Efficient Synthetic Routes to Terminal γ-Keto−Alkynes and Unsaturated Cyclic Carbene Complexes Based on Regio- and Diastereoselective Nucleophilic Additions of Enolates on Ruthenium(II) Indenyl Allenylidenes

Victorio Cadierno, Salvador Conejero, M. Pilar Gamasa, and José Gimeno*

Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

Enrique Pérez-Carreño and Santiago García-Granda

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

Received March 27, 2001

Ruthenium(II) indenyl allenylidene complexes [Ru{=C=C=C(R^1)Ph}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R^1 = Ph (**1**), H (**2**)) regioselectively react with lithium enolates $LiCH_2COR^2$ (R^2 = Ph, ^{i}Pr, Me, Fc, (*E*)-CH=CHPh) at the C_γ atom to yield the neutral σ-alkynyl derivatives [Ru{C≡CC(R^1)Ph(CH_2COR^2)}(η^5-C_9H_7)(PPh_3)$_2$] (**3a**−**e**, **4a**−**d**). Protonation of **3a**−**e** and **4a**−**d** with HBF_4·Et_2O affords the cationic vinylidene derivatives [Ru{=C=C(H)C(R^1)Ph(CH_2COR^2)}-(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**5a**−**e**, **6a**−**d**), which can be easily demetalated, by treatment with acetonitrile, to yield the terminal γ-keto-substituted alkynes HC≡CC(R^1)Ph(CH_2COR^2) (**7a**−**e**, **8a**−**d**) and the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**9**). The addition of lithium enolates $LiCH_2COR$ (R = Ph, ^{i}Pr, Me) on the optically active allenylidene complex [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**12**; C(C_9H_{16}) = (1*R*)-1,3,3-trimethylbicyclo-[2.2.1]hept-2-ylidene) proceeds in a regio- and diastereoselective manner, affording σ-alkynyl derivatives [Ru{C≡CC(C_9H_{16})(CH_2COR)}(η^5-C_9H_7)(PPh_3)$_2$] (**13a**−**c**). The X-ray crystal structure of **13b** shows that these enolate additions take place on the less sterically congested *exo* face of the allenylidene chain. Chiral alkynes HC≡CC(C_9H_{16})(CH_2COR) (**15a**−**c**) have been also prepared from **13a**−**c** via initial protonation with HBF_4·Et_2O and subsequent treatment of the resulting vinylidenes **14a**−**c** with acetonitrile. Cyclic alkenyl derivatives [Ru{C=CHC(R^1)(R^2)CH=C(R^3)O}(η^5-C_9H_7)(PPh_3)$_2$] (R^1 = R^2 = Ph, R^3 = Ph (**18a**), ^{i}Pr (**18b**); R^1R^2 = C_9H_{16}, R^3 = Ph (**20**)) have been obtained by treatment of dichloromethane solutions of σ-alkynyl complexes **3a**,**b** and **13a** with catalytic amounts of $AlCl_3$ at room temperature. Protonation of these species affords the cyclic carbenes [Ru{=CCH$_2$C(R^1)(R^2)CH=C(R^3)O}-(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**19a**,**b**, **21**).

Introduction

As a part of the continuous interest in the chemistry of carbene complexes, allenylidene derivatives [M]=C=C=CR_2 have attracted a great deal of attention in recent years due to their versatile reactivity.[1] Theoretical studies clearly indicate that the C_α and C_γ carbon atoms of the allenylidene chain are electrophilic centers, while the C_β is a nucleophilic site.[2] Nucleophilic attacks dominate the reactivity of allenylidene complexes, revealing the great potential of these species to promote novel C−C and C−heteroatom coupling reactions.[1] Moreover, it is now well-established that the regioselectivity of these nucleophilic additions is strongly dependent on the metallic fragment.[1] In general, allenylidene groups attached to bulky and/or electron-rich metallic fragments are unreactive toward weak nucleophiles but react with strong nucleophiles which

* To whom correspondence should be addressed. E-mail: jgh@sauron.quimica.uniovi.es.

(1) For comprehensive reviews on the synthesis and reactivity of allenylidene complexes see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Werner, H. *Chem. Commun.* **1997**, 903. (c) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (d) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178*−*180*, 409. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571.

(2) (a) Schilling, B. E. R.; Hoffman, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Berke, H.; Huttner, G.; von Seyerl, J. *Z. Naturforsch.* **1981**, *36B*, 1277. (c) Pérez-Carreño, E. Doctoral Thesis, University of Oviedo, 1996. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826. (e) Xia, H. P.; Ng, W. S.; Ye, J. S.; Li, X.-Y.; Wong, W. T.; Lin, Z.; Yang, C.; Jia, G. *Organometallics* **1999**, *18*, 4552. (f) Re, N.; Sgamellotti, A.; Floriani, C. *Organometallics* **2000**, *19*, 1115. (g) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585.

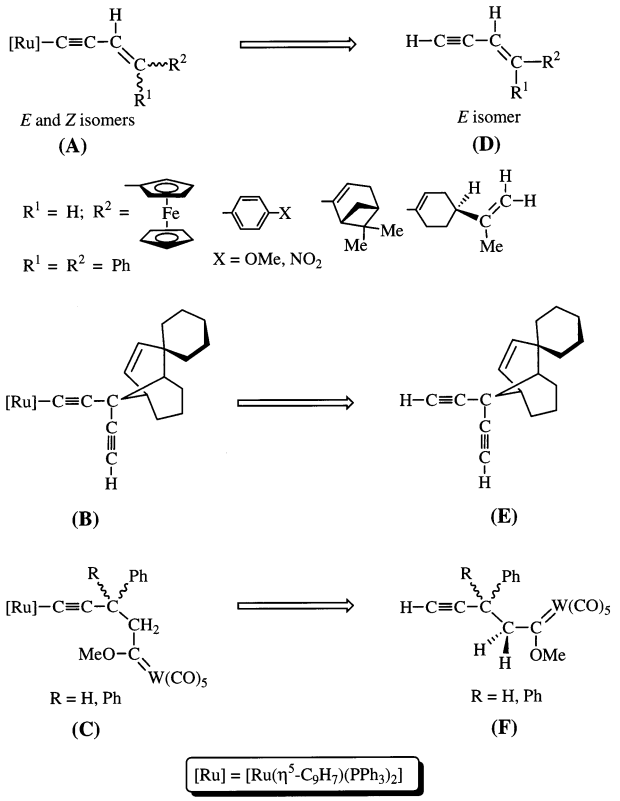
10.1021/om010252o CCC: $20.00
Publication on Web 06/12/2001

are added regioselectively at the C_γ atom, leading to the alkynyl species [M]−C≡CCR$_2$(Nu).[3] In contrast, the presence of metallic units bearing less sterically demanding and/or more π-electron-withdrawing ligands show a marked ability to add both soft and hard nucleophiles at the C_α atom.[4]

We have described an extensive series of allenylidene complexes containing η^5-indenyl−ruthenium(II) fragments and have investigated their influence on the reactivity of the cumulenic chain.[3h,5] Thus, we have shown that those allenylidene groups stabilized by the electron-rich [Ru(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ moiety are able to add regioselectively a large variety of neutral and anionic nucleophiles at the C_γ atom to afford the functionalized σ-alkynyl derivatives [Ru{C≡CCR^{1}R^2-(Nu)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^{n+}$ (n = 0, 1).[5c−i] Furthermore, we have designed an efficient synthetic approach to terminal alkynes. They can be obtained from vinylidene complexes, resulting from the protonation of the functionalized σ-alkynyl complexes, followed by a demetalation process via treatment with acetonitrile.[5g] This procedure allows the recovery of the metallic auxiliary as the insoluble complex [Ru(N≡CMe)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$, which can be separated quantitatively from the free alkynes. Chart 1 collects a number of alkynyl complexes (**A**−**C**) which can be used as efficient precursors of terminal alkynes (**D**−**F**).[5g,i,6] Although these examples prove the potential synthetic utility of allenylidene complexes in organic synthesis,[7] the scope of its application is still not comparable to that of the related vinylidenes [M]=C=CR$_2$ or the classical Fischer type metal carbenes [M]=C(X)R (X = OR′, NR′$_2$).[8−10]

Pursuing these studies aimed at exploiting the utility of this synthetic route, we describe in this paper the

Chart 1



(3) For representative examples see the following. [M] = *trans*-[RuClL$_2$]$^+$ (L$_2$ = dppm (bis(diphenylphosphino)methane), dppe (1,2-bis(diphenylphosphino)ethane)): (a) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980. (b) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. (c) Touchard, D.; Haquette, P.; Daridor, A.; Romero, A.; Dixneuf, P. H. *Organometallics* **1998**, *17*, 3844. (d) Rigaut, S.; Maury, O.; Touchard, D.; Dixneuf, P. H. *Chem. Commun.* **2001**, 373. [M] = [RuCl{N(CH$_2$-CH$_2$PPh$_2$)$_3$}]$^+$: (e) Wolinska, A.; Touchard, D.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, *420*, 217. [M] = [Ru(η^5-C$_5$R$_5$)LL′]$^+$ (R = H, L = L′ = PMe$_3$, PPh$_3$; R = H, L = PPh$_3$, L′ = PPh$_2$CH$_2$C(=O)^{t}Bu; R = H, LL′ = dippe (1,2-bis(diisopropylphosphino)ethane); R = Me, L = L′ = PEt$_3$; R = Me, LL′ = dippe): (f) Selegue, J. P. *Organometallics* **1982**, *1*, 217. (g) de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **1997**, *549*, 221. (h) Crochet, P.; Demerseman, B.; Vallejo, M. I.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 5406. (i) Bruce, M. I.; Low, P. J.; Tiekink, E. R. T. *J. Organomet. Chem.* **1999**, *572*, 3. (j) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. [M] = [Os(η^5-C$_5$H$_5$)(P^{i}Pr$_3$)$_2$]$^+$: see ref 2g.

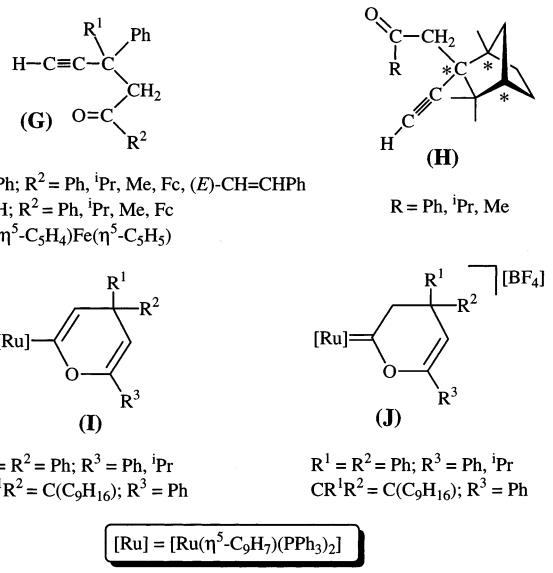
(4) For representative examples see the following. [M] = M(CO)$_5$ (M = Cr, W): (a) Fischer, H.; Roth, G.; Reindl, D.; Troll, C. *J. Organomet. Chem.* **1993**, *454*, 133. (b) Fischer, H.; Reindl, D.; Troll, C.; Leroux, F. *J. Organomet. Chem.* **1995**, *490*, 221. (c) Fischer, H.; Roth, G. *J. Organomet. Chem.* **1995**, *490*, 229. (d) Cosset, C.; del Rio, I.; Le Bozec, H. *Organometallics* **1995**, *14*, 1938. (e) Roth, G.; Fischer, H. *J. Organomet. Chem.* **1996**, *507*, 125. (f) Cosset, C.; del Rio, I.; Péron, V.; Windmüller, B.; Le Bozec, H. *Synlett* **1996**, 435. (g) Dötz, K. H.; Paetsch, D.; Le Bozec, H. *J. Organomet. Chem.* **1999**, *589*, 11. (h) Ulrich, K.; Porhiel, E.; Péron, V.; Ferrand, V.; Le Bozec, H. *J. Organomet. Chem.* **2000**, *601*, 78. [M] = [Mn(η^5-C$_5$H$_5$)(CO)$_2$]: (i) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *265*, 271. See also ref 2b. [M] = [RuCl(η^6-arene)(PR$_3$)]$^+$ (PR$_3$ = PMe$_3$, PPh$_3$): (j) Dussel, R.; Pilette, D.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 3287. (k) Pilette, D.; Le Bozec, H.; Romero, A.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1220. (l) Pilette, D.; Ouzzine, K.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809. (m) Ruiz, N.; Péron, D.; Sinbandith, S.; Dixneuf, P. H.; Baldoli, C.; Maiorana, S. *J. Organomet. Chem.* **1997**, *533*, 213. See also ref 4h. [M] = [Ru(η^5-C$_5$H$_5$)(CO)(PR$_3$)]$^+$ (PR$_3$ = P^{i}Pr$_3$, PPh$_3$): (n) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (o) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 2297. (p) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567. (q) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4959. (r) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1998**, *17*, 5434. (s) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606. (t) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995. (u) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **2000**, *19*, 4. (v) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 4327. See also ref 2d and 4h. [M] = *fac*,*cis*-[RuCl$_2${EtN(CH$_2$-CH$_2$PPh$_2$)$_2$}]: (w) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Lopez, C.; de los Rios, I.; Romerosa, A. *Chem. Commun.* **1999**, 443. [M] = [Re-(Triphos)(CO)$_2$]$^+$ (Triphos = 1,1,1-tris(diphenylphosphinomethyl)-ethane): (x) Bianchini, C.; Mantovani, N.; Marchi, A.; Marvelli, L.; Masi, D.; Peruzzini, M.; Rossi, R.; Romerosa, A. *Organometallics* **1999**, *18*, 4501. (y) Bianchini, C.; Mantovani, N.; Marvelli, L.; Peruzzini, M.; Rossi, R.; Romerosa, A. *J. Organomet. Chem.* **2001**, *617*−*618*, 23.

(5) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (b) Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 2483. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; Ienco, A. *Organometallics* **1998**, *17*, 5216. (f) 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. (g) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821. (h) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3235. (i) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **2000**, 451.

(6) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *J. Organomet. Chem.* **2001**, *621*, 39.

(7) Organic cumulenes have been prepared using rhodium(I) allenylidene complexes as starting materials: (a) Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1996**, *118*, 2495. (b) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561. (c) Werner, H.; Laubender, M.; Wiedemann, R.; Windmüller, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1237.

