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Synthesis of indenyl-ruthenium(II) σ-alkynyl complexes via nucleophilic addition of (1*R*)-(+)- and (1*S*)-(−)-camphor enolates on the allenylidene group of $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$: Efficient synthesis of novel optically pure vinylidene derivatives

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Abstract

The diphenylallenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**1**) regioselectively reacts at the C_γ atom with the lithium enolate derived from (1*R*)-(+)-camphor to yield σ-alkynyl derivative $[Ru\{C{\equiv}CCPh_2(C_{10}H_{15}O)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**2**). Complex **2** was obtained as a non-separable mixture of two diastereoisomers, i.e. (1*R*,3*S*,4*R*)-**2** and (1*R*,3*R*,4*R*)-**2** (ca. 3:2 ratio), in which the alkynyl fragment is located in *exo* or *endo* disposition on the camphor skeleton, respectively. Protonation of this mixture with $HBF_4{\cdot}Et_2O$ affords the vinylidene derivative $[Ru\{=C=C(H)CPh_2(C_{10}H_{15}O)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**3**) as a single diastereoisomer, i.e. (1*R*,3*S*,4*R*)-**3**, showing an *exo* disposition of the vinylidene group. The structure of complex (1*R*,3*S*,4*R*)-**3** has been confirmed by X-ray diffraction. The molecular structure shows the typical pseudo-octahedral three-legged piano-stool geometry around the ruthenium atom, which is linked to the phosphorus atoms of the PPh_3 ligands, to the η^5-bonded indenyl ligand, and to an almost linear vinylidene chain (Ru–C(1)–C(2) = 165.6 (18)°) with a Ru–C(1) bond length of 1.88 (2) Å. Demetalation of (1*R*,3*S*,4*R*)-**3**, by treatment with acetonitrile at reflux, yields the terminal alkyne $HC{\equiv}CCPh_2(C_{10}H_{15}O)$ (**4**) and the nitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**5**). Compound **4** was obtained as a non-separable mixture of two diastereoisomers, i.e. (1*R*,3*S*,4*R*)-**4** and (1*R*,3*R*,4*R*)-**4** (ca. 3:1 ratio). Related reactions starting from diphenylallenylidene **1** and the (1*S*)-(−)-camphor enolate are also reported.

Keywords: Allenylidene complexes; σ-Alkynyl complexes; Vinylidene complexes; Terminal alkynes; Indenyl; Ruthenium; Camphor

1. Introduction

The chemistry of transition-metal allenylidene complexes $[M]=C=C=CR^1R^2$ has been the subject of special attention in recent years due to the wealth of their applications in stoichiometric [1] and catalytic reactions [2]. Indeed, the unsaturated character of M=C=C=C chain as well as its alternating array of electrophilic/nucleophilic carbon sites [3] makes allenylidene complexes unique organometallic reagents for use in C–C and C–heteroatom coupling processes.

In the context of our studies in the chemistry of indenyl-ruthenium(II) complexes [4], we have reported the preparation of wide series of both neutral and cationic σ-alkynyl derivatives of general formula $[Ru\{C{\equiv}CC(Nu)R^1R^2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^{n+}$ ($n = 0$, 1) via regioselective nucleophilic additions at the C_γ atom of the allenylidene chain in complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ [3c,5]. Moreover, we have recently developed an efficient synthetic procedure for the propargylic substitution of 2-propyn-1-ols mediated by the metallic fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (Chart

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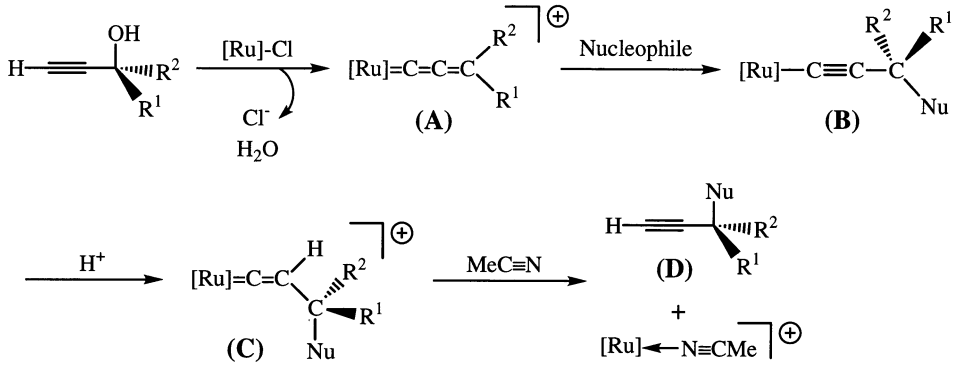


Chart 1. $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$-mediated propargylic substitution reactions.

1) [5d,5f,5g,5i,5j]. Thus, in a first step allenylidene complexes **A** are formed and subsequently transformed into the corresponding σ-alkynyl derivatives **B** which undergo a selective C_β protonation to afford vinylidene complexes **C** [6]. Finally, demetalation of **C** with acetonitrile leads to the functionalized terminal alkynes **D** in excellent yields [7]. This synthetic methodology constitutes an alternative to the well-known Nicholas reaction [8]. Although the same number of steps are required in both propargylic substitution reactions, the quantitative recovery of the metal fragment as the acetonitrile complex $[Ru(N{\equiv}CMe)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (Chart 1) represents a major advantage compared with the classical Nicholas reaction in which the metal auxiliary cannot be recovered after the oxidative decomplexation step.

The involvement of chiral nucleophiles in such nucleophilic addition processes is of special interest since functionalized optically active terminal alkynes could be readily accessible. In this respect, we have recently reported the preparation of the σ-alkynyl complex **E** and the γ-keto-acetylene **F** (Chart 2) in optically pure form from the addition of the (*R*)-(−)-carvone enolate on $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ [5i].

