recombination in PFD is at least 200 times faster than in CH, while cage escape in PFD is only 6 times slower than in CH.[35] Another possible cause of lower quantum yields is the variation in the decay pathways of the excited state of $Cr(CO)_6$ with solvent changes.[36] While we cannot exclude this possibility, it seems unlikely to be a major contribution to quantum yield differences, since PFD and PFH would be expected to give the same quantum yields (Table I). We conclude that the low quantum yield in PFD can be attributed primarily to a faster rate of cage recombination.

Inspection of the quantum yields reported by Wieland and van Eldik and our yields for DCE reveals deviations from the "$^2/_3$ rule" for "reactive" solvents of low viscosity. Wieland and van Eldik pointed out that the deviations cannot be explained by variations in viscosity. The quantum yields are significantly larger for some solvents and smaller for others. The differences are likely due to differences in microscopic properties of the solvent and how they contribute to the interaction with $Cr(CO)_5$. As an example, we wish to speculate about one possible contribution to the differences in quantum yields. In terms of the Turner and Poliakoff model, yields higher than $^2/_3$ may indicate occasional solvent intervention when the $Cr(CO)_5$ reopens to face the CO, and the lower yields indicate the solvent cannot completely trap $Cr(CO)_5$ even when it opens toward the solvent. Therefore, it is not just a matter of whether $Cr(CO)_5$ faces CO or solvent; CO's ultimate escape is also determined by how efficiently a cage solvent molecule can collapse to trap $Cr(CO)_5$ (as in the case of PFD). Wieland and van Eldik obtained quantum yields in short-chain alkanes that were larger than that for CH. This might be attributed to the availability of methyl groups that are sterically less demanding and more mobile than a methylene. An analogous argument may explain the relative quantum yields in PFD and PFH. Further studies of aromatic and halogenated compounds are in progress.

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(35) The rate constant for cage escape follows the form $k = a/\eta$, where a is a constant dependent on the size of the diffusing species.[14a]
(36) We thank a reviewer for this suggestion.

Platinum-Catalyzed Hydrosilylation of Alkynes

Larry N. Lewis,* Karen G. Sy, Garold L. Bryant, Jr., and Paul E. Donahue

GE Research and Development, Schenectady, New York 12301

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The reaction of terminal alkynes with several SiH compounds was investigated. The alkynes included phenylacetylene and 1-pentyne. Silanes investigated were triphenylsilane, diphenylmethylsilane, phenyldimethylsilane, triethylsilane, and triethoxysilane. All the reactions were catalyzed by highly active platinum catalysts. Comparison of product yields to those of reactions with other platinum catalysts and with rhodium catalysts were made in a few cases. Comprehensive analysis of product distribution and structure was made by GC and ^1H and ^{13}C NMR spectroscopy (APT and HETCOR). Further structural confirmation was achieved with single-crystal X-ray structures for *trans*-$Ph_3SiCH{=}C(H)Ph$ (1-trans) and for $Ph_3Si(Ph)C{=}CH_2$ (1-α). Compound 1-trans, $C_{26}H_{22}Si$, was monoclinic, $P2_1$, with a = 7.410 (6) Å, b = 11.349 (8) Å, c = 12.594 (10) Å, β = 99.43 (6)°, and Z = 2. Compound 1-α, $C_{26}H_{22}Si$, was monoclinic, $P2_1/c$, with a = 10.121 (7) Å, b = 10.225 (6) Å, c = 20.116 (11) Å, β = 93.03 (5)°, and Z = 4.

Introduction

The hydrosilylation reaction (eq 1) is remarkable in its speed and selectivity. Typically, in the presence of parts

$$R_3SiH + H_2C{=}CHR' \xrightarrow{\text{catalyst}} R_3SiCH_2CH_2R' \quad (1)$$

per million of catalyst, SiH containing compounds add to terminal olefins at or slightly above room temperature in minutes or a few hours. In addition, hydrosilylation is a selective reaction, generally giving >98% "β addition" (as shown in eq 1).[1-7] The mechanism and nature of the catalytic species in this reaction have recently been investigated by these laboratories.[8-11]

As described by us[9] and others,[1,2,4,6] several metals catalyze the hydrosilylation reaction but rhodium and platinum are the most active. The type of platinum compound that would generate the highest activity is one in which reduction to or formation of a single Pt^0 atom and concomitant loss of ligands are facile.[8,11] The most active catalysts are therefore Pt^0L_x complexes where L is olefinic and least active catalysts are Pt^{II} or Pt^{IV} complexes with strongly binding ligands such as phosphines, amines, and sulfides.

As we[8,9] and others[2,4,6] have discussed, the rate and selectivity of hydrosilylation is adversely affected by certain

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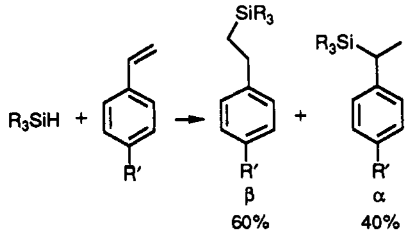
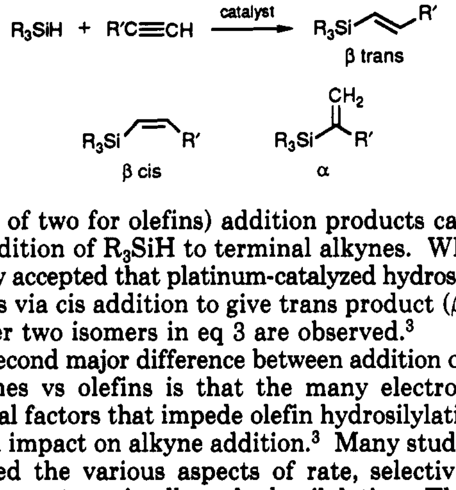
combinations of R_3SiH and/or unsaturated groups. For example, addition of a variety of R_3SiH compounds to styrenes gives a 60:40 mixture of β and α products (eq 2) as opposed to the high selectivity for β addition normally achieved with other olefins.



(2)

We have also shown that the electronic nature of the groups R and R′ (eq 1) affect the rate of hydrosilylation; electron-withdrawing R and electron-donating R′ dramatically enhance the rate of the reaction.[8] Finally, it is well-known that internal double bonds and substituted double bonds are reluctant to add R_3SiH; e.g., cyclohexene will not add R_3SiH under normal conditions.[4,6]

The hydrosilylation of alkynes has been discussed in several reviews.[1,2,4,6] The higher rate of addition of R_3SiH to alkynes vs olefins was recognized soon after Speier's work made "homogeneous"-catalyzed hydrosilylation a routine synthetic reaction.[6,12-15] In addition to the higher rates, two other aspects of alkyne hydrosilylation distinguish it from olefin hydrosilylation. The first difference is the additional complexity due to stereochemistry vis-a-vis olefins. For example, as shown in eq 3, three possible



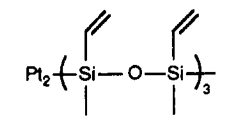
(3)

(instead of two for olefins) addition products can result from addition of R_3SiH to terminal alkynes. While it is generally accepted that platinum-catalyzed hydrosilylation proceeds via cis addition to give trans product (β trans), the other two isomers in eq 3 are observed.[3]

The second major difference between addition of R_3SiH to alkynes vs olefins is that the many electronic and structural factors that impede olefin hydrosilylation have minimal impact on alkyne addition.[3] Many studies have addressed the various aspects of rate, selectivity, and product structures in alkyne hydrosilylation. This paper describes our results on hydrosilylation of alkynes where we employ highly active Pt^0 olefin complexes as the catalyst.[8-11,17] We investigated the effect of the electronic nature of R and R′ in eq 3 on selectivity of the reaction. Finally, in the course of this investigation, we found that the assignment of the structure of the products was not always straightforward. Several unusual NMR results are reported and conclusions correlating NMR to structure are supported by single-crystal X-ray structural analyses.

Results and Discussion

Hydrosilylation of Terminal Alkynes with a Highly Active Platinum Catalyst. The reaction of several SiH compounds with several different terminal alkynes was examined. The data for the reactions in Table I were obtained via catalysis with the highly active platinum catalyst called the Karstedt catalyst.[8,11] This catalyst has recently been shown to have the following empirical formula:[18,19]



Karlstedt's catalyst

(The Lappert group refers to this platinum complex as "solution A".)

Product structural assignments are discussed below. Typically, reactions were run neat with ca. 100 ppm platinum. Gentle heating for about 5 min to initiate the reaction led to an exotherm and complete conversion to products in less than 1 h with formation of the characteristic yellow color.[17]

The effect of steric and electronic factors on product selectivity was investigated. With a sterically bulky group near the α position only β product is formed (entries 4 and 5, Table I) whereas entry 2 of Table I shows that 23% of α product was formed. The addition reaction of $Ph_{3-x}Me_xSiH$, x = 0–2, to 1-pentyne was insensitive to variations to the ratio of Ph/Me substitution at silicon; all three silanes gave roughly the same proportion of β and α products. A trend favoring more α product with more electron-withdrawing groups on silicon is shown in Tables II and III. The $(EtO)_3SiH$ reagent gives the highest degree of α product. While electronic factors are important,[8] we are beginning to learn the importance of steric factors as well.[20] Further modeling work will be required in order to accurately predict products such as the apparent anomaly in product distribution found for Ph_3SiH + PhC≡CH (Table III).

Structural Assignments. As shown in the results in the tables, the three possible isomers of alkyne addition products of eq 3 were observed. In the reaction of Ph_3SiH with PhC≡CH (entry 1 of Table I), the reaction mixture was heated to ca. 60 °C for 2 min. An exothermic reaction occurred; a yellow color formed and crystals deposited. Analysis of the entire product mixture by GC and ^1H NMR spectroscopy showed three products in the ratio shown in Table I. ^1H NMR analysis of the product mixture showed a large resonance at 6.98 ppm (doublet with J = 2 Hz), 1-trans, with a smaller singlet at 7.16, 1-cis, and a pair of doublets at 6.28 and 5.69 (J = 2 Hz), 1-α. Selective crystallization from CH_2Cl_2/methanol gave a single pure compound 1-trans, mp 151–152 °C, while crystals of compound 1-α, mp 117–121 °C, were obtained from the mother liquor. The ^1H NMR spectrum of the mother liquor from crystallization of 1-trans showed that 1-cis and 1-α were present.