Chart 2



R^1 = Ph; R^2 = Ph, ^{i}Pr, Me, Fc, (*E*)-CH=CHPh
R^1 = H; R^2 = Ph, ^{i}Pr, Me, Fc
Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$

R = Ph, ^{i}Pr, Me

$R^1 = R^2$ = Ph; R^3 = Ph, ^{i}Pr
$CR^1R^2 = C(C_9H_{16})$; R^3 = Ph

$R^1 = R^2$ = Ph; R^3 = Ph, ^{i}Pr
$CR^1R^2 = C(C_9H_{16})$; R^3 = Ph

[Ru] = $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$

synthesis of γ-keto-substituted alkynes **G** and **H** (Chart 2). The former alkynes have been obtained by starting from the allenylidene complexes $[Ru\{=C=C=C(R^1)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = Ph, H) through the addition of lithium enolates $LiCH_2COR^2$. Alkynes **H** have been synthesized diastereoselectively using similar additions on the optically active allenylidene derivative $[Ru\{=C=C=C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($C(C_9H_{16})$ = (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene). The preparation of unsaturated carbene complexes **J**, which are obtained via protonation of cyclic alkenyl derivatives **I**, is also reported. The alkenyl complexes **I** result from the intramolecular cyclization of the keto-functionalized σ-alkynyl species $[Ru\{C\equiv CCR^1R^2(CH_2COR^3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ in the presence of $AlCl_3$. Part of this work has been communicated in a preliminary report.[5e]

Results and Discussion

Synthesis of Terminal Alkynes $HC\equiv CC(R^1)Ph(CH_2COR^2)$. The synthetic route is based on the same procedure that we have previously described.[5g,i] Thus, with allenylidene complexes as the starting materials, the first step involves the preparation of the corresponding σ-alkynyl derivatives, which are transformed into vinylidene species. The treatment of these vinylidenes with acetonitrile finally gives the free alkynes through a demetalation process.

(a) Reactions of Allenylidene Complexes $[Ru\{=C=C=C(R^1)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ with Enolates Derived from Methyl Ketones. As expected from our previous studies,[5c–i] the allenylidene complexes $[Ru\{=C=C=C(R^1)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = Ph (**1**), H (**2**))[5a] react with lithium enolates $LiCH_2COR^2$ (R^2 = Ph, ^{i}Pr, Me, Fc, (*E*)-CH=CHPh) in tetrahydrofuran, at −20 °C, to afford the neutral σ-alkynyl derivatives $[Ru\{C\equiv CC(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**3a**–**e**, **4a**–**d**), resulting from the regioselective addition of the nucleophile at the C_γ atom. Complexes **3a**–**e** and **4a**–**d** have been isolated as air-stable orange solids in 62–83% yields (Scheme 1).

Analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) support the proposed formulations (see the Experimental Section and Tables 1 and 2). In particular, the formation of a γ-keto-substituted alkynyl chain was identified on the basis of (i) the presence of typical ν(C=O) and ν(C≡C) absorption bands in the IR spectra (KBr) at 1652–1721 and 2052–2092 cm^{-1}, respectively, and (ii) characteristic resonances in the ^{13}C{^{1}H} NMR spectra of the Ru–C≡C, C_γ, CH_2, and C=O carbon nuclei at δ 92.62–98.02 ($^2J_{CP}$ = 22.5–25.7 Hz, C_α), 111.77–115.99 (C_β), 37.88–50.67 (C_γ), 50.51–57.63 (CH_2), and 195.68–211.21 (C=O).

(b) Synthesis of Vinylidene Complexes $[Ru\{=C=C(H)C(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$. The treatment of σ-alkynyl complexes **3a**–**e** and **4a**–**d** with $HBF_4\cdot Et_2O$ in diethyl ether at −20 °C generates the air-stable vinylidene complexes $[Ru\{=C=C(H)C(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**5a**–**e** and **6a**–**d**; 74–94% yields) (Scheme 1). Elemental analyses and spectroscopic data are in accordance with the proposed formulations (see the Experimental Section and Tables 3 and 4 for details). The most remarkable feature in the ^{1}H NMR spectra of these complexes is the presence of a singlet (**5a**–**e**) or doublet (**6a**–**d**; ca. J_{HH} = 10 Hz) signal in the range 4.50–5.76 ppm attributed to the acidic vinylidene proton [Ru]=C=CH (Table 3). The characteristic deshielded C_α resonance appears, in the ^{13}C{^{1}H} NMR spectra, as a triplet ($^2J_{CP}$ = 15.1–17.9 Hz) at δ 340.50–344.41, while the C_β, C_γ, CH_2 and C=O carbon nuclei resonate as singlets at higher fields (δ 115.90–116.79 (C_β), 34.24–48.21 (C_γ), 48.12–53.24 (CH_2), and 196.89–213.36 (C=O); see Table 4).

(c) Demetalation Processes. Demetalation of complexes **5a**–**e** and **6a**–**d** proceeds rapidly (ca. 30 min) in refluxing acetonitrile to afford terminal γ-keto-substituted alkynes $HC\equiv CC(R^1)Ph(CH_2COR^2)$ (**7a**–**e** and **8a**–**d**) and the cationic nitrile complex $[Ru(N\equiv CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**9**)[5g] (Scheme 1). Keto–alkynes **7a**–**d** and **8a**–**d** have been purified from the reaction mixture by column chromatography on silica gel (72–86% yield) after filtering off the unsoluble complex **9**. They have been characterized by means of standard spectroscopic techniques and microanalysis (see the Experimental Section and Tables 5 and 6). The most relevant spectroscopic features of **7a**–**e** and **8a**–**d** are (i) (^{1}H NMR) the singlet (**7a**–**e**) or doublet (**8a**–**d**; ca. J_{HH} = 2 Hz) resonance for the acetylenic proton (δ 2.25–2.73) and (ii) (^{13}C{^{1}H} NMR) typical signals for the HC≡C carbons which appear in the ranges δ 70.71–75.10 and 84.87–87.84, respectively.[11]

(8) For recent reviews on the chemistry of vinylidene complexes see: (a) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 44. (b) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (c) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193–195*, 977. See also ref 1a.

(9) Extensive surveys and reviews have been published on the chemistry of Fischer type carbene complexes. For recent references see: (a) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (b) Zaragoza Dörwald, F. In *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999. (c) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187. (d) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911.

(10) A few examples of catalytic transformations of propargylic alcohols via ruthenium(II) allenylidene intermediates have been reported: (a) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476. (b) Trost, B. M.; Flygare, J. A. *Tetrahedron Lett.* **1994**, *35*, 4059. (c) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (d) The catalytic activity of ruthenium(II) allenylidene complexes in ring-closing metathesis (RCM) of olefins has been recently discovered: Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012 and references therein.

Scheme 1

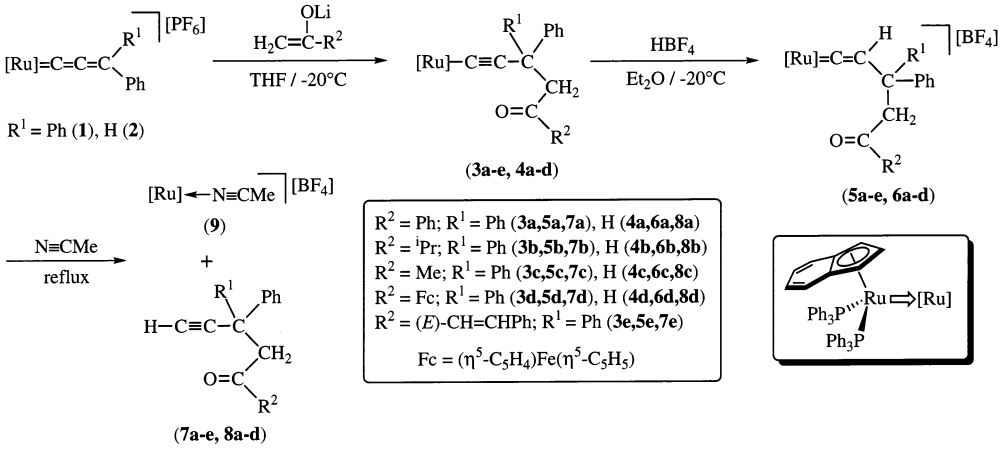
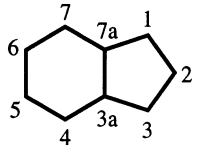


Table 1. $^{31}P\{^1H\}$ and ^1H NMR Data for Neutral σ-Alkynyl Complexes $[Ru\{C{\equiv}CC(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[a]

		^1H					
		η^5-C_9H_7[n]					
complex	$^{31}P\{^1H\}$	H-1,3	H-2	J_{HH}	H-4,5,6,7	CH_2	others
$R^1 = R^2 = Ph$ (**3a**)	53.14 s	4.75 d	5.64 t	2.3	6.53 m, 6.78 m	3.99 s	6.84−7.76 (m, Ph)
$R^1 = Ph$, $R^2 = {}^i$Pr (**3b**)	52.19 s	4.78 d	5.71 t	2.0	6.46 m, *b*	3.52 s	0.91 (d, $J_{HH} = 6.8$, CH_3); 2.29 (sept, $J_{HH} = 6.8$, CH); 6.81−7.63 (m, Ph)
$R^1 = Ph$, $R^2 = Me$ (**3c**)	52.24 s	4.73 d	5.63 t	2.5	6.42 m, *b*	3.48 s	1.85 (s, CH_3); 6.81−7.57 (m, Ph)
$R^1 = Ph$, $R^2 = Fc$ (**3d**)	53.42 s	4.70 d	5.63 t	2.3	6.56 m, 6.78 m	3.89 s	3.81 (s, C_5H_5); 4.03 and 4.61 (br, C_5H_4); 6.87−7.89 (m, Ph)
$R^1 = Ph$, $R^2 =$ (*E*)-CH=CHPh (**3e**)	52.00 s	4.80 d	5.83 t	2.0	6.35 m, 6.78 m	3.72 s	6.52 and 7.72 (d, $J_{HH} = 15.9$, =CH); 6.89−7.60 (m, Ph)
$R^1 = H$, $R^2 = Ph$ (**4a**)	52.47 br	4.54 br 4.71 br	5.40 br		6.27 m, 6.67 m	3.17 dd[c] 3.64 dd[d]	5.04 (dd, $J_{HH} = 9.0$, $J_{HH} = 5.3$, CH); 6.84−8.03 (m, Ph)
$R^1 = H$, $R^2 = {}^i$Pr (**4b**)	49.38 d[e] 49.87 d[e]	4.64 br 4.73 br	5.56 br		6.30 m, 6.71 m	2.76 dd[f] 3.04 dd[g]	0.91 (d, $J_{HH} = 7.0$, CH_3); 0.99 (d, $J_{HH} =$ 6.9, CH_3); 2.36 (m, $CH(CH_3)_2$); 4.85 (dd, $J_{HH} = 8.0$, $J_{HH} = 6.4$, CH); 6.85−7.53 (m, Ph)
$R^1 = H$, $R^2 = Me$ (**4c**)	51.88 d[h] 52.35 d[h]	4.67 br 4.73 br	5.53 br		6.35 m, 6.75 m	2.62 dd[i] 2.94 dd[j]	1.88 (s, CH_3); 5.20 (dd, $J_{HH} = 9.2$, $J_{HH} = 5.3$, CH); 6.88−7.53 (m, Ph)
$R^1 = H$, $R^2 = Fc$ (**4d**)	51.94 d[k] 52.52 d[k]	4.77 br 4.82 br	5.59 br		6.28 m, 6.69 m	3.26 dd[l] 3.37 dd[m]	3.89 (s, C_5H_5); 4.11 and 4.60 (br, C_5H_4); 5.13 (dd, $J_{HH} = 7.7$, $J_{HH} = 6.9$, CH); 6.88−7.67 (m, Ph)

[a] Spectra recorded in C_6D_6; δ in ppm and *J* in Hz. Abbreviations: s, singlet; br, broad; d, doublet; dd, doublet of doublets; t, triplet; sept, septuplet; m, multiplet. [b] Overlapped by Ph protons. [c] $J_{HH} = 15.5$, $J_{HH} = 5.3$. [d] $J_{HH} = 15.5$, $J_{HH} = 9.0$. [e] $^2J_{PP} = 30.3$. [f] $J_{HH} = 15.5$, $J_{HH} = 6.4$. [g] $J_{HH} = 15.5$, $J_{HH} = 8.0$. [h] $^2J_{PP} = 31.7$. [i] $J_{HH} = 14.8$, $J_{HH} = 5.3$. [j] $J_{HH} = 14.8$, $J_{HH} = 9.2$. [k] $^2J_{PP} = 29.9$. [l] $J_{HH} = 15.6$, $J_{HH} = 7.7$. [m] $J_{HH} = 15.6$, $J_{HH} = 6.9$. [n] Legend for indenyl skeleton:



Diastereoselective Synthesis of Terminal Alkynes $HC{\equiv}CC(C_9H_{16})(CH_2COR)$. The efficient access to alkynes **7a**−**e** and **8a**−**d** from allenylidene complexes **1** and **2** and methyl ketones prompted us to use chiral substrates in order to obtain optically active terminal alkynes. Toward this aim, a novel allenylidene complex bearing a chiral auxiliary derived from the commercially available ketone (−)-fenchone was prepared. The subsequent transformations leading to the formation of the desired terminal alkynes are similar to those previously mentioned.

(a) Synthesis of the Optically Active Allenylidene Ruthenium(II) Complex $[Ru\{{=}C{=}C{=}C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$. Following the well-known Selegue synthetic protocol,[3f] the chiral allenylidene derivative $[Ru\{{=}C{=}C{=}C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**12**) was prepared (80% yield) by refluxing $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**10**),[12] $NaPF_6$, and 2-*exo*-ethynyl-1,3,3-trimethyl-2-*endo*-norbornanol (**11**)[13] in methanol (Scheme 2). Spectroscopic data (see the Experimental Section) for **12** are similar to those reported for the related allenylidene complexes $[Ru(=C=C=CRR')(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$.[5a,h] Significantly, the presence of the cumulenic moiety was clearly identified on the basis of a strong ν(C=C=C) IR absorption at 1963 cm^{-1} and the

(11) To the best of our knowledge only the terminal alkyne **8a** has been previously reported: Caffyn, A. J. M.; Nicholas, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 6438.

(12) Oro, L. A.; Ciriano, M. A.; Campo, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *289*, 117.

