conjugates were separated from excess DNA by ion-exchange HPLC starting with 20 mM Tris (pH 7.2) and then using a 0.5 % min^{-1} gradient of a solution of 20 mM Tris and 1M NaCl at a flow rate of 1 mL min^{-1}, while monitoring the UV signal at 260 and 280 nm. The 1:0.4 streptavidin:DNA mixture showed two peaks at 45 and 56 min, while the 1:1 mixture showed four peaks at 45, 56, 67, and 71 min, which correspond to the 1:1, 2:1, 3:1, and 4:1 oligonucleotide:streptavidin complexes, respectively. The 1:4 mixture showed four peaks at the same positions but with increased intensity of the third (67 min) and fourth (71 min) peaks. The HPLC chromatogram of the 1:8 streptavidin:DNA mixture showed two main peaks, one at 59 min for recovered DNA and the other at 71 min for the 4:1 oligonucleotide:streptavidin complex. In addition, a shoulder at 67 min, assigned to the 3:1 complex, was also present. Purified streptavidin–biotinylated-DNA conjugates were concentrated and dispersed in 0.3 M PBS by ultrafiltration (centricon 30). Aggregates for TEM, thermal denaturation experiments, and SAXS measurements were prepared by freezing the solution containing **1**–STV, **2**–Au, and **3** in dry ice for 10 min, and thawing to facilitate hybridization prior to the measurement.

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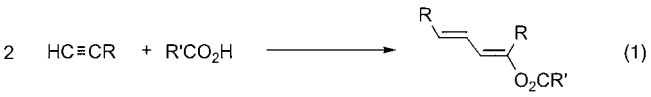
Ruthenium-Catalyzed One-Step Transformation of Propargylic Alcohols into Alkylidene Cyclobutenes: X-ray Characterization of an Ru(η^3-cyclobutenyl) Intermediate**

Jacques Le Paih, Sylvie Dérien, Christian Bruneau, Bernard Demerseman, Loïc Toupet, and Pierre H. Dixneuf*

Among unsaturated small cycles, cyclobutenes are especially useful as building-block precursors. They allow the general in situ generation of reactive functional 1,3-diene skeletons,[1] a key process for the synthesis of phytotoxic natural products[2] or polycyclic derivatives.[3] Cyclobutenes were also shown to be precursors of 1,5-dienes for access to pheromones by ring-opening catalysis.[4] The most general methods to produce simple cyclobutenes are based on the [2+2] cycloaddition of C≡C and C=C bonds, either photochemically[5] or with Lewis acids[6] and metal-based[7] catalysts, and on the zirconocene-catalyzed reaction of alkynyl halides with Grignard reagents.[8] In contrast, the access to alkylidenecyclobutenes is not straightforward and occurs by intramolecular thermal coupling of 1,5-diynes[9] or copper-mediated cyclization from 1,4-enynes.[10]

We have recently shown that the catalyst precursor [Cp*RuCl(cod)] (Cp* = C_5Me_5, cod = 1,5-cyclooctadiene) promotes the head-to-head coupling of two terminal alkynes, via a chelating biscarbene–ruthenium intermediate, which, upon addition of a carboxylic acid produces 1-acyloxybuta-1,3-dienes [Eq. (1)].[11] We now report that the same electron-rich precatalyst [Cp*RuCl(cod)] activates propargylic alcohols in a novel manner in the presence of a carboxylic acid. It leads to the one-step catalytic head-to-head cyclodimerization



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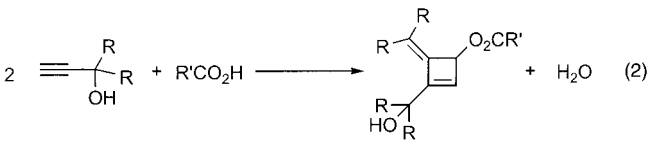
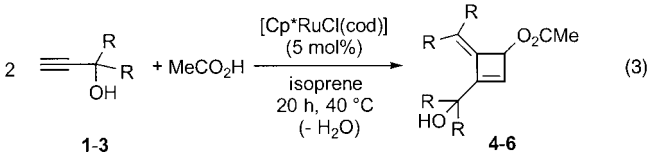
of propargyl alcohols and to the formation of alkylidenecyclobutene derivatives [Eq. (2)] via cyclobutadiene– and cyclobutenyl–ruthenium intermediates, dehydration, and carboxylate addition.