The observation of the doublet resonance for 1-trans with a small coupling constant in the ^1H NMR spectrum

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Table I. Reactions and Products from Hydrosilylation of Terminal Alkynes Catalyzed by Karstedt's Catalyst with Isomer % Ratio in Parentheses

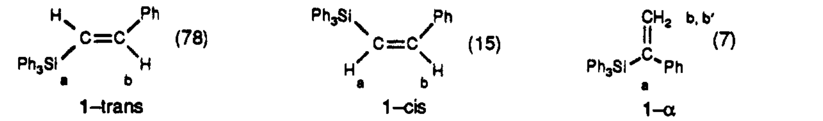
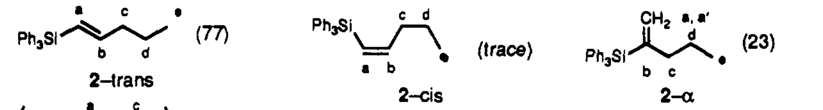
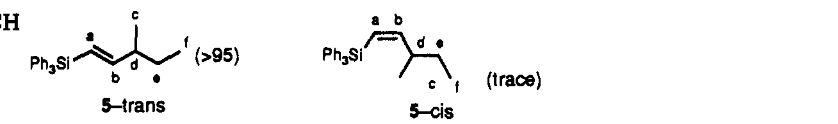
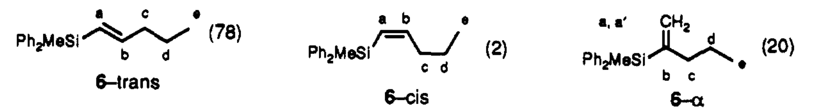
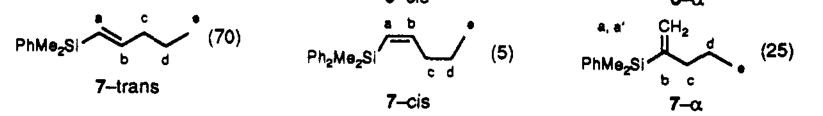
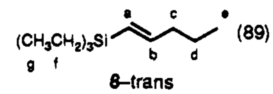
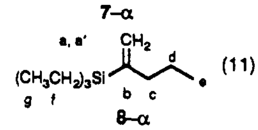
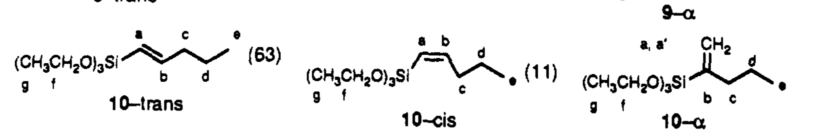
entry no.	R_3SiH	R'—C≡CH	β trans	β cis	α
1	Ph_3SiH	PhC≡CH			
2	Ph_3SiH	$CH_3CH_2CH_2C≡CH$			
3	Ph_3SiH	$HC≡C(CH_2)_4C≡CH$			
4	Ph_3SiH	$(CH_3)_3CC≡CH$			
5	Ph_3SiH	$CH_3CH_2(CH_3)CHC≡CH$			
6	Ph_2MeSiH	$CH_3CH_2CH_2C≡CH$			
7	$PhMe_2SiH$	$CH_3CH_2CH_2C≡CH$			
8	$(CH_3CH_2)_3SiH$	$CH_3CH_2CH_2C≡CH$		(see text) 8-cis (0)	
9	$(CH_3CH_2)_3SiH$	PhC≡CH			
10	$(CH_3CH_2O)_3SiH$	$CH_3CH_2CH_2C≡CH$			
11	$(CH_3CH_2O)_3SiH$	PhC≡CH			

Table II. Effect of R in R_3SiH on Product Selectivity with Addition to 1-Pentyne

	% product		
R_3SiH	β trans	β cis	α
Et_3SiH	89	0	11
$PhMe_2SiH$	70	5	25
Ph_2MeSiH	78	2	20
Ph_3SiH	77	0	23
$(EtO)_3SiH$	55.5	6	38.5

Table III. Effect of R in R_3SiH on Product Selectivity with Addition to PhC≡CH

	% product		
R_3SiH	β trans	β cis	α
Et_3SiH	81	1	18
Ph_3SiH	78	15	7
$(EtO)_3SiH$	70	0	30

led to an initial assignment for 1-trans as the α isomer. However, there was a single olefinic resonance for isomer 1-α as well. The use of 2D NMR spectroscopy partially resolved the structural assignment problem for 1-trans, 1-cis, and 1-α. 2D $^{13}C/^{1}H$ (heteronuclear correlation, HETCOR) NMR spectra for pure 1-trans (Figure 1) showed that the 6.98 resonance was correlated with two carbons; thus, the correct structure of 1-trans was either one of the β isomers, cis or trans. The 2D $^{13}C/^{1}H$ (HETCOR) NMR spectrum for the mother liquor showed that the singlet resonance of 1-cis was correlated with two carbons, β isomer either cis or trans, and that the protons giving rise to the pair of doublets in 1-α were connected to a single carbon. The 2D NMR (Figure 2) and ^{1}H NMR spectra also showed that there was a carbon in 1-α without attached protons. On the basis of the 2D NMR and the ^{13}C NMR spectra, which showed CH_2 and quaternary carbons to be present, 1-α was assigned as the α isomer.

Single-crystal X-ray structural analyses were carried out for 1-trans and 1-α. As shown in Figure 3, compound 1-trans was indeed the β-trans isomer. Relevant bond distances and angles are shown in Tables IV and V, respectively. As shown in Figure 4, compound 1-α was the α isomer. Relevant distances and angles are shown in Tables VI and VII, respectively. There was a slight lengthening of the C═C bond distance in going from the

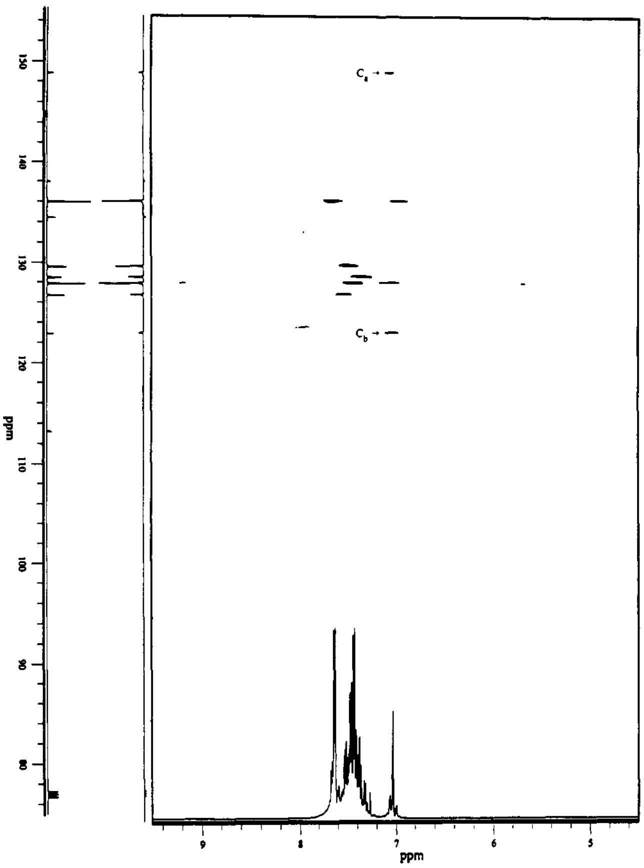


Figure 1. 2D $^{13}C/^{1}H$/(heteronuclear correlation, HETCOR) NMR spectrum for 1-trans.

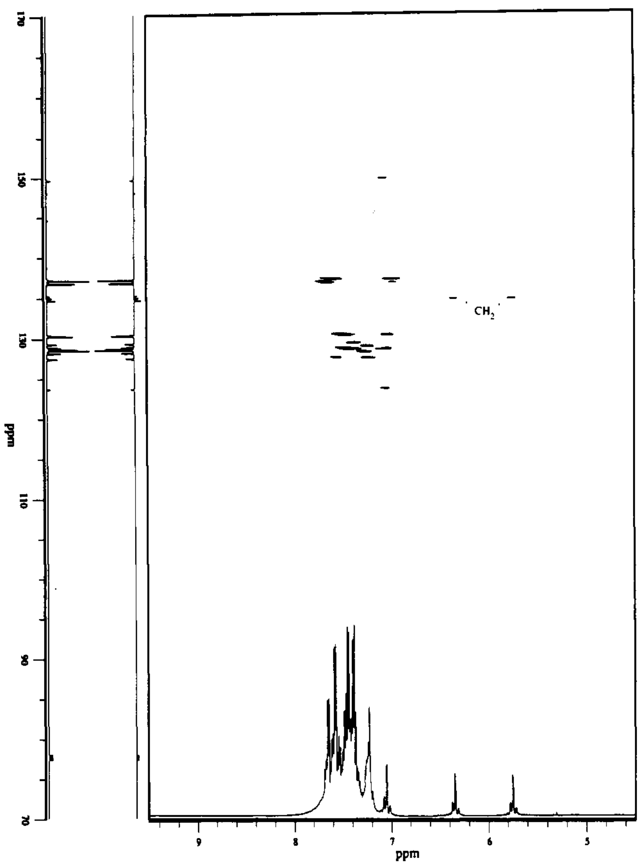


Figure 2. 2D $^{13}C/^{1}H$ (HETCOR) NMR spectrum from mother liquor (entry 1, Table I) containing 1-trans, 1-cis, and 1-α.

