Notes

Coupling of Alkynes Mediated by $[RuCp(PPh_2NHPh)(CH_3CN)_2]^+$: Formation of η^4-Butadiene Amido Complexes through Migration and N−H Activation of the PPh_2NHPh Ligand

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Summary: This is a continuation of our work on the reactions of $[RuCp(PR_3)(CH_3CN)_2]PF_6$ *with terminal alkynes and diynes. Here now we use, instead of* PR_3*, the phosphino-amine ligand* PPh_2NHPh*. The reaction pattern is found to be similar except that the N−H bond of the phosphine ligand is activated and not a C−H bond as before. Thus the reaction of* $[RuCp(PPh_2NHPh)(CH_3CN)_2]PF_6$ *with HC≡CR (R = Ph, n-Bu,* CH_2Ph*), 1,6-heptadiyne, and 1,7-octadiyne results in the formation of the* η^4*-butadiene amido complexes* $[RuCp(\eta^4\text{-}C_4H_3(R)_2\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$*,* $[RuCp(\eta^4\text{-}C_4H_3(CH_2)_3\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$*, and* $[RuCp(\eta^4\text{-}C_4H_3(CH_2)_4\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ *in good yields.*

Introduction

The labile complex $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = Me, Ph, Cy, etc.) is a useful starting material for a variety of transformations since it behaves as synthetic equivalent for the 14-electron fragment $[RuCp(PR_3)]^+$.[1] For instance, it reacts with many terminal alkynes to give ruthenium allyl carbenes.[2] These in turn appear as masked coordinatively unsaturated complexes that react readily with the donor ligands PR_3 and $P(OR)_3$ to give η^3-butadienyl complexes.[3] Furthermore, the ruthenium allyl carbenes are prone to convert into η^4-butadiene complexes according to Scheme 1.[4] The overall transformation is intriguing because of the involvement of phosphine migration and C−H bond activation in the phosphine substituent.

In this respect it was deemed worthwhile to switch over to the phosphino-amine ligand PPh_2NHPh instead of PR_3. Our intention was to see in what ways the course of reaction is changed when $[RuCp(PPh_2NHPh)(CH_3CN)_2]PF_6$ (**1**) is reacted with terminal alkynes and diynes. Specifically, will migration appear at the P or the N site? As another question, will there be N−H bond or C−H bond activation? These issues are addressed in the present contribution.

Results and Discussion

The starting complex **1** was obtained in 92% isolated yield by reacting $RuCp(CH_3CN)_3]PF_6$ with 1 equiv of PPh_2NHPh at room temperature. It is stable to air in the solid state but decomposes slowly in solutions exposed to air. The ^1H NMR spectrum bears no unusual features. The Cp ligand gives a singlet at 4.49 ppm. The NH proton of the PPh_2NHPh ligand gives rise to a doublet at 6.43 ppm ($^2J_{HP}$ = 8.37 Hz). In the $^{31}P\{^1H\}$ NMR spectrum the phosphino-amine ligand shows a singlet at 81.2 ppm.

Treatment of **1** with HC≡CR (R = Ph, *n*-Bu, CH_2Ph), 1,6-heptadiyne, and 1,7-octadiyne results in the formation of the η^4-butadiene amido complexes $[RuCp(\eta^4\text{-}C_4H_3(R)_2\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ (**2a**−**c**), $[RuCp(\eta^4\text{-}C_4H_3\text{-}(CH_2)_3\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ (**2d**), and $[RuCp(\eta^4\text{-}C_4H_3\text{-}(CH_2)_4\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ (**2e**) in 43−88% isolated yields (Schemes 2 and 3). These compounds, which are air-stable both in solution and in the solid state, were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy as well as elemental analysis. The ^1H NMR spectroscopic data for **2a** include characteristic resonances at 7.26 (d, $^3J_{HH}$ = 10.9 Hz, H^3), 4.81 (d, 1H, $^2J_{HP}$ = 15.8, H^1), and 4.47 (d, 1H, $^3J_{HH}$ = 10.9 Hz, H^4) assignable to the two terminal and the internal diene protons of the coordinated η^4-diene unit. 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 butadiene moiety exhibit resonances at 29.1 (d, $^1J_{CP}$ = 110.0 Hz), 114.2, 90.6, and 81.7 ppm, respectively. In the $^{31}P\{^1H\}$ NMR spectrum the phosphino-amine ligand exhibits a singlet at 46.2 ppm. Concurrent NMR spectra are observed for **2b**−**e**.

