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Reactions of Ruthenium–Aminophosphane Complexes with Diynes: P–N Bond Activation and Formation of Novel Phosphaallyl, Azaallyl, and Aminocarbene Complexes

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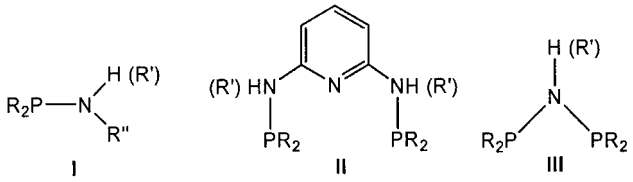
The aminophosphane complexes $[RuCp(PPh_2NRR'_2)(CH_3CN)_2]^+$ and $[RuCp^*(PPh_2NRR'_2)(CH_3CN)_2]^+$ (NRR′ = NH*n*Pr, NEt_2, NC_5H_5) react with 1,6-heptadiyne and 1,7-octadiyne to yield novel η^3-phosphaallyl–η^2-vinylamine complexes of the types $[RuCp\{\eta^3\text{-}(P,C,C)\text{-}PPh_2CH{=}C{-}(CH_2)_n{-}\eta^2\text{-}(C,C){-}C{=}CHNRR'_2\}]^+$ and $[RuCp^*\{\eta^3\text{-}(P,C,C)\text{-}PPh_2CH{=}C{-}(CH_2)_n{-}\eta^2\text{-}(C,C)\text{-}C{=}CHNRR'_2\}]^+$ (n = 3, 4). These complexes are the kinetic products but eventually form the η^1-phosphaallyl–η^3-azaallyl complexes $[RuCp\{\eta^1\text{-}(P)\text{-}PPh_2CH{=}C{-}(CH_2)_n{-}\eta^3\text{-}(C,C,N)\text{-}CCHNRR'_2\}]^+$ and $[RuCp^*\{\eta^1\text{-}(P)\text{-}PPh_2CH{=}C{-}(CH_2)_n{-}\eta^3\text{-}(C,C,N)\text{-}CCHNRR'_2\}]^+$, respectively. With n = 3 elevated temperatures are required, while with n = 4 this conversion takes places already at room temperature. The only exception is $[RuCp^*(PPh_2NH{n}Pr)(CH_3CN)_2]^+$ where amido butadiene complexes $[RuCp^*\{\eta^1\text{-}(N)\text{-}N{n}PrPPh_2\text{-}\eta^4\text{-}CH{=}C(CH_2)_nCH{=}CH_2\}]PF_6$ (n = 3, 4) are obtained instead. In the case of $[RuCp\{\eta^1\text{-}(P)\text{-}PPh_2CH{=}C{-}(CH_2)_3{-}\eta^3\text{-}(C,C,N)\text{-}CCHNRR'_2\}]^+$ with NRR′ = NEt_2 and NC_5H_5, a further rearrangement took place at elevated temperatures affording the aminocarbenes $[RuCp\{{=}C(NRR')\text{-}\eta^2\text{-}(C,C)\text{-}C(CH_2)_3C{-}CH_2{-}(\eta^1\text{-}(P)\text{-}PPh_2)\}]^+$. Representative X-ray structures are presented. Moreover, conceivable mechanisms for all these reaction sequences are established by means of DFT/B3LYP calculations.

Introduction

Aminophosphanes that contain one or more direct P^{III}–N bonds have received considerable attention in recent years as ligands for transition metals.[1] They are accessible in large quantities through the use of relatively simple condensation processes from inexpensive starting materials, that is, primary or secondary amines and PR_2Cl compounds which contain dialkyl or diaryl substituents as well as achiral and chiral P–O- and P–N-containing phosphane units. Accordingly, variations of electronic, steric, and stereochemical parameters may be achieved in a very facile fashion. The most common structural types of such ligands contain either one P–N unit (e.g. **I**),[2] two or more P–N units which are not directly bound (e.g. **II**),[3,4] or a P–N–P framework (e.g. **III**).[5,6] It should be noted that in some cases P^{III}–N bonds were found to be sensitive towards acid- or base-catalyzed hydrolysis during complexation reactions.[7] However, by choosing appropriate substituents on both phosphorus and nitrogen centers, P–N bond cleavage can be avoided.



I II III

We have recently started to investigate the chemistry of RuCp, RuCp*, and RuTp complexes that contain one or two aminophosphane ligands of the most simple PR_2NHR' type, **I**. In these compounds coordination takes place exclusively through the phosphorus donor leaving the N-site available for further reactions. We have shown, for instance, that in the vinylidene and allenylidene complexes $[RuCp(PPh_2NHR)_2\{{=}C{=}(C)_n{=}CHR'\}]^+$ and $[RuTp(PPh_2NHR)_2\{{=}C{=}(C)_n{=}CHR'\}]^+$ (n = 0, 1; R = Ph, *n*Pr; R′ = alkyl, aryl) an intramolecular addition of the NHR′ moiety to the α-carbon of the cumulene moiety takes place, resulting in the formation of novel four-membered aza-phospha-carbenes.[8] Complexes of the types $[RuCp(PPh_2NHPh)(CH_3CN)_2]^+$ and $[RuCp^*(PR_2NHR')(CH_3CN)_2]^+$ (R = Ph, *i*Pr, R′ = Ph, C_6F_5) have been found to react with terminal alkynes and diynes to give amido butadiene complexes.[9,10] In all these reactions, the N–H bond but not the P–N bond is cleaved unless larger amounts of water are present. Recently, when we switched over to a complex where the aminophosphane lacks a N–H bond viz. [RuCp-

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$(PPh_2NEt_2)(CH_3CN)_2]^+$, we discovered that it reacts with diynes to afford unusual and unprecedented phosphaallyl complexes which readily rearrange to give azaallyl complexes.[11] This process formally constitutes an insertion of an unsaturated carbon C4 chain into the P–N bond, that is, in the course of this reaction the P–N bond is cleaved. The present work is intended to investigate in detail the formation of phosphaallyl complexes and their conversion to azaallyl complexes and we report here the reaction of $[RuCp(PPh_2NRR')(CH_3CN)_2]PF_6$ and $[RuCp^*(PPh_2NRR')(CH_3CN)_2]PF_6$ (NRR′ = NH*n*Pr, NEt_2, NC_5H_{10}) with diynes. The mechanistic considerations will be supported by DFT/B3LYP calculations.

Results and Discussion

Starting Materials

The starting complexes **1a**–**c** were obtained in highly isolated yields by reacting $[RuCp(CH_3CN)_3]PF_6$ with 1 equiv. of the respective aminophosphane PPh_2NRR' (NRR′ = NH*n*Pr, NEt_2, NC_5H_{10}) at room temperature. The analogous RuCp* complexes were obtained in a similar fashion by reacting $[RuCp^*(CH_3CN)_3]PF_6$ with PPh_2NRR' affording complexes **2a**–**c**. All these complexes are stable to air in the solid state but decompose slowly in solutions on exposure to air. Complexes **1a**–**c** and **2a**–**c** exhibit a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum in the range of 83–102 ppm. Structural views of **1a** and **2c** are shown in Figure 1 and Figure 2 with selected bond lengths given in the captions.

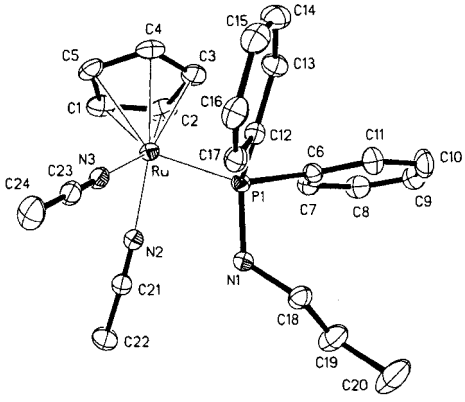


Figure 1. Structural view of $[RuCp(PPh_2NH{\it n}Pr)(CH_3CN)_2]PF_6$ (**1a**) showing 50% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: Ru–C(1–5)$_{av}$ 2.187(2), Ru–N(2) 2.064(2), Ru–N(3) 2.064(2), Ru–P(1) 2.2823(5), P(1)–N(1) 1.657(2).

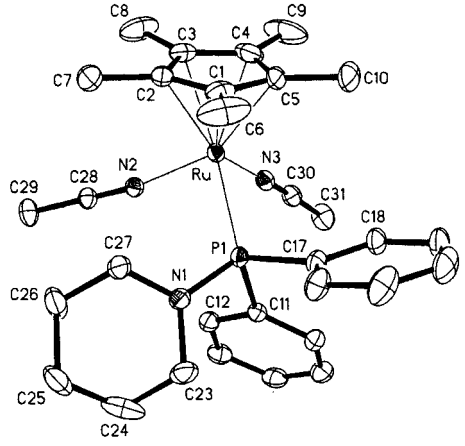
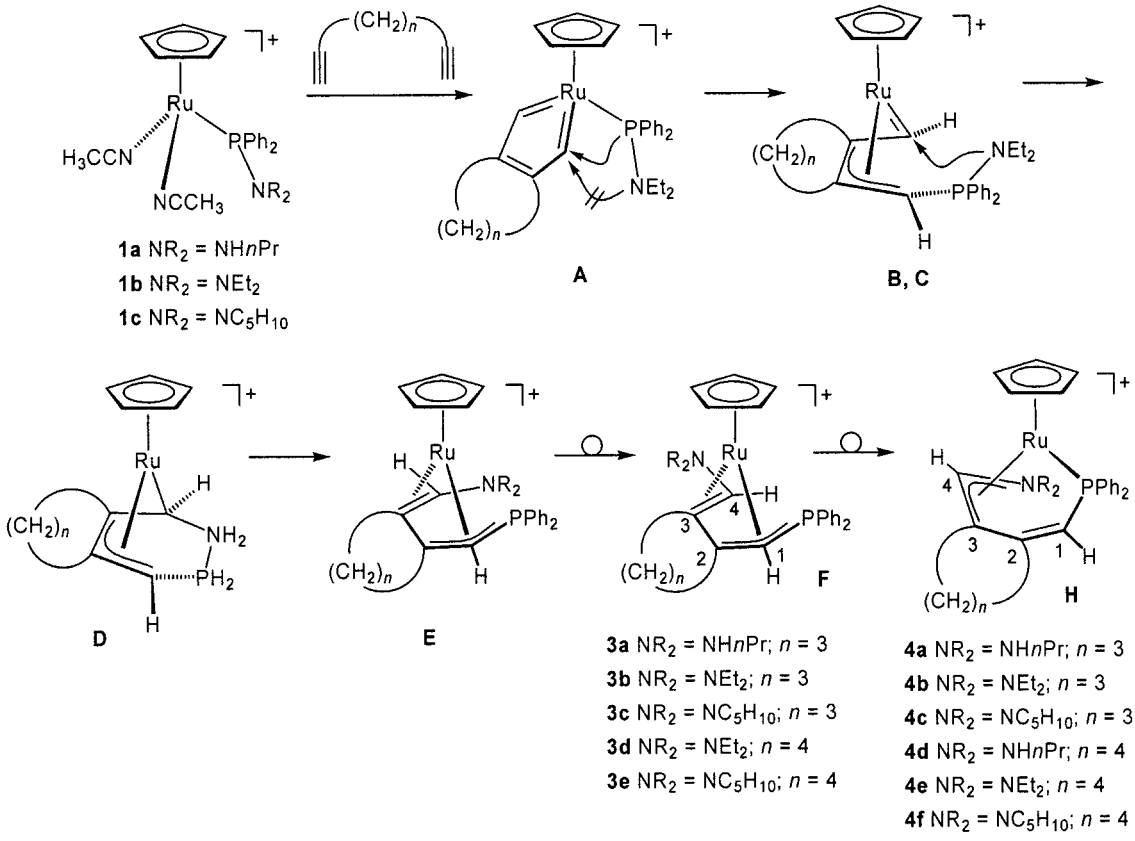


Figure 2. Structural view of $[RuCp^*(PPh_2NC_5H_{10})(CH_3CN)_2]PF_6$ (**2c**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: Ru–C(1–5)$_{av}$ 2.191(2), Ru–P(1) 2.3322(5), Ru–N(2) 2.064(2), Ru–N(3) 2.059 (2), P(1)–N(1) 1.668(2).

Reaction of $[RuCp(PPh_2NRR')(CH_3CN)_2]^+$ (NRR′ = NH*n*Pr, NEt_2, NC_5H_{10}) with Diynes

Within a few minutes, treatment of **1a**–**c** with 1,6-heptadiyne results in the formation of the η^3-phosphaallyl–η^2-vinylamine complexes $[RuCp\{\eta^3\text{-}(P,C,C)\text{-}PPh_2CH{=}C\text{–}(CH_2)_3\text{-}\eta^2\text{-}(C,C)\text{–}C{=}CH\text{–}NH{\it n}Pr\}]^+$ (**3a**), $[RuCp\{\eta^3\text{-}(P,C,C)\text{-}PPh_2CH{=}C\text{–}(CH_2)_3\text{–}\eta^2\text{-}(C,C)\text{-}C{=}CH\text{–}NEt_2\}]^+$ (**3b**), and $[RuCp\{\eta^3\text{-}(P,C,C)\text{-}PPh_2CH{=}C\text{–}(CH_2)_3\text{–}\eta^2\text{-}(C,C)\text{-}C{=}CH\text{–}NC_5H_{10}\}]^+$ (**3c**) in high yields (Scheme 1).[12,13] It is interesting to note that despite the fact that the aminophosphane ligand of **1a** bears a NH proton, a phosphaallyl complex rather than an amido butadiene complex is formed, as has been observed recently for $[RuCp(Ph_2PNHPh)(CH_3CN)_2]^+$. This may be attributed to the lower acidity of the NH proton (in other words, a stronger N–H bond) in $PPh_2NH{\it n}Pr$ as compared to the NH bond in PPh_2NHPh. Accordingly, P–*N* rather than N–H bond activation is favored. The phosphaallyl composition proved not to be the most stable one. In fact, if a solution of **3a**–**c** is kept at 90 °C for several hours, further rearrangement takes place, leading eventually to the thermodynamically more stable η^1-phosphaallyl–η^3-azaallyl complexes $[RuCp\{\eta^1\text{-}(P)\text{-}PPh_2CH{=}C\text{–}(CH_2)_3\text{–}\eta^3\text{-}(C,C,N)\text{-}C{=}CH\text{–}NH{\it n}Pr\}]^+$ (**4a**), $[RuCp\{\eta^1\text{-}(P)\text{-}PPh_2CH{=}C\text{–}(CH_2)_3\text{–}\eta^3\text{-}(C,C,N)\text{-}C{=}CH\text{–}NEt_2\}]^+$ (**4b**), and $[RuCp\{\eta^1\text{-}(P)\text{-}PPh_2CH{=}C\text{–}(CH_2)_3\text{–}\eta^3\text{-}(C,C,N)\text{-}C{=}CH\text{–}NC_5H_{10}\}]^+$ (**4c**) in essentially quantitative yields (Scheme 1).[14] On the other hand, with **1a** and 1,7-octadiyne no η^3-phosphaallyl–η^2-vinylamine complex could be observed and the η^1-phosphaallyl–η^3-azaallyl **4d** was obtained directly. In the case of **1b** and **1c** the respective η^3-phosphaallyl–η^2-vinylamine complexes **3d** and **3e** could be observed spectroscopically but rearranged rapidly at room temperature to afford the corresponding η^1-phosphaallyl–η^3-azaallyl complexes **4e** and **4f**. All compounds, which are air-stable both in solution and in the solid state, were fully characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy as well as elemental analysis.

