Reactions of the Cationic Fragments $[RuCp(PPh_2NHR)_2]^+$ and $[RuTp(PPh_2NHR)_2]^+$ (R = Ph, *n*-Pr) with Alkynes: Formation of Four-Membered Azaphosphacarbenes

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Received April 2, 2005

The synthesis of $RuCp(PPh_2NHR)_2Cl$ (**1a**,**b**; R = Ph, *n*-Pr) and $RuTp(PPh_2NHR)_2Cl$ (**2a**,**b**) is reported. Chloride abstraction from **1a** with $AgCF_3SO_3$ affords $RuCp(PPh_2NHPh)_2(\eta^1\text{-}OSO_2CF_3)$ (**3**), whereas when $AgSbF_6$ is used instead $[RuCp(\kappa^2(P,P)\text{-}PPh_2NHC_6H_4PPh_2)(NH_2Ph)]^+$ (**4**) is formed. In the course of this reaction the P−N bond of one PPh_2NHPh ligand is cleaved while a new P−C bond is formed, with concomitant formation of an aniline ligand. In the presence of Ag^+ ($CF_3SO_3^-$ or SbF_6^-) complexes **1** and **2** react with terminal alkynes HC≡CR′ (R′ = Ph, *p*-C_6H_4Me, *n*-Bu) and propargylic alcohols to give novel azaphosphacarbene complexes of the types $[RuCp(\kappa^2(C,P)\text{=}C(CH_2R')N(R)PPh_2)(\kappa^1(P)\text{-}PPh_2NHR)]^+$ (**5a**−**c**, **6a**−**c**), $[RuTp(\kappa^2(C,P)\text{=}C(CH_2R')N(R)PPh_2)(\kappa^1(P)\text{-}PPh_2NHR)]^+$ (**14a**,**b**, **15a**−**c**), $[RuCp(\kappa^2(C,P)\text{=}C(CH\text{=}CPh_2)N(Pr^n)PPh_2)(\kappa^1(P)\text{-}PPh_2NHPr^n)]^+$ (**12**), and $[RuTp(\kappa^2(C,P)\text{=}C(CH\text{=}CPh_2)N(Pr^n)\text{-}PPh_2)(\kappa^1(P)\text{-}PPh_2NHPr^n)]^+$ (**17**). These reactions proceed via vinylidene and allenylidene intermediates, respectively, which could be isolated in some cases: viz. $[CpRu(PPh_2NHPh)_2(\text{=}C\text{=}C\text{=}CPh_2)]^+$ (**11**) and $[RuTp(PPh_2NHR)_2(\text{=}C\text{=}C\text{=}CPh_2)]^+$ (**16a**,**b**). Furthermore, complexes **1a**,**b** react with 3-butyn-1-ol to yield the oxacyclopentylidene complexes $[CpRu(PPh_2NHR)_2(\text{=}C_4H_6O)]^+$ (**7a**,**b**). In sharp contrast to **6a**−**c** (R = *n*-Bu), **5a**−**c** (R = Ph) turned out to be quite sensitive toward traces of water, leading eventually to the formation of the aminocarbene complexes $[RuCp(\text{=}C(CH_2R)NHPh)(PPh_2NHPh)(\kappa^1(P)\text{-}PPh_2OH)]^+$ (**8a**,**b**) featuring a κ^1(P)-coordinated PPh_2OH ligand. This ligand could be easily deprotonated to yield the neutral complex $RuCp(\text{=}C(CH_2Ph)NHR)(PPh_2NHPh)(\kappa^1(P)\text{-}OPPh_2)$ (**10a**,**b**). The formation of these complexes is reversible. Finally, representative structures have been determined by X-ray crystallography.

Introduction

Ruthenium vinylidene and allenylidene complexes play an important role in organometallic chemistry, as emphasized in several recent reviews.[1] Interest in these compounds stems from the fact that they are intermediates in several stoichiometric and catalytic transformations of organic molecules. Moreover, they are readily accessible from terminal alkynes and propargylic alcohols. A key characteristic of all these complexes, particularly if they are cationic, is the electrophilicity of the α-carbon, adding, often easily, amines,[2] alcohols,[3] phosphines,[4] and even fluoride.[5] In this way heteroatom-stabilized carbene complexes become readily available. Such reactions have been shown to be particularly facile in the intramolecular mode[6] through utilizing bifunc-

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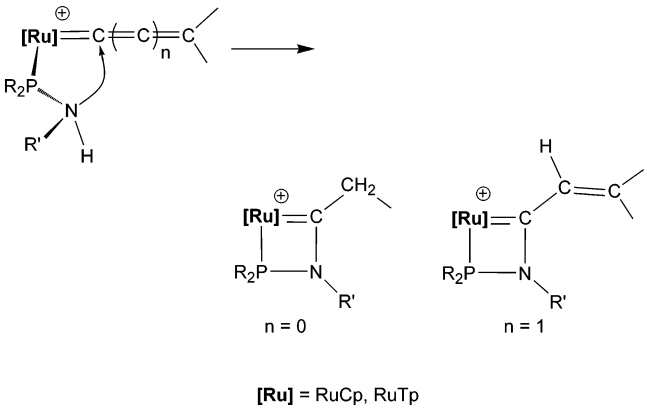
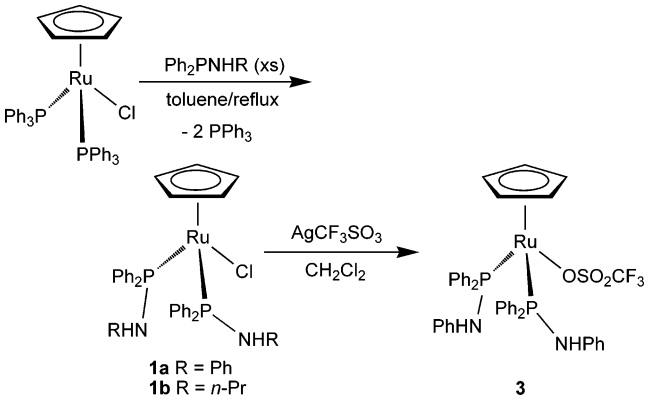
10.1021/om050247a CCC: $30.25 © 2005 American Chemical Society
Publication on Web 06/10/2005

Chart 1



Scheme 1



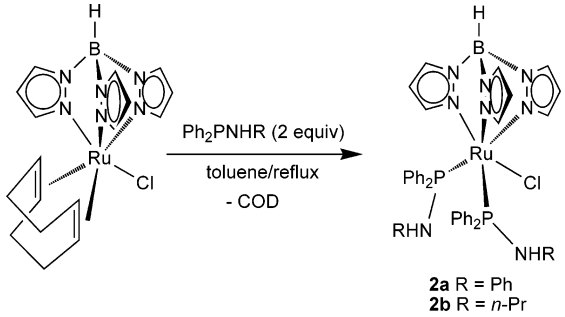
tional ligands such 2-aminopyridine[7] and 2-acetamidopyridines.[8]

In the present paper we report on the synthesis of RuCp and RuTp complexes containing phosphinoamine ligands of the type PPh_2NHR with R = Ph, *n*-Pr. We describe the reactivity of these complexes toward terminal acetylenes and propargylic alcohols, yielding novel cyclic four-membered azaphosphacarbenes via an intramolecular addition of the amine moiety of the bifunctional phosphinoamine ligand to vinylidene and allenylidene complexes according to Chart 1.

Results and Discussion

Treatment of $RuCp(PPh_3)_2Cl$ with an excess of PPh_2NHR (R = Ph, *n*-Pr) at 120 °C for 12 h in toluene affords $RuCp(PPh_2NHR)_2Cl$ (**1a**,**b**) in 88 and 91% yields, respectively (Scheme 1). The synthesis of **1a** has been already reported elsewhere.[9] The analogous RuTp complexes $RuTp(PPh_2NHR)_2Cl$ (**2a**,**b**) have been prepared by reacting RuTp(COD)Cl with 2 equiv of PPh_2NHR at 120 °C for 3 h in toluene according to Scheme 2. All of these complexes are air-stable and thermally robust orange to yellow solids. They have been characterized by a combination of elemental analysis and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. In addition, **1a** and **2a** have been characterized by X-ray crystallography.

Scheme 2



Structural views are depicted in Figures 1 and 2, with selected bond distances and angles given in the captions. In both complexes the steric requirements of the bulky aminophosphine ligands lead to an an asymmetric arrangement of the phenyl moieties. Both complexes are stabilized in the solid state by intramolecular hydrogen bonds between the two amino groups and/or between the amino groups and the chloride ligand. In **1a** two markedly bent N−H···Cl bonds with distinctly different N···C distances are observed (Figure 1), while in **2a**·$CHCl_3$ both an intramolecular N−H···N bond and an N−H···Cl hydrogen bond are present (Figure 2). In addition, **2a**·$CHCl_3$ also contains an intramolecular C−H···Cl hydrogen interaction from the $CHCl_3$ molecule to the Ru complex: $C(CHCl_3)$···Cl(Ru complex) = 3.40 Å.

In solution, even at temperatures of −90 °C in CD_2Cl_2 as the solvent, only one $^{31}P\{^1H\}$ signal is observed for both complexes **1** and **2**, indicating a rather weak hydrogen bond and thus apparently fast exchange. According to DFT/B3LYP calculations in the model complex $RuCp(PH_3)(PH_2NH_2)Cl$ intramolecular N−H···Cl hydrogen bonding provides a stabilization of merely 2.5 kcal/mol. It is, therefore, not surprising that this weak interaction cannot be observed in solution by NMR spectroscopy, even at very low temperatures.

Substitution of the chloride ligand in **1a** for the weakly nucleophilic $CF_3SO_3^-$ anion was investigated

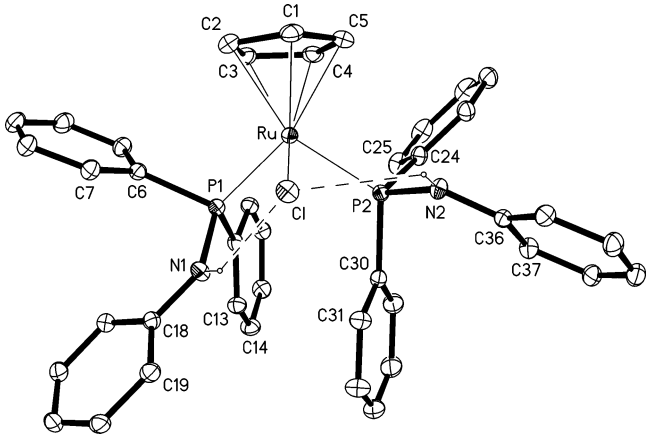


Figure 1. Structural view of $RuCp(PPh_2NHPh)_2Cl$ (**1a**) showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): $Ru-C(1-5)_{av}$ = 2.210(1), Ru−P(1) = 2.2798(3), Ru−P(2) = 2.2947(3), Ru−Cl = 2.4413(3), P(1)−N(1) = 1.681(1), P(2)−N(2) = 1.693(1), N(1)−C(18) = 1.398(2), N(2)−C(36) = 1.403(2); P(1)−Ru−P(2) = 97.52(1), P(1)−Ru−Cl = 90.78(1), P(2)−Ru−Cl = 89.56(2), P(1)−N(1)−C(18) = 133.5(1), P(2)−N(2)−C(36) = 129.5(1); N(1)···C = 3.094(1), N(2)···Cl = 3.335(1).

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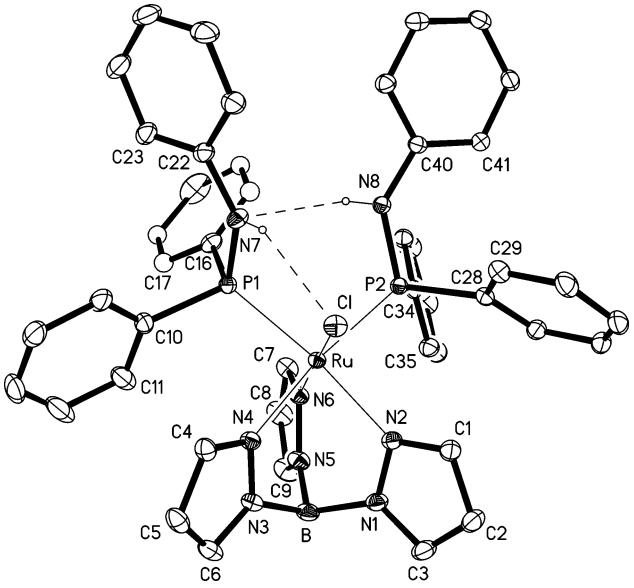


Figure 2. Structural view of $RuTp(PPh_2NHPh)_2Cl{\cdot}CHCl_3$ (**2a**·$CHCl_3$) showing 40% thermal ellipsoids ($CHCl_3$ omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−N(2) = 2.153(1), Ru−N(4) = 2.142(1), Ru−N(6) = 2.083(1), Ru−P(1) = 2.3105(5), Ru−P(2) = 2.3125(4), Ru−Cl = 2.4436(4), P(1)−N(7) = 1.695(1), P(2)−N(8) = 1.688(1); P(1)−Ru−P(2) = 96.29(1), P(1)−Ru−Cl = 89.96(1), P(2)−Ru−Cl = 90.64(1), P(1)−N(7)−C(22) = 134.5(1), P(2)−N(8)−C(40) = 134.2(1); N(7)···Cl = 3.096(1), N(8)···N(7) = 3.087(2).

with the intention of generating a reactive complex bearing a weakly coordinating ligand occupying a latent coordination site. In fact, chloride abstraction from **1a** with $AgCF_3SO_3$ (1 equiv) affords, on workup, the expected neutral complex $RuCp(PPh_2NHPh)_2(\eta^1\text{-}OSO_2CF_3)$ (**3**), where $CF_3SO_3^-$ is directly bound to the metal center (Scheme 1). A structural view of **3** is depicted in Figure 3 with selected bond distances and angles given in the caption. The overall geometry of the complex, which has the usual three-legged piano-stool structure, is very similar to that of **1a** with respect to Ru−C(Cp) and Ru−P bond lengths and also with respect to the spatial arrangement of the two aminophosphine ligands. The $CF_3SO_3^-$ anion is coordinated via the oxygen atom in an η^1 fashion with a Ru−O(1) distance of 2.234(2) Å and a Ru−O(1)−S angle of 128.7(2)°. Moreover, as outlined in Figure 3, there are two intramolecular N−H···O hydrogen bonds which contribute to the coherence and asymmetry of the complex. Several other ruthenium complexes with the η^1-OSO_2CF_3 ligand are known and have been structurally characterized.[10]

On the other hand, if chloride abstraction from **1a** is performed with $AgSbF_6$ instead of $AgCF_3SO_3$, a different reaction was observed, resulting in the formation of $[RuCp(\kappa^2(P,P)\text{-}PPh_2NHC_6H_4PPh_2)(NH_2Ph)]^+$ (**4**) in 90% yield (Scheme 3). In the ^1H NMR spectrum of **4** the Cp ring gives rise to a singlet at 4.61 ppm. The NH_2 hydrogen atoms of the aniline ligand exhibit two doublets centered at 3.80 and 3.11 ppm with P−C coupling constants of 11.2 and 10.7 Hz, respectively. In the $^{31}P\{^1H\}$ NMR spectrum the κ^2(P,P)-coordinated $PPh_2NHC_6H_4PPh_2$ ligand displays an AX pattern with two doublets centered at 103.1 and 48.5 ppm. The coupling constant J_{PP} is 63.3 Hz. In addition to spectroscopic and analytical characterization also the solid-state structure of **4** was determined by single-crystal X-ray diffraction. An ORTEP diagram is shown in Figure 4. Selected bond distances and angles are reported in the caption. Accordingly, the complex adopts a three-legged piano-stool

