$)$_3$), 7.93 (d, $^3J_{H,H}$ = 2.3, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 52.6 (d, $^1J_{C,P}$ = 14.9 Hz, P*C*H$_2$N), 73.1 (d, $^3J_{C,P}$ = 6.3 Hz, N*C*H$_2$N), 105.9 (s, HB-($C_3H_3N_2$)$_3$), 106.8 (s, HB($C_3H_3N_2$)$_3$), 107.6 (s, HB($C_3H_3N_2$)$_3$), 129.0−134.0 (*C* PPh$_3$), 144.6 (*C* PPh$_3$) 136.9 (s, HB($C_3H_3N_2$)$_3$), 137.4 (s, HB($C_3H_3N_2$)$_3$), 143.9 (s, HB($C_3H_3N_2$)$_3$), 144.4 (s, HB($C_3H_3N_2$)$_3$), 144.6 (s, HB($C_3H_3N_2$)$_3$), 145.0 (s, HB-($C_3H_3N_2$)$_3$), 163.1 (s, C=C=*C*Ph$_2$), 204.1 (s, C=*C*=CPh$_2$), 309.3 (t, br, $^2J_{C,P}$ = 18.4 Hz, *C*=C=CPh$_2$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ −144.1 (sept, $^1J_{P,F}$ = 710.4 Hz, *P*F$_6$), −46.5 (d, $^2J_{P,P}$ = 31.5 Hz, *P*PTA), 40.4 (d, $^2J_{P,P}$ = 31.2 Hz, *P*Ph$_3$) ppm.

Preparation of [TpRu(C=C=CPh$_2$)(PTA)(PPh$_3$)]BPh$_4$ (5·BPh$_4$). This compound was prepared exactly as described for **5**·PF$_6$, but using $NaBPh_4$ instead of $NaPF_6$. Yield: 50.2%. Anal. Calcd for $C_{72}H_{67}B_2N_9P_2Ru$ (1243.02 g/mol): C, 69.57; H, 5.43; N, 10.14. Found: C, 69.42; H, 5.58; N, 10.44. IR (KBr pellet): $\nu_{BH(Tp)}$ 2481 (w), $\nu_{C=C=C}$ 1938 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.63−3.82 (AB system, 6H, PCH_2N), 4.05−4.38 (AB system, 6H, NCH_2N), 5.82 (t, $^3J_{H,H}$ = 2.5 Hz, 1H, HB($C_3H_3N_2$)$_3$), 5.95 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.15 (t, br, $^3J_{H,H}$ = 2.1 Hz, 1H, HB($C_3H_3N_2$)$_3$), 6.23 (br, 1H, HB-($C_3H_3N_2$)$_3$), 6.59 (d, br, $^3J_{H,H}$ = 2.1, 1H, HB($C_3H_3N_2$)$_3$), 6.88 (t, *J* = 7.16 Hz, 4H, *Ph*), 7.04 (t, $^3J_{H,H}$ = 7.38 Hz, 8H, *Ph*), 7.22−7.49 (m, 28 H, *Ph*) 7.59 (br, 2H, HB($C_3H_3N_2$)$_3$), 7.61 (br, 1H, *Ph*), 7.74 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.75−7.81 (m, 4 H, *Ph*), 7.93 (d, br, $^3J_{H,H}$ = 2.0 Hz, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 52.3 (d, $^1J_{C,P}$ = 13.9 Hz, P*C*H$_2$N), 72.9 (d, $^3J_{C,P}$ = 6.3 Hz, N*C*H$_2$N), 105.9 (s, HB-($C_3H_3N_2$)$_3$), 106.7 (s, HB($C_3H_3N_2$)$_3$), 107.5 (s, HB($C_3H_3N_2$)$_3$), 122.0−136.3 (*C* PPh$_3$), 136.9 (s, HB($C_3H_3N_2$)$_3$), 137.1 (s, HB-($C_3H_3N_2$)$_3$), 137.4 (s, HB($C_3H_3N_2$)$_3$), 143.7 (s, HB($C_3H_3N_2$)$_3$), 144.4−145.2 (*C* PPh$_3$), 144.3 (s, HB($C_3H_3N_2$)$_3$), 144.7 (s, HB-($C_3H_3N_2$)$_3$), 163.0 (s, C=C=*C*Ph$_2$), 163.7−164.8 (*C* PPh$_3$), 203.5 (s, C=*C*=CPh$_2$), 308.7 (dd, $^2J_{C,P}$ = 18.9 Hz, $^2J_{C,P}$ = 17.7 Hz, *C*=C=CPh$_2$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ −46.0 (d, $^2J_{P,P}$ = 31.9 Hz, *P*PTA), 40.5 (d, $^2J_{P,P}$ = 31.9 Hz, *P*Ph$_3$) ppm.

