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Coupling of Propargylsilanes with α,β-Unsaturated Fischer Carbene Complexes: A New Synthesis of 1,3,5-Trienes

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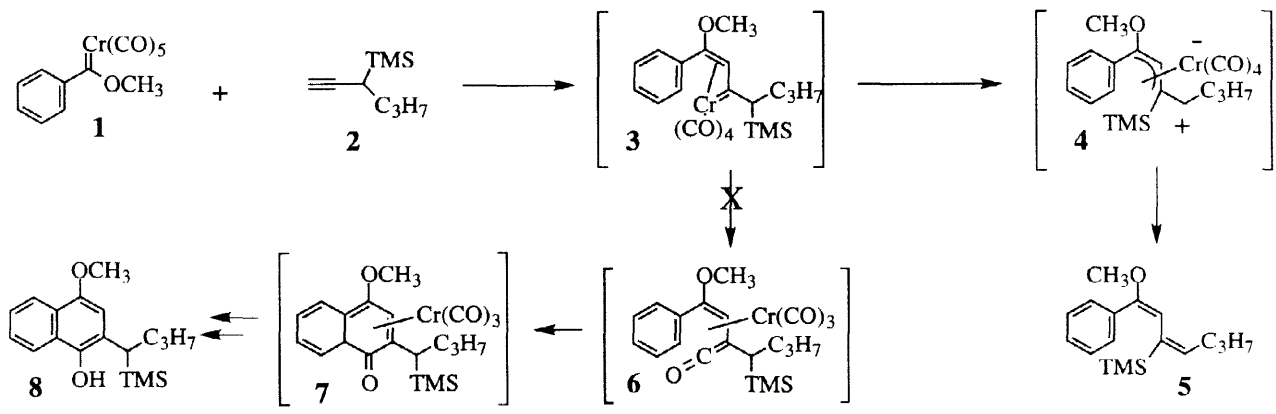
Abstract: The reaction of propargylsilanes with α,β-unsaturated Fischer carbene complexes has been investigated. The reaction provides 1,3,5-triene derivatives. Simple benzannulation involving the alkyne functionality of the propargylsilane does not appear to be a competitive reaction pathway in most cases.

Recently, the synthesis of conjugated dienes via the coupling of propargylsilanes and Fischer carbene complexes was reported (Scheme 1).[1] Reaction of phenylcarbene complex **1** with propargylsilane **2** afforded conjugated diene **5** (major stereoisomer depicted)[2] and not benzannulation (Dötz reaction)[3] product **7**. The mechanism for the diene synthesis involves formation of zwitterionic compound **4** through a 1,2-shift of silicon[4] in initially-produced vinylcarbene complex intermediate **3**, followed by decomplexation. Benzannulation would occur if vinylcarbene complex **3** underwent a CO-insertion to form vinylketene complex **6**, followed by subsequent electrocyclic ring closure, enolization, and decomplexation. Selectivity for formation of the diene has been attributed to a kinetic preference for silicon migration in vinylcarbene intermediate **3**.

Scheme 1



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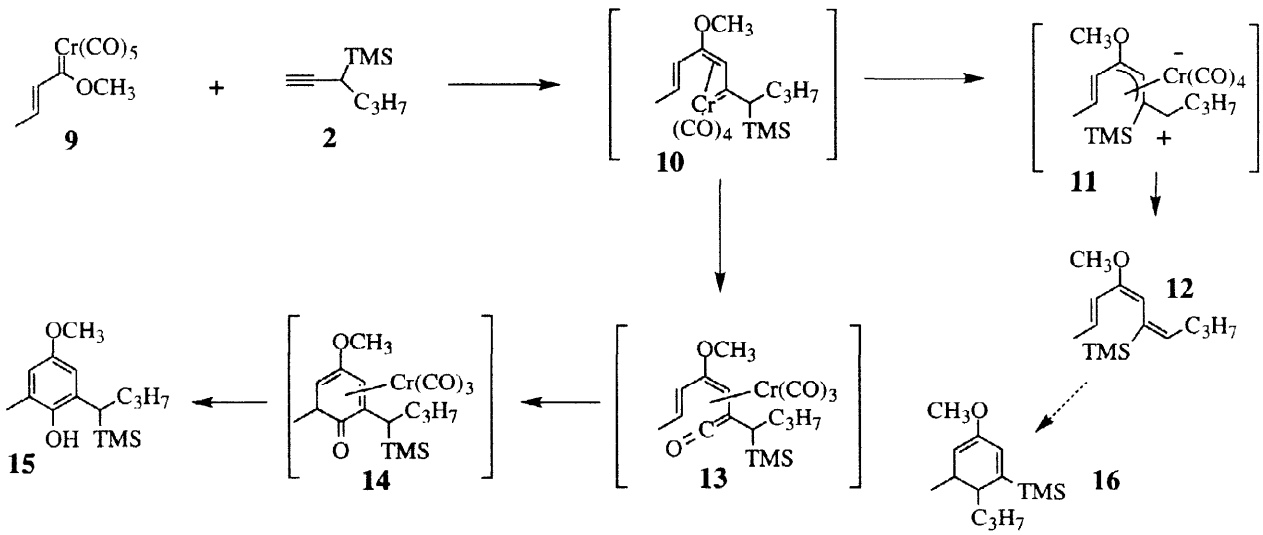
This manuscript focuses on the reaction of alkenylcarbene complexes with propargylsilanes (Scheme 2), which in theory can produce either conjugated trienes (*e.g.* **12**) or benzannulation products (*e.g.* **15**).[5] Although the benzannulation event should be more favorable for alkenylcarbene complexes (**13** → **14**) than for arylcarbene complexes (**6** → **7** of Scheme 1),[6] this step of the reaction occurs long after the proposed point of divergence, intermediate vinylcarbene complex **10**. The conjugated trienes produced in this reaction could prove to be very useful for the synthesis of six-membered ring derivatives. Conjugated trienes which possess the cis divinyl substitution pattern about the central double bond (*e.g.* **12**) can undergo electrocyclic ring closure processes (**12** → **16**), forming cyclohexadiene derivatives.[7] The overall transformation of propargylsilane **2** and propenylcarbene complex **9** to cyclohexadiene **16** would constitute a formal [3+3]-cycloaddition process.[8]