The ^1H NMR spectroscopic data for **3a** include characteristic resonances at 4.14 (d, J_{HP} = 4.4 Hz) and 3.99 ppm (d, $J_{H,P}$ = 7.6 Hz, 1 H) assignable to the protons H^1 and H^4 of the η^3-phosphaallyl and η^2-vinylamine units, respectively. In the $^{13}C\{^1H\}$ NMR spectrum the characteristic resonance of the coordinated sp^2 carbon atoms C^1, C^2, C^3, and C^4 of the η^3-phosphaallyl–η^2-vinylamine moiety exhi-



Scheme 1.

bit resonances at 41.6 (d, J_{CP} = 24.5 Hz), 82.1, 116.8 (d, J_{CP} = 3.8 Hz), and 106.9 ppm (d, J_{CP} = 6.1 Hz), respectively. In the $^{31}P\{^1H\}$ NMR spectrum the phosphaallyl ligand exhibits a singlet at 9.3 ppm. Concurrent NMR spectra are observed for **3b**–**e**.

The NMR spectroscopic data of **4a**–**f** are quite different from those of **3a**–**e**. As the overall spectroscopic features are very similar, we describe here only those of **4a**. The ^1H NMR spectrum exhibits resonances at 5.98 (d, J_{HP} = 10.1 Hz) and 6.02 ppm, which can be assigned to the olefinic hydrogen atom H^1 and the allyl proton H^4. The most characteristic features in the $^{13}C\{^1H\}$ NMR spectrum are a low-field doublet resonance at δ = 170.1 ppm (d, J_{CP} = 29.1 Hz) and doublet resonances at 111.9 (d, J_{CP} = 47.2 Hz), 85.8 (d, J_{CP} = 1.9 Hz), and 74.4 ppm assignable to the terminal allyl carbon atom C^3, the two olefinic carbon atoms C^1 and C^2, and the central allyl carbon atom C^4 bearing the NH*n*Pr unit. In the $^{31}P\{^1H\}$ NMR spectrum the η^1-(P)-phosphaallyl ligand exhibits a singlet at δ = 70.3 ppm (cf. 9.3 ppm in **3a**).

The solid-state structures of **3a**, **3c**, and **4f** were determined by single-crystal X-ray diffraction. ORTEP diagrams are depicted in Figure 3, Figure 4, and Figure 5 with selected bond lengths given in Table 1. The structures of **3a** and **3c** can be described as a three-legged piano stool geometry with the η^3-phosphaallyl moiety and the C=C bond of the vinylamine unit as the legs. The η^3-phosphaallyl functionality is nearly symmetrically bonded to the metal with the Ru–P, Ru–C(18), and Ru–C(19) bond lengths being 2.2763(5), 2.241(2), and 2.220(2) Å in **3a** and 2.2505(4), 2.239(2), and 2.203(2) Å in **3c**, respectively. The olefin part of the vinylamine moiety is strongly asymmetrically bonded to the metal center with the Ru–C bonds to the carbon

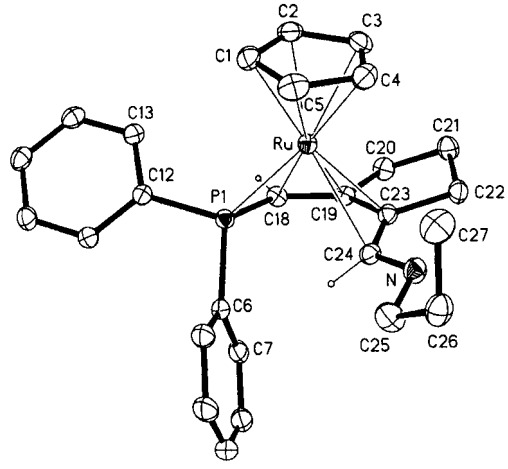


Figure 3. Structural view of [RuCp{η^3-(P,C,C)-$PPh_2CHC–(CH_2)_3$–η^2-(C,C)-CCHNH*n*Pr}]PF_6 (**3a**) showing 40% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: Ru–C(1–5)$_{av}$ 2.197(2), Ru–P(1) 2.2763(5), Ru–C(18) 2.241(2), Ru–C(19) 2.220(2), Ru–C(23) 2.236(2), Ru–C(24) 2.490(2), P(1)–C(18) 1.768(2), C(18)–C(19) 1.4129(34), C(19)–C(23) 1.437(3), C(23)–C(24) 1.396(3), C(24)–N 1.344(2).

atoms C(23) and C(24) being 2.236(2) and 2.490(2) Å in **3a** and 2.219(2) and 2.551(2) Å in **3c**, respectively. Strong alteration of olefin binding by π-donor substituents has also been observed in $[FeCp(CO)_2(H_2C{=}CHNMe_2)]^+$ where the vinylamine is essentially η^1-bound [the nonbonded Fe···C separation is 2.823(11) Å].[15] In turn, the C(24)–N bonds in **3a** and **3c** exhibit already double bond character being 1.344(2) and 1.359(2) Å, respectively. The bonding situation of the –C=CHNH*n*Pr and $-C{=}CHNC_5H_{10}$ units might be described as intermediate between the limiting vinylamine and imine forms or alternatively perhaps even as η^1-(C)-azaallyl. Accordingly, rotation about the C(23)–C(24) bond is expected to be facile, putting the amine moiety rapidly in a *syn*-conformation for steric reasons (conversion **D** to complexes **3** in Scheme 1).

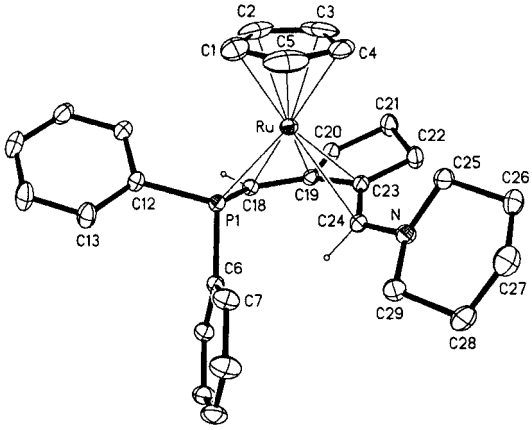


Figure 4. Structural view of $[RuCp\{\eta^1\text{-}(P)\text{-}PPh_2CH{=}C\text{–}(CH_2)_3\text{–}\eta^3\text{-}(C,C,N)\text{-}CCHNC_5H_{10}\}]PF_6$ (**3c**) showing 40% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: Ru–C(1–5)$_{av}$ 2.182(2), Ru–P(1) 2.2505(4), Ru–C(18) 2.239(2), Ru–C(19) 2.203(2), Ru–C(23) 2.219(2), Ru–C(24) 2.551(2), P(1)–C(18) 1.774(2), C(18)–C(19) 1.415(2), C(19)–C(23) 1.438(2), C(23)–C(24) 1.406(2), C(24)–N 1.359(2).

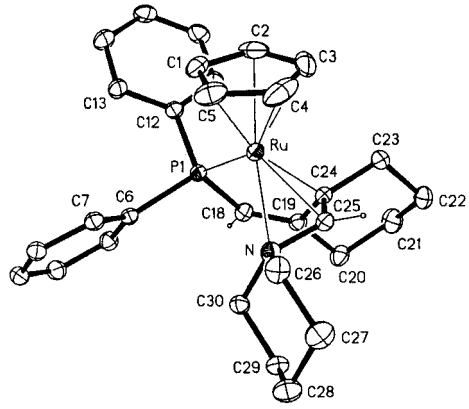


Figure 5. Structural view of $[RuCp\{\eta^1\text{-}(P)\text{-}PPh_2\text{-}CH{=}C(CH_2)_4\text{-}\eta^3\text{-}(C,C,N)\text{-}CH\text{-}NC_5H_{10}\}]PF_6$ (**4f**) showing 40% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: Ru–C(1–5)$_{av}$ 2.210(2), Ru–N 2.186(2), Ru–C(25) 2.089(2), Ru–C(24) 2.204(2), Ru–P(1) 2.2791(5), P(1)–C(18) 1.796(2), C(18)–C(19) 1.336(2), C(19)–C(24) 1.505(2), C(24)–C(25) 1.418(2), C(25)–N 1.415(2).

The structure of **4f** also adopts a three-legged piano stool conformation with the η^3-azaallyl moiety and the P atom as the legs. The η^3-azaallyl unit, being *exo*-oriented with respect to the phosphane moiety, is asymmetrically bonded

Table 1. Details for the crystal structure determinations of complexes **1a**, **2c**, **3a**, **3c**, **4f**, and **5a**.

	1a	**2c**	**3a**	**3c**	**4f**	**5a**
Empirical formula	$C_{24}H_{29}F_6N_3P_2Ru$	$C_{31}H_{41}F_6N_3P_2Ru$	$C_{27}H_{31}F_6NP_2Ru$	$C_{29}H_{33}F_6NP_2Ru$	$C_{30}H_{35}F_6NP_2Ru$	$C_{28}H_{33}F_6NP_2Ru$
Formula mass	636.51	732.68	646.54	672.57	686.60	660.56
Crystalsize [mm]	0.46×0.34×0.22	0.62×0.48×0.33	0.62×0.37×0.07	0.62×0.24×0.09	0.52×0.29×0.14	0.47×0.36×0.21
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	17.4288(10)	21.7560(17)	9.7404(5)	17.6384(8)	14.9183(7)	8.9199(4)
b [Å]	8.9607(5)	18.7520(14)	18.3098(9)	8.8425(4)	10.1274(5)	15.6117(7)
c [Å]	17.2306(10)	18.6960(14)	14.7423(8)	18.9241(9)	19.5913(9)	20.3315(10)
α [°]	90	90	90	90	90	90
β [°]	93.502(1)	120.954(1)	90.134(1)	108.100(1)	91.835(1)	93.219(1)
γ [°]	90	90	90	90	90	90
V [Å^3]	2686.0(3)	6541.1(9)	2629.2(2)	2805.5(2)	2958.4(2)	2826.8(2)
Z	4	8	4	4	4	4
ρ_{calcd} [g/cm^3]	1.574	1.488	1.633	1.592	1.542	1.552
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
μ [mm^{-1}] (Mo-K_α)	0.763	0.637	0.779	0.733	0.697	0.726
F(000)	1288	3008	1312	1368	1400	1344
θ_{max} [°]	30	30	30	30	30	27
Measured reflections	24957	48057	37914	40276	40996	25939
Unique reflections	7787	9522	7615	8167	8570	5719
No. of reflections $I > 2\sigma(I)$	6857	8133	6543	6947	7656	5024
Parameters	345	416	343	375	367	343
R_1 $[I > 2\sigma(I)]$[a]	0.0337	0.0343	0.0292	0.0282	0.0316	0.0899
R_1 (all data)	0.0396	0.0424	0.0380	0.0361	0.0360	0.0992
wR_2 (all data)	0.0838	0.0949	0.0823	0.0732	0.0881	0.2279
$\Delta\rho_{min/max}$ [e/Å^3]	–0.52/1.04	–0.50/0.77	–0.33/1.03	–0.43/0.80	–0.58/0.97	–1.08/1.96

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2–F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

to the metal with the Ru–C bond length to the central allyl carbon atom C(25) [2.089(2) Å] distinctly shorter than the Ru–N and Ru–C(24) bonds to the terminal allyl atoms N and C(24) [2.186(2) and 2.204(2) Å, respectively].

Upon keeping a CH_3CN solution of **4b** at 90 °C for 12 h, an unexpected rearrangement took place affording the aminocarbene $[RuCp\{=C(NEt_2)\text{-}\eta^2\text{-}(C,C)\text{-}C(CH_2)_3CCH_2\text{-}(\eta^1\text{-}(P)\text{-}PPh_2)\}]^+$ (**5a**) in essentially quantitative yield (71% isolated yield) as monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2). The same isomerization reaction was observed for **4c** yielding $[RuCp\{=C(NC_5H_{10})\text{-}\eta^2\text{-}(C,C)\text{-}C(CH_2)_3CCH_2\text{-}(\eta^1\text{-}(P)\text{-}PPh_2)\}]^+$ (**5b**) but the reaction was not quantitative. Attempts to isolate **5b** in pure form were unsuccessful and only mixtures of **4c** and **5b** were obtained. All other azaallyl complexes turned out to be thermally stable and there was no evidence for the formation of an aminocarbene. In the course of this process, the hydrogen of the central allyl carbon atom C^4 is transferred onto the olefinic carbon C^1. It is interesting to note that this reaction takes place only in the coordinating solvent CH_3CN, but not in CH_3NO_2. It may be speculated that such a formal 1,4 hydrogen shift reaction proceeds most likely by a metal mediated C–H activation step and the intermediacy of a hydride species (Scheme 2). Addition of the coordinating solvent may cause a hapticity change of the η^3 azaallyl moiety to give a η^2 vinylamine, thereby providing a latent vacant coordination site for a subsequent C–H bond activation step. Insertion of the noncoordinated olefin moiety into the Ru–H bond may then afford the aminocarbene complex. The conversion of activated olefins to heteroatom-stabilized carbenes is well documented.[16]

Characteristic features of **5a** and **5b** comprise, in the $^{13}C\{^1H\}$ NMR spectrum, a low-field doublet resonance in the range of 225.2 (d, J_{CP} = 13.0 Hz) and 222.9 (d, J_{CP} = 12.3 Hz) ppm, respectively, assignable to the carbene carbon atoms. The sp^3 carbon atom C^1 gives rise to a doublet resonance at 37.9 (d, J_{CP} = 35.3 Hz) and 36.7 (d, J_{CP} = 35.3 Hz). The $^{31}P\{^1H\}$ NMR spectrum reveals an unusually high-field shifted resonance at –34.3 and –37.8 ppm (cf. 9.3 and 4.3 ppm in **3b** and **3c**, and 74.1 and 73.3 ppm in **4b** and **4c**) with a small coupling constant of 36 Hz. The structural identity of **5a** was unequivocally proven by X-ray crystallography. The result is depicted in Figure 6 with important bond lengths given in the caption. Overall, **5a** adopts a typical three-legged piano stool conformation with PPh_2, the

