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Easy Entry to Terminal 1,5- and 1,6-Enynes from (Indenyl)ruthenium(II) Allenylidenes and Grignard Reagents

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Summary: The allenylidene complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ $(R^1 = R^2 = Ph$ (***1a***); $R^1 = H$, $R^2 = Ph$ (***1b***), $C(Me)=CPh_2$ (***1c***); $CR^1R^2 =$ *(1R)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene* (***1d***)) *react with Grignard reagents* $CH_2=CH(CH_2)_nMgBr$ $(n = 1, 2)$ *to yield the σ-alkynyl derivatives* $[Ru\{C\equiv CCR^1R^2(CH_2)_nCH=CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (***2a−d***, ***3a−c***). *Protonation of* ***2a−d*** *and* ***3a−c*** *with* $HBF_4{\cdot}Et_2O$ *leads to the vinylidene complexes* $[Ru\{=C=C(H)CR^1R^2(CH_2)_nCH=CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (***4a−d*** *and* ***5a−c***)*, which can be easily demetalated with acetonitrile to afford the terminal enynes* $HC\equiv CCR^1R^2(CH_2)_nCH=CH_2$ (***6a−d*** *and* ***7a−c***) *and the nitrile complex* $[Ru(N\equiv CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (***8***).

Introduction

The Nicholas reaction (Scheme 1; path A) has found elegant applications in organic synthesis, especially in the field of carbon−carbon bond formation.[1] This type of propargylic substitution proceeds via dicobalt hexacarbonyl−π-alkyne complexes containing coordinated propargyl cations (**A**).[2] These intermediates selectively react at C-3 with a wide variety of heteroatom- and carbon-centered nucleophiles to furnish functionalized propargylic derivatives after oxidative demetalation. In this regard, the cationic transition-metal allenylidene complexes $[M]^+=C=C=CR^1R^2$, readily available by dehydration of 2-propyn-1-ols upon coordination to an unsaturated metal center,[3] can be considered as stabilized propargyl cations, due to the extensive contribution of the metal−alkynyl resonance form $[M]-C\equiv CC^+R^1R^2$.[4] Although the reactivity of cationic allenylidenes is governed by the electron-deficient character of both the C_α and C_γ atoms of the cumulenic chain,[5] regioselective nucleophilic additions at C_γ are usually observed with electron-rich and/or bulky metallic fragments, leading to a wide variety of the functionalized σ-alkynyl complexes $[M]-C\equiv CC(Nu)R^1R^2$.[4] On the basis of these nucleophilic attacks, we have recently developed an alternative procedure for the propargylic substitution of 2-propyn-1-ols mediated by the (indenyl)ruthenium(II) moiety $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (Scheme 1; path B).[6] Thus, in the first step allenylidene complexes **B** are formed and subsequently transformed into the corresponding σ-alkynyl derivatives **C** ($Nu^- = HC\equiv C^-$, $R^3COCH_2^-$, $(CO)_5W=C(OMe)CH_2^-$), which undergo a selective C_β protonation to afford the vinylidene complexes **D**.[7] Finally, demetalation of **D** with acetonitrile leads to the functionalized terminal alkynes in excellent yields.

Pursuing our studies aimed at exploiting the utility of this synthetic route, in this paper we report an easy entry to terminal 1,5- and 1,6-enynes (see Chart 1) based on the regioselective coupling of Grignard reagents $CH_2=CH(CH_2)_nMgBr$ ($n = 1, 2$) with the allenylidene chain in the complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R^1 = R^2 = Ph$; $R^1 = H$, $R^2 = Ph$, $C(Me)=CPh_2$; $CR^1R^2 = (1R)$-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene ($C(C_9H_{16})$)), followed by the corresponding demetalation of the resulting σ-alkynyl complexes (Scheme 1; path B).

Results

The allenylidene complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R^1 = R^2 = Ph$ (**1a**);[5a] $R^1 = H$, $R^2 =$

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[6] (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821. (b) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **2000**, 451. (c) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **2001**, *20*, 3175. (d) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Falvello, L. R.; Llusar, R. M. *Organometallics*, in press.