(13) Keegan, D. S.; Midland, M. M.; Werley, R. T.; McLoughlin, J. I. *J. Org. Chem.* **1991**, *56*, 1185.

Table 2. $^{13}C\{^1H\}$ NMR Data for Neutral σ-Alkynyl Complexes $[Ru\{C{\equiv}CC(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[a]

	η^5−C_9H_7											
complex	C-1,3	C-2	C-3a,7a	Δδ(C-3a,7a)[b]	C-4,5,6,7	Ru−C_α	$^2J_{CP}$	C_β	C_γ	CH_2	C=O	others
3a	74.72	96.81	110.69	−20.01	124.56 *c*	95.42 t	22.7	115.24	50.40	51.94	196.30	126.07−150.05 (m, Ph)
3b	74.28	96.65	110.58	−20.12	124.35 126.01	96.94 t	22.5	114.76	50.37	54.43	211.19	18.81 (s, CH_3); 41.31 (s, CH); 127.76−149.78 (m, Ph)
3c	74.11	96.38	110.27	−20.43	124.07 125.82	97.40 t	22.6	113.92	49.72	57.63	206.18	31.41 (s, CH_3); 127.41−149.26 (m, Ph)
3d	75.23	96.48	110.71	−19.99	124.51 *c*	95.94 t	23.3	115.99	50.67	53.15	199.62	70.22 and 72.24 (s, CH of C_5H_4); 70.50 (s, C_5H_5); 82.31 (s, C of C_5H_4); 126.39−150.14 (m, Ph)
3e	74.35	96.74	110.18	−20.52	124.00 *d*	98.02 t	23.0	113.90	50.21	56.97	197.39	126.10−149.36 (m, Ph and =CH)
4a	75.16[e] 75.38[f]	96.38	109.08 110.72	−20.80	123.46 124.46 125.90 126.68	94.24 vt	24.3	112.16	38.92	50.51	198.86	126.76−146.84 (m, Ph)
4b	74.47[g] 74.57[h]	95.74	108.84 109.89	−21.33	123.02 123.58 125.47 c	92.73 vt	24.7	111.77	37.88	51.76	211.21	18.13 and 18.19 (s, CH_3); 41.32 (s, CH); 126.00−146.29 (m, Ph)
4c	75.18[i]	94.64	109.65 110.43	−20.66	123.87 124.29 126.25 126.59	94.64 vt	24.1	111.99	38.81	55.03	206.58	31.04 (s, CH_3); 127.93−146.66 (m, Ph)
4d	74.65 74.90	95.79	108.44 110.07	−21.44	122.81 123.74 125.26 126.09	92.62 vt	25.7	112.03	38.13	51.21	195.68	69.46, 70.30, 71.89 and 72.11 (s, CH of C_5H_4); 69.90 (s, C_5H_5); 80.81 (s, C of C_5H_4); 127.25−146.58 (m, Ph)

[a] Spectra recorded in C_6D_6; δ in ppm and *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet. [b] Δδ(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] Overlapped by Ph carbons. [d] 125.66 and 125.83 (s, =CH and C-4,7 or C-5,6). [e] d, $^2J_{CP}$ = 3.5. [f] d, $^2J_{CP}$ = 3.5. [g] d, $^2J_{CP}$ = 7.2. [h] d, $^2J_{CP}$ = 6.9. [i] Broad signal.

Table 3. $^{31}P\{^1H\}$ and ^1H NMR Data for Cationic Vinylidene Complexes $[Ru\{{=}C{=}C(H)C(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$[a]

		^1H						
		η^5-C_9H_7						
complex	$^{31}P\{^1H\}$	H-1,3	H-2	J_{HH}	H-4,5,6,7	Ru=C=CH	CH_2	others
R^1 = R^2 = Ph (**5a**)	36.51 s	5.03 d	6.08 t	2.1	5.14 m, 7.04 m	5.73 s	3.16 s	6.53−7.71 (m, Ph)
R^1 = Ph, R^2 = ^{i}Pr (**5b**)	36.56 s	5.07 d	6.09 t	2.1	5.16 m, 7.03 m	5.76 s	2.65 s	0.74 (d, J_{HH} = 6.8, CH_3); 2.20 (sept, J_{HH} = 6.8, CH); 6.56−7.53 (m, Ph)
R^1 = Ph, R^2 = Me (**5c**)	36.55 s	5.05 d	5.98 t	1.8	5.14 m, 7.05 m	5.45 s	2.48 s	1.67 (s, CH_3); 6.51−7.52 (m, Ph)
R^1 = Ph, R^2 = Fc (**5d**)	36.28 s	5.05 d	6.04 t	1.2	5.16 m, 7.03 m	5.33 s	2.53 s	3.72 (s, C_5H_5); 4.52 and 4.54 (br, C_5H_4); 6.44.7.51 (m, Ph)
R^1 = Ph, R^2 = (*E*)-CH=CHPh (**5e**)	36.40 s	5.06 d	6.07 t	1.9	5.16 m, 7.04 m	5.58 s	2.84 s	6.33 (d, J_{HH} = 16.0, =CH); 6.54−7.53 (m, Ph and =CH)
R^1 = H, R^2 = Ph (**6a**)	37.96 d[b] 40.16 d[b]	5.13 br *c*	6.25 br		*c*, *d*	4.77 d[e]	3.24 dd[f] 3.50 dd[g]	4.37 (m, CH); 6.52−8.14 (m, Ph)
R^1 = H, R^2 = ^{i}Pr (**6b**)	37.98 d[h] 40.29 d[h]	5.21 br *i*	6.34 br		*i*, *d*	4.75 d[j]	*k* 3.01 dd[l]	1.09 (d, J_{HH} = 6.9, CH_3); 1.19 (d, J_{HH} = 6.8, CH_3); 4.21 (m, CH); 6.51−7.42 (m, Ph)
R^1 = H, R^2 = Me (**6c**)	38.08 d[h] 40.52 d[h]	5.27 br 5.62 br	6.20 br		5.75 m, *d*	4.52 d[e]	2.80 m	2.20 (s, CH_3); 6.56−7.45 (m, Ph)
R^1 = H, R^2 = Fc (**6d**)	38.36 d[m] 39.89 d[m]	5.14 br 5.59 br	6.23 br		5.70 m, 6.85 m	*n*	2.99 m	4.25 (s, C_5H_5); 6.76−7.74 (m, Ph)

[a] Spectra recorded in $CDCl_3$; δ in ppm and *J* in Hz. Abbreviations: s, singlet; br, broad; d, doublet; dd, doublet of doublets; t, triplet; sept, septuplet; m, multiplet. [b] $^2J_{PP}$ = 23.5. [c] 5.64 (m, 3H, H-1 or H-3 and H-4, H-5, H-6 or H-7). [d] Overlapped by Ph protons. [e] J_{HH} = 10.2. [f] J_{HH} = 17.4, J_{HH} = 4.5. [g] J_{HH} = 17.4, J_{HH} = 9.6. [h] $^2J_{PP}$ = 23.4. [i] 5.67 (m, 3H, H-1 or H-3 and H-4, H-5, H-6 or H-7). [j] J_{HH} = 9.4. [k] 2.72 (m, 2H, C*H*(CH_3)$_2$ and CH_2). [l] J_{HH} = 17.4, J_{HH} = 8.9. [m] $^2J_{PP}$ = 32.1. [n] 4.50 (m, 6H, Ru=C=CH, CH and C_5H_4).

low-field resonances, in the $^{13}C\{^1H\}$ NMR spectrum, for the Ru=C=C=C carbon nuclei: δ 305.06 (vt, $^2J_{CP}$ = $^2J_{CP'}$ = 18.9 Hz, Ru=C_α), 202.01 (C_β), and 183.24 (C_γ).

(b) Reactions of $[Ru\{{=}C{=}C{=}C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ with Enolates Derived from Methyl Ketones. The allenylidene complex **12** reacts with lithium enolates derived from acetophenone, methyl isopropyl ketone, and acetone, affording the σ-alkynyl derivatives $[Ru\{C{\equiv}CC(C_9H_{16})(CH_2COR)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**13a**−**c**) in 68−77% yield after chromatographic workup (Scheme 3). Formation of compounds **13a**−**c** involves, as expected, the regioselective addition of the nucleophile at the C_γ atom of the allenylidene chain leading to the generation of a novel stereogenic center at C_γ. Enolate additions proceed in a diastereoselective manner, since only one diastereoisomer was detected

Table 4. $^{13}C\{^1H\}$ NMR Data for Cationic Vinylidene Complexes [Ru{=C=C(H)C(R^1)Ph(CH_2COR^2)}(η^5-C_9H_7)(PPh_3)$_2$][BF_4][a]

	η^5-C_9H_7												
complex	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3a,7a)[b]	C-4,5,6,7	Ru=C_α	$^2J_{CP}$	C_β	C_γ	CH_2	C=O	others
5a	80.45	98.09	117.60	−13.10	123.86 [c]	344.41 t	17.9	116.79	47.82	48.12	197.33	127.36−147.66 (m, Ph)
5b	80.23	98.30	117.48	−13.22	123.70 127.23	343.76 t	17.9	116.65	48.21	50.34	212.82	18.00 (s, CH_3); 42.19 (s, CH); 127.94−147.29 (m, Ph)
5c	80.33	97.94	117.51	−13.19	123.72 126.27	343.69 t	17.6	116.58	48.01	52.02	206.23	32.36 (s, CH_3); 127.65−147.31 (m, Ph)
5d	80.27	97.73	117.47	−13.23	123.70 127.31	342.24 t	17.9	115.90	47.91	48.42	200.53	66.08 and 70.05 (s, CH of C_5H_4); 69.89 (s, C_5H_5); 79.93 (s, C of C_5H_4); 127.46−147.89 (m, Ph)
5e	79.77	97.66	116.92	−13.78	123.16 126.67	343.39 t	17.7	116.27	47.80	50.47	196.89	126.38 and 141.86 (s, =CH); 126.92−146.81 (m, Ph)
6a	82.69[d] 82.87[e]	99.82	114.78 119.23	−13.69	122.65 124.71 [c] [c]	343.24 vt	16.2	116.69	35.31	48.86	199.21	127.62−144.09 (m, Ph)
6b	81.88[f] 82.32[g]	99.46	113.87 118.53	−14.50	121.93 124.16 126.81 [c]	342.89 vt	16.6	116.31	34.24	50.01	213.36	17.77 and 18.02 (s, CH_3); 41.37 (s, CH); 127.16−143.55 (m, Ph)
6c	82.66 83.12	99.39	114.53 119.01	−13.93	122.49 124.55 [c] [c]	340.50 vt	15.2	116.67	34.26	53.24	206.89	31.12 (s, CH_3); 127.30−143.89 (m, Ph)
6d	82.61 82.72	99.35	114.82 119.32	−13.63	122.44 124.62 127.29 127.38	342.41 vt	15.1	116.43	35.19	50.10	202.38	69.53, 70.00, 73.43 and 73.62 (s, CH of C_5H_4); 70.27 (s, C_5H_5); 79.63 (s, C of C_5H_4); 128.64−143.80 (m, Ph)

[a] Spectra recorded in $CDCl_3$; δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet. [b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] Overlapped by Ph carbons. [d] d, $^2J_{CP}$ = 10.1. [e] d, $^2J_{CP}$ = 7.9. [f] d, $^2J_{CP}$ = 7.7. [g] d, $^2J_{CP}$ = 7.3.

Table 5. IR[a] and ^{1}H NMR[b] Data for Terminal Alkynes HC≡CC(R^1)Ph(CH_2COR^2)

	IR			^{1}H		
compd	ν (HC≡)	ν (C≡C)	ν (C=O)	HC≡	CH_2	others
R^1 = R^2 = Ph (**7a**)	3280	2104	1698	2.63 s	4.07 s	7.21−7.94 (m, Ph)
R^1 = Ph, R^2 = ^{i}Pr (**7b**)	3244	2111	1709	2.66 s	3.52 s	1.02 (d, J_{HH} = 6.9, CH_3); 2.57 (sept, J_{HH} = 6.9, CH); 7.20−7.45 (m, Ph)
R^1 = Ph, R^2 = Me (**7c**)	3283	2118	1699	2.69 s	3.45 s	2.05 (s, CH_3); 7.22−7.44 (m, Ph)
R^1 = Ph, R^2 = Fc (**7d**)	3248	2109	1667	2.66 s	3.83 s	4.18 (s, C_5H_5); 4.47 and 4.76 (br, C_5H_4); 7.12−7.64 (m, Ph)
R^1 = Ph, R^2 = (*E*)-CH=CHPh (**7e**)	3247	2109	1677	2.73 s	3.68 s	6.65 (d, J_{HH} = 16.0, =CH); 7.21−7.52 (m, Ph and =CH)
R^1 = H, R^2 = Ph (**8a**)	3286	2113	1683	2.28 d[c]	3.37 dd[d] 3.62 dd[e]	4.47 (ddd, J_{HH} = 8.0, J_{HH} = 6.0, J_{HH} = 2.3, CH); 7.24−7.97 (m, Ph)
R^1 = H, R^2 = ^{i}Pr (**8b**)	3250	2113	1701	2.25 d[f]	2.83 dd[g] 2.94 dd[h]	1.02 (d, J_{HH} = 7.1, CH_3); 1.10 (d, J_{HH} = 6.9, CH_3); 2.53 (m, C*H*(CH_3)$_2$); 4.27 (ddd, J_{HH} = 8.7, J_{HH} = 6.4, J_{HH} = 2.5, CH); 7.25−7.43 (m, Ph)
R^1 = H, R^2 = Me (**8c**)	3279	2118	1696	2.26 d[i]	2.82 dd[j] 3.01 dd[k]	2.15 (s, CH_3); 4.21 (ddd, J_{HH} = 8.2, J_{HH} = 6.0, J_{HH} = 2.2, CH); 7.25−7.40 (m, Ph)
R^1 = H, R^2 = Fc (**8d**)	3301	2110	1664	2.29 d[l]	3.13 dd[m] 3.29 dd[n]	4.07 (s, C_5H_5); 4.46 (ddd, J_{HH} = 7.0, J_{HH} = 6.7, J_{HH} = 2.6, CH); 4.50 and 4.75 (br, C_5H_4); 7.26−7.52 (m, Ph)

[a] KBr; ν in cm^{-1}. [b] Spectra recorded in $CDCl_3$; δ in ppm and J in Hz. Abbreviations: s, singlet; br, broad; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; sept, septuplet; m, multiplet. [c] J_{HH} = 2.3. [d] J_{HH} = 17.1, J_{HH} = 6.0. [e] J_{HH} = 17.1, J_{HH} = 8.0. [f] J_{HH} = 2.5. [g] J_{HH} = 16.7, J_{HH} = 6.4. [h] J_{HH} = 16.7, J_{HH} = 8.7. [i] J_{HH} = 2.2. [j] J_{HH} = 16.8, J_{HH} = 6.0. [k] J_{HH} = 16.8, J_{HH} = 8.2. [l] J_{HH} = 2.6. [m] J_{HH} = 17.4, J_{HH} = 6.7. [n] J_{HH} = 17.4, J_{HH} = 7.0.

by NMR spectroscopy (see Tables 7 and 8).[14] Since the configuration of the new chiral atom could not be elucidated from the NMR data, a single-crystal X-ray structural determination was carried out on complex **13b**. An ORTEP view of the molecular geometry of this complex is shown in Figure 1. Selected bond distances and angles which are collected in the caption can be compared with those previously reported by us for other ruthenium(II) indenyl σ-alkynyl complexes [Ru(C≡CR)(η^5-C_9H_7)(PPh_3)$_2$][5d−f] (caution must be used in the comparison of these data, due to the relative imprecision of the crystallographic determination). As expected, the structure of **13b** clearly indicates that the addition of the [^{i}PrCOCH_2]$^-$ moiety takes place on the less sterically congested *exo* face of the allenylidene chain in [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**12**). On the basis of steric requirements, an analogous conformation is also proposed for σ-alkynyl derivatives **13a** and **13c**.