In order to exploit the efficiency of this selective synthetic approach to the synthesis of novel chiral γ-keto-acetylenes, in this paper we report our results using enolates derived from the commercially available and optically pure ketones (1*R*)-(+)- and (1*S*)-(−)-camphor.

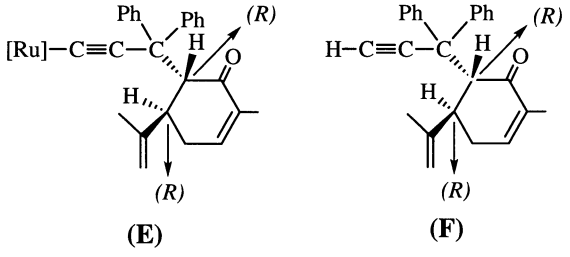


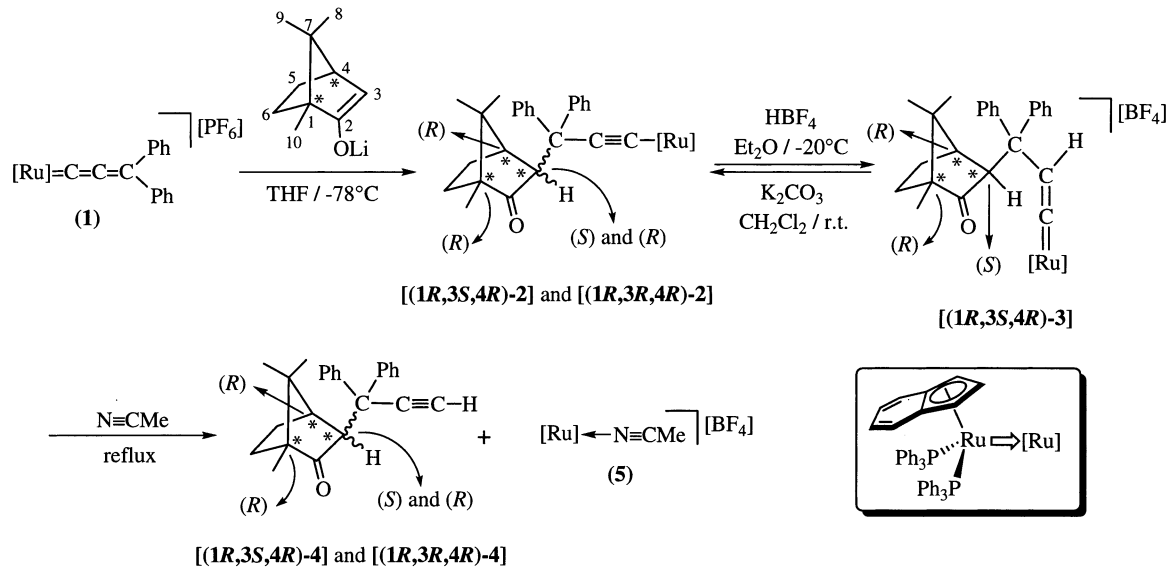
Chart 2. Structure of the optically active compounds **E** and **F**.

2. Results and discussion

2.1. Synthesis of σ-alkynyl complexes

As expected from our previous studies [5], lithium enolate of (1*R*)-(+)-camphor (prepared in situ by treatment with one equivalent of LDA in THF at −78 °C) adds regioselectively at the γ-position of the cumulenic chain in diphenylallenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**1**) to afford the neutral σ-alkynyl derivative $[Ru\{C{\equiv}CCPh_2\text{-}(C_{10}H_{15}O)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**2**), isolated as an air-stable orange solid in 88% yield (Scheme 1).

The $^{31}P\{^1H\}$-, ^1H-, and $^{13}C\{^1H\}$-NMR spectroscopic data for **2** (details are given in Section 4) indicate clearly that the nucleophilic attack of this chiral enolate is not stereoselective since two diastereoisomers are present in solution, i.e. (1*R*,3*S*,4*R*)-**2** and (1*R*,3*R*,4*R*)-**2** (ca. 3:2 ratio). Thus, the $^{31}P\{^1H\}$-NMR spectrum displays signals consistent with two AB spin systems [(1*R*,3*S*,4*R*)-**2**: $\delta = 49.19$ and 51.04 ($^2J_{PP} = 31.7$ Hz) ppm; (1*R*,3*R*,4*R*)-**2**: $\delta = 50.32$ and 51.11 ($^2J_{PP} = 33.6$ Hz) ppm], the non-equivalence of the phosphorus nuclei being a consequence of the presence of stereogenic centres on the organic fragment. The ^1H-NMR spectrum exhibits resonances for aromatic, indenyl and enolate groups, in accordance with the proposed structures. The comparison of these ^1H-NMR spectroscopic data with those reported in the literature for other 3-substituted camphor derivatives allowed us to elucidate the stereochemistry for each diastereoisomer. In particular, while for the major diastereoisomer (1*R*,3*S*,4*R*)-**2** the *endo*-hydrogen on C(3) (numbering for the camphor skeleton is shown in Scheme 1) resonates as a singlet at $\delta = 3.35$ ppm, a doublet signal ($J_{HH} = 4.2$ Hz) is observed for the H(3) *exo*-proton ($\delta = 3.97$ ppm) in the minor diastereoisomer (1*R*,3*R*,4*R*)-**2** due to the coupling with the methine hydrogen on C(4) [9]. The $^{13}C\{^1H\}$-NMR spectrum also shows the characteristic resonances for $Ru{-}C_\alpha{\equiv}C_\beta{-}C_\gamma{-}CH{-}C{=}O$ carbon nuclei of both diastereoisomers (see Section 4).



