Indenylruthenium(II) Aminoallenylidenes: New Building Blocks for the Synthesis of Highly Unsaturated Alkynyl and Allenylidene Complexes

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The allenylidene complexes [Ru(=C=C=CRPh)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R = Ph (**1**); R = H (**2**)) react with the ynamines R′C≡CNEt_2 (R′ = Me, $SiMe_3$), yielding the aminoallenylidenes [Ru{=C=C=C(NEt_2)[C(R′)=C(R)Ph]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R = Ph, R′ = Me (**3**); R = H, R′ = Me (**4**); R = Ph, R′ = $SiMe_3$ (**5**)). The reactions proceed regio- and stereoselectively, the insertion of the ynamine taking place exclusively at the C_β=C_γ bond of the unsaturated chain. The analogous allenylidene complex **6** (R′ = H, R = Ph) is obtained by desylilation of complex **5** with KF. The treatment of complex **3** with HBF_4 leads to the formation of the dicationic vinylidene [Ru{=C=C(H)C(=NEt_2)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$]$^{2+}$ (**7**). The aminoallenylidene complex **3** undergoes regioselective nucleophilic additions of acetylides and other carbanions at the C_γ atom, yielding (i) the disubstituted alkynylalkenylallenylidenes [Ru{=C=C=C(C≡CR)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (R = Ph (**8**), $SiMe_3$ (**9**)) from the addition of acetylides LiC≡CR, (ii) the 3-alkenyl-3,4,5-hexatrien-1-ynyl derivatives [Ru{C≡CC(=C=C=CRR′)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$] (R = R′ = Me (**10**); R = Ph, R′ = H (**11**)) from the reaction with LiC≡CCHRR′, and (iii) the 3-alkenyl-3-buten-1-ynyl species [Ru{C≡CC(=CHR)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$] (R = H (**12**), R = *n*-Pr (**13**)) and the 3-alkenyl-3,5-hexadien-1-ynyl complex [Ru{C≡CC(=CHCH=CH_2)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$] (**14**) from the treatment with $LiCH_2R$ (R = H, *n*-Pr) and $BrMgCH_2CH$=CH_2, respectively. The secondary allenylidenes [Ru{=C=C=C(H)[C(R)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R = Me (**16**), R = H (**17**)) are obtained in a one-pot synthesis from the reactions of aminoallenylidenes **3** and **6** with $LiBHEt_3$ and subsequent treatment with silica, respectively. Highly unsaturated alkenylaminoallenylidenes of the general formula [Ru{=C=C=C(NEt_2)[(CR=CH)$_n$C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (*n* = 1, R = Me (**18**), R = $SiMe_3$ (**19**); *n* = 2, R = Me (**22**)) have been synthesized by regio- and stereoselective sequential insertion of one or two ynamines RC≡CNEt_2 (R = Me, $SiMe_3$) into the C_β=C_γ bond of the cumulene group of complexes [Ru{=C=C=C(H)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**16**) and [Ru{=C=C=C(H)[(CMe=CH)C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**21**), respectively. Structures of complexes **3** and **18** have been confirmed by X-ray crystallography.

Introduction

The applications in organic synthesis of unsaturated Fischer type and other electrophilic carbenes continue disclosing efficient synthetic alternatives to classical procedures.[1] In particular, during the past few years the chemistry of the carbenes belonging to the cumulenylidene series [M]=C(=C)$_n$=CR^1R^2 has provided important developments in a number of stoichiometric and catalytic transformations. As part of the well-known applications of ruthenium complexes in organic synthesis, the reactivity of allenylidene and higher cumulenylidene ruthenium(II) complexes has attracted special attention.[2] To date, a wide number of C−C and C−heteroatom coupling reactions are well represented. Allenylidene and butatrienylidene complexes have emerged as useful starting materials for the synthesis of metal-bonded heterocycles.[3] The rapid development of this chemistry probably stems from the presence in the carbon chain of both electrophilic and nucleophilic sites, which provide an unusually versatile reactivity.[4] An interesting class of derivatives are those in which the cumulenylidene chains =C(=C)$_n$=CR^1R^2 also contain other types of α,β-unsaturated functional groups (R^1 and/or R^2 unsaturated hydrocarbon chain). The presence of such a type of highly unsaturated hydrocarbon moiety should increase the scope of the reactive sites. However,

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(1) (a) Furstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043. (b) Dörwald Zaragoza, F. *Metal Carbenes in Organic Chemistry*; Wiley-VCH: Weinheim, Germany, 1999. (c) Dötz, K. H.; Jahr, H. C. In *Carbene Chemistry*; Bertrand, G., Ed.; Marcel Dekker: New York, 2002; Chapter 8. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.* **2004**, *248*, 1627−1657.

(2) For recent reviews see: (a) Werner, H.; Ilg, K.; Lass, R.; Wolf, J. *J. Organomet. Chem.* **2002**, *661*, 137−147. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571−591. (c) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178−180*, 409−429. (d) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797−2858. (e) Werner, H. *Chem. Commun.* **1997**, 903−910. (f) Le Bozec, H.; Dixneuf, P. H. *Russ. Chem. Bull.* **1997**, *44*, 801.

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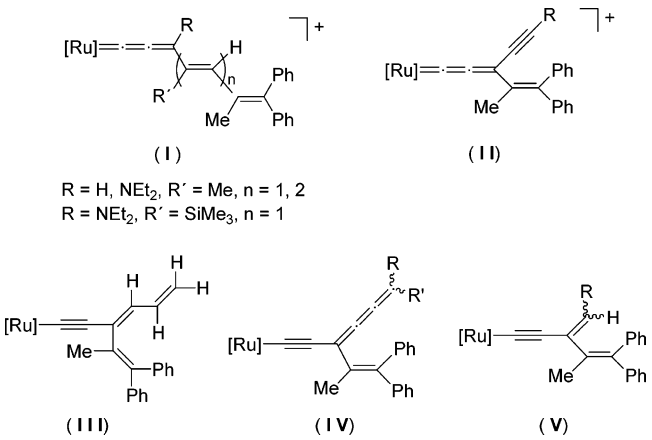
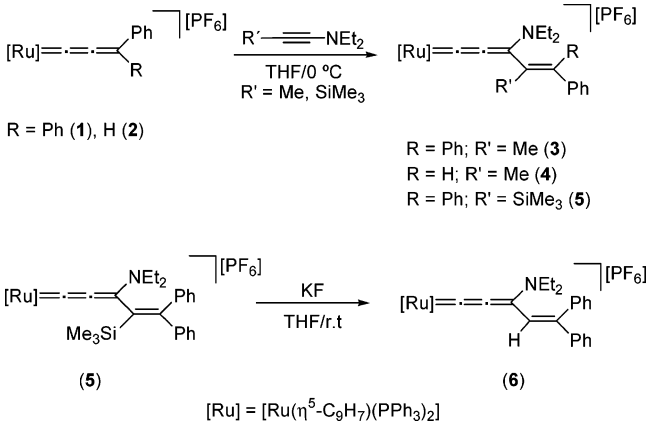
Chart 1



despite the potential synthetic applications only a few examples are known.[1d] The main drawback to achieving the desired unsaturated cumulenylidene precursors is the lack of systematic synthetic routes. Herein, we report an efficient and stereoselective synthetic methodology of indenylruthenium(II) complexes containing highly unsaturated hydrocarbon moieties, including (i) polyalkenylallenylidene chains {=C=C=C(R)[(CR′=CH)$_n$C(Me)=CPh$_2$]} (**I**: n = 1, 2, R = H, NEt$_2$, R′ = Me; n = 1, R = NEt$_2$, R′ = SiMe$_3$) (Chart 1), which are obtained via sequential insertion of ynamines, RC≡CNEt$_2$ (R = Me, SiMe$_3$), into the readily accessible cationic allenylidene precursors [Ru(=C=C=CRPh)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ and (ii) unsaturated allenylidene and alkynyl chains of the types **II** and **III**−**V**, respectively (Chart 1), prepared through regio- and stereoselective nucleophilic additions of carbanions onto the aminoallenylidene [Ru{=C=C=C(NEt$_2$)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$. These processes are representative examples of a new synthetic approach to building up unprecedented highly unsaturated hydrocarbon chains. Part of this work has been communicated previously.[5]

Scheme 1



Results and Discussion

Synthesis of Alkenylaminoallenylidene Complexes [Ru{=C=C=C(NEt$_2$)[C(R′)=C(R)Ph]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Ph, R′ = Me (3); R = H, R′ = Me (4); R = Ph, R′ = SiMe$_3$ (5); R = Ph, R′ = H (6)). Allenylidene complexes [Ru(=C=C=CRPh)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Ph (**1**), H (**2**))[4h] react rapidly with an excess of the ynamine MeC≡CNEt$_2$[6] in tetrahydrofuran at 0 °C, yielding regio- and stereoselectively the alkenylaminoallenylidene complexes **3** and **4** (71−87% yield) (Scheme 1).[7] Similarly, the treatment of a solution of complex **1** in tetrahydrofuran with Me$_3$SiC≡CNEt$_2$, at room temperature over 12 h, affords the analogous allenylidene complex **5** (64% yield). The desilylated complex **6** is readily obtained (96% yield) by the reaction of **5** with KF in methanol at room temperature (Scheme 1).

Complexes **3**−**6** are isolated as crystalline air-stable orange solids. Analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) of **3**−**6** support the proposed formulation (see Experimental Section). The most significant features of the spectroscopic data are (i) the characteristic ν(C=C=C) strong absorption at 1980−1992 cm^{-1} in the IR spectra, (ii) the low-field signals for the allenylidene carbon nuclei in the ^{13}C{^{1}H} NMR spectra, which appear in the ranges 195.87−206.68 (t, $^2J_{CP}$ = 20.6−21.4 Hz, C$_\alpha$), 149.95−156.79 (s, C$_\gamma$), and 121.11−122.76 (s, C$_\beta$) ppm, (iii) the hydrogen of the alkenyl group in the ^{1}H NMR spectrum as a singlet at 5.91 (**4**) and 6.20 ppm (**6**), and (iv) 2D NMR (NOESY) experiments for complex **4**, which are in accord with a trans arrangement of the hydrogen and methyl substituents in solution. Although the spectroscopic data of these aminoallenylidene complexes can be compared with those of the precursors **1** and **2**, some significant differences can be observed, in particular (i) the ν(C=C=C) absorption in the IR spectra, which appears at 1980−1992 cm^{-1}, between that shown by all-carbon-substituted allenylidenes and alkynylruthenium(II) complexes,[2] (ii) the higher field of the C$_\alpha$ (195.87−

(3) (a) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 5274−5284. (b) Harbort, R.-C.; Hartmann, S.; Winter, R. F.; Klinkhammer, K. W. *Organometallics* **2003**, *22*, 3171−3174. (c) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 162−171. (d) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *Organometallics* **2001**, *20*, 3175−3189. (e) Bernard, D. J.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 4327−4335. (f) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallis* **2000**, *19*, 4−14. (g) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606−1614. (h) Bruce, M. I.; Ke, M.; Kelly, B. D.; Low, P. J.; Smith, M. E.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1999**, *590*, 184−201. (i) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4959−4965. (j) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567−3573. (k) Bruce, M. I.; Hinterding, P.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1997**, 715−716.

(4) (a) Auger, N.; Touchard, D.; Rigaut, S.; Halet, J. F.; Saillard, J. Y. *Organometallics* **2003**, *22*, 1638−1644. (b) Marrone, A.; Re, N. *Organometallics* **2002**, *21*, 3562−3571. (c) Winter, R. F.; Klinkhammer, K. W.; Zális, S. *Organometallics* **2001**, *20*, 1317−1333. (d) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutierrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585−2596. (e) Re, N.; Sgamellotti, A.; Floriani, C. *Organometallics* **2000**, *19*, 1115−1122. (f) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826−5835. (g) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Modrego, J.; Oro, L. A. *Organometallics* **1996**, *15*, 3556−3562. (h) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137−2147. (i) Berke, H.; Huttner, G.; Von Seyerl, J. *Z. Naturforsch., B* **1981**, *36*, 1277−1288. (j) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585−591.

(5) Conejero, S.; Díez, J.; Gamasa, M. P.; Gimeno, J.; García-Granda, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3439−3442.

(6) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, The Netherlands, 1988; p 235.