(14) The formation of only one diastereoisomer was confirmed in the crude reaction mixture by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

(c) Synthesis of Vinylidene Complexes [Ru{=C=C(H)C(C_9H_{16})(CH_2COR)}(η^5-C_9H_7)(PPh_3)$_2$]-

Table 6. $^{13}C\{^1H\}$ NMR Data for Terminal Alkynes HC≡CC(R¹)Ph(CH₂COR²)[a]

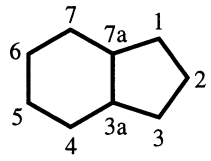
compd	≡CH	≡C	C_γ	CH_2	C=O	others
7a	74.24	87.77	47.04	49.50	195.51	127.14, 127.42, 128.41, 128.68, 128.80, and 133.33 (s, CH of Ph); 137.64 and 144.41 (s, C of Ph)
7b	74.38	87.63	46.79	51.52	210.42	18.31 (s, CH_3); 41.62 (s, CH); 127.16, 127.34, and 128.65 (s, CH of Ph); 144.36 (s, C of Ph)
7c	74.63	86.99	46.42	54.70	205.09	31.18 (s, CH_3); 126.96, 127.10, and 128.42 (s, CH of Ph); 143.66 (s, C of Ph)
7d	73.91	87.84	46.32	49.92	198.73	69.17 and 72.07 (s, CH of C_5H_4); 69.69 (s, C_5H_5); 79.16 (s, C of C_5H_4); 126.68, 127.07 and 128.22 (s, CH of Ph); 144.26 (s, C of Ph)
7e	75.10	87.38	47.21	53.04	196.16	126.29 and 142.52 (s, =CH); 127.26, 127.46, 128.59, 128.68, 129.12, and 130.65 (s, CH of Ph); 134.82 (s, C of Ph)
8a	70.95	85.23	32.57	47.01	196.67	127.10, 127.40, 128.06, 128.55, 128.66, and 133.23 (s, CH of Ph); 136.55 and 140.52 (s, C of Ph)
8b	70.72	85.19	32.45	48.63	211.09	17.59 and 17.65 (s, CH_3); 41.17 (s, CH); 127.29, 128.58, and 133.51 (s, CH of Ph); 140.45 (s, C of Ph)
8c	70.98	84.87	32.46	51.55	205.45	30.49 (s, CH_3); 127.12, 127.25, and 128.65 (s, CH of Ph); 140.17 (s, C of Ph)
8d	70.71	85.93	32.09	48.23	200.29	69.03, 69.24, and 72.35 (s, CH of C_5H_4); 69.61 (s, C_5H_5); 78.42 (s, C of C_5H_4); 127.18, 127.64, and 128.64 (s, CH of Ph); 140.83 (s, C of Ph)

[a] Spectra recorded in $CDCl_3$; δ in ppm.

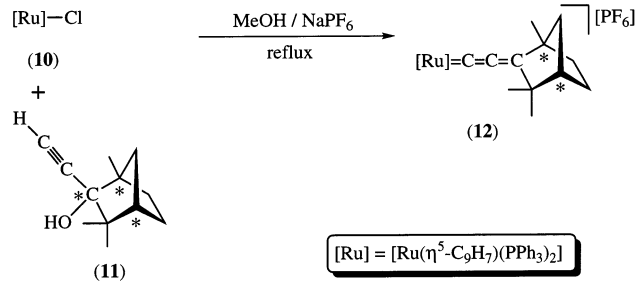
Table 7. $^{31}P\{^1H\}$ and ^1H NMR Data for Neutral σ-Alkynyl Complexes [Ru{C≡CC(C₉H₁₆)(CH₂COR)}(η⁵-C₉H₇)(PPh₃)₂][a]

			^1H				
			η^5-C_9H_7[h]				
complex	$^{31}P\{^1H\}$	$^2J_{PP}$	H-1,3	H-2	H-4,5,6,7	CH_2C=O	others
R = Ph (**13a**)	52.89 d 54.44 d	34.6	4.53 br 5.07 br	5.75 br	6.03 d,[b] *c*	3.32 br	0.98, 1.52, and 2.08 (m, CH_2); 1.17, 1.23, and 1.92 (s, CH_3); 3.06 (m, CH); 6.62−7.98 (m, Ph)
R = ^{i}Pr (**13b**)	53.23 d 54.29 d	36.6	4.34 br 5.20 br	5.64 br	6.00 d,[b] *c*	2.66 d[e] 2.79 d[e]	0.80 and 1.00 (d, J_{HH} = 6.8, $CH(CH_3)_2$); 0.86, 1.32, and 1.72 (s, CH_3); 0.93 and 1.58 (m, CH_2); 1.75−2.13 (m, CH_2 and $CH(CH_3)_2$); 3.14 (m, CH); 6.70−7.67 (m, Ph)
R = Me (**13c**)	53.00 d 53.98 d	34.6	4.44 br 5.10 br	5.65 br	6.00 d,[f] *c*	2.53 d[g] 2.67 d[g]	1.20, 1.23, 1.60, and 1.78 (s, CH_3); 1.22, 1.70, and 2.15 (m, CH_2); 3.08 (m, CH); 6.67−7.05 (m, Ph)

[a] Spectra recorded in C_6D_6; δ in ppm and J in Hz. Abbreviations: s, singlet; br, broad; d, doublet; sept, septuplet; m, multiplet. [b] J_{HH} = 8.5. [c] Overlapped by Ph protons. [d] J_{HH} = 8.2. [e] J_{HH} = 18.6. [f] J_{HH} = 8.7. [g] J_{HH} = 18.3. [h] Legend for indenyl skeleton:



Scheme 2



$[BF_4]$ and Demetalation Reactions. Transformation of complexes **13a**−**c** into the corresponding terminal alkynes HC≡CC(C_9H_{16})(CH_2COR) (**15a**−**c**) using our synthetic methodology proceeds efficiently (see Scheme 3). Thus, in a first step the air-sensitive vinylidene derivatives [Ru{=C=C(H)C(C_9H_{16})(CH_2COR)}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**14a**−**c**) were prepared by protonation of **13a**−**c** with HBF_4·Et_2O in diethyl ether at −20 °C (83−96% yield). Spectroscopic data of **14a**−**c** are in agreement with the proposed structures, being comparable to those observed for the related vinylidenes **5a**−**e** and **6a**−**d** (see Tables 9 and 10). We note, in particular, the presence of the expected low-field carbenic C_α resonance in $^{13}C\{^1H\}$ NMR spectra at ca. 328 ppm, which appears as a doublet of doublets due to the coupling with the two diastereotopic phosphorus nuclei ($^2J_{CP}$ = 14.1−19.5 Hz). Remarkably, demetalation of **14a**−**c** with acetonitrile takes place even at room temperature (ca. 30 min), giving the optically active terminal alkynes **15a**−**c**, which have been isolated in 70−97% yield. Confirmation of the identity of **15a**−**c** was achieved by IR and NMR spectroscopy, elemental analyses, and/or high-resolution mass spectrometry (see the Experimental Section and Tables 11 and 12). Assuming that the stereogenic C_γ atom in σ-alkynyl complexes **13a**−**c** is not involved in the protonation and demetalation processes, an *exo* disposition of the ketonic fragment is also proposed for vinylidenes **14a**−**c** and terminal alkynes **15a**−**c**.

Synthesis of Unsaturated Ruthenium(II) Cyclic Alkenyl and Carbene Complexes. Among the synthetic routes to oxacycloalkylidene complexes, those based on intramolecular nucleophilic additions of hydroxy groups at the C_α of vinylidene moieties are one of the most efficient.[15] It could be anticipated that the enol resonance form of the keto-substituted vinylidene complexes **5a**−**e**, **6a**−**d**, and **14a**−**c** would fulfill these expectations, driving the reaction to the formation of the desired intramolecular addition products. However, these vinylidene complexes are stable in solution and

(15) For a review see: Weyershausen, B.; Dötz, K. H. *Eur. J. Inorg. Chem.* **1999**, 1057.

Scheme 3

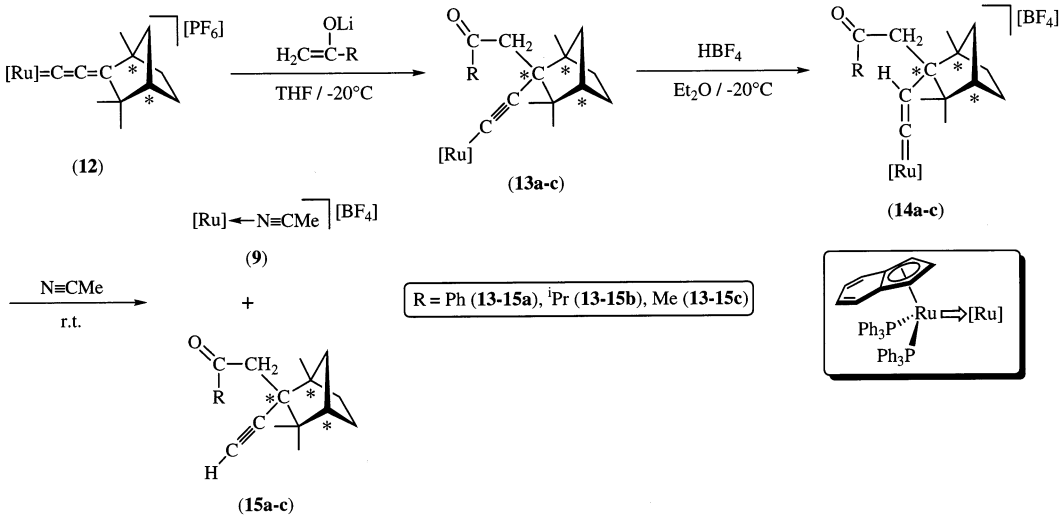


Table 8. $^{13}C\{^1H\}$ NMR Data for Neutral σ-Alkynyl Complexes $[Ru\{C{\equiv}CC(C_9H_{16})(CH_2COR)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[a]

	η^5-C_9H_7											
complex	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3a,7a)[b]	C-4,5,6,7	Ru−C_α	$^2J_{CP}$	C_β	C_γ	$CH_2C{=}O$	C=O	others
13a	75.26 dd[c] 75.50 d[d]	97.18	110.61 111.56	−19.61	123.86 125.21 125.88 126.88	85.29 vt	22.9	114.88	54.99	48.56	199.34	20.27, 28.37, and 28.48 (s, CH_3); 26.81, 35.67, and 42.34 (s, CH_2); 45.74 and 52.65 (s, C); 53.09 (s, CH); 127.74−140.78 (m, Ph)
13b	74.24	96.77	108.96 112.30	−20.07	122.52 124.66 125.61 127.13	84.36 vt	22.0	114.78	54.30	49.92	212.30	18.59, 19.69, 22.95, 27.67, and 29.56 (s, CH_3); 26.14, 35.10, and 41.60, (s, CH_2); 41.03 (s, 44.92 and 52.06 (s, C); $CH(CH_3)_2$); 44.92 and 52.06 (s, C); 51.94 (s, CH); 127.26−140.16 (m, Ph)
13c	74.06 vt[e] 74.45 vt[f]	96.56	109.38 111.77	−20.12	122.83 124.92 125.28 126.16	85.02 vt	22.4	114.62	54.20	51.88	206.74	19.67, 27.56, 27.78, and 30.76 (s, CH_3); 26.22, 35.04, and 41.56 (s, CH_2); 44.91 and 52.47 (s, C); 51.88 (s, CH); 127.16−140.09 (m, Ph)

[a] Spectra recorded in C_6D_6; δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; vt, virtual triplet; m, multiplet. [b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] $^2J_{CP}$ = 5.4, $^2J_{CP'}$ = 3.3. [d] $^2J_{CP}$ = 6.5. [e] $^2J_{CP}$ = $^2J_{CP'}$ = 2.5. [f] $^2J_{CP}$ = $^2J_{CP'}$ = 5.4.