Scheme 1. Nucleophilic addition of the (1R)-(+)-camphor enolate on the allenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$.

The chemical behaviour of the diphenylallenylidene derivative **1** towards the (1*S*)-(−)-camphor enolate has also been explored allowing the preparation of the σ-alkynyl complex **2** as a non-separable mixture of the (1*S*,3*R*,4*S*)- and (1*S*,3*S*,4*S*)-diastereoisomers (ca. 3:2 ratio; 85% yield) (see Fig. 1).

2.2. Synthesis of vinylidene complexes

In agreement with the strong nucleophilic character of C_β of a σ-alkynyl ligand [6], the addition of $HBF_4 \cdot Et_2O$ to a solution containing complexes (1*R*,3*S*,4*R*)-**2** and (1*R*,3*R*,4*R*)-**2**, in diethyl ether at −20 °C, affords the cationic vinylidene derivative $[Ru\{=C=C(H)CPh_2(C_{10}H_{15}O)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**3**) (91% yield) (Scheme 1). Surprisingly, complex **3** was obtained as a single diastereoisomer, i.e. (1*R*,3*S*,4*R*)-**3**, in which the vinylidene fragment $[Ru=C=C(H)CPh_2]$ is located in an *exo* disposition on the camphor skeleton [10]. This fact is clearly evidenced by the single resonance (δ = 4.63 ppm) observed in the ^{1}H-NMR spectrum for the CHC=O proton, typical of 3-*exo*-substituted camphor derivatives [9]. ^{1}H- and $^{13}C\{^1H\}$-NMR spectra also display characteristic spectroscopic features for the vinylidene unit (see Section 4). The proposed stereochemistry for complex **3** was confirmed by X-ray diffraction methods (see Fig. 2 and Table 1) [11]. The molecule exhibits the usual allylene structure of the η^5-indenyl ligand [12] in the pseudo-octahedral three-legged piano-stool geometry. The interligand angles P(1)–Ru–P(2), C(1)–Ru–P(1), and C(1)–Ru–P(2) and those between the centroid C* and the legs show values typical of a pseudo-octahedron. The vinylidene ligand is bound to ruthenium with a Ru–C(1) distance of 1.88 (2) Å, a C(1)–C(2) distance of 1.29 (2) Å, and a Ru–C(1)–C(2) angle of 165.6 (18)°. These bonding parameters can be compared with those reported for other ruthenium(II) vinylidene complexes [6,13]. As predicted by theoretical calculations [14], the preferred conformation of the indenyl ligand is such that the benzo ring is oriented almost *trans* to the vinylidene group (CA = 162.5 (6)°). As expected, the (1*S*,3*R*,4*S*)-diastereoisomer of vinylidene complex **3** (see Fig. 1) could also be obtained in optically pure form (93% yield) by treatment of a mixture containing (1*S*,3*R*,4*S*)- and (1*S*,3*S*,4*S*)-**2** with tetrafluoroboric acid.

Remarkably, deprotonation of the optically pure vinylidene complex (1*R*,3*S*,4*R*)-**3**, by treatment of a

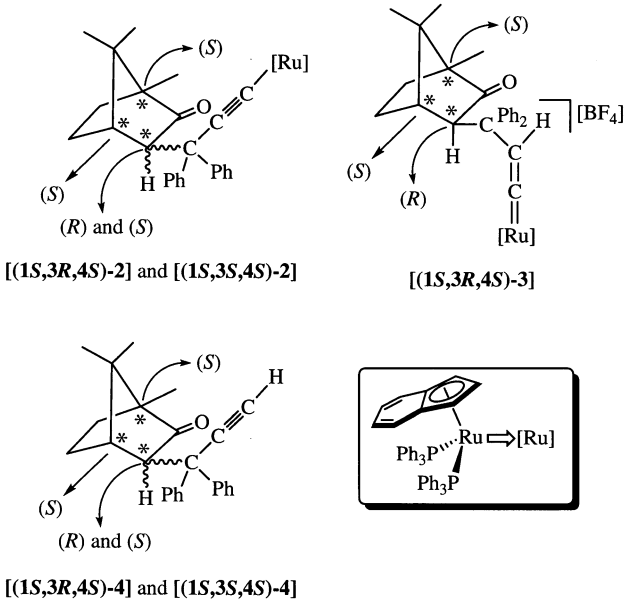


Fig. 1. Structure of the products derived from (1*S*)-(−)-camphor enolate.