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Scheme 1. Propargylic Substitution Reactions

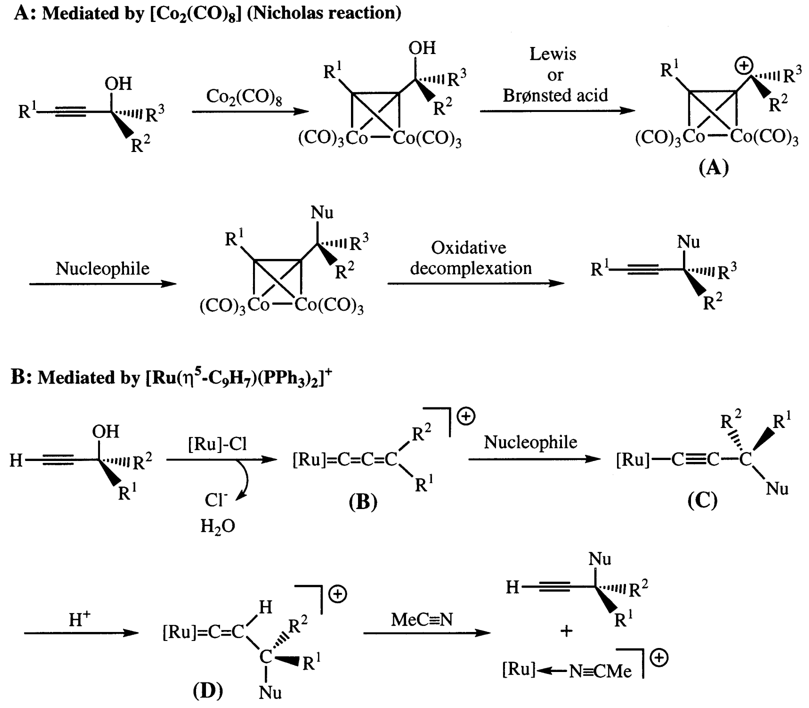
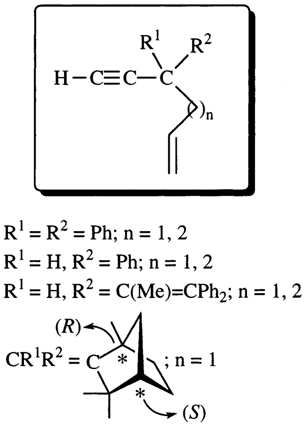


Chart 1



Ph (**1b**),[5a] C(Me)=CPh$_2$ (**1c**)[8e]) react with the Grignard derivatives CH$_2$=CH(CH$_2$)$_n$MgBr (n = 1, 2), in tetrahydrofuran at −20 °C, to afford the neutral σ-alkynyl derivatives [Ru(C≡CCR^{1}R^2(CH$_2$)$_n$CH=CH$_2$)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (R^1 = R^2 = Ph, n = 1 (**2a**), 2 (**3a**); R^1 = H, R^2 = Ph, n = 1 (**2b**), 2 (**3b**); R^1 = H, R^2 = C(Me)=CPh$_2$, n = 1 (**2c**), 2 (**3c**)) (Scheme 2).[8] Complexes **2a**−**c** and **3a**−**c** have been isolated as air-stable orange solids in 76−88% yield after chromatographic workup on neutral Al$_2$O$_3$. Attempts to synthesize the σ-alkynyl derivatives [Ru(C≡CCR^{1}R^{2}CH=CH$_2$)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] by reaction of the allenylidenes **1a**−**c** with vinylmagnesium bromide failed, and instead complicated mixtures of uncharacterized species were obtained.[9]

Analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) support the proposed formulations for **2a**−**c** and **3a**−**c**.[10] In particular, the formation of an enynyl chain was identified on the basis of (i) the presence of a typical ν(C≡C) absorption band in the IR spectra (KBr) at 2076−2090 cm^{-1} and (ii) characteristic resonances in the ^{13}C{^{1}H} NMR spectra of the Ru−C≡C, C$_\gamma$, CH$_2$, and CH=CH$_2$ carbon nuclei in the ranges δ 90.26−95.29 ($^2J_{CP}$ = 22.6−24.9 Hz, C$_\alpha$), 112.22−115.02 (C$_\beta$), 40.10−52.05 (C$_\gamma$), 30.85−46.97 (CH$_2$), 137.73−140.35 (=CH), and 113.91−115.81 (=CH$_2$).