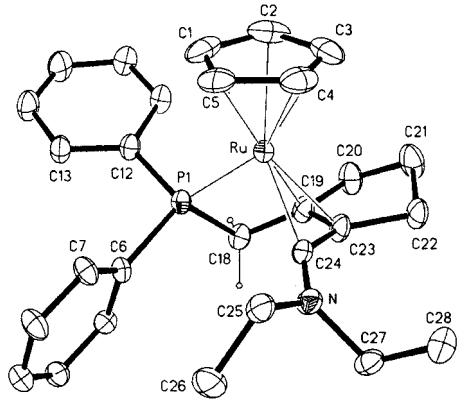
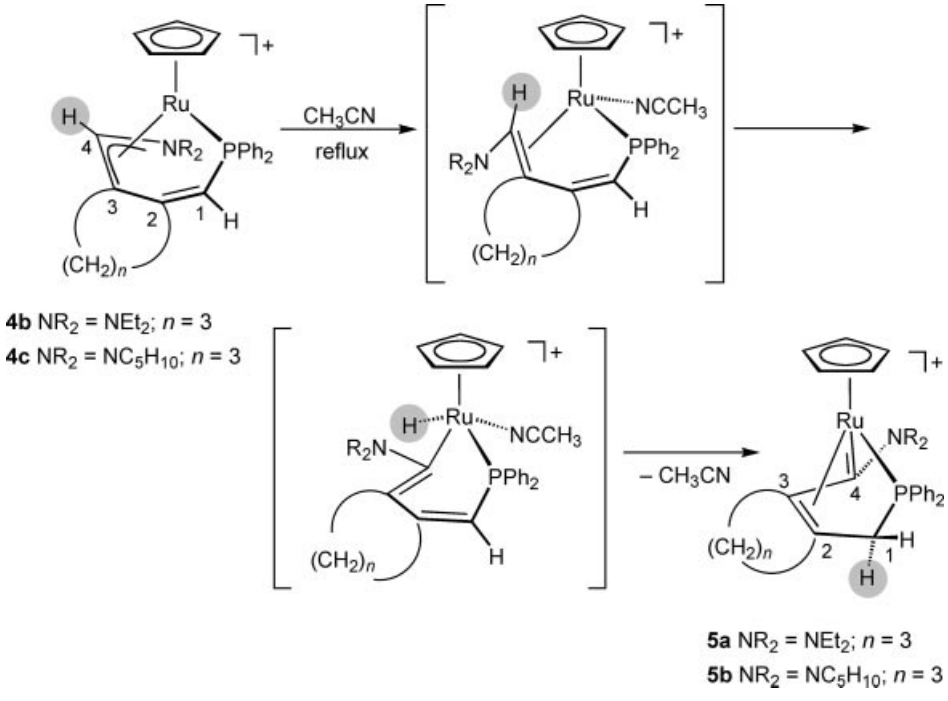


Figure 6. Structural view of $[RuCp\{=C(NEt_2)\text{-}\eta^2\text{-}(C,C)\text{-}C(CH_2)_3\text{-}C\text{–}CH_2\text{-}(\eta^1\text{-}(P)\text{-}PPh_2)\}]PF_6$ (**5a**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: $Ru\text{–}C(1\text{–}5)_{av}$ 2.204(9), Ru–C(24) 2.006(7), Ru–C(23) 2.201(7), Ru–C(19) 2.444(8), Ru–P(1) 2.263(2), P(1)–C(18) 1.818(7), C(18)–C(19) 1.493(12), C(19)–C(23) 1.421(12), C(23)–C(24) 1.508(11), C(24)–N 1.147(9).

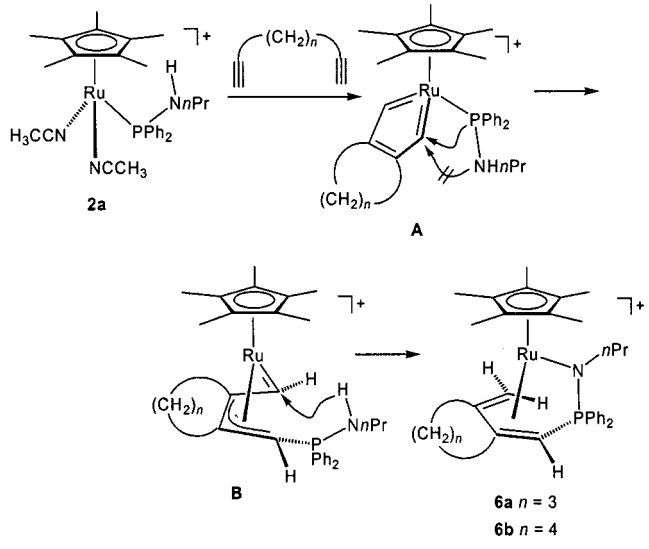


Scheme 2.

two C=C bonds of the vinyl moiety and the carbene carbon atom as the legs. The most notable feature is the comparatively short Ru–C(24) bond length of 2.006(7) Å reflecting metal carbon double bond character which is typical for aminocarbenes. The η^2-vinyl unit is asymmetrically bonded to the metal center with Ru–C(23) and Ru–C(19) bond lengths of 2.201(7) and 2.444(8) Å, respectively.

Reaction of $[RuCp^*(PPh_2NRR')(CH_3CN)_2]^+$ (NRR′ = NH*n*Pr, NEt_2, NC_5H_5) with Diynes

Given the previously observed behavior differences between $[CpRu(PR_3)(CH_3CN)_2]^+$ and the homologous $[Cp^*Ru(PR_3)(CH_3CN)_2]^+$ complexes with respect to the C–H activation processes,[17] we have addressed the question of whether P–N bond activation occurs also in the case of the Cp* aminophosphane complexes **2a**–**c**. In contrast to **1a**–**c**, the reaction of **2a** both with 1,6-heptadiyne and 1,7-octadiyne results in the clean formation of the amido butadiene complexes $[RuCp^*\{\eta^1\text{-}(N)\text{-}NnPrPPh_2\text{-}\eta^4\text{-}CH{=}C(CH_2)_3CH{=}CH_2\}]PF_6$ (**6a**) and $[RuCp^*\{\eta^1\text{-}(N)\text{-}NnPrPPh_2\text{-}\eta^4\text{-}CH{=}C(CH_2)_4CH{=}CH_2\}]PF_6$ (**6b**) in high yields (Scheme 3). There was no evidence that phosphaallyl or azaallyl complexes were formed. The same reaction has been found for $[RuCp(PPh_2NHPh)(CH_3CN)_2]^+$ and $[RuCp^*(PR_2NHR')(CH_3CN)_2]^+$ (R = Ph, *i*Pr, R′ = Ph, C_6F_5).[10,11] Compounds **6a** and **6b** are air-stable both in solution and in the solid state and were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy as well as elemental analysis.



Scheme 3.

As these compounds exhibit similar spectroscopic features to the RuCp η^4-butadiene amido complexes already described recently,[10,11] they are not discussed here. The solid-state structures of **6a** and **6b** were determined by single-crystal X-ray diffraction. ORTEP diagrams are depicted in Figure 7 and Figure 8 with selected bond lengths reported in the captions.

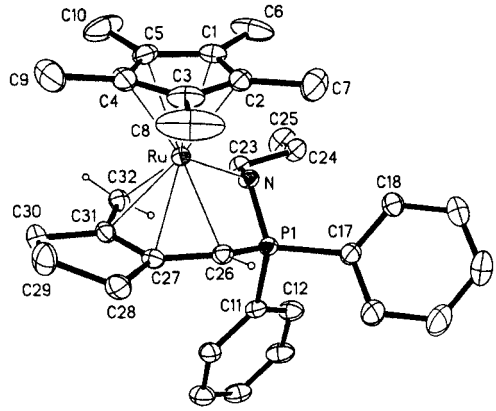


Figure 7. Structural view of $[RuCp^*\{\eta^1\text{-}(N)\text{-}NnPrPPh_2\text{-}\eta^4\text{-}CH{=}C(CH_2)_3CH{=}CH_2\}]PF_6$ (**6a**) showing 40% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: $Ru\text{–}C(1\text{–}5)_{av}$ 2.207(3), Ru–N = 2.183(2), Ru–C(26) 2.222(2), Ru–C(27) 2.232(2), Ru–C(31) 2.227(2), Ru–C(32) 2.204(2), P(1)–N 1.600(2), P(1)–C(26) 1.769(2), C(26)–C(27) 1.416(3), C(27)–C(31) 1.432(3), C(31)–C(32) 1.401(3).

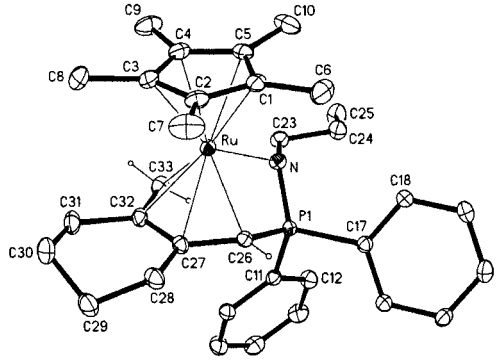
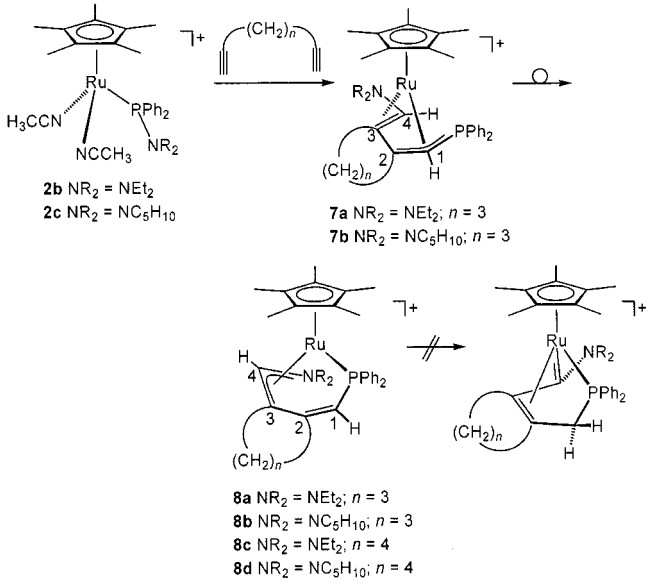


Figure 8. Structural view of $[RuCp^*\{\eta^1\text{-}(N)\text{-}NnPrPPh_2\text{-}\eta^4\text{-}CH{=}C(CH_2)_4CH{=}CH_2\}]PF_6$ (**6b**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity; only the first of three independent Ru complexes is shown). Selected bond lengths [Å]: $Ru\text{–}C(1\text{–}5)_{av}$ 2.220(2), Ru–N 2.184(2), Ru–C(26) 2.191 (2), Ru–C(27) 2.249(2), Ru–C(32) 2.244(2), Ru–C(33) 2.172(2), P(1)–N 1.600(2), P(1)–C(26) 1.771(2), C(26)–C(27) 1.423(3), C(27)–C(32) 1.436(3), C(32)–C(33) 1.406(4).

In similar fashion to the RuCp complexes **1a**–**c**, with 1,6-heptadiyne, 1,7-octadiyne, **2b**, and **2c**, the η^1-phosphaallyl–η^3-azaallyl complexes $[RuCp^*\{\eta^1\text{-}(P)\text{-}PPh_2\text{–}CH{=}C(CH_2)_3\text{-}\eta^3\text{-}(C,C,N)\text{-}CCHNEt_2\}]PF_6$ (**8a**), $[RuCp^*\{\eta^1\text{-}(P)\text{-}PPh_2\text{–}CH{=}C(CH_2)_3\text{-}\eta^3\text{-}(C,C,N)\text{-}CCHNC_5H_{10}\}]PF_6$ (**8b**), $[RuCp^*\{\eta^1\text{-}(P)\text{-}PPh_2\text{–}CH{=}C(CH_2)_4\text{-}\eta^3\text{-}(C,C,N)\text{-}CCHNEt_2\}]PF_6$ (**8c**), and $[RuCp^*\{\eta^1\text{-}(P)\text{-}PPh_2\text{–}CH{=}C(CH_2)_4\text{-}\eta^3\text{-}(C,C,N)\text{-}CCHNC_5H_{10}\}]PF_6$ (**8d**), respectively, are obtained in high isolated yields (Scheme 4). While in the case of 1,6-heptadiyne the intermediacy of η^3-phosphaallyl–η^2-vinylamine complexes **7a** and **7b** could be observed by NMR spectroscopy, in the case of 1,7-octadiyne no intermediates were detected. Again, all compounds were fully characterized by a combination of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. Overall, the spectroscopic features of complexes **7** and **8** are very similar to those of complexes **3** and **4** and are thus not discussed here. In ad-

dition, the solid-state structures of **8c** and **8d** were determined by single-crystal X-ray diffraction. ORTEP plots are depicted in Figure 9 and Figure 10 with selected bond lengths reported in the captions.



Scheme 4.

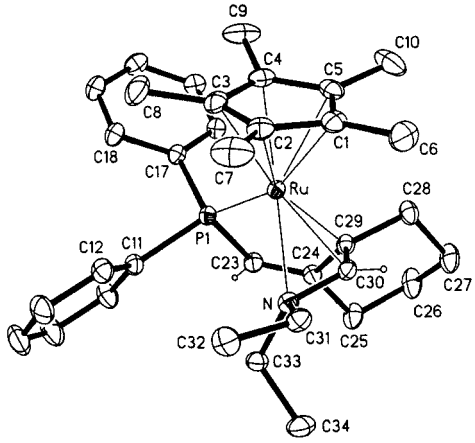


Figure 9. Structural view of [RuCp*{η^1-(P)-$PPh_2CH{=}C(CH_2)_4$-η^3-(C,C,N)-C=CH–NEt_2}]$PF_6{\cdot}CH_2Cl_2$ (**8c**·CH_2Cl_2) showing 30% thermal ellipsoids (PF_6^- and solvent omitted for clarity). Selected bond lengths [Å]: Ru–$C(1–5)_{av}$ 2.239(2), Ru–P(1) 2.3020(6), Ru–C(29) 2.253(2), Ru–C(30) 2.092(2), Ru–N 2.243(2), P(1)–C(23) 1.795(2), C(23)–C(24) 1.325(3), C(24)–C(29) 1.510(3), C(29)–C(30) 1.425(3), N–C(30) 1.421(3).