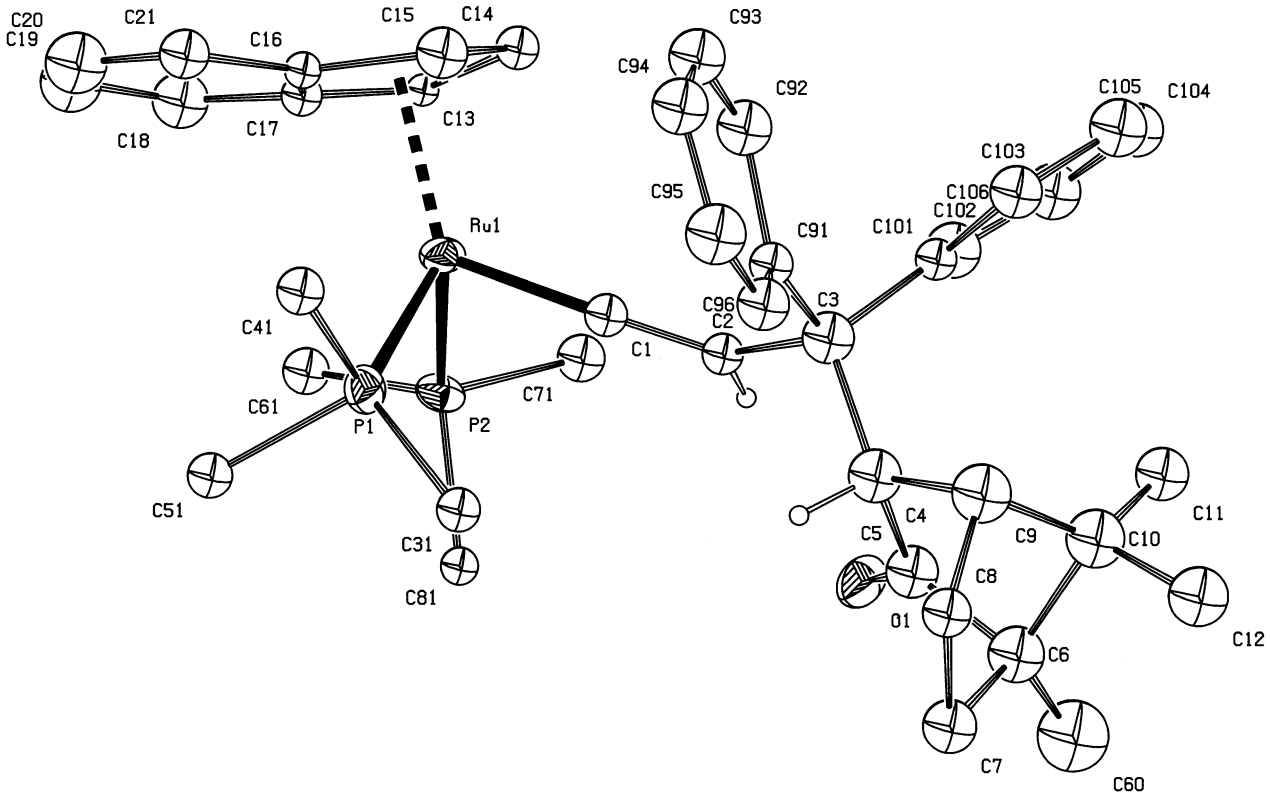


Fig. 2. ORTEP-type view of the structure of the cation (1*R*,3*S*,4*R*)-**3** showing the crystallographic labelling scheme. Thermal ellipsoids are drawn at the 30% probability level. Aryl groups of the triphenylphosphine ligands and hydrogen atoms (except those on C(2) and C(4) carbons) have been omitted for clarity.

dichloromethane solution with K_2CO_3 at room temperature, does not allow the selective formation of the expected σ-alkynyl diastereoisomer (1*R*,3*S*,4*R*)-**2**. Apparently, a spontaneous epimerization rapidly occurs yielding the equilibrium mixture of (1*R*,3*S*,4*R*)- and (1*R*,3*R*,4*R*)-**2** (ca. 3:2 ratio) (see Scheme 1).

2.3. Demetalation process

A related epimerization is also observed in the demetalation process of (1*R*,3*S*,4*R*)-**3** with acetonitrile which leads quantitatively [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**5**) and the corresponding γ-keto-acetylene **4** as a non-separable mixture of the *exo* [(1*R*,3*S*,4*R*)-**4**] and *endo* [(1*R*,3*R*,4*R*)-**4**] diastereoisomers in ca. 3:1 ratio (see Scheme 1). Analytical and spectroscopic data of the γ-keto-alkynes **4** are in accord with the proposed formulation (see Section 4). Noteworthy, activation of the diastereomeric mixture of **4** by the chloride complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**6**), in methanol at room temperature and in the presence of $NaPF_6$, regenerates the optically pure vinylidene derivative (1*R*,3*S*,4*R*)-**3** (see Scheme 2).

As expected, an epimerization also takes place during the demetalation of the optically pure vinylidene (1*S*,3*R*,4*S*)-**3**, which leads to an equilibrium mixture (ca. 3:1 ratio) of the diastereoisomers (1*S*,3*R*,4*S*)-**4** and (1*S*,3*S*,4*S*)-**4** (88% yield; see Fig. 1).

3. Conclusions

In contrast with our previous results using enolates derived from the optically active ketones (*R*)-(−)-carvone and (*R*)-(+)-pulegone [5i], the nucleophilic addition of the (1*R*)-(+)- and (1*S*)-(−)-camphor enolates at the C_γ atom of allenylidene complex [Ru(=C=C=CPh_2)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**1**) does not proceed in a diastereoselective manner affording the σ-alkynyl derivatives [Ru{C≡CCPh_2($C_{10}H_{15}O$)}(η^5-C_9H_7)(PPh_3)$_2$] (**2**) as a 3:2 mixture of two diastereoisomers for each one of the enolates. As expected, the major stereoisomers are those in which the metallic fragment is located on the less sterically demanding *exo* face of the (1*R*)-(+)- and (1*S*)-(−)-camphor skeletons, i.e. (1*R*,3*S*,4*R*)-**2** and (1*S*,3*R*,4*S*)-**2**, respectively. This *exo* conformation seems to be strongly favoured in the corresponding vinylidene complexes [Ru{=C=C(H)CPh_2($C_{10}H_{15}O$)}(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**3**) which are formed diastereoselectively, as the (1*R*,3*S*,4*R*)- and (1*S*,3*R*,4*S*)-enantiomers, by protonation of the corresponding diastereomeric mixture of the σ-alkynyl deri-

Table 1
Selected bond lengths (Å), slip parameter Δ [a] (Å), bond angles (°) and dihedral angles (°), fold angle (FA) [b], hinge angle (HA) [c], dihedral angle (DA) [d], and conformational angle (CA) [e], for complex (1*R*,3*S*,4*R*)-**3**