(7) Other vinylallenylidene complexes are known: (a) Péron, D.; Romero, A.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 3319−3326. (b) Touchard, D.; Pirio, N.; Toupet, L.; Fettouhi, M.; Ouahab, L.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 5263−5272.

Table 1. $^{13}C\{^1H\}$ NMR Selected Data for the Allenylidene Complexes[a]

compd	C_α	C_β	C_γ
[Ru{=C=C=C(NEt$_2$)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**3**)	199.39 dd (20.7, 20.7)	121.72 s	155.26 s
[Ru{=C=C=C(NEt$_2$)[C(Me)=C(H)Ph]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**4**)[b]	206.68 t (21.4)	122.76 s	156.79 s
[Ru{=C=C=C(NEt$_2$)[C(SiMe$_3$)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**5**)	195.87 t (20.6)	121.11 s	156.83 s
[Ru{=C=C=C(NEt$_2$)[C(H)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**6**)	202.33 t (22.0)	122.27 s	149.95 s
[Ru{=C=C=C(NEt$_2$)[(CR=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**18**; R = H)	202.21 t (21.2)	121.07 s	156.21 s
[Ru{=C=C=C(NEt$_2$)[(CR=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**19**; R = SiMe$_3$)	201.50 dd (21.7, 19.9)	121.27 s	159.14 s
[Ru{=C=C=C(NEt$_2$)[(CMe=CH)$_2$C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**22**)	202.61 t (21.5)	121.14 s	157.11 s
[Ru{=C=C=C(C≡CPh)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**8**)	281.78 t (18.7)	222.68 s	156.86 s
[Ru{=C=C=C(C≡CSiMe$_3$)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**9**)[b]	280.17 t (19.5)	221.88 s	152.95 s
[Ru{=C=C=C(H)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**16**)	295.05 t (19.7)	208.84 s	150.61 s
[Ru{=C=C=C(H)[C(H)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**17**)[b]	292.66 t (18.9)	215.69 s	146.60 s
[Ru{=C=C=C(H)[(CMe=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**21**)	290 93 t (19.2)	203.50 s	152.32 s

[a] Spectra recorded in $CDCl_3$. δ in ppm and J in Hz. Abbreviations: s, singlet; dd, doublet of doublets; t, triplet. $^2J_{CP}$ values are given in parentheses. [b] Spectrum recorded in CD_2Cl_2.

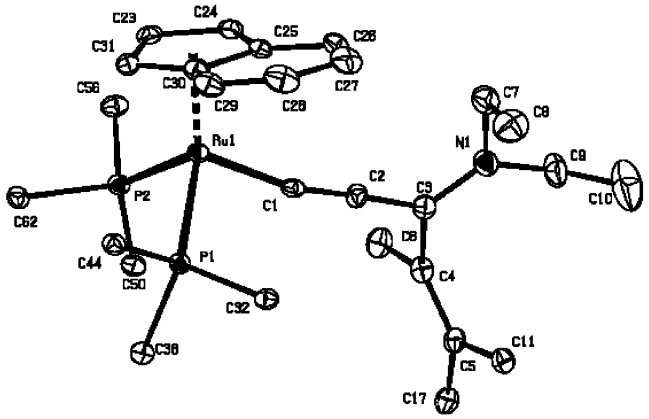


Figure 1. ORTEP view of the molecular structure of the cation of [Ru{=C=C=C(NEt$_2$)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$]·EtOH (**3**·EtOH), drawn at the 10% probability level. The hexafluorophosphate anion, EtOH molecule, and phenyl groups of PPh_3 have been omitted for clarity. Only the ipso carbon atoms of the aryl groups are depicted.

Table 2. Selected Bond Lengths and Slip Parameter Δ[a] (Å) and Bond Angles, Torsion Angles, and Dihedral (CA[b]) Angles (deg) for 3·EtOH

	Distances		
Ru−C*	1.9348(4)	Ru−P(1)	2.3402(12)
Ru−C(1)	1.956(5)	Ru−P(2)	2.2943(12)
C(1)−C(2)	1.235(6)	Ru−C(23)	2.207(4)
C(2)−C(3)	1.392(6)	Ru−C(24)	2.220(4)
C(3)−C(4)	1.520(6)	Ru−C(25)	2.352(4)
C(4)−C(5)	1.353(6)	Ru−C(30)	2.377(5)
C(3)−N(1)	1.314(6)	Ru−C(31)	2.249(4)
Δ	0.13(4)		
	Angles		
P(1)−Ru−P(2)	98.64(4)	C(4)−C(3)−N(1)	120.4(4)
P(1)−Ru−C(1)	96.01(13)	C(3)−N(1)−C(7)	119.7(4)
P(2)−Ru−C(1)	95.21(12)	C(3)−N(1)−C(9)	123.5(4)
C*−Ru−C(1)	119.73(12)	C(7)−N(1)−C(9)	116.7(4)
C*−Ru−P(1)	122.23(13)	C(2)−C(3)−C(4)	116.2(4)
C*−Ru−P(2)	119.22(3)	C(5)−C(4)−C(6)	125.0(4)
Ru−C(1)−C(2)	168.0(4)	C(5)−C(4)−C(3)	123.7(4)
C(1)−C(2)−C(3)	174.7(5)	C(6)−C(4)−C(3)	111.3(4)
C(2)−C(3)−N(1)	123.2(5)	C(17)−C(5)−C(11)	116.3(4)
CA	69.78(12)	C(6)−C(4)−C(3)−N(1)	99.0(5)

[a] Δ = d[Ru−C(25),C(30)] − d[Ru−C(24),C(31)]. [b] CA (conformational angle) = angle between normals to least-squares planes defined by [C**, C*, Ru] and [C*, Ru, C(1)]. C* = centroid of C(30), C(31), C(23), C(24), C(25). C** = centroid of C(30), C(29), C(28), C(27), C(26), C(25).

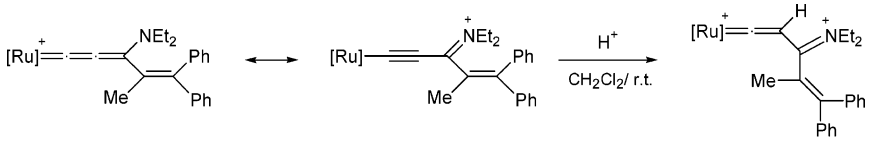
206.68 ppm) and C_β resonances (121.11−122.76 ppm) in the ^{13}C NMR spectra (see Table 1), and (iii) the nonequivalence of the ethyl substituents in the NEt_2 group (two resonance signals, one of the Et group pointing toward and one away from the metal) in the ^1H and ^{13}C NMR spectra. These facts point to a dominant contribution of the alkynyl resonance form.[3b,4c,8] To assess the existence of this contribution in the alkenylallenylidene complexes **3**−**6**, an X-ray diffraction study of complex **3** was undertaken.

An ORTEP type view of the cation complex **3** is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The molecular structure shows the typical pseudooctahedral three-legged piano-stool coordination around the ruthenium atom, which is η^5 bonded to the indenyl group, the two phosphorus atoms of PPh_3 ligands, and the C(1) of the alkenylaminoallenylidene group. Bond lengths in the aminoallenylidene chain (Ru−C(1) = 1.956(5) Å, C(1)−C(2) = 1.235(6) Å, C(2)−C(3) = 1.392(6) Å, and C(3)−N(1) = 1.314(6) Å) show an important contribution of the iminium−alkynyl resonance form [Ru]−C≡CC(=N$^+$Et$_2$)[C(Me)=CPh$_2$].[2b] In addition, the coordination environment of the nitrogen atom is similar to that expected for a typical N(sp^2) hybridization (angles C(3)−N(1)−C(7) = 119.7(4)°, C(7)−N(1)−C(9) = 116.7(4)°, and C(3)−N(1)−C(9) = 123.5(4)°). It is also worth noting the orientation of the methyl substituent with respect to the amino group of the alkenylaminoallenylidene chain, defined by the torsion angle C(6)−C(4)−C(3)−N(1) (99.0(5)°), which deviates notably from the s-trans stereochemistry (torsion angle of 180°). The orientation of the alkenylaminoallenylidene group with respect to the benzo ring of the indenyl ligand is established by the conformational angle (CA) of 69.78(12)° (CA = 0° for the cis orientation). The rest of the main structural parameters are rather similar to those found for analogous indenylruthenium(II) complexes reported by us and therefore do not merit further comments (see Table 2).

On the basis of this structural information, we then wondered whether the addition of electrophiles at the C_β atom would be feasible, in accordance with the reactivity generally observed by transition-metal alky-

(8) (a) Fischer, H.; Szesni, N.; Roth, G.; Burlaff, N.; Weibert, B. *J. Organomet. Chem.* **2003**, *683*, 301−312. (b) Winter, R. F.; Hartmann, S.; Zális, S.; Klinkhammer, K. W. *Dalton* **2003**, 2342−2352. (c) Slageren, J.-V.; Winter, R. F.; Klein, A.; Hartmann, S. *J. Organomet. Chem.* **2003**, *670*, 137−143. (d) Roth, G.; Reindl, D.; Gockel, M.; Troll, C.; Fischer, H. *Organometallics* **1998**, *17*, 1393−1401. (e) Bruce, M. I.; Hinterding, P.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans* **1998**, 467−473. (f) Winter, R. F.; Hornung, F. M. *Organometallics* **1997**, *16*, 4248−4250. (g) Fischer, H.; Leroux, F.; Stumpf, R.; Roth, G. *Chem. Ber.* **1996**, *129*, 1475−1482. (h) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157−11158.

Scheme 2



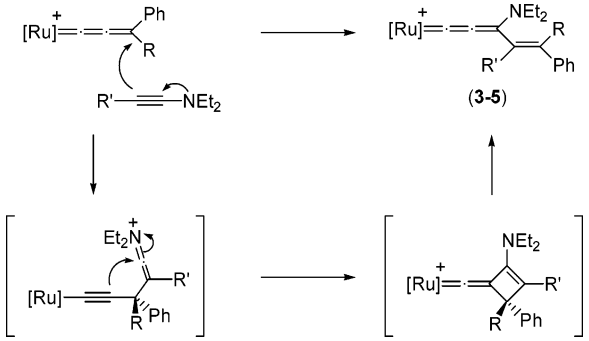
nyls. As expected, the treatment of complex **3** with $HBF_4{\cdot}OEt_2$, in dichloromethane at room temperature, leads to the dicationic vinylidene complex **7** in 96% yield (Scheme 2).

Complex **7** has been spectroscopically characterized (^1H and $^{13}C\{^1H\}$ NMR), showing the expected resonances of typical vinylidene groups attached to indenylruthenium(II) fragments[10] as well as those of the vinylidene−iminium group ($^{13}C\{^1H\}$ NMR δ 334.81 (t, $^2J_{CP}$ = 14.7 Hz, C_α), 110.49 (s, C_β), and 171.84 (s, C_γ=N); ^1H NMR δ 5.17 (s, br, =C=CH)). However, all attempts to isolate complex **7** with analytical purity failed, since it easily reverts to its allenylidene precursor **3** by loss of the C_β proton. The selective formation of the vinylidene **7** corroborates the dominant contribution of the alkynyl resonance form [Ru]−C≡CC(=N^+Et_2)-[C(Me)=CPh_2] vs [Ru]$^+$=C=C=C(NEt_2)[C(Me)=CPh_2] and contrasts with the typical electrophilic additions to the C_β atom of an allenylidene chain to give carbyne complexes.[11] The analogous aminoallenylidene complex *trans*-[RuCl{=C=C=C(NMe_2)(CH_2R)}(dppm)$_2$]$^+$ is also prone to undergo this favored protonation, affording the dicationic iminium-substituted vinylidene complex *trans*-[RuCl{=C=C(H)C(=NMe_2)(CH_2R)}(dppm)$_2$]$^{2+}$ (R = C_5H_5S).[3b]

The formation of complexes **3**−**5** probably proceeds through an initial nucleophilic addition of the ynamine at the C_γ atom of the cumulene moiety, leading to the formation of a cationic alkynyl intermediate complex. Further ring closure, involving the C_β atom, gives the [2 + 2] vinylidene cycloadduct. A subsequent cycloreversion would yield the alkenylaminoallenylidenes **3**−**5** (Scheme 3). It is worth noting that the synthesis of complex **5** requires a longer reaction time (12 h), probably due to the presence of a sterically demanding group (R′ = $SiMe_3$) in the nucleophilic carbon of the ynamine.

