In Search of Optically Active γ-Keto Acetylenes via Regioselective Coupling of Allenylidene Groups and Cyclic Enolates

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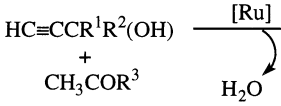
(Indenyl)ruthenium(II) allenylidene complexes [Ru{=C=C=C(R)Ph}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R = Ph (**1**), H (**2**)) regioselectively react with enolates derived from cyclopentanone and cyclohexanone at the C_γ atom to yield the σ-alkynyl derivatives [Ru{C≡CC(R)Ph(CHCOCH$_2$-(CH$_2$)$_n$CH$_2$)}(η^5-C_9H_7)(PPh_3)$_2$] (R = Ph, *n* = 1 (**3a**), 2 (**3b**); R = H, *n* = 1 (**4a**), 2 (**4b**)). Protonation of these species at C_β of the alkynyl chain with HBF_4 affords vinylidene complexes **5a**,**b** and **6a**,**b**, which can easily be demetalated with acetonitrile to yield the γ-keto acetylenes HC≡CC(R)Ph(CHCOCH$_2$(CH$_2$)$_n$CH$_2$) (**7a**,**b** and **8a**,**b**). Compounds **4a**,**b**, **6a**,**b** and **8a**,**b**, derived from the monosubstituted allenylidene complex **2**, have been obtained as nonseparable mixtures of two diastereoisomers. The optically active allenylidene [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**10**) (C_9H_{16}) = (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene) undergoes a selective exo addition of the cyclopentanone enolate to afford the σ-alkynyl diastereoisomers [Ru{C≡CC(C_9H_{16})(CHCOCH$_2$CH$_2$CH$_2$)}(η^5-C_9H_7)(PPh_3)$_2$] (**11a**,**b**). Demetalation of **11a** and **11b**, via their corresponding vinylidenes, allows the preparation of optically pure terminal alkynes HC≡CC(C_9H_{16})(CHCOCH$_2$CH$_2$CH$_2$) (**13a**,**b**, respectively). The oxacycloalkenyl derivative [Ru{C=C(H)C(C_9H_{16})C=C(CH$_2$CH$_2$CH$_2$)O}(η^5-C_9H_7)(PPh_3)$_2$] (**14**) has been obtained by treatment of **11a** or **11b** with a catalytic amount of $AlCl_3$. Protonation of **14** affords the corresponding cyclic carbene **15**. The reactivity of allenylidene complexes **1**, **2**, and **10** toward lithium enolates derived from the optically active ketones (*R*)-(−)-carvone and (*R*)-(+)-pulegone has been also explored. For diphenylallenylidene **1** diastereoselective additions are observed, yielding the optically pure σ-alkynyl complexes **16** and **19**, respectively. While attempts to demetalate **19** failed, demetalation of **16** yields the optically pure γ-keto alkyne HC≡CCPh$_2$($C_{10}H_{13}O$) (**18**) in excellent yield. The crystal structures of compounds **11b** and **14** have been determined by X-ray diffraction.

Introduction

In the context of our studies on the chemistry of allenylidene ruthenium(II) complexes, we have recently reported an efficient synthetic approach of γ-keto acetylenes based on the regio- and diastereoselective propargylic alkylation of 2-propyn-1-ols with methyl ketones mediated by the (indenyl)ruthenium(II) moiety [Ru(η^5-C_9H_7)(PPh_3)$_2$]$^+$ (see eq 1).[1]



(1)

The following processes are involved in this synthetic route (see Scheme 1): (i) initial formation of allenylidene complexes **A** as the result of the metal-mediated dehydration of propargylic alcohols HC≡CCR^{1}R^2(OH),[2,3] (ii)

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(1) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño. E.; García-Granda, S. *Organometallics* **2001**, *20*, 3175.

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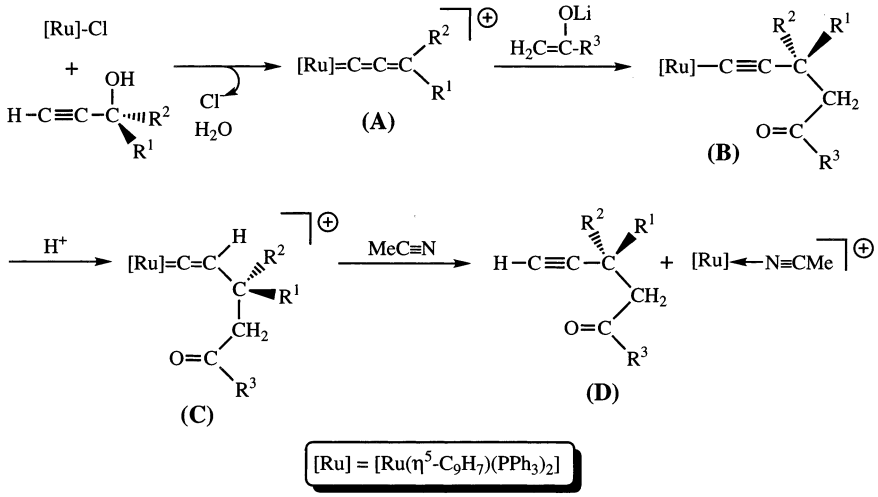
Scheme 1



regioselective nucleophilic addition of lithium enolates at the electrophilic C_γ atom of these metallacumulenes to give neutral keto alkynyl derivatives **B**,[4] (iii) selective C_β protonation of the σ-alkynyl complexes to afford the corresponding vinylidenes **C**,[5] and finally (iv) a vinylidene−π-terminal alkyne tautomerization in refluxing acetonitrile to generate transient π-alkyne complexes which readily exchange the coordinated alkyne by acetonitrile, leading to the free γ-keto acetylenes **D**. The metal fragment is quantitatively recovered as the acetonitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$.

This synthetic methodology constitutes an alternative to the well-known Nicholas coupling of 2-propyn-1-ol derivatives with ketones containing α-hydrogens via $[Co_2(CO)_6]$-stabilized propargylium cations.[6] Interestingly, Hidai and co-workers have recently reported a related ruthenium-catalyzed propargylic alkylation of monosubstituted propargylic alcohols with ketones to afford γ-keto acetylenes.[7] Remarkably, although the detailed reaction mechanism of this catalytic process is still unknown, the nucleophilic attack of an enolate carbon on the electrophilic C_γ atom in allenylidene intermediates has been proposed as the key step of the catalytic cycle.

To extend the scope of our synthetic approach, in this paper we report the efficient synthesis of novel optically active terminal alkynes which are prepared via regioselective reactions of the allenylidene derivatives $[Ru\{{=}C{=}C{=}C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = Ph, H)[3a] and $[Ru\{{=}C{=}C{=}C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($C(C_9H_{16})$ = (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)[1] with enolates derived from prochiral (i.e. cyclopentanone and cyclohexanone) and chiral (i.e. (*R*)-(−)-carvone and (*R*)-(+)-pulegone) cyclic ketones. The presence of prochiral or stereogenic centers in the allenylidene precursors permits the elucidation of the stereoselectivity of these nucleophilic additions. Part of this work has been communicated in a preliminary report.[3d]

Results

Reactions of Allenylidene Complexes with Enolates Derived from Prochiral Cyclic Ketones. Lithium enolates of cyclopentanone and cyclohexanone (prepared in situ from the corresponding ketone and LDA in THF at −20 °C) add regioselectively at the C_γ atom of the cumulenic chain in complexes $[Ru\{{=}C{=}C{=}C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = Ph (**1**), H (**2**)),[3a] to afford the neutral σ-alkynyl derivatives $[Ru\{C{\equiv}CC(R)\text{-}Ph(\overline{CHCOCH_2(CH_2)_nCH_2})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**3a**,**b** and **4a**,**b**) isolated as air-stable yellow solids in 63−89% yield after chromatographic workup (Scheme 2).

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

(3) For papers dealing with the synthesis and reactivity of (indenyl)ruthenium(II) allenylidenes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ see: (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) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; Ienco, A. *Organometallics* **1998**, *17*, 5216. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3235. (g) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **2000**, 451. (h) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Rodríguez, M. A. *Organometallics* **2002**, *21*, 203.

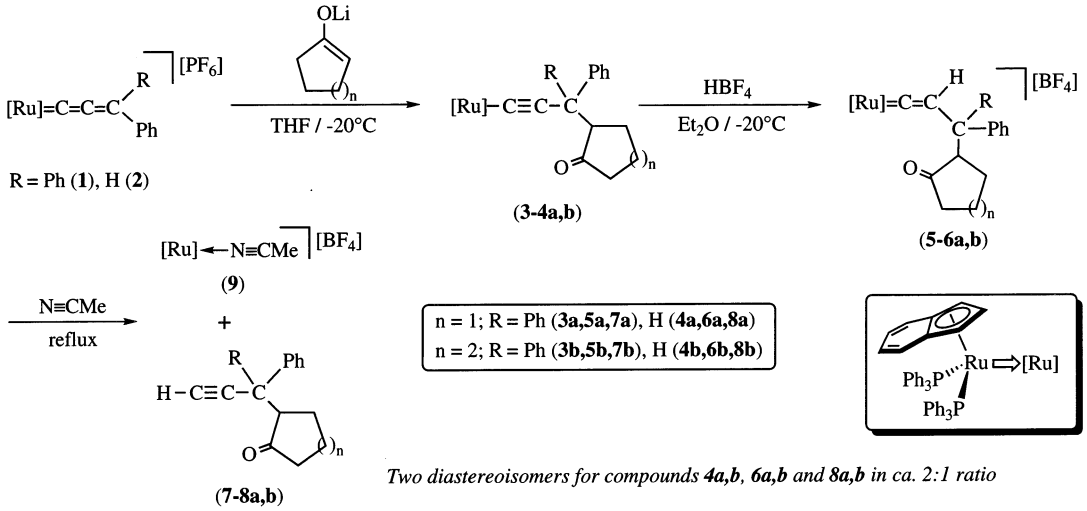
(4) Other regioselective nucleophilic additions of enolates derived from methyl ketones at C_γ in allenylidene complexes, i.e. $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)]^+$, $[Os(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$, $[Re(=C=C=CPh_2)(CO)_2\{MeC(CH_2PPh_2)_3\}]^+$, and $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5Me_5)(^iPr_2PCH_2CH_2P^iPr_2)]^+$, have been reported: (a) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826. (b) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585. (c) Mantovani, N.; Marvelli, L.; Rossi, R.; Bianchini, C.; de los Rios, I.; Romerosa, A.; Peruzzini, M. *J. Chem. Soc., Dalton Trans.* **2001**, 2353. (d) Bustelo, E.; Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903.