Table 9. $^{31}P\{^1H\}$ and ^1H NMR Data for Cationic Vinylidene Complexes $[Ru\{{=}C{=}C(H)C(C_9H_{16})(CH_2COR)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$[a]

			^1H					
			η^5-C_9H_7					
complex	$^{31}P\{^1H\}$	$^2J_{PP}$	H-1,3	H-2	H-4,5,6,7	Ru=C=CH	$CH_2C{=}O$	others
R = Ph (**14a**)	35.23 d 37.94 d	22.8	5.59 br	6.12 br	5.26 m, *b*	5.12 s	2.26 d[c] 3.13 d[c]	0.39, 0.75, and 1.39 (s, CH_3); 1.20, 1.64, and 1.87 (m, CH_2); 2.05 (m, CH); 6.44−7.87 (m, Ph)
R = ^{i}Pr (**14b**)	35.35 d 37.92 d	22.6	5.60 br	6.08 br	5.30 m, *b*	5.15 s	2.52 d[d] 2.71 d[d]	0.36, 0.77, and 1.30 (s, CH_3); 1.09 and 1.13 (d, J_{HH} = 6.9, $CH(CH_3)_2$); 1.44, 1.66, and 1.96 (m, CH_2); 2.15 (m, CH); 2.53 (m, $CH(CH_3)_2$); 6.48−7.51 (m, Ph)
R = Me (**14c**)	35.23 d 38.09 d	22.8	5.17 br 5.58 br	6.43 br	5.31 d,[e] 5.56 d,[f] *b*	5.05 s	1.75 d[g] 2.53 d[g]	0.32, 0.75, 1.26, and 2.12 (s, CH_3); 1.18, 1.53, and 1.62 (m, CH_2); 1.96 (m, CH); 6.89−7.49 (m, Ph)

[a] Spectra recorded in $CDCl_3$; δ in ppm and J in Hz. Abbreviations: s, singlet; br, broad; d, doublet; sept, septuplet; m, multiplet. [b] Overlapped by Ph protons. [c] J_{HH} = 18.8. [d] J_{HH} = 19.1. [e] J_{HH} = 8.0. [f] J_{HH} = 9.4. [g] J_{HH} = 18.5.

do not undergo such cyclization processes, even in refluxing toluene. It is apparent that the electron-releasing ability of the indenyl moiety [Ru(η^5-C_9H_7)-(PPh_3)$_2$] decreases the electrophilic character of the vinylidene Ru=C_α moiety, avoiding the effective cyclization reaction.[16] To facilitate this process, we set out to

Table 10. $^{13}C\{^1H\}$ NMR Data for Cationic Vinylidene Complexes [Ru{=C=C(H)C(C_9H_{16})(CH_2COR)}(η^5-C_9H_7)(PPh_3)$_2$][BF_4][a]

	η^5-C_9H_7											
complex	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3,7a)[b]	C-4,5,6,7	Ru=C_α	$^2J_{CP}$	C_β	C_γ	CH_2C=O	C=O	others
14a	79.96 d[c] 81.65 d[d]	97.27	113.67 119.88	−13.92	122.04 124.59 *e*	328.79 dd	19.5 14.6	108.87	57.49	44.53	199.98	18.80, 26.85, and 27.02 (s, CH_3); 25.27, 35.08, and 41.06 (s, CH_2); 46.47 and 52.71 (s, C); 49.77 (s, CH); 127.62−136.67 (m, Ph)
14b	80.41 d[f] 82.30 d[g]	97.55	113.59 121.07	−13.37	122.40 124.31 *e*	328.57 dd	18.9 14.8	109.05	59.29	46.65	216.15	18.83, 19.02, 19.43, 27.63, and 27.96 (s, CH_3); 26.14, 35.67, and 41.47 (s, CH_2); 42.42 (s, $CH(CH_3)_2$); 46.84 and 53.11 (s, C); 50.19 (s, CH); 125.37−135.91 (m, Ph)
14c	80.36 d[f] 82.29 d[f]	97.65	113.53 121.02	−13.42	122.39 125.34 *e*	328.25 dd	18.7 14.1	108.94	58.52	49.36	210.28	18.91, 26.95, 27.74, and 31.38 (s, CH_3); 25.99, 35.45, and 41.40 (s, CH_2); 46.92 and 52.78 (s, C); 50.13 (s, CH); 128.51−147.47 (m, Ph)

[a] Spectra recorded in CD_2Cl_2; δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; m, multiplet. [b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)), δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] $^2J_{CP}$ = 8.5. [d] $^2J_{CP}$ = 7.3. [e] Overlapped by Ph carbons. [f] $^2J_{CP}$ = 8.2. [g] $^2J_{CP}$ = 7.7.

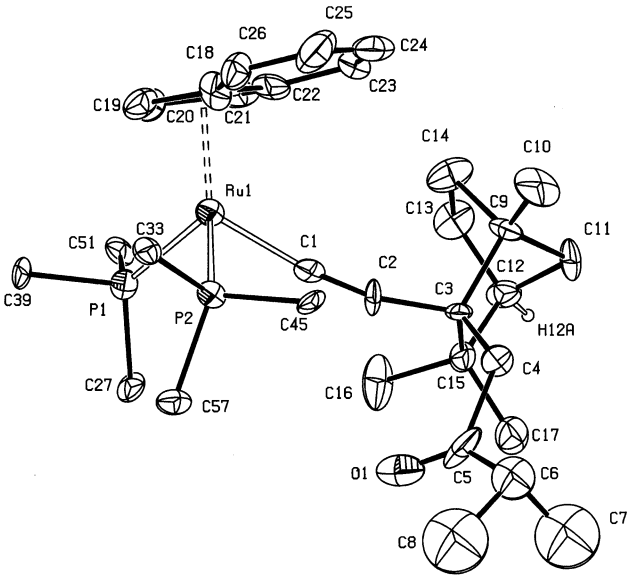


Figure 1. ORTEP view of the structure of the σ-alkynyl complex [Ru{C≡CC(C_9H_{16})(CH_2CO^iPr)}(η^5-C_9H_7)(PPh_3)$_2$] (**13b**). Aryl groups of the triphenylphosphine ligands have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−C* = 1.94(4); Ru−P1 = 2.235(8); Ru−P2 = 2.333(9); Ru−C1 = 2.03(3); C1−C2 = 1.21(3); C2−C3 = 1.55(4); C5−O1 = 1.18(5); C*−Ru−P1 = 119(1); C*−Ru−P2 = 123(1); C*−Ru−C1 = 121(3); Ru−C1−C2 = 173(3); C(1)−C(2)−C(3) = 168(3). C* = centroid of the indenyl ring (C18, C19, C20, C21, C22).

synthesize hydroxy−vinylidene complexes via reduction of the ketone group into the corresponding alcohol. Toward this aim the corresponding σ-alkynyl precursors were prepared. Thus, treatment of [Ru{C≡CCPh$_2$(CH_2-COR^2)}(η^5-C_9H_7)(PPh_3)$_2$] (R^2 = Ph (**3a**), ^{i}Pr (**3b**)) with a slight excess of LiMe in tetrahydrofuran, at −20 °C, and subsequent methanolysis allows the preparation of the γ-hydroxy−alkynyl derivatives [Ru(C≡CCPh$_2${CH_2C-(OH)MeR^2})(η^5-C_9H_7)(PPh_3)$_2$] (**16a,b**; 71% and 63% yields, respectively) (Scheme 4). We note that all attempts to promote related reactions on the corresponding vinylidene complexes **5a**,**b** were unsuccessful, recovering instead the starting σ-alkynyl derivatives **3a**,**b**.

Complexes **16a,b** have been analytically and spectroscopically characterized (see the Experimental Section). IR and $^{13}C\{^1H\}$ NMR spectra are very informative, since they show the disappearance of the typical carbonyl signals of **3a**,**b**, confirming the reduction of the ketone group. In addition, two novel singlet resonances in the ranges δ 25.49−32.09 and 75.53−75.91 assigned to the methyl and C−OH carbon nuclei, respectively, were observed in the $^{13}C\{^1H\}$ NMR spectra. However, protonation of **16a**,**b** does not yield the expected cyclic carbenes **17** (Scheme 5), giving instead the tetrafluoroborate salt of the diphenylallenylidene complex [Ru(=C=C=CPh$_2$)(η^5-C_9H_7)(PPh_3)$_2$]$^+$ (**1**) in almost quantitative yields. Apparently, the protonation of the alkynyl moiety in **16a**,**b** seems to be thermodynamically disfavored with respect to the protonation of the hydroxy function. Thus, an unstable carbocation is formed, which evolves into **1** by elimination of α-methylstyrene or 2,3-dimethyl-1-butene (Scheme 5).

Consequently, an alternative synthetic procedure was devised. As it is well-known, Lewis acid catalyzed intramolecular heterocyclizations of alkynes is a widely used and general method for the synthesis of unsaturated heterocycles.[17] This synthetic methodology proved to be appropriate to obtain the desired cyclization products. Thus, we have found that the treatment of

(16) In contrast, the protonation of the analogous keto-substituted σ-alkynyl complex [Ru{C≡CCPh$_2$(CH_2COCH_3)}(η^5-C_5H_5)(CO)(P^iPr_3)] with HBF_4 has been reported to give [Ru{=CCH_2CPh$_2$CH=C(CH_3)-O}(η^5-C_5H_5)(CO)(P^iPr_3)][BF_4], which is formed via an intramolecular nucleophilic addition at the electrophilic C_α atom of the enol resonance form in the highly reactive vinylidene intermediate [Ru{=C=C(H)-CPh$_2$(CH_2COCH_3)}(η^5-C_5H_5)(CO)(P^iPr_3)][BF_4].[2d]

(17) See for example: Harding, K. E.; Tiner, T. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 4, p 363.

Table 11. IR[a] and ^{1}H NMR[b] Data for Terminal Alkynes HC≡CC(C_9H_{16})(CH_2COR)

	IR			^{1}H		
compd	ν(HC≡)	ν(C≡C)	ν(C=O)	HC≡	CH_2	others
R = Ph (**15a**)	3307	2099	1692	2.03 s	3.05 d[c] 3.16 d[c]	0.96, 1.07, and 1.65 (s, CH_3); 1.00 and 1.82 (m, CH_2); 1.12−1.56 (m, CH_2); 2.52 (m, CH); 7.04−7.85 (m, Ph)
R = ^{i}Pr (**15b**)	3316	2104	1725	1.98 s	2.44 d[d] 2.60 d[d]	0.92 and 0.94 (d, J_{HH} = 6.8, CH(CH_3)$_2$); 0.93 and 1.02 (s, CH_3); 0.98−1.52 (m, CH_3 and CH_2); 2.23 (sept, J_{HH} = 6.8, C*H*(CH_3)$_2$); 2.43 (m, CH)
R = Me (**15c**)	3257	2103	1718	2.00 s	2.29 d[d] 2.39 d[d]	0.87, 0.95, 1.45, and 1.71 (s, CH_3); 1.06, 1.31, and 1.50 (m, CH_2); 2.38 (m, CH)

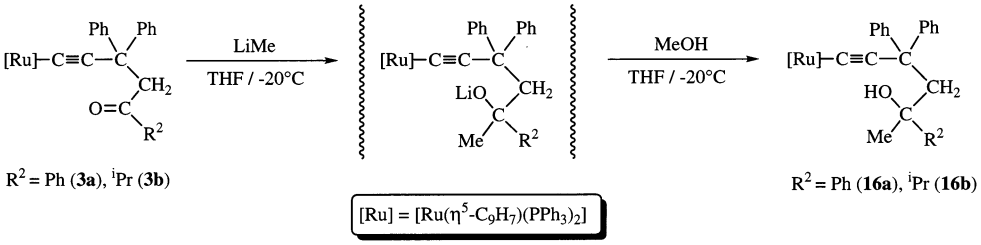
[a] KBr; ν in cm^{-1}. [b] Spectra recorded in C_6D_6; δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; sept, septuplet; m, multiplet. [c] J_{HH} = 18.1. [d] J_{HH} = 17.9.

Table 12. ^{13}C{^{1}H} NMR Data for Terminal Alkynes HC≡CC(C_9H_{16})(CH_2COR)[a]

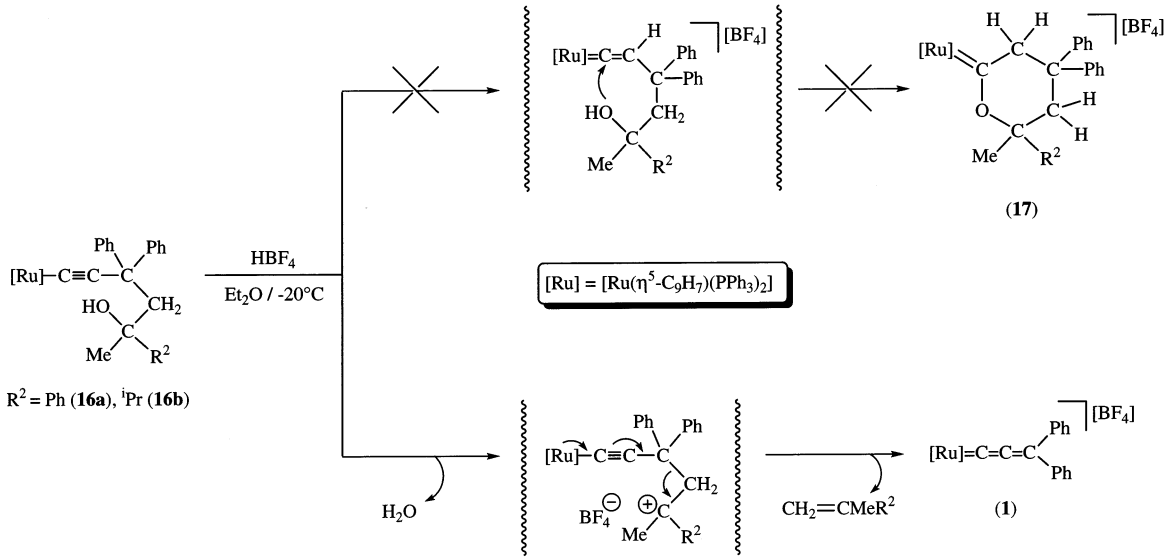
compd	≡CH	≡C	C_γ	CH_2C=O	C=O	others
15a	72.72	87.49	52.92	45.23	197.06	18.62, 25.93, and 26.70 (s, CH_3); 25.11, 34.28, and 40.99 (s, CH_2); 43.97 and 49.42 (s, C); 51.32 (s, CH); 127.97, 128.60, and 132.45 (s, CH of Ph); 138.31 (s, C of Ph)
15b	72.44	87.55	52.69	47.10	210.57	18.48, 18.51, 18.87, 25.81, and 28.68 (s, CH_3); 25.09, 34.24, and 40.91 (s, CH_2); 40.97 (s, *C*H(CH_3)$_2$), 43.69 and 49.18 (s, C); 51.16 (s, CH)
15c	72.71	87.40	52.70	49.81	204.60	18.36, 25.95, 26.66, and 30.24 (s, CH_3); 25.09, 34.07, and 40.80 (s, CH_2); 43.80 and 49.20 (s, C); 51.11 (s, CH)

[a] Spectra recorded in C_6D_6; δ in ppm.