Bond lengths	
Ru–C*	1.993 (2)
Ru–P(1)	2.329 (7)
Ru–P(2)	2.379 (7)
Ru–C(1)	1.88 (2)
C(1)–C(2)	1.29 (2)
C(2)–C(3)	1.54 (3)
C(3)–C(4)	1.57 (3)
C(4)–C(5)	1.59 (4)
C(4)–C(9)	1.59 (3)
C(5)–O(1)	1.20 (3)
C(5)–C(6)	1.55 (4)
C(6)–C(10)	1.60 (3)
C(6)–C(7)	1.59 (3)
C(7)–C(8)	1.59 (3)
C(8)–C(9)	1.47 (3)
C(9)–C(10)	1.60 (3)
Δ	0.20 (2)
Bond angles	
C*–Ru–C(1)	125.2 (8)
C*–Ru–P(1)	126.1 (2)
C*–Ru–P(2)	118.0 (2)
P(1)–Ru–P(2)	101.9 (3)
P(1)–Ru–C(1)	87.6 (7)
P(2)–Ru–C(1)	89.2 (8)
Ru–C(1)–C(2)	165.6 (18)
C(1)–C(2)–C(3)	129 (2)
C(2)–C(3)–C(4)	106.4 (19)
C(3)–C(4)–C(5)	119 (2)
C(3)–C(4)–C(9)	119 (2)
C(4)–C(5)–O(1)	127 (3)
C(4)–C(5)–C(6)	101 (3)
C(5)–C(6)–C(7)	107 (2)
C(5)–C(6)–C(10)	97 (2)
C(7)–C(6)–C(10)	106 (2)
C(6)–C(7)–C(8)	100.0 (19)
C(7)–C(8)–C(9)	108 (2)
C(8)–C(9)–C(4)	105 (2)
C(8)–C(9)–C(10)	102 (2)
FA	18 (1)
HA	11 (2)
DA	121 (1)
CA	162.5 (6)

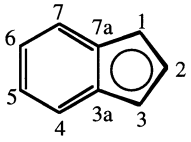
[a] $\Delta = d$[Ru–C(16), C(17)] − d[Ru–C(13), C(15)].
[b] FA = angle between the planes defined by [C(13), C(14), C(15)] and [C(16), C(17), C(18), C(19), C(20), C(21)].
[c] HA = angle between the planes defined by [C(13), C(14), C(15)] and [C(13), C(15), C(16), C(17)].
[d] DA = angle between the planes defined by [C*, Ru, C(1)] and [C(1), C(2), C(3)].
[e] CA = angle between the planes defined by [C**, C*, Ru] and [C*, Ru, C(1)]. C* = centroid of C(13), C(14), C(15), C(16), C(17). C** = centroid of C(16), C(17), C(18), C(19), C(20), C(21).

vatives **2**, via epimerization of the minor *endo* stereoisomers. Unfortunately, an epimerization process is also observed during the demetalation of the vinylidenes **3** to give the free γ-keto-acetylenes HC≡CCPh$_2$(C$_{10}$H$_{15}$O) (**4**) since the former *exo* preference is not maintained, and again an equilibrium between the *exo* and *endo* conformations is reached.

4. Experimental

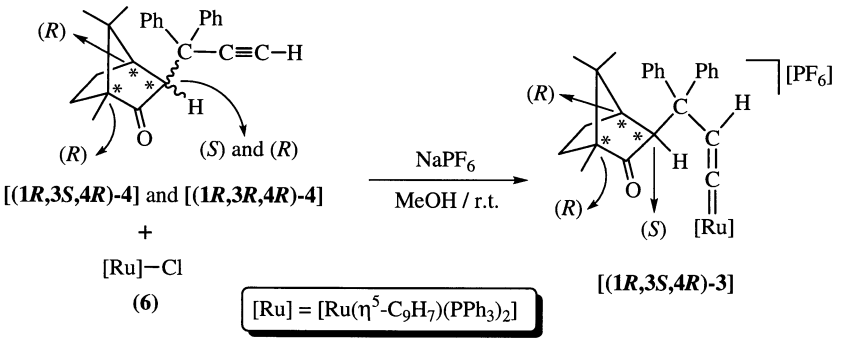
The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification except compounds [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**1**) [3c] and [RuCl(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (**6**) [15], which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature (r.t.), 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. NMR spectra were recorded on a Bruker AC300 instrument at 300 (^{1}H), 121.5 (^{31}P) or 75.4 MHz (^{13}C) using SiMe$_4$ or 85% H$_3$PO$_4$ as standards. DEPT experiments have been carried out for all the compounds reported. Abbreviations used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; and m, multiplet.

The numbering for the indenyl skeleton is as follows:



4.1. Synthesis of [Ru{C≡CCPh$_2$(C$_{10}$H$_{15}$O)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (2)

A solution of (1*R*)-(+)-camphor (0.152 g, 1 mmol) in 20 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$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**1**) (1.076 g, 1 mmol) in 50 ml of THF. The mixture was allowed to warm to r.t. and the solvent was then removed in vacuo. The resulting solid residue was dissolved in dichloromethane (ca. 5 ml) and transferred to an Al$_2$O$_3$ (neutral; activity grade I) chromatography column. Elution with a mixture of hexane–diethyl ether (5:1) gave an orange band from which complex **2** was isolated, after solvent removal, as a non-separable mixture of two diastereoisomers in ca. 3:2 ratio. Yield: 88% (0.952 g); Anal. Calc. for RuC$_{70}$H$_{62}$P$_2$O: C, 77.68; H, 5.77. Found: C, 77.76; H, 5.89%. Major diastereoisomer [(1*R*,3*S*,4*R*)-**2**] — IR (KBr, cm^{-1}): 1735 ν(C=O), 2072 ν(C≡C); ^{31}P{^{1}H}-NMR (C$_6$D$_6$) δ 49.19 and 51.04 (d, $^2J_{PP}$ = 31.7 Hz)