Finally, as part of our ongoing effort to investigate the chemistry of complexes with ligands which possess direct P^{III}–N bonds towards alkynes, we set out here to prepare a complex with a diphenylphosphanylhydrazide ligand, that is, a ligand having a P^{III}–N–N unit. It should be noted that transition-metal complexes with $R_2PNHNR'_2$ ligands are comparatively rare. With respect to late transition metals, they have been found to coordinate either as monodentate or bidentate ligands in κ^1-P and κ^2-P,N fashion, respectively.[18] Accordingly, treatment of [RuCp$(CH_3CN)_3$]PF_6 with 1 equiv. of PPh_2NHNMe_2 in CH_2Cl_2 as the solvent

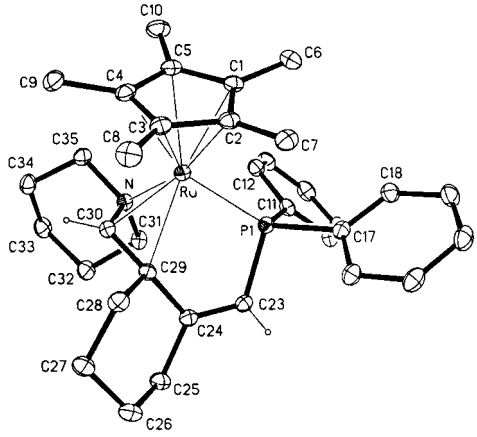
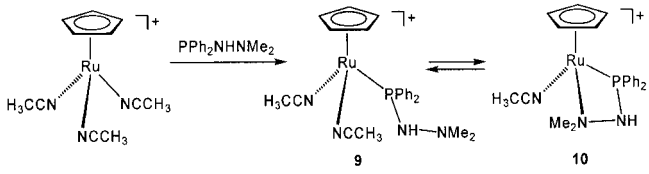


Figure 10. Structural view of [RuCp*{η^1-(P)-$PPh_2CH{=}C(CH_2)_4$-η^3-(C,C,N)-C=CH–$N(CH_2)_5$}]PF_6 (**8d**) showing 30% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å]: Ru–$C(1–5)_{av}$ 2.228(2), Ru–P(1) 2.2978(5), Ru–C(29) 2.252(2), Ru–C(30) 2.090(2), Ru–N 2.233(2), P(1)–C(23) 1.796(2), C(23)–C(24) 1.326(3), C(24)–C(29) 1.508(3), C(29)–C(30) 1.418(3), N–C(30) 1.418(2).

at room temperature yields, upon workup, a 5:1 mixture of [RuCp{κ^1(P)-PPh_2NHNMe_2}$(CH_3CN)_2$]PF_6 (**9**) and [RuCp{κ^2(P,N)-PPh_2NHNMe_2}(CH_3CN)]PF_6 (**10**) where the PPh_2NHNMe_2 ligand is attached to the metal center in the κ^1-P and κ^2-P,N mode, respectively (Scheme 5). Complex **9** is obtained in pure form, when the reaction is performed in the presence of 1 equiv. of CH_3CN. Both complexes were characterized by means of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis in the case of **9**. Crystals of **10** could be grown by diffusion of diethyl ether into a CH_2Cl_2 solution of a reaction mixture containing both **9** and **10**. A structural view of **10** is depicted in Figure 11 with selected bond lengths and angles reported in the caption.



Scheme 5.

Complexes **9** and **10** exhibit singlet resonances in the $^{31}P\{^1H\}$ NMR spectrum at 90.6 to 61.4 ppm, respectively. In the case of **10** where the PPh_2NHNMe_2 ligand is bound in κ^2-P,N fashion the ^1H and $^{13}C\{^1H\}$ NMR spectra show the two methyl groups to be inequivalent, giving rise to two signals at δ = 3.35 and 2.82 ppm and 63.9 and 57.8 ppm, respectively [cf. complex **9** exhibits one singlet at δ = 2.27 ppm and a doublet centered at δ = 49.9 ppm (J_{CP} = 3.4 Hz)].

Unfortunately, in contrast to the clean reactions of complexes **1** and **2** with diynes, the reaction of **9** with 1,6-heptadiyne and 1,7-octadiyne afforded only mixtures of intractable materials. Thus as yet no further reactions have been performed with **9**.

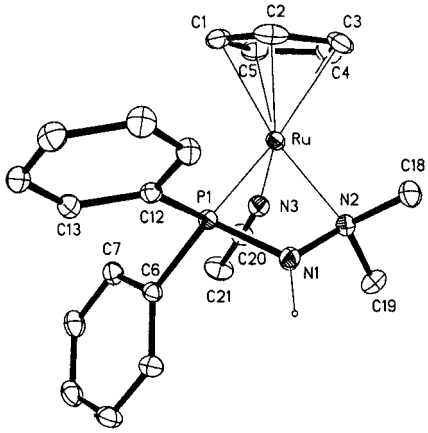


Figure 11. Structural view of $[RuCp\{\kappa^2\text{-}(P,N)\text{-}PPh_2NHNMe_2\}(CH_3CN)]PF_6$ (**10**) showing 30% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru–$C(1–5)_{av}$ 2.173(2), Ru–P(1) 2.2915(2), Ru–N(2) 2.216(2), Ru–N(3) 2.050(2), P(1)–N(2) 1.688(2), N(1)–N(2) 1.456(2), P(1)–Ru–N(2) 67.03(4).

Mechanistic Aspects

For the present conversion of **1** and **2** to the respective phosphaallyl complexes **4**, unfortunately, no intermediate products could be detected spectroscopically. From previous experimental data[19] it is reasonable to assume that the formation of the η^3-phosphaallyl–η^2-vinylamine proceeds via the intermediacy of the cationic metallacyclopentatriene **A** and the η^3-allyl carbene complex **B**. The formation of the latter involves migration of the κ^1(P) coordinated PPh_2NRR' ligand to one of the two electrophilic carbene carbon atoms of **A**.[19] Accordingly, we have chosen **B** (in the form of the two model complexes $[CpRu\{=CH\text{–}(\eta^3\text{-}CHCHCH\text{–}PH_2NH_2)\}]^+$ and $[CpRu\{=CH\text{-}(\eta^3\text{-}CHCHCH\text{–}PMe_2NHMe)\}]^+$) as the starting point of our theoretical mechanistic investigation based on DFT/B3LYP calculations. The energy profile for the conversion of **B** to the η^3-phosphaallyl–η^2-vinylamine complexes **4** is shown in Figure 12. The models of **4** with PH_2NH_2 and PMe_2NHMe will be called **F** (in Figure 12 the energy values in parentheses refer to PMe_2NHMe). The reliability of the computational method (details in Experimental Section) is supported by the good agreement between the calculated geometries of **F** with the X-ray structures of the related complexes (e.g. **3a** and **3c**).

The first step **B** to **C** constitutes a rotation of the aminophosphane substituent about the C–P bond, which is required to place the amine moiety in a position suitable for nucleophilic attack at the carbene carbon atom. This process is slightly endothermic by 3.2 kcal/mol and possesses a small activation barrier (6.7 kcal/mol). Subsequent nucleophilic attack of the amine moiety at the carbene carbon atom of **C** yields intermediate **D**, which features an unusual six-membered aza-phosphacycle. The transition state for this process, $\mathbf{TS_{CD}}$, is very similar to the structure of **D**, indicating that the transition state structure occurs quite late along the reaction coordinate and is merely 0.3 kcal/

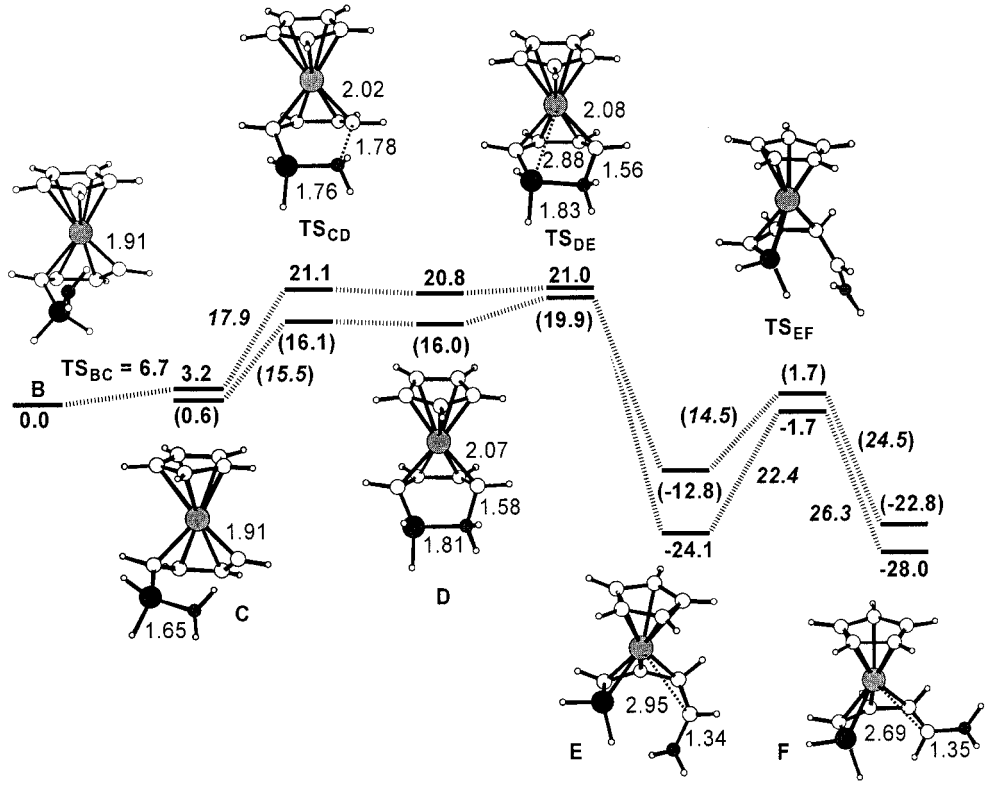


Figure 12. Energy profile (in kcal/mol, relative to **B**) for the conversion of **B** to **F** with PH_2NH_2 as model aminophosphane ligand. The numbers in parentheses refer to PMe_2NHMe as the model ligand.

mol higher in energy than **D**. In the course of this reaction, a new N···C bond starts to form. It is 1.78 Å in $\mathbf{TS_{CD}}$ and finally reaches 1.58 Å in species **D**. This process requires an activation energy of 17.9 kcal/mol. The P–N bond in **D** is rather weak as judged from the long P–N bond length of 1.81 Å. Accordingly, this bond is readily cleaved, yielding the η^3-phosphaallyl–η^2-vinylamine complex **E**. This transformation is strongly exothermic, releasing 44.9 kcal/mol. The transition state connecting **D** and **E** is reached at an early stage and thus its structure is very similar to **D**. In fact, the only noticeable change from **D** to $\mathbf{TS_{DE}}$ is a weak but apparently important Ru···P interaction of 2.88 Å. In **E** the Ru–P bond is fully developed (2.30 Å), while the Ru–C^4 bond becomes very weak or almost nonbonding (2.95 Å). On going from **D** to **E**, the amino substituent is initially placed in an *anti* position, that is, pointing towards the phosphane moiety, which is sterically unfavorable, especially if the amine is mono- or even disubstituted (repulsive interactions) such as in **3b**, **3c**, **3d**, or **3e**. Rotation of the amine unit about the C^3–C^4 bond yields the experimentally observed and isolated *syn* isomer **F**. Surprisingly, despite the fact that the Ru–C^4 bond is rather long (2.95 Å), the activation barrier for this rotation is relatively high, requiring 22.4 kcal/mol. However, in the case of the more realistic model ligand PMe_2NHMe, the activation barrier becomes significantly smaller (14.5 kcal/mol) and unfavorable steric interactions are better taken into account (Figure 12, numbers in parentheses).

Experimentally it has been observed that η^3-phosphaallyl–η^2-vinylamine complexes (**F**) are the kinetic products but isomerize (in some cases already at room temperature) to the thermodynamically more stable η^1-phosphaallyl–η^3-azaallyl complexes **H**. The energy profiles for this conversion are presented in Figures 12 (**F** → **E**) and 13 (**E** → **H**). In agreement with experimental data, the overall process is thermodynamically favored. This rearrangement exhibits a *syn–anti* isomerization of the NH_2 substituent and thus proceeds most likely again via the intermediacy of **E** (Figure 12). This first step needs an activation energy of 26.3 kcal/mol for the parent PH_2NH_2 ligand and 24.5 kcal/mol for PMe_2NHMe and is thus rate determining. Once **E** is re-formed, the subsequent processes are facile. Complex **E** proceeds through transition state $\mathbf{TS_{EG}}$ to afford the metallacycle **G**. This reaction is energetically slightly unfavorable by 6.7 kcal/mol with an activation energy of 12.1 kcal/mol. These values, however, are comparatively small taking into account that in the course of this reaction two Ru–C bonds are broken, which are counterbalanced only by one weak Ru–C interaction (2.65 Å). Moreover, as a consequence of that ongoing from **E** by $\mathbf{TS_{EG}}$ to **G**, the C4 chain experiences a severe distortion, as is apparent from the changes of the respective torsion angles C–C–C–C being 39.2, 58.1, and finally 111.5°, respectively. This may also explain why the formation of azaallyl complexes is far more facile in the case of 1,7-octadiyne where the phosphaallyl complexes contain a six-membered ring system than with 1,6-heptadiyne where these complexes feature a more rigid five-membered ring. The subsequent conversion of **G** to the η^1-phosphaallyl–η^3-azaallyl complexes **H** requires merely 0.4 kcal/mol activation energy and is energetically very favorable, releasing 18.5 kcal/mol (Figure 13).

Finally, we also looked for a plausible mechanism of the formation of amido-butadiene complexes (**I**) from allyl carbene complexes (**B**). This reaction is obviously restricted to aminophosphane ligands possessing NH protons. An energetically feasible pathway with the model complexes [CpRu{=CH-(η^3-CHCHCH–PH_2NH_2)}]$^+$ and [CpRu{=CH-(η^3-CHCHCH–PMe_2NHMe)}]$^+$ (**A**) is shown in Figure 14. Accordingly, the N–H proton in **B** is transferred to the carbene carbon atom by transition state $\mathbf{TS_{HI}}$ without any involvement of the metal center. This reaction has an activation barrier of 17.7 kcal/mol (18.1 kcal/mol for PMe_2NHMe) and is exothermic releasing 8.4 kcal/mol (11.0 kcal/mol for PMe_2NHMe). Therefore, in the case of complexes with

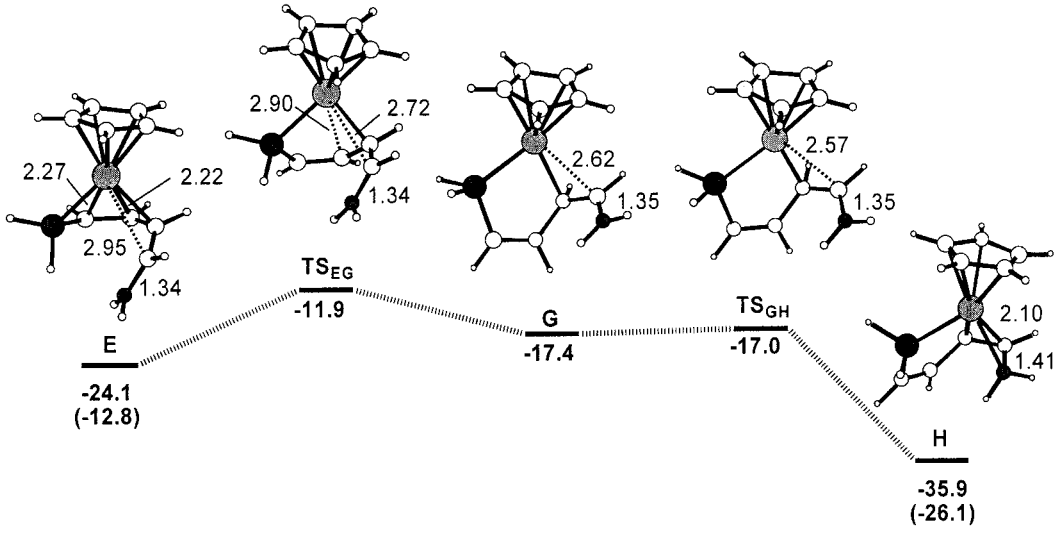


Figure 13. Energy profile (in kcal/mol, relative to **B**) for the conversion of **E** to **H** with PH_2NH_2 as model aminophosphane ligand. The numbers in parentheses refer to PMe_2NHMe as the model ligand.

aminophosphanes that contain N–H bonds, this pathway becomes competitive with the formation of phosphaallyl (**F**) and azaallyl complexes (**H**). It should be noted that we were unable to find an alternative pathway to obtain amido butadiene complexes by oxidative addition of the N–H bond to the metal center.

