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Reaction of Propargylsilanes with Chromium Carbene Complexes: Synthesis of Conjugated Diene Enol Ethers through a Tandem Alkyne Insertion−1,2-Silicon Shift Process

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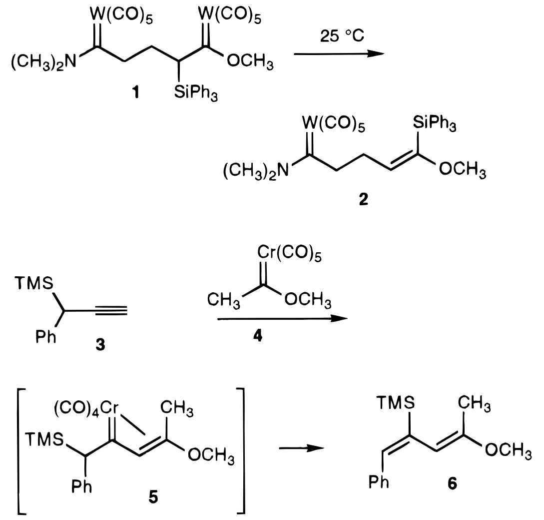
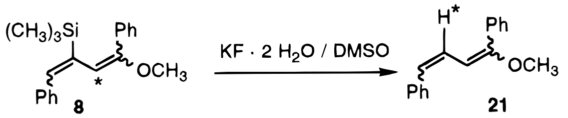
Scheme 1



Scheme 2



It has long been recognized that Fischer carbene complexes containing an α-silicon group (*e.g.*, **1**, Scheme 1) are relatively unstable.[1] Attempts to prepare this class of compounds often result in the synthesis of vinylsilanes (*e.g.*, **2**) and not stable carbene complexes. On the basis of these observations, it was predicted that carbene complex **5**, obtained from regioselective insertion of propargylsilane **3** into carbene complex **4**,[2] would spontaneously undergo this silicon migration process and afford the conjugated diene derivative **6**.[3] Examination of this reaction process is the subject of this paper.

The reaction of methylcarbene complex **4** and propargylsilane **3** in dioxane at 100 °C afforded conjugated diene **6** in 78% yield as a 67:22:11 mixture of diene stereoisomers. The scope and limit of the diene synthesis was tested using other carbene complexes and propargylsilanes; the results are presented in Table 1. In all cases tested, the diene was the exclusive product of the reaction. The reaction proceeds equally well when either an aryl group (entries A−D) or an alkyl group (entries E−G) is at the propargyl position of the silane. In cases where either a phenylcarbene or cyclopropylcarbene complex is employed (entries B, C, E, and F), well-established annulation processes[4,5] might conceivably compete with the diene synthesis; however, this process was not observed. The reaction of carbene complex **13** with propargylsilane **3** (entry D) produced only diene **14** with no competition from intramolecular Diels−Alder or cyclopropanation processes.[6]

In all of the cases, the enol ether of the major product was of the *E* configuration. This assignment was based on chemical shift comparisons of the asterisked carbon in the major and minor stereoisomers (Scheme 2); this carbon of the *E* enol ether is usually 10−20 ppm upfield relative to the same carbon in the Z isomer.[7] Formation of *E* enol ethers from the coupling of alkynes and chromium carbene complexes has ample precedent.[8] Assignment of the vinylsilane configuration was based upon fluoride-induced protiodesilylation studies of diene **8**; this process has been reported to proceed with retention of configuration.[9] Treatment of diene **8** (3:2:1 mixture of stereoisomers) with potassium fluoride dihydrate in DMSO at 40 °C afforded a similar ratio of desilylated dienes **21**. The asterisked proton was a triplet ($J = \sim 11$ Hz) in the major and minor isomers and a doublet of doublets ($J = 15.6, 10.8$ Hz) in the second most abundant stereoisomer. This implies that the original vinylsilane was of the *Z* configuration in the major and minor stereoisomers and of the *E* configuration in the second-most abundant stereoisomer. Similar stereochemical features were attributed to the major isomers of the other examples in Table 1. The *E* geometry of the vinylsilane is predicted based upon similar reactions where a carbene complex is transformed into an alkene via silicon or hydrogen migration.[1,10]

In summary, synthesis of dienes from propargylsilanes and carbene complexes is a general and efficient process. The key step of the reaction, migration of a trimethylsilyl group to an electrophilic center, is apparently a very facile process that occurs in preference to other well-established reaction pathways for vinylcarbene complex intermediates. Further examination of the synthetic potential of the new diene synthesis is currently underway in these laboratories.