The solid state structures of **2b** and **2d** were determined by single-crystal X-ray diffraction. ORTEP diagrams are depicted in Figures 1 and 2, with important bond distances reported in the captions. The overall

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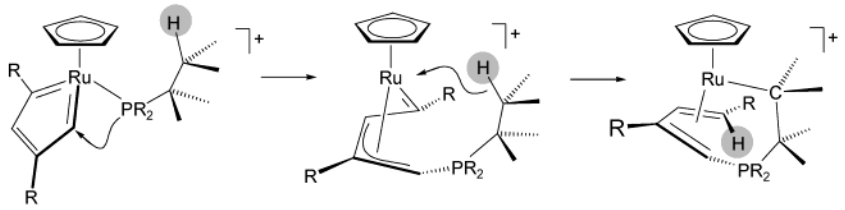
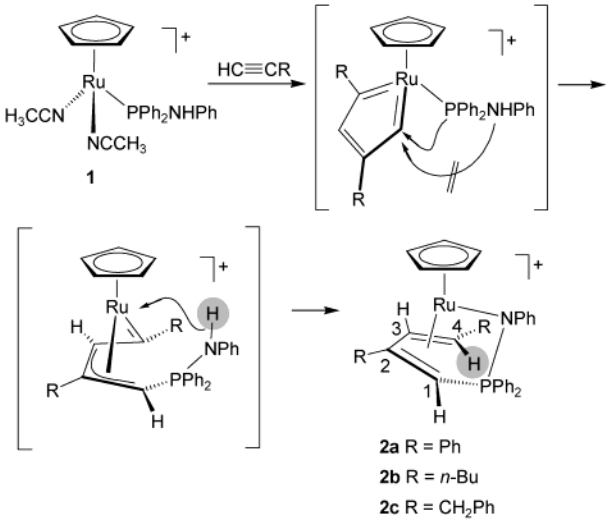
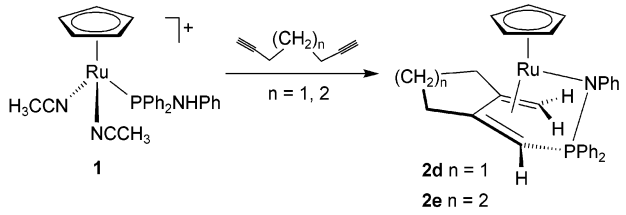
Scheme 1



Scheme 2



Scheme 3



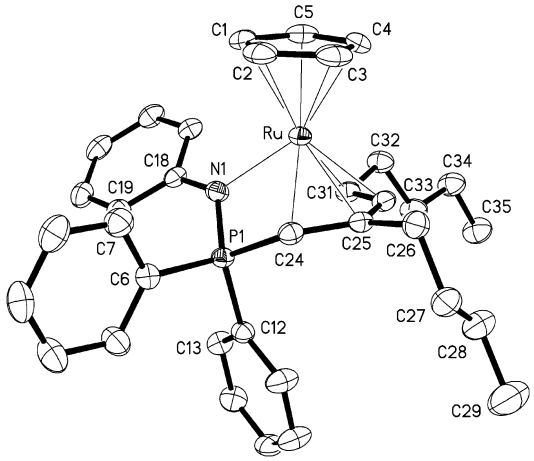


Figure 1. Structural view of [RuCp(η^4-C_4H_3(*n*-Bu)$_2$-PPh_2-κ^1-(N)-NPh)]PF_6 (**2b**) showing 50% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ 2.194(3), Ru−C(24) 2.229(3), Ru−C(25) 2.225(3), Ru−C(30) 2.181(3), Ru−C(31) 2.237(3), Ru−N(1) 2.173(2), N(1)−P(1) 1.599(2), C(24)−C(25) 1.416(4), C(25)−C(30) 1.427(4), C(30)−C(31) 1.406 (4), N(1)−Ru−C(24) 71.5-(1).