(5) For reviews on the synthesis and reactivity vinylidene complexes see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (d) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977.

(6) For reviews on the Nicholas reaction see: (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (b) Melikyan, G. G.; Nicholas, K. M. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995. (c) Caffyn, A. J. M.; Nicholas, K. M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, Chapter 7.1. (d) Müller, T. J. J. *Eur. J. Org. Chem.* **2001**, 2021.

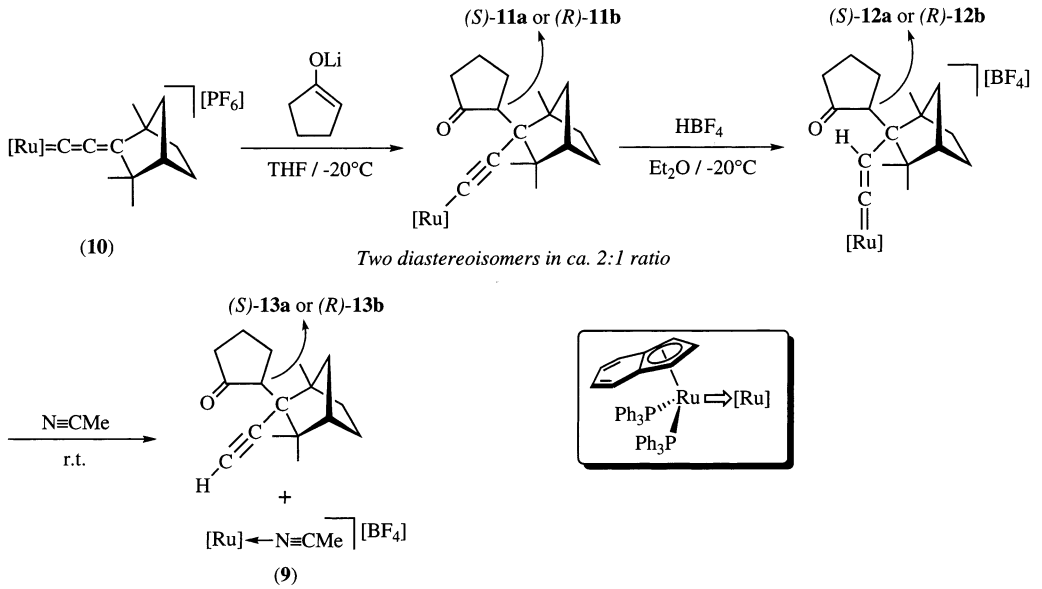
(7) (a) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393. Related ruthenium-catalyzed propargylic substitutions with heteroatom-centered nucleophiles have been also reported: (b) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019.

Scheme 2



*Two diastereoisomers for compounds **4a,b**, **6a,b** and **8a,b** in ca. 2:1 ratio*

Scheme 3



Spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) of **3a**,**b** and **4a**,**b** support the proposed formulations (see the Experimental Section and Tables S1 and S2, provided as Supporting Information). In particular, (i) the IR spectra show the expected ν(C=O) and ν(C≡C) absorption bands in the ranges 1708−1736 and 2072−2093 cm^{-1}, respectively, and (ii) the ^{13}C{^{1}H} NMR spectra display typical Ru−C$_\alpha$≡C$_\beta$ signals at δ 92.47−95.59 (dd, $^2J_{CP}$ = 22.2−26.2 Hz, C$_\alpha$) and 108.60−114.05 (s, C$_\beta$). Complexes **4a**,**b** have been isolated as a nonseparable mixture of two diastereoisomers (ca. 2:1 ratio), as inferred by NMR spectroscopy.

As expected on the basis of our previous results,[1] demetalation of **3a**,**b** and **4a**,**b** proceeds cleanly, yielding the terminal alkynes HC≡CC(R)Ph(CHCOCH$_2$(CH$_2$)$_n$CH$_2$) (**7a**,**b** and **8a**,**b**) in good overall yields (Scheme 2). Thus, in the first step the air-stable vinylidene derivatives [Ru{=C=C(H)CPh$_2$(CHCOCH$_2$(CH$_2$)$_n$CH$_2$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**5a**,**b**) were prepared by treatment of **3a**,**b** with HBF$_4$ (96 and 97% yields, respectively). Similarly, vinylidene complexes **6a**,**b** have been prepared (92 and 88% yields, respectively) and isolated as nonseparable mixtures of two diastereoisomers (ca. 2:1 ratio). Complexes **5a**,**b** and **6a**,**b** have been fully characterized by means of standard spectroscopic techniques and elemental analysis (see the Experimental Section and Tables S3 and S4, provided as Supporting Information). In a second step acetonitrile solutions of vinylidenes **5a**,**b** and **6a**,**b** were heated under reflux, resulting in the liberation of the γ-keto acetylenes **7a**,**b** and **8a**,**b** (as a mixture of two diastereoisomers in ca. 2:1 ratio) (78−83% isolated yields), and formation of the solvato complex [Ru(N≡CMe)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (**9**).[8] Relevant spectroscopic features of **7a**,**b** and **8a**,**b** are (i) (^{1}H NMR) the singlet (**7a**,**b**) or doublet (**8a**,**b**; J_{HH} = 2.6−3.3 Hz) signal for the acetylenic proton (δ 2.22−2.70; see Table S5 provided as Supporting Information) and (ii) (^{13}C{^{1}H} NMR) characteristic singlet resonances for the HC≡C carbons, which appear in the ranges 70.31−75.22 and 83.16−85.66 ppm, respectively (see Table S6, provided as Supporting Information).

(8) Terminal alkynes **8a**,**b** have been previously reported; see ref 7a and: Saha, M.; Nicholas, K. M. *Isr. J. Chem.* **1984**, *24*, 105.

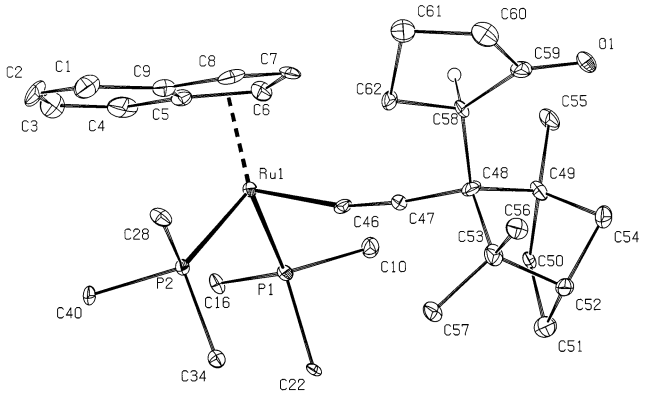


Figure 1. ORTEP view of the structure of the σ-alkynyl complex [Ru{C≡CC(C_9H_{16})(CHCOCH_2CH_2CH_2)}(η^5-C_9H_7)(PPh_3)$_2$] (**11b**). Aryl groups of the triphenylphosphine ligands have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru−C* = 1.948(5); Ru−P(1) = 2.290(2); Ru−P(2) = 2.314(2); Ru−C(46) = 2.027(7); C(46)−C(47) = 1.223(9); C(47)−C(48) = 1.504(9); C(48)−C(49) = 1.62(1); C(48)−C(53) = 1.61(1); C(48)−C(58) = 1.573(9); C(59)−O(1) = 1.214(8); C*−Ru−P(1) = 124.69(19); C*−Ru−P(2) = 124.42(18); C*−Ru−C(46) = 115.2(3); P(1)−Ru−P(2) = 99.84(8); C(46)−Ru−P(1) = 93.9(2); C(46)−Ru−P(2) = 90.0-(2); Ru−C(46)−C(47) = 168.1(7); C(46)−C(47)−C(48) = 172(1). C* denotes the centroid of the indenyl ring (C(5), C(6), C(7), C(8), C(9)).

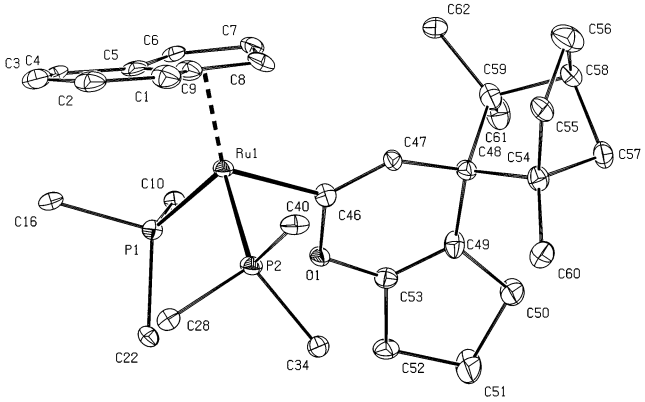


Figure 2. ORTEP view of the structure of the alkenyl complex [Ru{C=C(H)C(C_9H_{16})C=C(CH_2CH_2CH_2)O}(η^5-C_9H_7)(PPh_3)$_2$] (**14**). Aryl groups of the triphenylphosphine ligands have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru−C* = 1.976(7); Ru−P(1) = 2.306(2); Ru−P(2) = 2.314(2); Ru−C(46) = 2.063(6); C(46)−C(47) = 1.333(8); C(46)−O(1) = 1.428(8); C(53)−O(1) = 1.361(7); C(53)−C(49) = 1.335(8); C*−Ru−P(1) = 120.97(15); C*−Ru−P(2) = 124.33(14); C*−Ru−C(46) = 119.6(2); P(1)−Ru−P(2) = 103.72(8); C(46)−Ru−P(1) = 93.0(2); C(46)−Ru−P(2) = 86.5(2); Ru−C(46)−C(47) = 128.5(5); Ru−C(46)−O(1) = 113.8(4); C(46)−O(1)−C(53) = 116.0(5); O(1)−C(53)−C(49) = 128.3(6); C(52)−C(53)−C(49) = 128.3-(6). C* denotes the centroid of the indenyl ring (C(5), C(6), C(7), C(8), C(9)).

The reactivity of the optically active allenylidene complex [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C(C_9H_{16}) = (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene) (**10**)[1] toward lithium enolates derived from cyclopentanone and cyclohexanone has been also explored. While **10** remains unchanged upon addition of a large excess of the cyclohexanone enolate, it readily reacts with a slight excess (ca. 3:1) of the cyclopentanone enolate, affording the corresponding σ-alkynyl derivative **11** (Scheme 3).