Scheme 4



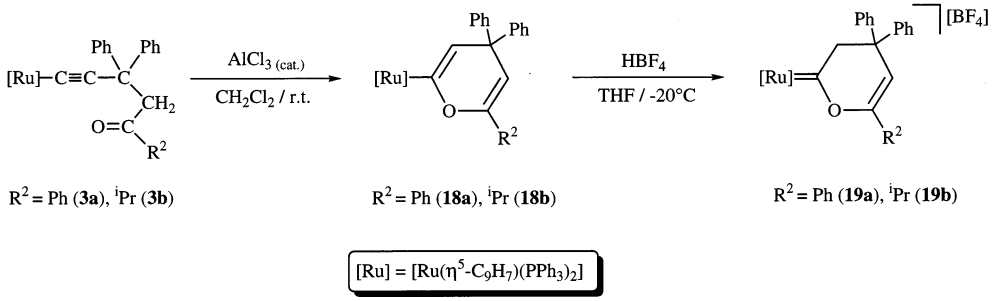
Scheme 5



σ-alkynyl complexes [Ru{C≡CCPh$_2$(CH_2COR^2)}(η^5-C_9H_7)(PPh_3)$_2$] (**3a**,**b**) with ca. 5 mol % $AlCl_3$ in dichloromethane at room temperature smoothly produces the cyclic alkenyl complexes [Ru{C=CHCPh$_2$CH=C(R^2)O}-(η^5-C_9H_7)(PPh_3)$_2$] (**18a**,**b**; 95% and 87% yields, respectively) (Scheme 6). These reactions can be monitored by IR spectroscopy, which shows the total disappearance of the typical ν(C≡C) and ν(C=O) absorptions of **3a**,**b**. In the NMR spectra, the most noticeable resonances are (i) (^{1}H NMR) two doublets (ca. J_{HH} = 2 Hz) in the range 4.74−5.57 ppm assigned to the olefinic protons of the six-membered ring and (ii) (^{13}C{^{1}H} NMR) a triplet signal (ca. $^2J_{CP}$ = 17 Hz) at ca. 163 ppm for the Ru−C_α atom[18] and singlets for the =CH (δ 99.50−117.64) and =C (δ 151.42−157.67) carbons.

As expected from the ability of alkenyl complexes to undergo electrophilic additions at the C_β atom to give carbene derivatives,[18,19] treatment of THF solutions of **18a**,**b** with HBF_4 at −20 °C leads to the formation of

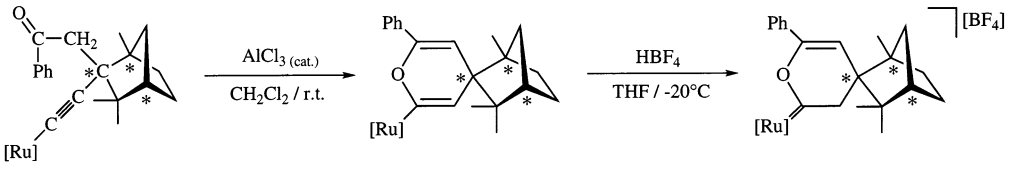
Scheme 6



R^2 = Ph (**3a**), ^{i}Pr (**3b**) R^2 = Ph (**18a**), ^{i}Pr (**18b**) R^2 = Ph (**19a**), ^{i}Pr (**19b**)

[Ru] = [Ru(η^5-C_9H_7)(PPh_3)$_2$]

Scheme 7



(**13a**) (**20**) (**21**)

[Ru] = [Ru(η^5-C_9H_7)(PPh_3)$_2$]

the air-stable oxacycloalkylidenes [Ru{=CCH$_2$CPh$_2$-CH=C(R^2)O}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (R^2 = Ph (**19a**), ^{i}Pr (**19b**)), which have been isolated in 83 and 89% yields, respectively (Scheme 6). The presence of the carbenic moiety is clearly confirmed by the $^{13}C\{^1H\}$ NMR spectra, which show the typical low-field resonance of the carbenic carbon nuclei at ca. δ 302 (t, $^2J_{CP}$ = 11.8−14.3 Hz). The spectra also show resonances assignable to the CH_2 (δ 67.62−68.39), =CH (δ 109.14−115.39), =C (δ 153.48−160.68), and *C*Ph$_2$ (δ 43.60−44.71) carbons of the six-membered heterocyclic skeletons.

To extend the scope of this synthetic route to optically active cyclic carbene complexes, we examined the behavior of the analogous chiral keto−alkynyl derivative **13a** toward $AlCl_3$. Under analogous reaction conditions, the chiral oxacycloalkenyl complex **20** was obtained and isolated (78% yield) as an air-stable solid. The subsequent protonation in THF with HBF_4 at −20 °C gives the desired oxacyclocarbene complex **21** in 83% yield (Scheme 7). Since the analytical and spectroscopic data of **20** and **21** are comparable to those observed for their achiral counterparts, **18a**,**b** and **19a**,**b** will not be further discussed.

Concluding Remarks

In this work a metal-mediated synthetic approach for γ-keto-substituted alkynes HC≡CCR$_2$(CH$_2$COR), which result from the formal coupling of 2-propyn-1-ols with methyl ketones, is reported. This methodology constitutes an alternative to the known coupling of propargylic alcohols with ketones containing α-hydrogens via [$Co_2(CO)_6$]-stabilized propargylium ions, which also yields γ-keto-substituted alkynes.[20]

The synthetic procedure is based on the electronic and/or steric ability of the fragment [Ru(η^5-C_9H_7)(PPh_3)$_2$] to promote the following processes involved in the synthetic route. (i) Stabilization of the coordinated allenylidene groups C=C=CR$_2$ which results from the dehydration of propargylic alcohols HC≡CC(OH)R$_2$. (ii) The regioselective addition of lithium enolates derived from methyl ketones at the C_γ atom of the allenylidene chain to give the keto−alkynyl complexes [Ru{C≡CC-R$_2$(CH$_2$COR)}(η^5-C_9H_7)(PPh_3)$_2$] (**3a**−**e** and **4a**−**d**). The steric protection of the electrophilic C_α allows the nucleophilic addition at the more accessible C_γ atom. (iii) The elimination of the free γ-keto-substituted alkyne HC≡CCR$_2$(CH$_2$COR) (**7a**−**e** and **8a**−**d**) which can be efficiently achieved via selective C_β protonation of **3a**−**e** and **4a**−**d** to afford vinylidene complexes [Ru{=C=C(H)CR$_2$(CH$_2$COR)}(η^5-C_9H_7)(PPh_3)$_2$]$^+$ (**5a**−**e** and **6a**−**d**), followed by the vinylidene−π-terminal alkyne tautomerization in refluxing acetonitrile, generating the species [Ru{η^2-HC≡CCR$_2$(CH$_2$COR)}(η^5-C_9H_7)(PPh_3)$_2$]$^+$. The ready exchange of the coordinated alkyne for acetonitrile leads to the free alkynes and the quantitative recovery of the metal fragment as the acetonitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**9**).

The generality of this synthetic procedure is shown by the synthesis of chiral γ-keto−alkynes **15a**−**c**, which are obtained from the formal coupling of 2-*exo*-ethynyl-1,3,3-trimethyl-2-*endo*-norbornanol (**11**) with methyl ketones. Thus, the synthesis of the first optically active allenylidene derivative, [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)-

(18) These chemical shifts and coupling constants are comparable to those found in related ruthenium(II) indenyl alkenyl derivatives [Ru{C(R)=C(H)R′}(η^5-C_9H_7)L_2] (L = PPh_3; L_2 = dppm): (a) Bassetti, M.; Casellato, P.; Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Martín-Vaca, B. *Organometallics* **1997**, *16*, 5470. (b) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M. *Organometallics* **1998**, *17*, 3707. See also ref 5c.

(19) For theoretical calculations on transition-metal alkenyl complexes see: Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(20) For general reviews on the synthetic utility of metal-complexed propargyl cations see: (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (b) Smit, W. A.; Caple, R.; Smoliakova, I. P. *Chem. Rev.* **1994**, *94*, 2359. (c) McGlinchey, M. J.; Girard, L.; Ruffolo, R. *Coord. Chem. Rev.*, **1995**, *143*, 331. (d) Amouri, H.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077. (e) Melikyan, G. G.; Nicholas, K. M. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995.

$(PPh_3)_2][PF_6]$ (**12**), is reported. This precursor has also proven to be an excellent substrate to promote regio- and diastereoselective additions of enolates $[CH_2COR]^-$, allowing, therefore, the diastereoselective synthesis of the final terminal alkynes of interest as building blocks in organic synthesis.

Moreover, a novel and general synthetic strategy for the preparation of unsaturated cyclic alkenyl and carbene ruthenium(II) complexes from γ-keto−alkynyl derivatives $[Ru\{C{\equiv}CCR_2(CH_2COR)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ has also been described. These alkynyl species are able to undergo $AlCl_3$-catalyzed intramolecular cyclization reactions to give oxacycloalkenyl complexes: i.e., **18a**,**b** and **20**. The subsequent protonation gives oxacyclocarbene complexes, i.e. **19a**,**b** and **21**, in high yields. Further studies concerning the scope and limitations of these processes are in progress.[5e]

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. Compounds $[Ru\{{=}C{=}C{=}C(R^1)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = Ph (**1**), H (**2**)),[5a] $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**10**),[12] and 2-*exo*-ethynyl-1,3,3-trimethyl-2-*endo*-norbornanol (**11**)[13] were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. High-resolution mass spectra were recorded using a MAT-95 spectrometer. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper.

(a) Synthesis of σ-Alkynyl Complexes $[Ru\{C{\equiv}CC(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (R^1 = Ph, R^2 = Ph (3a), ^{i}Pr (3b), Me (3c), $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (3d), (*E*)-CH=CHPh (3e); R^1 = H, R^2 = Ph (4a), ^{i}Pr (4b), Me (4c), $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (4d)). A solution of $LiCH_2COR^2$ (obtained in situ by treatment of the corresponding ketone (1 mmol) with LDA (0.179 g, 1 mmol) at −20 °C in 10 mL of THF for 30 min) was added at −20 °C to a solution of $[Ru\{{=}C{=}C{=}C(R^1)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = Ph (**1**), H (**2**); 1 mmol) in 30 mL of THF. 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 (1/2) gave an orange band from which σ-alkynyl complexes **3a**−**e** and **4a**−**d** were isolated as orange solids after solvent removal. **3a**: yield 83% (0.871 g); IR (KBr, cm^{-1}) ν 1702 (C=O), 2075 (C≡C). Anal. Calcd for $RuC_{68}H_{54}P_2O$ (1050.19): C, 77.77; H, 5.18. Found: C, 77.33; H, 5.19. **3b**: yield 65% (0.660 g); IR (KBr, cm^{-1}) ν 1721 (C=O), 2086 (C≡C). Anal. Calcd for $RuC_{65}H_{56}P_2O$ (1016.17): C, 76.83; H, 5.55. Found: C, 76.29; H, 5.33. **3c**: yield 63% (0.622 g); IR (KBr, cm^{-1}) ν 1697 (C=O), 2080 (C≡C). Anal. Calcd for $RuC_{63}H_{52}P_2O$ (988.13): C, 76.58; H, 5.30. Found: C, 76.46; H, 5.35. **3d**: yield 78% (0.903 g); IR (KBr, cm^{-1}) ν 1679 (C=O), 2082 (C≡C). Anal. Calcd for $RuFeC_{72}H_{58}P_2O$ (1158.11): C, 74.67; H, 5.05. Found: C, 75.27; H, 5.28. **3e**: yield 81% (0.871 g); IR (KBr, cm^{-1}) ν 1652 (C=O), 2052 (C≡C). Anal. Calcd for $RuC_{70}H_{56}P_2O$ (1076.23): C, 78.12; H, 5.24. Found: C, 77.91; H, 5.18. **4a**: yield 62% (0.604 g); IR (KBr, cm^{-1}) ν 1706 (C=O), 2073 (C≡C). Anal. Calcd for $RuC_{62}H_{50}P_2O$ (974.09): C, 76.45; H, 5.17. Found: C, 76.13; H, 5.09. **4b**: yield 65% (0.611 g); IR (KBr, cm^{-1}) ν 1705 (C=O), 2092 (C≡C). Anal. Calcd for $RuC_{59}H_{52}P_2O$ (940.07): C, 75.38; H, 5.57. Found: C, 74.92; H, 5.48. **4c**: yield 71% (0.647 g); IR (KBr, cm^{-1}) ν 1709 (C=O), 2089 (C≡C). Anal. Calcd for $RuC_{57}H_{48}P_2O$ (912.03): C, 75.06; H, 5.30. Found: C, 75.21; H, 5.17. **4d**: yield 69% (0.746 g); IR (KBr, cm^{-1}) ν 1658 (C=O), 2092 (C≡C). Anal. Calcd for $RuFeC_{66}H_{54}P_2O$ (1082.01): C, 73.26; H, 5.03. Found: C, 72.91; H, 5.18.