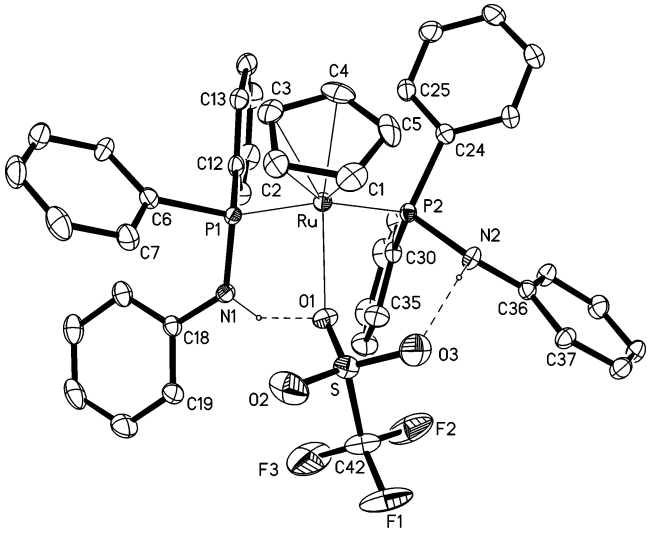
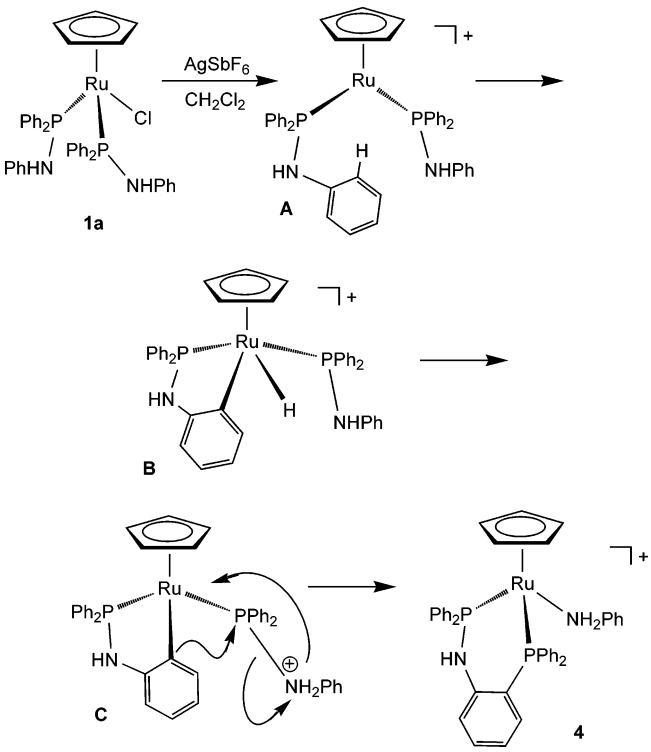


Figure 3. Structural view of $RuCp(PPh_2NHPh)_2(CF_3SO_3)$ (**3**) showing 40% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ = 2.188(4), Ru−P(1) = 2.305(1), Ru−P(2) = 2.315(1), Ru−O(1) = 2.234(3), P(1)−N(1) = 1.680(3), P(2)−N(2) = 1.680(3); P(1)−Ru−P(2) = 98.99(3), P(1)−Ru−O(1) = 86.4(1), P(2)−Ru−O(1) = 86.2(1), P(1)−N(1)−C(18) = 131.4(3), P(2)−N(2)−C(36) = 132.8(2); N(1)···O(1) = 2.935(4), N(2)···O(3) = 3.305(6).

Scheme 3



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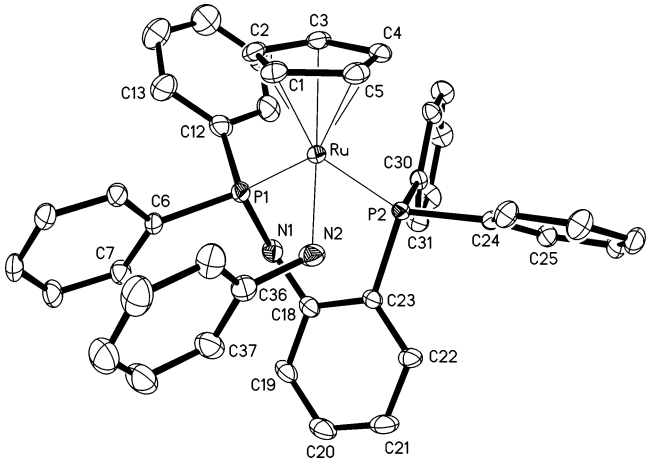

Figure 4. Structural view of [RuCp(κ^2(*P*,*P*)-$PPh_2NHC_6H_4PPh_2$)(NH_2Ph)]SbF_6·solv (**4**·solv) showing 40% thermal ellipsoids (SbF_6^- and solvent omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ = 2.214(5), Ru−P(1) = 2.271(2), Ru−P(2) = 2.285(2), Ru−N(2) = 2.238(5), P(1)−N(1) = 1.692(5); P(1)−Ru−P(2) = 86.92(5), P(1)−Ru−N(2) = 97.5(1), P(2)−Ru−N(2) = 87.4(1), P(1)−N(1)−C(18) = 122.2(4), Ru−N(2)−C(36) = 125.5(3).

conformation with the two phosphorus atoms of the $PPh_2NHC_6H_4PPh_2$ ligand and the nitrogen atom of the aniline ligand as the legs. The Ru−P(1) and Ru−P(2) bond distances are 2.271(2) and 2.285(2) Å, respectively, with a P(1)−Ru−P(2) bite angle of 86.92(5)°. The Ru−N(2) bond length is 2.238(5) Å with a Ru−N(2)−C(36) angle of 125.5(3)°. For comparison, the Ru−N(aniline) bond distances in the ruthenium aniline complexes [RuTp(PMe_3)(NH_2Ph)]$^+$ and [RuTp($P(OMe)_3$)(NH_2Ph)]$^+$ are 2.211(3) and 2.182(2) Å, respectively.[11] The respective Ru−N−C angles are 123.6(2) and 120.8(1)°.

Due to the absence of any observable intermediates the mechanism of this reaction can only be speculated upon. A possible mechanism is presented in Scheme 3. Chloride abstraction may initially afford the highly reactive coordinatively unsaturated 16e$^-$ complex [RuCp($PPh_2NHPh)_2$]$^+$ (**A**),[12] which then undergoes ortho metalation to yield the Ru(IV) hydride complex **B**. Intramolecular hydride abstraction by the "built-in" base PPh_2NHPh leads to the formation of **C**, which subsequently undergoes reductive elimination, thereby forming the new bidentate bisphosphine ligand $PPh_2NHC_6H_4PPh_2$ and releasing free aniline. The latter occupies the vacant coordination site, finally forming complex **4**. In the course of this reaction the P−N bond of one PPh_2NHPh ligand is cleaved while a new P−C bond is formed.

Reaction of the [RuCp($PPh_2NHR)_2$]$^+$ (R = Ph, *n*-Pr) Fragment with Terminal Alkynes. Treatment of **1a**,**b** with HC≡CR′ (R′ = Ph, *p*-C_6H_4Me, *n*-Bu) in the presence of $AgCF_3SO_3$ (1 equiv) at room temperature for 2−12 h in CH_2Cl_2 as the solvent results in the formation of the novel azaphosphacarbene complexes [RuCp(κ^2(*C*,*P*)=C(CH_2R′)N(R)PPh_2)(κ^1(*P*)-PPh_2NHR)]$^+$ (**5a**−**c**, **6a**−**c**) in high yields (Scheme 4). These compounds have again been characterized by elemental analysis and by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Characteristic features comprise, in the ^{13}C{^{1}H} NMR spectrum, a marked low-field doublet of doublets resonance in the range of 275.8−282.3 ppm (dd, J_{CP} = 31−33 Hz, J_{CP} = 12−14 Hz), assignable to the carbene carbon atom of the four-membered azaphosphacarbene moiety. The ^{31}P{^{1}H} NMR spectrum of complexes **5** and **6** reveal two doublets centered at about 88−82 and 78−72 ppm with a small coupling constant of 36 Hz. The NH proton of the PPh_2NHPh ligand gives rise to a doublet at about 6.5−5.5 ppm (J_{HP} = 16−17 Hz), whereas the NH proton of the PPh_2NHPr^n ligand could not be detected. Finally, the ^{1}H and ^{13}C{^{1}H} NMR resonances of the Cp ligand are in the expected ranges.

Metallacyclobutene complexes of the type **A**, where X and/or Y are, e.g., C, N, O, S, or P moieties are comparatively rare (Chart 2).[13] Four-membered azaphosphacarbene complexes where X = PR_2 and Y = NR, according to our knowledge, have not been described in the literature. In the last couple of years, Cavell and others reported the synthesis of a series of transition-metal bis(iminophosphorano)carbene complexes which are somewhat related to azaphosphacarbenes. In these compounds the carbene moiety is a four-membered chelate ligand coordinated in κ^2(C,N) fashions of the types **B**−**D**.[14] Structures of the "pincer type" **B** include group 4 metals,[15] samarium,[16] and molybdenum.[17] The bridged species **C** is observed in chromium,[18] aluminum,[19] and group 14 metals,[20] while bis(iminophosphorano)carbene complexes acting as a κ^2(C,N) bidentate ligand (**D**) are found in platinum[21] and ruthenium complexes.[22]

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Scheme 4

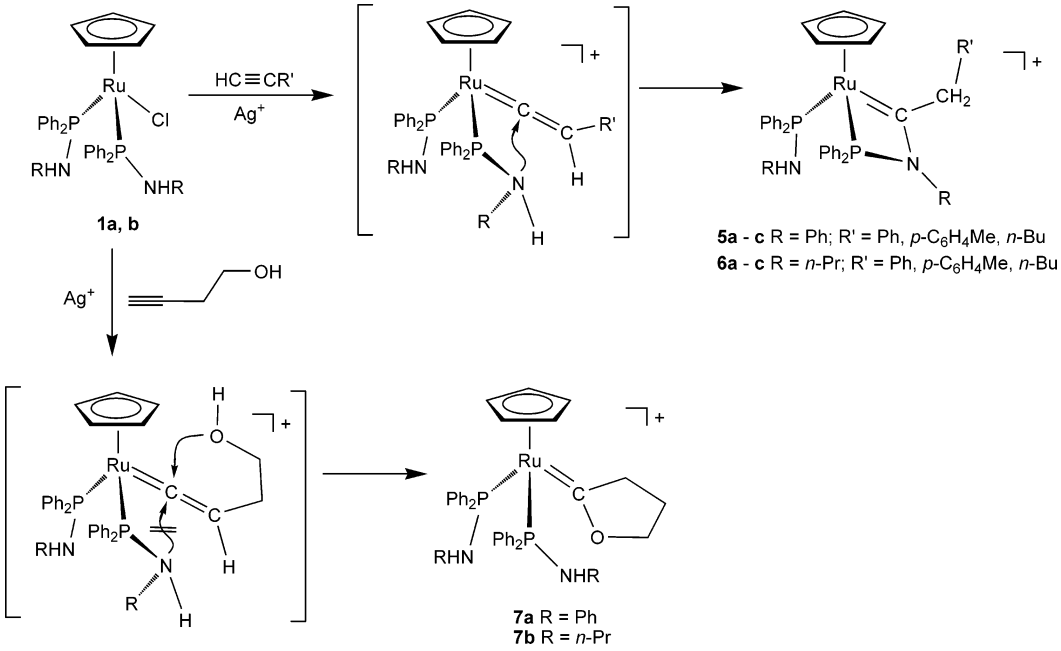
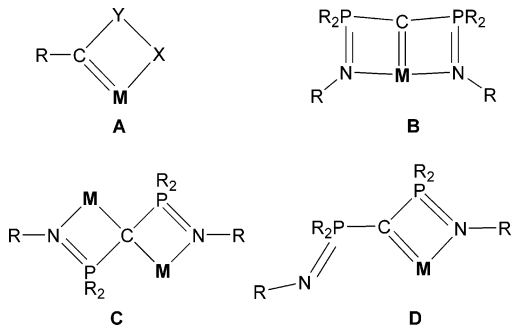


Chart 2



In contrast to the reactions of **1a**,**b** and simple terminal alkynes, with 3-butyn-1-ol oxacyclopentylidene complexes of the type $[CpRu(PPh_2NHR)_2(=C_4H_6O)]^+$ (**7a**,**b**) rather than azaphosphacarbenes are readily formed (Scheme 4).

The formation of both azaphosphacarbene and oxacyclopentylidene complexes likely proceeds via vinylidene intermediates according to Scheme 4. Although such intermediates could not be isolated in the case of the present RuCp systems, they could be spectroscopically detected. The tendency of vinylidene complexes to be readily attacked by nitrogen or oxygen donors to give Fischer carbene complexes is well-known.[2,3]

Such a process is especially facile when the nucleophilic attack occurs in an intramolecular, chelate-assisted fashion. In the case of 3-butyn-1-ol, nucleophilic addition of the hydroxy function of the alkynol at the α-carbon atom of the vinylidene intermediate is apparently kinetically favored over nucleophilic attack of the amine moiety, thus yielding exclusively oxacyclopentylidene complexes **7a**,**b**.

While complexes **5a**−**c** and **6a**−**c** are air stable in the solid state and to some extent also in solution, complexes **5a**−**c**, in sharp contrast to **6a**−**c**, turned out to be quite sensitive toward even traces of water. Accordingly, treatment of **5a** or **5c** (either isolated or prepared in situ by reacting **1a** with the respective acetylene and $AgCF_3SO_3$) with 1 equiv of water resulted in the formation of the aminocarbene complexes $[RuCp(=C(CH_2R)NHPh)(PPh_2NHPh)(\kappa^1(P)\text{-}PPh_2OH)]^+$ (**8a**,**b**), featuring a κ^1(P)-coordinated diphenylphosphinous acid (Scheme 5). Only a few examples of mononuclear complexes with a single PPh_2OH ligand have been reported in the literature, including $W(CO)_4(PPh_2OH)(PPh_2CH_2COR)$ (R = Ph, *p*-C_6H_4Me),[23] $PtCl_2(PPh_2OH)$,[24] $[RuCp(PPh_2OH)_2(PHPh_2)]^+$, and $[RuCp(PPh_2OH)(PHPh_2)_2]^+$.[25] In many cases, the PPh_2OH ligand is found in conjunction with the corresponding diphenylphosphinite ligand, $[PPh_2O]^-$, to form $Ph_2P{-}O{-}H\cdots O{-}PPh_2$ moieties with very strong and almost symmetric hydrogen bonds of O···O distances as low as 2.40 Å.

Complexes **8a**,**b** are obviously formed via nucleophilic attack of water at the phosphorus atom of the four-membered azaphosphacarbene accompanied by concomitant cleavage of the P−N bond. The ^{1}H NMR spectrum of **8a** displays an AB pattern for the CH_2Ph moiety, showing two doublets centered at 3.96 and 3.62 ppm with a coupling constant of 14.9 Hz. Furthermore, the OH proton of the κ^1(P)-coordinated PPh_2OH ligand in **8a** and **8b** gives rise to a low-field resonance at 11.68 and 10.75 ppm, respectively.