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[1] For recent references, see: Macomber, D. W.; Madhukar, P.; Rogers, R. D. *Organometallics* **1992**, *10*, 2121−2128.

[2] For a recent review of carbene complexes, see: Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 1065−1113.

[3] Similar 1,2-alkyl shifts of electrophilic carbene complexes are well-documented. (a) Bly, R. S.; Bly, R. K.; Hossain, M. M.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.* **1988**, *110*, 7723−7730. (b) Zora, M.; Herndon, J. W. *J. Org. Chem.* **1994**, *59*, 699−701.

[4] For a recent example of benzannulation using arylcarbene complexes and alkynes, see: Bao, J.; Wulff, W. D.; Fumo, M. J.; Grant, E. B.; Heller, D. P.; Whitcomb, M.C.; Yeung, S.-M. *J. Am. Chem. Soc.* **1996**, *118*, 2166−2181.

[5] For five-membered ring annulation using cyclopropylcarbene complexes and alkynes, see: Tumer, S. U.; Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 8394−8404.

[6] (a) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736−744. (b) Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113−3121.

[7] Strobel, P.; Andrieu, C. G.; Paquer, D.; Vazeaux, M.; Pham, C. C. *Nouv. J. Chim.* **1980**, *44*, 101−107.

[8] McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346−2360.

[9] Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1980**, *102*, 5004−5011.

[10] (a) Söderberg, B. C.; Turbeville, D. M. *Organometallics* **1991**, *10*, 3951−3953. (b) Harvey, D. F.; Neil, D. A. *Tetrahedron* **1993**, *49*, 2145−2150.

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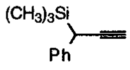
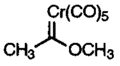
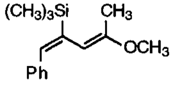
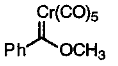
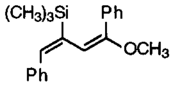
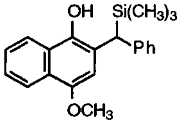
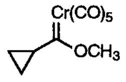
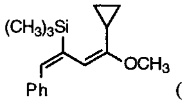
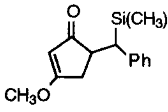
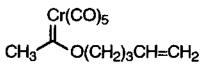
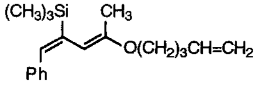
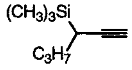
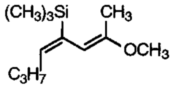
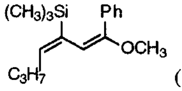
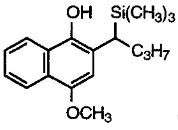
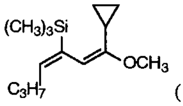
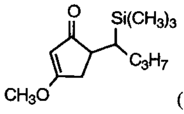
Table 1. Scope of the Synthesis of Dienes from Carbene Complexes and Propargylsilanes

Entry	Propargylsilane	Carbene Complex	Product, Yield[a] (Isomer Ratio)[b,c]	Hypothetical Annulation Product
A	 **(3)**	 **(4)**	 **(6)** 78% (63:19:18)	
B	**3**	 **(7)**	 **(8)** 82% (63:20:17)	 **(9)**
C	**3**	 **(10)**	 **(11)** 80% (83: 17)	 **(12)**
D	**3**	 **(13)**	 **(14)** 90% (77:23)	
E	 **(15)**	**4**	 **(16)** 85% (76:15:9)	
F	**15**	**7**	 **(17)** 75% (56:25:19)	 **(18)**
G	**15**	**10**	 **(19)** 90% (76:15:9)	 **(20)**

[a] The yield refers to the combined yield of all diene stereoisomers; complete separation of all isomers was not possible in most cases. [b] The major isomer was the *E*,*E* isomer as depicted. [c] The minor isomer(s) was assumed to differ from the major isomer in the configuration at one (not both) double bond.

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Supporting Information Available: Procedures for the synthesis of propargylsilanes and for the coupling of propargylsilanes with carbene complexes. Characterization data for compounds **3**, **6**, **8**, **11**, **14**–**17**, **19**, and **21** (6 pages).

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