Alkynyl complex **11** has been obtained as a mixture of two diastereoisomers (ca. 2:1 ratio) which are easily separated by column chromatography on neutral Al_2O_3 (**11a**, 48% yield; **11b**, 24% yield). Their analytical and spectroscopic data are fully consistent with the proposed formulation (see the Experimental Section). Since the configuration of the new chiral carbon atoms could not be elucidated from the NMR data, a single-crystal X-ray structural determination was carried out for the minor diastereoisomer **11b**. An ORTEP view of the molecular geometry is shown in Figure 1. Selected bond distances and angles are collected in the caption[9] and are in general comparable to those reported for the related σ-alkynyl derivative [Ru{C≡CC(C_9H_{16})(CH_2CO^{i}Pr)}(η^5-C_9H_7)(PPh_3)$_2$].[1] The structure shows that (i) the addition of the enolate fragment takes place on the less sterically demanding exo face of the allenylidene chain in [Ru{=C=C=C(C_9H_{16})}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**10**) and (ii) the absolute configuration for the new stereogenic carbon atom C(58) is *R*. As expected, demetalation of **11a** and **11b**, via vinylidene intermediates **12a** and **12b**, allowed the preparation of the optically pure γ-keto acetylenes **13a** and **13b** (98 and 92% yields, respectively; see Scheme 3).[10]

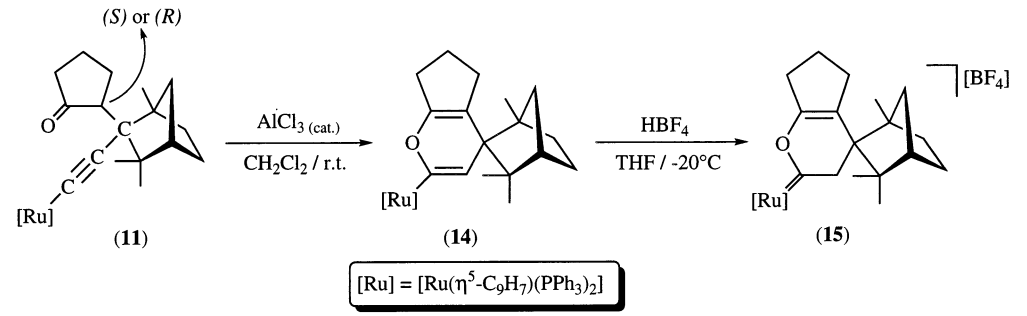
Assuming the preferred exo addition in **10**,[1] the major diastereoisomer **11a** should have an *S* configuration at C(58) (see Figure 1). In agreement with this, we have found that the treatment of **11a** and **11b** with a catalytic amount of $AlCl_3$, in dichloromethane at room temperature, yields in both cases the oxacycloalkenyl derivative **14**, as the result of the intramolecular cyclization of the keto alkynyl unit (94% yield, see Scheme 4).[11] Compound **14** exhibits analytical and spectroscopic data in accord with the proposed formulation (see the Experimental Section). Moreover, an unambiguous characterization by single-crystal X-ray analysis was undertaken (see Figure 2).[9] The molecule exhibits the usual pseudo-octahedral three-legged piano-stool geometry with the indenyl ligand in the usual η^5 coordination mode. The interligand angles P(1)−Ru−P(2), C(46)−Ru−P(1), and C(46)−Ru−P(2) and those between the centroid C* and the legs show values typical of a pseudooctahedron (see caption for Figure 2). The most interesting features of the structure are those concerning the alkenyl ligand.

(9) The crystals measured present two molecules in the asymmetric unit with very similar structural parameters. For brevity, only the bond distances and angles of one of them are listed in the caption.

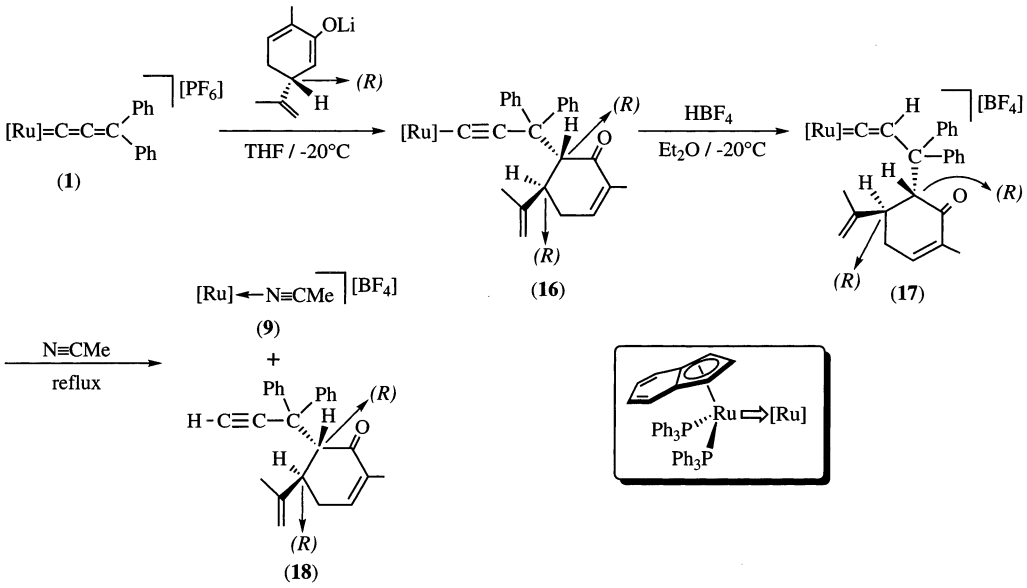
(10) The vinylidene complex **12b** has been characterized only by ^{31}P-{^1H} NMR spectroscopy (δ 36.07 and 38.16 (d, $^2J_{PP}$ = 21.6 Hz) ppm), since it is very unstable both in solution and in the solid state, generating complicated mixtures of uncharacterized products. Protonation of **11b** with 1 equiv of HBF_4·Et_2O in acetonitrile yields directly the terminal alkyne **13b** and the acetonitrile complex **9** (see the Experimental Section).

(11) (a) Lewis acid catalyzed intramolecular heterocyclization of alkynes is a well-known method for the synthesis of unsaturated heterocycles. See for example: Hardig, 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. (b) We have recently reported related cyclizations on the complexes [Ru{C≡CCR^{1}R^2(CH_2COR^3)}(η^5-C_9H_7)(PPh_3)$_2$] (R^1 = R^2 = Ph, R^3 = Ph, ^{i}Pr; CR^{1}R^2 = C(C_9H_{16}), R^3 = Ph).[1]

Scheme 4



Scheme 5



Thus, the Ru−C(46) bond length (2.063(6) Å) falls in the range 2.03−2.11 Å typical of a Ru−C(sp^2) single bond.[12] Similarly, the C(46)−O(1) (1.428(8) Å) and C(53)−O(1) (1.361(7) Å) distances compare well with those reported for other (oxacycloalkenyl)ruthenium(II) derivatives,[12f] and the C(46)−C(47) bond length (1.333(8) Å) shows also a coherent value for a C=C bond. The alkenyl function is located in an endo disposition with respect to the chiral auxiliary (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene, as was expected from the exo addition of the enolate group.

Treatment of **14** with HBF_4, in THF at −20 °C, leads to the novel optically active oxacycloalkylidene complex **15** in 84% yield (Scheme 4). Significantly, the $^{13}C\{^1H\}$ NMR spectrum gives clear evidence of the formation of a carbene moiety, displaying a typical low-field resonance for the Ru=C_α carbon atom at δ 299.49 (dd, $^2J_{CP}$ = 14.3 and 10.7 Hz). Electrophilic additions at C_β of alkenyl groups to give carbene species are well documented.[13,14]

Reactions of Allenylidene Complexes with Enolates Derived from Chiral Cyclic Ketones. The efficient access to terminal alkynes **7a**,**b**, **8a**,**b**, and **13a**,**b** from prochiral ketones (Schemes 2 and 3) prompted us to use the enolates derived from the commercially available chiral ketones (*R*)-(−)-carvone and (*R*)-(+)-pulegone in order to obtain the corresponding γ-keto alkynes bearing new stereogenic centers.

(a) Synthesis of the σ-Alkynyl Precursors. Treatment of (*R*)-5-isopropenyl-2-methyl-2-cyclohexenone ((*R*)-(−)-carvone) with LDA, in THF at −20 °C, and subsequent addition of 1 equiv of the complex [Ru(=C=C=CPh_2)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**) gives diastereoselectively, as determined by NMR spectroscopy, the σ-alkynyl derivative **16** (78% yield) (Scheme 5).

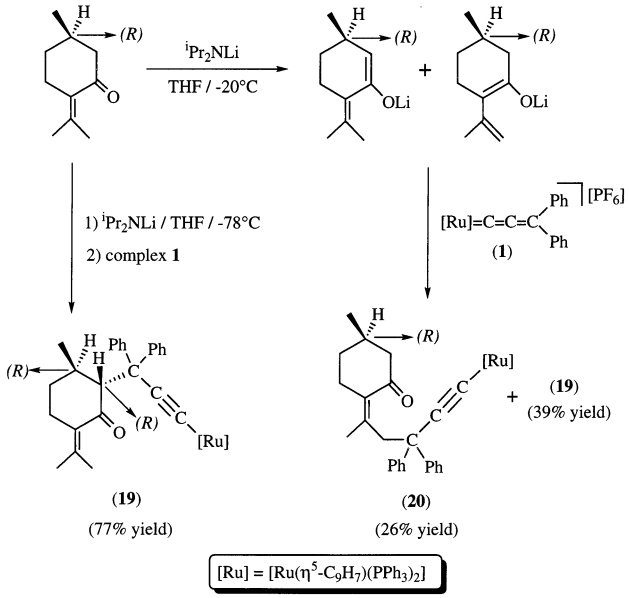
Similarly, complex **1** reacts with the enolate derived from (*R*)-2-isopropylidene-5-methylcyclohexanone (prepared in situ by treatment of (*R*)-(+)-pulegone with LDA in THF at −78 °C) to give the corresponding σ-alkynyl

(12) See for example: (a) Bruce, M. I.; Catlow, A.; Humphrey, M. G.; Koutsantonis, G. A.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *338*, 59. (b) Torres, M. R.; Santos, A.; Perales, A.; Ros, J. *J. Organomet. Chem.* **1988**, *353*, 321. (c) Romero, A.; Santos, A. Vegas, A. *Organometallics* **1988**, *7*, 1988. (d) López, J.; Santos, A.; Romero, A.; Echevarren, A. M. *J. Organomet. Chem.* **1993**, *443*, 221. (e) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685. (f) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 2297. (g) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567. (h) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606. (i) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **2001**, *20*, 5177.

