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Regio- and Diastereoselective Nucleophilic Additions of Lithium Enolates on the Allenylidene Complexes $[Ru\{{=}C{=}C{=}C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R = H, Ph): Synthesis of the First Chiral Keto-Functionalized (σ-Alkynyl)ruthenium(II) Complexes

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Summary: Indenylruthenium(II) allenylidene complexes undergo regioselective nucleophilic additions of lithium enolates at the C$_\gamma$ *atom of the unsaturated chain to afford keto-functionalized σ-alkynyl derivatives. Enolates derived from the chiral ketones (−)-carvone and (+)-pulegone are added regio- and diastereoselectively to give the first chiral keto-functionalized (σ-alkynyl)ruthenium(II) complexes.*

Transition-metal allenylidene complexes $[M]{=}C{=}C{=}CR_2$ are currently attracting interest either for their potential utility in organic synthesis[1] or for their physicochemical properties.[2] Despite the large number of allenylidene derivatives reported to date, the chemical reactivity of such complexes has only been sparsely investigated.[3] Nevertheless, there is ample experimental[3] and theoretical[4] evidence to conclude that the C$_\alpha$ and C$_\gamma$ atoms of the unsaturated chain are electrophilic centers, the regioselectivity of the nucleophilic additions being highly dependent on the metal fragment and nucleophile, as well as the C$_\gamma$ substituents. Thus, systematic studies of the reactivity of these metallacumulenes seem to be required in order to exploit their synthetic applications.

During the past few years, we have described[5] the synthesis of novel allenylidene complexes containing different (η^5-indenyl)ruthenium(II) moieties as metal auxiliaries and have investigated the influence of these metal fragments in the chemical behavior of the unsaturated chain.[5c,d,6] Thus, we have found that allenylidene complexes containing the $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ moiety exhibit an efficient steric protection of the C$_\alpha$ atom due to the preferred cis orientation of the indenyl group with respect to the allenylidene chain and to the presence of the bulky ancillary triphenylphosphine ligands. In contrast, the C$_\gamma$ atom is more accessible and a large variety of nucleophiles can be added at this position to yield functionalized σ-alkynyl complexes.[5b,6] Continuing with these studies, we report herein an easy entry to γ-substituted keto-alkynyl derivatives via regio- and diastereoselective carbon−carbon coupling reactions between lithium enolates and the allenylidene complexes $[Ru\{{=}C{=}C{=}C(R^1)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = Ph (**1**), H (**2**)).[5b]

As expected, complexes **1** and **2** add lithium enolates ($LiCH_2COR^2$) regioselectively at the C$_\gamma$ atom of the allenylidene chain to afford the neutral σ-alkynyl de-

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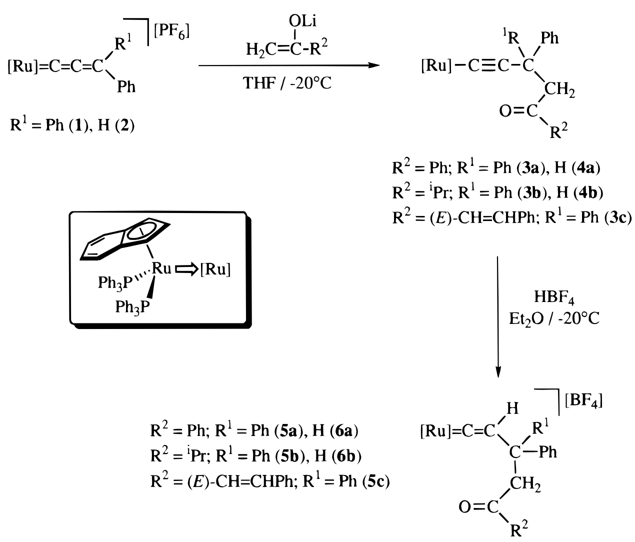
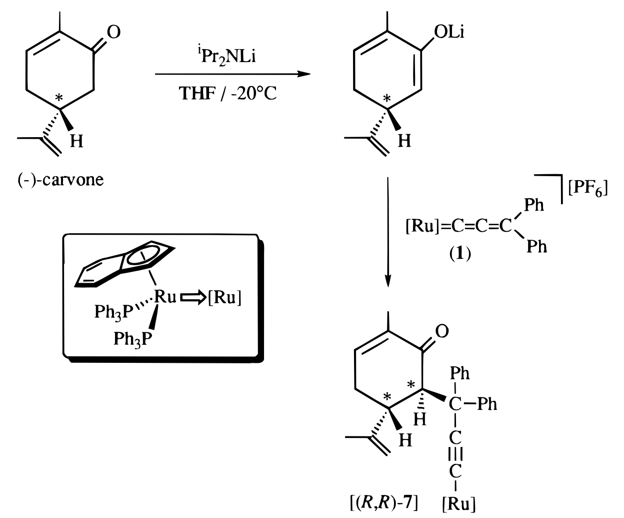
Scheme 1