Scheme 2. Activation of **4** by the complex $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (**6**).

ppm; ^{1}H-NMR (C_6D_6) δ 0.68, 0.88 and 0.90 (s, 3H each, CH_3), 1.39–1.93 (m, 4H, CH_2), 2.37 (m, 1H, CH), 3.35 (s, 1H, CHC=O), 4.72 and 4.75 (br, 1H each, H-1 and H-3), 5.75 (br, 1H, H-2), 5.93 (d, 1H, $J_{HH} = 8.6$ Hz, H-4, H-5, H-6 or H-7), 6.29 (d, 1H, $J_{HH} = 8.5$ Hz, H-4, H-5, H-6 or H-7), 6.75 (m, 2H, H-4, H-5, H-6 or H-7), 6.88–7.86 (m, 40H, Ph) ppm; ^{13}C{^{1}H}-NMR (C_6D_6) δ 10.37, 21.54 and 22.26 (s, CH_3), 27.20 and 31.94 (s, CH_2), 45.61 (s, *C*Me$_2$), 49.63 (s, CH), 54.74 (s, C_γ), 58.58 (s, *C*Me), 64.27 (s, *C*HC=O), 73.02 (d, $^2J_{CP} = 7.0$ Hz, C-1 or C-3), 75.58 (d, $^2J_{CP} = 5.7$ Hz, C-1 or C-3), 95.72 (dd, $^2J_{CP} =$ 25.1 and 21.0 Hz, Ru–C_α), 96.74 (s, C-2), 107.51 and 113.59 (s, C-3a and C-7a), 114.67 (s, C_β), 122.35, 123.94, 125.26 and 125.42 (s, C-4, C-5, C-6 and C-7), 126.73–151.65 (m, Ph), 216.13 (s, C=O) ppm; $\Delta\delta$(C-3a,7a) = −20.15 ppm. Minor diastereoisomer [(1*R*,3*R*,4*R*)-2] — IR (KBr, cm^{-1}): 1735 ν(C=O), 2072 ν(C≡C); ^{31}P{^{1}H}-NMR (C_6D_6) δ 50.32 and 51.11 (d, $^2J_{PP} = 33.6$ Hz) ppm; ^{1}H-NMR (C_6D_6) δ 0.47, 0.79 and 0.83 (s, 3H each, CH_3), 1.39–1.93 (m, 4H, CH_2), 2.86 (m, 1H, CH), 3.97 (d, 1H, $J_{HH} = 4.2$ Hz, CHC=O), 4.92 (br, 2H, H-1 and H-3), 5.70 (br, 1H, H-2), 5.98 (d, 1H, $J_{HH} = 8.2$ Hz, H-4, H-5, H-6 or H-7), 6.52 (d, 1H, $J_{HH} = 8.3$ Hz, H-4, H-5, H-6 or H-7), 6.75 (m, 2H, H-4, H-5, H-6 or H-7), 6.88–7.86 (m, 40H, Ph) ppm; ^{13}C{^{1}H}-NMR (C_6D_6) δ 10.95, 18.88 and 19.98 (s, CH_3), 22.96 and 30.72 (s, CH_2), 45.56 (s, *C*Me$_2$), 49.50 (s, CH), 53.06 (s, C_γ), 58.46 (s, *C*Me), 60.64 (s, *C*HC=O), 72.76 (d, $^2J_{CP} = 5.7$ Hz, C-1 or C-3), 75.72 (d, $^2J_{CP} = 5.9$ Hz, C-1 or C-3), 94.49 (dd, $^2J_{CP} =$ 23.8 and 21.0 Hz, Ru–C_α), 96.70 (s, C-2), 108.41 and 113.08 (s, C-3a and C-7a), 114.51 (s, C_β), 123.03, 124.57, 125.05 and 125.12 (s, C-4, C-5, C-6 and C-7), 126.73–151.65 (m, Ph), 215.55 (s, C=O) ppm; $\Delta\delta$(C-3a,7a) = −19.95 ppm.

Following the same synthetic procedure, a non-separable mixture (ca. 3:2 ratio) of (1*S*,3*R*,4*S*)-**2** and (1*S*,3*S*,4*S*)-**2** was prepared starting from $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**1**) (1.076 g, 1 mmol) and (1*S*)-(−)-camphor (0.152 g, 1 mmol). Yield: 85% (0.919 g); Anal. Calc. for $RuC_{70}H_{62}P_2O$: C, 77.68; H, 5.77. Found: C, 77.59; H, 5.66%.