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

(14) Transformations of (indenyl)ruthenium(II) alkenyl derivatives into carbene complexes are reported in: (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. (c) Bieger, K.; Díez, J.; Gamasa, M. P.; Gimeno, J.; Pavlista, M.; Rodríguez-Alvarez, Y.; García-Granda, S.; Santiago-García, R. *Eur. J. Inorg. Chem.* **2002**, 1647. See also ref 1.

Scheme 6

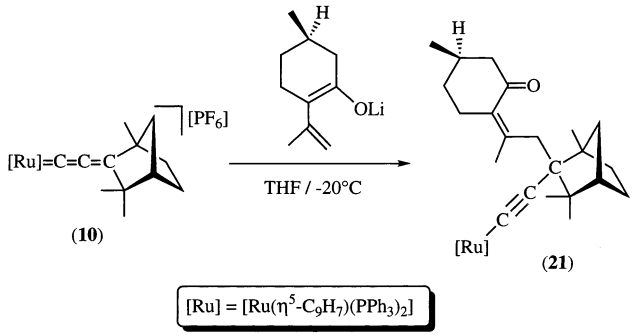


derivative **19** in a diastereoselective manner (77% yield; Scheme 6). When the in situ formation of the enolate takes place at −20 °C (instead of −78 °C) and the reaction with complex **1** is performed at this temperature, σ-alkynyl complexes **19** (39% yield) and **20** (26% yield) are obtained after chromatographic workup on neutral Al_2O_3 (Scheme 6). These complexes arise from the competitive deprotonation at $CH_2C{=}O$ vs CH_3 of (*R*)-(+)-pulegone. Compounds **16**, **19**, and **20** have been analytically and spectroscopically characterized (see the Experimental Section). The ^1H NMR spectra of **16** and **19** exhibit a doublet signal for the C*H*C=O proton at 4.30 (J_{HH} = 4.8 Hz) and 3.53 (J_{HH} = 4.4 Hz) ppm, respectively. On the basis of these data and the X-ray crystal structure of **16**, which shows an anti disposition of the two CH protons of the cyclohexenone ring (i.e. *R* configuration for C_δ),[3d] an *R* configuration is also assigned to the new stereogenic center in **19**. The $^{13}C\{^1H\}$ NMR spectrum of **20** is very informative, since it shows the presence of only two methyl groups (δ 22.63 and 24.06) and four CH_2 carbon resonances (δ 29.34, 33.99, 47.68, and 52.53) (assigned using DEPT experiments), in accord with the proposed formulation.

In contrast to complex **1**, the reaction of the chiral allenylidene complex [Ru{=C=C=C(C$_9$H$_{16}$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**10**) with the resulting (*R*)-(+)-pulegone enolates (prepared in situ at −20 °C) is chemoselective, affording the σ-alkynyl derivative **21** (51% yield; Scheme 7). On the basis of the stereochemistry found for the novel stereogenic carbon atom in the analogous σ-alkynyl complexes **11a** and **11b**, an exo addition is also proposed for the formation of complex **21**. Analytical and spectroscopic data for **21** confirm the proposed formulation (see the Experimental Section). Since these data can be compared to those observed for the analogous complex **20**, complex **21** will not be discussed further.

Although the allenylidene complex [Ru{=C=C=C(H)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**2**) also reacts with the enolates derived from (*R*)-(−)-carvone and (*R*)-(+)-pulegone, the reactions lead to complex mixtures of unidentified species, as inferred by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. All attempts to purify these mixtures by column chromatography or fractional crystallization failed. Moreover, no reaction has been observed between [Ru{=C=C=C(C$_9$H$_{16}$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**10**) and the lithium enolate derived from (*R*)-(−)-carvone.

Scheme 7



(b) Synthesis of the Terminal Alkynes. The terminal alkyne **18** has been obtained (83% yield) optically pure after protonation of **16** with HBF_4 and subsequent treatment of the resulting vinylidene derivative **17** with acetonitrile (Scheme 5). Analytical and spectroscopic data of **17** and **18** are in accord with the proposed formulations, being comparable with those observed for the related vinylidenes **5a**,**b** and **6a**,**b** and terminal alkynes **7a**,**b** and **8a**,**b** (see the Experimental Section). On the basis of the absolute configuration found for the σ-alkynyl precursor **16**,[3d] an *R* configuration is proposed for the corresponding new stereogenic centers in **17** and **18**. Unfortunatelly, all attempts to liberate the corresponding chiral γ-keto acetylene from σ-alkynyl complexes **19**−**21** failed, giving the starting materials, i.e. (*R*)-(+)-pulegone and allenylidene complexes **1** and **10**, respectively. This probably results from the selective protonation of the keto group in **19**−**21**.

Discussion

Stereoselectivity of the Nucleophilic Additions: Formation of Optically Active σ-Alkynyl Complexes. Previous studies from our laboratory have demonstrated the ability of (indenyl)ruthenium(II) allenylidene complexes [Ru(=C=C=CR^{1}R^2)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ to undergo regioselective nucleophilic additions, leading to the σ-alkynyl species [Ru{C≡CCR^{1}R^2(Nu)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$].[3] In accordance with this behavior the addition of methyl enolates leads to keto-functionalized σ-alkynyl derivatives [Ru{C≡CCR^{1}R^2(CH$_2$COR^3)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$].[1] As expected, the addition of the enolates derived from the prochiral cyclic ketones cyclopentanone and cyclohexanone to the allenylidenes **1** and **2** proceeds regioselectively to give σ-alkynyl complexes **3a**, **4a** and **3b**, **4b**, respectively (Scheme 2). Similarly, the chiral allenylidene complex **10** undergoes the regioselective addition of the enolate derived from cyclopentanone to give the σ-alkynyl complex **11**, although no reaction is observed with the cyclohexanone enolate (Scheme 3). This difference is probably produced by the effect of the steric hindrance between the chiral auxiliary (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene and the incoming bulkier enolate, which prevents the nucleophilic addition. Although the cyclopentanonic fragment adds stereoselectively through the exo face of

the chiral auxiliary, which is less hindered, the formation of **11** as a mixture of two diastereoisomers in a ca. 2:1 ratio shows that the overall diastereoselectivity of the nucleophilic addition is only moderate (33.3% de). This seems to indicate that the allenylidene substituent C_9H_{16} presents a poor chiral induction with respect to the incoming cyclic enolate. A similar chiral induction is also observed in the monosubstituted allenylidene **2**, since two *σ*-alkynyl diastereoisomers are also obtained for complexes **4a**,**b**. It is noteworthy that the *σ*-alkynyl complex **11** undergoes a Lewis acid promoted intramolecular cyclization of the keto alkynyl ligand to afford the optically active oxacycloalkenyl derivative **14** and the cyclic carbene **15** (Scheme 4).[1] The formation of these species clearly evidences the utility of transition-metal allenylidenes as building blocks for the preparation of complex molecules.[2]

To increase the stereoselectivity of the nucleophilic additions, a different approach was undertaken by using chiral enolates derived from (*R*)-(−)-carvone and (*R*)-(+)-pulegone. These nucleophiles react with the diphenylallenylidene **1** to give diastereoselectively the chiral *σ*-alkynyl complexes **16** and **19**, respectively (Schemes 5 and 6). The absolute configuration of the new stereogenic carbon atom (*R* as determined by X-ray diffraction analysis on **16**)[3d] seems to be the result of a sterically controlled addition, since the isopropenyl (**16**) and methyl (**19**) substituents of the cyclohexenone rings (C_ϵ) are located far away from the bulky CPh_2 moiety of the alkynyl chain. The influence of the steric hindrance between the incoming nucleophile and the allenylidene substituents is also clearly evidenced in the reaction of the chiral allenylidene **10** and the enolate derived from (*R*)-(+)-pulegone (Scheme 7). Despite the fact that at −20 °C the formation of the enolate is not chemoselective, giving rise to a mixture of two species (resulting from a competitive CH_2 vs CH_3 deprotonation), the addition occurs in a chemioselective manner, affording the isopropylidene-substituted isomer **21**. This is probably the result of the steric demands of the chiral auxiliary in the allenylidene chain, which prevents the addition of the other form of the enolate. The inertness of **10** toward the (*R*)-(−)-carvone enolate can be also explained on the basis of these steric demands.

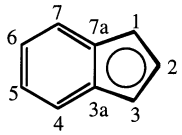
Demetalation Reactions: Synthesis of Optically Active Terminal Alkynes. We have recently reported an efficient synthetic approach to terminal functionalized alkynes starting from (allenylidene)ruthenium(II) complexes.[3e] Using the well-established sequence of reactions in this methodology (Scheme 1), novel *γ*-keto acetylenes have been prepared starting from the aforementioned *σ*-alkynyl derivatives **3a**,**b**, **4a**,**b**, **11a**,**b**, and **16**. These are transformed in a first step into the corresponding vinylidenes, which generate, by demetalation in refluxing acetonitrile, the desired terminal alkynes (Schemes 2, 3, and 5). Thus, optically active *γ*-keto alkynes **13a**,**b** and **18**, which represent a series of unusual examples containing up to four chiral centers, are obtained in good yields. Unfortunately, the competitive protonation of the keto alkynyl groups at the carbonyl function vs the formation of vinylidene complexes (protonation of **19**−**21**) constitutes a drawback which impedes the isolation of the desired optically active *γ*-keto acetylenes derived from (*R*)-(+)-pulegone.

In summary, novel *γ*-keto-functionalized terminal alkynes, some of them optically pure, have been prepared in good yields through regio- and stereoselective nucleophilic additions to appropriate allenylidene complexes. This efficient synthetic protocol follows previously reported examples which prove the utility of allenylidene complexes for the selective generation of C−C bonds.

Experimental Section

Synthetic procedures were performed under an atmosphere of dry nitrogen using vacuum line and other 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 $[Ru\{=C=C=C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = Ph (**1**), H (**2**))[3a] and $[Ru\{=C=C=C(C_9H_{16})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**10**)[1] were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. Conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Optical rotations (α) were measured on a Perkin-Elmer 343 polarimeter. High-resolution mass spectra were recorded using a MAT-95 spectrometer. FAB mass spectra were recorded using a VG-Autospec spectrometer operating in positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker DPX300 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 standard. DEPT experiments have been carried out for all the compounds reported in this paper. $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopic data for **3a**,**b** through **8a,b** are collected in Tables S1−S6, which have been provided as Supporting Information.