Demetalation of complexes **2a**−**c** and **3a**−**c** using our two-step method (path B; Scheme 1) proceeds cleanly, yielding the terminal 1,5- and 1,6-enynes HC≡CCR^{1}R^2(CH$_2$)$_n$CH=CH$_2$ (R^1 = R^2 = Ph, n = 1 (**6a**), 2 (**7a**); R^1 = H, R^2 = Ph, n = 1 (**6b**), 2 (**7b**); R^1 = H, R^2 = C(Me)=CPh$_2$, n = 1 (**6c**), 2 (**7c**)) in good overall yields (Scheme 2).[11] Thus, the air-stable vinylidene derivatives [Ru{=C=C(H)CR^{1}R^2(CH$_2$)$_n$CH=CH$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**4a**−**c** and **5a**−**c**) were initially prepared (85−95% yield), via selective C$_\beta$ protonation of **2a**−**c** and **3a**−**c**

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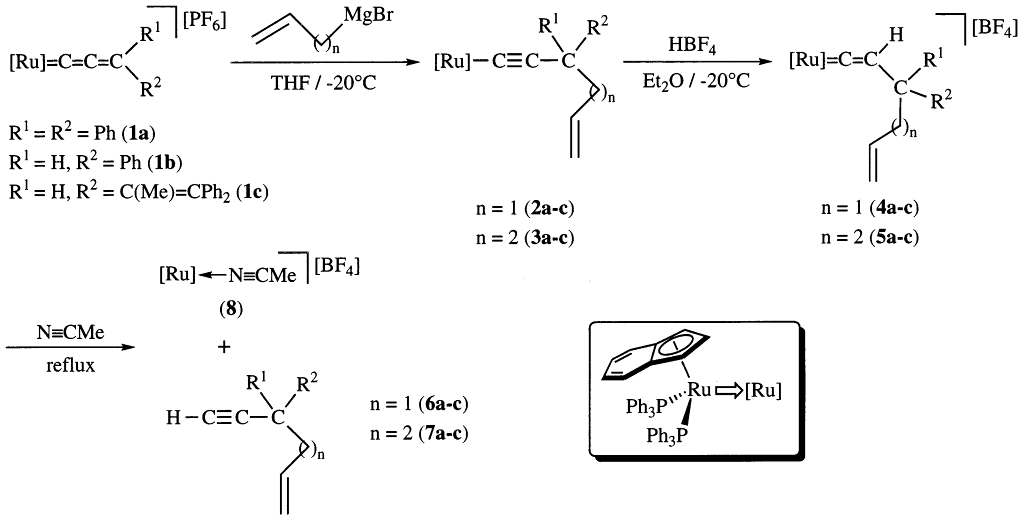
[8] Other regioselective nucleophilic additions at C$_\gamma$ of (indenyl)ruthenium(II) allenylidenes [Ru(=C=C=CR^{1}R^2)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ are reported in: (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3235. (d) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Rodríguez, M. A. *Organometallics* **2002**, *21*, 203. (e) Conejero, S. Ph.D. Thesis, University of Oviedo, 2001.

[9] We note that the coupling of the neutral diphenylallenylidenes *trans*-[RhCl(=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$], [RuCl(=C=C=CPh$_2$)(η^5-C$_5$Me$_5$)(κ^1P-^{i}Pr$_2$PCH$_2$CO$_2$Me)], and [OsCl(=C=C=CPh$_2$)(η^5-C$_5$H$_5$)(P^{i}Pr$_3$)] with CH$_2$=CHMgBr has been reported to produce the pentatrienyl derivatives [Rh{(3−5-η)-CH$_2$CHC=C=CPh$_2$}(P^{i}Pr$_3$)$_2$], [Ru{(3−5-η)-CH$_2$CHC=C=CPh$_2$}(η^5-C$_5$Me$_5$)(κ^1P-^{i}Pr$_2$PCH$_2$CO$_2$Me)], and [Os{(3−5-η)-CH$_2$CHC=C=CPh$_2$}(η^5-C$_5$H$_5$)(P^{i}Pr$_3$)], respectively, via initial substitution of the chloro ligand and subsequent migratory insertion of the allenylidene unit into the M-CH=CH$_2$ bond: (a) Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1996**, *118*, 2495. (b) Braun, T.; Meuer, P.; Werner, H. *Organometallics* **1996**, *15*, 4075. (c) Crochet, P.; Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479.