4.2. Synthesis of [Ru{=C=C(H)CPh$_2$(C$_{10}$H$_{15}$O)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] (3)

A solution of $HBF_4 \cdot Et_2O$ in diethyl ether (0.1 M) was added drop-wise, at −20 °C, to a stirred solution containing a mixture of (1*R*,3*S*,4*R*)-**2** and (1*R*,3*R*,4*R*)-**2** (1.082 g, 1 mmol) in 100 ml of diethyl ether. Immediately, an insoluble solid precipitated but the addition was continued until no further solid was formed (ca. 15 ml, 1.5 mmol). The solution was then decanted, the brown solid washed with diethyl ether (3 × 20 ml) and dried in vacuo. Complex **3** was obtained as a single diastereoisomer, i.e. (1*R*,3*S*,4*R*)-**3**. Yield: 91% (1.064 g); Anal. Calc. for $RuC_{70}H_{63}F_4P_2BO$: C, 71.85; H, 5.42. Found: C, 71.67; H, 5.46%; IR (KBr, cm^{-1}): 1662 ν(C=O), 1062 $\nu(BF_4^-)$; Conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 118; ^{31}P{^{1}H}-NMR ($CDCl_3$) δ 35.87 and 36.88 (d, $^2J_{PP} = 20.3$ Hz) ppm; ^{1}H-NMR ($CDCl_3$) δ −0.67, 0.63 and 0.71 (s, 3H each, CH_3), 0.82–1.59 (m, 4H, CH_2), 2.02 (m, 1H, CH), 4.63 (s, 1H, CHC=O), 5.10 (m, 3H, H-1 or H-3 and H-4, H-5, H-6 or H-7), 5.42 (br, 1H, H-1 or H-3), 5.80 (s, 1H, Ru=C=CH), 5.90 (m, 5H, Ph), 6.46 (br, 1H, H-2), 6.96–7.65 (m, 37H, Ph and H-4, H-5, H-6 or H-7) ppm; ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 9.41, 18.34 and 21.20 (s, CH_3), 29.17 and 31.36 (s, CH_2), 45.14 (s, CH), 45.38 (s, *C*Me$_2$), 53.13 (s, C_γ), 56.82 (s, *C*HC=O), 59.26 (s, *C*Me), 81.50 and 81.67 (s, C-1 and C-3), 97.00 (s, C-2), 116.23 (s, C_β), 120.41 (s, C-3a and C-7a), 121.89, 124.26, 126.99 and 127.35 (s, C-4, C-5, C-6 and C-7), 127.92–147.44 (m, Ph), 217.63 (s, C=O), 342.15 (dd, $^2J_{CP} = 21.5$ and 15.0 Hz, Ru=C_α) ppm; $\Delta\delta$(C-3a,7a) = −10.29 ppm.

Following the same synthetic procedure, complex (1*S*,3*R*,4*S*)-**3** was prepared starting from a mixture of (1*S*,3*R*,4*S*)-**2** and (1*S*,3*S*,4*S*)-**2** (1.082 g, 1 mmol). Yield: 93% (1.087 g); Anal. Calc. for $RuC_{70}H_{63}F_4P_2BO$: C, 71.85; H, 5.42. Found: C, 71.72; H, 5.51%.

4.3. Synthesis of HC≡CCPh$_2$(C$_{10}$H$_{15}$O) (4)

A solution of the vinylidene complex (1*R*,3*S*,4*R*)-**3** (1.170 g, 1 mmol) in acetonitrile (30 ml) was heated

under reflux for 30 min. The solution was then evaporated to dryness and the resulting solid residue extracted with diethyl ether (ca. 50 ml) and filtered. A yellow solid containing the nitrile complex [Ru(N≡CMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (**5**) remains insoluble. The extract was evaporated to dryness and the crude product purified by column chromatography on silica gel with hexane as eluent. Evaporation of the solvent gave terminal alkyne **4** as a white solid. This compound was obtained as a non-separable mixture of two diastereoisomers in ca. 3:1 ratio. Yield: 89% (0.305 g); Anal. Calc. for $C_{25}H_{26}O$: C, 87.67; H, 7.65. Found: C, 87.76; H, 7.60%. Major diastereoisomer [(1*R*,3*S*,4*R*)-**4**] — IR (KBr, cm^{-1}): 3310 ν(≡C-H), 2113 ν(C≡C), 1740 ν(C=O); ^{1}H-NMR ($CDCl_3$) δ 0.52, 0.79 and 0.92 (s, 3H each, CH_3), 1.17–1.67 (m, 4H, CH_2), 1.93 (m, 1H, CH), 2.27 (s, 1H, ≡CH), 3.31 (s, 1H, CHC=O), 6.96–7.69 (m, 10H, Ph) ppm; ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 10.06, 21.18 and 22.03 (s, CH_3), 29.82 and 31.91 (s, CH_2), 45.34 (s, *C*Me$_2$), 48.67 (s, HC≡C*C*), 48.81 (s, CH), 56.93 (s, *C*Me), 61.55 (s, *C*HC=O), 77.54 (s, ≡CH), 87.32 (s, ≡C), 126.93, 128.14, 128.87 and 129.39 (s, CH of Ph), 146.11 and 147.03 (s, C of Ph), 213.41 (s, C=O) ppm. Minor diastereoisomer [(1*R*,3*R*,4*R*)-**4**] — IR (KBr, cm^{-1}): 3310 ν(≡C–H), 2113 ν(C≡C), 1740 ν(C=O); ^{1}H-NMR ($CDCl_3$) δ 0.58, 0.75 and 0.97 (s, 3H each, CH_3), 1.17–1.67 (m, 4H, CH_2), 1.93 (m, 1H, CH), 2.14 (s, 1H, ≡CH), 3.86 (d, 1H, $J_{HH} = 3.9$ Hz, CHC=O), 6.96–7.69 (m, 10H, Ph) ppm; ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 10.52, 18.51 and 19.76 (s, CH_3), 29.82 and 30.88 (s, CH_2), 45.83 (s, *C*Me$_2$), 49.29 (s, HC≡C*C*), 51.11 (s, CH), 58.07 (s, *C*HC=O), 60.05 (s, *C*Me), 75.56 (s, ≡CH), 86.68 (s, ≡C), 126.71, 128.14, 128.87 and 129.39 (s, CH of Ph), 144.64 and 147.75 (s, C of Ph), 213.45 (s, C=O) ppm.

Following the same synthetic procedure, a non-separable mixture (ca. 3:1 ratio) of (1*S*,3*R*,4*S*)-**4** and (1*S*,3*S*,4*S*)-**4** was prepared starting from (1*S*,3*R*,4*S*)-**3** (1.170 g, 1 mmol). Yield: 88% (0.301 g); Anal. Calc. for $C_{25}H_{26}O$: C, 87.67; H, 7.65. Found: C, 87.58; H, 7.76%.