An analogous mechanism has been also proposed in the cycloaddition reactions of ynamines with group 6 allenylidene complexes[8d] [M{=C=C=C(C_6H_4R-*p*)$_2$}-(CO_5)] (M = Cr, W; R = H, Me, OMe, NMe_2). However, a mixture of two products, [M{=C=C=C(NEt_2)[C(R′)=C(C_6H_4R-*p*)$_2$]}(CO_5)] and [M{=CC(R′)=C(NEt_2)C=C(C_6H_4R-*p*)$_2$}(CO_5)] (M = Cr, W; R = H, Me, OMe, NMe_2, R′ = Ph, Me), are formed as a consequence of the insertion of the C≡C bond of the ynamine into both C_α=C_β and C_β=C_γ bonds of the cumulene moiety.

Scheme 3



The formal insertion selectivity promoted by allenylidene complexes **1** and **2** stems from the regioselectivity of the nucleophilic additions in these systems (see below).

Nucleophilic Additions onto the Aminoallenylidene Complex [Ru{=C=C=C(NEt_2)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (3): At present, it is well established that the reactivity of cationic transition-metal allenylidene complexes is dominated by the nucleophilic additions at the C_α and C_γ atoms of the cumulene chain.[2] During our investigations on the reactivity of allenylideneindenylruthenium(II) complexes [Ru(=C=C=CR^1R^2)(η^5-C_9H_7)(L)(L′)][PF_6], we have shown that the addition of nucleophiles to the unsaturated chain takes place regioselectively at the C_γ atom.[10a,12] The efficient and systematic accessibility to α,β-unsaturated allenylidene ruthenium complexes **3**−**5** prompted us to use them as precursors of highly unsaturated alkynyls through the corresponding nucleophilic additions of carbanions. To undertake a systematic reactivity study, the alkenylaminoallenylidene complex **3** was selected as the precursor model.

Reactions with Acetylides C≡CR^- (R = Ph, $SiMe_3$, Me_2CH, $PhCH_2$): Synthesis of [Ru{=C=C=C(C≡CR)[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (R = Ph (8), $SiMe_3$ (9)) and [Ru{C≡CC(=C=C=CRR′)-[C(Me)=CPh_2]}(η^5-C_9H_7)(PPh_3)$_2$] (R = R′ = Me (10); R = Ph, R′ = H (11)). Complex **3** reacts with an excess of LiC≡CR (R = Ph, $SiMe_3$; prepared in situ from the terminal alkyne and Li^{n}Bu) in tetrahydrofuran at −20 °C for 30 min. After removal of the solvent and extraction with diethyl ether, the subsequent addition of HBF_4 to the resulting solution leads to the formation of a solid precipitate, identified as the disubstituted alkynylalkenylallenylidene complexes **8** and **9** (Scheme 4). Complexes **8** and **9** were isolated after workup as air-stable blue-violet powders in 90 and 94% yields, respectively.

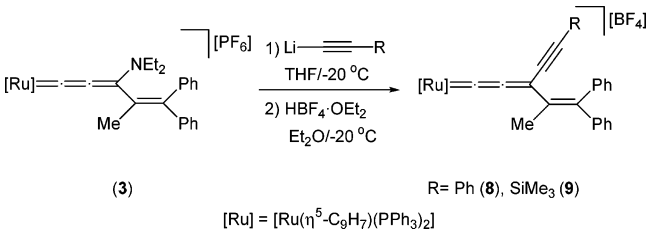
(9) Cadierno, V.; Díez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *Coord. Chem. Rev*. **1999**, *193*−*195*, 147−205.

(10) See for example: (a) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *Dalton* **2003**, 3060−3066. (b) Cadierno, V.; Conejero, S.; Díez, J.; Gamasa, M. P.; Gimeno, J.; García-Granda, S. *Chem. Commun*. **2003**, 840−841. (c) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *Organometallics* **2002**, *21*, 3837−3840. (d) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Falvello, L. R.; Llusar, R. M. *Organometallics* **2002**, *21*, 3716−3726.

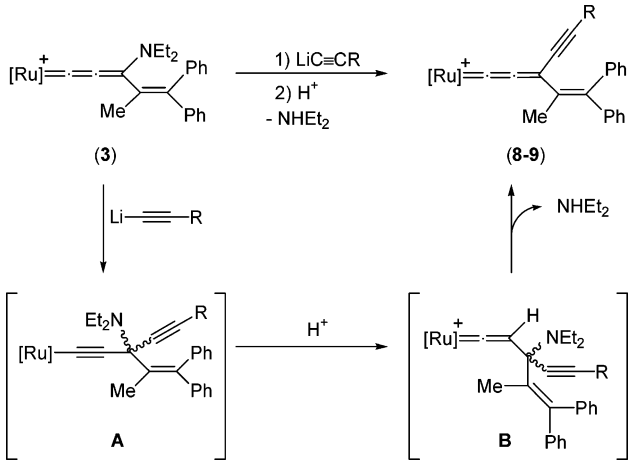
(11) (a) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 3980−3984. (b) Bustelo, E.; Jimenez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903−1911. (c) Jung, S.; Brandt, C. D.; Werner, H. *New J. Chem.* **2001**, *25*, 1101−1103. (d) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutierrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585−2596.

(12) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453−4463.

Scheme 4



Scheme 5



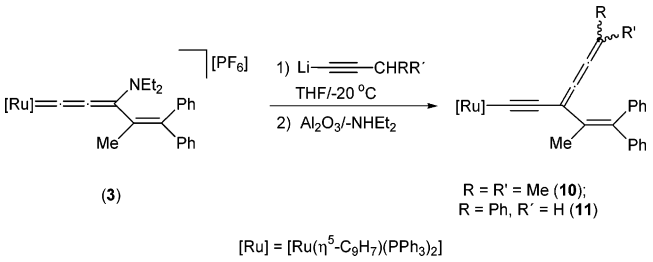
Spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR), elemental analyses, and mass spectra are in accordance with the proposed structures (see the Experimental Section). The most significant features of the spectroscopic data are (i) the characteristic ν(C=C=C) and ν(C≡C) absorptions in the IR spectra at 1918−1922 and 2131−2167 cm^{-1}, respectively, and (ii) the three low-field signals for the allenylidene carbon nuclei in the ^{13}C{^{1}H} NMR spectra, which appear in the ranges 280.17−281.78 (t, $^2J_{CP}$ = 18.7−19.5 Hz, C_α), 221.88−222.68 (s, C_β), and 152.95−156.86 (s, C_γ) ppm.

Likely, the reaction proceeds through the regioselective nucleophilic addition of lithium acetylide to the C_γ of the allenylidene chain of **3** to give the transient alkynyl-like complex **A**, which undergoes the electrophilic addition of a proton to form the vinylidene derivative **B** (Scheme 5). Finally, the spontaneous loss of diethylamine generates the difunctionalized allenylidene complexes. The overall processes formally result in an exchange reaction of the diethylamide substituent in the precursor complex by the acetylide group.[13]

Provided the effective attachment of alkynyl groups to the allenylidene chain through a regioselective coupling, we then explored the generalization of this methodology. To promote the amine elimination avoiding the protonation step, terminal alkynes containing an H_γ atom (i.e. $R_2C(H)C{\equiv}CH$) were used, expecting that an intramolecular elimination of $NHEt_2$ could be favored.

In a way similar to that described above, complex **3** reacts with an excess of LiC≡CCHRR′ (R = R′ = CH_3; R = Ph, R′ = H) (prepared in situ from the corresponding terminal alkynes and Li-*n*-Bu) in tetrahydrofuran at −20 °C. After 1 h of reaction at room temperature, evaporation of the solvent followed by extraction of the solid residue with diethyl ether and treatment with neutral alumina gives rise to the amine elimination. Removal of the solvent affords the 3-alkenyl-3,4,5-hexatrien-1-ynyl complexes **10** and **11**, isolated as red-orange air-stable solids in 83 and 89% yields, respectively (Scheme 6). The structures of **10** and **11** are fully supported by their spectroscopic data and elemental analyses. In particular, IR spectra exhibit the expected ν(C=C=C=C) and ν(C≡C) absorption bands at 1987−2008 and 2059−2062 cm^{-1}, respectively. ^{13}C{^{1}H} NMR spectra display (i) the typical triplet resonance for Ru−C_α at δ 121.03−138.71, which compares well with that of other unsaturated alkynyl complexes,[14] (ii) singlet signals for C_β at δ 113.57−114.64, and (iii) carbon nuclei resonances of the C=C=C=C side chain in the range δ 101.48−158.58. NMR spectra of **11** indicate that a mixture of the two *E*/*Z* isomers in a ca. 60:40 ratio is obtained. Significantly, two proton resonances of =CH appear in the ^{1}H NMR spectrum of **11** at δ 5.97 and 6.03. All attempts to form these compounds stereoselectively were unsuccessful.

Scheme 6



Although we have not undertaken mechanistic studies, it is likely that the reaction takes place through the formation of the corresponding intermediate amino-substituted alkynyl complex (analogous to **A** in Scheme 5), which in the presence of Al_2O_3 eliminates $NHEt_2$ intramolecularly, generating **10** and **11**.

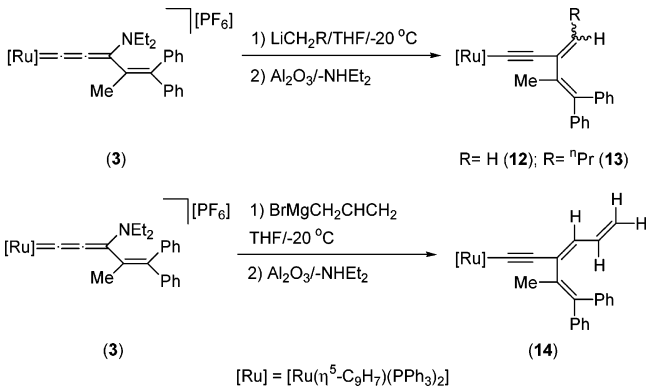
Reactions with Alkyl Carbanions: Synthesis of [Ru{C≡CC(=CHR)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (R = H (12), R = n-Pr (13), R = CH=CH$_2$ (14). The addition of LiMe or Li-*n*-Bu to a solution of alkenyl(amino)allenylidene **3** in tetrahydrofuran at −20 °C leads, after treatment with Al_2O_3, to the corresponding butadiene−alkynyl complexes **12** and **13**, isolated as air-stable orange solids in 76 and 87% yields, respectively (Scheme 7). Similarly, allylmagnesium bromide reacts with complex **3** in tetrahydrofuran. After treatment with Al_2O_3 and workup of the resulting solution, the hexatriene−alkynyl complex **14** is obtained (74%) as an air-stable orange solid (Scheme 7).

Complexes **12**−**14** have been characterized by elemental analyses and spectroscopic techniques, which support the proposed hydrocarbon moieties. Relevant spectroscopic features are as follows: (i) in the IR spectra (KBr), a weak ν(C≡C) stretching absorption at 2041−2096 cm^{-1}; (ii) in the ^{1}H NMR spectra, =CH resonances

(13) We have previously noted that addition of acids to the alkynyl complexes of general formula [Ru{C≡CCPh$_2$(NHCHMeR″)}(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$′)] (R = H, R′ = *i*-Pr, R″ = Ph, Cy; R = Me, R′= *i*-Pr, Ph, R″ = Ph, Cy) led to the formation of the allenylidene derivative [Ru(=C=C=CPh$_2$)(η^5-1,2,3-R$_3$C$_9$H$_4$)(CO)(PR$_3$)]$^+$ along with the elimination of NHR$_2$: Gamasa, M. P.; González-Bernardo, C.; Gimeno, J. Unpublished results.

(14) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Asselberghs, I.; Houbrechts, S.; Clays, K.; Persoons, A.; Borge, J.; García-Granda, S. *Organometallics* **1999**, *18*, 582−597.