Characteristic $^{13}C\{^1H\}$ NMR spectroscopic features of **8a** and **8b** comprise a marked low-field resonance at 254.3 and 258.7 ppm, respectively, assignable to the carbene carbon atom of the aminocarbene moiety. The $^{31}P\{^1H\}$ NMR spectrum of **8** displays an AX pattern, showing two doublets centered at about 140 and 80 ppm, assignable to the PPh_2OH and PPh_2NHPh ligands, respectively. Attempts to grow crystals of complex **8b** failed; instead, small amounts of crystals identified as the cationic $[RuCp(=C(CH_2Bu^n)NHPPh_2)(\kappa^2(P,P)\text{-}PPh_2\text{-}$

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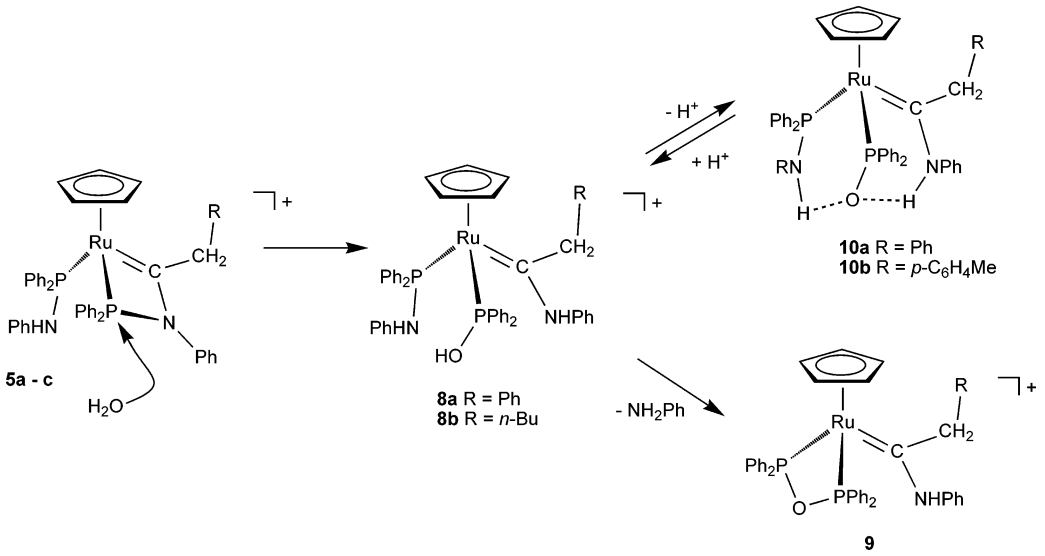
Scheme 5



$OPPh_2)]^+$ (**9**) could be obtained. Complex **9** contains a symmetric κ^2(P,P)-coordinated PPh_2OPPh_2 ligand, as is readily apparent from $^{31}P\{^1H\}$ NMR spectroscopy, exhibiting a singlet at 137.7 ppm. A structural view of **9** is depicted in Figure 5. Selected bond distances and angles are reported in the caption. This complex can be described in terms of a three-legged piano-stool conformation with the two P atoms of the PPh_2OPPh_2 ligand and the C atom of the aminocarbene moiety as the legs. The Ru−C(36) bond distance of 2.037(3) Å is comparable to that of other heteroatom-stabilized ruthenium carbene complexes. The bite angle of the chelating PPh_2-$OPPh_2$ ligand is 67.91(2)°, corresponding to a P−P distance of 2.51 Å. Only a very few complexes with a chelating PPh_2OPPh_2 ligand have been characterized by now, examples being $Cr(CO)_4(PPh_2OPPh_2)$[26] and $RuCl_2(PPh_2OPPh_2)(PPh_3)(Ph_2PO_2CCH{=}CH_2)$.[27] In other instances the ligand is acting as a bridging ligand,

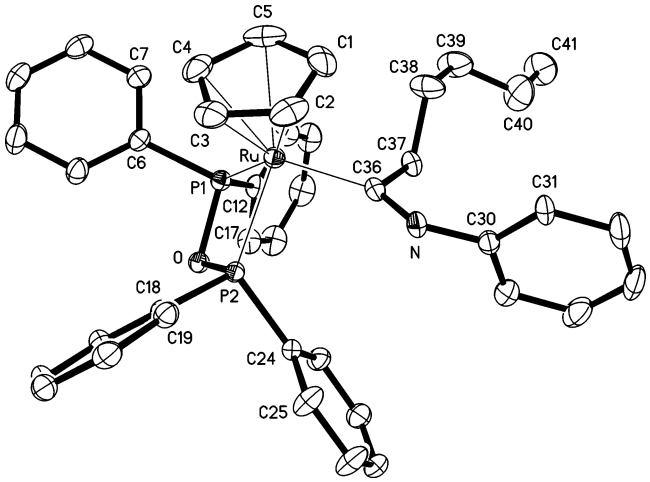
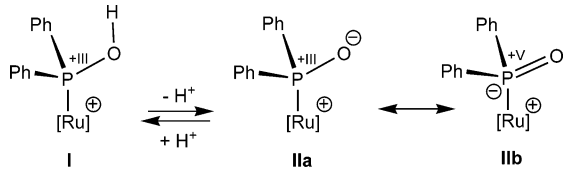


Figure 5. Structural view of $[RuCp(=C(CH_2Bu^n)NHPPh_2)$-$(\kappa^2(P,P)$-$PPh_2OPPh_2)]CF_3SO_3$ (**9**) showing 20% thermal ellipsoids ($CF_3SO_3^-$ omitted for clarity). Selected bond lengths (Å) and angles (deg): $Ru-C(1-5)_{av} = 2.234(2)$, Ru−P(1) = 2.2508(5), Ru−P(2) = 2.2439(5), Ru−C(36) = 2.037(2), P(1)−O = 1.673(1), P(2)−O = 1.675(1), C(36)−N = 1.313(2), C(36)−C(37) = 1.516; P(1)−Ru−P(2) = 67.91(2), P(1)−Ru−C(36) = 99.1(1), P(2)−Ru−C(36) = 90.8(1), P(1)−O−P(2) = 97.2(1); N···O(1) = 2.821(5).

showing in these cases P−P distances about 0.5 Å larger than in the chelating mode.[26]

When a solution of **8a** is passed through a column charged with neutral Al_2O_3, the PPh_2OH ligand is readily deprotonated and $RuCp(=C(CH_2Ph)NHPh)$-$(PPh_2NHPh)(\kappa^1(P)$-$PPh_2O)$ (**10a**) is obtained (Scheme 5). The diphenylphosphinite ligand is coordinated via the lone pair at P rather than via the oxygen lone pairs. This type of complex could be obtained also by directly reaction of **5** with water and subsequent treatment with acidic Al_2O_3, as shown for example for **5b**, affording **10b** upon workup. Complexes **10** exhibit spectroscopic features very similar to those of **8**, and it is sufficient to point out the $^{31}P\{^1H\}$ NMR resonances giving rise to two doublets centered at about 111 and 79.1 ppm, assignable to the $[PPh_2O]^-$ ligand and the aminophosphine PPh_2NHPh, respectively (cf. κ^1(P)-coordinated PPh_2OH in **8a**,**b** exhibits a $^{31}P\{^1H\}$ signal at 141.0 and 140.8 ppm, respectively). On the basis of the $^{31}P\{^1H\}$ NMR data the phosphorus atom in $[PPh_2O]^-$ may be considered as P(III) rather than as P(V), and thus the ligand is better described by structure **IIa** rather than **IIb**. The formation of complexes **10** is reversible. In fact,



addition of acid, e.g. CF_3COOH, leads to a clean back-transformation to **8**, as monitored by NMR spectroscopy.

To unequivocally establish the ligand arrangement around the metal center, the structure of **10a** has been determined by X-ray crystallography. A structural view of **10a** is depicted in Figure 6. Important bond distances and angles are given in the caption. The molecule exhibits the typical three-legged piano-stool geometry

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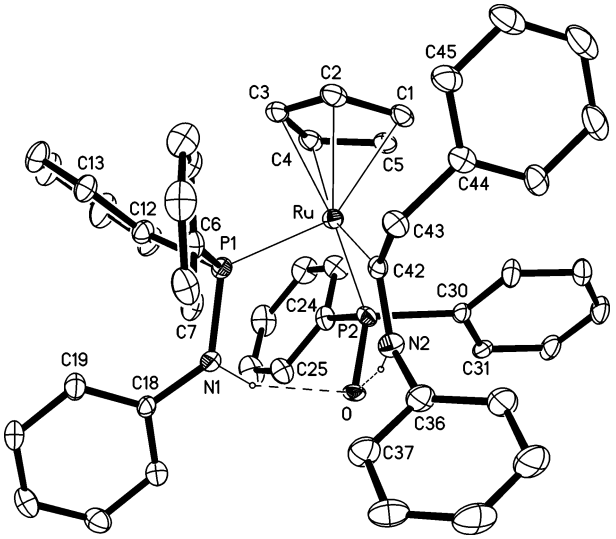

Figure 6. Structural view of [RuCp(=C(CH$_2$Ph)NHPh)(PPh$_2$NHPh)(κ^1(*P*)-O=PPh$_2$)] (**10a**) showing 20% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ = 2.237(9), Ru−P(1) = 2.228(5), Ru−P(2) = 2.282(5), Ru−C(42) = 1.984(12), P(1)−N = 1.678(10), P(2)−O = 1.534(7), C(42)−N(2) = 1.352(14), C(42)−C(43) = 1.509(15); P(1)−Ru−P(2) = 94.5(1), P(1)−Ru−C(42) = 87.3(4), P(2)−Ru−C(42) = 90.0(4), P(1)−N(1)−C(18) = 132.2(8); N(1)···O = 2.843(13), N(2)···O = 2.662(13).

with Ru−C(Cp), Ru−P, and Ru−C$_{carbene}$ bond lengths in accordance with other RuCp complexes of this work. Interestingly, the Ru−P bond to the phosphinoamine is slightly shorter than to the diphenylphosphinite (2.228 vs 2.282 Å), which is one argument supporting formula **IIa**. Another argument is the strong basicity of the phosphinite oxygen atom, which becomes apparent by the two outstandingly short intramolecular N−H···O hydrogen bonds of N···O = 2.66 and 2.84 Å present in **10a** (cf. Figure 6). The shorter of these two hydrogen bonds compares well with those between [HNEt$_3$]$^+$ cations and anionic phosphinite complexes.[28]

Next we have studied the reaction of complexes **1a**,**b** with the propargylic alcohol HC≡CCPh$_2$OH in the presence of AgCF$_3$SO$_3$. The outcome of this reaction depends strongly on the nature of the subtituent of the amine moiety in PPh$_2$NHR. In the case of R = Ph, the allenylidene complex [CpRu(PPh$_2$NHPh)$_2$(=C=C=CPh$_2$)]$^+$ (**11**) is obtained in high yield. On the other hand, with R = *n*-Pr the amine moiety is more basic as well as sterically less demanding; the reaction does not stop at the stage of the allenylidene complex, and nucleophilic attack of the amine moiety at the C$_\alpha$ atom of the allenylidene ligand leads to the formation of the azaphosphacarbene [RuCp(κ^2(*C*,*P*)=C(CH=CPh$_2$)N(Pr^n)-PPh$_2$)(κ^1(*P*)-PPh$_2$NHPr^n)]$^+$ (**12**), as outlined in Scheme 6. Complexes **11** and **12** are both air-stable solids and were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and elemental analysis. Characteristic spectroscopic features of **11** are the three resonances in the ^{13}C{^{1}H} NMR spectrum at 291.9, 201.5, and 161.2 ppm for the C$_\alpha$, C$_\beta$, and C$_\gamma$ allenyl carbon atoms. A view of the molecular geometry of **11** is shown in Figure 7, with selected bond distances and angles given in the

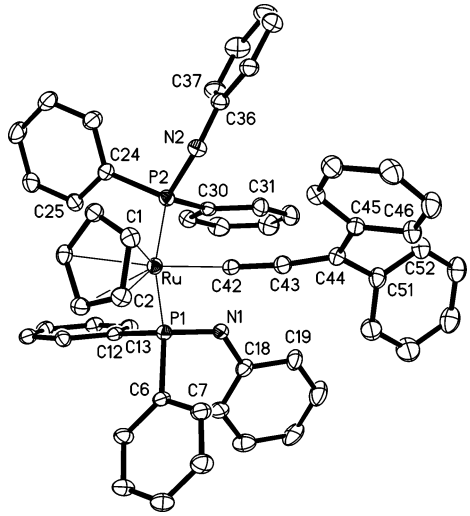

Figure 7. Structural view of [CpRu(PPh$_2$NHPh)$_2$(=C=C=CPh$_2$)]CF$_3$SO$_3$·CH$_2$Cl$_2$ (**11**·CH$_2$Cl$_2$) showing 40% thermal ellipsoids (CF$_3$SO$_3^-$ and CH$_2$Cl$_2$ omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ = 2.250(4), Ru−P(1) = 2.294(2), Ru−P(2) = 2.297(2), Ru−C(42) = 1.889(6), C(42)−C(43) = 1.270(8), C(43)−C(44) = 1.356(8), P(1)−N(1) = 1.680(5), P(2)−N(2) = 1.662(5); P(1)−Ru−P(2) = 97.92(6), P(1)−Ru−C(42) = 89.3(2), P(2)−Ru−C(42) = 88.6(2), Ru−C(42)−C(43) = 175.5(5), C(42)−C(43)−C(44) = 172.9(7), P(1)−N(1)−C(18) = 131.3(4), P(2)−N(2)−C(36) = 131.0(4); N(1)···C(31) = 3.464(7), N(2)···O(1) = 3.455(8).

caption. The structure shows the typical pseudo-octahedral three-legged piano-stool geometry, with a nearly linear allenylidene group coordinated to the ruthenium atom. The allenylidene chain shows typical Ru−C$_\alpha$, C$_\alpha$−C$_\beta$, and C$_\beta$−C$_\gamma$ bond lengths of 1.889(6), 1.270(8), and 1.356(8) Å comparing well with those of related allenylidene complexes.[3b,29]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **12** are consistent with the presence of an azaphosphacarbene structure containing a vinyl side chain. In the ^{13}C{^{1}H} NMR spectrum of **12** the carbene moiety is identified by a downfield signal at 275.2 ppm (dd, J_{CP} = 31.1 Hz, J_{CP} = 15.0 Hz). Other spectral changes accompanying the transformation to the azaphosphacarbene include characteristic resonances at 148.0 and 92.7 ppm assignable to the vinyl carbon atoms CH=*C*Ph$_2$ and *C*H=CPh$_2$, respectively. The vinyl proton gives rise to a singlet at 5.08 ppm.

Reaction of the [RuTp(PPh$_2$NHR)$_2$]$^+$ (R = Ph, *n*-Pr) Fragment with Terminal Alkynes. When **2a**,**b** is treated with HC≡CR′ (R′ = Ph, *p*-C$_6$H$_4$Me, *n*-Bu) in the presence of either AgSbF$_6$ or AgCF$_3$SO$_3$ (1 equiv) at room temperature for 4−24 h in CH$_2$Cl$_2$, the azaphosphacarbene complexes [RuTp(κ^2(*C*,*P*)=C(CH$_2$R′)N(R)PPh$_2$)(κ^1(*P*)-PPh$_2$NHR)]$^+$ (**14a**,**b**, **15a**−**c**) are obtained in high yields as air-stable dark yellow solids (Scheme 7). The only exception is when HC≡CBu^n is reacted with **2a**, where the vinylidene complex [RuTp(PPh$_2$NHPh)$_2$(=C=CH(Bu^n)]SbF$_6$ (**13**) was isolated. Complex **13** did not undergo rearrangement to the corresponding azaphosphacarbene even under reflux conditions for 24 h.