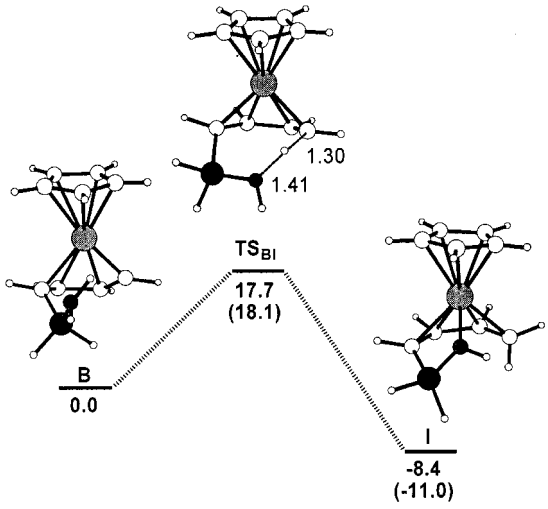


Figure 14. Energy profile (in kcal/mol, relative to **B**) for the reaction of **B** to **I** with PH_2NH_2 as model aminophosphane ligand. The numbers in parentheses refer to PMe_2NHMe as the model ligand.

Experimental Section

General: Manipulations were performed under inert purified argon by using Schlenk techniques and/or a glovebox. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[20] The deuterated solvents were purchased from Aldrich and dried with 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$,[21] $[RuCp^*(CH_3CN)_3]PF_6$,[22] and PPh_2NHNMe_2[23] were prepared according to the literature. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with Bruker Avance-250 and -300 spectrometers and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively. ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, 135-DEPT, and HSQC(^1H-^{13}C) experiments.

$[RuCp(PPh_2NH$*n*$Pr)(CH_3CN)_2]PF_6$ (1a): PPh_2NH*n*Pr (185 mg, 0.76 mmol) was added to a solution of $[RuCp(CH_3CN)_3]PF_6$ (300 mg, 0.69 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 2 h at room temperature. After removal of the solvent, a yellow powder was obtained which was collected on a glass frit, washed with Et_2O (3 × 10 mL), and dried under vacuum. Yield: 421 mg (95%). $C_{24}H_{29}F_6N_3P_2Ru$ (636.52): calcd. C 45.29, H 4.59, N 6.60; found C 45.23, H 4.79, N 6.74. ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.69–7.42 (m, 10 H, Ph), 4.43 (s, 5 H, Cp), 2.85–2.66 (m, 2 H, *n*Pr), 2.50–2.32 (m, 1 H, N*H**n*Pr), 2.20 (d, J_{HP} = 1.4 Hz, 6 H, CH_3CN), 1.51 –1.30 (m, 2 H, *n*Pr), 0.80 (t, J_{HH} = 7.4 Hz, 3 H, *n*Pr) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 136.1 (d, $^1J_{CP}$ = 48.7 Hz, Ph^1), 131.6 (d, $^2J_{CP}$ = 11.9 Hz, Ph^{2,6}), 130.0 (d, $^4J_{CP}$ = 1.9 Hz, Ph^4), 128.2 (d, $^3J_{CP}$ = 10.0 Hz, Ph^{3,5}), 126.7 (CH_3CN), 76.6 (d, J_{CP} = 2.3 Hz, Cp), 45.8 (d, J_{CP} = 8.0 Hz, CH_2), 24.9 (d, J_{CP} = 5.8 Hz, CH_2), 11.0 (CH_3), 3.7 (CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 86.0 (PPh_2), –143.0 ($^1J_{FP}$ = 708.3 Hz, PF_6) ppm.

$[RuCp(PPh_2NEt_2)(CH_3CN)_2]PF_6$ (1b): This complex has been prepared analogously to **1a** with $[RuCp(CH_3CN)_3]PF_6$ (300 mg, 0.69 mmol) and PPh_2NEt_2 (179 mg, 0.69 mmol) as starting materials. Yield: 416 mg (93%). $C_{25}H_{31}F_6N_3P_2Ru$ (650.55): calcd. C 46.16, H 4.80, N 6.46; found C 46.10, H 4.72, N 6.55. ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.61–7.30 (m, 10 H, Ph), 4.26 (s, 5 H, Cp), 3.42–3.20 (m, 4 H, Et), 2.22 (6 H, CH_3CN), 0.96 (t, J_{HH} = 7.1 Hz, 3 H, Et) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 137.4 (d, $^1J_{CP}$ = 46.0 Hz, Ph^1), 131.4 (d, $^2J_{CP}$ = 11.5 Hz, Ph^{2,6}), 129.7 (d, $^4J_{CP}$ = 1.9 Hz, Ph^4), 128.0 (d, $^3J_{CP}$ = 9.6 Hz, Ph^{3,5}), 127.3 (CH_3CN), 77.4 (d, J_{CP} = 2.3 Hz, Cp), 42.4 (d, J_{CP} = 6.5 Hz, CH_2), 13.6 (d, J_{CP} = 2.3 Hz, CH_3), 3.7 (CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 102.1 (PPh_2), –143.0 ($^1J_{FP}$ = 711.8 Hz, PF_6) ppm.

$[RuCp(PPh_2NC_5H_{10})(CH_3CN)_2]PF_6$ (1c): This complex has been prepared analogously to **1a** with $[RuCp(CH_3CN)_3]PF_6$ (374 mg, 0.86 mmol) and $PPh_2NC_5H_{10}$ (232 mg, 0.86 mmol) as starting materials. Yield: 500 mg (88%). $C_{26}H_{31}F_6N_3P_2Ru$ (662.56): calcd. C 47.13, H 4.72, N, 6.34; found C 46.66, H 4.89, N 6.51. ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.66–7.26 (m, 10 H, Ph), 4.23 (s, 5 H, Cp), 3.30–3.01 (m, 4 H, NC_5H_{10}), 2.20 (d, J_{HP} = 1.0 Hz, 6 H, CH_3CN), 1.72–1.36 (m, 6 H, NC_5H_{10}) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 136.6 (d, $^1J_{CP}$ = 46.0 Hz, Ph^1), 131.2 (d, $^2J_{CP}$ = 11.1 Hz, Ph^{2,6}), 129.7 (d, $^4J_{CP}$ = 1.9 Hz, Ph^4), 128.1 (d, $^3J_{CP}$ = 9.6 Hz, Ph^{3,5}), 127.3 (CH_3CN), 77.4 (d, J_{CP} = 2.3 Hz, Cp), 50.1 (d, J_{CP} = 3.4 Hz, CH_2), 27.0 (d, J_{CP} = 5.4 Hz, CH_2), 24.4 (CH_2), 3.7 (CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 98.8 (PPh_2), –143.0 ($^1J_{FP}$ = 710.5 Hz, PF_6) ppm.

$[RuCp^*(PPh_2NH$*n*$Pr)(CH_3CN)_2]PF_6$ (2a): PPh_2NH*n*Pr (145 mg 0.60 mmol) was added to a solution of $[RuCp^*(CH_3CN)_3]PF_6$ (300 mg, 0.60 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred for 2 h at room temperature. The volume of the solution was then reduced to about 1 mL and Et_2O (5 mL) was added. A yellow precipitate was formed, which was washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 336 mg (80%) $C_{29}H_{39}F_6N_3P_2Ru$ (706.66): calcd. C 49.29, H 5.56, N 5.95; found: C 48.94,; H 6.09, N 5.59. ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.65–7.40 (m, 10 H, Ph), 3.09–2.85 (m, 1 H, NH), 2.74 (m, J_{HH} = 6.9 Hz, 2 H, CH_2), 2.23 (d, J_{HP} = 1.3 Hz, 6 H, CH_3CN), 1.49 (d, J_{HP} = 1.7 Hz, 15 H, Cp*), 1.27–1.21 (m, 2 H, CH_2), 0.84 (t, J_{HH} = 7.5 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 135.4 (d, $^1J_{CP}$ = 43.7 Hz, Ph^1), 132.0 (d, $^2J_{CP}$ = 11.5 Hz, Ph^{2,6}), 129.7 (Ph^4), 128.0 (d, $^3J_{CP}$ = 9.2 Hz, Ph^{3,5}), 124.7 (CH_3CN), 86.8 (Cp*), 46.0 (d, J_{CP} = 9.2 Hz, CH_2), 25.0 (d, J_{CP} = 6.1 Hz, CH_2), 10.5 (CH_3), 9.1 (Cp*), 3.8 (CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 82.9 (PPh_2), –144.5 ($^1J_{FP}$ = 710.2 Hz, PF_6) ppm.

$[RuCp^*(PPh_2NEt_2)(CH_3CN)_2]PF_6$ (2b): This complex has been prepared analogously to **2a** with $[RuCp^*(CH_3CN)_3]PF_6$ (300 mg, 0.60 mmol) and PPh_2NEt_2 (153 mg 0.60 mmol) as starting materials. Yield: 350 mg (82%) $C_{30}H_{41}F_6N_3P_2Ru$ (720.68): calcd. C 50.00, H 5.73, N 5.83; found C 50.24, H 5.44, N 5.59. ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.58–7.18 (m, 10 H, Ph), 3.30–3.13 (m, 4 H, CH_2), 2.74 (m, $^3J_{HH}$ = 6.9 Hz, 2 H, CH_2), 2.24 (d, J_{HP} = 1.1 Hz, 6 H, CH_3CN), 1.32 (d, J_{HP} = 1.7 Hz, 15 H, Cp*′), 1.00 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 136.7 (d, $^1J_{CP}$ = 41.4 Hz, Ph^1), 131.8 (d, $^2J_{CP}$ = 11.5 Hz, Ph^{2,6}), 129.4 (Ph^4), 127.9 (d, $^3J_{CP}$ = 9.2 Hz, Ph^{3,5}), 125.5 (CH_3CN), 87.2 (Cp*), 41.6 (d, J_{CP} = 7.7 Hz, CH_2), 12.9 (d, J_{CP} = 3.1 Hz, CH_3), 8.7 (Cp*), 3.8 (CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 101.3 (PPh_2), –144.4 ($^1J_{FP}$ = 712.0 Hz, PF_6) ppm.

$[RuCp^*(PPh_2NC_5H_{10})(CH_3CN)_2]PF_6$ (2c): This complex has been prepared analogously to **2a** with $[RuCp^*(CH_3CN)_3]PF_6$ (300 mg, 0.60 mmol) and $PPh_2NC_5H_{10}$ (160 mg 0.60 mmol) as starting mate-

rials. Yield: 380 mg (87%) $C_{31}H_{41}F_6N_3P_2Ru$ (732.69): calcd. C 50.82, H 5.64, N 5.74; found C 50.14, H 5.46, N 5.78. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.51–7.35 (m, 10 H, Ph), 3.06–2.90 (m, 4 H, CH_2), 2.24 (d, J_{HP} = 1.26 Hz, 6 H, CH_3CN), 1.62–1.48 (m, 6 H, CH_2), 1.32 (d, J_{HP} = 1.7 Hz, 15 H, Cp*′) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 135.8 (d, $^1J_{CP}$ = 40.6 Hz, Ph^1), 131.5 (d, $^2J_{CP}$ = 10.7 Hz, Ph^{2,6}), 129.3 (Ph^4), 128.0 (d, $^3J_{CP}$ = 9.2 Hz, Ph^{3,5}), 125.3 (CH_3CN), 87.2 (Cp*), 50.4 (d, J_{CP} = 3.8 Hz, CH_2), 26.9 (d, J_{CP} = 6.9 Hz, CH_2), 24.3 (CH_2), 8.7 (Cp*), 3.8 (CH_3CN) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 96.1 (PPh_2), –144.4 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

[RuCp{η³-(P,C,C)-PPh₂CHC–(CH₂)₃–η²-(C,C)-CCHNH*n*Pr}]PF₆ (3a): 1.1 equiv. of 1,6-heptadiyne (26.7 μL, 0.23 mmol) was added to a solution of **1a** (135 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 2 h at room temperature. After removal of the solvent under reduced pressure, an orange solid was obtained, which was washed with Et_2O (5 mL), and dried under vacuum. Yield: 99 mg (73%). $C_{27}H_{31}F_6NP_2Ru$ (646.56): calcd. C 50.16, H 4.83, N 2.17; found C 49.88, H 5.02, N 2.22. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.79–7.25 (m, 10 H, Ph), 5.05 (s, 5 H, Cp), 4.30–4.09 (m, 1 H, N*H*nPr), 4.14 (d, $^2J_{HP}$ = 5.4 Hz, 1 H, H^1), 3.99 (d, J_{HP} = 7.6 Hz, 1 H, H^4), 3.37–3.20 (m, 1 H), 2.97–2.66 (m, 3 H), 2.62–2.39 (m, 2 H), 2.36–2.17 (m, 1 H), 2.09–1.86 (m, 1 H), 1.46–1.08 (m, 2 H), 0.77 (t, J_{HH} = 7.4, 3 H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 133.8 (d, $^2J_{CP}$ = 11.5 Hz, Ph^{2,6}), 132.4 (d, $^2J_{CP}$ = 12.3 Hz, Ph$^{2',6'}$), 131.6 (d, $^4J_{CP}$ = 3.4 Hz, Ph^4), 131.7–131.6 (d, $^4J_{CP}$ = 3.4 Hz, Ph$^{4'}$), 129.9 (d, $^3J_{CP}$ = 12.3 Hz, Ph^{3,5}), 129.1 (d, $^3J_{CP}$ = 12.3 Hz, Ph$^{3',5'}$), 122.1 (d, $^1J_{CP}$ = 52.1 Hz, Ph^1), 116.8 (d, J_{CP} = 3.8 Hz, C^3), 106.9 (d, J_{CP} = 6.1 Hz, C^4), 82.1 (C^2), 81.7 (Cp), 50.4 (CH_2), 41.6 (d, J_{CP} = 24.5 Hz, C^1), 37.1 (d, J_{CP} = 7.7 Hz, CH_2), 31.6 (CH_2), 22.6 (CH_2), 21.9 (CH_2), 11.8 (CH_3) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 9.3 (PPh_2), –142.9 ($^1J_{FP}$ = 711.5 Hz, PF_6) ppm.