Scheme 7



as two doublets (δ 4.94 (d) and 5.05 (d); J_{HH} = 2.6 Hz) (**12**), one triplet (4.95 (t); J_{HH} = 7.1 Hz) (**13**), and a doublet (δ 6.11 (d); J_{HH} = 10.8 Hz) (**14**) signals and, in addition, the =CH_2 resonances of **14** as two doublets of doublets at δ 4.88 and 5.00 (J_{HH} = 10.3−17.1 Hz, J_{HH} = 1.9 Hz); (iii) in the $^{13}C\{^1H\}$ NMR spectra, a Ru−C_α triplet (δ 112.07 (**12**), 113.00 (**13**), and 120.94 (**14**), $^2J_{CP}$ = 23.8−24.5 Hz) and a single C_β resonance (δ 113.12−114.90).

It is interesting to note that the formation of complex **13** proceeds in a stereoselective manner, although the spectroscopic data do not allow establishing the cis−trans disposition.

Synthesis of Alkenylallenylidenes [Ru{=C=C=C(H)[C(R)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Me (16), H (17)), Butadienylaminoallenylidenes [Ru{=C=C=C(NEt$_2$)[(CR=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Me (18), SiMe$_3$ (19)), and Butadienylallenylidene [Ru{=C=C=C(H)[(CMe=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (21). The ability of the allenylidene precursors **1** and **2** to undergo the insertion of one molecule of ynamines R′C≡CNEt_2 prompted us to use the new alkenylaminoallenylidenes [Ru{=C=C=C(NEt_2)[C(R′)=C(R)Ph]}(η^5-C_9H_7)(PPh_3)$_2$]-[PF_6] (**3**−**5**) as precursors in further insertion reactions. However, the treatment of complexes **3**−**5** with an excess of the ynamine in tetrahydrofuran, even under reflux conditions for several hours, gives the starting complexes unchanged. This fact probably arises from the dominant alkynyl resonance form [Ru]−C≡C−C(=N^+Et_2)[CMe=CPh_2] (see above, X-ray discussion), which precludes the insertion reaction. Since the presence of the diethylamino substituent favors the stabilization of the C≡C bond, we sought the transformation of the alkenylaminoallenylidene complex into the corresponding secondary derivative.

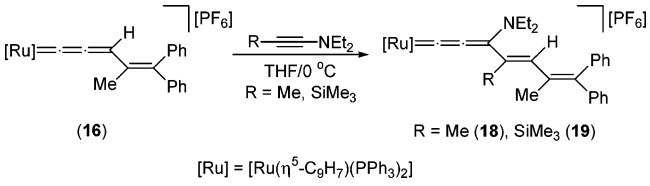
The treatment of complex **3** with $LiBHEt_3$ in tetrahydrofuran at 0 °C affords the alkynyl derivative **15**, generated by the nucleophilic addition of the hydride to the C_γ atom of the allenylidene chain (Scheme 8).

Complex **15** is isolated as an orange unstable solid. Although no analytically pure sample could be obtained, it has been characterized by NMR spectroscopy. The most characteristic resonances are as follows: (i) in the $^{31}P\{^1H\}$ NMR, the two doublets δ 52.43 and 52.73 ($^2J_{PP}$ = 34.0 Hz), in agreement with the AB system arising from the presence of a stereogenic center at C_γ; (ii) in the ^1H NMR, the singlet signal at δ 4.42 for the $CHNEt_2$ proton; (iii) the low-field signals at δ 93.60 (C_α) and 58.79 (C_γ) in the $^{13}C\{^1H\}$ NMR spectrum.

One-pot synthesis of alkenylallenylidene complexes **16** and **17** is achieved by the treatment of **3** and **6** with $LiBHEt_3$ after elimination of the resulting lithium salt and $NHEt_2$ on a short silica column[15] (see Scheme 8). Therefore, the overall process results in the formal substitution of the NEt_2 group by hydrogen. Complexes **16** (82%) and **17** (86%) have been isolated as violet air-stable powders.[16]

As was described above for the allenylidene complex **2**, the secondary allenylidene **16** also reacts with the ynamines RC≡CNEt_2 (R = Me, $SiMe_3$) in tetrahydrofuran, affording the butadienylaminoallenylidene complexes **18** (60%) and **19** (80%), which are isolated as air-stable orange solids (Scheme 9).

Scheme 9

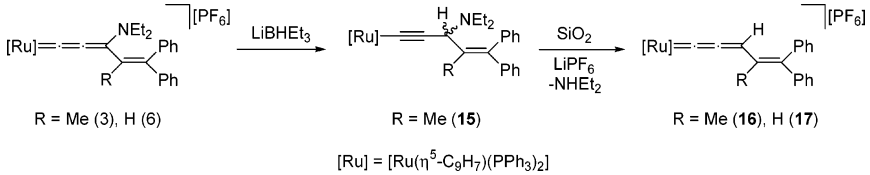


The transformation of the butadienylaminoallenylidene complex into the corresponding secondary allenylidene derivative is straightforward, following the methodology used above for the synthesis of **16.** Thus, the reaction of **18** with a slight excess of $LiBHEt_3$ in tetrahydrofuran, followed by purification of the concentrated solution on a silica column, yields the desired secondary butadienylallenylidene complex **21**, isolated as a violet solid in 83% yield after workup (Scheme 10). The formation of the intermediate alkynyl species **20** is observed in situ by NMR spectroscopy (see the Experimental Section for details).

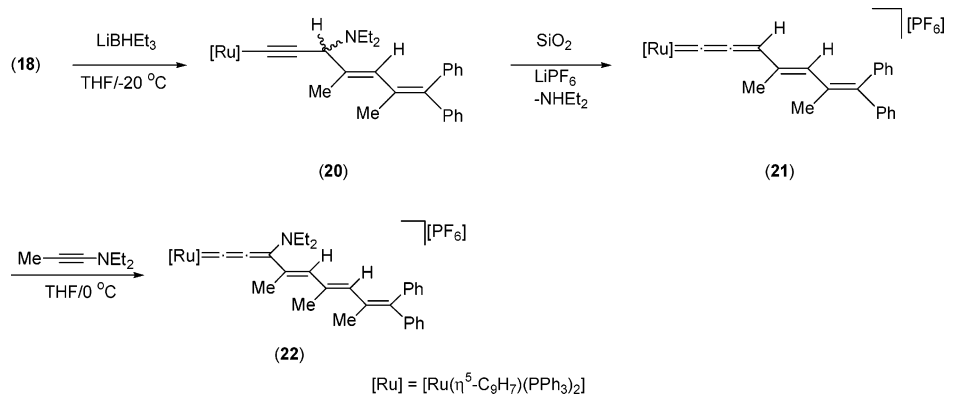
Complexes **16**−**19** and **21** have been fully characterized by elemental analysis, spectroscopic techniques (IR and multinuclear NMR spectroscopy), and X-ray crystallography for complex **18**. Selected bond lengths (Å) and angles (deg) are collected in Figure 2. For further structural data see ref 5.

IR spectra (KBr) show the expected ν(C=C=C) absorptions, in accordance with the type of allenylidene chain: (i) secondary allenylidenes **16**, **17**, and **21** (1932−1938 cm^{-1}) and (ii) aminoallenylidenes **18** and **19** (1987−1992 cm^{-1}). ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **16**−**19** and **21** display resonances, in ac-

Scheme 8



Scheme 10



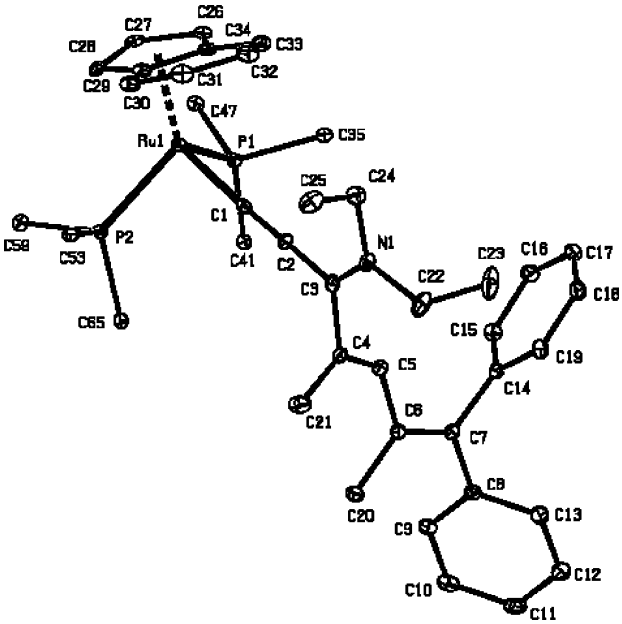


Figure 2. ORTEP view of the molecular structure of the cation of [Ru{=C=C=C(NEt$_2$)[(CMe=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**18**), drawn at the 10% probability level. The hexafluorophosphate anion and phenyl groups of PPh$_3$ have been omitted for clarity. Only the ipso carbon atoms of the aryl groups are depicted. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): Ru−P(1) = 2.299(9), Ru−P(2) = 2.305(9), Ru−C(1) = 1.946(4), C(1)−C(2) = 1.229(5), C(2)−C(3) = 1.390(5), C(3)−C(4) = 1.500(5), C(4)−C(5) = 1.340(6), C(5)−C(6) = 1.510(5), C(6)−C(7) = 1.355(5), C(3)−N(1) = 1.319(5); Ru−C(1)−C(2) = 174.6(3), C(1)−C(2)−C(3) = 177.8(4), C(2)−C(3)−N(1) = 122.1(3), C(4)−C(3)−N(1) = 119.0(3), C(2)−C(3)−C(4) = 118.4(2), C(3)−N(1)−C(24) = 121.7(3), C(3)−N(1)−C(22) = 122.1(4), C(24)−N(1)−C(22) = 116.2(4); C(20)−C(6)−C(5)−H(5) = 162.8(3), N(1)−C(3)−C(4)−C(21) = 78.8(5).

cordance with the presence of the methyl, ethyl, and phenyl substituents of the alkenyl groups (see Experimental Section). The most remarkable features arise from the carbon resonances of the allenylidene chain in the ^{13}C{^{1}H} NMR spectra (see Table 1), which appear at δ 290.93−295.05 (C$_\alpha$), 203.50−215.69 (C$_\beta$), and 146.60−152.32 (C$_\gamma$) (complexes **16**, **17**, and **21**) and δ 201.50−202.21 (C$_\alpha$), 121.07−121.27 (C$_\beta$), and 156.21−159.14 (C$_\gamma$) (complexes **18** and **19**). The latter values can be compared to those shown by the parent aminoallenylidene **3**.

Synthesis of the Hexatrienylaminoallenylidene Complex [Ru{=C=C=C(NEt$_2$)[(CMe=CH)$_2$C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (22). The secondary alkenylallenylidene **21** is also able to insert one further molecule of ynamine. Thus, when a solution of **21** in tetrahydrofuran is reacted with an excess of MeC≡CNEt$_2$ at 0 °C, the violet color turns immediately to orange. After workup of the resulting solution the hexatrienylaminoallenylidene complex **22** is obtained regio- and stereoselectively (45% yield) as an orange air-stable solid (Scheme 10).

Analytical and spectroscopic data support the proposed formulation (see the Experimental Section for details). ^{1}H and ^{13}C{^{1}H} NMR spectra display resonances in accord with the presence of the allenylidene and hexatrienyl groups, although unambiguous stereochemical information cannot be obtained. Since these data can be compared with those by the analogous alkenyl allenylidenes **18** and **19**, no further comments are warranted.

Final Remarks

Organometallic complexes bearing highly unsaturated hydrocarbon chains are one of the most challenging goals in organometallic chemistry, since they can provide unusual approaches to organic synthesis. Despite this fact, the construction of a desired unsaturated chain in a chemo- and regioselective manner is not always straightforward. In this context, the chemistry of cumulenylidene complexes has provided a general approach to achieve long cumulenic hydrocarbon chains.[1] However, only a few ruthenium complexes bearing unsaturated substituents are known.[1d] Since the generation of these cumulenic chains attached to metal fragments are generally achieved using the corresponding unsaturated propargyl alcohol, the metallacumulenic complex is only accessible, providing the availability of the appropriate alcohol. This synthetic drawback limits the access to this type of derivative.

(15) The synthesis of allenylidene complexes by dehydration of hydroxivinylidene species in the presence of SiO_2 or Al_2O_3 has been previously described: (a) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721−2727. (b) Gauss, C.; Veghini, D.; Orama, O.; Berke, H. *J. Organomet. Chem.* **1997**, *541*, 19−38.