Table IV. Bond Lengths (Å) for 1-trans

Si(1)–C(1)	1.862 (4)	Si(1)–C(9)	1.869 (5)
Si(1)–C(15)	1.886 (5)	Si(1)–C(21)	1.876 (4)
C(1)–C(2)	1.294 (7)	C(2)–C(3)	1.492 (6)
C(3)–C(4)	1.387 (7)	C(3)–C(8)	1.377 (7)
C(4)–C(5)	1.372 (8)	C(5)–C(6)	1.380 (10)
C(6)–C(7)	1.355 (10)	C(7)–C(8)	1.399 (7)
C(9)–C(10)	1.395 (6)	C(9)–C(14)	1.386 (7)
C(10)–C(11)	1.392 (8)	C(11)–C(12)	1.355 (10)
C(12)–C(13)	1.359 (8)	C(13)–C(14)	1.398 (8)
C(15)–C(16)	1.389 (7)	C(15)–C(20)	1.388 (8)
C(16)–C(17)	1.379 (8)	C(17)–C(18)	1.369 (9)
C(18)–C(19)	1.390 (9)	C(19)–C(20)	1.361 (8)
C(21)–C(22)	1.382 (6)	C(21)–C(26)	1.400 (7)
C(22)–C(23)	1.387 (6)	C(23)–C(24)	1.366 (9)
C(24)–C(25)	1.363 (8)	C(25)–C(26)	1.386 (6)

Table V. Bond Angles (deg) for 1-trans

C(1)–Si(1)–C(9)	107.3 (2)	C(1)–Si(1)–C(15)	112.3 (2)
C(9)–Si(1)–C(15)	108.7 (2)	C(1)–Si(1)–C(21)	109.8 (2)
C(9)–Si(1)–C(21)	109.7 (2)	C(15)–Si(1)–C(21)	109.0 (2)
Si(1)–C(1)–C(2)	123.4 (3)	C(1)–C(2)–C(3)	127.3 (4)
C(2)–C(3)–C(4)	117.1 (4)	C(2)–C(3)–C(8)	124.0 (5)
C(4)–C(3)–C(8)	118.9 (4)	C(3)–C(4)–C(5)	120.1 (5)
C(4)–C(5)–C(6)	120.6 (6)	C(5)–C(6)–C(7)	120.0 (6)
C(6)–C(7)–C(8)	119.9 (6)	C(3)–C(8)–C(7)	120.5 (5)
Si(1)–C(9)–C(10)	119.6 (4)	Si(1)–C(9)–C(14)	123.1 (3)
C(10)–C(9)–C(14)	117.3 (5)	C(9)–C(10)–C(11)	119.9 (5)
C(10)–C(11)–C(12)	121.5 (5)	C(11)–C(12)–C(13)	120.0 (6)
C(12)–C(13)–C(14)	119.5 (5)	C(9)–C(14)–C(13)	121.7 (4)
Si(1)–C(15)–C(16)	119.7 (4)	Si(1)–C(15)–C(20)	122.8 (4)
C(16)–C(15)–C(20)	117.4 (5)	C(15)–C(16)–C(17)	121.3 (5)
C(16)–C(17)–C(18)	120.2 (5)	C(17)–C(18)–C(19)	119.0 (6)
C(18)–C(19)–C(20)	120.5 (6)	C(15)–C(20)–C(19)	121.4 (5)
Si(1)–C(21)–C(22)	122.2 (3)	Si(1)–C(21)–C(26)	120.4 (3)
C(22)–C(21)–C(26)	117.4 (3)	C(21)–C(22)–C(23)	121.6 (5)
C(22)–C(23)–C(24)	119.6 (5)	C(23)–C(24)–C(25)	120.3 (4)
C(24)–C(25)–C(26)	120.4 (5)	C(21)–C(26)–C(25)	120.6 (5)

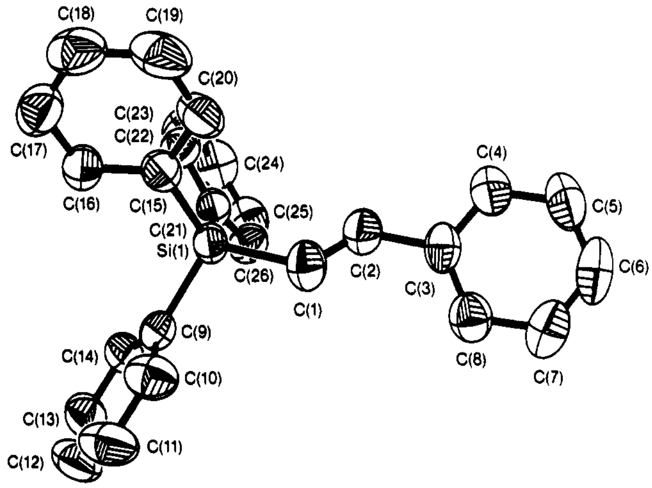


Figure 3. Thermal ellipsoids for 1-trans, 50% probability plot.

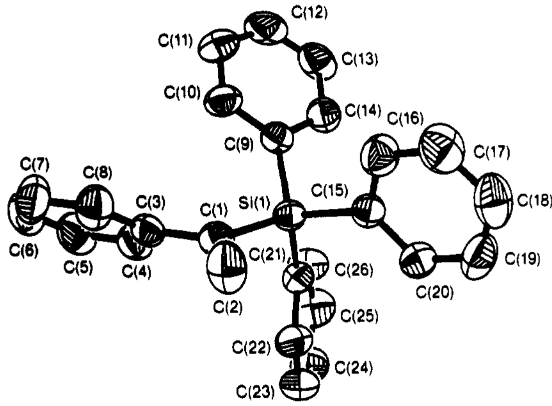


Figure 4. Thermal ellipsoids for 1-α, 50% probability plot.

Table VI. Bond Lengths (Å) for 1-α

Si(1)–C(1)	1.879 (3)	Si(1)–C(9)	1.875 (3)
Si(1)–C(15)	1.874 (3)	Si(1)–C(21)	1.881 (3)
C(1)–C(2)	1.320 (4)	C(1)–C(3)	1.494 (4)
C(3)–C(4)	1.386 (4)	C(3)–C(8)	1.386 (4)
C(4)–C(5)	1.375 (4)	C(5)–C(6)	1.360 (6)
C(6)–C(7)	1.373 (6)	C(7)–C(8)	1.379 (5)
C(9)–C(10)	1.387 (4)	C(9)–C(14)	1.394 (4)
C(10)–C(11)	1.385 (4)	C(11)–C(12)	1.369 (5)
C(12)–C(13)	1.367 (5)	C(13)–C(14)	1.385 (4)
C(15)–C(16)	1.393 (4)	C(15)–C(20)	1.395 (3)
C(16)–C(17)	1.375 (4)	C(17)–C(18)	1.368 (5)
C(18)–C(19)	1.365 (4)	C(19)–C(20)	1.392 (4)
C(21)–C(22)	1.398 (3)	C(21)–C(26)	1.385 (4)
C(22)–C(23)	1.384 (4)	C(23)–C(24)	1.355 (5)
C(24)–C(25)	1.357 (5)	C(25)–C(26)	1.391 (4)

Table VII. Bond Angles (deg) for 1-α

C(1)–Si(1)–C(9)	111.9 (1)	C(1)–Si(1)–C(15)	108.4 (1)
C(9)–Si(1)–C(15)	107.6 (1)	C(1)–Si(1)–C(21)	107.6 (1)
C(9)–Si(1)–C(21)	111.6 (1)	C(15)–Si(1)–C(21)	109.8 (1)
Si(1)–C(1)–C(2)	119.0 (2)	Si(1)–C(1)–C(3)	121.4 (2)
C(2)–C(1)–C(3)	119.5 (2)	C(1)–C(3)–C(4)	121.5 (2)
C(1)–C(3)–C(8)	120.7 (2)	C(4)–C(3)–C(8)	117.8 (2)
C(3)–C(4)–C(5)	121.0 (3)	C(4)–C(5)–C(6)	120.6 (3)
C(5)–C(6)–C(7)	119.4 (3)	C(6)–C(7)–C(8)	120.6 (3)
C(3)–C(8)–C(7)	120.6 (3)	Si(1)–C(9)–C(10)	124.2 (2)
Si(1)–C(9)–C(14)	119.4 (2)	C(10)–C(9)–C(14)	116.4 (2)
C(9)–C(10)–C(11)	121.8 (3)	C(10)–C(11)–C(12)	119.8 (3)
C(11)–C(12)–C(13)	120.4 (3)	C(12)–C(13)–C(14)	119.3 (3)
C(9)–C(14)–C(13)	122.2 (3)	Si(1)–C(15)–C(16)	119.7 (2)
Si(1)–C(15)–C(20)	123.7 (2)	C(16)–C(15)–C(20)	116.5 (2)
C(15)–C(16)–C(17)	122.1 (3)	C(16)–C(17)–C(18)	120.1 (3)
C(17)–C(18)–C(19)	119.7 (3)	C(18)–C(19)–C(20)	120.4 (3)
C(15)–C(20)–C(19)	121.1 (2)	Si(1)–C(21)–C(22)	119.5 (2)
Si(1)–C(21)–C(26)	124.3 (2)	C(22)–C(21)–C(26)	116.2 (2)
C(21)–C(22)–C(23)	121.8 (3)	C(22)–C(23)–C(24)	120.2 (3)
C(23)–C(24)–C(25)	120.0 (3)	C(24)–C(25)–C(26)	120.3 (3)
C(21)–C(26)–C(25)	121.5 (3)		

β-trans isomer of 1.293 (4) Å to 1.320 (4) Å in the α isomer. There were no significant differences between 1-trans and 1-α in the C–C bond distances from C(olefin) to C(phenyl-ipso) nor was any difference found between the two isomers for the Si–C(phenyl-ipso) bond distances. Finally, no significant differences were found among the C–C bond distances in the phenyl rings bound to Si vs the phenyl rings bound to carbon.