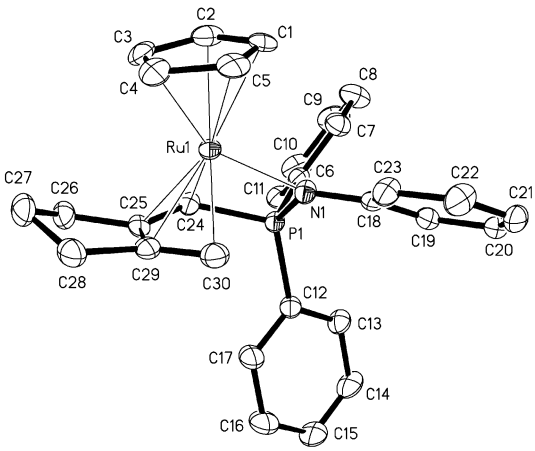


Figure 2. Structural view of [RuCp(η^4-$C_4H_3(CH_2)_3$-PPh_2-κ^1-(N)-NPh)]PF_6 (**2d**) showing 50% thermal ellipsoids (PF_6^- omitted for clarity). Only one of the two crystallographically independent complexes is shown. Selected bond lengths (Å) and angles (deg): Ru(1)−C(1−5)$_{av}$ 2.210(4), Ru(1)−C(24) 2.227(3), Ru(1)−C(25) 2.229(3), Ru(1)−C(29) 2.212(4), Ru-(1)−C(30) 2.217(4), Ru(1)−N(1) 2.145(3), N(1)−P(1) 1.605-(3), C(24)−C(25) 1.426(5), C(25)−C(29) 1.436(6), C(29)−C(30) 1.408 (6), N(1)−Ru(1)−C(24) 71.9(1).

structures of **2a** and **2d** are very similar and can be described as a three-legged piano stool conformation with the N atom of the PPh_2NHPh group and the two C=C bonds of the butadiene moiety as the legs.

In **2b** the butadiene C−C bonds C(24)−C(25), C(25)−C(30), and C(30)−C(31) reveal slightly alternating bond distances, i.e., a short−long−short pattern (1.416(4), 1.427(4), and 1.406(6) Å). Similar behavior is encountered in **2d** with C(24)−C(25), C(25)−C(29), and C(29)−C(30) being 1.426(5), 1.436(6), and 1.408(6) Å, respectively. The C_{1-4} chain in either compound is nearly planar, with a torsion angle of −4.4(5)°. All Ru−C distances are rather uniform, ranging from 2.181 to 2.237 Å. The Ru−N bonds in **2b** and **2d** are 2.173(2) and 2.145(3) Å, respectively, typical of a Ru−N amido single bond in Ru(II) complexes. For comparison, the Ru-amido nitrogen bond distances of $RuTp(CO)(PPh_3)$-(NHPh),[5] *cis*-$Ru(PMe_3)_4(H)$(NHPh),[6] and Ru(η^6-C_6Me_6)-(Ph)(PMe_3)(NHPh)[7] are 2.076(3), 2.160(4), and 2.121(3) Å, respectively. The N−Ru−C angles in **2b** and **2d** are 71.5(1)° and 71.9(1)°, respectively. The four-membered Ru−N−P−C ring system is essentially planar, with torsion angles of −3.8(1)° and −3.4(1)°.

For the present conversions, unfortunately, no intermediate products could be detected spectroscopically. However, it is plausible to speculate that the formation

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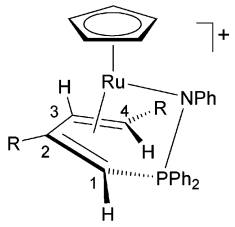
of the η^4-butadiene amido complexes proceeds via a metallacylopentatriene and an allyl carbene species as depicted in Scheme 2. Thus, there is migration of the κ^1(P)-coordinated PPh_2NHPh ligand analogously to the η^3-allyl carbene complex already described.[2c] In contrast, however, instead of a C−H bond activation step involving the phenyl substituents of the PPh_2NHPh ligand, there is facile N−H activation of the NHPh moiety. In this way novel RuCp η^4-butadiene amido complexes are afforded. This is also noteworthy in view of the comparatively strained four-membered Ru−N−P−C ring system formed, in contrast to a five-membered Ru−C−C−P−C ring system in the case of C−H bond activation.[4]

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[8] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$ and PPh_2NHPh have been prepared according to the literature.[9,10] ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer 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.