Scheme 2

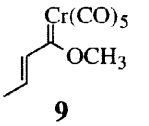
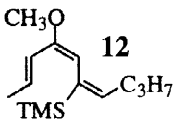
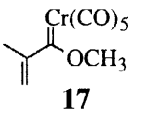
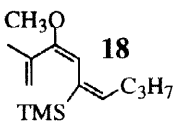
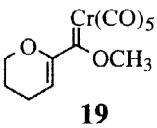
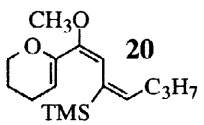
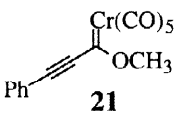
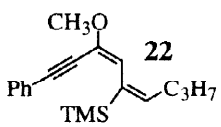


The reaction of carbene complex **9** (pure trans isomer) with propargylsilane **2** afforded triene **12** in 70% yield as a 5:1:1 mixture of stereoisomers; hypothetical benzannulation product **15** was not detected in the crude reaction mixture. The stereochemistry of the major isomer of triene **12** was assigned as EEE (depicted); assignments were based on the studies in reference 1. A similar reaction using complex **9** (2:1 trans:cis mixture) and propargylsilane **2** led to a mixture of at least five stereoisomers of **12**. A variety of alkenyl-carbene complexes were coupled with propargylsilane **2**; the results are presented in Table 1. For the reactions in the Table, benzannulation does not appear to be a competing process. The major product in all cases was assigned as the EE isomer (by analogy to reference 1), which constitutes at least 69% of the reaction mixture. Conjugated dienynes can be synthesized using alkynylcarbene complexes (Entry D) . Alkynylcarbene complex **21** was thermally unstable, and very few examples of the coupling of alkynes with alkynylcarbene complexes have been reported.[9] Successful coupling in this case might be due to the nucleophilicity of propargylsilanes.

The intramolecular coupling of a propargylsilane with an alkenylcarbene complex generated *in situ* from a two-alkyne coupling sequence[10] was also tested (Scheme 3). Treatment of diyne derivative **23**[11] with methylcarbene complex **24** afforded only benzannulation product **31** (20% yield) and not the expected triene **28**. Selective reaction of the carbene complex with the less substituted alkyne affords vinylcarbene complex **25**, which then couples with the second alkyne group, forming dienylcarbene complex **26**. Since benzannulation is the preferred pathway, either the CO insertion step (**26** → **29**) is accelerated, or the silicon

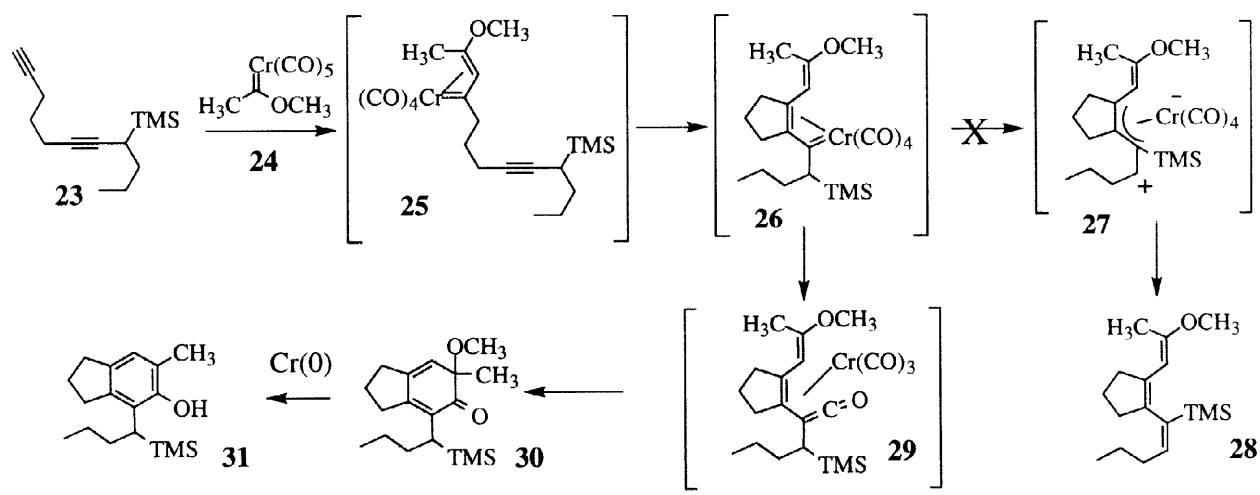
migration step (**26** → **27**) is retarded. Since electron-donating groups retard CO-insertion processes for carbene complexes,[12] the CO-insertion step for intermediate vinylcarbene complex **26** is anticipated to be faster than for intermediate **3** of Scheme 1 or **10** of Scheme 2 since the electron-donating methoxy group is located further away from the carbene complex functionality.