Preparation of [TpRuCl(C=C=CPh$_2$)(PTA)] (6). A 200.0 mg portion (0.26 mmol) of compound **1** was dissolved in toluene (80 mL, molecular sieves), and 273.5 mg (1.30 mmol) of 1-phenyl-2-propyn-1-ol was added. This solution was refluxed for 24 h, during which time the color changed from yellow to purple. The mixture was filtered to eliminate impurities, and the solvent was removed in vacuo. The residue was treated with diethyl ether (3 mL) and *n*-hexane (3 mL), and a purple solid precipitated. Yield: 142.1 mg (78.3%). Anal. Calcd for $C_{30}H_{32}BN_9PClRu$ (696.95 g/mol): C, 51.70; H, 4.63; N, 18.09. Found: C, 51.59; H, 4.70; N, 18.20. IR (KBr pellet): $\nu_{BH(Tp)}$ 2467 (w), $\nu_{C=C=C}$ 1931 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.18 (s, 6H, PCH_2N), 4.29−4.48 (AB system, 6H, NCH_2N), 6.14 (br, 2H, HB($C_3H_3N_2$)$_3$), 6.49 (t, br, $^3J_{H,H}$ = 2.6 Hz, 1H, HB($C_3H_3N_2$)$_3$), 7.06 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.36 (t, $^3J_{H,H}$ = 7.64 Hz, 4H, *Ph*), 7.48 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.63 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.68−7.76 (t, br, $^3J_{H,H}$ = 7.5, 2H, *Ph*), 7.71 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.92 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.94 (d, $^3J_{H,H}$ = 8.3, 4H, *Ph*), 8.13 (br, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 52.5 (d, $^1J_{C,P}$ = 16.0 Hz, PCH_2N), 73.4 (d, $^3J_{C,P}$ = 6.4 Hz, NCH_2N), 105.6 (d, J_{CP} = 2.57 Hz, HB($C_3H_3N_2$)$_3$), 106.5 (s, HB($C_3H_3N_2$)$_3$), 106.5 (s, HB($C_3H_3N_2$)$_3$), 129.3, 129.5, 130.0, 147.0 (*C* PPh$_3$), 134.4 (s, HB($C_3H_3N_2$)$_3$), 135.7 (s, HB($C_3H_3N_2$)$_3$), 136.6 (s, HB($C_3H_3N_2$)$_3$), 142.7 (s, HB($C_3H_3N_2$)$_3$), 143.9 (s, HB($C_3H_3N_2$)$_3$), 145.2 (s, HB($C_3H_3N_2$)$_3$), 147.9 (s, C=C=*C*Ph$_2$), 226.8 (s, C=*C*=CPh$_2$), 307.8 (d, $^2J_{C,P}$ = 24.5 Hz, *C*=C=CPh$_2$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ −40.4 (s, *P* PTA).