$[RuCp(PPh_2NHPh)(CH_3CN)_2]PF_6$ (1). To a solution of $[RuCp(CH_3CN)_3]PF_6$ (300 mg, 0.691 mmol) in CH_2Cl_2 (5 mL) was added PPh_2NHPh (211 mg, 0.760 mmol), 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: 426 mg (92%). Anal. Calcd for $C_{27}H_{27}F_6N_3P_2Ru$: C, 48.36; H, 4.06; N, 6.27. Found: C, 48.39; H, 4.02; N, 6.31. ^1H NMR (δ, acetone-d_6, 20 °C): 7.84−7.35 (m, 10H, Ph), 7.23−7.00 (m, 2H, NH*Ph*), 6.95−6.73 (m, 3H, NH*Ph*), 6.43 (d, $^2J_{HP}$ = 8.37 Hz, 1H, N*H*Ph), 4.49 (s, 5H, Cp), 2.28 (d, J_{HP} = 1.26 Hz, 6H, *CH*$_3$CN). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 143.7 (d, J_{CP} = 3.2 Hz, 1C, NPh^1), 135.7 (d, $^1J_{CP}$ = 46.2 Hz, 2C, Ph^1), 131.6 (d, $^2J_{CP}$ = 12 Hz, 4C, Ph^{2,6}), 130.2 (d, $^4J_{CP}$ = 2.3 Hz, 2C, Ph^4), 128.4 (2C, N−Ph^{3,5}), 128.4 (d, $^3J_{CP}$ = 10.1 Hz, 4C, Ph^{3,5}), 127.9 (s, 2C, CH$_3$*C*N), 120.2 (d, J_{CP} = 1.2 Hz, 1C, NPh ^{4}), 118.9 (dd, $J_{CP} = J_{CP}$ = 6.0 Hz, 2C, NPh^{2,6}), 77.2 (d, J_{CP} = 2.3 Hz, 5C, Cp), 2.6 (s, 2C, *C*H$_3$CN). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 81.2 (PPh_2), −144.1 ($^1J_{FP}$ = 709.6 Hz, PF_6).

$[RuCp(\eta^4\text{-}C_4H_3(Ph)_2\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ (2a). To a solution of **1** (160 mg, 0.239 mmol) in CH_2Cl_2 (10 mL) was added 2.5 equiv of HC≡CPh (65.5 μL, 0.598 mmol), and the mixture was stirred for 2 h at room temperature. After removal of the solvent under reduced pressure, a dark red solid was obtained, which was washed with Et_2O (5 mL) and dried under vacuum. The crude product was purified by column chromatography (neutral Al_2O_3/CH_3CN). The red band was collected. Yield: 116 mg (61%). Anal. Calcd for $C_{39}H_{33}F_6NP_2Ru$: C, 59.09; H, 4.20; N, 1.77. Found: C, 59.15; H, 4.16; N, 1.83. ^1H NMR (δ, acetone-d_6, 20 °C): 8.48−6.51 (m, 25 H, Ph, N*Ph*), 7.26 (d, $^3J_{HH}$ = 10.9 Hz, H^3), 5.48 (s, 5H, Cp), 4.81 (d, $^2J_{HP}$ = 15.8 Hz, H^1), 4.47 (d, $^3J_{HH}$ = 10.9 Hz, H^4). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C):144.2 (s, 1C, N−Ph^1), 140.1−126.8 (26C, Ph, N−Ph^{3,5}), 122.2 (d, J_{CP} = 11.3 Hz, 1C, N−Ph^4), 120.9 (s, 2C, N−Ph^{2,6}), 114.2 (s, 1C, C^2), 90.6 (s, 1C, C^3), 87.7 (s, 5C, Cp), 81.7 (s, 1C, C^4), 29.1 (d, $^1J_{CP}$ = 110.0 Hz, 1C, C ^{1}). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 46.2 (PPh_2), −144.1 ($^1J_{FP}$ = 707.2 Hz, PF_6).