[RuCp{η³-(P,C,C)-PPh₂CHC–(CH₂)₃–η²-(C,C)-CCHNEt₂}]PF₆ (3b): This complex has been prepared analogously to **3a** with **1b** (100 mg, 0.15 mmol) and 1,6-heptadiyne (19.5 μL, 0.17 mmol) as the starting materials. Yield: 75 mg (76%). $C_{28}H_{33}F_6NP_2Ru$ (660.58): calcd. C 50.91, H 5.09, N 2.12; found C 50.83, H 5.11, N 2.19. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.68–7.41 (m, 10 H, Ph), 5.09 (s, 5 H, Cp), 4.01 (d, $^2J_{HP}$ = 4.7 Hz, 1 H, H^1), 3.58 (d, J_{HP} = 5.7 Hz, 1 H, H^4), 3.01–2.86 (m, 2 H), 2.82–2.51 (m, 6 H), 2.39–2.27 (m, 2 H), 0.96 (t, J_{HH} = 7.1 Hz, 3 H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 133.2 (d, $^2J_{CP}$ = 11.9 Hz, Ph^{2,6}), 132.4 (d, $^2J_{CP}$ = 12.3 Hz, Ph$^{2',6'}$), 132.1 (d, $^4J_{CP}$ = 3.5 Hz, Ph^4), 131.6 (d, $^4J_{CP}$ = 2.3 Hz, Ph$^{4'}$), 129.8 (d, $^3J_{CP}$ = 11.5 Hz, Ph^{3,5}), 129.0 (d, $^3J_{CP}$ = 11.9 Hz, Ph$^{3',5'}$), 125.9 (d, $^1J_{CP}$ = 47.9 Hz, Ph^1), 117.8 (d, J_{CP} = 6.9 Hz, C^4), 117.4 (d, J_{CP} = 4.6 Hz, C^3), 79.1 (d, J_{CP} = 1.5 Hz, Cp), 75.8 (C^2), 46.8 (CH_2), 40.8 (d, J_{CP} = 24.2 Hz, C^1), 36.0 (d, J_{CP} = 7.3 Hz, CH_2), 33.2 (CH_2), 23.1 (CH_2), 12.1 (CH_3) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 4.2 (PPh_2), –143.0 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

[RuCp{η³-(P,C,C)-PPh₂CHC–(CH₂)₃–η²-(C,C)-CCHNC₅H₁₀}]PF₆ (3c): This complex has been prepared analogously to **3a** with **1c** (105 mg, 0.16 mmol) and 1,6-heptadiyne (19 μL, 0.17 mmol) as the starting materials. Yield: 74 mg (69%). $C_{29}H_{33}F_6NP_2Ru$ (672.59): calcd. C 51.79, H 4.95, N 2.08; found C 51.87, H 5.09, N 2.14. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.72–7.31 (m, 10 H, Ph), 5.14 (s, 5 H, Cp), 4.03 (d, $^2J_{HP}$ = 4.7 Hz, 1 H, H^1), 3.30 (d, J_{HP} = 5.7 Hz, 1 H, H^4), 3.24–3.09 (m, 1 H), 2.99–2.64 (m, 5 H), 2.39–2.13 (m, 4 H), 1.63–1.37 (m, 6 H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 133.6 (d, $^2J_{CP}$ = 11.9 Hz, Ph^{2,6}), 132.2 (d, $^2J_{CP}$ = 12.3 Hz, Ph$^{2',6'}$), 132.2 (d, $^4J_{CP}$ = 3.3 Hz, Ph^4), 131.4–131.6 (d, $^4J_{CP}$ = 3.4 Hz, Ph$^{4'}$), 129.7 (d, $^3J_{CP}$ = 12.3 Hz, Ph^{3,5}), 129.7 (d, $^3J_{CP}$ = 12.3 Hz, Ph^{3,5}), 129.0 (d, $^3J_{CP}$ = 12.3 Hz, Ph$^{3',5'}$), 126.5 (d, $^1J_{CP}$ = 50.6 Hz, Ph^1), 117.8 (d, J_{CP} = 3.8 Hz, C^3), 116.8 (d, J_{CP} = 5.8 Hz, C^4), 79.1 (d, J_{CP} = 1.5 Hz, Cp), 76.1 (C^2), 52.4 (CH_2), 41.3 (d, J_{CP} = 24.2 Hz, C^1), 35.7 (d, J_{CP} = 6.9 Hz, CH_2), 33.3 (CH_2), 24.9 (CH_2), 23.2 (CH_2), 23.1 (CH_2) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 8.1 (PPh_2), –142.9 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

Reaction of 1b with 1,7-Octadiyne in CD_2Cl_2. Formation of [RuCp{η³-(P,C,C)–PPh₂–CH–C(CH₂)₄-η²-(C,C)-CCHNEt₂}]PF₆ (3d) and [RuCp{η¹-(P)-PPh₂–CH=C(CH₂)₄-η³-(C,C,N)-CCHNEt₂}]PF₆ (4e): A 5-mm NMR tube was charged with **1b** (30 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) and 1,7-octadiyne (6,1 μL, 0.05 mmol) was added by syringe. The reaction was then monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 20 min both **3d** and **4e** were formed in an approximately 3:1 ratio. After 5 h this ratio changed to about 1:6. Because of spectral overlap with **4e** only the most characteristic signals of **3d** could be unequivocally assigned. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 5.10 (s, 5 H, Cp), 3.53 (d, $^2J_{HP}$ = 4.7 Hz, 1 H, H^1), 2.90 (d, J_{HP} = 7.6 Hz, 1 H, H^4), 0.83 (t, J_{HH} = 7.1 Hz, 6 H, Et) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 3.3 (PPh_2), –143.0 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm. After heating at 40 °C for 8 h, the **3d** was completely converted to **4e**.

Reaction of 1c with 1,7-Octadiyne in CD_2Cl_2. Formation of [RuCp-{η³-(P,C,C)–PPh₂–CH–C(CH₂)₄-η²-(C,C)-CCHNC₅H₁₀}]PF₆ (3e) and [RuCp{η¹-(P)-PPh₂–CH=C(CH₂)₄-η³-(C,C,N)-CCHNC₅H₁₀}]PF₆ (4f): A 5-mm NMR tube was charged with **1c** (34 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) and 1,7-octadiyne (6,1 μL, 0.05 mmol) was added by syringe. The reaction was then monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 30 min both **3e** and **4f** were formed in an approximately 8:1 ratio. After 5 h this ratio changed to about 3:1. Because of spectral overlap with **4f** only the most characteristic signals of **3e** could be unequivocally assigned. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 5.20 (s, 5 H, Cp), 3.51 (d, $^2J_{HP}$ = 5.1 Hz, 1 H, H^1), 2.62 (d, J_{HP} = 7.0 Hz, 1 H, H^4) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 7.9 (PPh_2), –142.9 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm. After heating at 40 °C for 8 h, **3e** was completely converted to **4f**.

[RuCp{η¹-(P)-PPh₂CH=C–(CH₂)₃–η³-(C,C,N)-CCHNH*n*Pr}]PF₆ (4a): A stirred solution of **3a** (50 mg, 0,08 mmol) in CH_3NO_2 (5 mL) was kept at 90 °C for 3 h. After removal of the solvent under reduced pressure, an orange solid was obtained which was washed with Et_2O (5 mL), and dried under vacuum. Yield: 37 mg (73%). $C_{27}H_{31}F_6NP_2Ru$ (646.56): calcd. C 50.16, H 4.83, N 2.17; found C 49.68, H 4.82, N 2.23. ^{1}H NMR (CD_3NO_2, 20 °C): δ = 8.01–7.87 (m, 2 H, Ph), 7.68–7.45 (m, 6 H, Ph), 7.33–7.18 (m, 2 H, Ph), 6.02 (1 H, H^4), 5.98 (d, J_{HP} = 10.1 Hz, 1 H, H^1), 4.85 (s, 5 H, Cp), 3.06–2.89 (m, 1 H), 2.86–2.40 (m, 5 H), 2.21–2.00 (m, 2 H), 1.47–1.11 (m, 2 H), 0.59 (t, J_{HH} = 7.4 Hz, 3 H) ppm. The NH proton could not be detected. ^{13}C{^{1}H} NMR (CD_3NO_2, 20 °C): δ = 170.1 (d, J_{CP} = 29.1 Hz, C^3), 136.4 (d, $^1J_{CP}$ = 52.1 Hz, Ph^1), 134.2 (d, $^2J_{CP}$ = 11.5 Hz, Ph^{2,6}), 131.3 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 131.2 (d, $^1J_{CP}$ = 41.4 Hz, Ph$^{1'}$), 130.4 (d, $^2J_{CP}$ = 11.1 Hz, Ph$^{2',6'}$), 130.0 (d, $^4J_{CP}$ = 2.7 Hz, Ph$^{4'}$), 128.8 (d, $^3J_{CP}$ = 10.4 Hz, Ph^{3,5}), 128.7 (d, $^3J_{CP}$ = 11.1 Hz, Ph$^{3',5'}$), 111.9 (d, J_{CP} = 47.2 Hz, C^1), 85.8 (d, J_{CP} = 1.9 Hz, C^2), 81.3 (d, J_{CP} = 1.9 Hz, Cp), 74.4 (C^4), 57.5 (CH_2), 35.6 (CH_2), 28.9 (d, J_{CP} = 19.2 Hz, CH_2), 25.2 (CH_2), 24.1 (CH_2), 9.6 (CH_3) ppm. ^{31}P{^{1}H} NMR (CD_3NO_2, 20 °C): δ = 70.3 (PPh_2), –143.2 ($^1J_{FP}$ = 707.4 Hz, PF_6) ppm.

[RuCp{η¹-(P)-PPh₂CH=C–(CH₂)₃–η³-(C,C,N)-CCHNEt₂}]PF₆ (4b): A stirred solution of **3b** (50 mg, 0,08 mmol) in CH_3NO_2 (5 mL) was kept overnight at 80 °C. After removal of the solvent under reduced pressure, an orange solid was obtained, which was

washed with Et_2O (5 mL), and dried under vacuum. Yield: 45 mg (85%). $C_{28}H_{33}F_6NP_2Ru$ (660.58): calcd. C 50.91, H 5.04, N 2.12; found C 50.60,; H 4.98, N 2.00. ^1H NMR (CD_3NO_2, 20 °C): δ = 8.08–7.88 (m, 2 H, Ph), 7.73–7.34 (m, 6 H, Ph), 7.33–7.16 (m, 2 H, Ph), 6.35 (d, J_{HP} = 9.8 Hz, 1 H, H^1), 6.03 (s, 1 H, H^4), 4.76 (s, 5 H, Cp), 3.72–3.51 (m, 1 H), 3.03–2.44 (m, 4 H), 2.27–1.84 (m, 5 H), 1.21 (t, J_{HH} = 7.1 Hz, 3 H), 0.81 (t, J_{HH} = 7.1 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (CD_3NO_2, 20 °C): δ = 172.0 (d, J_{CP} = 27.2 Hz, C^3), 137.5 (d, $^1J_{CP}$ = 54.4 Hz, Ph^1), 134.0 (d, $^2J_{CP}$ = 12.3 Hz, $Ph^{2,6}$), 131.6 (d, $^1J_{CP}$ = 47.2 Hz, $Ph^{1'}$), 131.3 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 130.4 (d, $^2J_{CP}$ = 10.7 Hz, $Ph^{2',6'}$), 129.9 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 128.7 (d, $^3J_{CP}$ = 10.0 Hz, $Ph^{3,5}$), 128.6 (d, $^3J_{CP}$ = 10.7 Hz, $Ph^{3',5'}$), 117.4 (d, J_{CP} = 47.9 Hz, C^1), 91.3 (d, J_{CP} = 3.1 Hz, C^2), 82.2 (d, J_{CP} = 1.9 Hz, Cp), 79.1 (d, J_{CP} = 1.5 Hz, C^4), 58.3 (CH_2), 44.1 (d, J_{CP} = 8.8 Hz, CH_2), 38.4 (CH_2), 28.8 (d, J_{CP} = 19.6 Hz, CH_2), 25.1 (CH_2), 13.8 (CH_3), 12.1 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 74.1 (PPh_2), –143.3 ($^1J_{FP}$ = 707.1 Hz, PF_6) ppm.

[RuCp{η¹-(P)-PPh₂CH=C–(CH₂)₃–η³-(C,C,N)-CCHNC₅H₁₀}]PF₆ (4c): A stirred solution of **3c** (50 mg, 0,07 mmol) in CH_3NO_2 (5 mL) was kept at 90 °C for 3 h. After removal of the solvent under reduced pressure, an orange solid was obtained, which was washed with Et_2O (5 mL) and dried under vacuum. Yield: 38 mg (81%). $C_{29}H_{33}F_6NP_2Ru$ (672.59): calcd. C 51.79, H 4.95, N 2.08; found C 51.33, H 5.03, N 2.11. ^1H NMR (CD_3NO_2, 20 °C): δ = 8.06–7.89 (m, 2 H, Ph), 7.68–7.32 (m, 6 H, Ph), 7.30–7.14 (m, 2 H, Ph), 6.33 (d, J_{HP} = 9.8 Hz, 1 H, H^1), 6.12 (1 H, H^4), 4.73 (s, 5 H, Cp), 3.39–3.05 (m, 2 H), 2.99–0.96 (m, 14 H) ppm. $^{13}C\{^1H\}$ NMR (CD_3NO_2, 20 °C): δ = 171.7 (d, J_{CP} = 28.0 Hz, C^3), 137.8 (d, $^1J_{CP}$ = 54.1 Hz, Ph^1), 134.1 (d, $^2J_{CP}$ = 11.9 Hz, $Ph^{2,6}$), 131.9 (d, $^1J_{CP}$ = 44.9 Hz, $Ph^{1'}$), 131.2 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 130.3 (d, $^2J_{CP}$ = 10.7 Hz, $Ph^{2',6'}$), 129.8 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 128.9 (d, $^3J_{CP}$ = 10.0 Hz, $Ph^{3,5}$), 128.6 (d, $^3J_{CP}$ = 10.4 Hz, $Ph^{3',5'}$), 117.3 (d, J_{CP} = 47.9 Hz, C^1), 91.5 (d, J_{CP} = 3.1 Hz, C^2), 82.3 (d, J_{CP} = 1.9 Hz, Cp), 79.0 (C^4), 68.0 (CH_2), 52.6 (d, J_{CP} = 7.7 Hz, CH_2), 38.1 (CH_2), 28.9 (d, J_{CP} = 19.9 Hz, CH_2), 27.3 (CH_2), 24.8 (d, J_{CP} = 1.5 Hz, CH_2), 22.3 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2, 20 °C): δ = 73.3 (PPh_2), –143.2 ($^1J_{FP}$ = 707.1 Hz, PF_6) ppm.