(2)

The reaction of 1,1-dimethylprop-2-ynol (**1**) with acetic acid in the presence of 5 mol% of [Cp*RuCl(cod)],[12] in isoprene as solvent at 40 °C for 20 h, affords the alkylidenecyclobutene derivative **4** in 57% yield [Eq. (3)]. Similarly, the prop-2-yn-1-ols **2** and **3** are catalytically converted into alkylidenecyclobutenes **5** (51%) and **6** (66%), respectively. The structures of compounds **4**–**6** were established by ^{1}H and ^{13}C NMR spectroscopy. A conclusive 2D NMR (NOESY) experiment showed that the alkene and methyne protons within the four-membered cycle are in the 1,2 positions.



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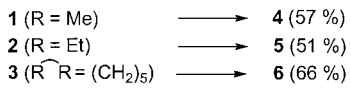
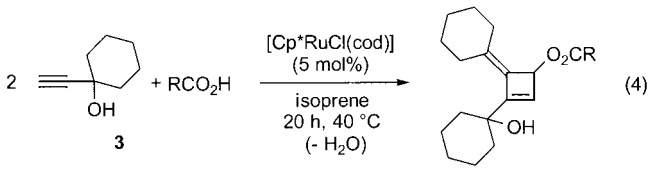


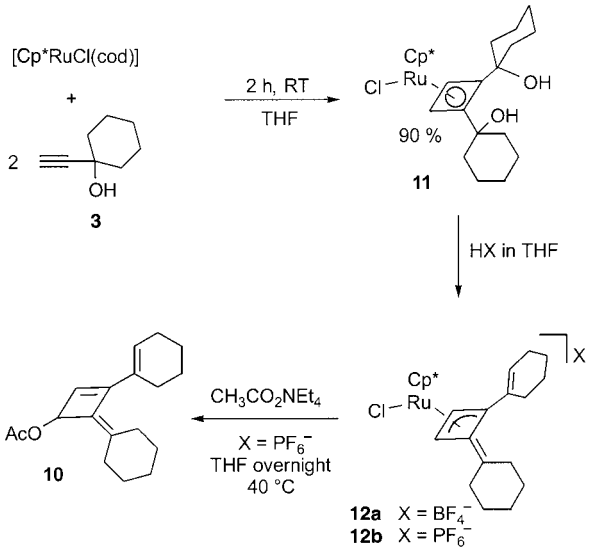
It is noteworthy that the reaction was restricted to propargylic alcohols bearing a terminal triple bond. However, the scope of the reaction was investigated in the cyclodimerization of propargyl alcohol **3** with a variety of carboxylic acids. The addition of acetic, benzoic, methoxyacetic, or pent-4-enoic acid to compound **3** in the presence of 5 mol% of catalyst [Cp*RuCl(cod)] selectively leads, under the previous conditions, to the catalytic formation of alkylidenecyclobutenes **6**–**9** isolated in 50–66% yield [Eq. (4)]. However, the reaction appears inhibited with stronger acids ($pK_a < 3.5$) such as cyanoacetic acid for which no conversion was observed.