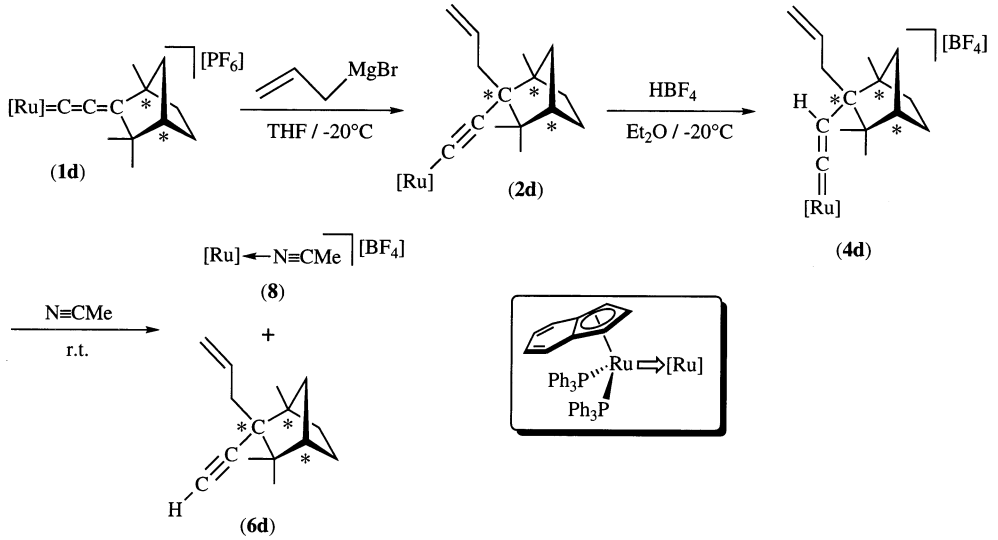
[10] Analytical and spectroscopic data for compounds **2a**−**d** through **7a**−**c** have been provided as Supporting Information.

[11] To the best of our knowledge only terminal enynes **6b** and **7b** have been previously reported: (a) O'Boyle, J. E.; Nicholas, K. M. *Tetrahedron Lett.* **1980**, *21*, 1595. (b) Khun, O.; Rau, D.; Mayr, H. *J. Am. Chem. Soc.* **1998**, *120*, 900. (c) Caporusso, A. M.; Filippi, S.; Barontini, F.; Salvadori, P. *Tetrahedron Lett.* **2000**, *41*, 1227.

Scheme 2



Scheme 3



with HBF$_4$[7] and fully characterized by means of standard spectroscopic techniques and elemental analysis.[10] The most relevant spectroscopic features of **4a**−**c** and **5a**−**c** are (i) (^{1}H NMR) the singlet (**4a** and **5a**) or doublet (**4b**,**c** and **5b**,**c**; J_{HH} = 6.9−9.1 Hz) signal for the acidic vinylidene proton [Ru]=C=CH at δ 4.26−4.63 and (ii) ($^{13}C\{^1H\}$ NMR) the characteristic deshielded Ru=C$_\alpha$ resonance, which appears as a triplet (**4a** and **5a**) or a doublet of doublets (**4b**,**c** and **5b**,**c**) in the range 343.53−354.55 ppm ($^2J_{CP}$ = 15.9−17.4 Hz). In a second step acetonitrile solutions of vinylidenes **4a**−**c** and **5a**−**c** were heated under reflux, affording the terminal enynes **6a**−**c** and **7a**−**c** and the cationic nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)($PPh_3)_2$][BF_4] (**8**).[6a] Enynes **6a**−**c** and **7a**−**c** were purified from the reaction mixture by column chromatography on silica gel (86−95% isolated yields) after filtering off the unsoluble complex **8**. Spectroscopic data of **6a**−**c** and **7a**−**c** are in agreement with the proposed structures.[10] Thus, the IR spectra show the expected ν(C≡C) absorption in the range 2113−2132 cm^{-1}. The acetylenic C≡CH proton appears, in the ^{1}H NMR spectra, as a singlet (**6a** and **7a**) or a doublet (**6b**,**c** and **7b**,**c**; J_{HH} = ca. 2 Hz) at 1.92−2.66 ppm, and the HC≡C carbons resonate, in the $^{13}C\{^1H\}$ NMR, in the ranges δ 70.32−74.14 (HC≡) and 85.29−87.77 (≡C).