[RuCp{η¹-(P)-PPh₂–CH=C–(CH₂)₄–η³-(C,C,N)-CH–N*n*Pr}]PF₆ (4d): 1.1 equiv. of 1,7-octadiyne (21.9 μL, 0.17 mmol) was added to a solution of **1a** (100 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) and the mixture was heated for 8 h at 40 °C. After removal of the solvent under reduced pressure, an orange solid was obtained, which was washed with Et_2O (5 mL) and dried under vacuum. Yield: 82 mg (78%). $C_{29}H_{35}F_6NP_2Ru$ (674.61): calcd. C 51.63, H 5.23, N 2.08; found C 51.60, H 5.11, N 2.04. ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.92–7.76 (m, 2 H, Ph), 7.68–7.40 (m, 6 H, Ph), 7.37–7.20 (m, 2 H, Ph), 6.17 (d, J_{HP} = 7.1 Hz, 1 H, H^4), 5.95 (d, $^2J_{HP}$ = 10.1 Hz, 1 H, H^1), 4.78 (s, 5 H, Cp), 3.16–2.88 (m, 2 H), 2.84–2.62 (m, 1 H), 2.47–2.07 (m, 4 H), 1.94–1.61 (m, 2 H), 1.57–1.23 (m, 3 H), 0.72 (t, J_{HH} = 7.4 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 165.8 (d, J_{CP} = 26.5 Hz, C^3), 136.5 (d, $^1J_{CP}$ = 52.5 Hz, Ph^1), 134.1 (d, $^2J_{CP}$ = 11.9 Hz, $Ph^{2,6}$), 131.8 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 130.9 (d, $^1J_{CP}$ = 48.7 Hz, $Ph^{1'}$), 130.4 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 130.3 (d, $^2J_{CP}$ = 11.5 Hz, $Ph^{2',6'}$), 129.2 (d, $^3J_{CP}$ = 10.4 Hz, $Ph^{3,5}$), 129.0 (d, $^3J_{CP}$ = 10.7 Hz, $Ph^{3',5'}$), 119.9 (d, J_{CP} = 46.0 Hz, C^1), 84.2 (d, J_{CP} = 1.9 Hz, C^2), 81.8 (d, J_{CP} = 1.9 Hz, Cp), 72.0 (C^4), 57.6 (CH_2), 41.1 (CH_2), 35.7 (d, J_{CP} = 20.3 Hz, CH_2), 29.1 (CH_2), 27.7 (CH_2), 24.7 (CH_2), 10.4 (CH_3) ppm.

[RuCp{η¹-(P)-PPh₂–CH=C–(CH₂)₄–η³-(C,C,N)-CH–NEt₂}]PF₆ (4e): This complex was prepared analogously to **4d** with **1b** (100 mg, 0.15 mmol) and 1,7-octadiyne (20.8 μL, 0.17 mmol) as starting materials. Yield: 56 mg (55%). $C_{30}H_{37}F_6NP_2Ru$ (688.64): calcd. C 52.33 H 5.42, N 2.03; found C 52.25, H 5.46, N 2.12.^1H NMR (CD_2Cl_2, 20 °C): δ = 7.96–7.79 (m, 2 H, Ph), 7.66–7.39 (m, 6 H, Ph), 7.34–7.18 (m, 2 H, Ph), 6.21 (d, J_{HP} = 9.8 Hz, 1 H, H^1), 6.06 (s, 1 H, H^4), 4.69 (s, 5 H, Cp), 3.78–3.57 (m, 1 H), 3.28–3.12 (m, 1 H), 2.72–2.40 (m, 2 H), 2.34–1.68 (m, 8 H), 1.22 (t, J_{HH} = 7.0 Hz, 3 H), 0.89 (t, J_{HH} = 7.1 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 169.5 (d, J_{CP} = 25.3 Hz, C^3), 137.8 (d, $^1J_{CP}$ = 54.1 Hz, Ph^1), 134.1 (d, $^2J_{CP}$ = 12.3 Hz, $Ph^{2,6}$), 131.8 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 131.1 (d, $^1J_{CP}$ = 45.6 Hz, $Ph^{1'}$), 130.3 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 130.3 (d, $^2J_{CP}$ = 10.7 Hz, $Ph^{2',6'}$), 129.0 (d, $^3J_{CP}$ = 10.3 Hz, $Ph^{3,5}$), 122.5 (d, J_{CP} = 48.0 Hz, C^1), 90.8 (d, J_{CP} = 2.7 Hz, C^2), 82.7 (d, J_{CP} = 1.9 Hz, Cp), 79.8 (C^4), 58.4 (CH_2), 44.9 (CH_2), 43.8 (d, J_{CP} = 6.5 Hz, CH_2), 36.2 (d, J_{CP} = 21.5 Hz, CH_2), 29.9 (CH_2), 28.3 (CH_2), 14.2 (CH_3), 12.9 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 76.3 (PPh_2), –142.9 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

[RuCp{η¹-(P)-PPh₂–CH=C–(CH₂)₄–η³-(C,C,N)-CH–NC₅H₁₀}]PF₆ (4f): This complex was prepared analogously to **4d** with **1b** (100 mg, 0.15 mmol) and 1,7-octadiyne (20.8 μL, 0.17 mmol) as starting materials. Yield: 72 mg (70%). $C_{30}H_{35}F_6NP_2Ru$ (686.62): calcd. C 52.48, H 5.14, N 2.04; found C 52.27, H 5.18, N 2.18. ^1H NMR (CD_2Cl_2, 20 °C): δ = 8.00–7.77 (m, 2 H, Ph), 7.72–7.36 (m, 6 H, Ph), 7.33–7.14 (m, 2 H, Ph), 6.18 (d, $^2J_{HP}$ = 9.5 Hz, 1 H, H^1), 6.14 (1 H, H^4), 4.68 (s, 5 H, Cp), 3.41–3.07 (m, 3 H), 2.66–2.40 (m, 1 H), 2.38–1.51 (m, 11 H), 1.43–0.99 (m, 3 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 169.3 (d, J_{CP} = 25.7 Hz, C^3), 138.1 (d, $^1J_{CP}$ = 53.7 Hz, Ph^1), 134.2 (d, $^2J_{CP}$ = 12.3 Hz, $Ph^{2,6}$), 131.7 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 131.3 (d, $^1J_{CP}$ = 45.6 Hz, $Ph^{1'}$), 130.2 (d, $^2J_{CP}$ = 11.1 Hz, $Ph^{2',6'}$), 130.1 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 129.2 (d, $^3J_{CP}$ = 10.0 Hz, $Ph^{3,5}$), 128.9 (d, $^3J_{CP}$ = 10.7 Hz, $Ph^{3',5'}$), 122.2 (d, J_{CP} = 47.5 Hz, C^1), 91.0 (d, J_{CP} = 2.7 Hz, C^2), 82.7 (d, J_{CP} = 1.9 Hz, Cp), 77.2 (C^4), 68.7 (CH_2), 44.6 (CH_2), 36.5 (d, J_{CP} = 21.5 Hz, CH_2), 30.0 (CH_2), 28.3 (CH_2), 27.9 (CH_2), 27.4 (CH_2), 22.7 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 76.2 (PPh_2), –142.9 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

[RuCp{=C(NEt₂)-η²-(C,C)-C–(CH₂)₃–CCH₂-(η¹-(P)-PPh₂)}]PF₆ (5a): A solution of **4b** (96 mg, 0.15 mmol) in acetonitrile was heated at 90 °C for 12 h. After removal of the solvent under reduced pressure, an orange solid was obtained, which was washed with Et_2O (5 mL) and dried under vacuum. Yield: 70 mg (71%). $C_{29}H_{35}F_6NP_2Ru$ (688.64): calcd. C 52.33, H 5.42, N 2.03; found C 52.57, H 5.27, N 2.11. ^1H NMR (CD_3CN, 20 °C): δ = 7.68–7.31 (m, 10 H, Ph), 4.95 (s, 5 H, Cp), 4.06–3.79 (m, 3 H, CH_2, H^1), 3.77–3.47 (m, 3 H, CH_2, $H^{1'}$), 2.82–2.55 (m, 2 H), 2.27–2.07 (m, 1 H), 2.03–1.74 (m, 2 H), 1.58–1.35 (m, 1 H), 1.12 (t, J_{HH} = 7.3 Hz, 3 H), 0.84 (t, J_{HH} = 7.3 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ = 225.2 (d, J_{CP} = 13.0 Hz, C^4), 137.5 (d, $^1J_{CP}$ = 46.8 Hz, Ph^1), 132.4 (d, $^2J_{CP}$ = 12.3 Hz, $Ph^{2,6}$), 131.3 (d, $^1J_{CP}$ = 36.0 Hz, $Ph^{1'}$), 131.0 (d, $^2J_{CP}$ = 11.5 Hz, $Ph^{2',6'}$), 130.9 (d, $^4J_{CP}$ = 3.1 Hz, Ph^4), 130.4 (d, $^4J_{CP}$ = 3.1 Hz, $Ph^{4'}$), 128.9 (d, $^3J_{CP}$ = 10.7 Hz, $Ph^{3,5}$), 128.6 (d, $^3J_{CP}$ = 10.7 Hz, $Ph^{3',5'}$), 83.3 (Cp), 73.8 (d, J_{CP} = 16.1 Hz, C^2), 71.7 (d, J_{CP} = 3.1 Hz, C^3), 51.7 (d, J_{CP} = 26.8 Hz, CH_2), 37.7 (d, J_{CP} = 7.7 Hz, CH_2), 37.0 (d, J_{CP} = 35.3 Hz, CH_2, C^1), 32.7 (CH_2), 22.5 (CH_2), 13.2 (CH_3), 12.4 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ = –34.3 (PPh_2), –143.1 ($^1J_{FP}$ = 706.8 Hz, PF_6) ppm.

Isomerization of 3c to 4c and [RuCp{=C(NC₅H₁₀)-η²-(C,C)-C–(CH₂)₃–CCH₂-(η¹-(P)-PPh₂)}]PF₆ (5b): A 5-mm NMR tube was charged with **3c** (30 mg, 0.04 mmol) in CD_3CN (0.5 mL) and heated to 90 °C. The reaction was then monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 48 h both **4c** and **5b** were formed in an approximately 3:1 ratio. Because of spectral overlap

with **4c** only the most characteristic signals of **5b** could be unequivocally assigned. ^{1}H NMR (CD_3CN, 20 °C): δ = 4.93 (s, 5 H, Cp), 3.66–3.49 (m, 2 H, H^1) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 20 °C): δ = 222.9 (d, J_{CP} = 12.3 Hz, C^4), 83.2 (Cp), 74.3 (d, J_{CP} = 16.9 Hz, C^2), 71.2 (C^3), 36.7 (d, J_{CP} = 35.3 Hz, CH_2, C^1) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ = –37.8 (PPh_2), –144.6 ($^1J_{FP}$ = 707.7 Hz, PF_6) ppm.

[RuCp*{η^1-(N)-N*n*PrPPh$_2$–η^4-CH=C–(CH$_2$)$_3$–C=CH$_2$}]PF$_6$ (6a): 1 equiv. of 1,6-heptadiyne (16 μL, 0.14 mmol) was added to a solution of **2a** (100 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred for 2 h at room temperature. After that the volume of the solution was reduced to about 1 mL and Et_2O (5 mL) was added whereupon a precipitate was formed. The yellow solid was washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 68 mg (68%). $C_{32}H_{41}F_6NP_2Ru$ (716.69): calcd. C 53.63, H 5.77, N 1.95; found C 54.01, H 5.56, N 2.06. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.78–7.32 (m, 10 H, Ph), 3.88 (d, J_{HH} = 3.5 Hz, 1 H, H^4), 3.52–3.31 (m, 2 H), 3.18 (d, $^2J_{HP}$ = 16.3 Hz, 1 H, H^1), 2.64 (d, J_{HH} = 3.3 Hz, 1 H, $H^{4'}$), 2.56–2.40 (m, 1 H), 2.39–2.28 (m, 2 H), 2.27–2.06 (m, 3 H), 1.67 (s, 15 H, Cp*), 1.34–1.20 (m, 2 H), 0.70 (t, J_{HH} = 7.3 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 133.5–128.5 (Ph), 119.1 (C^2), 112.5 (C^3), 98.1 (Cp*), 50.4 (CH_2), 46.7 (C^4), 37.0 (d, J_{CP} = 7.7 Hz, CH_2), 35.3 (CH_2), 29.8 (CH_2), 22.0 (d, J_{CP} = 112.7 Hz, C^1), 20.5 (CH_2), 11.2 (CH_3), 9.2 (Cp*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 47.5 (PPh_2), –144.4 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

[RuCp*{η^1-(N)-N*n*PrPPh$_2$–η^4-CH=C–(CH$_2$)$_4$–C=CH$_2$}]PF$_6$ (6b): This complex was prepared analogously to **6a** with **2a** (100 mg, 0.14 mmol) and 1,7-octadiyne (19 μL, 0.14 mmol) as the starting materials. Yield: 64 mg (63%). $C_{33}H_{43}F_6NP_2Ru$ (730.72): calcd. C 54.24, H 5.93, N 1.29; found C 54.35, H 5.88, N 1.22. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.78–7.26 (m, 10 H, Ph), 3.70 (d, J_{HH} = 3.5 Hz, 1 H, H^4), 3.15–2.87 (m, 2 H), 2.76 (d, $^2J_{HP}$ = 13.6 Hz, 1 H, H^1), 2.61–2.28 (m, 2 H), 2.43 (d, J_{HH} = 3.8 Hz, 1 H, $H^{4'}$), 1.90–1.72 (m, 4 H), 1.69 (s, 15 H, Cp*), 1.59–1.49 (m, 4 H), 0.74 (t, J_{HH} = 7.3 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 135.9–126.9 (Ph), 113.3 (C^2), 105.4 (C^3), 99.1 (Cp*), 51.3 (d, J_{CP} = 3.1 Hz, CH_2), 48.6 (C^4), 30.7 (d, J_{CP} = 8.4 Hz, CH_2), 30.4 (CH_2), 29.7 (CH_2), 23.5 (d, J_{CP} = 108.1 Hz, C^1), 21.7 (d, J_{CP} = 1.2 Hz, CH_2), 21.4 (CH_2), 11.2 (CH_2), 9.5 (Cp*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 55.7 (PPh_2), –142.9 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

Reaction of 2b with 1,6-Heptadiyne in CD_2Cl_2. Formation of [RuCp*{η^3-(P,C,C)–PPh$_2$–CH–C(CH$_2$)$_4$–η^2-(C,C)-CCHNEt$_2$}]PF$_6$ (7) and [RuCp*{η^1-(P)-PPh$_2$–CH=C–(CH$_2$)$_3$–η^3-(C,C,N)-CCHNEt$_2$}]PF$_6$ (8a): A 5-mm NMR tube was charged with **2b** (56 mg, 0.08 mmol) in CD_2Cl_2 (0.5 mL) and 1,6-heptadiyne (8.9 μL, 0.08 mmol) was added by syringe. The reaction was then monitored by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. After 10 min both **7** and **8a** were formed in an approximately 1:1 ratio. Because of spectral overlap with one another only the most characteristic signals of **7** and **8a** could be unequivocally assigned. **7:** ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 4.17 (d, $^2J_{HP}$ = 4.3 Hz, 1 H, H^1), 3.7 (d, J_{HP} = 4.4 Hz, 1 H, H^4), 1.67 (d, J_{HP} = 1.9 Hz, 15 H, Cp*) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = –10.0 (PPh_2), –144.4 ($^1J_{FP}$ = 710.2 Hz, PF_6). **8a**: ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 6.08 (d, $^2J_{HP}$ = 8.4 Hz, 1 H, H^1), 5.17 (s, 1 H, H^4), 1.48 (d, J_{HP} = 1.6 Hz, 15 H, Cp*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 67.8 (PPh_2), –144.4 ($^1J_{FP}$ = 710.2 Hz, PF_6) ppm.