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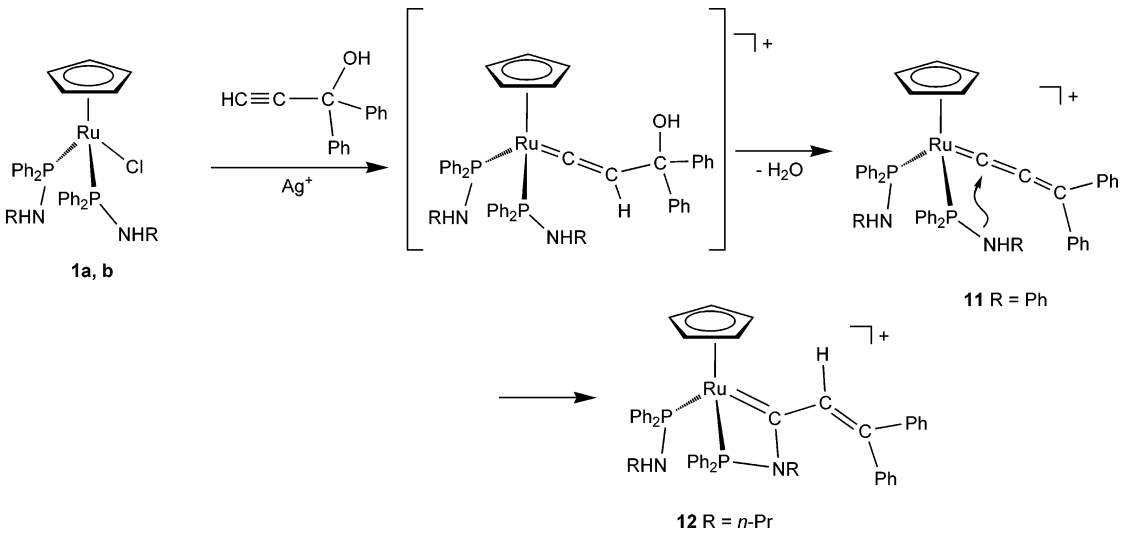
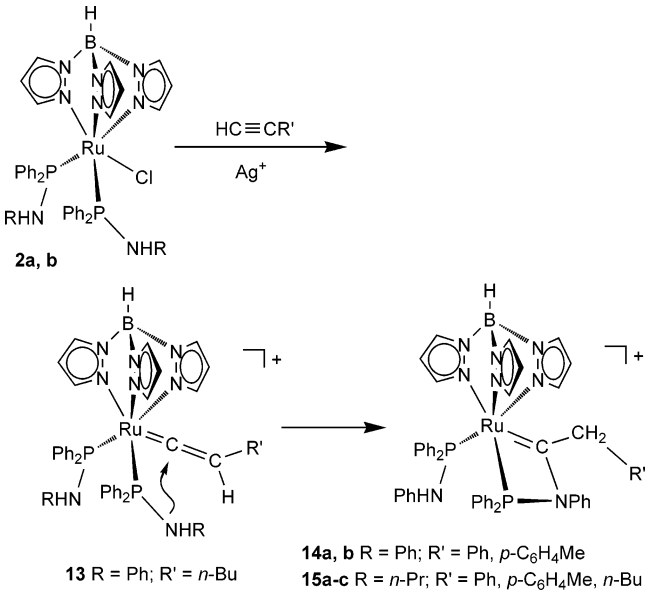
(29) (a) Bustelo, E.; Jimenez Tenorio, M.; Puerta, M. C.; Valerga, P. *Eur. J. Inorg. Chem.* **2001**, 2391. (b) Bustelo, E.; Jimenez Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; Garcia-Granda, S. *Organometallics* **1994**, *13*, 745.

Scheme 6



Scheme 7



Complexes **14** and **15** exhibit three distinct sets of pyrazol-1-yl resonances in a 1:1:1 ratio in the ^{1}H and ^{13}C{^{1}H} NMR spectrum, due to three distinct pyrazol-1-yl rings differing in their trans ligand atoms. In the ^{13}C{^{1}H} NMR spectrum the most noticeable resonance is again the low-field resonance of the carbene carbon atom, observed as a doublet of doublets in the range 288.5−283.7 ppm with P−C coupling constants between 20−23 Hz and 10−11 Hz. Finally, the ^{1}H and ^{13}C{^{1}H} NMR resonances of Tp and the phosphinoamine ligands are in the expected ranges.

The identities of the chemical structures of **14a** and **15b** were unequivocally proven by X-ray crystallography. The result is depicted in Figures 8 and 9, respectively, with important bond distances and angles given in the captions. The coordination geometry around ruthenium is a distorted octahedron. The three Ru−N(Tp) bond lengths show only minor variations and are within the range of those for other RuTp complexes. In **14a** the Ru−C(28) bond distance is 2.007(14) Å, which is comparable to those in other aminocarbene complexes. The Ru−P(1) and Ru−P(2) distances are 2.241(4) and 2.333(4) Å, respectively. Similar bond distances are found for **15b**: Ru−C(40) is 1.993(1) Å, and Ru−P(1) and Ru−P(2) distances are 2.323(1) and 2.253(1) Å, respectively.

Upon treatment of **2a**,**b** with the propargylic alcohol HC≡CPh$_2$OH and AgCF$_3$SO$_3$ in CH$_2$Cl$_2$ for 8 h at room temperature, the allenylidene complexes [RuTp(PPh$_2$NHR)$_2$(=C=C=CPh$_2$)]$^+$ (**16a**,**b**) are obtained in high yields (Scheme 8). These complexes are readily identified by ^{13}C{^{1}H} NMR spectroscopy, exhibiting triplets at 312.9 and 316.9 ppm with P−C coupling constants of 19.1 and 19.9 Hz, respectively, which are assigned to the C$_\alpha$ carbon atom of the allenylidene unit. The C$_\beta$ and C$_\gamma$ carbon atoms give rise to singlets at 199.6 and 206.1 and at 164.1 and 160.9, respectively. While allenylidene **16a** is stable even at elevated temperatures, **16b** slowly rearranges at 50 °C to afford the vinyl azaphosphacarbene complex [RuTp(κ^2(*C*,*P*)=C(CH=CPh$_2$)N(Pr^n)PPh$_2$)-

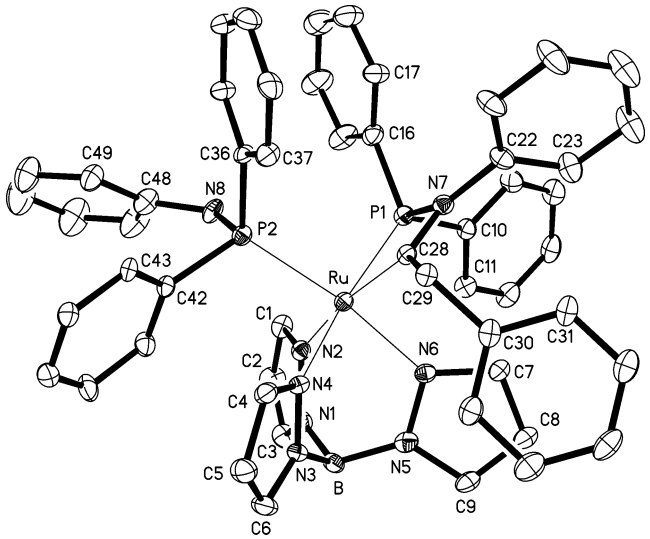
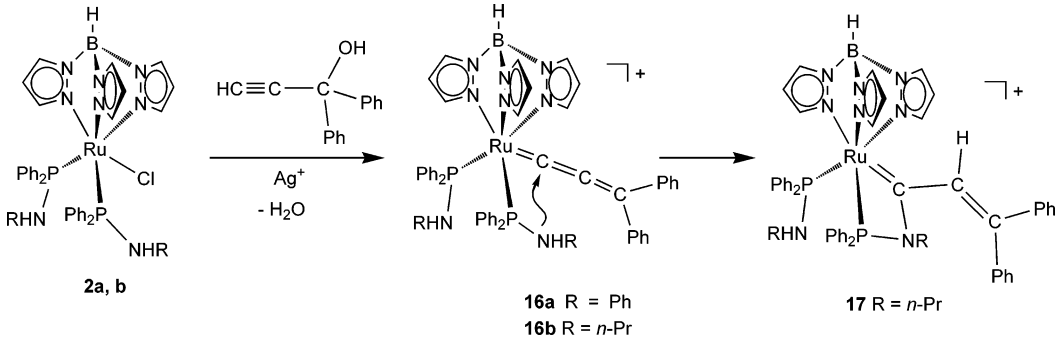


Figure 8. Structural view of [RuTp(κ^2(*C*,*P*)=C(CH$_2$Ph)N(Ph)PPh$_2$)(κ^1(*P*)-PPh$_2$NHPh)]SbF$_6$·2C$_6$H$_5$F (**14a**·2C$_6$H$_5$F) showing 20% thermal ellipsoids (SbF$_6^-$ and C$_6$H$_5$F omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−N(2) = 2.174(7), Ru−N(4) = 2.112(7), Ru−N(6) = 2.121(7), Ru−P(1) = 2.241(4), Ru−P(2) = 2.333(4), Ru−C(28) = 2.007(14), C(28)−N(7) = 1.334(16), P(1)−N(7) = 1.782(12), P(2)−N(8) = 1.675(11); P(1)−Ru−P(2) = 94.7(2), P(1)−Ru−C(28) = 68.7(4), P(2)−Ru−C(28) = 98.2(4).

Scheme 8



($\kappa^1(P)$-PPh_2NHPr^n)]CF_3SO_3 (**17**) in high isolated yield (Scheme 8). The NMR spectroscopic features are similar to those of **5**, **6**, **14**, and **15**. The characteristic resonance of the carbene carbon atom is 274.8 ppm (dd, J_{CP} = 22.2 Hz, J_{CP} = 13.0 Hz). In the ^{1}H NMR spectrum the vinyl C*H*=CPh_2 hydrogen atom gives rise to a doublet at 5.07 ppm (J_{HP} = 7.3 Hz). The solid-state structure of **17** has been confirmed by single-crystal X-ray diffraction (Figure 10). Selected bond distances and angles are reported in the caption. The coordination geometry around ruthenium is distorted octahedral. The Ru−N(Tp) bond distances are all very similar. The bond lengths in the Ru−azaphosphacarbene ring are comparable to those of complexes **14a** and **15b**: e.g. Ru−P(2) = 2.260 Å, Ru−C(40) = 2.012 Å, P(2)−N(8) = 1.766 Å, and N(8)−C(40) = 1.353 Å in **17**. Unlike in **14a** but as in **15b** this ring is not planar in **17**, as the nitrogen N(8) deviates by 0.25 Å from the plane defined by Ru, P(2), and C(40).

Concluding Remarks

In the present study RuCp and RuTp complexes featuring two phosphinoamine ligands of the type PPh_2-NHR with R = Ph, *n*-Pr have been synthesized. We have demonstrated that both the [RuCp($PPh_2NHR)_2$]$^+$ and [RuTp($PPh_2NHR)_2$]$^+$ fragments prepared in situ promote the formation of vinylidene, allenylidene, and oxacyclopentyldiene complexes upon treatment with terminal alkynes. The strong electrophilic character of the α-carbon atom of the vinylidene and allenylidene unit, respectively, is demonstrated by the fact that the weakly nucleophilic nitrogen atom of the bifunctional phosphinoamine reacts readily with the vinylidene and allenylidene moieties in an intramolecular fashion to give novel cyclic azaphosphacarbene complexes. Azaphosphacarbenes belong to a rare series of transition-metal complexes in which the carbene moiety is part of a four-membered chelate ligand coordinated in a κ^2(C,P) mode.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of purified argon by using Schlenk techniques and/or a glovebox. All chemicals were standard

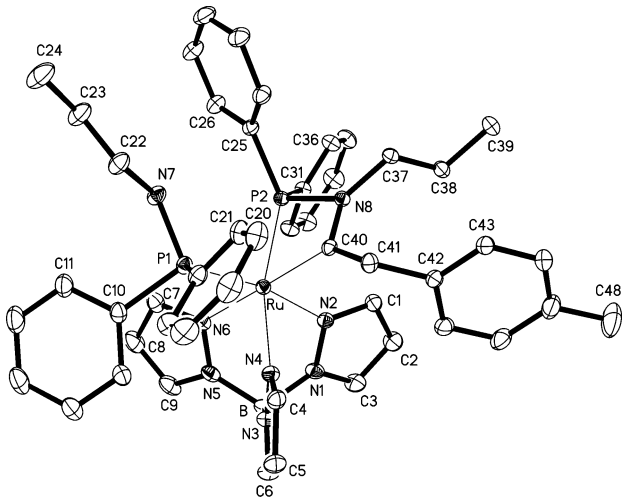


Figure 9. Structural view of [RuTp($\kappa^2(C,P)$=C(CH_2-C_6H_4Me)N(Pr^n)PPh_2)($\kappa^1(P)$-PPh_2NHPr^n)]CF_3SO_3·CH_2Cl_2-(**15b**·CH_2Cl_2) showing 30% thermal ellipsoids ($CF_3SO_3^-$ and CH_2Cl_2 omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−N(2) = 2.166(1), Ru−N(4) = 2.144-(1), Ru−N(6) = 2.168(1), Ru−P(1) = 2.323(1), Ru−P(2) = 2.253(1), Ru−C(40) = 1.993(1), C(40)−N(8) = 1.351(2), P(2)−N(8) = 1.754(1), P(1)−N(7) = 1.670(1); P(1)−Ru−P(2) = 99.18(1), P(1)−Ru−C(40) = 98.67(3), P(2)−Ru−C(40) = 67.46(3), P(1)−N(7)−C(22) = 124.7(1), P(2)−N(8)−C(40) = 98.6(1), P(2)−N(8)−C(37) = 131.4(1).

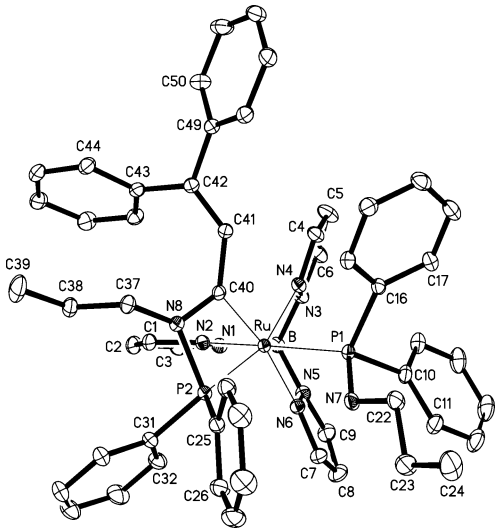


Figure 10. Structural view of [RuTp($\kappa^2(C,P)$=C(CH=CPh_2)N(Pr^n)PPh_2)($\kappa^1(P)$-PPh_2NHPr^n)]CF_3SO_3 (**17**) showing 30% thermal ellipsoids ($CF_3SO_3^-$ omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−N(2) = 2.163(1), Ru−N(4) = 2.129(1), Ru−N(6) = 2.154(1), Ru−P(1) = 2.3354(3), Ru−P(2) = 2.2595(3), Ru−C(40) = 2.012-(1), C(40)−N(8) = 1.353(1), P(2)−N(8) = 1.766(1), P(1)−N(7) = 1.667(1); P(1)−Ru−P(2) = 99.49(1), P(1)−Ru−C(40) = 100.68(3), P(2)−Ru−C(40) = 67.32(3), P(1)−N(7)−C(22) = 124.4(1), P(2)−N(8)−C(40) = 98.4(1), P(2)−N(8)−C(37) = 131.0(1).

reagent grade and used without further purification. The solvents were purified according to standard procedures.[30] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $RuCp(PPh_3)_2Cl$ and RuTp(COD)Cl were prepared according to the literature.[31,32] ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance 250 and 300 spectrometers and were referenced to $SiMe_4$ (^1H and $^{13}C\{^1H\}$) and H_3PO_4 (85%) ($^{31}P\{^1H\}$). ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, 135-DEPT, and HSQC($^1H-^{13}C$) experiments.

$RuCp(PPh_2NHPh)_2Cl$ (1a). A suspension of $RuCp(PPh_3)_2Cl$ (1.5 g, 2.01 mmol) and PPh_2NHPh (4.6 g, 15.5 mmol) in toluene (15 mL) was heated for 12 h at reflux. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 and precipitated with petroleum ether. The product was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield: 1.4 g (88%). Anal. Calcd for $C_{41}H_{37}ClN_2P_2Ru$ (mol wt 756.23): C, 65.12; H, 4.93; N, 3.70. Found: C, 65.09; H, 5.02; N, 4.67. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.56−7.09 (m, 20H, Ph), 6.84 (t, J_{HH} = 8.0 Hz, 4H, NH*Ph*), 6.59 (t, J_{HH} = 7.4 Hz, 2H, NH*Ph*), 6.33 (d, J_{HH} = 7.7 Hz, 4H, NH*Ph*), 6.17 (pt, $^2J_{HP}$ = 6.6 Hz, 2H, N*H*Ph), 4.07 (5H, Cp). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 143.2 (t, J_{CP} = 6.7 Hz, NPh^1), 139.0 (t, $^1J_{CP}$ = 25.0 Hz, Ph^1), 135.5 (t, $^1J_{CP}$ = 25.1 Hz, $Ph^{1\prime}$), 131.6 (t, $^2J_{CP}$ = 5.5 Hz, $Ph^{2,6}$), 131.2 (t, $^2J_{CP}$ = 5.5 Hz, $Ph^{2,6\prime}$), 129.2 (d, $^4J_{CP}$ = 3.7 Hz, $Ph^{4,4\prime}$), 128.3 ($NPh^{3,5}$), 127.8 (t, $^3J_{CP}$ = 5.3 Hz, $Ph^{3,5}$), 127.7 (t, $^3J_{CP}$ = 5.3 Hz, $Ph^{3,5\prime}$), 119.5 (NPh^4), 117.9 (t, J_{CP} = 2.5 Hz, $NPh^{2,6}$), 81.5 (t, J_{CP} = 2.5 Hz, Cp). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 71.9.