Scheme 2



rivatives $[Ru\{C{\equiv}CC(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (R^1 = Ph, R^2 = Ph (**3a**), ^{i}Pr (**3b**), (*E*)-CH=CHPh (**3c**); R^1 = H, R^2 = Ph (**4a**), ^{i}Pr (**4b**); 62−83% yield) (Scheme 1). The spectroscopic properties of **3a**−**c** and **4a**,**b** are consistent with the presence of a γ-substituted keto-alkynyl chain,[7] in particular, the ν(C=O) and ν(C≡C) IR absorptions (1652−1721 and 2052−2092 cm^{-1}, respectively) and the typical chemical shifts in the $^{13}C\{^1H\}$ NMR spectrum of the Ru−C≡C and C=O carbon nuclei (δ 92.73−98.02 ($^2J_{CP}$ = 22.5−24.7 Hz, C_α), 108.84−115.24 (C_β), and 196.30−211.21 ppm (C=O)). The analogous complex $[Ru\{C{\equiv}CCPh_2(CH_2COCH_3)\}(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)]$ has been recently reported.[4b]

Addition of electrophiles at C_β of σ-alkynyl complexes has been described as one of the most versatile entries into vinylidene derivatives.[3a] Thus, the protonation of **3a**−**c** and **4a**,**b** with an excess of $HBF_4{\cdot}Et_2O$, in diethyl ether at −20 °C, leads to the formation of the monosubstituted cationic vinylidene derivatives $[Ru\{{=}C{=}C(H)C(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (R^1 = Ph, R^2 = Ph (**5a**), ^{i}Pr (**5b**), (*E*)-CH=CHPh (**5c**); R^1 = H, R^2 = Ph (**6a**), ^{i}Pr (**6b**); 82−89% yield) (Scheme 1). Analytical and spectroscopic data are in accord with the proposed formulations.[8] In particular, the presence of the vinylidene moiety was identified on the basis of (i) (^{1}H NMR) the singlet (**5a**−**c**) or doublet resonance (J_{HH} = 10.2 (**6a**) and 9.4 (**6b**) Hz) of the Ru=C=CH proton (δ 4.75−5.76 ppm) and (ii) ($^{13}C\{^1H\}$ NMR) the low-field resonance of the carbene carbon $Ru{=}C_\alpha$ (δ 342.89−344.41 ppm; $^2J_{CP}$ = 16.2−17.9 Hz). It is interesting to note that the protonation of the analogous keto-substituted alkynyl complex $[Ru\{C{\equiv}CCPh_2(CH_2COCH_3)\}(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)]$ also leads to the formation of the vinylidene $[Ru\{{=}C{=}C(H)CPh_2(CH_2COCH_3)\}(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)][BF_4]$.[4b] However, this complex has not been isolated, since in contrast to **5a**−**c** and **6a**,**b** it undergoes an intramolecular nucleophilic addition of the enol resonance form at the carbenic C_α atom to afford the unsaturated cyclic carbene complex $[Ru\{{=}CCH_2CPh_2C(H){=}C(CH_3)O\}(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)][BF_4]$.[4b,9]

The regioselective and efficient access to complexes **3a**−**c** and **4a**,**b** prompted us to use chiral enolates in order to obtain optically active (σ-alkynyl)ruthenium(II) derivatives. Thus, treatment of (*R*)-5-isopropenyl-2-methyl-2-cyclohexenone ((−)-carvone) with LDA, in THF at −20 °C, and subsequent addition of 1 equiv of the diphenylallenylidene complex $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**1**) gives the σ-alkynyl derivative **7** (61% yield) (Scheme 2).