The optically active 1,5-enyne HC≡CC(C_9H_{16})CH_2-CH=CH_2 (**6d**) has been also prepared by starting from the chiral allenylidene complex [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)($PPh_3)_2$][PF_6] (**1d**)[6c] by reaction with allylmagnesium bromide (see Scheme 3). Compounds **2d**, **4d**, and **6d** were obtained in a diastereoselective manner as the result of the selective exo addition of the 2-propen-1-yl fragment to the allenylidene chain in **1d**. We have recently reported analogous stereoselective nucleophilic exo additions to **1d**.[6c,d,8e] Since the analytical and spectroscopic data of these species are comparable to those observed for their achiral counterparts, **2a**−**c**, **4a**−**c**, and **6a**−**c** are not worth further discussion.

Discussion

As expected, nucleophilic addition of the Grignard reagents CH_2=CH($CH_2)_n$MgBr (n = 1, 2) to [Ru(=C=C=CR^1R^2)(η^5-C_9H_7)($PPh_3)_2$][PF_6] (**1a**−**d**) proceeds regioselectively at the C$_\gamma$ atom of the allenylidene chain, affording the σ-alkynyl complexes [Ru{C≡CCR^1R^2($CH_2)_n$-CH=CH_2}(η^5-C_9H_7)($PPh_3)_2$] (**2a**−**d** and **3a**−**c**). As we have extensively reported,[6,8] this process is based on the ability of the moiety [Ru(η^5-C_9H_7)($PPh_3)_2$] to sterically protect the electrophilic C$_\alpha$ atom of the allenylidene chain, which allows the selective formation of σ-alkynyl complexes. Taking advantage of this behavior and the well-established synthetic methodology of functionalized alkynes mediated by the (indenyl)ruthenium moiety $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (path B; Scheme 1), 1,5- and 1,6-enynes $HC{\equiv}CCR^1R^2(CH_2)_nCH{=}CH_2$ ($n = 1,2$; **6a**−**d** and **7a**−**c**) have been synthesized in high yields. This synthetic approach can be regarded as the result of the formal coupling of 2-propyn-1-ols with 1-propene or 1-butene (see eq 1).

$$\begin{matrix} HC{\equiv}CCR^1R^2(OH) \\ + \\ CH_2{=}CH(CH_2)_nCH_3 \\ n = 0, 1 \end{matrix} \xrightarrow[H_2O]{[Ru]} \begin{matrix} HC{\equiv}CCR^1R^2(CH_2)_nCH{=}CH_2 \\ n = 1, 2 \end{matrix} \qquad (1)$$

The overall processes of Schemes 2 and 3 constitute an efficient alternative to the known coupling of propargylic alcohols with allylsilanes or -stannanes via $[Co_2(CO)_6]$-stabilized propargyl cations (Nicholas reaction).[1,11a,b] Although the same number of steps are required in both propargylic substitution reactions (see Scheme 1), the quantitative recovery of the metal fragment as the acetonitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**8**) represents an advantage compared with the classical Nicholas reaction in which the metal auxiliary cannot be recovered after the oxidative decomplexation step.[12] Further studies directed to the preparation of novel functionalized terminal alkynes using the allenylidene complexes $[Ru({=}C{=}C{=}CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ as synthons of propargyl cations $HC{\equiv}CC^+R^1R^2$ are in progress.

Experimental Section

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. Allenylidene complexes $[Ru({=}C{=}C{=}CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R^1 = R^2 = Ph$ (**1a**);[5a] $R^1 = H$, $R^2 = Ph$ (**1b**),[5a] $C(Me){=}CPh_2$ (**1c**);[8e] $CR^1R^2 = C(C_9H_{16})$ (**1d**)[6c]) were prepared by following the methods reported in the literature.