Table 1. Synthesis of Conjugated Trienes via Coupling of Alkenylcarbene Complexes with Propargylsilane **2**.

Entry	Carbene Complex[a]	Conjugated Triene[b]	Yield[c]	Stereochemistry[d]
A	 *e* **9**	 **12**	70%	72: 14: 14
B	 *e* **17**	 **18**	72%	69: 25: 6
C[f]	 *h* **19**	 **20**	79%	84:16
D	 **21**	 **22**	40%	70: 23: 7

[a]Carbene complexes were prepared from the corresponding organolithium reagents using a literature procedure.[13] [b]The major stereoisomer is the one depicted. [c]Combined yield of all alkene stereoisomers. [d]The major isomer was the E,E isomer; the minor isomer(s) was assumed to differ from the major isomer in the configuration at one (not both) double bond. [e]The requisite organolithium reagent was prepared via a halogen-metal exchange reaction using the appropriate alkenyl halide. [f]For a procedure, see reference 14. [g]The requisite organolithium reagent was prepared by deprotonation of dihydropyran.[13]

Scheme 3



In summary, a general synthesis of conjugated triene derivatives has been presented. Benzannulation is not competitive with the triene synthesis except for the highly-specialized case noted in Scheme 3. We are presently examining ring closure processes for the trienes produced in these studies.

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6 . This has been demonstrated in a mechanistically similar process involving metal carbonyl-induced ring expansion of cyclopropenes. Semmelhack, M.F.; Ho, S.; Cohen, D.; Steigerwald, M.; Lee, M.C.; Lee, G.; Gilbert, A.M.; Wulff, W.D.; Ball, R.G. *J. Am. Chem. Soc.* **1994**, *116*, 7108-7122.

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11. This compound was prepared by coupling the lithium salt of alkyne **2** with 5-iodo-1-pentyne. This lithium salt *must* be generated by treatment of the dianion of 1-hexyne with one eq of chlorotrimethylsilane and not from lithiation of **2**. Hommes, H.; Verkruijsse, H.D.; Brandsma, L. *Rec. Trav. Chim.* **1980**, *99*, 113-114.

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14. A solution of carbene complex **19** (0.302 g, 1.00 mmol) and propargylsilane **2** (0.414 g, 2.65 mmol) in THF (100 mL) was heated at reflux for a 6h period. The reaction mixture was cooled to 25 °C and hexane (10 mL) was added. The green solution was filtered through Celite and washed with 4:1 hexane: ethyl acetate. After removal of the solvent on a rotary evaporator, the residue was purified by Flash Chromatography on silica gel (prewashed with 1% triethylamine in hexane) using 9:1 hexane: ethyl acetate. A single fraction was isolated (0.220 g, 79%) and identified as an 84:16 mixture of stereoisomers. Further purification using preparative TLC and partial band cutting provided a pure sample of the major stereoisomer. ^{1}H NMR ($CDCl_3$): δ 5.65 (dt, 1 H, J = 6.7, 2.0 Hz), 5.13 (br s, 1 H), 4.90 (t, 1 H, J = 3.9 Hz), 3.96 (t, 2 H, J = 5.1 Hz), 3.58 (s, 3 H), 2.05 (m, 2 H), 1.77 (m, 2 H), 1.75 (m, 4 H), 1.37 (m, 2 H), 0.88 (t, 3 H, J = 7.2 Hz), 0.03 (s, 9 H); ^{13}C NMR ($CDCl_3$): δ 148.3, 142.6, 140.6, 137.7, 102.9, 101.8, 66.0, 55.3, 32.3, 22.2, 22.0, 20.4, 13.9, -1.0; MS (EI): 280 (M), 265, 251, 237, 207; HRMS: calcd for $C_{16}H_{28}O_2Si$ 280.1859, found 280.1869.