(4)

This novel catalytic reaction formally corresponds to a regioselective head-to-head carbon–carbon coupling of the alkynes with addition of carboxylic acid and elimination of water. This reaction drastically depends on the nature of the solvent. The conversion of **3** into **6** at 40 °C for 20 h in 2 mL of the two-electron coordinating solvents tetrahydrofuran or acetonitrile was always under 5%, and only 20% in dioxane. However, this conversion significantly increased when the reaction was performed in a diene as solvent. Thus, the conversion of **3** into **6** after 20 h at 40 °C in 2 mL of 1,3-cyclohexadiene, 1,5-cyclooctadiene, or isoprene, reached 60, 65, or 80%, respectively. The use of an excess of diene shows that the cyclodimerization of the alkyne is the favored process, as no codimerization of alkyne and diene takes place, whereas it does with allyl alcohol in the absence of acid.[13]

The nature of the products **4**–**9** suggested that one key intermediate was a cyclobutadiene–ruthenium complex rather than a chelating biscarbene complex as found for other terminal alkynes.[11] To investigate the mechanism, a set of stoichiometric reactions were successively performed. The reaction of [Cp*RuCl(cod)] with 5 equivalents of ethynylcyclohexanol (**3**), but in THF, for 2 h at room temperature afforded 90% of the cyclobutadiene complex **11**[14] (Scheme 1). As no X-ray structure of **11** could be determined,



Scheme 1.

complex **11** was treated in THF at −60 °C with 1.1 equivalents of HBF_4 or HPF_6, which gave complexes **12a** and **12b**, respectively, in 90% yield (Scheme 1). The X-ray diffraction structure of single crystals of **12b** is shown in Figure 1.[15] It confirms the four-membered ring formation with the head-to-head alkyne coupling. However, it shows an unprecedented alkylidenecyclobutenyl ligand coordinated by an η^3-allyl C12-C13-C14 group (C12–C13 1.426(9), C13–C14 1.428(7), C11–C12 1.499(7), C11–C14 1.506(7) Å) and η^2-C11=C21 bond. This C11=C21 bond (1.364(8) Å) is bent 28.7° towards the metal with a strong Ru–C11 (2.194(4) Å) and a weak Ru–C21 (2.674(4) Å) interaction. The structure of complex **12b** dramatically contrasts with that of the (η^3-methylidenecyclobutenyl)Pd complex [(CH_2=C–C(*t*Bu)–C(*t*Bu)–CMe)-Pd(acac)][16] (acac = 2,4-pentanedione) for which the non-

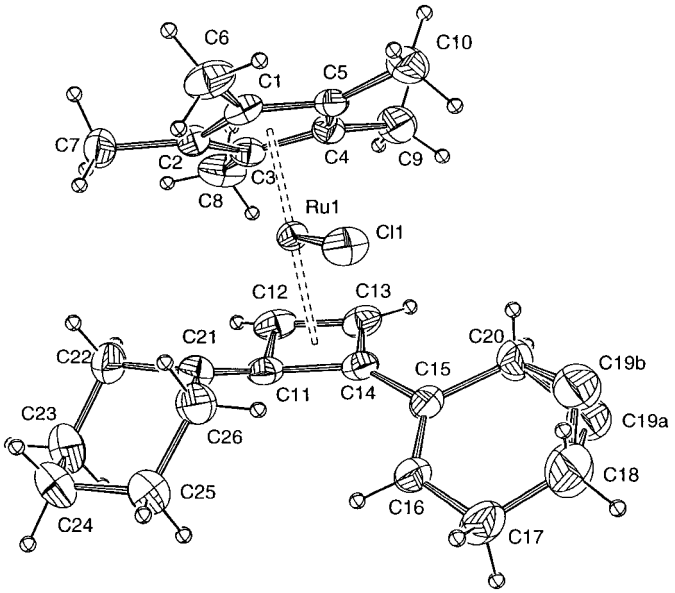


Figure 1. ORTEP drawing of the molecular structure of **12b** (thermal ellipsoids set at the 50% probability level): the PF_6 anion is omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ru-Cl 2.3845(12), Ru-C11 2.194(4), Ru-C12 2.114(4), Ru-C13 2.237(5), Ru-C14 2.315(4), C11-C12 1.499(7), C12-C13 1.426(9), C13-C14 1.428(7), C14-C11 1.506(7), C14-C15 1.448(7), C15-C16 1.330(7), C21-C11 1.364(8); C11-C12-C13 90.7(4), C12-C13-C14 92.4(5), C13-C14-C11 90.3(4), C14-C11-C12 86.6(4).

coordinated C=CH_2 bond is bent away from the palladium atom and makes an angle of 20.4° with the allyl plane.