$RuCp(PPh_2NHPr^n)_2Cl$ (1b). This complex has been prepared analogously to **2a** with $RuCp(PPh_3)_2Cl$ (300 mg, 0.41 mmol) and PPh_2NHPr^n (603 mg, 2.5 mmol) as the starting materials. Yield: 256 mg (91%). Anal. Calcd for $C_{35}H_{41}ClN_2P_2Ru$ (mol wt 688.19): C, 61.09; H, 6.00; N, 4.07. Found: C, 60.94; H, 6.12; N, 4.00. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.75−7.64 (m, 4H, Ph), 7.38−7.22 (m, 8H, Ph), 7.20 − 7.09 (m, 4H, Ph), 4.07−6.93 (m, 4H, Ph), 4.28−3.29 (m, 2H, N*H*Pr^n), 4.14 (5H, Cp), 2.52−2.36 (m, 2H, Pr^n), 2.33−2.16 (m, 2H, Pr^n), 1.52−1.33 (m, 4H, Pr^n), 0.81 (t, J_{HH} = 7.4 Hz, 6H, Pr^n). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 140.2 (t, $^1J_{CP}$ = 21.0 Hz, Ph^1), 137.8 (t, $^1J_{CP}$ = 28.3 Hz, $Ph^{1\prime}$), 132.6 (t, $^2J_{CP}$ = 5.3 Hz, $Ph^{2,6}$), 130.9 (t, $^2J_{CP}$ = 5.8 Hz, $Ph^{2,6\prime}$), 129.0 (Ph^4), 128.3 ($Ph^{4\prime}$), 127.6 (t, $^3J_{CP}$ = 4.8 Hz, $Ph^{3,5}$), 127.4 (t, $^3J_{CP}$ = 4.8 Hz, $Ph^{3,5\prime}$), 80.7 (t, J_{CP} = 2.5 Hz, Cp), 45.9 (t, $^2J_{CP}$ = 5.8 Hz, CH_2), 24.6 (t, $^3J_{CP}$ = 3.4 Hz, CH_2), 11.7 (CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 84.8.

$RuTp(PPh_2NHPh)_2Cl$ (2a). A suspension of RuTp(COD)Cl (100 mg, 0.22 mmol) and PPh_2NHPh (133.3 mg, 0.480 mmol) in toluene (5 mL) was heated for 3 h at reflux. After removal of the solvent the remaining residue was dissolved in CH_2Cl_2 (2 mL) and the product was precipitated by addition of Et_2O and petroleum ether. The yellow powder was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield: 171 mg (86%). Anal. Calcd for $C_{45}H_{42}BClN_8P_2Ru$ (mol wt 904.16): C, 59.78; H, 4.68; N, 12.39. Found: C, 59.89; H, 4.56; N, 12.44. ^1H NMR (δ, C_6D_6, 20 °C): 8.32 (pt, $^2J_{HP}$ = 7.3 Hz, 2H, N*H*Ph), 7.75−6.71 (36H, Ph, NH*Ph*, Tp), 5.71 (d, J = 1.6 Hz, 1H, Tp), 5.66 (dd, $J_1 = J_2$ = 2.2 Hz, 1H, Tp), 5.60 (dd, $J_1 = J_2$ = 1.9 Hz, 1H, Tp). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 147.7 (Tp), 143.9 (Tp), 142.6 (t, J_{CP} = 5.9 Hz, NPh^1), 136.0 (Tp), 137.3 (t, $^1J_{CP}$ = 21.1 Hz, Ph^1), 134.3 (Tp), 132.9 (t, $^2J_{CP}$ = 5.0 Hz, $Ph^{2,6}$), 132.2 (t, $^2J_{CP}$ = 5.0 Hz, $Ph^{2,6\prime}$), 131.2 (t, $^1J_{CP}$ = 23.2 Hz, $Ph^{1\prime}$), 129.1 (Ph^4), 128.8 ($Ph^{4\prime}$), 128.6 ($NPh^{3,5}$), 127.6 (t, $^3J_{CP}$ = 4.6 Hz, $Ph^{3,5}$), 127.4 (t, $^3J_{CP}$ = 5.3 Hz, $Ph^{3,5\prime}$), 119.9 (NPh^4), 118.5 ($NPh^{2,6}$), 104.8 (Tp), 104.5 (Tp). $^{31}P-\{^1H\}$ NMR (δ, C_6D_6, 20 °C): 76.8.

$RuTp(PPh_2NHPr^n)_2Cl$ (2b). This complex has been prepared analogously to **2a** with RuTp(COD)Cl (150 mg, 0.20 mmol) and PPh_2NHPr^n (642.3 mg, 2.64 mmol) as starting materials. Yield: 664 mg (90%). Anal. Calcd for $C_{39}H_{46}BClN_8P_2Ru$ (mol wt 836.13): C, 56.02; H, 5.55; N, 13.40. Found: C, 56.11; H, 5.67; N, 13.37. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.86−7.02 (m, 23H, Ph, Tp), 6.75 (d, J = 1.9 Hz, 2H, Tp), 5.75 (d, J = 1.9 Hz, 1H, Tp), 5.62 (dd, $J_1 = J_2$ = 2.1 Hz, 2H, Tp), 5.41 (dd, $J_1 = J_2$ = 2.2 Hz, 1H, Tp), 4.47−4.27 (m, 2H, N*H*Pr^n), 2.91−2.74 (m, 2H, Pr^n), 2.70−2.47 (m, 2H, Pr^n), 1.78−1.54 (m, 4H, Pr^n), 0.91 (t, J_{HH} = 7.4 Hz, 6H, Pr^n). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 147.0 (Tp), 143.7 (Tp), 136.3 (t, $^1J_{CP}$ = 18.9 Hz, Ph^1), 135.4 (Tp), 134.9 (t, $^1J_{CP}$ = 13.1 Hz, $Ph^{1\prime}$), 134.2 (Tp), 132.8 (t, $^2J_{CP}$ = 4.6 Hz, $Ph^{2,6}$), 132.5 (t, $^2J_{CP}$ = 4.6 Hz, $Ph^{2\prime,6\prime}$), 128.7 (Ph^4), 128.5 ($Ph^{4\prime}$), 127.4 (t, $^3J_{CP}$ = 4.2 Hz, $Ph^{3,5}$), 127.1 (t, $^3J_{CP}$ = 4.2 Hz, $Ph^{3\prime,5\prime}$), 104.6 (Tp), 104.4 (Tp), 46.8 (t, J_{CP} = 5.4 Hz, CH_2), 25.3 (t, J_{CP} = 3.1 Hz, CH_2), 11.9 (CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 88.3.

$RuCp(PPh_2NHPh)_2(\eta^1\text{-}OSO_2CF_3)$ (3). A solution of **1a** (100 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was treated with $AgCF_3SO_3$ (41 mg, 0.16 mmol) and stirred at room temperature for 2 h. The solution was then evaporated to dryness, and the residue was redissolved in CH_2Cl_2. Insoluble materials were removed by filtration. On addition of Et_2O a yellow precipitate was formed, which was collected on a glass frit, washed with Et_2O, and dried under vacuum. Yield: 82 mg (72%). Anal. Calcd for $C_{42}H_{37}F_3N_2O_3P_2RuS$ (mol wt 869.8): C, 57.99; H, 4.29; N, 3.22. Found: C, 57.80; H, 4.28; N, 3.17. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.40−7.03 (m, 20H, Ph), 6.80 (t, J_{HH} = 7.8 Hz, 4H, NH*Ph*), 6.57 (t, J_{HH} = 7.2 Hz, 2H, NH*Ph*), 6.28 (d, J_{HH} = 7.9 Hz, 4H, NH*Ph*), 5.49 (pt, $^2J_{HP}$ = 8.0 Hz, 2H, N*H*Ph), 4.20 (5H, Cp). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 142.2 (t, J_{CP} = 6.2 Hz, NPh^1), 137.0 (t, $^1J_{CP}$ = 26.0 Hz, Ph^1), 134.3 (t, $^1J_{CP}$ = 24.6 Hz, $Ph^{1\prime}$), 131.3 (t, $^2J_{CP}$ = 5.8 Hz, $Ph^{2,6}$), 131.0 (t, $^2J_{CP}$ = 6.0 Hz, $Ph^{2,6\prime}$), 129.9 (Ph^4), 129.7 ($Ph^{4\prime}$), 128.4 ($NPh^{3,5}$), 128.3 (t, $^3J_{CP}$ = 5.1 Hz, $Ph^{3,5}$), 128.3 (t, $^3J_{CP}$ = 5.3 Hz, $Ph^{3,5\prime}$), 119.8 (NPh^4), 117.9 (t, J_{CP} = 2.8 Hz, $NPh^{2,6}$), 84.0 (Cp). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 77.3.

$[RuCp(\kappa^2(P,P)\text{-}PPh_2NHC_6H_4PPh_2)(NH_2Ph)]SbF_6$ (4). A solution of complex **1a** (100 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was treated with $AgSbF_6$ (54.5 mg, 0.16 mmol) and stirred at room temperature for 2 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of Et_2O a yellow precipitate was formed, which was collected on a glass frit, washed with Et_2O, and dried under vacuum. Yield: 112 mg (90%). Anal. Calcd for $C_{41}H_{37}F_6N_2P_2RuSb$ (mol wt 956.5): C, 51.48; H, 3.90; N, 2.93. Found: C, 51.39; H, 3.99; N, 2.97. ^1H NMR (δ, CD_2Cl_2, 20 °C): 7.93−6.29 (m, 29H, Ph), 5.64 (d, $^2J_{HP}$ = 6.6 Hz, 1H, N*H*), 4.61 (5H, Cp), 3.80 (d, J_{HP} = 11.2 Hz, 1H, N*H*$_2$Ph), 3.11 (d, J_{HP} = 10.7 Hz, 1H, N*H*$_2$Ph). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 148.9 ($NHPh^1$), 146.0 (NH_2Ph^1), 135.7−119.4 (Ph), 82.1 (Cp). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 103.1 (d, J_{PP} = 63.3 Hz), 48.5 (d, J_{PP} = 63.3 Hz).

$[RuCp(\kappa^2(C,P)\text{=}C(CH_2Ph)N(Ph)PPh_2)(\kappa^1(P)\text{-}PPh_2NHPh)]CF_3SO_3$ (5a). A solution of **1a** (100 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) and phenylacetylene (42.8 μL, 0.39 mmol) was treated with $AgCF_3SO_3$ (41 mg, 0.16 mmol) and stirred at room temperature for 12 h. The solution was then evaporated to dryness and the residue redissolved in CH_2Cl_2. Insoluble materials were removed by filtration. On addition of Et_2O and petroleum ether a dark yellow precipitate was formed, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 76 mg (78%). Anal. Calcd for $C_{50}H_{43}F_3N_2O_3P_2RuS$ (mol wt 972.0): C, 61.74; H, 4.46; N, 2.86. Found: C, 61.69; H, 4.50; N, 2.87. ^1H NMR (δ, CD_2Cl_2, 20 °C): 7.85−6.62 (m, 31H, Ph), 6.28 (d, J_{HH} = 7.7 Hz, 2H, NH*Ph*), 6.11 (d, J_{HH} = 7.7 Hz, 2H, NH*Ph*), 5.53 (d, $^2J_{HP}$ = 16.8 Hz, 1H, N*H*Ph), 4.49 (5H, Cp), 4.14 (dd, $J_{1,HH}$ = 14.3 Hz, $J_{2,HP}$ = 4.0 Hz, 1H, C*H*$_2$Ph), 3.82 (dd, $J_{1,HH}$ = 14.3 Hz, $J_{2,HP}$ = 1.2 Hz, 1H, C*H*$_2$-Ph).$^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 276.8 (dd, $J_{1,CP}$ = 32.2

(30) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.
(31) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synthesis* **1990**, *28*, 270.
(32) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998.

Hz, $J_{2,CP}$ = 13.8 Hz, =*C*), 141.8−118.7 (Ph), 86 2 (Cp), 53.3 (d, J_{CP} = 11.5 Hz, CH_2). ^{31}P NMR (δ, CD_2Cl_2, 20 °C): 83.7 (d, J_{PP} = 36.0 Hz), 77.2 (d, J_{PP} = 36.0 Hz).

[RuCp(κ²(*C*,*P*)=C(CH₂C₆H₄CH₃)N(Ph)PPh₂)(κ¹(*P*)-PPh₂NHPh)]CF₃SO₃ (5b). This complex has been prepared analogously to **5a** with **1a** (150 mg, 0.20 mmol), *p*-tolylacetylene (75.4 μL, 0.6 mmol), and $AgCF_3SO_3$ (61 mg, 0.24 mmol) as starting materials. Yield: 119 mg (60%). Anal. Calcd for $C_{51}H_{45}F_3N_8O_3P_2RuS$ (mol wt 986.0): C, 62.13; H, 4.60; N, 2.84. Found: C, 62.24; H, 4.71; N, 2.57. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.98−6.57 (m, 30H, Ph), 6.42 (d, $^2J_{HP}$ = 13.1 Hz, 1H, N*H*Ph), 6.21 (d, J_{HH} = 7.8 Hz, 2H, NH*Ph*), 6.15 (d, J_{HH} = 7.8 Hz, 2H, NH*Ph*), 4.46 (5H, Cp), 4.08 (dd, $J_{1,HH}$ = 14.3 Hz, $J_{2,HP}$ = 3.8 Hz, 1H, C*H*$_2$C$_6$H$_4$CH$_3$), 3.68 (d, J_{HH} = 14.3 Hz, 1H, C*H*$_2$C$_6$H$_4$-CH$_3$), 2.41 (3H, CH$_3$).^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 277.0 (dd, $J_{1,CP}$ = 32.2 Hz, $J_{2,CP}$ = 13.8 Hz, =*C*), 141.5−118.7 (Ph), 86 2 (Cp), 52.8 (d, J_{CP} = 10.7 Hz, CH_2), 20.9 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 83.6 (d, J_{PP} = 35.6 Hz), 77.9 (d, J_{PP} = 35.6 Hz).

[RuCp(κ²(*C*,*P*)=C(CH₂Bu^n)N(Ph)PPh₂)(κ¹(*P*)-PPh₂NHPh)]CF₃SO₃ (5c). This complex has been prepared analogously to **5a** using **1a** (150 mg, 0.20 mmol), 1-hexyne (68.9 μL, 0.6 mmol), and $AgCF_3SO_3$ (61 mg, 0.24 mmol) as starting materials. Yield: 102 mg (54%). Anal. Calcd for $C_{48}H_{47}F_3N_8O_3P_2RuS$ (mol wt 952.0): C, 60.50; H, 4.98; N, 2.94. Found: C, 60.38; H, 4.88; N, 2.85. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.98−6.65 (m, 26H, Ph), 6.23 (d, J_{HH} = 8.0 Hz, 2H, NH*Ph*), 6.13 (d, J_{HH} = 7.8 Hz, 2H, NH*Ph*), 5.46 (d, $^2J_{HP}$ = 16.7 Hz, N*H*Ph), 4.84 (5H, Cp), 2.88−2.53 (m, 2H), 1.94−1.62 (m, 1H), 1.60−1.34 (m, 1H), 1.33−1.06 (m, 5H), 0.95−0.74 (m, 3H).^{13}C-{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 282.3 (dd, $J_{1,CP}$ = 33.0 Hz, $J_{2,CP}$ = 13.8 Hz, =*C*), 141.8−116.2 (Ph), 86.2 (Cp), 48.8 (d, J_{CP} = 10.7 Hz, CH_2), 33.1 (CH_2), 21.8 (CH_2), 18.5 (CH_2), 13.8 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 81.9 (d, J_{PP} = 37.2 Hz), 77.6 (d, J_{PP} = 37.2 Hz).