Preparation of [TpRuCl(CO)(PTA)] (7). A nitrogen-purged solution of 100.0 mg of [TpRuCl(PTA)(PPh$_3$)] in toluene (20 mL) was placed in a Schlenk flask equipped with a Teflon stopcock under an atmosphere of CO (p_{CO} = 1 atm). The Schlenk tube was tightly closed and heated at reflux for 4 h. Removal of the solvent under vacuum and precipitation of the residue with Et$_2$O (3 × 5 mL) gave a white solid. Yield: 75%. Anal. Calcd for $C_{16}H_{22}BClN_9OPRu$ (534.72 g/mol): C, 35.94; H, 4.15; N, 23.58. Found: C, 35.12; H, 4.09; N, 23.70. IR (KBr pellet): ν(BH) 2481, ν(CO) 1963 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.21 (s, 6H, PCH_2N), 4.40−4.57 (AB system, 6H, NCH_2N), 6.22 (br s, 1H, HB($C_3H_3N_2$)$_3$), 6.25 (t, $^3J_{H,H}$ = 2.2 Hz, 1H, HB($C_3H_3N_2$)$_3$), 6.35 (t, $^3J_{H,H}$ = 2.1 Hz, 1H, HB($C_3H_3N_2$)$_3$), 7.39 (br s, 1H, HB($C_3H_3N_2$)$_3$), 7.64 (br s, 1H, HB($C_3H_3N_2$)$_3$), 7.74 (br,d, $^3J_{H,H}$ = 2.1 Hz, 1H, HB($C_3H_3N_2$)$_3$), 7.78 (br d, $^3J_{H,H}$ = 2.1 Hz, 1 H, HB($C_3H_3N_2$)$_3$), 7.80 (br s, 1H, HB($C_3H_3N_2$)$_3$), 7.91 (br d, $^3J_{H,H}$ = 2.4 Hz, 1 H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 52.07 (d, $^1J_{C,P}$ = 16.43 Hz, PCH_2N), 73.33 (d, $^3J_{C,P}$ = 6.32 Hz, NCH_2N), 106.10 (d, $^4J_{C,P}$ = 2.53 Hz, HB($C_3H_3N_2$)$_3$), 106.19 (s, HB($C_3H_3N_2$)$_3$), 106.96 (s, HB($C_3H_3N_2$)$_3$), 135.21 (s, HB($C_3H_3N_2$)$_3$), 136.02 (s, HB($C_3H_3N_2$)$_3$), 137.03 (s, HB($C_3H_3N_2$)$_3$), 143.25 (s, HB($C_3H_3N_2$)$_3$), 145.44 (s, HB($C_3H_3N_2$)$_3$), 146.11 (s, HB($C_3H_3N_2$)$_3$), 201.81 (d, J = 17.69, CO) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz): δ −35.40 (s)

In Situ NMR Formation of [TpRu{C(PPh$_2$Me)=C=CPh$_2$}(PTA)(PPh$_3$)]PF$_6$ (8). A solution of **5** (20.9 mg, 0.019 mmol) in 0.5 mL of MeOD was placed in an NMR tube, and PPh$_2$Me (3.67 μL, mL, 0.019 mmol) was added through the serum cap via a microsyringe at room temperature. ^{31}P{^{1}H} NMR (MeOD, 161 MHz, 0 °C): δ −144.3 (sept, $^1J_{P,F}$ = 707.6 Hz, *P*F$_6$), −31.2 (br d, $^2J_{P,P}$ = 31.2 Hz *P* PTA), 22.6 (br s, *P*Ph$_2$Me), 53.9 (br d, $^2J_{P,P}$ = 35.6 Hz, *P*Ph$_3$) ppm.

Preparation of [TpRu{C(PTA)=C=CPh$_2$}(PTA)(PPh$_3$)]PF$_6$ (9). A 14.7 mg portion (0.093 mmol) of PTA was added to a solution of **5** (100.0 mg, 0.093 mmol) in 20 mL of MeOH. The mixture was concentrated by slow evaporation of the solvent under a stream of nitrogen. A yellow crystalline precipitate was obtained. Yield: 62.9 mg (54.9%). Anal. Calcd for $C_{54}H_{59}BF_6N_{12}P_4Ru$ (1225.91 g/mol): C, 52.91; H, 4.85; N, 13.71. Found: C, 53.01; H, 4.75; N, 13.60. IR (KBr pellet): $\nu_{BH(Tp)}$ 2518 (w), $\nu_{C=C=C}$ 1840 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz, 0 °C): δ 2.81−4.24 (m, 24H, PTA), 5.80 (t, br, $^3J_{H,H}$ = 2.4, 1H, HB($C_3H_3N_2$)$_3$), 6.08 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.33 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.40 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.82 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.99−7.80 (m, 25H, *Ph*), 7.71 (d, br, $^3J_{H,H}$ = 2.3, 1H, HB($C_3H_3N_2$)$_3$), 7.95 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.98 (br, 1H, HB($C_3H_3N_2$)$_3$), 8.01 (br, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, 0 °C): δ 52.5 (d, $^1J_{C,P}$ = 23.4 Hz, PCH_2N), 51.8 (d, $^1J_{C,P}$ = 12.3 Hz, PCH_2N), 71.4 (d, $^3J_{C,P}$ = 7.4 Hz, NCH_2N), 72.1 (d, $^3J_{C,P}$ = 6.1 Hz, NCH_2N), 105.7 (s, HB($C_3H_3N_2$)$_3$), 106.6 (s, HB($C_3H_3N_2$)$_3$), 108.2 (s, HB($C_3H_3N_2$)$_3$), 126.0−131.4 (*C* PPh$_3$), 136.6 (s, HB($C_3H_3N_2$)$_3$), 137.9 (s, HB($C_3H_3N_2$)$_3$), 138.7 (s, HB($C_3H_3N_2$)$_3$), 144.3 (s, HB($C_3H_3N_2$)$_3$), 144.7 (s, HB($C_3H_3N_2$)$_3$), 146.9 (s, HB($C_3H_3N_2$)$_3$), 102.7 (d, $^3J_{CP}$ = 25.89 Hz, C=C=*C*Ph$_2$), 209.7 (m, C=*C*=CPh$_2$) ppm. The signal corresponding to C$_\alpha$ could not be safely localized, likely due to superimposition with signals of the PTA backbone at ca. 70 ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz, 0 °C): δ −144.2 (sept, $^1J_{P,F}$ = 711.2 Hz, *P*F$_6$), −46.8 (s, *P*PTA), −44.1 (d, $^2J_{P,P}$ = 32.3 Hz, *P*PTA), 49.2 (d, $^2J_{P,P}$ = 32.3 Hz, *P*Ph$_3$) ppm.