[RuCp*{η^1-(P)-PPh$_2$CH=C–(CH$_2$)$_3$–η^3-(C,C,N)-C=CH–N-(CH$_2$)$_5$}]PF$_6$ (8b): 1,6-Heptadiyne (16 μL, 0.14 mol) was added to a solution of **2c** (100 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred for 2 h at room temperature. The volume of the solution was then reduced to about 1 mL. Addition of 5 mL of Et_2O resulted in the formation of a yellow precipitate, which was washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 83 mg (82%). $C_{34}H_{43}F_6NP_2Ru$ (742.73): calcd. C 54.98, H 5.84, N 1.89; found C 54.84, H 5.76, N 1.93. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.76–6.99 (m, 10 H, Ph), 6.05 (d, J_{HP} = 8.7 Hz, 1 H, H^1), 5.07 (s, 1 H, H^4), 3.23–2.92 (m, 2 H), 2.88–2.69 (m, 2 H), 2.66–2.43 (m, 2 H), 2.41–1.92 (m, 3 H), 1.91–1.53 (m, 3 H), 1.48 (s, 15 H, Cp*), 1.35–1.01 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 169.8 (d, J_{CP} = 28.4 Hz, C^3), 134.1 (d, $^1J_{CP}$ = 49.8 Hz, Ph^1), 132.3 (d, $^2J_{CP}$ = 10.7 Hz, $Ph^{2,6,2',6'}$), 131.6 (Ph^4), 131.5 (d, $^1J_{CP}$ = 40.6 Hz, $Ph^{1'}$), 130.3 ($C^{4'}$), 129.2 (d, $^3J_{CP}$ = 9.2 Hz, $Ph^{3,5}$), 128.7 (d, $^3J_{CP}$ = 9.2 Hz, $Ph^{3',5'}$), 119.7 (d, $^1J_{CP}$ = 46.0 Hz, C^1), 92.8 (Cp*), 91.4 (d, J_{CP} = 3.1 Hz, C^2), 85.9 (C^4), 64.7 (CH_2), 51.4 (d, J_{CP} = 6.9 Hz, CH_2), 36.5 (CH_2), 29.1 (d, J_{CP} = 19.2 Hz, CH_2), 27.7 (d, J_{CP} = 17.6 Hz, CH_2), 25.7 (CH_2), 22.8 (CH_2), 9.6 (Cp*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 68.7 (PPh_2), –144.4 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

[RuCp*{η^1-(P)-PPh$_2$CH=C–(CH$_2$)$_4$–η^3-(C,C,N)-C=CH–NEt$_2$}]PF$_6$ (8c): This complex was prepared analogously to **8b** with **2b** (100 mg, 0.14 mmol) and 1,7-octadiyne (16 μL, 0.14 mmol) as the starting materials. Yield: 75 mg (72%). $C_{34}H_{45}F_6NP_2Ru$ (744.74): calcd. C 54.83, H 6.09, N 1.88; found C 54.62, H 6.19, N 1.98. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.90–7.10 (m, 10 H, Ph), 6.08 (d, $^2J_{HP}$ = 8.5 Hz, 1 H, H^1), 5.22 (s, 1 H, H^4), 3.58 (m, 1 H), 3.16 (m, 1 H′), 2.59 (m, 1 H), 2.27–1.94 (m, 5 H), 1.93–1.53 (m, 4 H), 1.46 (d, J_{HP} = 1.8 Hz 15 H, Cp*), 1.16 (t, J_{HH} = 7.2 Hz, 3 H, CH_3), 0.84 (t, J_{HH} = 7.2 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 167.1 (d, J_{CP} = 26.8 Hz, C^3), 134.6 (d, $^1J_{CP}$ = 49.8 Hz, Ph^1), 132.5 (d, $^2J_{CP}$ = 10.7 Hz, $Ph^{2,6,2',6'}$), 131.7 (d, $^1J_{CP}$ = 41.4 Hz, $Ph^{1'}$), 131.6 (d, J_{CP} = 2.3 Hz, Ph^4), 130.4 (d, J_{CP} = 3.1 Hz, $Ph^{4'}$), 128.9 (d, J_{CP} = 9.2 Hz, $Ph^{3,5}$), 128.7 (d, J_{CP} = 10.0 Hz, $Ph^{3',5'}$), 126.1 (d, J_{CP} = 46.8 Hz, C^1), 92.9 (Cp*), 88.9 (d, J_{CP} = 3.1 Hz, C^2), 88.1 (C^4), 55.7 (CH_2), 42.0 (CH_2), 41.7 (d, J_{CP} = 6.1 Hz, CH_2), 35.9 (d, J_{CP} = 20.7 Hz, CH_2), 29.6 (CH_2), 27.9 (CH_2), 12.8 (CH_3), 12.6 (CH_3), 9.2 (Cp*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 70.5 (PPh_2), –144.4 ($^1J_{FP}$ = 710.5 Hz, PF_6) ppm.

[RuCp*{η^1-(P)-PPh$_2$CH=C–(CH$_2$)$_4$–η^3-(C,C,N)-C=CH–N-(CH$_2$)$_5$}]PF$_6$ (8d): This complex was prepared analogously to **8b** with **2c** (100 mg, 0.14 mmol) and 1,7-octadiyne (19 μL, 0.14 mmol) as the starting materials. Yield: 80 mg (77%). $C_{35}H_{45}F_6NP_2Ru$ (756.75): calcd. C 55.55, H 5.99, N 1.85; found C 56.00, H 5.89, N 1.69. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.77–7.32 (m, 10 H, Ph), 6.02 (d, J_{HP} = 8.5 Hz, 1 H, H^1), 5.17 (s, 1 H, H^4), 3.18–2.90 (m, 4 H), 2.48–2.20 (m, 2 H), 2.19–2.96 (m, 4 H), 1.90–1.50 (m, 6 H), 1.45 (d, J_{HP} = 1.7 Hz, 15 H, Cp*), 1.39–1.24 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 166.4 (d, J_{CP} = 26.1 Hz, C^3), 134.7 (d, $^1J_{CP}$ = 49.8 Hz, Ph^1), 132.6 (d, $^2J_{CP}$ = 10.0 Hz, $Ph^{2,6}$), 132.2 (d, $^2J_{CP}$ = 9.2 Hz, $Ph^{2',6'}$), 131.6 (Ph^4), 131.6 (d, $^1J_{CP}$ = 48.3 Hz, $Ph^{1'}$), 130.4 ($C^{4'}$), 129.1 (d, $^3J_{CP}$ = 10.0 Hz, $Ph^{3,5}$), 128.7 (d, $^3J_{CP}$ = 10.0 Hz, $Ph^{3',5'}$), 126.2 (d, $^1J_{CP}$ = 46.0 Hz, C^1), 92.8 (Cp*), 89.5 (C^2), 84.4 (C^4), 65.2 (CH_2), 52.6 (d, J_{CP} = 4.6 Hz, CH_2), 45.8 (CH_2), 41.8 (CH_2), 36.1 (d, J_{CP} = 20.7 Hz, CH_2), 29.7 (CH_2), 28.0 (d, J_{CP} = 17.6 Hz, CH_2), 27.9 (CH_2), 23.0 (CH_2), 9.7 (Cp*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 72.2 (PPh_2), –144.4 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm.

Formation of [RuCp{κ^1(P)-PPh$_2$NHNMe$_2$}(CH$_3$CN)$_2$]PF$_6$ (9) and [RuCp{κ^2(P,N)-PPh$_2$NHNMe$_2$} (CH$_3$CN)]PF$_6$ (10): PPh_2NHNMe_2 (188 mg, 0.77 mmol) was added to a solution of $[RuCp(CH_3CN)_3]$-PF_6 (335 mg, 0.77 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred for 2 h at room temperature. The volume of the solution was then reduced to about 1 mL and Et_2O (5 mL) was added. A

yellow precipitate was formed, which was collected on a glass frit, washed with Et_2O (3 × 10 mL), and dried under vacuum. ^1H NMR spectroscopy revealed that **9** and **10** were formed in an approximately 5:1 ratio. If the same reaction was performed in the presence of acetonitrile (40 μL, 0.77 mmol), complex **9** was exclusively obtained. Yield: 398 mg (84%). $C_{23}H_{28}F_6N_4P_2Ru$ (637.51): calcd. C 43.33, H 4.43, N 8.79; found C 42.98; H 4.50, N 8.61. ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.74–7.54 (m, 4 H, Ph), 7.53–7.39 (m, 6 H, Ph), 4.45 (s, 5 H, Cp), 3.51 (d, $^2J_{HP}$ = 34.1 Hz, 1 H, N*H*), 2.27 (6 H, CH_3), 2.26 (d, J_{HP} = 1.3 Hz, 6 H, CH_3CN) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 136.2 (d, $^1J_{CP}$ = 51.7 Hz, Ph^1), 132.6 (d, $^2J_{CP}$ = 12.1 Hz, $Ph^{2,6}$), 130.2 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 127.9 (d, $^3J_{CP}$ = 9.8 Hz, $Ph^{3,5}$), 127.0 (CH_3CN), 76.4 (d, J_{CP} = 2.9 Hz, Cp), 49.9 (d, J_{CP} = 3.4 Hz, CH_3) 3.8 (d, J_{CP} = 1.2 Hz, CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 90.6 (PPh_2), –142.9 ($^1J_{FP}$ = 710.8 Hz, PF_6) ppm. All attempts to grow crystals of **9** were unsuccessful. Crystals of **10** were grown by diffusion of diethyl ether into a CH_2Cl_2 solution of the reaction mixture containing **9** and **10**. **10**: ^1H NMR (CD_2Cl_2, 20 °C): δ = 7.72–7.36 (m, 10 H, Ph), 4.48 (s, 5 H, Cp), 3.35 (s, 3 H, Me), 2.82 (s, 3 H, Me), 2.14 (d, J_{HP} = 1.6 Hz, CH_3CN) ppm. The NH proton could not be detected. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 132.9–128.5 (Ph), 128.1 (CH_3CN), 73.0 (Cp), 63.9 (CH_3), 57.8 (CH_3), 3.85 (CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ = 61.4 (PPh_2), –142.9 ($^1J_{FP}$ = 711.5 Hz, PF_6) ppm.

X-ray Structure Determination: Crystals of **1a**, **2a**, **3c**, **3f**, **4a**, **5a**, **6a**, **6b**, **8c·CH_2Cl_2**, **8d**, and **10** were obtained by diffusion of Et_2O or pentane into CH_2Cl_2 solutions. Crystal data and experimental details are given in Table 1 and Table 2. X-ray data were collected with a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering mostly complete spheres of the reciprocal space. Corrections for absorption (multi-scan method), $\lambda/2$ effects, and crystal decay were applied.[24] The structures were solved by direct methods using the program SHELXS97.[25] Structure refinement on F^2 was carried out with the program SHELXL97.[24] 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.[26] Compound **6b** crystallizes in the acentric triclinic space group *P*1 (no. 1) with three independent Ru complexes in the unit cell. Two of these three complexes adopt a pseudocentric arrangement (pseudo space group $P\bar{1}$) while the third complex does not comply with this symmetry. In Figure 8 only the first of these three complexes is shown as a representative example.

CCDC-286740 to -286750 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: All calculations were performed using the Gaussian98 software package on the Silicon Graphics Origin 2000 of the Vienna University of Technology.[27] The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level[28] with the Stuttgart/Dresden ECP (SDD) basis set[29] to describe the electrons of the ruthenium atom. For the C, N, P, and H atoms the 6-31g** basis set was employed.[30] A vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequency. Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel et al.[31] Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. The vibrational eigenvectors corresponding to the reaction coordinate (with imaginary frequency) of all transition states were visually checked to confirm the connectivity of transition states with the reactants and the products. Crucial transition states have been confirmed by IRC calculations. All geometries were optimized without symmetry constraints.

Table 2. Details for the crystal structure determinations of complexes **6a**, **6b**, **8c·CH_2Cl_2**, **8d**, and **10**.

	6a	**6b**	**8c·CH_2Cl_2**	**8d**	**10**
Empirical formula	$C_{32}H_{41}F_6NP_2Ru$	$C_{33}H_{43}F_6NP_2Ru$	$C_{35}H_{47}Cl_2F_6NP_2Ru$	$C_{35}H_{45}F_6NP_2Ru$	$C_{21}H_{25}F_6N_3P_2Ru$
Formula mass	716.67	730.69	829.65	756.73	596.45
Crystal size [mm]	0.48 × 0.26 × 0.22	0.71 × 0.32 × 0.22	0.56 × 0.48 × 0.42	0.40 × 0.27 × 0.17	0.62 × 0.33 × 0.26
Space group	$P2_12_12_1$ (no. 19)	*P*1 (no. 1)	$Pna2_1$ (no. 33)	*Pbca* (no. 61)	$P2_12_12_1$ (no. 19)
a [Å]	9.8943(4)	10.9184(5)	17.2512(7)	18.9953(9)	7.9113(49)
b [Å]	16.3485(7)	12.1773(5)	13.7579(6)	18.2714(8)	15.3880(8)
c [Å]	19.3928(8)	20.3660(8)	15.7043(7)	19.2964(9)	19.3607(10)
α [°]	90	96.037(1)	90	90	90
β [°]	90	103.790(1)	90	90	90
γ [°]	90	109.460(1)	90	90	90
V [Å^3]	3136.9(2)	2428.6(2)	3727.3(3)	6697.2(5)	2357.0(2)
Z	4	3	4	8	4
ρ_{calcd} [g/cm^3]	1.517	1.499	1.478	1.501	1.681
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)
μ [mm^{-1}] (Mo-K_α)	0.661	0.642	0.706	0.623	0.863
F(000)	1472	1128	1704	3120	1200
θ_{max} [°]	30	30	30	30	30
Measured reflections	35175	45589	80284	96310	35290
Unique reflections	9048	28007	10830	9743	6675
No. of reflections $I > 2\sigma(I)$	8633	27374	10223	7562	6858
Parameters	385	1202	435	417	302
R_1 [$I > 2\sigma(I)$][a]	0.0313	0.0271	0.0288	0.0325	0.0211
R_1 (all data)	0.0335	0.0279	0.0325	0.0505	0.0219
wR_2 (all data)	0.0846	0.0714	0.0807	0.0765	0.0540
$\Delta\rho_{min/max}$ [e/Å^3]	–0.34/0.80	–0.42/0.94	–0.77/1.01	–0.34/0.46	–0.44/0.46

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2–F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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