(b) Synthesis of Vinylidene Complexes $[Ru\{{=}C{=}C(H)C(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (R^1 = Ph, R^2 = Ph (5a), ^{i}Pr (5b), Me (5c), $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (5d), (*E*)-CH=CHPh (5e); R^1 = H, R^2 = Ph (6a), ^{i}Pr (6b), Me (6c), $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (6d)). 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 $[Ru\{C{\equiv}CC(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**3a**−**e** and **4a**−**d**; 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 vacuum-dried. **5a**: yield 88% (1.001 g); IR (KBr, cm^{-1}) ν 1065 (BF_4^-), 1689 (C=O). Anal. Calcd for $RuC_{68}H_{55}F_4P_2BO$ (1138.00): C, 71.77; H, 4.87. Found: C, 71.08; H, 5.06. **5b**: yield 89% (0.982 g); IR (KBr, cm^{-1}) ν 1061 (BF_4^-), 1710 (C=O). Anal. Calcd for $RuC_{65}H_{57}F_4P_2BO$ (1103.98): C, 70.72; H, 5.20. Found: C, 69.95; H, 5.06. **5c**: yield 87% (0.935 g); IR (KBr, cm^{-1}) ν 1059 (BF_4^-), 1712 (C=O). Anal. Calcd for $RuC_{63}H_{53}F_4P_2BO$ (1075.43): C, 70.33; H, 4.96. Found: C, 70.12; H, 4.81. **5d**: yield 88% (1.096 g); IR (KBr, cm^{-1}) ν 1061 (BF_4^-), 1660 (C=O). Anal. Calcd for $RuFeC_{72}H_{59}F_4P_2BO$ (1245.92): C, 69.41; H, 4.77. Found: C, 69.45; H, 4.95. **5e**: yield 82% (0.954 g); IR (KBr, cm^{-1}) ν = 1057 (BF_4^-), 1662 (C=O). Anal. Calcd for $RuC_{70}H_{57}F_4P_2BO$ (1064.04): C, 72.22; H, 4.93. Found: C, 72.79; H, 4.93. **6a**: yield 89% (0.945 g); IR (KBr, cm^{-1}) ν 1058 (BF_4^-), 1657 (C=O). Anal. Calcd for $RuC_{62}H_{51}F_4P_2BO$ (1061.90): C, 70.12; H, 4.84. Found: C, 70.52; H, 4.52. **6b**: yield 84% (0.863 g); IR (KBr, cm^{-1}) ν 1060 (BF_4^-), 1705 (C=O). Anal. Calcd for $RuC_{59}H_{53}F_4P_2BO$ (1027.88): C, 68.94; H, 5.20. Found: C, 68.51; H, 5.23. **6c**: yield 94% (0.940 g); IR (KBr, cm^{-1}) ν 1060 (BF_4^-), 1712 (C=O). Anal. Calcd for $RuC_{57}H_{49}F_4P_2BO$ (999.84): C, 68.47; H, 4.94. Found: C, 68.52; H, 4.88. **6d**: yield 74% (0.866 g); IR (KBr, cm^{-1}) ν 1061 (BF_4^-), 1654 (C=O). Anal. Calcd for $RuFeC_{66}H_{55}F_4P_2BO$ (1169.82): C, 67.76; H, 4.73. Found: C, 68.02; H, 4.69.

(c) Synthesis of Terminal Alkynes $HC{\equiv}CC(R^1)Ph(CH_2COR^2)$ (R^1 = Ph, R^2 = Ph (7a), ^{i}Pr (7b), Me (7c), $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (7d), (*E*)-CH=CHPh (7e); R^1 = H, R^2 = Ph (8a), ^{i}Pr (8b), Me (8c), $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (8d)). A solution of the corresponding vinylidene complex $[Ru\{{=}C{=}C(H)C(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**5a**−**e** and **6a**−**d**; 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 mainly the nitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**9**) remains insoluble. The extract was evaporated to dryness and the crude product purified by column chromatography on silica gel with a mixture of hexane and diethyl ether (6/1) as eluent. Evaporation of the solvents gave terminal alkynes **7a**−**e** and **8a**−**d**. **7a**: white solid; yield 86% (0.267 g). Anal. Calcd for $C_{23}H_{18}O$ (310.94): C, 89.00; H, 5.84. Found: C, 88.91; H, 5.90. **7b**: white solid; yield 80% (0.221 g). Anal. Calcd for $C_{20}H_{20}O$ (276.37): C, 86.92; H, 7.29. Found: C, 86.45; H, 7.34. **7c**: white solid; yield 93% (0.231 g). Anal. Calcd for $C_{18}H_{16}O$ (248.32): C, 87.06; H, 6.49. Found: C, 86.91; H, 6.55. **7d**: orange solid; yield 73% (0.305 g). Anal. Calcd for $FeC_{27}H_{22}O$ (418.31): C, 77.52; H, 5.30. Found: C, 77.27; H, 5.48. **7e**: white solid; yield 78% (0.262 g). Anal. Calcd for $C_{25}H_{20}O$ (336.43): C, 89.25; H, 5.99. Found: C, 89.12; H, 6.14. **8a**: white solid; yield 82% (0.192 g). Anal. Calcd for $C_{17}H_{14}O$ (234.30): C, 87.14; H, 6.02. Found: C, 87.21; H, 6.12. **8b**: white solid; yield 76% (0.152 g). Anal. Calcd for $C_{14}H_{16}O$ (200.28): C, 83.96; H, 8.05.

Found: C, 83.78; H, 8.10. **8c**: colorless oil; yield 80% (0.138 g); HRMS *m*/*z* calcd for $C_{12}H_{12}O$ (found) M^+ = 172.088 809 (172.088 527). **8d**: orange solid; yield 72% (0.246 g). Anal. Calcd for $FeC_{21}H_{18}O$ (342.22): C, 73.70; H, 5.30. Found: C, 73.60; H, 5.22.

(d) Synthesis of the Allenylidene Complex [Ru{=C=C=C(C$_9$H$_{16}$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (12). To a solution of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**10**; 0.776 g, 1 mmol) in 50 mL of MeOH were added $NaPF_6$ (0.336 g, 2 mmol) and 2-*exo*-ethynyl-1,3,3-trimethyl-2-*endo*-norbornanol (**11**; 0.356 g, 2 mmol). The reaction mixture was heated under reflux for 30 min. The solvent was then removed under vacuum, the crude product extracted with CH_2Cl_2, and the extract filtered. Concentration of the resulting solution to ca. 5 mL followed by the addition of 50 mL of diethyl ether precipitated a red solid, which was washed with diethyl ether (2 × 20 mL) and dried in vacuo. Yield: 80% (0.837 g). IR (KBr, cm^{-1}): ν 1963 (C=C=C), 838 (PF_6^-). Anal. Calcd for $RuC_{57}H_{53}F_6P_3$ (1046.02): C, 65.45; H, 5.10. Found: C, 64.83; H, 5.09. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.09 and 47.21 (d, $^2J_{PP}$ = 23.2 Hz) ppm. ^1H NMR ($CDCl_3$): δ 1.04, 1.05, and 1.14 (s, 3H each, CH_3), 1.30, 1.54, 1.62, and 1.87 (m, 1H each, CH_2), 1.77 (m, 2H, CH_2), 2.27 (m, 1H, CH), 5.19 (br, 2H, H-1 and H-3), 5.35 (br, 1H, H-2), 6.28 and 6.36 (d, 1H each, J_{HH} = 7.7 Hz, H-4, H-5, H-6 or H-7), 6.91−7.67 (m, 32H, Ph and H-4, H-5, H-6 or H-7) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.87, 25.19, and 26.51 (s, CH_3), 25.24, 34.38, and 44.95 (s, CH_2), 47.72 (s, CH), 57.57 and 64.34 (s, C), 83.52 and 84.60 (br, C-1 and C-3), 98.10 (s, C-2), 112.55 and 114.07 (s, C-3a and C-7a), 123.21, 124.09, 129.17, and 131.39 (s, C-4, C-5, C-6 and C-7), 123.21−135.27 (m, Ph), 183.24 (s, C_γ), 202.01 (s, C_β), 305.06 (vt, $^2J_{CP} = {}^2J_{CP'}$ = 18.9 Hz, Ru=C_α) ppm; $\Delta\delta$(C-3a,7a) = −17.39.

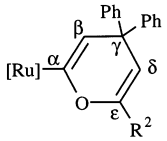
(e) Synthesis of σ-Alkynyl Complexes [Ru{C≡CC(C$_9$H$_{16}$)(CH$_2$COR)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (R = Ph (13a), ^{i}Pr (13b), Me (13c)). These complexes were prepared as described for **3a**−**e** and **4a**−**d** by starting from the allenylidene derivative [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**12**; 1.046 g, 1 mmol) and the corresponding ketone (1 mmol). Products were purified by column chromatography on Al_2O_3 (neutral; activity grade I) with a mixture of hexane and diethyl ether (1/1) as eluent. Evaporation of the solvents gave complexes **13a**−**c** as red solids. **13a**: yield 77% (0.785 g); IR (KBr, cm^{-1}) ν 2070 (C≡C), 1694 (C=O). Anal. Calcd for $RuC_{65}H_{60}P_2O$ (1020.22): C, 76.52; H, 5.94. Found: C, 76.56; H, 6.29. **13b**: yield 68% (0.670 g); IR (KBr, cm^{-1}) ν 2070 (C≡C), 1718 (C=O). Anal. Calcd for $RuC_{62}H_{62}P_2O$ (986.20): C, 75.51; H, 6.33. Found: C, 75.47; H, 6.60. **13c**: yield 76% (0.728 g); IR (KBr, cm^{-1}) ν 2072 (C≡C), 1723 (C=O). Anal. Calcd for $RuC_{60}H_{58}P_2O$ (958.15): C, 75.21; H, 6.10. Found: C, 74.86; H, 6.21.

(f) Synthesis of Vinylidene Complexes [Ru{=C=C(H)C(C$_9$H$_{16}$)(CH$_2$COR)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (R = Ph (14a), ^{i}Pr (14b), Me (14c)). These complexes were obtained as brown solids as described for **5a**−**e** and **6a**−**d**, starting from the corresponding σ-alkynyl complex [Ru{C≡CC(C_9H_{16})(CH_2-COR)}(η^5-C_9H_7)(PPh_3)$_2$] (**13a**−**c**) (1 mmol). **14a**: yield 83% (0.920 g); IR (KBr, cm^{-1}) ν 1663 (C=O), 1060 (BF_4^-). **14b**: yield 85% (0.913 g); IR (KBr, cm^{-1}) ν 1702 (C=O), 1058 (BF_4^-). **14c**: yield 96% (1.004 g); IR (KBr, cm^{-1}) ν 1711 (C=O), 1057 (BF_4^-). Complexes **14a**−**c** were too sensitive to moisture and oxygen to give satisfactory elemental analyses.

(g) Synthesis of Terminal Alkynes HC≡CC(C$_9$H$_{16}$)(CH$_2$COR) (R = Ph (15a), ^{i}Pr (15b), Me (15c)). These compounds were prepared as described for **7a**−**e** and **8a**−**d**, starting from the corresponding vinylidene complex [Ru{=C=C(H)C(C_9H_{16})(CH_2COR)}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**14a**−**c**; 1 mmol). **15a**: white solid; yield 79% (0.221 g). Anal. Calcd for $C_{20}H_{24}O$ (280.41): C, 85.67; H, 8.63. Found: C, 86.02; H, 8.84. **15b**: colorless oil; yield 70% (0.172 g); HRMS *m*/*z* calcd for $C_{20}H_{24}O$ (found) M^+ 246.198 869 (246.198 365). **15c**: white solid; yield 97% (0.212 g). Anal. Calcd for $C_{15}H_{22}O$ (218.34): C, 82.51; H, 10.15. Found: C, 81.73; H, 10.34.

(h) Synthesis of σ-Alkynyl Complexes [Ru(C≡CCPh$_2$-{CH$_2$C(OH)MeR^2})(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (R^2 = Ph (16a), ^{i}Pr (16b)). LiMe (1.5 M in diethyl ether; 1 mL, 1.5 mmol) was added at −20 °C to a solution of the corresponding σ-alkynyl complex [Ru{C≡CCPh$_2$(CH_2COR^2)}(η^5-C_9H_7)(PPh_3)$_2$] (R^2 = Ph (**3a**), ^{i}Pr (**3b**); 1 mmol) in 20 mL of THF. The mixture was stirred at −20 °C for 45 min, and MeOH (5 mL) was then added. The resulting solution was warmed to room temperature, and the solvent was then removed in vacuo. The resulting solid residue was extracted with hexane (ca. 80 mL) and filtered. Evaporation of the solvent gave complexes **16a**,**b** as orange solids. **16a**: yield 71% (0.757 g); IR (KBr, cm^{-1}) ν 2065 (C≡C), 3317 (O−H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 50.70 and 51.91 (d, $^2J_{PP}$ = 23.2 Hz) ppm; ^1H NMR (C_6D_6) δ 1.61 (s, 3H, CH_3), 3.10 and 3.17 (d, 1H each, J_{HH} = 13.7 Hz, CH_2), 3.22 (br, 1H, OH), 4.75 and 5.16 (br, 1H each, H-1 and H-3), 5.45 (br, 1H, H-2), 6.61−8.04 (m, 49H, Ph and H-4, H-5, H-6 and H-7) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 32.09 (s, CH_3), 50.04 (s, C_γ), 54.02 (s, CH_2), 71.71 and 73.02 (s, C-1 and C-3), 75.53 (s, C−OH), 96.48 (s, C-2), 104.29 (vt, $^2J_{CP} = {}^2J_{CP'}$ = 21.6 Hz, Ru−C_α), 110.48 and 110.80 (s, C-3a and C-7a), 116.18 (s, C_β), 124.62−152.20 (m, Ph, C-4, C-5, C-6 and C-7) ppm; $\Delta\delta$(C-3a,7a) = −20.06. Anal. Calcd for $RuC_{69}H_{58}P_2O$ (1066.23): C, 77.72; H, 5.48. Found: C, 78.10; H, 5.31. **16b**: yield 63% (0.650 g); IR (KBr, cm^{-1}) ν 2062 (C≡C), 3332 (O−H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 50.30 and 52.10 (d, $^2J_{PP}$ = 33.4 Hz) ppm; ^1H NMR (C_6D_6) δ 1.08 (d, 3H, J_{HH} = 8.2 Hz, CH(CH_3)$_2$), 1.11 (s, 3H, CH_3), 1.23 (d, 3H, J_{HH} = 6.7 Hz, CH(CH_3)$_2$), 1.95 (m, 1H, C*H*(CH_3)$_2$), 2.86 (br, 2H, CH_2), 3.52 (br, 1H, OH), 4.50 and 5.25 (br, 1H each, H-1 and H-3), 5.40 (br, 1H, H-2), 6.42−7.83 (m, 44H, Ph and H-4, H-5, H-6 and H-7) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 18.25 and 18.91 (s, CH(CH_3)$_2$), 25.49 (s, C(CH_3)OH), 42.10 (s, *C*H(CH_3)$_2$), 47.92 (s, C_γ), 49.42 (s, CH_2), 71.97 and 74.14 (s, C-1 and C-3), 75.91 (s, C−OH), 97.09 (s, C-2), 105.45 (vt, $^2J_{CP} = {}^2J_{CP'}$ = 23.4 Hz, Ru−C_α), 111.30 (s, C-3a and C-7a), 115.98 (s, C_β), 125.91−152.71 (m, Ph, C-4, C-5, C-6 and C-7) ppm; $\Delta\delta$(C-3a,7a) = −20.40. Anal. Calcd for $RuC_{66}H_{60}P_2O$ (1032.22): C, 76.79; H, 5.85. Found: C, 77.01; H, 5.90.

