Ruthenium-Mediated Insertion of an Unsaturated C4 Unit into the P−N Bond of an Aminophosphine Ligand

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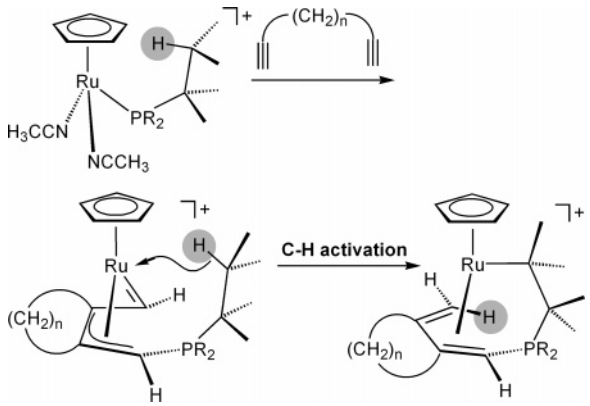
Summary: The reactions of 1,6-heptadiyne and 1,7-octadiyne with $[RuCp(PPh_2NEt_2)(CH_3CN)_2]^+$ *afford the* η^3*-phosphaallyl−*η^2*-vinylamine complexes* $[RuCp(\eta^3\text{-}(P,C,C)\text{-}PPh_2CH{=}C(CH_2)_n\text{-}\eta^2(C,C)\text{-}C{=}CHNEt_2)]^+$ *(*$n = 3$*, 4), which cleanly rearrange to give the* η^1*-phosphaallyl−*η^3*-azaallyl complexes* $[RuCp(\eta^1(P)\text{-}PPh_2CH{=}C(CH_2)_n\text{-}\eta^3\text{-}(C,C,N)\text{-}CCHNEt_2)]^+$ *(*$n = 3, 4$*).*

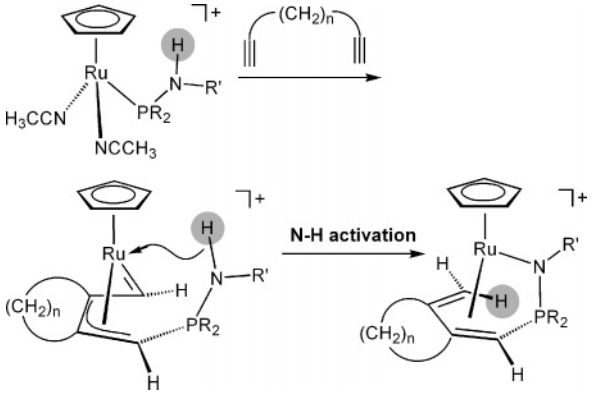
The labile complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = alkyl, aryl) are synthons for the 14-electron fragments $[RuCp(PR_3)]^+$, promoting the oxidative coupling of alkynes to eventually give ruthenium allyl carbenes.[1] These, in turn, behave as masked 16e complexes which are capable of activating C−H bonds of alkyl and aryl substituents of the phosphine ligands to afford η^4-butadiene complexes according to Scheme 1.[2] With aminophosphine ligands of the type PR_2NHR' instead of PR_3, N−H bond activation rather than C−H bond activation is observed. In this way amido-η^4-butadiene complexes are obtained (Scheme 2).[3,4] In this context we found it interesting to switch over to aminophosphine ligands lacking N−H bonds in order to see whether C−H bond activation processes become predominant again. Here we give a preliminary account of these investigations and report the reaction of $[RuCp(PPh_2NEt_2)(CH_3CN)_2]PF_6$ (**1**) with diynes, revealing an unusual insertion of an unsaturated carbon C4 chain into the P−N bond of the aminophosphine ligand. As a result of this transformation, phosphaallyl and azaallyl complexes are formed.

Treatment of **1** with 1,6-heptadiyne results within a few minutes in the formation of the η^3-phosphaallyl−η^2-vinylamine $[RuCp(\eta^3(P,C,C)\text{-}PPh_2CHC(CH_2)_3\text{-}\eta^2(C,C)\text{-}C{=}CHNEt_2)]^+$ (**2a**) in high yield (Scheme 3).[6,7] At elevated temperature (80 °C) **2a** isomerizes cleanly to

Scheme 1



Scheme 2



afford the thermodynamically more stable η^1-phosphaallyl−η^3-azaallyl complex $[RuCp(\eta^1(P)\text{-}PPh_2CH{=}C(CH_2)_3\text{-}\eta^3(C,C,N)\text{-}CCHNEt_2)]^+$ (**3a**) in 85% isolated yield.[8] With 1,7-octadiyne the analogous phosphaallyl−azaallyl complex **2b** is formed, as monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, but rearranges already at room temperature to give the corresponding η^1-phosphaallyl−η^3-azaallyl complex **3b**. Compounds **2a**, **3a**, and **3b**, 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 by elemental analysis. The ^1H NMR spectroscopic data for **2a** include characteristic resonances at 4.01 (d, $^2J_{HP} = 4.7$ Hz) and