[RuCp(κ²(*C*,*P*)=C(CH₂Ph)N(Pr^n)PPh₂)(κ¹(*P*)-PPh₂NHPr^n)]CF₃SO₃ (6a). This complex has been prepared analogously to **5a** using **1b** (100 mg, 0.15 mmol), phenylacetylene (32 μL, 0.29 mmol), and $AgCF_3SO_3$ (41.1 mg, 0.16 mmol) as starting materials. Yield: 105 mg (77%). Anal. Calcd for $C_{44}H_{47}F_3N_2P_2O_3RuS$ (mol wt 903.94): C, 58.46; H, 5.24; N, 3.10. Found: C, 58.39; H, 5.32; N, 3.17. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.88−6.82 (m, 25H, Ph), 4.27 (5H, Cp), 3.48−3.24 (m, 1H, C*H*$_2$Ph), 3.48−3.24 (m, 1H, C*H*$_2$Ph), 2.71−2.46 (m, 1H, Pr^n), 2.43−2.2 (m, 1H, Pr^n), 1.95−1.63 (m, 1H, Pr^n), 1.59−1.32 (m, 1H, Pr^n), 1.31−0.93 (m, 4H, Pr^n), 0.81 (t, J_{HH} = 6.7 Hz, 3H, Pr^n), 0.62 (t, J_{HH} = 7.3 Hz, 3H, Pr^n). The NH proton could not be detected. ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 276.8 (dd, J_{CP} = 32.2 Hz, J_{CP} = 14.6 Hz, =*C*), 135.7−127.8 (Ph), 85.0 (Cp), 54.1 (CH_2), 51.5 (CH_2), 46,0 (CH_2), 24.8 (CH_2), 23.1 (CH_2), 11.0 (CH_3), 10.8 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 88.7 (d, J_{PP} = 37.2 Hz), 74.5 (d, J_{PP} = 37.2 Hz).

[RuCp(κ²(*C*,*P*)=C(CH₂C₆H₄CH₃)N(Pr^n)PPh₂)(κ¹(*P*)-PPh₂NHPr^n)]CF₃SO₃ (6b). This complex has been prepared analogously to **5a** with **1b** (100 mg, 0.15 mmol), *p*-tolylacetylene (36.8 μL, 0.29 mmol), and $AgCF_3SO_3$ (41.1 mg, 0.16 mmol) as starting materials. Yield: 103 mg (75%). Anal. Calcd for $C_{45}H_{49}F_3N_2O_2P_2RuS$ (mol wt 917.97): C, 58.88; H, 5.39; N, 3.05. Found: C, 58.89; H, 5.44; N, 3.08. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.97−6.71 (m, 25H, Ph), 4.26 (5H, Cp), 3.84−3.55 (m, 1H, *CH*$_2$C$_6$H$_4$Me), 3.51−3.27 (m, 1H, *CH*$_2$C$_6$H$_4$Me), 2.89−2.69 (m, 1H, Pr^n), 2.67−2.47 (m, 1H, Pr^n), 2.46−2.22 (m, 1H, Pr^n), 2.38 (3H, CH$_3$), 1.87−1.65 (1H, Pr^n), 1.58−1.05 (m, 4H, Pr^n), 0.81 (t, J_{HH} = 7.4 Hz, 3H, Pr^n), 0.60 (t, J_{HH} = 7.3 Hz, 3H, Pr^n). The NH proton could not be detected. ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 275.8 (dd, J_{CP} = 31.4 Hz, J_{CP} = 14.6 Hz, =*C*), 138.1−118.1 (Ph), 84.9 (Cp), 54.0 (d, J_{CP} = 3.2 Hz, CH_2), 51.0 (d, J_{CP} = 12.3 Hz, CH_2), 45.8 (d, J_{CP} = 10.0 Hz, CH_2), 24.3 (d, J_{CP} = 6.9 Hz, CH_2), 23.2 (CH_2), 20.8 (CH_3), 11.0 (CH_3), 10.8 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 88.8 (d, J_{PP} = 37.2 Hz), 74.4 (d, J_{PP} = 37.2 Hz).

[RuCp(κ²(*C*,*P*)=C(CH₂Bu^n)N(Pr^n)PPh₂)(κ¹(*P*)-PPh₂NHPr^n)]CF₃SO₃ (6c). This complex has been prepared analogously to **5a** using **1b** (100 mg, 0.15 mmol), 1-hexyne (50.0 μL, 0.44 mmol), and $AgCF_3SO_3$ (41.1 mg, 0.16 mmol) as starting materials. Yield: 111 mg (84%). Anal. Calcd for $C_{42}H_{51}F_3N_2O_3P_2RuS$ (mol wt 883.95): C, 57.07; H, 5.82; N, 3.17. Found: C, 57.12; H, 5.69; N, 3.22. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.98−6.91 (m, 20H, Ph), 4.72 (5H, Cp), 3.69−3.40 (m, 1H), 3.37−3.13 (m, 1H), 3.09−2.86 (m, 1H), 2.79−2.60 (m, 1H), 2.59−2.35 (m, 2H), 2.33−2.10 (m, 2H), 1.83−1.18 (m, 8H), 0.93 (t, J_{HH} = 7.0 Hz, 3H), 0.80 (t, J_{HH} = 7.3 Hz, 3H), 0.56 (t, J_{HH} = 7.4 Hz, 3H). The NH proton could not be detected. ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 280.5 (dd, J_{CP} = 32.2 Hz, J_{CP} = 14.6 Hz, =*C*), 138.5−118.1 (Ph), 84.9 (Cp), 53.7 (CH_2), 46.4 (d, J_{CP} = 11.5 Hz, CH_2), 45.7 (d, J_{CP} = 10.5 Hz, CH_2), 31.8 (CH_2), 27.8 (CH_2), 24.2 (d, J_{CP} = 6.9 Hz, CH_2), 22.8 (CH_2), 22.3 (CH_2), 13.8 (CH_3), 10.9 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 88.4 (d, J_{PP} = 37.2 Hz), 72.2 (d, J_{PP} = 37.2 Hz).

[CpRu(PPh₂NHPh)₂(=C₄H₆O)]CF₃SO₃ (7a). A solution of **1a** (100 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) and 3-butyn-1-ol (20 μL, 0.45 mmol) was treated with $AgCF_3SO_3$ (37.4 mg, 0.15 mmol) and stirred at room temperature for 12 h. The solution was then evaporated to dryness, and the residue was redissolved in CH_2Cl_2. Insoluble materials were removed by filtration. On addition of Et_2O and petroleum ether a light brown precipitate was formed, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 85 mg (70%). Anal. Calcd for $C_{46}H_{43}F_3N_2O_4P_2RuS$ (mol wt 939.93): C, 58.78; H, 4.61; N, 2.98. Found: C, 58.09; H, 4.73; N, 2.99. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.59−7.27 (m, 20H, Ph), 6.97 (t, J_{HH} = 8.0 Hz, 4H, NH*Ph*), 6.79 (t, J_{HH} = 7.4 Hz, 2H, NH*Ph*), 6.45 (d, J_{HH} = 7.7 Hz, 4H, NH*Ph*), 6.42 (pt, $^2J_{HP}$ = 7.6 Hz, 2H, N*H*Ph), 4.85 (5H, Cp), 4.49 (t, J_{HH} = 7.4 Hz, 2H, CH_2), 3.27 (t, J_{HH} = 7.7 Hz, 2H, CH_2), 1.84 (q, J_{HH} = 7.5 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 298.8 (t, J_{CP} = 13.3 Hz, =*C*), 141.5 (t, J_{CP} = 5.7 Hz, NPh^1), 136.2 (t, $^1J_{CP}$ = 27.5 Hz, Ph^1), 135.7 (t, $^1J_{CP}$ = 29.1 Hz, Ph$^{1'}$), 131.2−128.4 (Ph), 121.2 (NPh^4), 118.5 (t, J_{CP} = 2.8 Hz, NPh^{2,6}), 92.2 (t, J_{CP} = 1.8 Hz, Cp), 82.2 (CH_2), 59.5 (CH_2), 22.4 (CH_2). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 80.3.

[CpRu(PPh₂NHPr^n)₂(=C₄H₆O)]CF₃SO₃ (7b). This complex has been prepared analogously to **7a** using **1b** (100 mg, 0.15 mmol), 3-butyn-1-ol (109.7 μL, 1.45 mmol), and $AgCF_3SO_3$ (41.1 mg, 0.16 mmol) as starting materials. Yield: 88 mg (68%). Anal. Calcd for $C_{40}H_{47}F_3N_2O_4P_2RuS$ (mol wt 871.89): C, 55.10; H, 5.43; N, 3.21. Found: C, 55.06; H, 5.33; N, 3.12. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.98−7.23 (m, 20H, Ph), 4.83 (5H, Cp), 4.51 (t, J_{HH} = 7.4 Hz, 2H), 4.27−4.09 (m, 2H, N*H*Pr^n), 3.75 (t, J_{HH} = 6.0 Hz, 2H), 2.85 (t, J_{HH} = 7.7 Hz, 2H), 2.62−2.33 (m, 5H), 1.74−1.58 (m, 1H), 1.58−1.39 (m, 2H), 0.87 (t, J_{HH} = 7.7 Hz, 6H). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 297.8 (t, J_{CP} = 14.2 Hz, =*C*), 137.8 (t, $^1J_{CP}$ = 28.0 Hz, Ph^1), 136.8 (t, $^1J_{CP}$ = 29.5 Hz, Ph$^{1'}$), 133.9−128.3 (Ph), 91.9 (Cp), 81.6 (CH_2), 58.9 (CH_2), 45.6 (t, J_{CP} = 5.0 Hz, CH_2), 24.6 (t, J_{CP} = 3.5 Hz, CH_2), 22.2 (CH_2), 11.3 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 87.3.

[RuCp(=C(CH₂Ph)NHPh)(PPh₂NHPh)(κ¹(*P*)-PPh₂OH)]CF₃SO₃ (8a). A solution of **1** (150 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) and phenylacetylene (65 μL, 0.6 mmol) was treated with $AgCF_3SO_3$ (56 mg, 0.22 mmol). H_2O (8 μL, 0.4 mmol,) was added, and the reaction mixture was stirred at room temperature for 12 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were removed by filtration. Upon addition of Et_2O and petroleum ether an orange precipitate was formed, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 115 mg (58%). Anal. Calcd for $C_{50}H_{45}F_3N_2O_4P_2RuS$ (mol wt 990.0): C, 60.66; H, 4.58; N, 2.83. Found: C, 60.78; H, 4.50; N, 2.77. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 11.68 (1H, PPh$_2$O*H*), 7.96−6.84 (m, 29H, Ph), 6.82−6.53 (m, 6H, Ph), 6.46 (d, $^2J_{HP}$ = 7.2 Hz, 1H, N*H*Ph), 6.23 (d, $^2J_{HP}$ = 7.5 Hz, 1H, N*H*Ph), 4.46 (5H, Cp), 3.96 (d, J_{HH} = 14.7 Hz, 1H, C*H*$_2$Ph), 3.62 (d, J_{HH} =

14.9 Hz, 1H, CH_2Ph). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 254.3 (t, J_{CP} = 15.7 Hz, =*C*), 142.9−118.6 (Ph), 88.8 (Cp), 54.6 (CH_2). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 141.0 (d, J_{PP} = 47.1 Hz), 80.5 (d, J_{PP} = 47.1 Hz).

[RuCp(=C(CH$_2$Bu^n)NHPh)(PPh$_2$NHPh)(κ^1-(P)-PPh$_2$OH)]CF$_3$SO$_3$ (8b). This complex has been prepared analogously to **8a** using **1** (150 mg, 0.20 mmol), 1-hexyne (68.9 μL, 0.6 mmol), $AgCF_3SO_3$ (61 mg, 0.24 mmol), and H_2O (8 μL, 0.4 mmol,) as starting materials. Yield: 108 mg (56%). Anal. Calcd for $C_{48}H_{49}F_3N_2O_4P_2RuS$ (mol wt 970.0): C, 59.44; H, 5.09; N, 2.89. Found: C, 59.39; H, 5.13; N, 2.67. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 10.75 (1H, PPh$_2$O*H*), 7.99−6.30 (m, 32H, Ph, N*H*Ph), 4.71 (5H, Cp), 2.70−2.41 (m, 2H, CH_2), 1.15−0.57 (m, 9H, Bu^n). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 258.7 (t, J_{CP} = 15.3 Hz, =*C*), 142.6 (d, $^1J_{PC}$ = 51.3 Hz, Ph^1), 142.2 (d, J_{CP} = 12.2 Hz, NPh^1), 140.4 (d, $^1J_{PC}$ = 47.5 Hz, Ph^1), 139.3 (NPh^1), 138.1 (d, $^1J_{PC}$ = 52.9 Hz, Ph^1), 135.9 (d, $^1J_{PC}$ = 55.2 Hz, Ph^1), 132.7−118.5 (Ph), 89.1 (Cp), 51.2 (CH_2), 31.5 (CH_2), 25.6 (CH_2), 21.8 (CH_2), 13.4 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 140.8 (d, J_{PP} = 46.0 Hz), 80.7 (d, J_{PP} = 45.9 Hz).

Attempts to Crystallize 7a. Formation of [RuCp(=C(CH$_2$Bu^n)NHPPh$_2$)(κ^2(*P*,P)-PPh$_2$OPPh$_2$)]CF$_3$SO$_3$ (9). Crystals of **9** were obtained by diffusion of Et_2O into a CH_2Cl_2 solution of **7a**. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.93−7.70 (m, 4H), 7.69−7.37 (m, 16H), 7.28−7.01 (m, 4H), 5.79 (d, J_{HH} = 7.4 Hz, 2H), 5.2 (5H, Cp), 2.71−2.56 (m, 2H, CH_2), 1.35−0.65 (m, 9H, Bu^n). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 254.1 (=*C*), 142.5−124.6 (Ph), 88.8 (Cp), 51.6 (CH_2), 31.5 (CH_2), 25.9 (CH_2), 21.8 (CH_2), 13.3 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 137.7.

[RuCp(=C(CH$_2$Ph)NHPh)(PPh$_2$NHPh)(κ^1(*P*)-PPh$_2$O)] (10a). A solution of **7a** (100 mg, 0.10 mmol) in CH_2Cl_2 was passed through a column charged with neutral Al_2O_3. The yellow product was eluted with acetonitrile, evaporated to dryness and dried under vacuum. Yield: 47 mg (56%). Anal. Calcd for $C_{49}H_{44}N_2OP_2Ru$ (mol wt 839.9): C, 70.07; H, 5.28; N, 3.34. Found: C, 69.89; H, 5.07; N, 3.37. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.90−6.62 (m, 37H, Ph, N*H*Ph), 4.46 (5H, Cp), 3.82 (d, J_{HH} = 15.0 Hz, 1H, CH_2Ph), 3.56 (d, J_{HH} = 15.1 Hz, 1H, CH_2Ph). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 251.4 (dd, $J_{1,CP}$ = 17.6 Hz, $J_{2,CP}$ = 14.6 Hz, =*C*), 149.7 (d, $^1J_{PC}$ = 48.3 Hz, Ph^1), 148.3 (d, $^1J_{PC}$ = 42.9 Hz, Ph^1), 144.0 (d, J_{CP} = 12.3 Hz, NPh^1), 140.3 (d, $^1J_{PC}$ = 42.9 Hz, Ph^1), 138.8 (d, $^1J_{PC}$ = 40.0 Hz, Ph^1), 138.3 (NPh^1), 137.6 (CH$_2$Ph^1), 133.8−118.0 (Ph), 87.7 (Cp), 55.3 (CH_2). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 110.6 (d, J_{PP} = 48.4 Hz), 79.1 (d, J_{PP} = 48.4 Hz).