The formation of **7** involves the generation of a second stereogenic center, but surprisingly only one diastereoisomer was detected by NMR spectroscopy.[10] Since the configuration of the new chiral carbon could not be elucidated unambiguously from the NMR data, a single-crystal X-ray structural determination was carried out.[11] The molecular structure (Figure 1) shows the typical pseudooctahedral three-legged piano-stool geometry around the ruthenium atom, which is linked to the two phosphorus atoms of the triphenylphosphine ligands in addition to a nearly linear alkynyl fragment (Ru−C(1)−C(2) = 172(1)°, C(1)−C(2)−C(3) = 172(1)°). The alkynyl chain also shows typical Ru−C(1) (2.02(1) Å) and C(1)−C(2) (1.22(2) Å) bond lengths. The indenyl ligand orientation is in a position between the formal cis and trans arrangements with respect to the hydrocarbon chain, in contrast to the cis orientation shown by the indenyl group in the precursor allenylidene complex $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**1**).[5b] The most interesting feature in this structure is the *R* configuration shown by the new stereogenic carbon atom C(100) generated in the stereoselective nucleophilic addition, which leads to the formation of the diastereoisomer R_C,R_C (**7**). This seems to be the result of the sterically

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[7] Synthesis, spectroscopic, and analytical data for complexes **3a**−**c** and **4a**,**b** have been provided as Supporting Information.

[8] Synthesis, spectroscopic, and analytical data for complexes **5a**−**c** and **6a**,**b** have been provided as Supporting Information.

(9) A related cyclization process, induced by $^nBu_4NOH$, has been recently reported to occur on the vinylidene derivative $[Ru\{{=}C{=}C(Ph)CH_2COOMe\}(\eta^5\text{-}C_5H_5)(PPh_3)_2][PF_6]$ to yield the neutral furan complex $[Ru\{C{=}C(Ph)CH{=}C(OMe)O\}(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ via initial deprotonation of the methylene group and subsequent nucleophilic addition of the resulting enol ester group to the C_α atom of the vinylidene chain: Ting, P. C.; Lin, Y. C.; Lee, G. H.; Cheng, M. C.; Wang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6433. Attempts to promote such a type of cyclization on complexes **5a**−**c** and **6a**,**b** using different bases were unsuccessful, recovering in all the cases the starting σ-alkynyl derivatives **3a**−**c** and **4a**,**b** in almost quantitative yields.

(10) For complexes **7** and **8** the $^{31}P\{^1H\}$ NMR spectra from the crude reaction mixtures confirm the formation of only one diastereoisomer.

(11) Crystal data for (*R,R*)-**7** have been provided as Supporting Information.

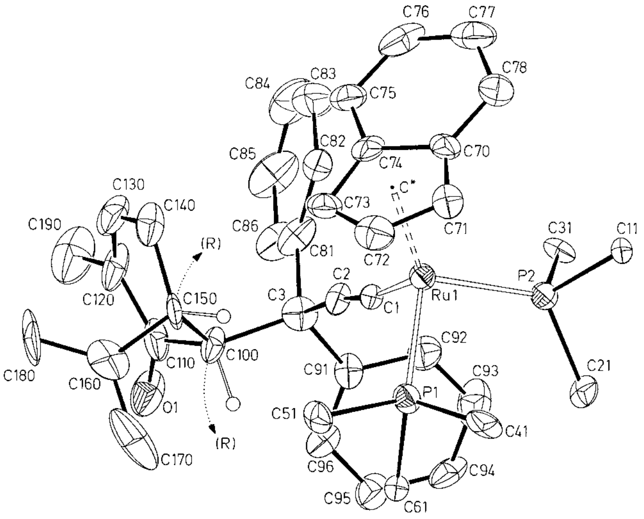
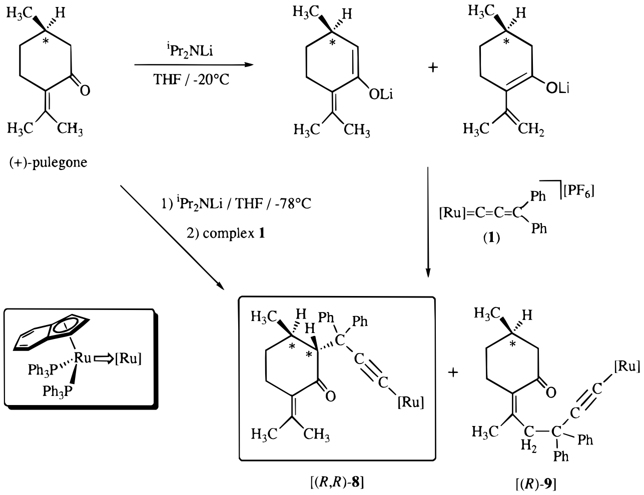