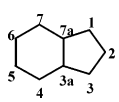
(16) The reaction of **3** with NaBH$_4$ proceeds in a different way, giving instead the alkynyl complex [Ru{C≡CCH$_2$[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (**23**), which has been isolated as an air-stable yellow powder in 77% yield. Characterization follows from elemental analysis and NMR spectroscopy (see the Supporting Information).

Herein an unprecedented synthetic methodology of highly unsaturated allenylidenes is described. The synthetic approach is based on the regio- and stereoselective sequential insertions of ynamines into the allenylidene moieties. The systematic and efficient method allows the synthesis of alkenyl-, butadienyl- and hexatrienylallenylidene complexes of the types [Ru{=C=C=C(NEt$_2$)[(CR=CH)$_n$C(R′)=C(R″)Ph]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (n = 0−2; **3**−**6**, **18**, **19**, and **22**), [Ru{=C=C=C(H)[(CMe=CH)$_n$C(R)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (n = 0, 1; **16**, **17**, and **21**), and [Ru{=C=C=C(C≡CR)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**8** and **9**). The ability of the aminoallenylidene **3** to undergo regioselective C−C coupling with carbanions is also exploited to build up organometallic species bearing unusual highly unsaturated alkynyl complexes of the typew [Ru{C≡CC(=CHR)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (**12**−**14**) and [Ru{C≡CC(=C=C=CRR′)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (**10** and **11**), the latter showing three distinct unsaturated carbon−carbon chains arising from the presence of alkynyl, alkenyl, and butatrienyl groups.

The utility of this synthetic methodology in organic synthesis through demetalation processes is currently being investigated. We have recently shown an efficient approach to synthesizing functionalized terminal alkynes starting from the appropriate alkynylruthenium(II) complexes.[10a]

Experimental Section

General Procedures. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of the compounds Me$_3$SiC≡CNEt$_2$[17] and [Ru(=C=C=CRPh)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Ph, H),[4h] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer (inconsistent analyses were found for complexes **8** and **9** due to incomplete combustion). Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using SiMe$_4$ or 85% H$_3$PO$_4$ as standard. DEPT experiments have been carried out for all the compounds reported. Legend for atoms of the indenyl group:



[Ru{=C=C=C(NEt$_2$)[C(Me)=C(R)Ph]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Ph (3), H (4)). The addition of a solution of the allenylidene complex [Ru(=C=C=CRPh)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R= Ph (**1**), H (**2**); 1 mmol) in tetrahydrofuran (40 mL) to a solution of the ynamine MeC≡CNEt$_2$ (2 mmol) in tetrahydrofuran (10 mL) at 0 °C gave an orange solution, which was stirred for 15 min. The solvent was then removed under vacuum, and the orange solid was washed with diethyl ether (2 × 30 mL) and dried in vacuo. Data for **3** are as follows. Yield: 1.03 g (87%). IR (KBr, cm^{-1}): ν(C=C=C) 1989, ν(C=N) 1532, ν(PF$_6^-$) 840. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 49.50 and 49.35 (d, $^2J_{PP}$ = 27.5 Hz). ^{1}H NMR (CDCl$_3$): δ 0.94 and 1.06 (t, 3H each, $^3J_{HH}$ = $^3J_{HH'}$ = 7.1 Hz, CH$_2$C*H*$_3$), 1.79 (s, 3H, =CCH$_3$), 3.17, 3.45, 3.73, and 4.12 (m, 1H each, C*H*$_2$CH$_3$), 4.82 and 4.88 (br, 1H each, H-1 and H-3), 5.26 (br, 1H, H-2), 6.06 and 6.28 (d, 1H each, $^3J_{HH}$ = 7.7 Hz, H-4, H-5, H-6, or H-7), 6.99−7.78 (m, 42H, Ph, H-4, H-5, H-6, or H-7). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 11.74 and 12.94 (s, CH$_2$*C*H$_3$), 20.22 (s, =C*C*H$_3$), 45.75 and 47.11 (s, *C*H$_2$CH$_3$), 76.09 and 76.73 (s, C-1 and C-3), 95.88 (s, C-2), 109.75 and 111.72 (s, C-3a and C-7a), 121.72 (s, C$_\beta$), 122.86 and 123.76 (s, C-4, C-5, C-6, or C-7), 126.05−142.20 (m, Ph, =*C*CH$_3$, =*C*Ph$_2$, C-4, C-5, C-6, or C-7), 155.26 (s, C$_\gamma$N), 199.39 (dd, $^2J_{CP}$ = $^2J_{CP'}$ = 20.7 Hz, Ru=C$_\alpha$). Anal. Calcd for C$_{67}$H$_{60}$F$_6$NP$_3$Ru: C, 67.76; H, 5.10; N, 1.33. Found: C, 67.50; H, 5.33; N, 1.18. Λ_M = 121 Ω^{-1} cm^2 mol^{-1} (acetone). Data for **4** are as follows. Yield: 0.79 g (71%). IR (KBr, cm^{-1}): ν(C=C=C) 1989, ν(C=N) 1540, ν(PF$_6^-$) 840. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 49.58 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.33 and 1.41 (t, 3H each, $^3J_{HH}$ = 6.9 Hz, CH$_2$C*H*$_3$), 1.88 (s, 3H, =CCH$_3$), 3.62 and 3.91 (q, 2H each, $^3J_{HH}$ = 6.9 Hz, C*H*$_2$CH$_3$), 4.90 (d, 2H, $^3J_{HH}$ = 2.6 Hz, H-1 and H-3), 5.21 (t, 1H, $^3J_{HH}$ = 2.6 Hz, H-2), 6.18 (m, 2H, H-4, H-5, H-6, or H-7), 6.20 (s, 1H, =CH), 6.99−7.35 (m, 37H, Ph, H-4, H-5, H-6, or H-7). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 13.35 and 14.14 (s, CH$_2$*C*H$_3$), 17.54 (s, =C*C*H$_3$), 46.72 and 47.78 (s, *C*H$_2$CH$_3$), 77.42 (s, C-1 and C-3), 95.93 (s, C-2), 111.00 (s, C-3a and C-7a), 122.76 (s, C$_\beta$), 123.63 (s, C-4, C-5, C-6, or C-7), 127.39−136.92 (m, Ph, =*C*CH$_3$, =CH, C-4, C-5, C-6, or C-7), 156.79 (s, C$_\gamma$N), 206.68 (t, $^2J_{CP}$ = 21.4 Hz, Ru=C$_\alpha$). Anal. Calcd for C$_{61}$H$_{56}$F$_6$NP$_3$Ru: C, 65.94; H, 5.08; N, 1.26. Found: C, 65.59; H, 4.78; N, 0.98. Λ_M = 124 Ω^{-1} cm^2 mol^{-1} (acetone).

[Ru{=C=C=C(NEt$_2$)[C(SiMe$_3$)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (5). Me$_3$SiC≡CNEt$_2$ (0.26 mL, 2 mmol) was added, at room temperature, to a solution of allenylidene [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (1.08 g, 1 mmol) in 40 mL of tetrahydrofuran. The reaction mixture was stirred for 12 h, and the solvent was removed in vacuo. The solid residue was transferred to a silica chromatography column and washed with diethyl ether, and compound **5** was eluted with a diethyl ether/dichloromethane (3/1) mixture. Removal of the solvents led to the title compound as an orange solid. Yield: 0.79 g (64%). IR (KBr, cm^{-1}): ν(C=C=C) 1980, ν(C=N) 1519, ν(PF$_6^-$) 840. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 47.71 s. ^{1}H NMR (CDCl$_3$): δ 0.09 (s, 9H, Si(CH$_3$)$_3$), 0.71 (dd, 3H, $^3J_{HH}$ = $^3J_{HH'}$ = 7.0 Hz, NCH$_2$C*H*$_3$), 1.10 (dd, 3H, $^3J_{HH}$ = $^3J_{HH'}$ = 7.2 Hz, NCH$_2$C*H*$_3$), 3.43, 3.50, 3.64, and 3.82 (m, 1H each, N(C*H*$_2$CH$_3$)$_2$), 4.75 and 5.00 (br, 1H each, H-1 and H-3), 5.47 (t, 1H, $^3J_{HH}$ = 2.4 Hz, H-2), 5.81 (d, 1H, $^3J_{HH}$ = 8.3 Hz, H-4, H-5, H-6, or H-7), 5.99 (d, 1H, $^3J_{HH}$ = 7.9 Hz, H-4, H-5, H-6, or H-7), 6.74−7.48 (m, 42H, Ph, H-4, H-5, H-6, or H-7). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 1.41 (s, Si(CH$_3$)$_3$), 11.96 and 12.44 (s, N(CH$_2$*C*H$_3$)$_2$), 44.78 and 45.24 (s, N(*C*H$_2$CH$_3$)$_2$), 74.37 and 76.05 (s, C-1 and C-3), 95.97 (s, C-2), 109.98 and 114.34 (s, C-3a and C-7a), 121.11 (s, C$_\beta$), 122.28, 124.35, and 127.03 (s, C-4, C-5, C-6, or C-7), 127.52−140.95 (m, Ph, =*C*SiMe$_3$, C-4, C-5, C-6, or C-7), 155.58 (s, =*C*Ph$_2$), 156.83 (s, C$_\gamma$N), 195.87 (t, $^2J_{CP}$ = 20.6 Hz, Ru=C$_\alpha$). Anal. Calcd for C$_{69}$H$_{66}$F$_6$NP$_3$SiRu: C, 66.55; H, 5.34; N, 1.12. Found: C, 66.20; H, 5.55; N, 1.19. Λ_M = 120 Ω^{-1} cm^2 mol^{-1} (acetone).

[Ru{=C=C=C(NEt$_2$)(CH=CPh$_2$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (6). KF (0.035 g, 0.6 mmol) was added, at room temperature, to a solution of **5** (0.59 g, 0.5 mmol) in 40 mL of methanol. The resulting solution was stirred for 1 h. The solvent was then removed under vacuum, the solid residue was extracted with dichloromethane, and the extract was filtered off. Removal of the solvent under vacuum led to the title compound as an orange solid. Yield: 0.56 g (96%). IR (KBr, cm^{-1}): ν(C=C=C) 1992, ν(C=N) 1531, ν(PF$_6^-$) 837. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 49.66 s. ^{1}H NMR (CDCl$_3$): δ 0.86 (t, 3H, $^3J_{HH}$ = 7.1 Hz, NCH$_2$C*H*$_3$), 1.21 (t, 3H, $^3J_{HH}$ = 7.0 Hz, NCH$_2$C*H*$_3$), 3.33 (q, 2H, $^3J_{HH}$ = 7.1 Hz, NC*H*$_2$CH$_3$), 3.84 (q, 2H, $^3J_{HH}$ = 7.0 Hz, NC*H*$_2$CH$_3$) 4.79 (d, 2H, $^3J_{HH}$ = 2.3 Hz, H-1 and H-3), 5.09 (t, 1H, $^3J_{HH}$ = 2.3 Hz, H-2), 5.91 (s, 1H, =CH), 6.10 (m, 2H,

(17) Himbert, G.; Nabhan, H.; Gerulet, O. *Synthesis* **1997**, 293.

H-4, H-5, H-6, or H-7), 6.89−7.44 (m, 42H, Ph, H-4, H-5, H-6, or H-7). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.31 (s, $N(CH_2CH_3)_2$), 46.18 and 47.20 (s, $N(CH_2CH_3)_2$), 77.35 (s, C-1 and C-3), 94.91 (s, C-2), 110.27 (s, C-3a and C-7a), 121.42 and 123.02 (s, C-4, C-5, C-6, and C-7), 122.27 (s, C_β), 127.49−140.03 (m, Ph and =CH), 148.22 (s, $=CPh_2$), 149.95 (s, $C_\gamma N$), 202.33 (t, $^2J_{CP}$ = 22.0 Hz, $Ru=C_\alpha$). Anal. Calcd for $C_{66}H_{58}F_6NP_3Ru$: C, 67.59; H, 4.98; N, 1.19. Found: C, 67.40; H, 4.82; N, 1.24. Λ_M = 118 Ω^{-1} cm^2 mol^{-1} (acetone).