The numbering for the indenyl skeleton is as follows:



Synthesis of the *σ*-Alkynyl Complexes $[Ru\{C{\equiv}CC(R)Ph(CHCOCH_2(CH_2)_nCH_2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (*n* = 1, R = Ph (3a), H (4a); *n* = 2, R = Ph (3b), H (4b)). A solution of the corresponding lithium enolate (prepared in situ by treatment of the corresponding ketone (1 mmol) with LDA (0.179 g, 1 mmol) in 10 mL of THF at −20 °C for 30 min) was added at −20 °C to a solution of $[Ru\{=C=C=C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = 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 a silica gel chromatography column. Elution with a hexane/diethyl ether mixture (2/1) gave a yellow band from which *σ*-alkynyl complexes **3a**,**b** and **4a**,**b** were isolated as yellow solids after solvent removal. Complexes **4a**,**b** have been obtained as a nonseparable mixture of diastereoisomers in ca. 2:1 ratio. **3a**: yield 89% (0.902 g); IR (KBr, cm^{-1}) *ν* 1736 (C=O), 2072 (C≡C). Anal. Calcd for $RuC_{65}H_{54}P_2O$ (1014.16): C, 76.98; H, 5.36. Found: C, 77.12; H, 5.12. **3b**: yield 69% (0.709 g); IR (KBr, cm^{-1}) *ν* 1715 (C=O), 2077 (C≡C). Anal. Calcd for $RuC_{66}H_{56}P_2O$ (1028.18): C, 77.09; H, 5.49. Found: C, 77.21; H, 5.60. **4a**: yield 69% (0.647 g); IR (KBr, cm^{-1}) *ν* 1735 (C=O), 2090 (C≡C). Anal. Calcd for $RuC_{59}H_{50}P_2O$ (938.06): C, 75.54; H, 5.37. Found: C, 76.12; H, 5.20. **4b**: yield 63% (0.600 g); IR (KBr, cm^{-1}) *ν* 1708 (C=O), 2093 (C≡C). Anal. Calcd for $RuC_{60}H_{52}P_2O$ (952.08): C, 75.69; H, 5.50. Found: C, 75.80; H, 5.39.

Synthesis of the Vinylidene Complexes [Ru{=C=C(H)-C(R)Ph(CHCOCH$_2$(CH$_2$)$_n$CH$_2$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (*n* = 1, R = Ph (5a), H (6a); *n* = 2, R = Ph (5b), H (6b)). A dilute solution of HBF$_4$·Et$_2$O in diethyl ether was added dropwise at −20 °C to a stirred solution of the corresponding σ-alkynyl complex **3a**,**b** and **4a**,**b** (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. Complexes **6a**,**b** have been obtained as a nonseparable mixture of diastereoisomers in ca. 2:1 ratio. **5a**: yield 96% (1.058 g); IR (KBr, cm^{-1}) ν 1059 (BF$_4^-$), 1730 (C=O); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 107. Anal. Calcd for RuC$_{65}$H$_{55}$F$_4$P$_2$BO (1101.97): C, 70.84; H, 5.03. Found: C, 71.03; H, 4.98. **5b**: yield 97% (1.082 g); IR (KBr, cm^{-1}) ν 1057 (BF$_4^-$), 1702 (C=O); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 112. Anal. Calcd for RuC$_{66}$H$_{57}$F$_4$P$_2$BO (1115.99): C, 71.03; H, 5.14. Found: C, 71.40; H, 5.20. **6a**: yield 92% (0.944 g); IR (KBr, cm^{-1}) ν 1060 (BF$_4^-$), 1732 (C=O); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 109. Anal. Calcd for RuC$_{59}$H$_{51}$F$_4$P$_2$BO (1025.87): C, 69.07; H, 5.01. Found: C, 69.28; H, 5.17. **6b**: yield 88% (0.915 g); IR (KBr, cm^{-1}) ν 1059 (BF$_4^-$), 1701 (C=O); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 111. Anal. Calcd for RuC$_{60}$H$_{53}$F$_4$P$_2$BO (1039.89): C, 69.30; H, 5.13. Found: C, 69.68; H, 5.21.

Synthesis of the Terminal Alkynes HC≡CC(R)Ph-(CHCOCH$_2$(CH$_2$)$_n$CH$_2$) (*n* = 1, R = Ph (7a), H (8a); *n* = 2, R = Ph (7b), H (8b)). A solution of the corresponding vinylidene complex **5a**,**b** and **6a**,**b** (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≡CMe)(η^5-C$_9$H$_7$)(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 hexane/diethyl ether mixture (6/1) as eluent. Evaporation of the solvents gave terminal alkynes **7a**,**b** and **8a**,**b** as white solids. Compounds **8a**,**b** have been obtained as a nonseparable mixture of diastereoisomers in a ca. 2:1 ratio. **7a**: yield 79% (0.216 g). Anal. Calcd for C$_{20}$H$_{18}$O (274.36): C, 87.55; H, 6.61. Found: C, 87.28; H, 6.70. **7b**: yield 80% (0.230 g). Anal. Calcd for C$_{21}$H$_{20}$O (288.39): C, 87.46; H, 6.99. Found: C, 87.21; H, 6.83. **8a**: yield 83% (0.164 g). Anal. Calcd for C$_{14}$H$_{14}$O (198.26): C, 84.81; H, 7.11. Found: C, 84.74; H, 7.23. **8b**: yield 78% (0.165 g). Anal. Calcd for C$_{15}$H$_{16}$O (212.28): C, 84.87; H, 7.59. Found: C, 84.93; H, 7.42.

Synthesis of the σ-Alkynyl Complex [Ru{C≡CC(C$_9$H$_{16}$)-(CHCOCH$_2$CH$_2$CH$_2$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (11). Complex **11** was prepared as described for **3a**,**b** and **4a**,**b** starting from the allenylidene derivative [Ru{=C=C=C(C$_9$H$_{16}$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**10**) (1.046 g, 1 mmol) and cyclopentanone (0.265 mL, 3 mmol). It was obtained as a mixture of two diastereoisomers which were separated by column chromatography on Al$_2$O$_3$ (neutral; activity grade I) using a hexane/diethyl ether mixture (3/1) as eluent (orange bands). Major diastereoisomer (**11a**): yield 48% (0.472 g). IR (KBr, cm^{-1}) ν 2069 (C≡C), 1739 (C=O). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 52.28 and 54.41 (d, $^2J_{PP}$ = 34.5 Hz) ppm; ^{1}H NMR (C$_6$D$_6$) δ 1.16, 1.18, and 1.83 (s, 3H each, CH$_3$), 1.24 (m, 4H, CH$_2$), 1.53, 1.76, 1.88, and 2.18 (m, 2H each, CH$_2$), 2.50 (dd, 1H, J_{HH} = 13.8 Hz, $J_{HH'}$ = 7.2 Hz, CHC=O), 3.13 (m, 1H, CH), 4.63 and 5.17 (br, 1H each, H-1 and H-3), 5.85 (br, 1H, H-2), 6.00 (d, 1H, J_{HH} = 8.7 Hz, H-4, H-5, H-6, or H-7), 6.65−7.63 (m, 33H, Ph and H-4, H-5, H-6 or H-7) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 19.78, 29.27, and 30.08 (s, CH$_3$), 21.04, 25.75, 31.53, 36.62, 37.30, and 41.39 (s, CH$_2$), 46.35 and 54.38 (s, C), 51.53 (s, CH), 56.14 (s, C$_γ$), 62.77 (s, *C*HC=O), 74.18 (br, C-1 or C-3), 74.91 (d, $^2J_{CP}$ = 5.4 Hz, C-1 or C-3), 83.76 (dd, $^2J_{CP}$ = 22.4 Hz, $^2J_{CP}$ = 22.4 Hz, Ru−C$_α$), 96.56 (s, C-2), 109.94 and 111.41 (s, C-3a and C-7a), 115.60 (s, C$_β$), 123.09, 124.94, and 125.83 (s, C-4, C-5, C-6 or C-7), 127.15−140.18 (m, Ph and C-4, C-5, C-6 or C-7), 216.59 (s, C=O) ppm; Δδ(C-3a,7a) = −20.02. Anal. Calcd for RuC$_{62}$H$_{60}$P$_2$O (984.18): C, 75.66; H, 6.14. Found: C, 76.42; H, 6.02. Minor diastereoisomer (**11b**): yield 24% (0.236 g); IR (KBr, cm^{-1}) ν 2064 (C≡C), 1724 (C=O). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 52.74 and 53.72 (d, $^2J_{PP}$ = 34.9 Hz) ppm. ^{1}H NMR (C$_6$D$_6$) δ 0.97, 1.05, and 1.25 (s, 3H each, CH$_3$), 1.15, 1.45, 1.71, and 1.90 (m, 2H each, CH$_2$), 2.20 (m, 1H, CHC=O), 2.37 (m, 4H, CH$_2$), 2.97 (m, 1H, CH), 4.48 and 4.71 (br, 1H each, H-1 and H-3), 5.38 (br, 1H, H-2), 6.12 and 6.31 (d, 1H each, J_{HH} = 7.6 Hz, H-4, H-5, H-6, or H-7), 6.73−7.25 (m, 32H, Ph and H-4, H-5, H-6, or H-7) ppm; ^{13}C{^{1}H} (C$_6$D$_6$) δ 19.33, 28.33, and 28.91 (s, CH$_3$), 20.33, 24.51, 32.64, 37.51, 41.14, and 41.44 (s, CH$_2$), 46.69 and 53.50 (s, C), 50.49 (s, CH), 56.71 (s, *C*HC=O), 59.07 (s, C$_γ$), 73.14 (d, $^2J_{CP}$ = 4.5 Hz, C-1 or C-3), 73.51 (br, C-1 or C-3), 85.42 (dd, $^2J_{CP}$ = 22.3 Hz, $^2J_{CP}$ = 22.3 Hz, Ru−C$_α$), 95.28 (s, C-2), 109.37 and 110.55 (s, C-3a and C-7a), 116.17 (s, C$_β$), 122.89, 123.80, 125.07, and 125.63 (s, C-4, C-5, C-6 and C-7), 126.91−139.11 (m, Ph), 219.96 (s, C=O) ppm; Δδ(C-3a,7a) = −20.74. Anal. Calcd for RuC$_{62}$H$_{60}$P$_2$O (984.18): C, 75.66; H, 6.14. Found: C, 75.53; H, 6.27.