[RuCp(=C(CH$_2$C$_6$H$_4$Me)NHPh)(PPh$_2$NHPh)(κ^1(*P*)-PPh$_2$O)] (10b). A solution of **5b** (80 mg, 0.08 mmol) in CH_2Cl_2 was passed through a column charged with neutral Al_2O_3. The yellow product was eluted with acetonitrile, evaporated to dryness, and dried in vacuo. Yield: 56 mg (82%). Anal. Calcd for $C_{50}H_{46}N_2OP_2Ru$ (mol wt 853.9): C, 70.33; H, 5.43; N, 3.28. Found: C, 70.39; H, 5.36; N, 3.36. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.88−6.56 (m, 36H, Ph, N*H*Ph), 4.46 (5H, Cp), 3.76 (d, J_{HH} = 14.9 Hz, 1H, CH_2Ph), 3.48 (d, J_{HH} = 15.0 Hz, 1H, CH_2Ph), 2.35 (3H, CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 251.5 (dd, $J_{1,CP}$ = 17.6 Hz, $J_{2,CP}$ = 14.6 Hz, =*C*), 149.8 (d, $^1J_{PC}$ = 47.5 Hz, Ph^1), 148.3 (d, $^1J_{PC}$ = 42.9 Hz, Ph$^{1'}$), 144.0 (d, J_{CP} = 12.3 Hz, NPh^1), 140.2 (d, $^1J_{PC}$ = 42.9 Hz, Ph^1), 138.8 (d, $^1J_{PC}$ = 42.2 Hz, Ph$^{1'}$), 137.6 (NPh$^{1'}$), 135.5 (CH$_2$*C*$_6$H$_4$CH$_3$, Ph), 135.1 (CH$_2$*C*$_6$H$_4$CH$_3$, Ph), 131.6−118.0 (Ph), 87.6 (Cp), 53.8 (CH_2), 20.8 (CH_3). ^{31}P-{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 111.1 (d, J_{PP} = 47.1 Hz), 79.1 (d, J_{PP} = 47.1 Hz).

[CpRu(PPh$_2$NHPh)$_2$(=C=C=CPh$_2$)]CF$_3$SO$_3$ (11). A solution of complex **1** (150 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) and 1,1-diphenylpropyn-1-ol (124 mg, 0.6 mmol) was treated with AgO_3SCF_3 (56 mg, 0.22 mmol) and stirred at room temperature for 8 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of Et_2O a dark red solid was formed, which was washed with Et_2O and dried under vacuum. Yield: 173 mg (82%). Anal. Calcd for $C_{57}H_{47}F_3N_2P_2O_3RuS$ (mol wt 1060.1): C, 64.58; H, 4.47; N, 2.64. Found: C, 64.63; H, 4.50; N, 2.72. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.97−6.96 (m, 30H, Ph), 6.84 (t, J_{HH} = 7.9 Hz, 4H, NH*Ph*), 6.71 (t, J_{HH} = 7.3 Hz, 2H, NH*Ph*), 6.38 (dd, $J_{1,HP}$ = 19.0 Hz, $J_{2,HP}$ = 7.8 Hz, 2H, N*H*Ph), 6.00 (d, J_{HH} = 7.5 Hz, 4H, NH*Ph*), 5.1 (5H, Cp). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 291.9 (=*C*), 201.5 (=C=*C*=CPh$_2$), 161.2 (=C=C=*C*Ph$_2$), 143.6−128.2 (Ph), 120.8 (NPh^4), 118.1 (NPh^{2,6}), 93.0 (Cp). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 74.1.

[RuCp(κ^2(*C*,*P*)=C(CH=CPh$_2$)N(Pr^n)PPh$_2$)(κ^1(*P*)-PPh$_2$NHPr^n)]CF$_3$SO$_3$ (12). A solution of **1b** (100 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) and 1,1-diphenylpropyn-1-ol (91 mg, 0.44 mmol) was treated with $AgCF_3SO_3$ (41.1 mg, 0.16 mmol) and stirred at room temperature for 1 h. The solution was then evaporated to dryness and the residue redissolved in CH_2Cl_2. Insoluble materials were removed by filtration. On addition of Et_2O and petroleum ether a brown precipitate was formed, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 93 mg (63%). Anal. Calcd for $C_{51}H_{51}F_3N_2P_2O_3RuS$ (mol wt 992.05): C, 61.75; H, 5.18; N, 2.82. Found: C, 61.69; H, 5.22; N, 2.77. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.91−6.99 (m, 30H, Ph), 5.08 (1H, −C*H*=CPh$_2$), 4.16 (5H, Cp), 4.02−3.78 (m, 1H, Pr^n), 3.52−3.28 (m, 1H, Pr^n), 2.69−2.42 (m, 1H, Pr^n), 2.40−2.20 (m, 1H, Pr^n), 1.97−1.76 (m, 1H, N*H*Pr^n), 1.51−1.24 (m, 2H, Pr^n), 1.22−1.00 (m, 2H, Pr^n), 0.71 (t, J_{HH} = 7.1 Hz, 3H, Pr^n), 0.59 (t, J_{HH} = 7.3 Hz, 3H, Pr^n). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 275.2 (dd, $J_{1,CP}$ = 31.1 Hz, $J_{2,CP}$ = 15.0 Hz, =*C*), 148.0 (−CH=*C*Ph$_2$), 138.2−125.4 (Ph), 92.7 (−*C*H=CPh$_2$), 85.0 (Cp), 54.7 (d, J_{CP} = 2.3 Hz, CH_2), 45.9 (d, J_{CP} = 10.0 Hz, CH_2), 24.3 (d, J_{CP} = 6.9 Hz, CH_2), 22.8 (CH_2), 11.0 (CH_3), 10.8 (CH_3). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 88.6 (d, J_{PP} = 36.0 Hz), 75.1 (d, J_{PP} = 36.0 Hz).

[RuTp(PPh$_2$NHPh)$_2$(=C=CH(Bu^n))]SbF$_6$ (13). A solution of **2a** (150 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) and 1-hexyne (55 μL, 0.48 mmol) was treated with $AgSbF_6$ (65.2 mg, 0.19 mmol) and stirred at room temperature for 24 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of Et_2O and petroleum ether a dark yellow solid was formed, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 118 mg (62%). Anal. Calcd for $C_{51}H_{52}BF_6N_8P_2RuSb$ (mol wt 1185.6): C, 51.62; H, 4.42; N, 9.44. Found: C, 51.59; H, 4.47; N, 9.47. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 8.04−6.47 (m, 33H, Ph, Tp), 6.27−6.13 (m, 4H, Tp), 5.89−5.78 (m, 2H, Tp), 5.29 (pt, $^2J_{HP}$ = 7.3 Hz, 2H, N*H*Ph), 4.31−4.20 (m, 1H, =C=C*H*Bu^n), 2.22−2.08 (m, 2H, Bu^n), 1.36−1.22 (m, 2H, Bu^n), 1.20−1.01 (m, 2H, Bu^n), 0.66 (t, J_{HH} = 7.1 Hz, 3H, Bu^n). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 369.8 (t, J_{CP} = 17.6 Hz, =*C*=CHBu^n), 144.9 (Tp), 144.4 (Tp), 140.4 (t, J_{CP} = 4.6 Hz, NPh^1), 137.8 (Tp), 136.4 (Tp), 132.9 (Tp), 132.3−128.6 (Ph), 121.9 (NPh^4), 118.6 (NPh^{2,6}), 107.0 (=C=*C*HBu^n), 106.4 (Tp), 105.9 (Tp), 33.1 (CH_2), 21.8 (CH_2), 18.5 (CH_2), 13.8 (CH_3). ^{31}P-{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 67.2.

[RuTp(κ^2(*C*,*P*)=C(CH$_2$Ph)N(Ph)PPh$_2$)(κ^1(*P*)-PPh$_2$NHPh)]SbF$_6$ (14a). A solution of complex **2a** (100 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) and phenylacetylene (36 μL, 0.33 mmol) was treated with $AgSbF_6$ (41.2 mg, 0.12 mmol) and stirred at room temperature for 24 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of Et_2O and petroleum ether a dark yellow solid was formed, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 108 mg (81%). Anal. Calcd for $C_{53}H_{48}BF_6N_8P_2RuSb$ (mol wt 1206.6): C, 52.76; H, 4.01; N, 9.29. Found: C, 52.84; H, 4.00; N, 9.16. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 8.13−6.39 (m, 37H, Ph, Tp), 6.15−5.93 (m, 4H, Ph, Tp), 5.41−5.37 (m, 1H, Tp), 5.27−5.16 (m, 2H, Tp), 5.03 (d, J_{HH} = 11.5 Hz, 1H, CH_2Ph), 4.27 (d, $^2J_{HP}$ = 16.1 Hz, 1H, N*H*Ph), 4.09 (dd, J_{HH} = 11.8 Hz, J_{HP} = 3.5 Hz, 1H, CH_2Ph). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 286.4 (dd, J_{CP} = 20.7 Hz, J_{CP} = 12.3 Hz, =*C*), 145.4 (Tp), 145.2 (Tp), 143.6 (Tp), 141.6 (d, J_{CP} = 10.7 Hz, NPh^1), 140.0 (d, J_{CP} = 4.6 Hz, NPh$^{1'}$), 137.6 (Tp), 135.9 (Tp), 135.7 (Tp), 133.2−126.7 (Ph),

120.9 (NPh^4), 117.5 (d, J_{PC} = 4.6 Hz, $NPh^{2,6}$), 107.0 (Tp), 106.4 (Tp), 104.7 (Tp), 48.5 (d, J_{CP} = 10.0 Hz, CH_2). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 84.2 (d, J_{PP} = 39.7 Hz), 82.2 (d, J_{PP} = 39.7 Hz).

[RuTp(κ^2(*C*,*P*)=C($CH_2C_6H_4Me$)N(Ph)PPh_2)(κ^1(*P*)-PPh_2NHPh)]CF_3SO_3 (14b). This complex has been prepared analogously to **14a** using **2a** (150 mg, 0.16 mmol), *p*-toluene-acetylene (63.2 μL, 0.48 mmol), and AgO_3SCF_3 (56 mg, 0.22 mmol) as starting materials. The solution was stirred at 50 °C for 48 h. Yield: 102 mg (56%). Anal. Calcd for $C_{55}H_{50}BF_3N_8O_3P_2RuS$ (mol wt 1133.9): C, 58.26; H, 4.44; N, 9.88. Found: C, 58.09; H, 4.49; N, 9.92. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.23−6.25 (m, 36H, Ph, Tp), 6.13−5.97 (m, 4H, Ph, Tp), 5.44−5.37 (m, 1H, Tp), 5.17−5.07 (m, 2H, Tp), 4.96 (d, J_{HH} = 11.5 Hz, 1H, CH_2C$_6$H$_4$CH$_3$), 4.27 (d, $^2J_{HP}$ = 15.9 Hz, 1H, N*H*Ph), 4.07 (dd, $J_{1,HH}$ = 11.3 Hz, $J_{2,HP}$ = 3.7 Hz, 1H, CH_2Ph), 1.99 (3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 286.5 (dd, $J_{1,CP}$ = 20.7 Hz, $J_{2,CP}$ = 11.5 Hz, =*C*), 145.5 (Tp), 145.3 (Tp), 143.8 (Tp), 141.7 (d, J_{CP} = 10.7 Hz, NPh^1), 140.0 (d, J_{CP} = 4.6 Hz, $NPh^{1'}$), 137.6 (Tp), 135.9 (Tp), 135.7 (Tp), 133.3−125.4 (Ph), 120.9 (NPh^4), 117.6 ($NPh^{2,6}$), 107.0 (Tp), 106.4 (Tp), 104.5 (Tp), 48.2 (d, J_{CP} = 10.0 Hz, CH_2), 20.5 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 83.9 (d, J_{PP} = 39.7 Hz), 82.4 (d, J_{PP} = 39.7 Hz).

[RuTp(κ^2(*C*,*P*)=C(CH_2Ph)N(Pr^n)PPh_2)(κ^1(*P*)-PPh_2NHPr^n)]CF_3SO_3 (15a). A solution of complex **2b** (100 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) and phenylacetylene (39 μL, 0.36 mmol) was treated with $AgSbF_6$ (34 mg, 0.13 mmol) and stirred at room temperature for 4 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of Et_2O and petroleum ether a yellow solid was formed, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 103 mg (82%). Anal. Calcd. for $C_{48}H_{52}BF_3N_8O_3P_2RuS$ (mol wt 1051.87): C, 54.81; H, 4.98; N, 10.65. Found: C, 54.84; H, 5.09; N, 10.58. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.21−6.15 (m, 33H, Ph, Tp), 6.00−5.84 (m, 1H, Tp), 5.76−5.61 (m, 1H, Tp), 4.98 (d, J_{HH} = 13.6 Hz, 1H, CH_2Ph), 4.12−3.56 (m, 2H, Pr^n), 3.82 (d, J_{HH} = 13.6 Hz, 1H, CH_2Ph), 2.26−1.87 (m, 2H, Pr^n), 1.46−1.10 (m, 4H, Pr^n), 0.90 (t, J_{HH} = 7.6 Hz, 3H, Pr^n), 0.56 (t, J_{HH} = 7.6 Hz, 3H, Pr^n). The NH proton could not be detected. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 283.7 (dd, $J_{1,CP}$ = 23.0 Hz, $J_{2,CP}$ = 11.5 Hz, =*C*), 146.1 (Tp), 144.9 (d, J_{CP} = 3.1 Hz, Tp), 142.7 (Tp), 136.9 (Tp), 136.5 (Tp), 136.0 (Tp), 135.9−127.0 (Ph), 106.3 (Tp), 106.2 (Tp), 104.5 (Tp), 54.8 (d, J_{CP} = 2.3 Hz, CH_2), 48.9 (d, J_{CP} = 10.7 Hz, CH_2), 46.4 (d, J_{CP} = 10.0 Hz, CH_2), 24.6 (d, J_{CP} = 5.4 Hz, CH_2), 22.7 (CH_2), 11.0 (CH_3), 10.3 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 86.7 (d, J_{PP} = 38.5 Hz), 78.6 (d, J_{PP} = 38.5 Hz).

[RuTp(κ^2(*C*,*P*)=C($CH_2C_6H_4Me$)N(Pr^n)PPh_2)(κ^1(*P*)-PPh_2NHPr^n)]CF_3SO_3 (15b). This complex has been prepared analogously to **15a** using **2b** (100 mg, 0.12 mmol), *p*-toluene-acetylene (30.2 μL, 0.24 mmol), and AgO_3SCF_3 (34 mg, 0.13 mmol) as starting materials. Yield: 116 mg (91%). Anal. Calcd for $C_{49}H_{54}BF_3N_8O_3P_2RuS$ (mol wt 1065.90): C, 55.22; H, 5.11; N, 10.51. Found: C, 55.19; H, 5.19; N, 10.63. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.08−6.06 (m, 32H, Ph, Tp), 5.94−5.84 (m, 1H, Tp), 5.78−5.67 (m, 1H, Tp), 4.90 (d, J_{HH} = 13.9 Hz, 1H, CH_2-Ph), 4.08−3.57 (m, 2H, Pr^n), 3.79 (dd, $J_{1,HH}$ = 14.1 Hz, $J_{2,HP}$ = 2.1 Hz, 1H, CH_2Ph), 2.54−1.87 (m, 2H, Pr^n), 2.11 (3H, CH_3), 1.50−1.21 (m, 2H, Pr^n), 1.08−0.87 (m, 2H, Pr^n), 0.67 (t, J_{HH} = 6.5 Hz, 3H, Pr^n), 0.55 (t, J_{HH} = 7.3 Hz, 3H, Pr^n). The NH proton could not be detected. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 284.0 (dd, J_{CP} = 22.6 Hz, J_{CP} = 11.1 Hz, =*C*), 146.1 (Tp), 145.0 (d, J_{CP} = 3.1 Hz, Tp), 142.8 (Tp), 137.0 (Tp), 136.4 (d, J_{CP} = 51.4 Hz), 136.4 (Tp), 135.9 (Tp), 135.3−127.6 (Ph), 106.3 (Tp), 106.1 (d, J_{CP} = 3.1 Hz, Tp), 104.5 (Tp), 54.7 (d, J_{CP} = 3.1 Hz, CH_2), 48.6 (d, J_{CP} = 10.7 Hz, CH_2), 46.4 (d, J_{CP} = 10.0 Hz, CH_2), 24.5 (d, J_{CP} = 6.1 Hz, CH_2), 22.7 (CH_2), 20.5 (CH_3), 11.0 (CH_3), 10.3 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 87.0 (d, J_{PP} = 38.5 Hz), 78.4 (d, J_{PP} = 38.5 Hz).