The C(Ph)–Si–C(Ph) angles for the two structures were within 2° of each other. The largest C–Si–C angle (111.9°) was in the α isomer and may suggest a slight difference in packing between 1-trans and 1-α. The three angles centered about C_1 in the α isomer were from 119 to 121.4°, whereas the C_3–C_2–C_1 and C_2–C_1–Si angles in the β-trans isomer were 127.3 and 123.4°, respectively, consistent with the fact that hydrogen is less sterically demanding than methyl.

The crystal structures of 1-trans and 1-α confirmed the assignments of the structures for these isomers based on NMR spectra. It was quite surprising that the olefin CH in 1-trans gave rise to a single resonance; the CH's of 1-trans had almost the same chemical shift and a small coupling constant between them. The same NMR spectroscopic result was obtained for the CH's of 1-cis.

The structural assignments of the other alkyne products were based on information gleaned from the two crystal structures above and by use of the APT routine in the ^{13}C NMR spectra and by HETCOR ($^{13}C/^{1}H$). For example, the product 5-trans (Table I) was determined by these NMR techniques, which showed that there was a pair of closely spaced olefinic proton resonances around 6.1 ppm. The ^{13}C NMR spectrum showed two olefinic carbons (both CH by APT) at 121.1 and 158.7 ppm. The 2D HETCOR

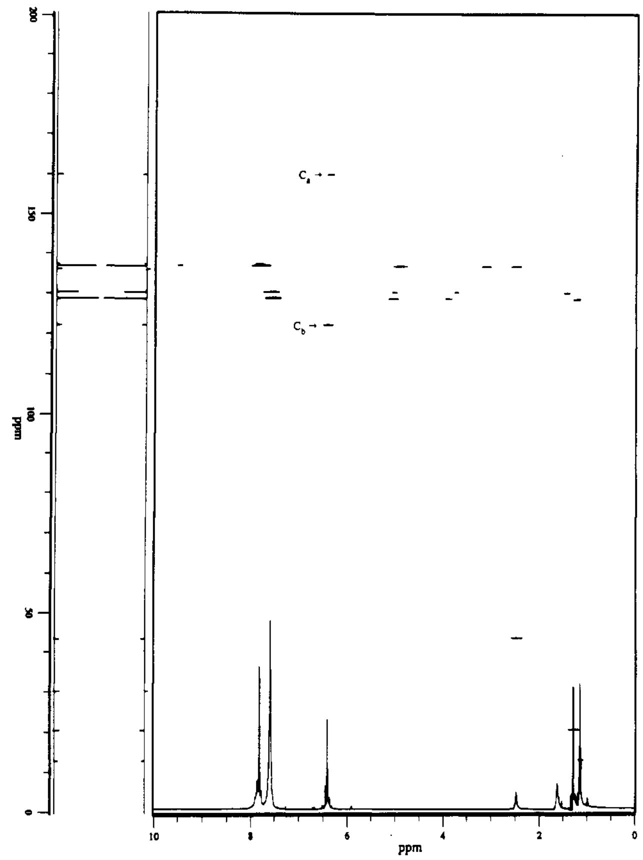


Figure 5. 2D $^{13}C/^{1}H$ (HETCOR) NMR spectrum for 5-trans.

(Figure 5) showed that the ^{1}H resonances correlate to the ^{13}C resonances. These data were consistent with the β-trans isomer. In addition, several general trends aided in the assignment of NMR peaks and therefore the confirmation of the various product structures. The phenyl groups on silicon usually gave uninformative multiplets by ^{1}H NMR spectroscopy but a very common and reproducible pattern in the ^{13}C NMR spectra. The ortho and para resonances were the most upfield ones and could be distinguished from each other on the basis of intensity (ortho > para); typically ortho resonances were between 127 and 128 ppm, while the para resonances were ca. 129 ppm. The meta resonances were always quite a bit downfield from ortho and para and typically were found at ca. 136 ppm. The ipso was easily distinguished from the other resonances via APT and by the fact that quaternary carbons typically had lower intensity (due to NOE) than other carbons.

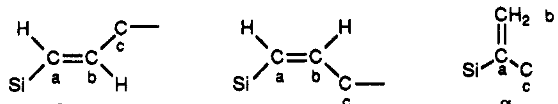
The compounds in Table I, entries 6–11, exhibit several characteristic features.[20,21] Table VIII summarizes some of the ^{1}H NMR data for these compounds. As shown in Table VIII for the β-trans compounds, hydrogen on C_a occurred upfield of the hydrogen on C_b. The characteristic large trans coupling constant was observed (J_{ab} = 18.5–19.5 Hz). The J_{bc} coupling constant was about 6 Hz, and the longer range J_{ac} was also observed and was about 1.5 Hz. These results contrasted to the cis isomers, where the coupling was not well resolved. The chemical shift of the olefin hydrogens on the β-cis isomers occurred about 0.5 ppm upfield of those on the trans isomer. The proton resonances for the vinylidene in the α isomer were also found upfield of the olefin protons in the β trans isomers.

(21) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1525.
(22) Tsipis, C. A. *J. Organomet. Chem.* **1980**, *187*, 427.

Table VIII. ^{1}H NMR Data for Compounds of Table I[a]

entry no. (Table I)	β trans						β cis			α		
	δ(a)	δ(b)	δ(c)	J_{ab}	J_{bc}	J_{ac}	δ(a)	δ(b)	δ(c)	δ(b)	δ(b′)	$J_{bb'}$
6	5.95	6.16	2.14	18.5	6.0	1.1	5.30	5.30	1.94	5.40	5.83	
7	5.78	6.11	2.09	18.5	6.3	1.3	5.31	5.31	1.95	5.40	5.66	3
8	5.57	6.05	2.11	18.7	6.2	1.4	5.40	5.40		5.32	5.65	
9	6.44	6.91		19.3						5.58	5.88	3
10	5.43	6.44	2.14	18.8	6.3	1.6	5.42	5.42	2.27	5.64	5.72	
11	6.18	7.23		19.5						5.97	6.14	3

[a] Key:



β trans β cis α

Table IX. ^{13}C NMR Data for the Compounds in Table I

entry no. (Table I)	β trans			β cis			α		
	δ(a)	δ(b)	δ(c)	δ(a)	δ(b)	δ(c)	δ(a)	δ(b)	δ(c)
1	148.80	122.82		128.02	126.64		143.80	134.10	
2	153.30	123.23	39.07	132.80			146.47	130.22	38.40
3	153.11	123.51	36.73						
4	164.54	116.38	35.74						
5	158.87	119.73	42.32	136.37	135.84	42.00			
6	151.35	125.37	38.98	132.21	123.74	25.87	148.24	128.37	38.25
7	149.07	124.28	38.94	143.51	131.38	25.91	150.00	125.86	38.27
8	148.52	125.77	39.19	150.08	125.11	36.06	148.45	125.07	38.63
9	144.85	125.88					150.44	138.52	
10	153.86	119.11	38.76	132.50	122.37	25.87	143.68	129.22	38.80
11	149.19	117.72					143.42	137.66	

A $J_{bb'}$ value of 3 Hz was observed in each case. The J_{H-H} coupling constant between CH_3 and CH_2 in the ethyl group of $(EtO)_3Si$– was 7 Hz, while it was 8 Hz in $(CH_3CH_2)_3Si$–.

The other compounds of Table I, entries 1–5, were characterized by a lack of resolution of the olefin protons for the β isomers. The 2D HETCOR spectra and crystallography were crucial to the assignment of resonances for these compounds. Additional observations in the ^{1}H NMR spectra for some of these compounds included the characteristic multiplet observed for CH_2 next to Si.[23]

There were also several characteristic features in the ^{13}C NMR spectra of the compounds studied here. Table IX summarizes some of the ^{13}C NMR data. Whereas the olefinic proton nearest silicon gave the most upfield resonance in the ^{1}H NMR spectrum, the olefinic carbon nearest silicon gave the most *downfield* resonance in the ^{13}C NMR spectrum. The carbon attached to Si in the β-trans and α isomers was considerably more downfield than the corresponding carbon in the β-cis isomers. The carbon attached to Si was usually shifted much further downfield in the β-trans and α isomers vs the same carbon in the β-cis isomer. Finally, it was noted that the carbon of CH_2 (where present) in entries 6, 7, and 10 adjacent to the olefinic carbons was shifted upfield by 13–15 ppm in the β-cis isomers vs CH_2 in either the β-trans or α isomers.

In a recent publication the mechanism of Pt metal catalyzed olefin hydrosilylation was discussed.[8] This report suggested that the reaction proceeds via nucleophilic attack of olefin on an activated R_3SiH–Pt complex. Thus, the higher activity of alkynes vs olefins could be due to the higher degree of nucleophilicity of alkynes vs olefins. As discussed above, unlike the normally high regioselectivity of olefin hydrosilylation products, alkyne hydrosilylation was less selective. One cause for the lower selectivity of alkyne hydrosilylation vs olefins may be geometric considerations of the alkyne. As discussed for eq 2, hydrosilylation of styrene gives 60:40 β:α product mixtures. The origin of the high selectivity in normal hydrosilylation may be steric in nature, e.g. the only facile approach of the olefin to the activated SiH bond results in a β product. However, for the flat styrene molecule, there may be a negligible energy difference between approach of the β or α end of the molecule. Formation of the α product may become a lower energy process than for olefins due to the lower steric bulk around the unsaturated group.

Comparison to Literature Results Using Other Catalysts. The results obtained here may explain the apparent difficulty of assigning structures to products in the work of others. In one case in the literature, several workers report that dramatic differences in product distribution were obtained depending on the nature of the Pt catalyst.[24] We found that the product distribution obtained for the reaction between Ph_3SiH and 1-pentyne (entry 2, Table I) was the same if Karstedt's catalyst was used or if H_2PtCl_6 (β:α = 77:23) was used. Our conditions closely matched those reported.[24] These same workers reported that using $CODPtCl_2$, the β:α ratio = 32:68 for the addition of Et_3SiH to 1-hexyne. We found for this reaction (entry 8, Table I) that the product distribution was β:α = 89:11 ± 1 for the Karstedt catalyst or $CODPtCl_2$. We do not believe altering the Pt catalyst affects product distribution, and we feel the product ratios reported here are correct.