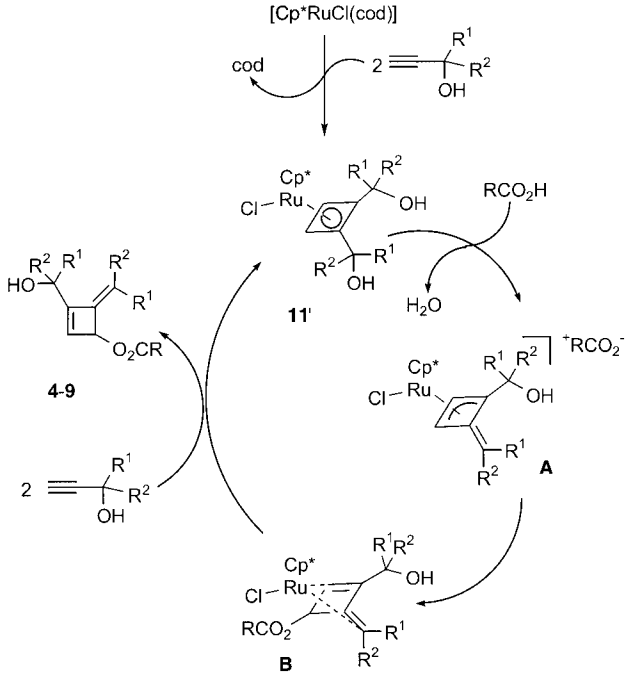
Addition of an excess of acetic acid to complex **11** in THF at 40 °C leads to the quantitative formation of derivative **6**. Complex **11** also catalyses the formation of derivative **6** under the conditions in Equation (3). Complex **12b** was also treated with 1.1 equivalents of $CH_3CO_2^-Et_4N^+$ in THF at 40 °C and 41% of derivative **10** was isolated (Scheme 1). The latter corresponds to the addition of the acetate to the nonsubstituted terminal carbon atom of the allyl group of **12b**, for example, to the dehydrated derivative of **6**.

On the basis of the nature of the isolated intermediates **11** and **12b** and on their reactivity, the realistic catalytic cycle described in Scheme 2 can be proposed. Protonation of **11′** is expected to give the cationic alkenylidenecyclobutenyl–metal intermediate **A** to which the carboxylate group adds at the unsubstituted allyl carbon giving intermediate **B**. The complexes **12a** and **12b** correspond to the dehydrated intermediate **A**.

This novel catalytic reaction constitutes a remarkable example of the combination of three molecules to afford only one high-value, multifunctional substrate with atom economy.

Experimental Section

General procedure for the catalytic synthesis of **4**–**9**: the propargylic alcohol (2.5 mmol) and the carboxylic acid (1.25 mmol) were added successively to a stirred solution of [Cp*RuCl(cod)] (0.125 mmol, 47 mg) in isoprene (2 mL) under a nitrogen atmosphere. The reaction mixture was then heated at 40 °C for 20 h. The solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel with a diethyl ether/pentane mixture as eluent. The isolated yields are based on the propargylic alcohol. All compounds were fully characterized by spectroscopic methods (see Supporting Information). Selected data for



Scheme 2. Catalytic cycle.

6: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.4-1.75$ (m, 17H, cyclohexyl CH_2 + OH), 2.01 (s, 3H, Me), 1.96–2.08 (m, 2H, cyclohexyl CH_2), 2.37–2.47 (m, 2H, cyclohexyl CH_2), 5.59 (d, 1H, $J = 0.5$ Hz, CH), 6.27 (s, 1H, =CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 21.2$ (Me), 21.6, 21.7, 25.5, 26.4, 27.7, 27.9, 30.8, 31.4, 35.6, 35.8 (CH_2), 69.4 (C–OH), 72.4 (CH–O), 127.8 (=C), 129.3 (=C), 130.7 (=CH), 162.0 (=C), 171.3 (C=O); high resolution MS *m*/*z* calcd for [M^+] ($C_{18}H_{26}O_3$): 290.1882; found 290.1879.