4.4. Synthesis of vinylidene complex [Ru{=C=C(H)CPh$_2$($C_{10}H_{15}O$)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (**3**) starting from [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**6**) and HC≡CCPh$_2$($C_{10}H_{15}O$) (**4**)

To a solution of [RuCl(η^5-C_9H_7)(PPh_3)$_2$] (**6**) (0.155 g, 0.2 mmol) in 10 ml of MeOH were added $NaPF_6$ (0.067 g, 0.4 mmol) and a mixture of (1*R*,3*S*,4*R*)-**4** and (1*R*,3*R*,4*R*)-**4** (0.068 g, 0.2 mmol). The reaction mixture was stirred at r.t. for 5 h. The solvent was then removed under vacuum, the crude product extracted with CH_2Cl_2 (ca. 20 ml) 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 brown solid which was washed with diethyl ether (3 × 20 ml) and dried in vacuo. Complex **3** was obtained as a single diastereoisomer, i.e. (1*R*,3*S*,4*R*)-**3**. Yield: 88% (0.216 g); Anal. Calc. for $RuC_{70}H_{63}F_6P_3O$: C, 68.45; H, 5.17. Found: C, 68.28; H, 5.05%; IR (KBr, cm^{-1}): 1662 ν(C=O), 840 ν(PF_6^-); conductivity (acetone, 20 °C; Ω^{-1} cm^2 mol^{-1}) 107.

4.5. X-ray crystal structure determination of [Ru{=C=C(H)CPh$_2$($C_{10}H_{15}O$)}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] [(1*R*,3*S*,4*R*)-**3**]

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of cyclopentane into a saturated solution of the complex in dichloromethane. Data collection, crystal and refinement parameters are collected in Table 2. Diffraction data were recorded at 200 K on a Nonius Kappa CCD single-crystal diffractometer using Cu–K_α radiation. Crystal–detector distance was fixed at 29 mm and a total of 133 images were collected using the oscillation method, with 2° oscillation and 40 s exposure time per image. Data collection strategy was calculated with the program Collect [16]. Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack [17]. A total of 6468 reflections were collected with θ between 3° and

Table 2
Crystallographic data for [(1*R*,3*S*,4*R*)-**3**]·C_5H_{10}

Empirical formula	$RuC_{70}H_{63}F_6P_3OC_5H_{10}$
Formula weight	1298.31
Temperature (K)	200 (2)
Wavelength (Å)	1.54184
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	14.838 (2)
b (Å)	14.693 (3)
c (Å)	15.416 (4)
α (°)	90
β (°)	107.94 (5)
γ (°)	90
Volume (Å^3)	3197.5 (11)
Z	2
Density (calculated) (g cm^{-3})	1.349
Absorption coefficient (mm^{-1})	3.204
F(000)	1348
Crystal size (mm^3)	0.16 × 0.06 × 0.06
Theta range for data collection (°)	3.01–43.54
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 13$, $-13 \le l \le 13$
Reflections collected/unique	6468/4199 [R(int) = 0.0921]
Completeness to theta = 43.54°	94.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4199/1/368
Goodness-of-fit on F^2	0.971
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0893$, $wR_2 = 0.2025$
R indices (all data)	$R_1 = 0.1581$, $wR_2 = 0.2399$
Absolute structure parameter	0.02 (3)
Largest difference peak and hole (e Å^{-3})	0.529 and −0.898

44°. Unit cell dimensions were determined from 734 reflections. Multiple observations were averaged, $R_{merge} = 0.092$, resulting in 4199 unique reflections of which 2086 were observed with $I > 2\sigma(I)$. Final mosaicity was 0.55°. All data completeness was 94.1%. Intensity–error ratio for all reflections was 400:25.

Crystal structure was solved by Patterson methods, using the program DIRDIF-99 [18]. Anisotropic least-squares refinement was carried out with SHELXL-97 [19]. Only the ruthenium and phosphorus atoms were anisotropically refined. A mixture of independent and constrained refinement treated all hydrogen atoms. The final cycle of full-matrix least-squares refinement based on 4199 reflections and 368 parameters converged to a final value of $R(F^2 > 2\sigma(F^2)) = 0.089$; $wR(F^2 > 2\sigma(F^2)) = 0.202$; $R(F^2) = 0.158$; $wR(F^2) = 0.240$. Final difference Fourier maps showed no peaks higher than 0.53 and -0.90 e Å^{-3}. One strongly disordered cyclopentane molecule and hexafluorophosphate anion were isotropically refined. The absolute configuration was determined with a Flack parameter of 0.02 (3) [20].

Atomic scattering factors were taken from International Tables for X-ray Crystallography [21]. Geometrical calculations were made with PARST [22]. The crystallographic plots were made with PLATON [23]. All calculations were made at the University of Oviedo on the Scientific Computer Centre and X-Ray group DEC/AXP-computers.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 189632 for compound (1*R*,3*S*,4*R*)-**3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[10] Apparently, the tetrafluoroboric acid not only protonate **2** but also induces its *endo*/*exo* isomerization. Acid/base-catalyzed *endo*/*exo* isomerizations in 3-substituted camphor derivatives are well-documented [9].

[11] Only the hexafluorophosphate salt of **3** (see Scheme 2) gave crystals suitable for X-ray diffraction.

[12] Although the indenyl group is η^5-bonded to ruthenium, the structure shows moderate distortions of the five-carbon ring from planarity (see Δ, FA and HA values in Table 1), which are similar to those shown by analogous indenyl-ruthenium(II) vinylidene derivatives [4]. The moderate distortions toward an η^3-binding mode in the solid state appear to be maintained in solution according to the value $\Delta\delta$(C-3a,7a) = −10.29 ppm obtained from the $^{13}C\{^1H\}$-NMR spectrum: (a) R.T. Baker, T.H. Tulip, Organometallics 5 (1986) 839;
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