Ojima and co-workers[25] reported that the cis:trans ratio of the reaction product of Et_3SiH + 1-pentyne catalyzed by $(PPh_3)_3RhCl$ was 69:31. We obtained no cis product in this reaction catalyzed by Pt. We reran the reaction of entry 8 with $(PPh_3)_3RhCl$ in place of Pt and indeed found

(23) This characteristic multiplet has been dubbed a Colborn multiplet (CM): Colborn, R. E. *J. Chem. Educ.* **1990**, *67*, 438.

(24) Pukhnarevich, V. B.; Tsykhanskaya, I. I.; Ushakova, N. I.; Gel'fman, M. I.; Voronkov, M. G. *Bull. Acad. Sci. USSR* **1984**, *33*, 2540.

(25) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1974**, *66*, C14.

a β-cis:β-trans:α product ratio of 72:22:6. We then reran the reaction with $RhCl_3$ in *i*-PrOH (which unlike $(PPh_3)_3RhCl$ should give colloidal Rh)[26] and obtained nearly identical results (see Experimental Section). Thus, it appeared that a different mechanism was operative in the Rh-catalyzed reaction.[27] Pt-catalyzed hydrosilylation of alkynes is characterized by cis addition giving trans product (or α product).

The Rh-catalyzed reaction between Et_3SiH and 1-pentyne apparently resulted in the kinetic product mixture, assuming cis olefinic product is thermodynamically less stable than trans. Ojima and co-workers[28] have proposed a mechanism that accounts for the predominance of cis products from Rh-catalyzed hydrosilylation of alkynes. Their mechanism can explain the results found here for Rh. A reaction between Et_3SiH and 1-pentyne, catalyzed by the Karstedt Pt catalyst, was carried out. The Pt-catalyzed product mixture was divided into two aliquots. In one aliquot additional 1-pentyne and Et_3SiH were added and the mixture was heated. The added 1-pentyne/Et_3SiH completely converted to the hydrosilylation mixture containing 89% *trans*-$Et_3SiCH{=}CHCH_2CH_2CH_3$ and 11% *cis*-$Et_3SiCH({=}CH_2)CH_2CH_2CH_3$. This result showed that Pt was still active in this mixture. The second aliquot from the Pt-catalyzed reaction was combined with an equal portion of a Rh-catalyzed product mixture. The initial mixture contained about 18% *cis*-, 62% *trans*-, and 20% α-olefin products. Heating this mixture at 55 °C for 3 days in the presence of active Pt catalyst did *not* produce any change in isomer mixture. No cis to trans isomerization occurred. Thus, a mechanism by which cis "kinetic product" formed and then subsequently converted to trans in the presence of Pt is ruled out. In a second set of experiments the Rh catalyst did not promote isomerization of the Pt catalyst product mixture; e.g., the 89% trans 11% α was unchanged upon heating in the presence of Rh; no cis product was observed.

Finally, it is well-known that I_2 will catalyze conversion of a kinetic mixture of olefins to the thermodynamic one.[29] For example, refluxing *cis*-stilbene in toluene in the presence of a few crystals of I_2 cleanly converts the stilbene to the trans isomer. Unfortunately, heating the silyl olefin products formed from 1-pentyne and Et_3SiH with I_2 resulted in formation of products based on Si–C bond cleavage.

Experimental Section

General Procedures. Reactions were carried out in air in virgin glass vials. Care was taken to use "Pt-only" syringes (only used for Pt catalysts) to introduce catalysts. The Pt catalyst used throughout, unless specified otherwise, was the Karstedt catalyst described previously.[8-11] The catalyst (also available from Huls Petrarch Systems as PC072) was prepared by combining $H_2PtCl_6{\cdot}6H_2O$ (5 g, 10.0 mmol) with 5 mL of ethanol and divinyltetramethyldisiloxane (DVTMDS) (50 g, 0.27 mol). The mixture was heated for 5 h at 60 °C. A homogeneous orange solution was obtained to which solid $NaHCO_3$ (1.7 g, 70.8 mmol) was added. This mixture was stirred for 1 h and then filtered. The filter cake was washed with two 10-g portions of DVTMDS. The liquid at this point was analyzed and showed 2.27% Pt. The filtrate was concentrated in vacuo at 40 °C, ca. 30 mmHg, to give a dark oil to which sufficient xylene was added to give 5% by weight platinum (ca. 40 mL). This solution was 5% by weight Pt and was added by microliter syringe: 1 μL delivers 0.25 μmol of Pt or about 50 μg of Pt. NMR spectra were recorded on a GE QE-300 instrument (^1H and ^{13}C, 300.15 and 75.48 MHz, respectiely) in $CDCl_3$, 7.26 ppm lock signal, all shifts, δ, relative to TMS = 0 internal standard. All ^{13}C NMR spectra were rerun by using the APT sequence with the orientation of CH_3 and CH up and CH_2 and C(quat) down. Two-dimensional NMR spectra were obtained on a General Electric GN-Omega 500 NMR spectrometer. A standard HETCOR (heteronuclear carbon–proton chemical shift correlated) pulse sequence was employed by using 1k data points by 128 increments. A 10-mm broad-band probe was used. Typical parameters for ^{13}C (at 125 MHz) were a sweep width of 20 kHz, a 90° pulse width of 14.5 μs, and waltz-16 decoupling. Typical ^1H parameters (observed at 500 MHz) were a 5-kHz sweep width and a decoupler 90° pulse width of 65.7 μs at the power level used. A predelay time of 0.5 s was also used.

GC product analyses were carried out by using a Hewlett Packard Model 5890 instrument coupled to a Model 3393 integrator. A 6-ft OV 101 column was employed, and a thermal conductivity detector was used. GCMS analyses were performed by using a Varian Model MAT311A instrument at 70-eV (EI mode) resolution set at 850, with a 30-m long x 0.32-mm i.d. DB FSWOCT column.

HRGCMS spectra were recorded on a VG Analytical Model ZAB-2F gas chromatograph mass spectrometer, run in the accurate mass mode at 5500 resolution. High-resolution electron-impact mass spectra (HREIMS) were recorded on a MAT731 instrument at 10000 resolution at 80 eV.

Crystallographic data are listed in Tables X–XII.

Ph_3SiH + PhC≡CH, Entry 1 of Table I. Ph_3SiH (4.74 g, 18.2 mmol) was combined with PhC≡CH (2 g, 18.2 mmol). The mixture was heated to melt the Ph_3SiH, and then the Karstedt catalyst was added (3 μL, 0.8 μmol of Pt). An exothermic reaction was noted after 2–3 min with formation of a yellow color. Analysis by GC showed, in increasing RT (retention time), α 7%, β cis 15%, and β trans 78%.

1-trans: ^1H NMR 6.98 (d, J = 2.7 Hz, 2H, a, b); ^{13}C NMR 122.82 (b), 148.8 (a). HETCOR showed 6.98 proton resonance correlated to 122.8/148.8 carbon resonances.

1-α: ^1H NMR 5.69 (d, J = 2 Hz, 1 H, b), 6.28 (d, J = 2 Hz, 1 H, b′); ^{13}C NMR 134.1 (b), 143.8 (a). HETCOR showed 5.69/6.28

Table X. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for Compound 1-trans

	x	y	z	U(eq)[a]
Si(1)	3191 (1)	0	2371 (1)	52 (1)
C(1)	2177 (5)	−60 (6)	3629 (3)	68 (1)
C(2)	563 (6)	−475 (5)	3668 (3)	64 (1)
C(3)	−395 (5)	−516 (5)	4621 (3)	59 (1)
C(4)	−1753 (6)	−1358 (6)	4613 (4)	72 (2)
C(5)	−2681 (8)	−1448 (7)	5467 (5)	91 (2)
C(6)	−2335 (8)	−673 (8)	6320 (4)	96 (2)
C(7)	−1052 (7)	179 (8)	6325 (4)	85 (2)
C(8)	−70 (6)	263 (5)	5470 (3)	71 (2)
C(9)	4664 (6)	1344 (5)	2452 (3)	55 (1)
C(10)	6046 (7)	1502 (5)	3336 (4)	76 (2)
C(11)	7182 (7)	2485 (6)	3387 (6)	94 (2)
C(12)	6972 (7)	3308 (5)	2597 (6)	91 (2)
C(13)	5623 (8)	3187 (5)	1732 (5)	82 (2)
C(14)	4473 (7)	2204 (5)	1659 (4)	67 (1)
C(15)	4648 (6)	−1331 (5)	2211 (3)	56 (1)
C(16)	6003 (6)	−1260 (5)	1571 (3)	65 (1)
C(17)	7053 (6)	−2225 (6)	1407 (4)	80 (2)
C(18)	6794 (8)	−3278 (6)	1890 (5)	89 (2)
C(19)	5465 (8)	−3357 (5)	2548 (5)	89 (2)
C(20)	4417 (6)	−2405 (5)	2698 (4)	70 (2)
C(21)	1325 (5)	109 (5)	1173 (3)	55 (1)
C(22)	1261 (6)	−618 (5)	287 (3)	66 (1)
C(23)	−140 (7)	−539 (6)	−587 (3)	81 (2)
C(24)	−1453 (6)	309 (6)	−601 (4)	80 (2)
C(25)	−1426 (6)	1048 (6)	255 (4)	77 (2)
C(26)	−54 (6)	958 (5)	1142 (4)	67 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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(29) Egger, K. W. *J. Am. Chem. Soc.* **1967**, *89*, 504.
(30) *International Tables for X-ray Crystallography*; Kluwer Academic Publishing: Dordrecht, The Netherlands, 1974.