$[RuCp(\eta^4\text{-}C_4H_3(n\text{-}Bu)_2\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ (2b). This complex has been prepared analogously to **2a** with **1** (150 mg, 0.224 mmol) and 1-hexyne (64.3 μL, 0.559 mmol) as the starting materials. Yield: 74 mg (43%). Anal. Calcd for $C_{35}H_{41}F_6NP_2Ru$: C, 55.85; H, 5.49; N, 1.86. Found: C, 55.76; H, 5.44; N, 1.90. ^1H NMR (δ, CD_2Cl_2 20 °C): 7.96−7.27 (m, 10H, Ph), 7.24−7.04 (m, 2H, N*Ph*), 6.93−6.62 (m, 3H, N*Ph*), 7.97 (d, $^3J_{HH}$ = 10.7 Hz, H^3), 5.30 (s, 5H, Cp), 4.01 (d, $^2J_{HP}$ = 15.3 Hz, 1H, H^1), 3.43 (m, 1H, H^4), 2.71−2.30 (m, 2H), 2.26−2.04 (m, 2H), 2.02−1.76 (m, 2H), 1.68−1.38 (m, 4H), 1.36−1.12 (m, 2H), 1.03 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_3$), 0.85 (t, $^3J_{HH}$ = 7 Hz, 3H, CH$_3$). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 145.1 (s, 1C, N−Ph^1), 134.6 (d, $^4J_{CP}$ = 2.8 Hz, 1C, Ph^4), 134.2 (d, $^4J_{CP}$ = 2.8 Hz, 1C, Ph$^{4'}$), 131.2 (d, $^2J_{CP}$ = 11.0 Hz, 2C, Ph^{2,6}), 131.0 (d, $^2J_{CP}$ = 11.3 Hz, 2C, Ph$^{2,6'}$), 130.1 (d, $^3J_{CP}$ = 12.3 Hz, 2C, Ph^{3,5}), 129.3 (d, $^3J_{CP}$ = 12.0 Hz, 2C, Ph$^{3,5'}$), 129.3 (d, $^1J_{CP}$ = 50.0 Hz, 1C, Ph^1), 129.0 (s, 2C, NPh^{3,5}), 127.9 (d, $^1J_{CP}$ = 52.4 Hz, 1C, Ph$^{1'}$), 121.7 (d, J_{CP} = 12.3 Hz, 1C, NPh^4), 120.3 (s, 2C, N−Ph^{2,6}), 116.2 (s, 1C, C^2), 94.0 (s, 1C, C^3), 85.3 (s, 5C, Cp), 83.8 (s, 1C, C^4), 43.0 (d, J_{CP} = 9 Hz, 1C, CH$_2$), 37.4 (s, 1C, CH$_2$), 35.5 (s, 1C, CH$_2$), 34.1 (s, 1C, CH$_2$), 28.4 (d, $^1J_{CP}$ = 111.8 Hz, 1C, C^1), 22.4 (s, 1C, CH$_2$), 21.9 (s, 1C, CH$_2$), 13.6 (s, 1C, CH$_3$), 13.5 (s, 1C, CH$_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 42.6 (PPh_2), −144.1 ($^1J_{FP}$ = 708.4 Hz, PF_6).

$[RuCp(\eta^4\text{-}C_4H_3(CH_2Ph)_2\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ (2c). This complex has been prepared analogously to **2a** with **1** (160 mg, 0.239 mmol) and benzylacetylene (74.3 μL, 0.598 mmol) as the starting materials. Yield: 108 mg (55%). Anal. Calcd for $C_{41}H_{37}F_6NP_2Ru$: C, 60.00; H, 4.54; N, 1.71. Found: C, 60.08; H, 4.47; N, 1.66. ^1H NMR (δ, CD_2Cl_2 20 °C): 8.12−6.55 (m, 25H, Ph, N*Ph*), 6.21 (d, $^3J_{HH}$ = 9.7 Hz, 1H, H^3), 5.44 (s, 5H, Cp), 4.25 (d, $^2J_{HP}$ = 14.0 Hz, 1H, H^1), 3.91−3.43 (m, 5H, CH$_2$, H^4). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 145.1 (s, 1C, N−Ph^1), 140.0−126.6 (26C, Ph, NPh^{3,5}), 121.7 (d, J_{CP} = 13.2 Hz, 1C, NPh^4), 120.4 (s, 2C, NPh^{2,6}), 114.9 (s, 1C, C^2), 94.1 (s, 1C, C^3), 85.7 (s, 5C, Cp), 83.0 (s, 1C, C^4), 48.0 (d, J_{CP} = 9.5 Hz, 1C, CH$_2$), 42.9 (s, 1C, CH$_2$), 28.3 (d, $^1J_{CP}$ = 112.5 Hz, 1C, C^1). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 44.2 (PPh_2), −144.6 ($^1J_{FP}$ = 701.9 Hz, PF_6).