[RuTp(κ^2(*C*,*P*)=C(CH_2Bu^n)N(Pr^n)PPh_2)(κ^1(*P*)-PPh_2NHPr^n)]CF_3SO_3 (15c). This complex has been prepared analogously to **15a** using **2b** (100 mg, 0.12 mmol), 1-hexyne (0.24 mmol, 27.3 μL), and AgO_3SCF_3 (34 mg, 0.13 mmol) as starting materials. Yield: 103 mg (83%). Anal. Calcd for $C_{46}H_{56}BF_3N_8O_3P_2RuS$ (mol wt 1031.88): C, 53.54; H, 5.47; N, 10.86. Found: C, 53.49; H, 5.49; N, 10.90. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.05−6.22 (m, 29H, Ph, Tp), 5.99−5.76 (m, 2H, Tp), 4.07−3.62 (m, 2H, CH_2), 3.15−2.94 (m, 1H), 2.89−2.68 (m, 1H), 2.23−1.90 (m, 2H), 1.81−1.53 (m, 3H), 1.01−0.79 (m, 10H), 0.61−0.48 (m, 6H). The NH proton could not be detected. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 286.2 (dd, $J_{1,CP}$ = 22.2 Hz, $J_{2,CP}$ = 10.7 Hz, =*C*), 146.1 (Tp), 144.5 (d, J_{CP} = 3.8 Hz, Tp), 142.6 (Tp), 136.9 (Tp), 136.3 (d, J_{CP} = 2.3 Hz, Tp), 135.7 (Tp), 135.6−127.6 (Ph), 106.2 (Tp), 105.8 (d, J_{CP} = 2.3 Hz, Tp), 104.1 (Tp), 53.5 (d, J_{CP} = 3.1 Hz, CH_2), 46.4 (d, J_{CP} = 10.0 Hz, CH_2), 43.6 (d, J_{CP} = 10.7 Hz, CH_2), 31.9 (CH_2), 25.0 (CH_2), 24.5 (d, J_{CP} = 6.1 Hz, CH_2), 24.2 (CH_2), 21.7 (CH_2), 13.1 (CH_3), 11.0 (CH_3), 10.9 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 87.7 (d, J_{PP} = 38.5 Hz), 78.1 (d, J_{PP} = 38.5 Hz).

[RuTp(PPh_2NHPh)$_2$(=C=C=CPh_2)]CF_3SO_3 (16a). A solution of complex **2a** (150 mg, 0.17 mmol) and 1,1-diphenyl-propyn-1-ol (104 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was treated with AgO_3SCF_3 (47 mg, 0.18 mmol) and stirred at room temperature for 8 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of Et_2O and petroleum ether a dark purple solid was obtained, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 138 mg (69%). Anal. Calcd for $C_{61}H_{52}BF_3N_8P_2O_3RuS$ (mol wt 1208.0): C, 60.65; H, 4.34; N, 8.28. Found: C, 60.77; H, 4.41; N, 8.15. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.10−6.72 (m, 41H, Ph, Tp), 6.29−6.14 (m, 6H, Ph, Tp), 5.72−5.64 (m, 2H, Tp), 5.51 (pt, $^2J_{HP}$ = 7.9 Hz, 2H, N*H*Ph). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 312.9 (t, J_{CP} = 19.1 Hz, =*C*=C=CPh_2), 199.6 (=C=*C*=CPh_2), 164.1 (=C=C=*C*Ph_2), 145 4 (Tp), 144.0 (Tp), 143.4 (Ph^1), 140.9 (t, J_{CP} = 5.0 Hz, NPh^1), 137.6 (Tp), 136.0 (Tp), 133.1 (Tp), 132.3−127.8 (Ph), 121.5 (NPh^4), 118.2 ($NPh^{2,6}$), 106.5 (Tp), 105.4 (Tp). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 71.5.

[RuTp(PPh_2NHPr^n)$_2$(=C=C=CPh_2)]CF_3SO_3 (16b). A solution of complex **2b** (100 mg, 0.12 mmol) and 1,1-diphenyl-propyn-1-ol (50 mg, 0.24 mmol) in CH_2Cl_2 (5 mL) was treated with AgO_3SCF_3 (34 mg, 0.13 mmol) and stirred at room temperature for 1 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2. Insoluble materials were filtered off. On addition of Et_2O and petroleum ether a dark purple solid was obtained, which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 114 mg (83%). Anal. Calcd for $C_{55}H_{56}BF_3N_8P_2O_3RuS$ (mol wt 1139.98): C, 57.95; H, 4.95; N, 9.83. Found: C, 58.08; H, 4.99; N, 9.91. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.13−6.93 (m, 33H, Ph, Tp), 6.65−6.46 (m, 4H, Ph, Tp), 6.43−6.32 (m, 2H, Tp), 5.77−5.68 (m, 1H, Tp), 2.85−2.25 (m, 4H, Pr^n), 1.71−1.44 (m, 4H, Pr^n), 0.91 (t, J_{HH} = 7.3 Hz, 6H, Pr^n). The NH proton could not be detected. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 316.9 (t, J_{CP} = 19.9 Hz, =*C*=C=CPh_2), 206.1 (=C=*C*=CPh_2), 160.9 (=C=C=*C*Ph_2), 146.9−127.6 (Tp, Ph), 106.6 (Tp), 106.1 (Tp), 105.3 (Tp), 46.8 (t, J_{CP} = 4.6 Hz, CH_2), 25.9 (t, J_{CP} = 3.5 Hz, CH_2), 11.5 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 78.8.

[RuTp(κ^2(*C*,*P*)=C(CH=CPh_2)N(Pr^n)PPh_2)(κ^1(*P*)-PPh_2NHPr^n)]CF_3SO_3 (17). A solution of complex **16b** (100 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) was heated at 50 °C for 8 h. The solution was reduced to about 1 mL. On addition of Et_2O and petroleum ether a red solid was obtained which was washed with Et_2O and petroleum ether and dried under vacuum. Yield: 83 mg (81%). Anal. Calcd. for $C_{55}H_{56}BF_3N_8P_2O_3RuS$ (mol wt 1139.98): C, 60.65; H, 4.34; N, 8.28. Found: C, 60.59; H, 4.38; N, 8.16. ^1H NMR (δ, CD_2Cl_2, 20 °C): 8.15−6.69 (m, 33H, Ph, Tp), 6.64−6.47 (m, 2H, Ph, Tp), 6.44−6.23 (m, 4H, Ph, Tp), 5.88−5.81 (m, 1H, Tp), 5.07 (d, J_{HP} = 7.3 Hz, 1H, CH), 3.70−3.46 (m, 1H), 3.25−2.97 (m, 1H), 2.63−2.28 (m,

Table 1. Details for the Crystal Structure Determinations of Complexes 1a, 2a·$CHCl_3$, 3, 4·solv, and 9

	1a	**2a**·$CHCl_3$	**3**	**4**·solv	**9**
formula	$C_{41}H_{37}ClN_2P_2Ru$	$C_{46}H_{43}BCl_4N_8P_2Ru$	$C_{42}H_{37}F_3N_2O_3P_2RuS$	$C_{41}H_{37}F_6N_2P_2RuSb$	$C_{42}H_{42}F_3NO_4P_2RuS$
fw	756.19	1023.50	869.81	956.49	876.84
cryst size, mm	0.62 × 0.54 × 0.40	0.60 × 0.36 × 0.20	0.6 × 0.4 × 0.3	0.70 × 0.25 × 0.20	0.75 × 0.42 × 0.22
space group (No.)	$P2_1$ (4)	$P2_1/n$ (14)	Pn (7)	$P2_1/n$ (14)	$P\bar{1}$ (2)
a, Å	10.0363(6)	11.005(2)	9.9429(12)	11.142(2)	11.6571(7)
b, Å	18.0314(11)	21.850(3)	21.374(3)	15.037(3)	12.9967(8)
c, Å	10.3864(6)	20.272(3)	18.606(2)	24.940(4)	15.1889(9)
α, deg	90	90	90	90	77.718(1)
β, deg	113.968(1)	103.544(2)	98.610(2)	100.654(3)	68.636(1)
γ, deg	90	90	90	90	71.892(1)
V, Å^3	1717.5(2)	4738.7(12)	3909.6(8)	4106.5(12)	2024.0(2)
Z	2	4	4	4	2
ρ_{calcd}, g cm^{-3}	1.462	1.435	1.478	1.547	1.439
T, K	100(2)	123(2)	297(2)	173(2)	300(2)
μ(Mo Kα), mm^{-1}	0.660	0.666	0.592	1.161	0.574
F(000)	776	2088	1776	1904	900
θ_{max}, deg	30	30	30	25	30
no. of rflns measd	32 068	67 859	29 072	27 305	28 295
no. of unique rflns	9955	13 633	19 397	6922	11 591
no. of rflns $I > 2\sigma(I)$	9932	11 898	15 960	5232	9669
no. of params	430	598	987	508	629
R1 ($I > 2\sigma(I)$)[a]	0.0167	0.0291	0.0315	0.0468	0.0344
R1 (all data)	0.0168	0.0360	0.0450	0.0735	0.0444
wR2 (all data)[a]	0.0443	0.0738	0.0745	0.1076	0.0912
diff Fourier peaks min/max, e Å^{-3}	−0.26/0.40	−0.50/0.76	−0.42/0.35	−0.70/1.47	−0.74/0.77

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table 2. Details for the Crystal Structure Determinations of Complexes 10a, 11·CH_2Cl_2, 14a·2C_6H_5F, 15b·CH_2Cl_2, and 17

	10a	**11**·CH_2Cl_2	**14a**·2C_6H_5F	**15b**·CH_2Cl_2	**17**
formula	$C_{49}H_{44}N_2OP_2Ru$	$C_{58}H_{49}Cl_2F_3N_2O_3P_2RuS$	$C_{65}H_{58}BF_8N_8P_2RuSb$	$C_{50}H_{56}BCl_2F_3N_8O_3P_2RuS$	$C_{55}H_{56}BF_3N_8O_3P_2RuS$
fw	839.87	1144.96	1398.76	1150.81	1139.96
cryst size, mm	0.2 × 0.1 × 0.1	0.53 × 0.36 × 0.22	0.12 × 0.04 × 0.02	0.70 × 0.50 × 0.32	0.68 × 0.33 × 0.19
space group (No.)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a, Å	19.82(4)	13.280(2)	11.403(2)	12.8141(5)	12.3228(5)
b, Å	8.626(15)	12.787(2)	17.341(4)	13.9087(6)	13.8390(5)
c, Å	23.59(4)	31.996(5)	31.492(7)	18.1289(7)	17.7616(7)
α, deg	90	90	90	86.685(1)	79.910(1)
β, deg	100.61(5)	100.455(3)	96.726(7)	69.964(1)	83.886(1)
γ, deg	90	90	90	62.774(1)	63.820(1)
V, Å^3	3964(13)	5343.1(14)	6184(2)	2680.2(2)	2674.7(2)
Z	4	4	4	2	2
ρ_{calcd}, g cm^{-3}	1.407	1.423	1.502	1.426	1.415
T, K	300(2)	173(2)	300(2)	173(2)	173(2)
μ(Mo Kα), mm^{-1}	0.517	0.549	0.805	0.550	0.454
F(000)	1736	2344	2824	1184	1176
θ_{max}, deg	25	25	23.1	30	30
no. of rflns measd	9230	30 407	28 346	50 111	50 109
no. of unique rflns	6115	9336	8639	15 449	15 487
no. of rflns $I > 2\sigma(I)$	2442	5480	3246	14 225	14 512
no. of params	410	583	555	676	717
R1 ($I > 2\sigma(I)$) [a]	0.0905	0.0641	0.0874	0.0272	0.0249
R1 (all data)	0.2121	0.1245	0.2321	0.0303	0.0268
wR2 (all data)[a]	0.2007	0.1834	0.2634	0.0743	0.0667
diff Fourier peaks min/max, e Å^{-3}	−0.62/0.85	−0.78/1.11	−0.53/0.77	−0.66/0.53	−0.32/0.46

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

2H), 2.27−2.09 (m, 1H), 2.03−1.84 (m, 1H), 1.67−1.39 (m, 2H), 0.88−0.75 (m, 3H), 0.64−0.44 (m, 3H). The NH proton could not be detected. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 274.8 (dd, J_{CP} = 22.2 Hz, J_{CP} = 13.0 Hz, =*C*), 152.5 (−CH=*C*Ph_2), 146.3−129.9 (Tp, Ph), 129.7 (−*C*H=*C*Ph_2), 129.6−127.0 (Ph), 106.7 (Tp), 106.0 (Tp), 105.1 (Tp), 56.9 (d, J_{CP} = 2.3 Hz, CH_2), 46.0 (d, J_{CP} = 10.0 Hz, CH_2), 24.5 (d, J_{CP} = 6.1 Hz, CH_2), 22.2 (CH_2), 11.0 (CH_3), 10.9 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 83.4 (d, J_{PP} = 39.7 Hz), 80.2 (d, J_{PP} = 39.7 Hz).

X-ray Structure Determination. Crystals of **1a**, **2a**·$CHCl_3$, **3**, **4**·solv, **9**, **10a**, **11**·CH_2Cl_2, **14a**·2C_6H_5F, **15b**·CH_2Cl_2, and **17** were obtained by diffusion of Et_2O or pentane (**4**·solv, **15b**·CH_2Cl_2, **17**) into CH_2Cl_2 or $CHCl_3$ (**2a**·$CHCl_3$) solutions. Compound **9** cocrystallized with **10a** from CH_2Cl_2/Et_2O. In the case of complex **14a** this method gave only very unstable solvates, which were not measurable at all. Finally, evaporation crystallization from fluorobenzene was successful and yielded well-developed stable crystals of a corresponding solvate with the disadvantage of a very small size. Crystal data and experimental details are given in Tables 1 and 2. X-ray data were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and 0.3° ω-scan frames covering either hemispheres or complete spheres of the reciprocal space, except for **9**, where a quarter-sphere was measured. Corrections for absorption (multiscan method), $\lambda/2$ effects, and crystal

decay were applied.[33] The structures were solved by direct methods using the program SHELXS97.[34] Structure refinement on F^2 was carried out with the program SHELXL97.[33] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded, except for N-bound hydrogen atoms, which were refined in *x*, *y*, *z* if permitted by data quality.[35]

Computational Details. All calculations were performed using the Gaussian98 software package.[36] The geometries of the model complexes and the transition states were optimized at the B3LYP level[37] with the Stuttgart/Dresden ECP (SDD) basis set.[38] For all other atoms the 6-31G(d,p) basis set was employed.[39] A vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequency. The geometries were optimized without symmetry constraints.

Acknowledgment. Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" is gratefully acknowledged (Project No. P16600-N11).

Supporting Information Available: Complete crystallographic data and technical details in CIF format for **1a**, **2a**·$CHCl_3$, **3**, **4**·solv, **9**, **10a**, **11**·CH_2Cl_2, **14a**·$2C_6H_5F$, **15b**·CH_2Cl_2, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050247A

(33) Bruker programs: SMART, version 5.054; SAINT, version 6.2.9; SADABS, version 2.03; XPREP, version 5.1; SHELXTL, version 5.1 (Bruker AXS Inc., Madison, WI, 2001).

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