Table XI. Details of the Crystallographic Data Collection[a]

	$C_{26}H_{22}Si$ (1-trans)	$C_{26}H_{22}Si$ (1-α)
habit	clear prism	clear prism
dimens, mm	0.45 × 0.40 × 0.30	0.40 × 0.35 × 0.10
cryst system	monoclinic	monoclinic
temp, K	299	299
space group	$P2_1$	$P2_1/c$
a, Å	7.410 (6)	10.121 (7)
b, Å	11.349 (8)	10.225 (6)
c, Å	12.594 (10)	20.116 (11)
β, deg	99.43 (6)	93.03 (5)
Z	2	4
V, $Å^3$	1044.8 (14)	2079 (2)
ρ(calcd), Mg/m^3	1.152	1.158
abs coeff, mm^{-1}	0.114 (not applied)	0.115 (not applied)
scan type	2θ–θ	2θ–θ
2θ range, deg	3.5–55.0	3.5–55.0
scan speed, deg/min	variable; 1.5–15.00 in ω	variable; 1.5–15.00 in ω
index ranges	$0 \le h \le 9, 0 \le k \le 14, -16 \le l \le 16$	$0 \le h \le 13, 0 \le k \le 13, -26 \le l \le 26$
tot. no. of reflcns	2725	5350
no. of independent reflcns	2531 (R_{int} = 3.36%)	4797 (R_{int} = 1.87%)
no. of obsd reflcns ($F > 4.0\sigma(F)$)	2048	2875
R, %	0.0511	0.0548
R_w, %	0.0792	0.0435
GOF	0.91	1.77
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0060F^2$	$w^{-1} = \sigma^2(F) + 0.0001F^2$
largest and mean Δ/σ	0.096, −0.004	0.041, 0.002
data-to-param ratio	8.4:1	11.7:1
largest diff peak, e $Å^{-3}$	0.31	0.29
largest diff hole, e $Å^{-3}$	−0.23	−0.23

[a] Diffractometer: Siemens R3m/v upgrade of a Nicolet P3F. Radiation: Mo Kα (λ = 0.71072 Å). Monochromator: highly oriented graphite crystal. Solution system: Siemens SHELXTL PLUS (Micro VAX II). Solution: direct methods. Refinement: full-matrix least squares. Atomic scattering factors and anomalous dispersion corrections were taken from ref 30.

Table XII. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × 10^3) for Compound 1-α

	x	y	z	U(eq)[a]
Si(1)	2252 (1)	2919 (1)	779 (1)	44 (1)
C(1)	2650 (2)	4698 (2)	913 (1)	50 (1)
C(2)	3537 (3)	5255 (3)	547 (1)	77 (1)
C(3)	2013 (2)	5479 (3)	1436 (1)	50 (1)
C(4)	1785 (2)	4952 (3)	2054 (1)	62 (1)
C(5)	1189 (3)	5675 (4)	2530 (2)	83 (1)
C(6)	798 (3)	6928 (4)	2402 (2)	95 (2)
C(7)	1008 (3)	7470 (3)	1792 (2)	94 (2)
C(8)	1605 (3)	6754 (3)	1311 (2)	72 (1)
C(9)	426 (2)	2603 (2)	762 (1)	45 (1)
C(10)	−518 (2)	3556 (3)	864 (1)	60 (1)
C(11)	−1857 (3)	3269 (3)	844 (2)	78 (1)
C(12)	−2278 (3)	2016 (4)	720 (1)	78 (1)
C(13)	−1384 (3)	1047 (3)	611 (1)	70 (1)
C(14)	−48 (2)	1344 (3)	631 (1)	59 (1)
C(15)	2852 (2)	2416 (2)	−48 (1)	46 (1)
C(16)	2158 (3)	2809 (3)	−631 (1)	66 (1)
C(17)	2584 (3)	2513 (3)	−1251 (1)	82 (1)
C(18)	3716 (3)	1801 (3)	−1312 (2)	79 (1)
C(19)	4425 (3)	1392 (3)	−754 (2)	71 (1)
C(20)	3999 (2)	1687 (2)	−125 (1)	58 (1)
C(21)	3159 (2)	1970 (2)	1462 (1)	48 (1)
C(22)	4473 (2)	2286 (3)	1644 (1)	61 (1)
C(23)	5185 (3)	1615 (3)	2142 (2)	73 (1)
C(24)	4616 (3)	618 (3)	2466 (2)	78 (1)
C(25)	3341 (3)	281 (3)	2307 (2)	83 (1)
C(26)	2615 (3)	948 (3)	1807 (1)	67 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

proton resonances correlated to a 134.1 carbon resonance.

1-cis: ^{1}H NMR 7.16 (s, 2 H, a, b); ^{13}C NMR 126.64 (b), 128.02 (a). HETCOR showed that the 7.15 proton resonance was correlated to the 126.6/128 carbon resonances.

First crystallization from the reaction mixture from CH_2Cl_2/MeOH gave pure 1-trans, mp 151–152 °C. A second crop of crystals was obtained from the mother liquor, which was nearly pure 1-α, mp 117–121 °C.

Ph_3SiH + 1-Pentyne, Entry 2 of Table I. Ph_3SiH (5.28 g, 20.3 mmol) was heated to melt, and then 1-pentyne (1.38 g, 20.3 mmol) and the Karstedt catalyst (3 μL, 0.8 μmol of Pt) were added. Analysis by GC after 1 h at ambient temperature showed complete conversion to a low-RT product (20%) and a high-RT product (80%). ^{1}H NMR integration showed 77% β trans, 23% α, and <1% β cis were present in the reaction mixture. Anal. Calcd for $C_{23}H_{24}Si$: C, 84.09; H, 7.36; Si 8.55. Found: C, 83.73; H, 7.50; Si 8.77.

2-trans: ^{1}H NMR 0.85 (t, J = 7 Hz, 3 H, e), 1.45 (m, 2 H, d), 2.21 (t of m, J = 7 Hz, 1 Hz, 2 H, c), 6.10 (t, J = 3 Hz, 2 H, a, b); ^{13}C NMR 13.73 (e), 21.70 (d), 39.07 (c), 123.23 (b), 127.75 (o), 129.34 (p), 134.99 (i), 135.94 (m), 153.30 (a). Recrystallization of the entire product mixture in CH_2Cl_2/MeOH gave the pure β-trans isomer (confirmed by ^{1}H NMR), mp 48–49° C.

2-α: ^{1}H NMR 0.80 (t, J = 7 Hz, 3 H, e), 1.40 (m, 2 H, d), 2.20 (m, 2 H, c), 5.57 (m, 1 H, a), 5.99 (m, 1 H, a′); ^{13}C NMR 13.91 (e), 21.98 (d), 38.43 (c), 127.70 (o), 129.40 (p), 130.22 (a), 134.18 (i), 136.21 (m), 146.47 (b).

2-cis: ^{1}H NMR 0.71 (t, J = 7 Hz, 3 H, e), 1.92 (pent, J = 7 Hz, 2 H, d), 2.28 (d of t, J = 7 Hz, 1 Hz, 2 H, c), 5.41 (m, 10–12 lines, 2 H, a, b); ^{13}C NMR 14.04 (e), 19.12 (d), 25.84 (c), 123.30 (b), 134.7 (i), 127.80 (o), 129.3 (p), 132.8 (a), 135.9 (m).

The reactions between Ph_3SiH and 1-pentyne were repeated by using H_2PtCl_6 in i-PrOH in place of the Karstedt catalyst, and the identical product mixture was obtained.

Ph_3SiH + 1,7-Octadiyne, Entry 3 of Table I. 1,7-Octadiyne (5 g, 47 mmol) was combined with 2 equiv of Ph_3SiH (24.5 g, 92 mmol), which was heated to melt the triphenylsilane. The Karstedt catalyst was then added (20 μL, 5 μmol of Pt). A yellow color formed after 5 min at ambient temperature. Analysis by ^{1}H NMR spectroscopy showed 100% yield of a single product. The solid product was recrystallized from CH_2Cl_2/MeOH, mp 108–110 °C. HREIMS (direct probe): calcd for $C_{44}H_{42}Si_2$ (M^+), m/e 626.2825; found, m/e 626.2825. Anal. Calcd: C, 84.29; H, 6.75. Found: C, 84.22; H, 7.08.

3: ^{1}H NMR 1.46 (m, 2 H, d), 2.24 (m, 2 H, c), 6.16 (t, J = 2 Hz, 2 H, a, b), 7.34 (m, 15 H, arom); ^{13}C NMR 27.95 (d), 36.73 (c), 123.51 (b), 127.70 (o), 129.30 (p), 135.83 (m), 136.10 (i), 153.11 (a).

Ph_3SiH + 3,3′-Dimethyl-1-butyne, Entry 4 of Table I. 3,3′-Dimethyl-1-butyne (10 g, 0.122 mol) was combined with Ph_3SiH (31.69 g, 0.122 mol), which was heated to melt, and then the Karstedt catalyst (20 μL, 5 μmol of Pt) was added. A yellow color formed almost immediately. ^{1}H NMR analysis showed that a single isomer was produced in 100% yield. The product was recrystallized from CH_2Cl_2/MeOH, mp 84–86 °C.

4: ^{1}H NMR 1.05 (s, 9 H, d), 6.14 (d of d, J = 19 Hz, 37 Hz, 2 H, a, b), 7.3 + 7.6 (m, 15 H, arom); ^{13}C NMR 28.98 (d), 35.74 (c), 116.38 (b), 127.76 (o), 129.34 (p), 135.12 (i), 135.93 (m), 163.54 (a). HREIMS: calcd for $C_{24}H_{26}Si$ (M^+), m/e 342.1804; found, m/e 342.1803. Anal. Calcd: C, 84.15; H, 7.65. Found: C, 84.53; H, 7.83.

Ph_3SiH + 3-Methyl-1-pentyne, Entry 5 of Table I. Ph_3SiH (4.46 g, 17.2 mmol) was combined with 3-methyl-1-pentyne (1.40 g, 17.1 mmol) and the Karstedt catalyst (3 μL, 0.8 μmol of Pt). Analysis of the reaction mixture after about 1 h at ambient temperature showed complete conversion to a mixture of products that contained >95% β trans and had a trace of β cis. The assignments below were confirmed by HETCOR.