[Ru{=C=CHC=(NEt$_2$)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]-[X]$_2$ (7). To a solution of [Ru{=C=C=C(NEt$_2$)[C(Me)=CPh$_2$]}-(η^5-C_9H_7)(PPh_3)$_2$][PF_6] in dichloromethane was added, at room temperature, a slight excess of HBF_4·OEt_2. The solvent was removed under vacuum, and the solid residue was washed with diethyl ether (3 × 20 mL) and dried in vacuo to give an orange solid. Yield: 96%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.44 and 31.95 (d, $^2J_{PP}$ = 20.3 Hz). ^1H NMR ($CDCl_3$): δ 0.91 (m, 6H, $N(CH_2CH_3)_2$), 1.88 (s, 3H, CH_3), 3.35 and 3.66 (m, 4H, $N(CH_2CH_3)_2$), 5.17 (s, 1H, =C=CH), 5.52 (d, 1H, $^3J_{HH}$ = 6.5 Hz, H-4, H-5, H-6, or H-7), 5.64 (d, 1H, $^3J_{HH}$ = 8.3 Hz, H-4, H-5, H-6, or H-7), 5.68 and 5.74 (br, 1H each, H-1 and H-3), 6.42 (br, 1H, H-2), 6.66−7.57 (m, 42H, Ph, H-4, H-5, H-6, or H-7). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.52 and 12.65 (s, $N(CH_2CH_3)_2$), 21.59 (s, $=CCH_3$), 48.23 and 49.68 (s, $N(CH_2CH_3)_2$), 84.53 and 86.09 (d, $^2J_{CP}$ = 6.5 Hz, C-1 and C-3), 97.60 (s, C-2), 110.49 (s, C_β), 119.00 and 121.01 (s, C-3a and C-7a), 123.35, 124.79 and 127.25 (s, C-4, C-5, C-6, or C-7), 127.81−146.02 (m, Ph, $=CPh_2$, $=CCH_3$, C-4, C-5, C-6, or C-7), 171.84 (s, C_γ=N), 334.81 (t, $^2J_{CP}$ = 14.7 Hz, $Ru=C_\alpha$).

[Ru{=C=C=C(C≡CR)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]-[BF$_4$] (R = Ph (8), SiMe$_3$ (9)). A solution of [Ru{=C=C=C(NEt$_2$)[C(Me)=CPh$_2$]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (1.19 g, 1 mmol) in 50 mL of tetrahydrofuran was slowly added over the corresponding alkynyllithium (5 mmol) (generated in situ by addition of Li-*n*-Bu to a solution of the alkyne in 20 mL of tetrahydrofuran, at −20 °C), at −20 °C. The reaction mixture was warmed to room temperature and stirred for a further 30 min. The solvent was then removed under vacuum, the solid residue was extracted with ca. 40 mL of diethyl ether, and the orange solution was filtered off. This solution was cooled at −20 °C, and HBF_4·Et_2O was added dropwise. Immediately, an insoluble blue-violet solid precipitated, but the addition was continued until no further solid was formed. The solution was then decanted and the solid washed with diethyl ether (3 × 20 mL) and dried in vacuo. The solid was transferred to a silica gel chromatography column. Elution with a dichloromethane/MeOH (10/1) mixture gave a blue-violet band from which complexes **8** and **9** were isolated after solvent removal. Data for **8** are as follows. Yield: 90% (1.04 g). IR (KBr, cm^{-1}): ν(C≡C) 2167, ν(C=C=C) 1918, $\nu(BF_4^-)$ 1064. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.75 s. ^1H NMR ($CDCl_3$): δ 2.39 (s, 3H, $=CCH_3$), 5.08 (t, 1H, $^3J_{HH}$ = 2.8 Hz, H-2), 5.41 (d, 2H, $^3J_{HH}$ = 2.8 Hz, H-1 and H-3), 6.52 (m, 2H, H-4, H-5, H-6, or H-7), 6.85−7.45 (m, 47H, Ph, H-4, H-5, H-6, or H-7). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.89 (s, $=CCH_3$), 89.25 (s, C-1 and C-3), 99.23 (s, ≡C), 100.72 (s, C-2), 102.21 (s, ≡C), 115.61 (s, C-3a and C-7a), 127.09−146.76 (m, Ph, $=CCH_3$), $=CPh_2$, C-4, C-5, C-6, and C-7), 156.86 (s, C_γ), 222.68 (s, C_β), 281.78 (t, $^2J_{CP}$ = 18.7 Hz, $Ru=C_\alpha$). MS (FAB): *m/z* 1071 [M$^+$], 741 [M$^+$ − R], 479 [M$^+$ − R − PPh_3], 363 [M$^+$ − R − PPh_3 − C_9H_8] (R = [C=C=C(C≡CPh){C(Me)=CPh$_2$}]). Λ_M = 118 Ω^{-1} cm^2 mol^{-1} (acetone). Data for **9** are as follows. Yield: 94% (1.08 g). IR (KBr, cm^{-1}): ν(C≡C) 2131, ν(C=C=C) 1922, $\nu(BF_4^-)$ 1058. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 48.22 s. ^1H NMR (CD_2Cl_2): δ −0.05 (s, 9H, $Si(CH_3)_3$), 2.33 (s, 3H, $=CCH_3$), 5.05 (t, 1H, $^3J_{HH}$ = 2.6 Hz, H-2), 5.47 (d, 2H, $^3J_{HH}$ = 2.6 Hz, H-1 and H-3), 6.60 (m, 2H, H-4, H-5, H-6, or H-7), 7.04−7.46 (m, 42H, Ph, H-4, H-5, H-6, or H-7). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −0.13 (s, $Si(CH_3)_3$), 23.78 (s, $=CCH_3$), 86.61 (s, C-1 and C-3), 97.51 (s, C-2), 101.99 and 110.84 (s, C≡C), 112.51 (s, C-3a and C-7a), 123.96 (s, C-4, C-5, C-6, and C-7), 128.66−143.87 (m, Ph, $=CCH_3$ and $=CPh_2$), 152.95 (s, C_γ), 221.88 (s, C_β), 280.17 (t, $^2J_{CP}$ = 19.5 Hz, $Ru=C_\alpha$). MS (FAB): *m/z* 1067 [M$^+$], 741 [M$^+$ − R], 479 [M$^+$ − R − PPh_3], 363 [M$^+$ − R − PPh_3 − C_9H_8] (R = [C=C=C(C≡CSiMe$_3$){C(Me)=CPh$_2$}]). Λ_M = 122 Ω^{-1} cm^2 mol^{-1} (acetone).

[Ru{C≡CCR[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (10−14). General Procedure. LiC≡$CCHMe_2$ (3 mmol), LiC≡CCH_2Ph (3 mmol; generated in situ by addition of Li-*n*-Bu (1.6 M) to a solution of the corresponding alkyne in 10 mL of tetrahydrofuran, at −20 °C), LiMe (1.6 M; 1.56 mL, 2.5 mmol), Li-*n*-Bu (1.6 M; 1.56 mL, 2.5 mmol), or $BrMgCH_2CH=CH_2$ (1.0 M; 1.25 mL, 2 mmol) was added, at −20 °C, to a solution of [Ru{=C=C=C(NEt$_2$)[C(Me)=CPh$_2$]}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**3**; 1.19 g, 1 mmol) in 50 mL of tetrahydrofuran. The reaction mixture was brought to room temperature and stirred for further 1 h. The solvent was then removed under vacuum, the solid residue was extracted with diethyl ether (ca. 10 mL), and the resulting solution was transferred to an Al_2O_3 (neutral: activity grade I) chromatography column. Elution with diethyl ether and removal of the solvent under vacuum led to the title compounds.

[Ru{C≡CC[=C=C=C(Me)$_2$][C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)-(PPh$_3$)$_2$] (10). Orange solid. Yield: 83% (0.85 g). IR (KBr, cm^{-1}): ν(C≡C) 2062, ν(C=C=C=C) 2008. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 52.14 s. ^1H NMR (C_6D_6): δ 1.75 (s, 6H, $=C(CH_3)_2$), 2.59 (s, 3H, $=CCH_3$), 4.75 (d, 2H, $^3J_{HH}$ = 2.4 Hz, H-1 and H-3), 5.45 (t, 1H, $^3J_{HH}$ = 2.4 Hz, H-2), 6.50 and 6.80 (m, 2H each, H-4, H-5, H-6, and H-7), 7.07−7.70 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.97, 24.16, and 24.75 (s, $=CCH_3$ and $=C(CH_3)_2$), 75.28 (t, $^2J_{CP}$ = 3.8 Hz, C-1 and C-3), 95.48 (s, C-2), 106.74 and 107.45 (s, C_γ=C=C=C), 109.61 (s, C-3a and C-7a), 114.64 (s, C_β), 121.03 (t, $^2J_{CP}$ = 24.6 Hz, $Ru-C_\alpha$), 123.41 and 126.26 (s, C-4, C-5, C-6, and C-7), 125.94−145.32 (m, Ph and C_γ), 136.85 (s, $=CCH_3$), 147.15 (s, $=CPh_2$), 158.58 (s, C_γ=C=C=$C(CH_3)_2$). Anal. Calcd for $C_{68}H_{56}P_2Ru$: C, 78.82; H, 5.45. Found: C, 78.63; H, 5.54.

[Ru{C≡CC[=C=C=CHPh][C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)-(PPh$_3$)$_2$] (11). Red solid. Yield: 89% (0.96 g). IR (KBr, cm^{-1}): ν(C≡C) 2059, (C=C=C=C) 1987. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51.46 and 51.62 s. ^1H NMR (C_6D_6): δ 2.50 and 2.64 (s, 3H each, $=CCH_3$), 4.76 (br, 2H, 2H-1 and 2H-3), 5.40 (m, 2H, 2H-2), 5.97 and 6.03 (s, 1H each, =CH), 6.43−6.51 (m, 4H, H-4, H-5, H-6, or H-7), 6.80−6.83 (m, 4H, H-4, H-5, H-6, or H-7), 6.95−7.21 (m, 90H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.02 and 22.13 (s, $=CCH_3$), 75.37 (m, 2C-1 and 2C-3), 95.33 and 95.95 (s, C-2), 101.48 (s, 2=CH), 109.57 and 109.79 (s, 2C-3a and 2C-7a), 113.57 and 113.89 (s, C_β), 118.42 and 118.99 (s, C_γ=C=C=C), 123.22, 123.37, 126.27, and 126.33 (s, 2C-4, 2C-5, 2C-6, and 2C-7), 126.72−138.71 (m, Ph, $Ru-C_\alpha$), 136.53 and 137.01 (s, $=CCH_3$), 139.56 (s, $2=CPh_2$), 140.06−145.25 (m, C_{ipso} and C_γ), 155.39 and 155.80 (s, C_{ipso}). Anal. Calcd for $C_{72}H_{56}P_2Ru$: C, 79.76; H, 5.21. Found: C, 79.67; H, 5.14.

[Ru{C≡CC(=CH$_2$)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (12). Yellow solid. Yield: 76% (0.74 g). IR (KBr, cm^{-1}): ν(C≡C) 2055. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.02 s. ^1H NMR (C_6D_6): δ 2.43 (s, 3H, $=CCH_3$), 4.68 (s br, 2H, H-1 and H-3), 4.94 and 5.05 (d, 1H each, $^2J_{HH}$ = 2.6 Hz, =CH), 5.39 (s br, 1H, H-2), 6.38 and 6.70 (m, 2H each, H-4, H-5, H-6, and H-7), 6.92−7.21 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.80 (s, $=CCH_3$), 74.91 (s br, C-1 and C-3), 95.10 (s, C-2), 109.34 (s, C-3a and C-7a), 112.07 (t, $^2J_{CP}$ = 24.5 Hz, $Ru-C_\alpha$), 114.90 (s, C_β), 115.94 (s, $=CH_2$), 123.29 and 126.09 (s, C-4, C-5, C-6, and C-7), 125.92−144.62 (m, Ph, $=CMe$, $C=CH_2$ and $=CPh_2$); Anal. Calcd for $C_{64}H_{52}P_2Ru$: C, 78.11; H, 5.32. Found: C, 78.44; H, 4.94.