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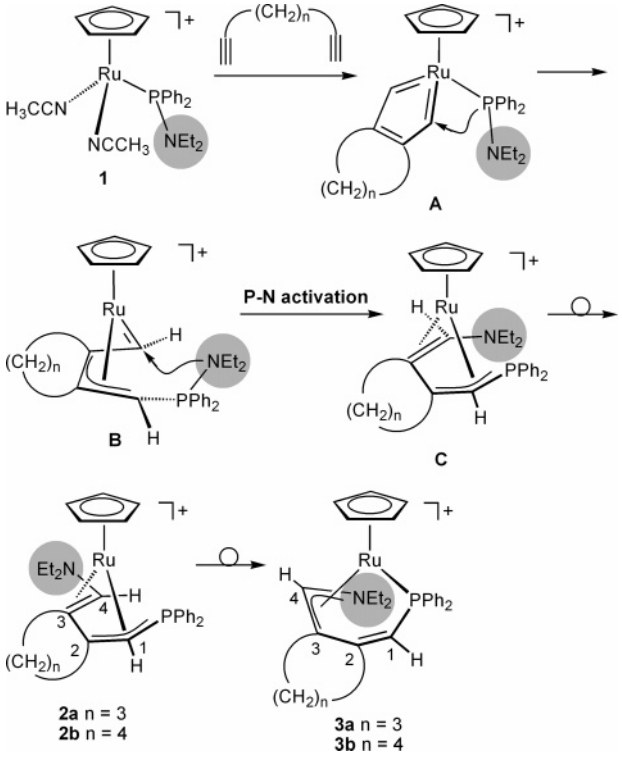
Scheme 3



3.58 ppm (d, 1H, $J_{HP} = 5.7$ Hz) 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 coordinated sp^2 carbon atoms C^1, C^2, C^3, and C^4 of the η^3-phosphaallyl−η^2-vinylamine moiety exhibit characteristic resonances at 40.8 (d, $^1J_{CP} = 24.2$ Hz), 75.8, 117.4 (d, $J_{CP} = 4.6$ Hz), and 117.8 ppm (d, $J_{CP} = 6.9$ Hz), respectively. In the $^{31}P\{^1H\}$ NMR spectrum the phosphaallyl ligand exhibits a singlet at 4.3 ppm. Concurrent NMR spectra are observed for **2b**. However, due to spectral overlap with **3b**, not all signals could be unequivocally assigned.

The NMR data of **3a** are quite different from those of **2a**. The ^1H NMR spectrum exhibits resonances at 6.35 (d, $J_{HP} = 9.8$ Hz) and 6.03 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 172.0 ppm (d, $J_{CP} = 27.2$ Hz) and doublet resonances at 117.4 (d, $J_{CP} = 47.9$ Hz), 91.3 (d, $J_{CP} = 3.1$ Hz), and 79.1 ppm (d, $J_{CP} = 1.5$ Hz) 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 NEt_2 unit. In the $^{31}P\{^1H\}$ NMR spectrum the η^1-(*P*)-phosphaallyl ligand exhibits a singlet at 74.1 ppm (cf. 4.3 ppm in **2a**). The NMR spectra of **3b** are similar to those of **3a** and are not discussed here.

The solid-state structures of **2a** and **3b** were determined by single-crystal X-ray diffraction. ORTEP diagrams are depicted in Figures 1 and 2, respectively, with important bond distances reported in the captions. The structure of **2a** can be described as a three-legged pianostool coordination with the η^3(*P*)-phosphaallyl moiety and the carbon atoms 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 distances being 2.269(1), 2.231(3),

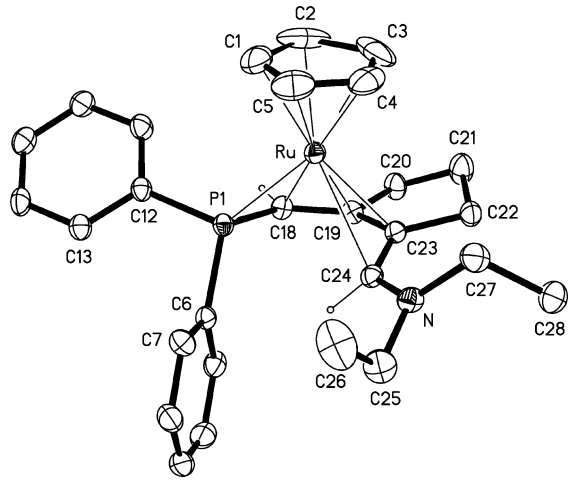


Figure 1. Structural view of **2a** showing 30% thermal ellipsoids (PF_6^- and most H atoms omitted for clarity). Selected bond lengths (Å): Ru−P(1) = 2.2690(9), Ru−C(18) = 2.231(3), Ru−C(19) = 2.227(3), Ru−C(23) = 2.239(4), Ru−C(24) = 2.547(3), P(1)−C(18) = 1.764(4), C(18)−C(19) = 1.412(5), C(19)−C(23) = 1.425(5), C(23)−C(24) = 1.392(5), C(24)−N = 1.358(4).