5-trans: ^{1}H NMR 0.88 (t, J = 7.5 Hz, 3 H, f), 1.03 (d, J = 7 Hz, 3 H, c), 1.35 (m, 2 H, e), 2.20 (m, 1 H, d), 6.10 (d, J = 3 Hz, 1 H, b), 6.12 (s, 1 H, a); ^{13}C NMR 1.82 (f), 19.42 (c), 29.08 (e), 42.32 (d), 119.73 (b), 127.74 (o), 129.31 (p), 135.06 (i), 135.89 (m), 158.87 (a). HRGCMS: cacd for $C_{24}H_{26}Si$ (M^+), m/e 342.1804; found, 342.1774.

5-cis: ^{1}H NMR 0.71 (t, J = 7 Hz, 3 H, f), 0.94 (d, J = 7 Hz, 3 H, c), 1.35 (m, 2 H, e), 2.33 (m, 1 H, d), 6.04 (4 lines, J = 18.6, 2 H, a, b); ^{13}C NMR 12.0 (f), 19.0 (c), 29.1 (e), 42.0 (d), 135.84 (b), 136.37 (a). No HRGCMS signal was obtained because the signal was too weak.

Ph_2MeSiH + 1-Pentyne, Entry 6 of Table I. Ph_2MeSiH (3.99 g, 20.3 mmol) and 1-pentyne (1.38 g, 20.3 mmol) were combined with the Karstedt catalyst (3 μL, 0.8 μmol of Pt). Analysis by GC and ^{1}H NMR spectroscopy showed complete conversion to products, which by integration in the NMR spectrum was a mixture of 78% β trans, 20% α, and 2% β cis.

6-trans: ^{1}H NMR 0.59 (s, 3 H, Si*Me*), 0.90 (t, *J* = 7 Hz, 3 H, e), 1.45 (1:2:3:3:2:1, *J* = 7 Hz, 2 H, d), 2.14 (t of m, *J* = 6 Hz, 1 Hz, 2 H, c), 5.95 (d of t, *J* = 18.5 Hz, 1.1 Hz, 1 H, a), 6.16 (d of t, *J* = 18.5 Hz, 6 Hz, 1 H, b); ^{13}C NMR -3.62 (s, Si*Me*), 13.72 (e), 21.74 (d), 38.98 (c), 125.37 (b), 127.77 (o), 129.12 (p), 134.84 (m), 137.12 (i), 151.35 (a). HRGCMS: calcd for $C_{18}H_{22}Si$ (M^+), *m/e* 266.1491; found, *m/e* 266.1495.

6-α: ^{1}H NMR 0.64 (s, 3 H, SiMe), 0.82 (t, *J* = 7 Hz, 3 H, e), 1.37 (1:2:3:3:2:1, *J* = 7 Hz, 2 H, d), 1.60 (d of t, *J* = 7 Hz, 1 Hz, 1 H, c), 1.96 (d, J = 7 Hz, 1 H, c′), 5.4 (m, 1 H, a), 5.83 (m, 1 H, a′); ^{13}C NMR -3.92 (s, Si*Me*), 14.29 (e), 21.99 (d), 38.25 (c), 127.77 (o), 128.37 (a), 129.21 (p), 135.07 (m), 136.19 (i), 148.24 (b).

6-cis: ^{1}H NMR 0.53 (s, 3 H, Si*Me*), 0.88 (t, *J* = 7 Hz, 3 H, e), 1.43 (1:2:3:3:2:1, *J* = 7 Hz, 2 H, d), 1.94 (m, 2 H, c), 5.3 (m, a, b); ^{13}C NMR −4.68 (Si*Me*), 13.96 (e), 20.06 (d), 25.87 (c), 123.74 (b), 132.21 (a). No HRGCMS signal was obtained for either **6**-α or **6**-cis because their signals were too weak.

$PhMe_2SiH$ + 1-Pentyne, Entry 7 of Table I. $PhMe_2SiH$ (2.76 g, 20.3 mmol) and 1-pentyne (1.38 g, 20.3 mmol) were combined with the Karstedt catalyst (3 μL, 0.8 μmol of Pt). Analysis by GC showed complete conversion after ca. 1 h at ambient temperature to a mixture of low-RT product (21.5%) and a high-RT product (78.5%). HRGCMS: calcd for $C_{13}H_{20}Si$ (M^+), *m/e* 204.1334; found for the low-RT product, *m/e* 204.1316, high-RT product, *m/e* 204.1321. ^{1}H NMR integration showed the mixture contained 70% β trans, 25% α, and 5% β cis.

7-trans: ^{1}H NMR 0.31 (s, 6 H, Si*Me*), 0.91 (t, *J* = 7 Hz, 3 H, e), 1.40 (1:2:3:3:2:1, *J* = 7 Hz, 2 H, d), 2.09 (1:2:2:1, *J* = 7 Hz, 2 H, c), 5.76 (d of t, *J* = 18.5 Hz, 1.3 Hz, 1 H, a), 6.11 (d of t, *J* = 18.5 Hz, 6.3 Hz, 1 H, b), ^{13}C NMR −2.38 (Si*Me*), 13.70 (e), 21.84 (d), 38.94 (c), 124.28 (b), 127.68 (o), 128.77 (p), 133.79 (m), 139.18 (i), 149.07 (a).

7-α: ^{1}H NMR 0.35 (s, 6 H, Si*Me*), 0.82 (t, *J* = 7 Hz, 3 H, e), 1.35 (1:2:3:3:2:1, *J* = 7 Hz, 2 H, d), 1.62 (d, *J* = 7 Hz, 1 H, c), 2.09 (d, *J* = 7 Hz, 1 H, c′), 5.40 (d of t, *J* = 3 Hz, 1 Hz, 1 H, a), 5.66 (m, 1 H, a′). ^{13}C NMR -3.42 (Si*Me*), 14.42 (e), 21.57 (d), 38.27 (c), 125.86 (b), 127.61 (o), 128.77 (p), 133.59 (m), 139.0 (i), 150.0 (a).

7-cis: ^{1}H NMR 0.25 (s, 6 H, Si*Me*), 0.88 (t, *J* = 7 Hz, 3 H, e), 1.37 (1:2:3:3:2:1, *J* = 7 Hz, 2 H, d), 1.95 (sex, *J* = 7 Hz, 2 H, c), 5.31 (m, 2 H, a, b); ^{13}C NMR −2.86 (Si*Me*), 13.93 (e), 22.05 (d), 25.91 (c), 127.57 (o), 128.77 (p), 131.38 (b), 133.53 (m), 138.9 (i), 143.51 (a).

Et_3SiH + 1-Pentyne, Entry 8 of Table I. Et_3SiH (2.36 g, 19.8 mmol) was combined with 1-pentyne (1.38 g, 20.3 mmol) and the Karstedt catalyst (3 μL, 0.8 μmol of Pt). Analysis by GC after ca. 1 h at ambient temperature showed complete conversion to product but with no separation of isomers by GC. HRGCMS: calcd for $C_{11}H_{24}Si$ (M^+), *m/e* 184.1647; found, *m/e* 184.1644. HREIMS (direct probe): found, *m/e* 184.1647. By ^{1}H NMR integration the product mixture contained a mixture of 89% β trans and 11% α.

8-trans: ^{1}H NMR 0.57 (q, *J* = 8 Hz, 6 H, f), 0.96 (t, *J* = 8 Hz, 9 H, g), 0.92 (t, *J* = 8 Hz, 3 H, e), 1.44 (sex, *J* = 7 Hz, 2 H, d), 2.11 (m, 2 H, c), 5.57 (d of t, *J* = 18.7 Hz, 1.4 Hz, 1 H, a), 6.05 (d of t, *J* = 18.7 Hz, 6.2 Hz, 1 H, b); ^{13}C NMR 3.56 (f), 7.31 (g), 13.54 (e), 22.01 (d), 39.19 (c), 125.77 (b), 148.52 (a).

8-α: ^{1}H NMR 0.60 (q, *J* = 8 Hz, 6 H, f), 0.96 (t, *J* = 8 Hz, 9 H, g), 5.32 (m, 1 H, a), 5.65 (m, 1 H, a′); ^{13}C NMR 2.96 (f), 6.52 (g), 14.0 (e), 21.90 (d), 38.63 (c), 125.07 (a), 148.45 (b). These results agree with those reported for pentyne[22,27] and for 1-butyne in place of 1-pentyne.[21]

The above reaction was rerun with Et_3SiH (1 g, 6.3 mmol), 1-pentyne (0.62 g, 6.3 mmol), and $CODPtCl_2$ (COD = 1,5-cyclooctadiene, 5 mg, 13 μmol). ^{1}H NMR analysis showed complete conversion to 88% β trans and 12% α.

Et_3SiH + 1-Pentyne Catalyzed by Rh Catalysts. The reaction described immediately above was rerun exactly except that $(PPh_3)_3RhCl$ (3.8 mg, 4.1 μmol) was used in place of $CODPtCl_2$. Analysis of the product distribution by ^{1}H NMR spectroscopy using this Rh catalyst showed 72% β cis, 22% β trans, and 6% α.

8-cis: ^{1}H NMR 5.40 (d of q, *J* = 14 Hz, 1.4 Hz, 2 H, a, b); ^{13}C NMR 5.76 (f), 6.54 (g), 13.80 (e), 22.89 (d), 36.06 (c), 125.11 (b), 150.08 (a). These data agreed with those reported.[25,27]

The reaction was rerun by combining Et_3SiH (0.73 g, 6.8 mmol) and 1-pentyne (0.43 g, 6.3 mmol) and then using $RhCl_3$ (0.050 g, 0.19 mmol) in 0.5 mL of *i*-PrOH in place of $(PPh_3)_3RhCl$. The products were separated by distillation through a 15-cm long x 1-cm diameter column packed with glass beads, 30 °C, 0.3 mmHg. ^{1}H NMR integration established that the mixture contained 64.5% β cis, 28.5% β trans, and 7% α.