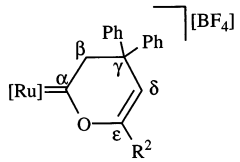
(i) Synthesis of Alkenyl Complexes [Ru{C=CHCPh$_2$-CH=C(R^2)O}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (R^2 = Ph (18a), ^{i}Pr (18b)). A solution of the corresponding σ-alkynyl complex [Ru{C≡CCPh$_2$(CH_2COR^2)}(η^5-C_9H_7)(PPh_3)$_2$] (R^2 = Ph (**3a**), ^{i}Pr (**3b**); 1 mmol) in 20 mL of dichloromethane was treated with $AlCl_3$ (0.007 g, 0.05 mmol) at room temperature for 2 h. The solution was then evaporated to dryness and the resulting solid residue extracted with diethyl ether (ca. 100 mL) and filtered over Al_2O_3 (neutral; activity grade I). Evaporation of the solvent gave complexes **18a**,**b** as yellow solids. The labeling scheme is



18a: yield 95% (0.997 g); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 49.44 (s) ppm; ^1H NMR (C_6D_6) δ 4.96 (br, 2H, H-1,3), 5.25 and 5.57 (d, 1H each, J_{HH} = 2.4 Hz, =CH), 5.84 (m, 2H, H-4,7 or H-5,6), 5.93 (br, 1H, H-2), 6.69−7.48 (m, 47H, Ph and H-4,7 or H-5,6) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 49.21 (s, C_γ), 74.25 (s, C-1,3), 100.94 (s, C-2), 106.39 and 117.64 (s, C_β and C_δ), 113.34 (s, C-3a,7a), 123.47 and 125.57 (s, C-4,7 and C-5,6), 127.74−152.74 (m, Ph), 151.42 (s, C_ϵ), 163.86 (t, $^2J_{CP}$ = 16.2 Hz, Ru−C_α) ppm; $\Delta\delta$(C-3a,7a) = −17.36. Anal. Calcd for $RuC_{68}H_{54}P_2O$ (1050.19): C, 77.77; H, 5.18. Found: C, 77.53; H, 5.07. **18b**: yield 87% (0.884 g); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 50.10 (s) ppm; ^1H NMR (C_6D_6) δ 0.64 (d, 6H, J_{HH} = 6.8 Hz, CH_3), 1.64 (sept, 1H, J_{HH} = 6.8 Hz, CH), 4.74 and 5.45 (d, 1H each, J_{HH} = 2.3 Hz, =CH), 4.89 (br, 2H, H-1,3), 5.73 and 6.76 (m, 2H each, H-4,7 and H-5,6), 5.86

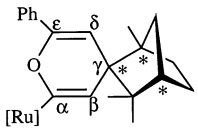
(br, 1H, H-2), 6.99−7.50 (m, 40H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 20.96 (s, CH_3), 30.76 (s, CH), 48.33 (s, C_γ), 74.38 (s, C-1,3), 99.50 and 116.84 (s, C_β and C_δ), 101.89 (s, C-2), 112.81 (s, C-3a,7a), 122.98 and 125.18 (s, C-4,7 and C-5,6), 127.45−153.17 (m, Ph), 157.67 (s, C_ϵ), 162.65 (t, $^2J_{CP}$ = 17.0 Hz, Ru−C_α) ppm; $\Delta\delta$(C-3a,7a) = −17.89. Anal. Calcd for $RuC_{65}H_{56}P_2O$ (1016.17): C, 76.83; H, 5.55. Found: C, 77.01; H, 5.48.

(j) Synthesis of Carbene Complexes [Ru{C=CCH$_2$CH=C(R^2)O}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] [BF$_4$] (R^2 = Ph (19a), ^{i}Pr (19b)). To a solution of the corresponding alkenyl complex **18a**,**b** (1 mmol) in 30 mL of THF was added dropwise, at −20 °C, an excess of a diluted solution of HBF_4·Et_2O in diethyl ether (3 mmol). The resulting solution was stirred at room temperature for 30 min and then concentrated to ca. 5 mL. Addition of diethyl ether (ca. 100 mL) precipitated complexes **19a**,**b** as brown solids, which were washed with diethyl ether (3 × 20 mL) and vacuum-dried. The labeling scheme is



19a: yield 83% (0.944 g); IR (KBr, cm^{-1}) ν 1057 (BF_4^-); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 41.63 (s) ppm; ^1H NMR (CD_2Cl_2) δ 3.79 (br, 2H, CH_2), 5.05 (d, 2H, J_{HH} = 1.7 Hz, H-1,3), 5.30 (t, 1H, J_{HH} = 1.7 Hz, H-2), 5.61 (br, 1H, =CH), 6.45−7.52 (m, 49H, Ph, H-4,7 and H-5,6) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 44.71 (s, C_γ), 68.39 (s, C_β), 77.88 (s, C-1,3), 96.35 (s, C-2), 115.39 (s, C_δ), 117.88 (s, C-3a,7a), 123.67 (s, C-4,7 or C-5,6), 127.36−144.94 (m, Ph and C-4,7 or C-5,6), 153.48 (s, C_ϵ), 303.11 (t, $^2J_{CP}$ = 11.8 Hz, Ru=C_α) ppm; $\Delta\delta$(C-3a,7a) = −12.82. Anal. Calcd for $RuC_{68}H_{55}F_4P_2BO$ (1138.00): C, 71.77; H, 4.87. Found: C, 72.15; H, 4.91. **19b**: yield 89% (0.982 g); IR (KBr, cm^{-1}) ν = 1060 (BF_4^-); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 43.43 (s) ppm; ^1H NMR (CD_2Cl_2) δ 0.72 (d, 6H, J_{HH} = 6.8 Hz, CH_3), 1.89 (sept, 1H, J_{HH} = 6.8 Hz, CH), 3.53 (br, 2H, CH_2), 4.10 (br, 1H, =CH), 5.06 (d, 2H, J_{HH} = 2.3 Hz, H-1,3), 5.24 (t, 1H, J_{HH} = 2.3 Hz, H-2), 6.72−7.47 (m, 44H, Ph, H-4,7 and H-5,6) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 21.22 (s, CH_3), 30.03 (s, CH), 43.60 (s, C_γ), 67.62 (s, C_β), 79.39 (s, C-1,3), 96.86 (s, C-2), 109.14 (s, C_δ), 117.06 (s, C-3a,7a), 123.51 (s, C-4,7 or C-5,6), 127.40−145.36 (m, Ph and C-4,7 or C-5,6), 160.68 (s, C_ϵ), 301.48 (t, $^2J_{CP}$ = 14.3 Hz, Ru=C_α) ppm; $\Delta\delta$(C-3a,7a) = −13.64. Anal. Calcd for $RuC_{65}H_{57}F_4P_2BO$ (1103.98): C, 70.72; H, 5.20. Found: C, 71.01; H, 5.12.

(k) Synthesis of the Alkenyl Complex [Ru{C=CHC(C$_9$H$_{16}$)CH=CPhO}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (20). This complex was obtained as a yellow solid as described for **18a**,**b**, starting from the σ-alkynyl complex [Ru{C≡CC(C_9H_{16})(CH_2COPh)}(η^5-C_9H_7)(PPh_3)$_2$] (**13a**) (1.02 g, 1 mmol). The labeling scheme is

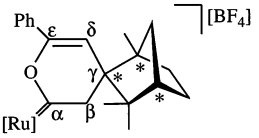


Yield: 78% (0.796 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 47.03 and 49.85 (d, $^2J_{PP}$ = 30.5 Hz) ppm. ^1H NMR (C_6D_6): δ 1.10, 1.18, and 1.28 (s, 3H each, CH_3), 1.24 and 1.83 (m, 2H each, CH_2), 1.57 and 1.96 (m, 1H each, CH_2), 2.19 (m, 1H, CH), 4.90 and 5.48 (d, 1H each, J_{HH} = 2.3 Hz, =CH), 5.12 and 5.18 (br, 1H each, H-1 and H-3), 5.55 (m, 2H, H-4, H-5, H-6 or H-7), 6.13 (br, 1H, H-2), 6.26−6.86 (m, 37H, Ph and H-4, H-5, H-6 or H-7) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.30, 25.60, and 28.69 (s, CH_3), 26.81, 29.39, and 40.63 (s, CH_2), 46.53, 48.80, and 53.95 (s, C and C_γ), 49.47 (s, CH), 74.40 and 74.58 (d, $^2J_{CP}$ = 9.8 Hz, C-1 and C-3), 103.00 (s, C-2), 105.70 and 110.39 (s, C_β and C_δ), 113.31 and 115.65 (s, C-3a and C-7a), 122.34, 123.60, 124.50, and 125.33 (s, C-4, C-5, C-6 and C-7), 126.99−138.70 (m, Ph), 151.29 (s, C_ϵ), 162.79 (vt, $^2J_{CP}$ = 17.0 Hz, Ru−C_α) ppm; $\Delta\delta$(C-3a,7a) = −16.22. Anal. Calcd for $RuC_{65}H_{60}P_2O$ (1020.22): C, 76.52; H, 5.94. Found: C, 76.93; H, 5.72.

Table 13. Crystal Data and Structure Refinement for 13b

empirical formula	$RuC_{62}H_{62}P_2O$·$2CH_2Cl_2$
fw	1155.98
temp	293(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1$
unit cell dimens	
a	15.12(3) Å
b	11.763(10) Å
c	18.574(14) Å
α	90°
β	112.85(9)°
γ	90°
V	3045(6) Å^3
Z	2
density (calcd)	1.261 g cm^{-3}
abs coeff	0.524 mm^{-1}
F(000)	1200
cryst size	0.20 × 0.13 × 0.04 mm^3
θ range for data collecn	1.19−25.99°
index ranges	$-18 \le h \le 18$, $-14 \le k \le 14$, $-22 \le l \le 22$
no. of rflns collected	13 029
no. of indep rflns	11 946 (R(int) = 0.2370)
completeness to θ = 25.99°	99.8%
abs cor	empirical
max and min transmissn	0.978 and 0.900
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	11 946/1/595
goodness of fit on F^2	0.905
final R indices ($I > 2\sigma(I)$)	R1 = 0.1073, wR2 = 0.2366
R indices (all data)	R1 = 0.4440, wR2 = 0.3977
absolute structure param	0.1(1)
largest diff peak and hole	0.669 and −0.829 e Å^{-3}

(l) Synthesis of the Carbene Complex [Ru=CCH$_2$C(C$_9$H$_{16}$)CH=CPhO(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (21). This complex was obtained as a brown solid as described for **19a**,**b**, starting from alkenyl complex **20** (1.02 g, 1 mmol). The labeling scheme is



Yield: 83% (0.920 g). IR (KBr, cm^{-1}): ν 1058 (BF_4^-). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.58 and 44.23 (br) ppm. ^1H NMR ($CDCl_3$): δ 0.68, 0.94, and 1.02 (s, 3H each, CH_3), 1.19 (m, 2H, CH_2), 1.46−1.69 (m, 4H, CH_2), 2.32 (m, 1H, CH), 3.78 and 4.02 (br, 1H each, =CCH_2), 5.00 (br, 1H, =CH), 5.20 and 5.94 (m, 1H each, H-4, H-5, H-6 or H-7), 5.31 (br, 1H, H-2), 5.48 (br, 2H, H-1 and H-3), 6.26−7.48 (m, 37H, Ph and H-4, H-5, H-6 or H-7) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.88, 24.87, and 28.11 (s, CH_3), 25.99, 29.19, and 40.91 (s, CH_2), 44.07, 46.01, and 52.17 (s, C and C_γ), 48.73 (s, CH), 59.81 (s, C_β), 75.89 (br, C-1 and C-3), 95.92 (s, C-2), 113.37 (s, C_δ), 121.51 (s, C-3a and C-7a), 124.35, 125.28, and 127.42 (s, C-4, C-5, C-6 or C-7), 128.25−133.36 (m, Ph and C-4, C-5, C-6 or C-7), 151.13 (s, C_ϵ), 302.45 (vt, $^2J_{CP}$ = 12.5 Hz, Ru=C_α) ppm; $\Delta\delta$(C-3a,7a) = −9.19. Complex **21** was too sensitive to moisture and oxygen to give satisfactory elemental analyses.

X-ray Diffraction. Data collection, crystal, and refinement parameters are collected in Table 13. The unit-cell parameters

were obtained from the least-squares fit of 25 reflections with θ between 5 and 8°. The intensity data were measured using the $\omega-2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The final drift correction factors were between 0.90 and 0.98. On all reflections, profile analysis was performed.[21,22] Lorentz and polarization corrections were applied, and the data were reduced to F_o^2 values. The structure was solved by Patterson methods and phase expansion using the program DIRDIF[23] and refined by least squares using SHELXL97.[24] The hydrogen atoms were geometrically placed. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of most of the non-H atoms were refined, except for the highly disordered carbon atoms (C6, C7, C8, C40 and C47) and the molecules of CH_2Cl_2, which were isotropically refined. The hydrogen atoms were isotropically refined riding with a common thermal parameter to CH_2Cl_2 hydrogen atoms an other to the rest. The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.1353P)^2 + (0.0000P)]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma(F_o^2)^2$ from counting statistics. The maximum shift-to-esd ratio in the last full-matrix least-squares cycle was 0.041. The final difference Fourier map showed no peaks higher than 0.67 e Å^{-3} or deeper than −0.83 e Å^{-3}. The absolute configuration was determined with a Flack parameter of 0.1(1).[25] Atomic scattering factors were taken from ref 26. Geometrical calculations were made with PARST.[27] The figure showing the coordination and the atomic numbering scheme was drawn by PLATON.[28] All calculations were performed at the University of Oviedo on the Scientific Computer Center and X-ray group DEC-ALPHA computers.

Acknowledgment. This work was supported by the Dirección General de Investigación Científica y Técnica (DGICYT, Project PB96-0558) and the EU (Human Capital Mobility program, Project ERBCHRXCT 940501). S.C. thanks the Ministerio de Educación y Cultura (MEC) for the award of a Ph.D. grant.

Supporting Information Available: Crystal structure data for **13b**, including tables of atomic parameters, anisotropic thermal parameters, and bond distances and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010252O

(21) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.
(22) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.
(23) 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; Technical Report of the Crystallographic Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.
(24) Sheldrick, G. M. SHELX97: Programs for Crystal Structure Analysis; Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
(25) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.
(26) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.
(27) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.
(28) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; University of Utrecht, Utrecht, The Netherlands, 2001.