Figure 1. Molecular structure of the σ-alkynyl complex (R,R)-**7**. For clarity aryl groups of the triphenylphosphine ligands are omitted (C* = centroid of the indenyl ring). Selected bond distances (Å) and angles (deg): Ru−C* = 1.956(1), Ru−C(1) = 2.02(1), C(1)−C(2) = 1.22(2), C(2)−C(3) = 1.45(2), C(3)−C(81) = 1.60(2), C(3)−C(91) = 1.51(2), C(3)−C(100) = 1.62(2), Ru−P(1) = 2.271(4), Ru−P(2) = 2.334(3); Ru−C(1)−C(2) = 172(1), C(1)−C(2)−C(3) = 172(1), C(2)−C(3)−C(81) = 111(1), C(2)−C(3)−C(91) = 107(1), C(2)−C(3)−C(100) = 109(1), P(1)−Ru−P(2) = 96.8(1).

Scheme 3



controlled addition, since the isopropenyl group of the cyclohexenone ring is located far away from the bulky CPh_2 moiety of the alkynyl chain (see Figure 1).[12]

The nucleophilic addition of the enolate derivative of (R)-2-isopropylidene-5-methylcyclohexanone ((+)-pulegone) also proceeds in a diastereoselective manner. Thus, the treatment of (+)-pulegone with LDA, in THF at −78 °C, and subsequent addition of **1** leads to the formation of the σ-alkynyl derivative **8** (68% yield) (Scheme 3).

IR and NMR ($^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$) data confirm the presence of only one diastereoisomer.[10] We propose, in accordance with the formation of complex (R,R)-**7**, that the diastereoselectivity is also sterically controlled. Assuming in this case a steric hindrance between the methyl group of the cyclohexanone ring and the CPh_2 fragment of the σ-alkynyl chain, an analogous R,R configuration can be assigned for complex **8**. This formulation is supported by the ^1H NMR spectrum, which exhibits a doublet signal for the C*H*C=O proton at δ 3.53 ppm with a coupling constant $J_{HH} = 4.4$ Hz. This value can be compared to that found in the complex (R,R)-**7** for the analogous C*H*C=O proton ($J_{HH} = 4.8$ Hz) for which an anti conformation has been assigned unequivocally.

However, when the reaction is carried out at −20 °C, the nucleophilic addition proceeds in a different way, affording instead a mixture from which the complexes (R,R)-**8** (39% yield) and (R)-**9** (26% yield) have been separated after chromatographic workup (Scheme 3). Complex **9** has been characterized by the $^{13}C\{^1H\}$ NMR spectrum, which shows the presence of only two CH_3 groups (δ 22.63 and 24.06 ppm) and four CH_2 carbons (δ 29.34, 33.99, 47.68, and 52.53 ppm) (assigned using DEPT experiments).[10] This result can be explained by taking into account that a competitive deprotonation at CH_2 vs CH_3 of (+)-pulegone has occurred at this temperature followed by the nucleophilic addition of both anionic species to the C_γ atom of the diphenylallenylidene complex **1**.

In summary, in this work we report unprecedented examples of regio- and stereoselective additions at C_γ of an allenylidene moiety promoted by the special electronic and steric properties of the indenylruthenium(II) fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$. The following facts are of interest. (a) The first keto-functionalized vinylidene complexes $[Ru\{=C=C(H)C(R^1)Ph(CH_2COR^2)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**5a**−**c**, **6a**,**b**) have been isolated, which have proven to be reluctant toward intramolecular cyclization to give the corresponding carbene species. This is in contrast with the behavior of the analogous fragment $[Ru(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)]$, probably due to the remarkably lower electrophilicity of the $Ru=C_\alpha$ atom in the indenyl complex as well as to the more effective steric protection of the vinylidene chain.[4b,13] (b) The regio- and diastereoselective nucleophilic additions of chiral enolates yield complexes (R,R)-**7**, (R,R)-**8**, and (R)-**9**, which are to date the first reported examples of ruthenium(II) complexes containing enantiomerically pure σ-alkynyl chains. Further studies concerning the scope of these enolate additions on other ruthenium(II) allenylidene complexes[5c,d] are in progress.

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Supporting Information Available: Text giving experimental procedures and IR, $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR, and analytical data for **3**−**9** and tables of crystal structure data, positional and thermal parameters, bond lengths and angles, torsion angles, and least-squares planes for (R,R)-**7** (31 pages). Ordering information is given on any current masthead page.

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[12] The molecular model of the corresponding diasteromer R,S shows a significant steric hindrance between the isopropenyl and phenyl groups of the hydrocarbon chain.

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