Synthesis of the Vinylidene Complex [Ru{=C=C(H)C-(C$_9$H$_{16}$)(CHCOCH$_2$CH$_2$CH$_2$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (12a). Complex **12a**, isolated as a brown solid, was obtained as described for **5a**,**b** and **6a**,**b** starting from the σ-alkynyl complex **11a** (0.984 g, 1 mmol): yield 92% (0.986 g); IR (KBr, cm^{-1}) ν 1720 (C=O), 1057 (BF$_4^-$); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 109; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 35.19 and 38.48 (d, $^2J_{PP}$ = 23.0 Hz) ppm; ^{1}H NMR (CDCl$_3$) δ 0.42, 0.82, and 1.31 (s, 3H each, CH$_3$), 1.13, 1.52, 1.71, 1.86, and 2.00 (m, 2H each, CH$_2$), 2.12 (m, 3H, CH$_2$ and CHC=O), 2.31 (m, 1H, CH), 5.22 (s, 1H, Ru=C=CH), 5.32 (d, 1H, J_{HH} = 8.3 Hz, H-4, H-5, H-6, or H-7), 5.57 (br, 2H, H-1 and H-3), 5.60 (d, 1H, J_{HH} = 9.1 Hz, H-4, H-5, H-6, or H-7), 6.10 (br, 1H, H-2), 6.82−7.50 (m, 32H, Ph and H-4, H-5, H-6, or H-7) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 20.81, 30.55, and 32.17 (s, CH$_3$), 22.27, 27.36, 33.34, 39.11, 40.20, and 42.84 (s, CH$_2$), 46.96 and 54.77 (s, C), 51.52 (s, CH), 61.10 (s, *C*HC=O), 65.31 (s, C$_γ$), 81.92 and 84.04 (d, $^2J_{CP}$ = 8.7 Hz, C-1 and C-3), 99.19 (d, $^2J_{CP}$ = 3.3 Hz, C-2), 111.43 (s, C$_β$), 114.81 (d, $^2J_{CP}$ = 3.3 Hz, C-3a or C-7a), 123.02 (s, C-3a or C-7a), 123.95 and 127.21 (s, C-4, C-5, C-6, or C-7), 130.28−135.84 (m, Ph and C-4, C-5, C-6, or C-7), 222.97 (s, C=O), 326.99 (dd, $^2J_{CP}$ = 19.1 Hz, $^2J_{CP}$ = 13.6 Hz, Ru=C$_α$) ppm; Δδ(C-3a,7a) = −11.78. Anal. Calcd for RuC$_{62}$H$_{61}$F$_4$P$_2$BO (1071.99): C, 69.47; H, 5.73. Found: C, 68.34; H, 5.86.

Synthesis of the Terminal Alkyne HC≡CC(C$_9$H$_{16}$)-(CHCOCH$_2$CH$_2$CH$_2$) (13a). Compound **13a**, isolated as a white solid, was prepared as described for **7a**,**b** and **8a**,**b** starting from the vinylidene **12a** (room temperature; 30 min): yield 98% (0.239 g); IR (KBr, cm^{-1}) ν 3298 (H−C≡), 2096 (C≡C), 1743 (C=O). ^{1}H NMR (CDCl$_3$) δ 0.84, 1.09, and 1.48 (s, 3H each, CH$_3$), 0.99, 1.13, 1.30, and 1.88 (m, 2H each, CH$_2$), 1.54−1.78 (m, 4H, CH$_2$), 2.18 (s, 1H, ≡CH), 2.36 (dd, 1H, J_{HH} = 13.2 Hz, J_{HH} = 7.5 Hz, CHC=O), 2.49 (m, 1H, CH) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$) δ 18.39, 28.47, and 28.63 (s, CH$_3$), 20.73, 24.72, 30.44, 35.48, 36.79, and 40.92 (s, CH$_2$), 45.20 (s, C), 50.80 (s, CH), 52.74 and 52.92 (s, C and C$_γ$), 60.41 (s, *C*HC=O), 72.94 (s, ≡CH), 88.47 (s, ≡C), 214.71 (s, C=O) ppm; $[\alpha]^{20}_D$ = −102.5° mL dm^{-1} g^{-1} (*c* = 0.04 M in ethanol). Anal. Calcd for C$_{17}$H$_{24}$O (244.38): C, 83.55; H, 9.89. Found: C, 83.71; H, 9.66.

Synthesis of the Terminal Alkyne HC≡CC(C$_9$H$_{16}$)-(CHCOCH$_2$CH$_2$CH$_2$) (13b). A solution of the σ-alkynyl complex **11b** (0.984 g, 1 mmol) in 30 mL of acetonitrile was treated at room temperature with a very dilute solution of HBF$_4$·Et$_2$O in diethyl ether (1 mmol). The reaction mixture was stirred at room temperature for 30 min and then evaporated to dryness. The yellow solid residue was transferred to a silica gel chromatography column. Elution with a hexane/diethyl

ether mixture (6/1) gave **13b** as a colorless oil: yield 92% (0.224 g); IR (KBr, cm^{-1}) ν 3314 (H−C≡), 2102 (C≡C), 1735 (C=O); ^1H NMR ($CDCl_3$) δ 0.95, 1.30, and 1.37 (s, 3H each, CH_3), 1.13, 1.40, 1.52, 1.78, and 1.99 (m, 2H each, CH_2), 2.01 (s, 1H, ≡CH), 2.25−2.50 (m, 3H, CH_2 and CHC=O), 2.61 (m, 1H, CH) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 19.68, 27.39, and 27.67 (s, CH_3), 20.32, 24.14, 31.39, 37.44, 40.24, and 41.66 (s, CH_2), 46.40 (s, C), 50.75 (s, CH), 52.98 and 54.97 (s, C and C_γ), 54.53 (s, *C*HC=O), 73.73 (s, ≡CH), 88.68 (s, ≡C), 215.80 (s, C=O) ppm; HRMS *m*/*z* calcd (found) for $C_{17}H_{24}O$, M^+ 244.182 716 (244.184 215); $[\alpha]^{20}_D = 74.2°$ mL dm^{-1} g^{-1} (*c* = 0.04 M in ethanol).

Synthesis of the Alkenyl Complex [Ru{C=C(H)C(C$_9$H$_{16}$)C=C(CH$_2$CH$_2$CH$_2$)O}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (14). A solution of the σ-alkynyl complex **11a** or **11b** (0.984 g, 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 complex **14** as a yellow solid: yield 94% (0.925 g); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 49.43 and 50.24 (d, $^2J_{PP}$ = 30.5 Hz) ppm; ^1H NMR ($CDCl_3$) δ 0.70, 0.90, and 1.13 (s, 3H each, CH_3), 0.97, 1.27, 1.40, 1.68, 1.93, and 2.33 (m, 2H each, CH_2), 2.10 (m, 1H, CH), 4.67 and 4.89 (br, 1H each, H-1 and H-3), 4.93 (s, 1H, =CH), 5.19 and 5.47 (m, 1H each, H-4, H-5, H-6, or H-7), 5.84 (br, 1H, H-2), 6.68−7.28 (m, 32H, Ph and H-4, H-5, H-6, or H-7) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 19.26, 26.55, and 28.50 (s, CH_3), 19.83, 25.65, 30.00, 30.93, 35.26, and 41.57 (s, CH_2), 48.55, 51.96, and 52.45 (s, C), 49.17 (s, CH), 73.62 (d, $^2J_{CP}$ = 10.9 Hz, C-1 or C-3), 74.34 (d, $^2J_{CP}$ = 9.5 Hz, C-1 or C-3), 102.09 (s, C-2), 109.54 (s, =CH), 109.79, 110.49, and 114.18 (s, C-3a, C-7a and =C), 121.54, 123.20, 123.36, and 124.85 (s, C-4, C-5, C-6, and C-7), 126.74−134.26 (m, Ph), 152.06 (s, =C−O), 160.80 (dd, $^2J_{CP}$ = 20.2 Hz, $^2J_{CP}$ = 15.9 Hz, Ru−C_α) ppm. Anal. Calcd for $RuC_{62}H_{60}P_2O$ (984.18): C, 75.66; H, 6.14. Found: C, 75.63; H, 6.05.

Synthesis of the Carbene Complex [Ru{=CCH$_2$C(C$_9$H$_{16}$)C=C(CH$_2$CH$_2$CH$_2$)O}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (15). To a solution of the alkenyl complex **14** (0.984 g, 1 mmol) in 30 mL of THF was added dropwise, at −20 °C, an excess of a diluted solution of $HBF_4 \cdot Et_2O$ 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 complex **15** as a brown solid, which was washed with diethyl ether (3 × 20 mL) and vacuum-dried: yield 84% (0.900 g); IR (KBr, cm^{-1}) ν 1060 (BF_4^-); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 115; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 41.37 and 46.58 (br) ppm; ^1H NMR ($CDCl_3$) δ 0.54, 0.86, and 1.31 (s, 3H each, CH_3), 1.06, 1.25, 1.55, and 2.22 (m, 2H each, CH_2), 1.74−1.82 (m, 4H, CH_2), 1.95 (m, 1H, CH), 4.17 (m, 2H, =CCH_2), 5.18 (br, 1H, H-2), 5.50 (br, 2H, H-1 and H-3), 6.32 (m, 4H, H-4, H-5, H-6, and H-7), 7.06−7.48 (m, 30H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 18.10, 28.41, and 28.53 (s, CH_3), 19.60, 24.80, 29.25, 31.27, 33.96, and 41.55 (s, CH_2), 45.07, 50.01, and 52.37 (s, C), 48.89 (s, CH), 59.85 (s, =*C*CH_2), 78.20 (br, C-1 and C-3), 97.76 (s, C-2), 111.21 (s, =CH), 120.24 (s, C-3a and C-7a), 121.28, 125.43, and 127.19 (s, C-4, C-5, C-6, or C-7), 128.08−134.31 (m, Ph and C-4, C-5, C-6, or C-7), 151.58 (s, =C−O), 299.49 (dd, $^2J_{CP}$ = 14.3 Hz, $^2J_{CP}$ = 10.7 Hz, Ru=C_α) ppm; $\Delta\delta$(C-3a,7a) = −10.46; mass spectrum (FAB, *m*/*e*) for $RuC_{62}H_{61}F_4P_2BO$ (1071.99) [M^+] 986, [M^+ − PPh_3] 724, [{Ru(η^5-C_9H_7)(PPh_3)}$^+$] 479. Complex **15** was too sensitive to moisture and oxygen to give satisfactory elemental analyses.