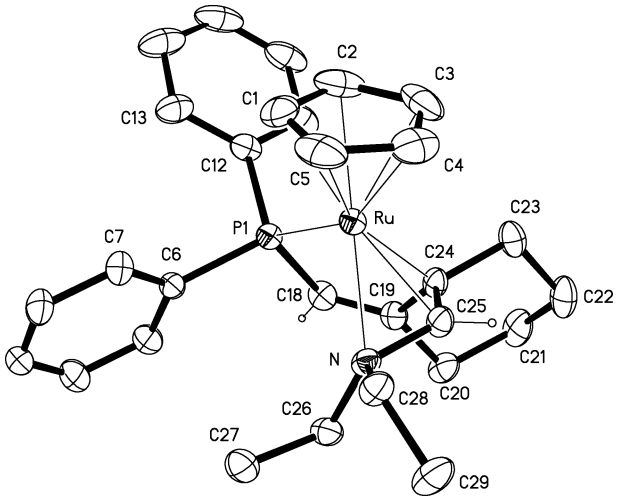


Figure 2. Structural view of **3b** showing 30% thermal ellipsoids (PF_6^- and most H atoms omitted for clarity). Selected bond lengths (Å): Ru−N = 2.212(2), Ru−C(25) = 2.083(2), Ru−C(24) = 2.203(3), Ru−P(1) = 2.2758(6), P(1)−C(18) = 1.806(2), C(18)−C(19) = 1.323(4), C(19)−C(24) = 1.498(4), C(24)−C(25) = 1.420(3), C(25)−N = 1.424(3).

and 2.227(3) Å, respectively. The C−C part of the moiety is strongly asymmetrically bonded to the metal center, with the Ru−C bonds to the carbon atoms C(23) and C(24) being 2.239(4) and 2.547(3) Å, respectively. Strong alteration of olefin binding by π-donor substituents has been also 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).[8] In turn, the C(24)−N bond already exhibits double-bond character, being 1.358(4) Å (cf. 1.456(5) and 1.474(5) Å for N−C(25) and N−C(27), respectively), and the N atom is essentially planar. The bonding situation of the $-C{=}CHNEt_2$ unit 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 NEt_2 substituent rapidly in a

syn conformation for steric reasons (conversion of **C** to **2** in Scheme 3).

The structure of **3b** is also of the three-legged piano-stool type, 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 phosphine moiety, is asymmetrically bonded to the metal with the Ru−C bond distance to the central allyl carbon atom C(25) (2.083(2) Å) distinctly shorter than the Ru−N and Ru−C(24) bonds to the terminal allyl atoms N and C(24) (2.212(2) and 2.203(3) Å, respectively).

For the present conversions, unfortunately, no intermediates could be detected spectroscopically. However, from previous experimental data it is apparent that the formation of η^3-phosphaallyl−η^2-vinylamine and η^1-phosphallyl−η^3-azaallyl complexes proceeds via the intermediacy of the highly electrophilic metallacyclopentatriene **A** and the allyl carbene complex **B**, as depicted in Scheme 3.[1] There is apparently migration of the κ^1(P)-coordinated PPh_2NEt_2 ligand, analogously to the η^3-allyl carbene complexes already described.[1] In contrast, however, instead of C−H bond activation involving either the phenyl or ethyl subtituents of the aminophosphine ligand, P−N bond activation occurs. Preliminary DFT/B3LYP calculations strongly suggest that direct NEt_2 attack at the carbene carbon atom of **B** takes place with concomitant P−N bond cleavage.[9] In this way RuCp η^3-phosphaallyl−η^2-vinylamine complexes **C** are afforded with the NEt_2 substituent initially in an anti position. However, rotation about the C−C bond to give the more stable syn isomers **2** is facile, since the Ru−C4 bond is weak or even nonbonding. Complexes **2** are the kinetic products, which rearrange eventually to the thermodynamically more stable η^1-phosphaallyl−η^3-azaallyl complexes **3**. The final conversion again requires a syn−anti isomerization of the NEt_2 substituent. Detailed mechanistic investigations, supported by theoretical DFT calculations, are currently underway and will be reported in due course.

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Supporting Information Available: Text giving experimental procedures and CIF files giving complete crystallographic data and technical details for **2a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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