In Situ NMR Formation of [TpRuCl{C(PPh$_2$Me)=C=CPh$_2$}(PTA)] (10). A solution of **6** (30.0 mg, 0.043 mmol) in 0.5 mL of CD_2Cl_2 was placed in an NMR tube, and PPh$_2$Me (0.043 mmol, 8.08 μL) was added through the serum cap via a microsyringe at room temperature. Once the NMR study was completed, the solvent was removed and the residue was used to prepare the KBr pellet to record the IR spectrum. IR: $\nu_{BH(Tp)}$ 2472 (w), $\nu_{C=C=C}$ 1853 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.80−4.21 (m, 15H, PTA + PPh$_2$*Me*), 6.15 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.42 (br, 2H, HB($C_3H_3N_2$)$_3$), 6.83 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.11−7.62 (m, 20H, *Ph*), 7.00 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.64 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.68 (br, 1H, HB($C_3H_3N_2$)$_3$), 7.85 (br, 1H, HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 52.6 (d, br, $^3J_{C,P}$ = 9.0 Hz, PCH_2N), 73.3 (br, NCH_2N + PPh$_2$*Me*), 105.2 (s, 2 HB($C_3H_3N_2$)$_3$), 125.5−133.9 (*C* PPh$_3$, HB($C_3H_3N_2$)$_3$), 136.4 (s, HB($C_3H_3N_2$)$_3$), 143.7 (s, HB($C_3H_3N_2$)$_3$), 144.9 (s, HB($C_3H_3N_2$)$_3$), 147.4 (s, HB($C_3H_3N_2$)$_3$), 100.7 (d, $^3J_{CP}$ = 24.06 Hz, C=C=*C*Ph$_2$), 214.9 (br, C=*C*=CPh$_2$) ppm. The signal corresponding to C$_\alpha$ could not be safely localized, likely due to superimposition with signals of the PTA backbone at ca. 70 ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz, 0 °C): δ −47.3 (s, *P* PTA), −18.4 (s, C−*P* PTA) ppm.