[Ru{C≡CC(=CHPr)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$](13). Orange solid. Yield: 87% (0.89 g). IR (KBr, cm^{-1}): ν(C≡C) 2052. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.09 s. ^1H NMR (C_6D_6): δ 0.64 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3), 1.14 (m, 2H, CH_2), 1.84 (s, 3H, $=CCH_3$), 2.23 (m, 2H, CH_2), 4.51 (d, $^3J_{HH}$ = 2.4 Hz, H-1 and H-3), 4.95 (t, $^3J_{HH}$ = 7.1 Hz, =CH), 5.14 (t, $^3J_{HH}$ = 2.4 Hz, H-2), 6.43 and 6.80 (m, 2H each, H-4, H-5, H-6, and H-7), 7.06−7.36 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ14.32 (s, CH_3), 21.90

(s, =C*C*H$_3$), 22.99 (s, CH$_2$), 32.86 (s, =C*C*H$_2$), 74.78 (s, C-1 and C-3), 95.76 (s, C-2), 109.99 (s, C-3a and C-7a), 113.00 (t, $^2J_{CP}$ = 23.8 Hz, Ru−C$_\alpha$), 113.12 (s, C$_\beta$), 123.68 and 126.14 (s, C-4, C-5, C-6, and C-7), 132.55 (s, =CH), 125.70−144.90 (m, Ph, =*C*Me, =*C*Ph$_2$, *C*=C). Anal. Calcd for $C_{67}H_{58}P_2Ru$: C, 78.42; H, 5.69. Found: C, 78.62; H, 5.46.

[Ru{C≡CC(=CHCH=CH$_2$)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (14). Orange solid. Yield: 74% (0.74 g). IR (KBr, cm^{-1}): ν(C≡C) 2041. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 53.30 s. ^{1}H NMR (C$_6$D$_6$): δ 2.24 (s, 3H, =CCH$_3$), 4.68 (d, 2H, $^3J_{HH}$ = 2.6 Hz, H-1 and H-3), 4.88 (dd, 1H, $^3J_{HH}$ = 10.3 Hz, $^2J_{HH}$ = 1.9 Hz, =C*H*$_a$H$_b$), 5.00 (dd, 1H, $^3J_{HH}$ = 17.1 Hz, $^2J_{HH}$ = 1.9 Hz, CH$_a$C*H*$_b$), 5.32 (t, 1H, $^3J_{HH}$ = 2.6 Hz, H-2), 6.11 (d, 1H, $^3J_{HH}$ = 10.8 Hz, =CH), 6.51 and 6.77 (m, 2H each, H-4, H-5, H-6, and H-7), 6.93−7.50 (m, 41H, Ph and =CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 22.09 (s, =C*C*H$_3$), 75.11 (m, C-1 and C-3), 95.43 (s, C-2), 110.01 (s, C-3a and C-7a), 113.43 (s, =CH$_2$), 114.33 (s, C$_\beta$), 120.94 (t, $^2J_{CP}$ = 23.8 Hz, Ru−C$_\alpha$), 123.82 and 126.50 (s, C-4, C-5, C-6, and C-7), 126.19−139.33 (m, Ph), 132.99 and 138.06 (s, =CH), 133.41 (s, =*C*CH$_3$), 137.18 (s, C$_\gamma$), 139.73 (s, =*C*Ph$_2$), 144.42 and 144.81 (s, C$_{ipso}$). Anal. Calcd for $C_{66}H_{54}P_2Ru$: C, 78.47; H, 5.39. Found: C, 78.32; H, 5.25.

[Ru{C≡CCH(NEt$_2$)[C(Me)=CPh$_2$]})(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (15). LiBHEt$_3$ (1 M in tetrahydrofuran; 0.090 mL, 0.08 mmol) was added to a solution of **3** (0.090 g, 0.08 mmol) in [D$_8$]-tetrahydrofuran at 0 °C, in a NMR tube. Total conversion of complex **3** took place instantaneously. ^{31}P{^{1}H} NMR ([D$_8$]-tetrahydrofuran): δ 52.43 and 52.73 (d, $^2J_{PP}$ = 34.0 Hz). ^{1}H NMR ([D$_8$]tetrahydrofuran): δ 0.80 (m, 6H, CH$_2$C*H*$_3$), 1.99 (s, 3H, =CCH$_3$), 2.65 and 2.72 (q, 2H each, $^3J_{HH}$ = 6.8 Hz, C*H*$_2$-CH$_3$), 4.40 and 4.47 (br, 1H each, H-1 and H-3), 4.42 (s, 1H, CH), 5.13 (t, 1H, $^3J_{HH}$ = $^3J_{HH'}$ = 2.4 Hz, H-2), 6.29 and 6.68 (m, 2H each, H-4, H-5, H-6, and H-7), 6.84−7.37 (m, 40H, Ph). ^{13}C{^{1}H} NMR ([D$_8$]tetrahydrofuran): δ 10.82 (s, CH$_2$*C*H$_3$), 16.82 (s, =C*C*H$_3$), 42.09 (s, *C*H$_2$CH$_3$), 58.79 (s, C$_\gamma$H), 73.22 and 73.36 (s, C-1 and C-3), 93.60 (t, $^2J_{CP}$ = $^2J_{CP}$ = 22.7 Hz, Ru−C$_\alpha$), 94.83 (s, C-2), 109.11, 109.64, and 110.24 (s, C-3a, C-7a, and C$_\beta$), 122.74 and 123.27 (s, C-4, C-5, C-6, or C-7), 125.10−138.89 (m, Ph, C-4, C-5, C-6, or C-7), 142.89 and 143.94 (s, =*C*CH$_3$ and =*C*Ph$_2$).

[Ru{=C=C=C(H)[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (16). A solution of **15** (0.5 mmol) in tetrahydrofuran (5 mL) was transferred to a silica gel column (20 cm). Elution with a hexane/diethyl ether mixture (3/1) produced a change of color from orange to violet. Once the transformation of color finished, the elution with a mixture of dichloromethane/MeOH (10/1) gave a violet band. Evaporation of the solvents yields complex **16** as a violet powder. Yield: 0.53 g, 86%. IR (KBr, cm^{-1}): ν(C=C=C) 1932, ν(PF$_6^-$) 839. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 46.99 (s). ^{1}H NMR (CDCl$_3$): δ 2.30 (s, 3H, =CCH$_3$), 5.31 (br, 2H, H-1 and H-3), 5.39 (br, 1H, H-2), 6.33 (m, 2H, H-4, H-5, H-6, or H-7), 7.14−7.57 (m, 42H, Ph, H-4, H-5, H-6, or H-7), 8.34 (s, 1H, =C=C=CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 19.13 (s, =C*C*H$_3$), 84.92 (s, C-1 and C-3), 96.81 (s, C-2), 111.65 (s, C-3a and C-7a), 123.25 (s, C-4, C-5, C-6, or C-7), 126.47−142.35 (m, Ph, =*C*CH$_3$, C-4, C-5, C-6, or C-7), 150.61 (s, C$_\gamma$), 161.70 (s, =*C*Ph$_2$), 208.84 (s, C$_\beta$), 295.05 (t, $^2J_{CP}$ = 19.7 Hz, Ru=C$_\alpha$). Anal. Calcd for $C_{63}H_{51}F_6P_3Ru$: C. 67.80; H, 4.60. Found: C, 67.64; H, 4.75. Λ$_M$ = 127 Ω^{-1} cm^2 mol^{-1} (acetone). MS (FAB): *m/z* 971 [M$^+$], 741 [M$^+$ − R], 479 [M$^+$ − R − PPh$_3$] (R = [C=C=CH{C(Me)=CPh$_2$}]).

[Ru{=C=C=C(H)(CH=CPh$_2$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (17). LiBHEt$_3$ (1 M; 1.2 mL, 1.2 mmol) was added, at −20 °C, to a solution of [Ru{=C=C=C(NEt$_2$)(CH=CPh$_2$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]-[PF$_6$] (**6**; 1.17 g, 1 mmol) in 50 mL of tetrahydrofuran. The mixture was warmed to room temperature, and the solvent was concentrated to ca. 5 mL. The orange solution was transferred to a silica gel chromatography column (20 cm high). Elution with a hexane/diethyl ether (3/1) mixture led to a color change from orange to violet. Once the orange color totally disappeared, elution with a dichloromethane/MeOH mixture (10/1) gave the title compound after solvent removal as a violet solid. Yield: 82% (0.90 g). IR (KBr, cm^{-1}): ν(C=C=C) 1934, ν(PF$_6^-$) 837. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 46.97 s. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.34 (d, 2H, $^3J_{HH}$ = 2.9 Hz, H-1 and H-3), 5.46 (t, 1H, $^3J_{HH}$ = 2.9 Hz, H-2), 6.37 (m, 2H, H-4, H-5, H-6, or H-7), 6.45 (d, 1H, $^3J_{HH}$ = 12.1 Hz, =CH), 6.82−7.65 (m, 42H, Ph, H-4, H-5, H-6, or H-7), 8.48 (d, 1H, $^3J_{HH}$ = 12.1 Hz, =C=C=CH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 85.45 (s, C-1 and C-3), 97.50 (s, C-2), 112.47 (s, C-3a and C-7a), 123.65−141.63 (m, Ph, C-4, C-5, C-6, and C-7), 138.79 (s, =CH), 146.60 (s, C$_\gamma$), 160.67 (s, =*C*Ph$_2$), 215.69 (s, C$_\beta$), 292.66 (t, $^2J_{CP}$ = 18.9 Hz, Ru=C$_\alpha$). Anal. Calcd for $C_{62}H_{49}F_6P_3Ru$: C, 67.57; H, 4.48. Found: C, 67.39; H, 4.21. Λ$_M$ = 125 Ω^{-1} cm^2 mol^{-1} (acetone).

[Ru{=C=C=C(NEt$_2$)[(CMe=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (18). This complex was prepared as described for **3** and **4** by starting from the allenylidene derivative **16** (0.077 mL, 1 mmol) and the ynamine MeC≡CNEt$_2$ (83 mL, 2 mmol) as an orange powder. Yield: 0.49 g (80%). IR (KBr, cm^{-1}): ν(C=C=C) 1992, ν(C=N) 1536, ν(PF$_6^-$) 840. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 49.40 (s). ^{1}H NMR (CDCl$_3$): δ 1.08 and 1.21 (t, 3H each, $^3J_{HH}$ = 6.8 Hz, CH$_2$C*H*$_3$), 1.51 and 1.86 (s, 3H each, =CCH$_3$), 3.08 and 3.76 (q, 2H each, $^3J_{HH}$ = 6.8 Hz, C*H*$_2$CH$_3$), 4.83 (br, 2H, H-1 and H-3), 5.26 (br, 1H, H-2), 5.88 (s, 1H, =CH), 6.05 (m, 2H, H-4, H-5, H-6, or H-7), 6.90−7.35 (m, 42H, Ph, H-4, H-5, H-6, or H-7). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 12.90 and 13.78 (s, CH$_2$*C*H$_3$), 17.33 and 20.60 (s, =C*C*H$_3$), 45.91 and 47.02 (s, *C*H$_2$CH$_3$), 76.39 (s, C-1 and C-3), 95.46 (s, C-2), 110.51 (s, C-3a and C-7a), 121.07 (s, C$_\beta$), 123.05 (s, C-4, C-5, C-6, or C-7), 126.98−143.33 (m, Ph, =*C*CH$_3$, =*C*Ph$_2$, C-4, C-5, C-6, or C-7), 132.41 (s, =CH), 156.21 (s, C$_\gamma$N), 202.21 (t, $^2J_{CP}$ = 21.2 Hz, Ru=C$_\alpha$). Anal. Calcd for $C_{70}H_{64}F_6NP_3Ru$: C, 68.51; H, 5.26; N, 1.14. Found: C, 68.14; H, 5.14; N, 1.19. Λ$_M$ = 121 Ω^{-1} cm^2 mol^{-1} (acetone). MS (FAB): *m/z* 1082 [M$^+$], 820 [M$^+$ − PPh$_3$], 479 [M$^+$ − PPh$_3$ − R] (R = [C=C=C(NEt$_2$){CMe=CHC(Me)=CPh$_2$}]).