Synthesis of the σ-Alkynyl Complex [Ru{C≡CCPh$_2$(C$_{10}$H$_{13}$O)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (16). Complex **16** was prepared as described for **3a**,**b** and **4a**,**b** by starting from the allenylidene derivative [Ru(=C=C=CPh_2)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**; 1.076 g, 1 mmol) and (*R*)-(−)-carvone (0.156 mL, 1 mmol). The product was purified by column chromatography on silica gel with a hexane/diethyl ether mixture (4/1) as eluent. Evaporation of the solvents gave complex **16** as an orange solid: yield 78% (0.843 g); IR (KBr, cm^{-1}) ν 2064 (C≡C), 1652 (C=O). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 51.56 and 52.05 (d, $^2J_{PP}$ = 33.4 Hz) ppm; ^1H NMR (C_6D_6) δ 1.48 and 1.74 (s, 3H each, CH_3), 2.12 and 2.82 (m, 1H each, CH_2), 4.30 (d, 1H, J_{HH} = 4.8 Hz, CHC=O), 4.37 (m, 1H, CH), 4.58 (br, 1H, H-1 or H-3), 4.92 (m, 2H, H-1 or H-3 and =CH_2), 5.04 (m, 2H, H-2 and =CH_2), 5.45 (br, 1H, =CH), 5.84−7.89 (m, 44H, Ph, H-4, H-5, H-6, and H-7) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 17.04 and 22.36 (s, CH_3), 27.58 (s, CH_2), 45.17 and 55.92 (s, CH), 57.40 (s, C_γ), 73.07 and 73.61 (s, C-1 and C-3), 96.42 (s, C-2), 99.72 (dd, $^2J_{CP}$ = 22.1 Hz, $^2J_{CP}$ = 22.1 Hz, Ru−C_α), 110.04 and 111.31 (s, C-3a and C-7a), 111.58 (s, =CH_2), 115.36 (s, C_β), 123.82−150.38 (m, Ph, C-4, C-5, C-6, and C-7), 136.49 (s, CH=*C*CH_3), 139.91 (s, *C*H=CCH_3), 148.94 (s, CH_2=*C*CH_3), 200.78 (s, C=O) ppm; $\Delta\delta$(C-3a,7a) = −20.02. Anal. Calcd for $RuC_{70}H_{60}P_2O$ (1080.26): C, 77.83; H, 5.59. Found: C, 77.95; H, 5.89.

Synthesis of the Vinylidene Complex [Ru{=C=C(H)CPh$_2$(C$_{10}$H$_{13}$O)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (17). Complex **17**, isolated as a brown solid, was prepared as described for **5a**,**b** and **6a**,**b** by starting from the σ-alkynyl derivative **16** (1.080 g, 1 mmol): yield 90% (1.051 g); IR (KBr, cm^{-1}) ν 1685 (C=O), 1064 (BF_4^-); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 113; $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) δ 36.74 and 41.69 (d, $^2J_{PP}$ = 23.0 Hz) ppm; ^1H NMR ($(CD_3)_2CO$) δ 1.34 and 1.46 (s, 3H each, CH_3), 2.89 and 3.06 (m, 1H each, CH_2), 4.10 (m, 1H, CH), 4.39 and 4.62 (s, 1H each, =CH_2), 4.85 (br, 1H, CHC=O), 5.20−5.60 (m, 6H, H-1, H-2, H-3, Ru=C=CH and H-4, H-5, H-6, or H-7), 6.53−7.50 (m, 43H, Ph, =CH and H-4, H-5, H-6, or H-7) ppm; $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$) δ 13.08 and 22.39 (s, CH_3), 31.27 (s, CH_2), 42.07 and 54.64 (s, CH), 62.87 (s, C_γ), 77.40 and 82.46 (s, C-1 and C-3), 98.25 (s, C-2), 110.93 (s, =CH_2), 115.82 (s, C_β), 119.78 (s, C-3a and C-7a), 124.13, 125.48, 127.47, and 127.68 (s, C-4, C-5, C-6, and C-7), 129.15−151.16 (m, Ph), 135.77 (s, CH=*C*CH_3), 147.34 (s, *C*H=CCH_3), 148.10 (s, CH_2=*C*CH_3), 206.05 (s, C=O), 358.29 (dd, $^2J_{CP}$ = 15.8 Hz, $^2J_{CP}$ = 14.3 Hz, Ru=C_α) ppm; $\Delta\delta$(C-3a,7a) = −10.92. Anal. Calcd for $RuC_{70}H_{61}F_4P_2BO$ (1168.04): C, 71.98; H, 5.26. Found: C, 72.23; H, 5.29.

Synthesis of the Terminal Alkyne HC≡CCPh$_2$(C$_{10}$H$_{13}$O) (18). Compound **18**, isolated as a white solid, was prepared as described for **7a,b** and **8a,b** starting from the vinylidene complex **17** (1.168 g, 1 mmol): yield 83% (0.282 g); IR (KBr, cm^{-1}) ν 3255 (H−C≡), 2115 (C≡C), 1652 (C=O). ^1H NMR ($CDCl_3$) δ 1.67 and 1.74 (s, 3H each, CH_3), 2.15 (m, 1H, CH_2), 2.67 (s, 1H, ≡CH), 3.02 (m, 2H, CH_2 and CH), 3.72 (d, 1H, J_{HH} = 1.0 Hz, CHC=O), 4.65 and 4.76 (s, 1H each, =CH_2), 6.54 (br, 1H, =CH), 7.15−7.63 (m, 10H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.40 and 21.40 (s, CH_3), 27.87 (s, CH_2), 42.45 and 55.26 (s, CH), 53.14 (s, HC≡*C*C), 76.53 (s, ≡CH), 85.73 (s, ≡C), 111.65 (s, =CH_2), 126.74, 126.90, 127.56, 127.64, 127.73, and 128.31 (s, CH of Ph), 136.10 (s, CH=*C*CH_3), 142.66 and 143.00 (s, C of Ph), 142.83 (s, *C*H=CCH_3), 148.48 (s, CH_2=*C*CH_3), 198.22 (s, C=O) ppm; $[\alpha]^{20}_D = -179.9°$ mL dm^{-1} g^{-1} (*c* = 0.04 M in ethanol). Anal. Calcd for $C_{25}H_{24}O$ (340.46): C, 88.19; H, 7.10. Found: C, 87.92; H, 7.23.

Synthesis of the σ-Alkynyl Complex [Ru{C≡CCPh$_2$(C$_{10}$H$_{15}$O)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (19). A solution of (*R*)-(+)-pulegone (0.162 mL, 1 mmol) in 10 mL of THF was treated, at −78 °C, with LDA (0.179 g, 1 mmol) for 30 min and then transferred to a solution of [Ru(=C=C=CPh_2)(η^5-C_9H_7)(PPh_3)$_2$]-[PF_6] (**1**; 1.076 g, 1 mmol) in 50 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 a silica gel chromatography column. Elution with a hexane/diethyl ether mixture (4/1) gave an orange band from which the σ-alkynyl complex **19** was isolated after solvent removal: yield 77% (0.833 g); IR (KBr, cm^{-1}) ν 2073 (C≡C), 1694 (C=O). $^{31}P\{^1H\}$

NMR (C_6D_6) δ 51.54 and 52.12 (d, $^2J_{PP}$ = 33.5 Hz) ppm; ^{1}H NMR (C_6D_6) δ 0.79 (d, 3H, J_{HH} = 6.6 Hz, CHCH_3), 1.23, 1.75, 2.21, and 2.45 (m, 1H each, CH_2), 1.50 and 2.00 (s, 3H each, =C(CH_3)$_2$), 2.95 (m, 1H, CHCH$_3$), 3.53 (d, 1H, J_{HH} = 4.4 Hz, CHC=O), 4.68 and 4.96 (br, 1H each, H-1 and H-3), 5.74 (br, 1H, H-2), 6.31−7.72 (m, 44H, Ph, H-4, H-5, H-6, and H-7) ppm; ^{13}C{^{1}H} NMR (C_6D_6) δ 21.87, 22.95 and 23.60 (s, CH_3), 27.28 and 31.53 (s, CH_2), 34.60 and 65.02 (s, CH), 56.60 (s, C_γ), 74.81 (d, $^2J_{CP}$ = 5.2 Hz, C-1 or C-3), 75.41 (d, $^2J_{CP}$ = 2.9 Hz, C-1 or C-3), 93.27 (dd, $^2J_{CP}$ = 22.4 Hz, $^2J_{CP}$ = 22.4 Hz, Ru−C$_\alpha$), 97.81 (s, C-2), 109.88 and 112.30 (s, C-3a and C-7a), 114.76 (s, C_β), 123.76−149.57 (m, Ph, C-4, C-5, C-6, C-7, and C=C(CH$_3$)$_2$), 205.26 (s, C=O) ppm; $\Delta\delta$(C-3a,7a) = −19.61. Anal. Calcd for $RuC_{70}H_{62}P_2O$ (1082.28): C, 77.68; H, 5.77. Found: C, 77.64; H, 5.68.

Synthesis of the σ-Alkynyl Complex [Ru{C≡CCPh$_2$(C$_{10}$H$_{15}$O)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (20). A solution of (*R*)-(+)-pulegone (0.162 mL, 1 mmol) in 10 mL of THF was treated, at −20 °C, with LDA (0.179 g, 1 mmol) for 30 min and then transferred to a solution of **1** (1.076 g, 1 mmol) in 50 mL of THF. The mixture was wamred 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 hexane/diethyl ether mixture (4/1) gave an orange band from which complex **19** was isolated in 39% (0.422 g) yield. Further elution with diethyl ether gave a new orange band from which the σ-alkynyl complex **20** was isolated after solvent removal: yield 26% (0.281 g); IR (KBr, cm^{-1}) ν 2077 (C≡C), 1683 (C=O); ^{31}P{^{1}H} NMR (C_6D_6) δ 51.52 and 51.99 (d, $^2J_{PP}$ = 33.8 Hz) ppm; ^{1}H NMR (C_6D_6) δ 0.70 (d, 3H, J_{HH} = 6.5 Hz, CHCH_3), 1.26−1.54 (m, 4H, CH_2), 1.86 (dd, 1H, J_{HH} = 14.2 Hz, J_{HH} = 11.4 Hz, C=OCH_2CHCH$_3$), 2.21 (m, 1H, C=OCH$_2$CHCH$_3$), 2.48 (dd, 1H, J_{HH} = 14.2 Hz, J_{HH} = 2.9 Hz, C=OCH_2CHCH$_3$), 2.97 (s, 3H, CH_3), 3.32 (br, 2H, CH_2), 4.68 and 4.76 (br, 1H each, H-1 and H-3), 5.37 (br, 1H, H-2), 6.46−7.46 (m, 44H, Ph, H-4, H-5, H-6 and H-7) ppm; ^{13}C{^{1}H} NMR (C_6D_6) δ 22.63 and 24.06 (s, CH_3), 29.34, 33.99, 47.68, and 52.53 (s, CH_2), 33.06 (s, CH), 52.22 (s, C_γ), 73.59 and 73.84 (s, C-1 and C-3), 96.79 (s, C-2), 96.81 (dd, $^2J_{CP}$ = 22.5 Hz, $^2J_{CP}$ = 22.5 Hz, Ru−C$_\alpha$), 110.98, and 111.29 (s, C-3a and C-7a), 117.84 (s, C_β), 124.93, 125.17, 126.14, and 126.47 (s, C-4, C-5, C-6, and C-7), 127.48−150.89 (m, Ph and C=C(CH$_3$)$_2$), 204.19 (s, C=O) ppm; $\Delta\delta$(C-3a,7a) = −19.56. Anal. Calcd for $RuC_{70}H_{62}P_2O$ (1082.28): C, 77.68; H, 5.77. Found: C, 77.21; H, 5.83.