$[RuCp(\eta^4\text{-}C_4H_3(CH_2)_3\text{-}PPh_2\text{-}\kappa^1\text{-}(N)\text{-}NPh)]PF_6$ (2d). This complex has been prepared analogously to **2a** with **1** (300 mg, 0.447 mmol) and 1,6-heptadiyne (61.5 μL, 0.537 mmol) as the starting materials. Yield: 268 mg (88%). Anal. Calcd for $C_{30}H_{29}F_6NP_2Ru$: C, 52.95; H, 4.29; N, 2.06. Found: C, 52.99; H, 4.32; N, 1.97. ^1H NMR (δ, acetone-d_6, 20 °C): 8.07−7.42 (m, 10H, Ph), 7.12−7.01 (m, 2H, N*Ph*), 6.85−6.69 (m, 3H, N*Ph*), 5.53 (s, 5H, Cp), 5.42 (d, $^2J_{HH}$ = 2.8 Hz, 1H, H^4), 4.60 (d, $^2J_{HP}$ = 16.4 Hz, 1H, H^1), 3.67−3.45 (m, 2H, CH$_2$), 2.65−2.45 (m, 2H, CH$_2$), 2.31 (d, $^2J_{HH}$ = 2.8 Hz, 1H, H$^{4'}$), 1.41−1.15 (m, 2H, CH$_2$). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 144.1 (s, 1C, NPh ^{1}), 134.6 (d, $^4J_{CP}$ = 2.9 Hz, 1C, Ph^4), 134.3 (d, $^4J_{CP}$ = 2.9 Hz, 1C, Ph$^{4'}$), 131.5 (d, $^2J_{CP}$ = 10.8 Hz, 2C, Ph^{2,6}), 131.5 (d, $^2J_{CP}$ = 10.8 Hz, 2C, Ph$^{2,6'}$), 130.0 (d, $^3J_{CP}$ = 12.4 Hz, 2C, Ph^{3,5}), 129.3 (d, $^3J_{CP}$ = 11.7 Hz, 2C, Ph$^{3,5'}$), 128.9 (s, 2C, NPh^{3,5}), 128.5 (d, $^1J_{CP}$ = 70.4 Hz, 1C, Ph^1), 126.8 (d, $^1J_{CP}$ = 92.6 Hz, 1C, Ph$^{1'}$), 121.6 (d, J_{CP} = 12.7 Hz, 1C, NPh^4), 120.2 (d, J_{CP} = 2.0 Hz, 2C, NPh^{2,6}), 114.4 (d, $^2J_{CP}$ = 1.6 Hz, 1C, C^2), 85.7 (s, 5C, Cp), 80.5 (s, 1C, C^3), 52.4 (s, 1C, C^4), 40.0 (d, J_{CP} = 8.8 Hz, 1C, CH$_2$), 38.6 (s, 1C, CH$_2$), 25.0 (d, $^1J_{CP}$ = 113.5 Hz, 1C, C^1), 22.1 (s,

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1C, CH_2). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 42.9 (PPh_2), −144.4 ($^1J_{FP}$ = 719.5 Hz, PF_6).