[Ru{=C=C=C(NEt$_2$)[(C(SiMe$_3$)=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (19). A solution of [Ru{=C=C=C(H)-[C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**16**; 1.17 g, 1 mmol) in 50 mL of tetrahydrofuran was slowly added to a solution of Me$_3$SiC≡CNEt$_2$ (0.34 g, 2 mmol) in 10 mL of tetrahydrofuran at room temperature. The solution became immediately orange, and the reaction mixture was stirred for a further 1 h. The solvent was then removed under vacuum and the residue washed with diethyl ether (2 × 30 mL). The solid residue was purified by chromatography column on silica gel with diethyl ether/dichloromethane (4/1) as eluant, giving an orange band. Evaporation of the solvents yielded complex **19** as an orange solid. Yield: 0.77 g (60%). IR (KBr, cm^{-1}): ν(C=C=C) 1987, ν(C=N) 1533, ν(PF$_6^-$) 839. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 47.60 and 48.32 (d, $^2J_{PP}$ = 26.1 Hz). ^{1}H NMR (CDCl$_3$): δ 0.41 (s, 9H, Si(CH$_3$)$_3$), 0.84 and 0.92 (t, 3H each, $^3J_{HH}$ = 7.1 Hz, N(CH$_2$C*H*$_3$)$_2$), 2.13 (s, 3H, =CCH$_3$), 3.02 and 3.19 (m, 1H each, NC*H*$_2$CH$_3$), 3.02−3.44 (m, 2H, NC*H*$_2$CH$_3$), 4.76 and 4.86 (br, 1H each, H-1 and H-3), 5.38 (t, 1H, $^3J_{HH}$ = $^3J_{HH'}$ = 2.6 Hz, H-2), 5.74 and 5.90 (d, 1H each, $^3J_{HH}$ = 7.1 Hz, H-4, H-5, H-6, or H-7), 6.61 (s, 1H, =CH), 6.66−7.39 (m, 42H, Ph, H-4, H-5, H-6, or H-7). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 0.67 (s, Si(CH$_3$)$_3$), 12.37 and 13.23 (s, N(CH$_2$*C*H$_3$)$_2$), 21.70 (s, =C*C*H$_3$), 45.19 and 45.65 (s, N(*C*H$_2$-CH$_3$)$_2$), 74.71 (d, $^2J_{CP}$ = 6.5 Hz, C-1 or C-3), 75.66 (d, $^2J_{CP}$ = 5.5 Hz, C-1 or C-3), 96.13 (s, C-2), 110.90 and 111.27 (s, C-3a and C-7a), 121.27 (s, C$_\beta$), 123.05 and 123.25 (s, C-4, C-5, C-6, or C-7), 127.28−137.18 (m, Ph, C-4, C-5, C-6, or C-7), 130.79 (s, =*C*CH$_3$), 141.10, 141.80, 141.94, and 144.46 (s, C$_{ipso}$, =*C*Ph$_2$ and =*C*SiMe$_3$), 145.30 (s, =CH), 159.14 (s, C$_\gamma$N), 201.50 (dd, $^2J_{CP}$ = 21.7 Hz, $^2J_{CP'}$ = 19.9 Hz, Ru=C$_\alpha$). Anal. Calcd for $C_{72}H_{70}F_6NP_3SiRu$: C. 67.28; H, 5.49; N, 1.08. Found: C, 66.91; H, 5.52; N, 0.99. Λ$_M$ = 122 Ω^{-1} cm^2 mol^{-1} (acetone).

[Ru{C≡CCH(NEt$_2$)[(CMe=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (20). This complex was prepared in a NMR tube as described for **16** by starting from the allenylidene complex **18** (0.080 g, 0.07 mmol) and LiBHEt$_3$ (1 M in tetrahydrofuran;

0.080 mL, 0.07 mmol). Total conversion of complex **18** took place instantaneously. $^{31}P\{^1H\}$ NMR ([D$_8$]tetrahydrofuran): δ 52.18 and 52.95 (d, $^2J_{PP}$ = 31.7 Hz). ^1H NMR ([D$_8$]tetrahydrofuran): δ 0.83 (t, 6H, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3), 1.47 and 1.66 (s, 3H each, =CCH_3), 2.36 (q, 4H, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3), 3.99 (s, 1H, CH), 4.39 and 4.45 (br, 1H each, H-1 and H-3), 5.15 (br, 1H, H-2), 6.14 and 6.61 (m, 2H each, H-4, H-5, H-6, and H-7), 6.74 (s, 1H, =CH), 7.01−7.28 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR ([D$_8$]-tetrahydrofuran): δ 13.35 and 13.38 (s, CH_2CH_3), 16.02 and 21.36 (s, =CCH_3), 42.75 and 43.84 (s, CH_2CH_3), 62.57 (s, $C_\gamma H$), 73.58 and 73.86 (s, C-1 and C-3), 94.57 (s, C-2), 95.87 (t, $^2J_{CP} = {}^2J_{CP'}$ = 24.8 Hz, Ru−C_α), 107.19, 108.53, and 109.34 (s, C-3a, C-7a, and C_β), 122.34, 122.93, 124.93, and 125.95 (s, C-4, C-5, C-6, and C-7), 125.39−143.92 (m, Ph, =CH, =CCH_3, =CPh_2).

[Ru{=C=C=C(H)[(CMe=CH)C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (21). This complex was prepared as described for **16** starting from complex **20** (0.5 mmol) to give a violet powder. Yield: 0.48 g (83%). IR (KBr, cm^{-1}): ν(C=C=C) 1938, $\nu(PF_6^-)$ 839. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.06 (s). ^1H NMR ($CDCl_3$): δ 2.00 and 2.25 (s, 3H each, =CCH_3), 5.22 (t, 1H, $^3J_{HH}$ = 2.6 Hz, H-2), 5.27 (d, 2H, $^3J_{HH}$ = 2.6 Hz, 1H, H-1 and H-3), 6.32 (m, 2H, H-4, H-5, H-6, or H-7), 6.92−7.44 (m, 43H, Ph, =CH, H-4, H-5, H-6, or H-7), 8.17 (s, 1H, =C=C=CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.71 and 20.06 (s, =CCH_3), 84.73 (s, C-1 and C-3), 96.68 (s, C-2), 111.31 (s, C-3a and C-7a), 123.08 (s, C-4, C-5, C-6, and C-7), 126.95−134.69 (m, Ph, =CCH_3), 142.41 and 142.71 (s, C_{ipso}), 145.39 (s, =CCH_3), 150.60 (s, =CPh_2), 152.32 (s, C_γ), 158.49 (s, =CH), 203.50 (s, C_β), 290.93 (t, $^2J_{CP}$ = 19.2 Hz, Ru=C_α). Anal. Calcd for $C_{66}H_{55}F_6P_3Ru$: C, 68.56; H, 4.79. Found: C, 68.21; H, 4.88. Λ_M = 119 Ω^{-1} cm^2 mol^{-1} (acetone). MS (FAB): *m/z* 1010 [M$^+$], 741 [M$^+$ − R], 479 [M$^+$ −R − PPh_3] (R = [C=C=C(H){(CMe=CH)C(Me)=CPh_2}]).

[Ru{=C=C=C(NEt$_2$)[(CMe=CH)$_2$C(Me)=CPh$_2$]}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (22). This complex was prepared as described for **3** and **4** by starting from the allenylidene derivative **21** (0.29 g, 0.25 mmol) and the ynamine MeC≡$CNEt_2$ (0.039 mL, 0.5 mmol) to give an orange powder. Yield: 0.14 g (45%). IR (KBr, cm^{-1}): ν(C=C=C) 1990, ν(C=N) 1533, $\nu(PF_6^-)$ 840. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.59 (s). ^1H NMR ($CDCl_3$): δ 1.26 and 1.31 (t, 3H each, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.49, 1.65, and 1.88 (s, 3H each, =CCH_3), 3.54 and 3.88 (q, 2H each, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 4.82 (d, 2H, $^3J_{HH}$ = 2.6 Hz, H-1 and H-3), 5.20 (t, 1H, $^3J_{HH}$ = 2.6 Hz, H-2), 5.50 and 5.97 (s, 1H each, =CH), 6.12 (m, 2H, H-4, H-5, H-6, or H-7), 6.90−7.50 (m, 42H, Ph, H-4, H-5, H-6, or H-7). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.02 and 13.76 (s, CH_2CH_3), 16.78, 18.22, and 21.09 (s, =CCH_3), 46.40 and 47.55 (s, CH_2CH_3), 76.70 (s, C-1 and C-3), 95.43 (s, C-2), 110.42 (s, C-3a and C-7a), 121.14 (s, C_β), 123.15 (s, C-4, C-5, C-6, and C-7), 126.60−143.18 (m, Ph, =CCH_3, =CPh_2, =CH), 157.11 (s, C_γN), 202.61 (t, $^2J_{CP}$ = 21.5 Hz, Ru=C_α). Anal. Calcd for $C_{73}H_{68}F_6NP_3Ru$: C, 69.18; H, 5.41; N, 1.10. Found: C, 69.34; H, 5.15; N, 1.06. Λ_M = 115 Ω^{-1} cm^2 mol^{-1} (acetone).

X-ray Structure Determination of 3·EtOH. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of the complex in ethanol. Data collection, crystal, and refinement parameters are collected in Table 3. Diffraction data were recorded at 200(2) K on a Nonius KappaCCD single-crystal diffractometer using Cu Kα radiation. The crystal-to-detector distance was fixed at 29 mm, and a total of 1210 frames were collected using the oscillation method, with 2° oscillation and 40 s exposure time per frame. The data collection strategy was calculated with the program Collect.[18] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[19] Unit cell dimensions were determined from 10 681 reflections. All data completeness was 98%.

Table 3. Crystal Data and Structure Refinement Details for 3·EtOH

chem formula	$C_{66}H_{58}F_6NP_3Ru$·EtOH
fw	1225.69
T (K)	200(2)
wavelength (Å)	1.54184
cryst system	triclinic
space group	$P\bar{1}$
a (Å)	13.0687(6)
b (Å)	13.7345(6)
c (Å)	18.4915(7)
α (deg)	110.983(2)
β (deg)	104.348(2)
γ (deg)	90.063(3)
V (Å^3)	2987.5(2)
Z	2
ρ_{calcd} (g cm^{-3})	1.363
μ (mm^{-1})	3.401
F(000)	1267
cryst size (mm)	0.23 × 0.075 × 0.075
monochromator	graphite
θ range (deg)	2.65−69.88
index ranges	$-15 \le h \le 15$
	$-16 \le k \le 15$
	$0 \le l \le 22$
no. of rflns collected	27 340
no. of indep rflns	11 083 (R(int) = 0.076)
no. of params/restraints	712/3
goodness of fit on F^2	0.892
R ($I > 2\sigma(I)$)[a]	R1 = 0.0503, wR2 = 0.1166
R (all data)	R1 = 0.0778, wR2 = 0.1275
largest diff peak and hole (e Å^{-3})	0.961 and −0.649 e

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

The structure was solved by Patterson methods using the program DIRDIF.[20] A multiscan absorption correction was applied using SORTAV[21] (ratio of minimum to maximum apparent transmission 077099). Full-matrix least-squares refinement on F^2 was carried out with SHELXL-97.[22] All non-H atoms were anisotropically refined except the F atoms and C68, C69, and O1 atoms of the disordered PF_6^- and ethanol solvent molecules, respectively, which were isotropically refined. The H atoms were geometrically placed, and their coordinates were refined riding on their parent atoms. The final cycle of full-matrix least-squares refinement based on 11 083 reflections and 712 parameters converged to a final value of R1 ($F^2 > 2\sigma(F^2)$) = 0.0503. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0324P)^2]$ with $\sigma^2(F_o^2)$ from counting statistics and P = (Max (F_o^2,0) + $2F_c^2$)/3. Atomic scattering factors were taken from ref 23. Geometrical calculations were made with PARST.[24] The crystallographic plots were made with PLATON.[25]

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(18) Collect, Nonius BV, Delft, The Netherlands, 1997−2000.
(19) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.
(20) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Techical Report of the Crystallographic Laboratory; University of Nijimegen, Nijimegen, The Netherlands, 1996.
(21) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
(22) Sheldrick, G. M. SHELXL-97: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.
(23) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV (present distrubutor: Kluwer Academic Publishers, Dordrecht, The Netherlands).
(24) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.
(25) Spek, A. L. PLATON, a Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2003.

Supporting Information Available: Text giving synthesis details and characterization data for complex **23** and tables and a CIF file giving crystallographic data for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 235820 (**3**) and 179713 (**18**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (internat.) (+44)1223/336-033; e-mail deposit@ccdc.cam.ac.uk).

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