11: 5 equivalents of 1-ethynylcyclohexanol (**3**; 3.7 mmol, 460 mg) were added to a solution of [Cp*RuCl(cod)] (0.74 mmol, 282 mg) in THF (10 mL) under a nitrogen atmosphere. After stirring at room temperature for 2 h the solvent was removed under vacuum, the solid residue was washed with anhydrous diethyl ether (3 × 15 mL), and dried under vacuum. The complex **11** was obtained as a brown powder (350 mg, 90%). ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 0.94-1.09$ (m, 4H, cyclohexyl CH_2), 1.30–1.65 (m, 14H, cyclohexyl CH_2), 1.68 (s, 15H, C_5Me_5), 2.08–2.14 (m, 2H, cyclohexyl CH_2), 3.42 (s, 2H, =CH), 3.93 (s, 2H, OH); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 10.5$ (C_5Me_5), 21.7, 21.9, 25.8, 36.0, 42.2 (cyclohexyl CH_2), 69.4(C–OH), 69.8 (=CH), 92.5 (=C), 99.6 (C_5Me_5); IR (nujol): $\tilde{\nu} = 1654$, 3403, 3443 cm^{-1}; high resolution MS *m*/*z* calcd for [M^+] ($C_{26}H_{39}O_2ClRu$): 520.1686; found 520.1660.

12a and **12b**: 1.1 equivalents of acid HX (HBF_4 or HPF_6) were added to a solution of complex **11** (1 mmol, 520 mg) in THF (20 mL) under nitrogen atmosphere at −60 °C. The stirred reaction mixture was allowed to warm to room temperature and kept at this temperature for 3 h. The solvent was removed under vacuum, the solid washed with diethyl ether (3 × 15 mL) and dried under vacuum. For **12a** a solution of HBF_4 (155 μL; 60% w/w in diethyl ether) was used and **12a** was obtained as a dark red powder (510 mg, 90%). ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 1.46-1.58$ (m, 14H, cyclohexyl CH_2), 1.83–1.90 (m, 2H, cyclohexyl CH_2), 1.83 (s, 15H, C_5Me_5), 2.23–2.29 (m, 2H, cyclohexyl CH_2), 5.06 (s, 1H, =CH), 5.56 (s, 1H, =CH), 6.05 (t, 1H, $J = 4$ Hz, cyclohexenyl =CH); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta =$ 10.6 (C_5Me_5), 21.5, 21.8, 24.2, 25.6, 26.3, 28.8, 31.4, 33.9, 35.9 (CH_2), 77.6, 86.8 (=CH), 93.5, 103.8, 128.9, 134.7 (=CH), 140.2 (=CH), 149.1 (=C); IR (nujol): $\tilde{\nu} = 1041$, 1559, 1632, 3095 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{36}RuClBF_4$: C 54.60, H 6.34, Cl 6.19; found: C 54.25, H 6.77, Cl 6.32.

For **12b** a solution of HPF_6 (175 μL, 60% w/w in water) was used and **12b** was obtained as a dark red powder (570 mg, 90%). ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 1.46-1.59$ (m, 14H, cyclohexyl CH_2), 1.83–1.90 (m, 2H, cyclohexyl CH_2), 1.82 (s, 15H, C_5Me_5), 2.24–2.30 (m, 2H, cyclohexyl CH_2), 4.89 (s, 1H, =CH), 5.48 (s, 1H, =CH), 6.06 (t, 1H, $J = 4$ Hz, cyclohexenyl =CH); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 10.6$ (C_5Me_5), 21.4, 21.7, 24.2, 25.6,

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26.3, 28.9, 31.5, 34.0, 35.4 (CH_2), 77.3, 86.3 (=CH), 93.4, 103.8, 128.8, 135.3 (=C), 140.7 (=CH), 149.3 (=C); IR (nujol): $\tilde{\nu} = 844$, 1561, 1630, 3103 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{36}RuClPF_6$: C 49.57, H 5.76, Cl 5.63; found: C 49.23, H 5.50, Cl 6.27. Microcrystals of complex **12b** were obtained in a dichloromethane/diethyl ether biphasic system.