[RuCp(η^4-$C_4H_3(CH_2)_4$-PPh_2-κ^1-(N)-NPh)]PF_6 (2e). This complex has been prepared analogously to **2a** with **1** (150 mg, 0.224 mmol) and 1,7-octadiyne (35.7 μL, 0.269 mmol) as the starting materials. Yield: 96 mg (62%). Anal. Calcd for $C_{31}H_{31}F_6NP_2Ru$: C, 53.61; H, 4.50; N, 2.02. Found: C, 53.58; H, 4.53; N, 2.11. ^1H NMR (δ, CD_3NO_2, 20 °C): 7.95−7.33 (m, 10H, Ph), 7.16−6.97 (m, 2H, N*Ph*), 6.90−6.68 (m, 3H, N*Ph*), 5.40 (s, 5H, Cp), 5.12 (d, $^2J_{HH}$ = 3.3 Hz, 1H, H^4), 4.01 (d, $^2J_{HP}$ = 13.3 Hz, 1H, H^1), 3.37−3.15 (m, 1H, CH_2), 2.74−2.23 (m, 2H, CH_2), 2.05 (d, $^2J_{HH}$ = 2.5 Hz, 1H, $H^{4'}$), 1.98−1.52 (m, 4H, CH_2), 1.32−1.14 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 144.5 (s, 1C, NPh^1), 134.6 (d, $^4J_{CP}$ = 2.9 Hz, 1C, Ph^4), 134.2 (d, $^4J_{CP}$ = 2.9 Hz, 1C, $Ph^{4'}$), 131.3 (d, $^2J_{CP}$ = 11.1 Hz, 2C, $Ph^{2,6}$), 131.3 (d, $^2J_{CP}$ = 11.4 Hz, 2C, $Ph^{2,6'}$), 130.2 (d, $^1J_{CP}$ = 70.4 Hz, 1C, Ph^1), 130.0 (d, $^3J_{CP}$ = 12.4 Hz, 2C, $Ph^{3,5}$), 129.3 (d, $^3J_{CP}$ = 11.7 Hz, 2C, $Ph^{3,5'}$), 128.9 (s, 2C, $NPh^{3,5}$), 128.6 (d, $^1J_{CP}$ = 68.1 Hz, 1C, $Ph^{1'}$), 122.3 (d, J_{CP} = 11.4 Hz, 1C, NPh^4), 120.7 (s, 2C, $NPh^{2,6}$), 115.0 (s, 1C, C^2), 108.1 (d, $^3J_{CP}$ = 2 Hz, 1C, C^3), 87.5 (s, 5C, Cp), 54.5 (s, 1C, C^4), 34.2 (d, J_{CP} = 3.9 Hz, 1C, CH_2), 34.1 (s, 1C, CH_2), 25.7 (d, $^1J_{CP}$ = 110.5 Hz, 1C, C^1), 22.1 (d, J_{CP} = 2.0 Hz 1C, CH_2), 21.5 (s, 1C, CH_2). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 48.9 (PPh_2), −144.4 ($^1J_{FP}$ = 719.5 Hz, PF_6).

X-ray Structure Determination for 2b and 2d. Crystals of **2b** and **2d** were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, 0.3° ω−scan frames covering complete spheres of the reciprocal space). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. The structures were solved by direct methods using the program SHELXS97.[11] Structure refinement on F^2 was carried out with the program SHELXL97.[12] 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.

2b: $C_{35}H_{41}F_6NP_2Ru$, M_r = 752.70, monoclinic, space group $P2_1/n$ (No. 14), T = 153(2) K, a = 14.406(2) Å, b = 11.217(2) Å, c = 21.209(3) Å, β = 96.731(2)°, V = 3404(1) Å^3, Z = 4, μ = 0.613 mm^{-1}. Of 48 352 reflections collected (θ < 30°), 9810 were independent; R_{int} = 0.037; final R values: R_1 = 0.061 (all data), wR_2 = 0.115 (all data).

2d: $C_{30}H_{29}F_6NP_2Ru$, M_r = 680.55, monoclinic, space group $P2_1/c$ (No. 14), T = 173(2) K, a = 9.204(2) Å, b = 20.107(4) Å, c = 30.886(6) Å, β = 95.402(4)°, V = 5691(2) Å^3, Z = 8, μ = 0.724 mm^{-1}. Of 39 379 reflections collected (θ < 27°), 12 306 were independent; R_{int} = 0.052; final R values: R_1 = 0.067 (all data), wR_2 = 0.126 (all data).

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, and bond lengths and angles for **2b** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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