Synthesis of the σ-Alkynyl Complexes $[Ru\{C{\equiv}CCR^1R^2(CH_2)_nCH{=}CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ ($R^1 = R^2 = Ph$, $n = 1$ (2a), 2 (3a); $R^1 = H$, $R^2 = Ph$, $n = 1$ (2b), 2 (3b); $R^1 = H$, $R^2 = C(Me){=}CPh_2$, $n = 1$ (2c), 2 (3c); $CR^1R^2 = C(C_9H_{16})$, $n = 1$ (2d)). A solution of the corresponding allenylidene complex $[Ru({=}C{=}C{=}CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**1a**−**d**; 1 mmol) in 30 mL of THF was treated at −20 °C with $CH_2{=}CHCH_2MgBr$ (1.0 M in Et_2O; 1.1 mL, 1.1 mmol) or $CH_2{=}CH(CH_2)_2MgBr$ (0.5 M in THF; 2.2 mL, 1.1 mmol) for 30 min. The mixture was warmed to room temperature, and the solvent was then removed in vacuo. The resulting solid residue was dissolved in dichloromethane (ca. 5 mL) and transferred to an Al_2O_3 (neutral; activity grade I) chromatography column. Elution with a mixture of hexane and diethyl ether (3/1) gave an orange band from which complexes **2a**−**d** and **3a**−**c** were isolated after solvent removal. **2a**: yield 79% (0.768 g). **3a**: yield 81% (0.799 g). **2b**: yield 82% (0.735 g). **3b**: yield 88% (0.801 g). **2c**: yield 87% (0.881 g). **3c**: yield 76% (0.780 g). **2d**: yield 84% (0.791 g).

Synthesis of the Vinylidene Complexes $[Ru\{{=}C{=}C(H)CR^1R^2(CH_2)_nCH{=}CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ ($R^1 = R^2 = Ph$, $n = 1$ (4a), 2 (5a); $R^1 = H$, $R^2 = Ph$, $n = 1$ (4b), 2 (5b); $R^1 = H$, $R^2 = C(Me){=}CPh_2$, $n = 1$ (4c), 2 (5c); $CR^1R^2 = C(C_9H_{16})$, $n = 1$ (4d)). A diluted solution of $HBF_4{\cdot}Et_2O$ in diethyl ether was added dropwise at −20 °C to a stirred solution of the corresponding σ-alkynyl complex $[Ru\{C{\equiv}CCR^1R^2(CH_2)_nCH{=}CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**2a**−**d** and **3a**−**c**; 1 mmol) in 100 mL of diethyl ether. Immediately, an insoluble solid precipitated but the addition was continued until no further solid was formed. The solution was then decanted and the brown solid washed with diethyl ether (3 × 20 mL) and dried in vacuo. **4a**: yield 93% (0.986 g). **5a**: yield 95% (1.020 g). **4b**: yield 89% (0.876 g). **5b**: yield 85% (0.848 g). **4c**: yield 89% (0.979 g). **5c**: yield 87% (0.969 g). **4d**: yield 95% (0.978 g).

Synthesis of Terminal Enynes $HC{\equiv}CCR^1R^2(CH_2)_nCH{=}CH_2$ ($R^1 = R^2 = Ph$, $n = 1$ (6a), 2 (7a); $R^1 = H$, $R^2 = Ph$, $n = 1$ (6b), 2 (7b); $R^1 = H$, $R^2 = C(Me){=}CPh_2$, $n = 1$ (6c), 2 (7c); $CR^1R^2 = C(C_9H_{16})$, $n = 1$ (6d)). A solution of the corresponding vinylidene complex $[Ru\{{=}C{=}C(H)CR^1R^2(CH_2)_nCH{=}CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**4a**−**d** and **5a**−**c**; 1 mmol) in acetonitrile (30 mL) was heated under reflux for 30 min. The solution was then evaporated to dryness and the resulting solid residue extracted with diethyl ether (ca. 50 mL) and filtered. A yellow solid containing the nitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**8**) remains insoluble. The extract was evaporated to dryness and the crude product purified by column chromatography on silica gel with hexane as eluent. Evaporation of the solvent gave terminal enynes **6a**−**d** and **7a**−**c** as colorless oils. **6a**: yield 88% (0.204 g). **7a**: yield 90% (0.222 g). **6b**: yield 86% (0.134 g). **7b**: yield 89% (0.151 g). **6c**: yield 95% (0.259 g). **7c**: yield 93% (0.266 g). **6d**: yield 98% (0.198 g).

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Supporting Information Available: Text giving analytical and spectroscopic data for compounds **2a**−**d** through **7a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Related ruthenium-catalyzed propargylic substitutions of monosubstituted propargylic alcohols, via allenylidene intermediates, have been recently reported: (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (b) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393.