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[14] The NMR spectra with a single resonance (^1H) at $\delta = 3.42$ and a single resonance (^{13}C) at $\delta = 69.8$ for the alkenyl unit of the cycle show the symmetry of the complex **11**.

[15] Crystal structure analysis: $RuClC_{26}H_{36} \cdot PF_6$, $M_r = 630.04$, monoclinic, *I2/a*, $a = 22.704(1)$, $b = 11.221(1)$, $c = 23.530(2)$ Å, $\beta = 114.57(1)$, $V = 5451.8(7)$ Å^{-3}, $Z = 8$, $\rho = 1.535$ Mg m^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 7.86$ cm^{-1}, $F(000) = 2576$, $T = 293$ K. The crystal, dimensions $0.37 \times 0.27 \times 0.23$ mm was studied on a NONIUS Kappa CCD diffractometer with graphite monochromatized $Mo_{K\alpha}$ radiation. The cell parameters are obtained with 10 frames (psi rotation: 1° per frame). The data collection (Nonius, 1999) ($2\theta_{max} = 60°$, 176 frames (117 via 1.6° phi rotation and 16 s per frame, 52 via 1.6° omega rotation) range *hkl*: *h* −25.29, *k* 0.14, *l* −25.30) gives 22884 reflections. The data reduction leads to 6103 independent reflections from which 4681 with $I > 2.0\sigma(I)$. The absorption correction is made with a faces indexed crystal. The structure was solved with SIR-97 which reveals the non-hydrogen atoms of the cation and the anion. One atom (C19) of the cyclohexene ring appears disordered between two positions. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL 97 by the full-matrix least-square techniques (use of F^2 magnitude; *x*, *y*, *z*, β_{ij} for Ru, Cl, P, C, and F atoms, *x*, *y*, *z* in riding mode for H atoms ; 316 variables and 4681 observations with $I > 2.0\sigma(I)$; calcd $w = 1/[\sigma^2(F_o^2) + (0.122P)^2 + 10.23P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.058$, $R_w = 0.169$ and $S_w = 1.024$ (residual $\Delta\rho < 1.37$ e Å^{-3}). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160045. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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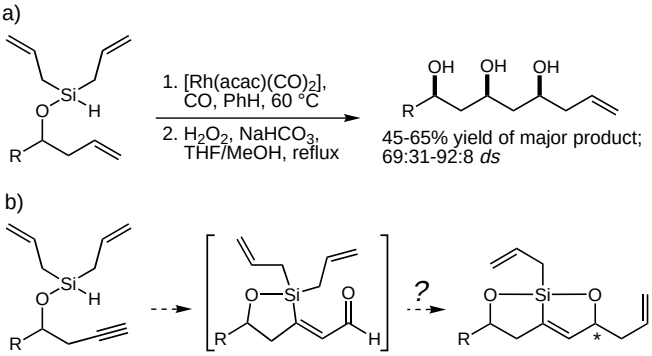
Tandem Intramolecular Alkyne Silylformylation – Allylsilylation: A Case of Remote 1,5-Asymmetric Induction**

Steven J. O'Malley and James L. Leighton*

Dedicated to Professor David A. Evans on the occasion of his 60th birthday

As part of a program dedicated to the development of stereoselective catalytic methods for the synthesis of polyols, we have recently reported the tandem intramolecular silylformylation – allylsilylation of alkenes (Scheme 1a).[1, 2] Alkynes are well-known substrates for silylformylation,[3] and it seemed plausible that tandem allylsilylation of the resultant unsaturated aldehydes might occur as well (Scheme 1b). Interestingly, in this system the silicon-substituted carbon atom is no longer stereogenic. Thus, any diastereoselectivity



Scheme 1. a) Tandem alkene silylformylation – allylsilylation and b) proposed tandem alkyne silylformylation – allylsilylation. Hacac = acetylacetone.

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