Synthesis of the σ-Alkynyl Complex [Ru{C≡CC(C$_9$H$_{16}$)(C$_{10}$H$_{15}$O)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (21). A solution of (*R*)-(+)-pulegone (0.810 mL, 5 mmol) in 20 mL of THF was treated, at −20 °C, with LDA (0.895 g, 5 mmol) for 30 min and then transferred to a solution of **10** (1.046 g, 1 mmol) in 50 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 a silica gel chromatography column. Elution with a hexane/diethyl ether mixture (5/1) gave a red band from which complex **21** was isolated after solvent removal: yield 51% (0.536 g); IR (KBr, cm^{-1}) ν 2064 (C≡C), 1706 (C=O); ^{31}P{^{1}H} NMR (C_6D_6) δ 51.38 and 52.67 (d, $^2J_{PP}$ = 33.9 Hz) ppm; ^{1}H (C_6D_6) δ 0.75 (d, 3H, J_{HH} = 6.3 Hz, CHCH_3), 1.06, 1.19, 1.63, and 2.83 (s, 3H each, CH_3), 1.24 (m, 4H, CH_2), 1.52, 1.74, and 2.69 (m, 2H each, CH_2), 1.95 (m, 3H, CH_2), 2.26 (m, 1H, CHCH$_3$), 2.46 (m, 1H, CH_2), 3.27 (m, 1H, CH), 4.77 and 4.89 (br, 1H each, H-1 and H-3), 5.68 (br, 1H, H-2), 6.16 and 6.78 (m, 2H each, H-4, H-5, H-6, and H-7), 6.95−7.32 (m, 30H, Ph) ppm; ^{13}C{^{1}H} NMR (C_6D_6) δ 19.40, 21.96, 22.29, 27.83, and 28.14 (s, CH_3), 26.39, 28.43, 32.92, 34.59, 41.49, 43.39, and 51.11 (s, CH_2), 31.04 and 52.53 (s, CH), 44.95 and 54.01 (s, C), 56.22 (s, C_γ), 73.35 and 73.85 (d, $^2J_{CP}$ = 5.4 Hz, C-1 and C-3), 86.92 (dd, $^2J_{CP}$ = 23.8 Hz, $^2J_{CP}$ = 20.7 Hz, Ru−C$_\alpha$), 96.18 (s, C-2), 109.76 and 111.33 (s, C-3a and C-7a), 116.24 (s, C_β), 123.39, 124.22, 125.26, and 126.07 (s, C-4, C-5, C-6, and C-7), 127.24−139.88 (m, Ph), 130.37 (s, =CCH$_3$), 151.42 (s, =C-C=O), 201.53 (s, C=O) ppm; $\Delta\delta$(C-3a,7a) = −20.15. Anal. Calcd for $RuC_{67}H_{68}P_2O$ (1052.30): C, 76.47; H, 6.51. Found: C, 76.57; H, 6.39.

Table 1. Crystal Data and Structure Refinement for Complexes 11b and 14[a]

	11b	14
empirical formula	$C_{64.5}H_{66}OP_2Ru$	$C_{62}H_{60}OP_2Ru$
fw	1020.19	984.11
T, K	293(2)	150(1)
λ, Å	0.710 73 (graphite monochromated)	
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
a, Å	21.096(15)	14.852(4)
b, Å	16.632(12)	15.413(2)
c, Å	30.39(2)	21.198(3)
β, deg	90	99.909(14)
V, Å^3	10 662(13)	4780.1(16)
Z	8	4
ρ_{calcd}, Mg/m^3	1.271	1.367
μ, mm^{-1}	0.396	0.439
F(000)	4280	2056
cryst size, mm	0.37 × 0.30 × 0.27	0.54 × 0.39 × 0.10
θ range, deg	1.18−30.58	2.04−27.47
limits (hkl)	−29 to +29; −23 to +18; −43 to +37	0−19; 0−19; −27 to +27
no. of rflns collected/unique	83 463/31 094	11 289/11 289
R(int)	0.0916	0.000
completeness to θ_{max}, %	97.3	99.4
abs cor	multiscan	ψ scans
T_{max}, T_{min}	1.000, 0.651	0.902, 0.844
refinement method	full-matrix least squares on F^2	
no. of data/restraints	31 094/98	11 289/7
no. of params	1276	1196
weighting params g_1, g_2	0.0605, 0.00	0.0455, 3.7799
goodness of fit on F^2	0.988	1.018
R1 ($I > 2\sigma(I)$)	0.0513	0.0454
wR2 (all data)	0.1440	0.1150
Flack param, est	−0.02(3)	−0.01(4)
Flack param, ref	0.00(3)	0.00(9)
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	1.177, −1.062	0.587, −0.601

[a] The function minimized was in both cases $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + (g_2P)]$, where $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$.

X-ray Diffraction. The crystal structures of complexes **11b** and **14** were analyzed by X-ray diffraction (data collection, crystal, and refinement parameters are collected in Table 1), and it quickly became clear that both structures were characterized by severe pseudosymmetry. This arises because a large portion of the molecule in each case is superimposable on its mirror image, while only parts of the chiral ligand, at the periphery of the molecule and representing roughly 12% of the scattering power for **11b** and 19% for **14**, are not. In both cases, the crystals have two molecules in the asymmetric unit, and in each case the two molecules are in fact mirror images of each other in all but the portion of the chiral ligand distal to the innermost chiral carbon atom. For **11b**, the space group would be *Pbca* in the absence of the chiral moiety, but this ligand has the same absolute configuration in both molecules, giving an asymmetric unit that can be formally described as consisting of a pair of diastereoisomers and lowering the overall symmetry of the crystal to $P2_12_12_1$. An analogous situation holds for **14**, which also has $Z' = 2$ ($Z = 4$) and would have space group $P2_1/n$ if not for the chiral fragment, which lowers the symmetry to $P2_1$. Again, a large part of the scattering density forms a centric pattern, broken only by the fixed stereochemistry of the outermost part of the chiral ligand. As can be imagined, it was of utmost importance in both cases to measure the diffraction data with care, and especially so for the systematically weak data that would have been systematic absences in *Pbca* but not $P2_12_12_1$ or in $P2_1/n$

but not $P2_1$. For **11b** data were measured using a SMART diffractometer,[15] with scan times set so as to achieve acceptable measurements of the weakest data. For **14**, data were gathered at $T = 150$ K on a CAD-4 diffractometer[16] using a variable scan speed algorithm in which no datum was skipped because of a poor showing on the preliminary scan. That is, the weakest data were measured for the longest time.

For **11b**, absorption corrections to the SMART data were applied by the multiscan procedure using the program SADABS.[17] For **14**, absorption corrections[18] were based on full or partial ψ scans of 20 reflections with Eulerian-equivalent angle χ distributed through the range -30.6 to $+48.7°$, so as to maximize the solid volume covered by the set of incident and scattered beams.

Both structures were solved by direct methods[19] and developed and refined in the usual sequence of least-squares refinements and difference Fourier maps.[20] In each case the uniform stereochemistry of the chiral groups was observed with no ambiguity and with no special treatment to the structural model (i.e., no constraints or restraints were needed for these ligands). In both cases, hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameters of their respective parent atoms. For **14**, in addition to the two molecules of the complex, the asymmetric unit contains one formula unit of *n*-pentane, disordered over two sites sharing one of the carbon atoms. For this interstitial solvent, restraints were placed on the 1,2- and 1,3-distances; similar restraints were placed on the two disordered congeners. The anisotropic displacement parameters of the atoms of the disordered solvent were also restrained, to a rigid-bond model and to isotropic behavior. For **11b**, a restraint to isotropic behavior was placed on one of the atoms of the indenyl ligand, C(7). Otherwise, all nonhydrogen atoms of both structures were refined freely with anisotropic displacement parameters.

The refined values of the Flack parameter[21] were 0.00(3) for **11b** and 0.00(9) for **14**, for the absolute structures reported. For **11b**, the anisotropic displacement parameters for the five-membered ring of the chiral ligand showed elongation perpendicular to the best plane of the ring, which is symptomatic of conformational disorder—this does not reflect on the determination of the absolute configurations of the chiral carbon atoms. For **14**, no signs of even the slightest conformational disorder were observed for the five-membered rings of the chiral ligands; it was observed that both independent molecules in the asymmetric unit have the same conformations for this group. Both refinements were stable and convergent.

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Supporting Information Available: Tables giving crystal structure data for **11b** and **14**, including tables of atomic parameters, anisotropic thermal parameters, and bond distances and bond angles, and Tables S1−S6, containing $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopic data for compounds **3a**,**b** through **8a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Diffractometer control: SMART V5.624, copyright 1997−2001, Bruker AXS, Inc. (b) Integration: SAINT+ V6.02, copyright 1997−1999, Bruker AXS, Inc.

(16) (a) Diffractometer control: CAD4/PC Version 2.0, copyright 1996, Nonius bv, Delft, The Netherlands. (b) Data reduction: XCAD4B (K. Harms, 1996).

(17) SADABS: Area-Detector Absorption Correction, copyright 1996, Siemens Industrial Automation, Inc., Madison, WI.

(18) SHELXTL release 5.05/VMS, copyright 1996, Siemens Analytical X-ray Instruments, Inc.

(19) SHELXS-97: Fortran program for crystal structure solution, copyright 1997, George M. Sheldrick.

(20) SHELXL-97: A program for crystal structure refinement, release 97-2, copyright 1997, George M. Sheldrick, University of Göttingen, Germany, 1997.

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