In Situ NMR Formation of [TpRuCl{C(PTA)=C=CPh$_2$}(PTA)] (11). A solution of **6** (30.0 mg, 0.043 mmol) in 0.5 mL of CD_2Cl_2 was placed in an NMR tube, and a CD_2Cl_2 solution of PTA (85.0 μL, 0.043 mmol, 0.5 M) was added through the serum cap via a microsyringe at room temperature. Once the reaction was completed (NMR monitoring), the solvent was removed in vacuo and the residue was used to prepare the KBr pellet to record the IR spectrum. IR: $\nu_{BH(Tp)}$ 2472 (w), $\nu_{C=C=C}$ 1851 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.76−3.93 (m, 6H, PCH_2N), 4.21−4.34 (m, 6H, NCH_2N), 4.34−4.49 (m, 6H, NCH_2N), 4.65−4.90 (m, 6H, PCH_2N), 5.65 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.13 (br, 2H, HB($C_3H_3N_2$)$_3$), 6.56 (br, 1H, HB($C_3H_3N_2$)$_3$), 6.86−7.85 (m, 15H, *Ph* + HB($C_3H_3N_2$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 72.7 (d, $^3J_{C,P}$ = 9.0 Hz, NCH_2N), 73.7 (d, $^3J_{C,P}$ = 5.1 Hz, NCH_2N), 105.0 (s, HB($C_3H_3N_2$)$_3$), 125.5−129.7 (*C* PPh$_3$, HB($C_3H_3N_2$)$_3$), 134.5 (s, HB($C_3H_3N_2$)$_3$), 135.2 (s, HB($C_3H_3N_2$)$_3$), 135.4 (s, HB($C_3H_3N_2$)$_3$), 142.3 (s, HB($C_3H_3N_2$)$_3$), 143.2 (s, HB($C_3H_3N_2$)$_3$), 143.9 (s, HB($C_3H_3N_2$)$_3$), 102.8 (d, $^3J_{CP}$ = 25.76 Hz, C=C=*C*Ph$_2$), 210.7 (br, C=*C*=CPh$_2$) ppm. A careful inspection of the ^{1}H,^{13}C-HSQC experiment indicates that the signal corresponding to the PCH_2N group (54.6 ppm) is partially obscured by the solvent resonance. The signal corresponding to C$_\alpha$ could not be safely localized, likely due to superimposition with signals of the PTA backbone at ca. 70 ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161 MHz, 0 °C): δ −47.3 (s, *P* PTA), −18.4 (s, C−*P* PTA) ppm.

X-ray Structure Determination. Suitable crystals for X-ray diffraction studies were obtained for compounds **2** and **9**.

Table 4. Crystal Data and Structure Refinement Details for Compounds 2 and 9

	2	9
empirical formula	$C_{41}H_{42}BN_9P_2Ru$	$C_{54}H_{59}BF_6N_{12}P_4Ru$
formula wt	834.66	1225.89
temp (K)	293(2)	100
wavelength (Å)	0.71073	
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens		
a (Å)	10.180(2)	12.0938(14)
b (Å)	10.678(2)	14.2160(16)
c (Å)	19.582(4)	17.962(2)
α (deg)	81.850(5)	72.991(2)
β (deg)	79.352(4)	70.925(2)
γ (deg)	67.111(4)	67.592(2)
V (Å^3)	1921.4(7)	2647.8(5)
Z	2	2
calcd density (Mg/m^3)	1.443	1.538
abs coeff (mm^{-1})	0.535	0.490
F(000)	860	1260.0
cryst size (mm)	0.20 × 0.20 × 0.15	0.24 × 0.10 × 0.02
θ range for data collecn (deg)	2.08−23.00	1.22−28.85
index ranges	$-11 \le h \le 11$; $-8 \le k \le 11$; $-21 \le l \le 21$	$-16 \le h \le 16$; $-18 \le k \le 18$; $-24 \le l \le 23$
no. of rflns collected	8238	251 950
no. of indep rflns	5300 (R(int) = 0.0707)	12 370 (R(int) = 0.0334)
no. of obsd rflns ($>2\sigma$)	3031	98 870
data completeness	0.990	0.980
abs cor	semiempirical from equivalents	
max and min transmissn	1.000 and 0.660	0.872 and 0.990
refinement method	full-matrix least squares on F^2	
no. of data/restraints/parameters	5300/0/488	12 370/0/706
goodness of fit on F^2	1.026	1.101
final R indices ($I > 2\sigma(I)$)	R1 = 0.0925, wR2 = 0.2304	R1 = 0.0479, wR2 = 0.1027
R indices (all data)	R1 = 0.1528, wR2 = 0.2895	R1 = 0.0658, wR2 = 0.1124
largest diff peak and hole (e Å^{-3})	1.556 and −1.259	1.095 and −0.532

For compound **2**, the data collection was carried out on a Siemens Smart CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. For compound **9**, the data collection was carried out on a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. Absorption corrections were carried out using SADABS.[27]

The structures of compounds were solved with the Oscail[28] (**2**) and Shelx programs[29] (**9**) by Patterson methods and refined by full-matrix least squares based on F^2.[29] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from ref 30. Details of crystal data and structural refinement are given in Table 4.

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Supporting Information Available: CIF files giving crystallographic data for compounds **2** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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