Attempted Isomerization Experiments. The Pt-catalyzed reaction of entry 8, Table I, was repeated; ^{1}H NMR and GC analyses confirmed complete conversion to the 89% *β-trans-* and 11% α-olefinic products, "Pt reaction mixture". The Pt reaction mixture (2 mL) was combined with 1-pentyne (0.3 g, 3 mmol) and Et_3SiH (0.5 g, 3.1 mmol) and heated at 55 °C for 3 days. At the same time 1 mL of the Pt reaction mixture was combined with 1 mL of a Rh reaction mixture. [The Rh reaction mixture was prepared by reaction of 1-pentyne (4.49 g, 65.9 mmol), Et_3SiH (7.31 g, 62.6 mmol), and $[CODRhCl]_2$ (0.025 g, 0.05 mmol) to give 64.5% β cis, 28.5% β trans, and 7% α.] Heating the mixed Pt reaction mixture (1 mL) with Rh reaction mixture (1 mL) for 3 days at 55 °C gave no change in isomer mixture by ^{1}H NMR and GC analysis.

A portion of the Pt reaction mixture (1 mL) was combined with $[CODRhCl]_2$ (0.03 g, 0.06 mmol) and heated at 80 °C for 17 h. Analysis by ^{1}H NMR spectroscopy and GC showed no change in isomer composition.

Et_3SiH + PhC≡CH, Entry 9 of Table I. Et_3SiH (2.12 g, 18.2 mmol) and PhC≡CH (1.86 g, 18.2 mmol) were combined with the Karstedt catalyst (3 μL, 0.8 μmol of Pt). The mixture was heated at 60 °C for 1 h. Analysis by GC showed complete conversion to two isomers, 30:70 low-RT:high-RT ratio. HRGCMS: calcd for $C_{14}H_{22}Si$ (M^+), *m/e* 218.1491, $M^+ - C_2H_5$, *m/e* 189.1100; found for low-RT product, *m/e* 189.1067, high-RT product, *m/e* 218.1481. HREIMS (direct probe): found, *m/e* 189.1096. ^{1}H NMR integrated ratio of products showed 81.5% β trans, 17.8% α, and 0.8% β cis.

9-trans: ^{1}H NMR 0.69 (q, *J* = 8 Hz, 6 H, c), 1.00 (t, *J* = 8 Hz, 9 H, d), 6.44 (d of d, *J* = 19.3 Hz, 1.2 Hz, 1 H, a), 6.91 (d, *J* = 19.3 Hz, 1 H, b); ^{13}C NMR 3.31 (d), 7.31 (c), 125.88 (b), 126.32 (o), 126.65 (p), 128.09 (m), 128.81 (i), 144.85 (a).

9-α: ^{1}H NMR 0.66 (q, *J* = 8 Hz, 6 H, c), 0.94 (t, *J* = 8 Hz, 9 H, d), 5.58 (d of d, *J* = 3 Hz, 1.3 Hz, 1 H, a), 5.88 (d of d, *J* = 3 Hz, 1.2 Hz, 1 H, a′); ^{13}C NMR 3.54 (c), 7.42 (d), 126.1 (o), 127.89 (p), 128.49 (m), 138.52 (a), 150.44 (b). These analytical data agree with those reported.[19]

$(EtO)_3SiH$ + 1-Pentyne, Entry 10 of Table I. $(EtO)_3SiH$ (3.33 g, 20.3 mmol) and 1-pentyne (1.38 g, 20.3 mmol) were combined with the Karstedt catalyst (3 μL, 0.8 μmol of Pt). Analysis of the reaction by GC after 1 h at ambient temperature showed complete conversion to a mixture of a low-RT product (23%) and a high-RT shoulder (3%) followed by a well-resolved high-RT product peak (74%). HRGCMS: calcd for $C_{11}H_{24}O_3Si$ (M^+), *m/e* 232.1494, $M^+ - C_2H_5$, *m/e* 217.1259; found for the low-RT product, *m/e* 217.0556, high-RT product, *m/e* 232.1444. HREIMS (direct probe): found, *m/e* 232.1495. ^{1}H NMR integration of product mixture showed 63% β trans, 26% α, and 11% β cis.

10-trans: ^{1}H NMR 0.92 (t, *J* = 7 Hz, 3 H, e), 1.24 (t, *J* = 7 Hz, 9 H, g), 1.46 (m, 2 H, d), 2.14 (m, 2 H, c), 3.83 (q, *J* = 7 Hz, 6 H, f), 5.43 (d of q, *J* = 18.8 Hz, 1.6 Hz, 1 H, a), 6.44 (d of t, *J* = 18.8 Hz, 6.3 Hz, 1 H, b); ^{13}C NMR 13.67 (e), 18.27 (g), 21.52 (d), 38.76 (c), 58.46 (f), 119.11 (b), 153.86 (a).

10-cis: ^{1}H NMR 0.94 (t, *J* = 7 Hz, 3 H, e), 1.23 (t, *J* = 7 Hz, 9 H, g), 1.46 (m, 2 H, d), 2.27 (m, 2 H, c), 3.82 (q, *J* = 7 Hz, 6 H, f), 5.42 (m, a, b); ^{13}C NMR 13.97 (e), 16.31 (d), 18.27 (g), 25.87 (c), 58.39 (f), 122.37 (b), 132.50 (a).

These analytical data agree with those reported for 1-butyne in place of 1-pentyne.[21]

10-α: ^{1}H NMR 0.92 (t, *J* = 7 Hz, 3 H, e), 1.24 (t, *J* = 7 Hz, 9 H, g), 1.46 (m, 2 H, d), 1.58 (m, 1 H, c), 2.00 (m, 1 H, c′), 3.81 (q, *J* = 7 Hz, 6 H, f), 5.64 (m, 1 H, a), 5.72 (m, 1 H, a′); ^{13}C NMR 14.07 (e), 18.27 (g), 21.96 (d), 38.80 (c), 58.57 (f), 129.22 (a), 143.68 (b).

$(EtO)_3SiH$ + PhC≡CH, Entry 11 of Table I. $(EtO)_3SiH$ (2.98 g, 18.3 mmol) and PhC≡CH (1.38 g, 18.2 mmol) were combined with the Karstedt catalyst (3 μL, 0.8 μmol of Pt).

Analysis of the reaction mixture by GC after 1 h at ambient temperature showed a low-RT product (30%) and a high-RT product (70%). The product ratio was confirmed by ^1H NMR integration, 70% β trans and 30% α. HRGCMS: calcd for $C_{14}H_{22}O_3Si$ (M^+), m/e 266.1338; found for low-RT product, m/e 266.1344, high-RT product, m/e 266.1292. HREIMS (direct probe): found m/e 266.1292.

11-trans: ^1H NMR 1.27 (t, J = 7 Hz, 9 H, d), 3.88 (q, J = 7 Hz, 6 H, c), 6.18 (d, J = 19.5 Hz, 1 H, a), 7.23 (d, J = 19.5 Hz, 1 H, b); ^{13}C NMR 18.32 (d), 58.74 (c), 117.72 (b), 126.81 (o), 128.30 (p), 128.57 (m), 131.58 (i), 149.19 (a).

11-α: ^1H NMR 1.20 (t, J = 7 Hz, 9 H, d), 3.83 (q, J = 7 Hz, 6 H, c), 5.97 (d, J = 3 Hz, 1 H, a), 6.14 (d, J = 3 Hz, 1 H, a'); ^{13}C NMR 18.16 (d), 58.16 (c), 126.88 (o), 126.94 (p), 128.76 (m), 137.66 (a), 143.42 (b).

These results agree with those reported.[21]

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Supplementary Material Available: Tables of isotropic and anisotropic displacement coefficients and H atom coordinates for 1-trans and 1-α and ^1H and ^{13}C NMR spectra (33 pages); listings of structure factor amplitudes for 1-trans and 1-α (27 pages). Ordering information is given on any current masthead page.

Reactions of Triiron Dodecacarbonyl with Alkynyl- and Allenyllithium Reagents: Formation of Dinuclear Products

Dietmar Seyferth,* Colin M. Archer, and John C. Dewan

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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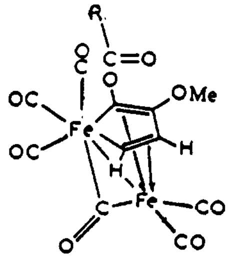
Reactions of alkynyllithium reagents with $Fe_3(CO)_{12}$ result in formation of Li[(μ-CO)(μ-RC≡C)$Fe_2(CO)_6$], whose reaction with a sulfenyl chloride, R'SCl, gives (μ-RC≡C)(μ-R'S)$Fe_2(CO)_6$ in moderate yield. The reaction of CH_2=C=C(OMe)Li with $Fe_3(CO)_{12}$, followed by addition of an acid chloride yields a ferrole complex.



2 **a**, R = Ph
b, R = t-Bu

The structure of the PhC(O)Cl-derived product (**2a**, R = Ph) was determined by X-ray diffraction. This compound crystallizes in the space group $P2_1/a$ with a = 12.444 (2) Å, b = 8.837 (2) Å, c = 18.429 (3) Å, β = 105.77 (1)°, and Z = 4. Final R_1 = 0.050 and R_2 = 0.058.

Introduction

Our earlier studies have shown that lithium and sodium thiolates react with $Fe_3(CO)_{12}$ to form a dinuclear anion, [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$. This species shows broad reactivity toward electrophilic substrates that are potential 3-electron donors.[1-10] In an attempt to determine how general the concept shown in eq 1 is, we have investigated the reactions of $Fe_3(CO)_{12}$ with two types of unsaturated organolithium reagents whose organic groups are potential 3-electron donors.

$$Fe_3(CO)_{12} \xrightarrow{Nu^-} [(\mu\text{-CO})(\mu\text{-Nu})Fe_2(CO)_6]^- \xrightarrow{E^+} [(\mu\text{-E})(\mu\text{-Nu})Fe_2(CO)_6] \quad (1)$$

Results and Discussion

Alkynyllithium Reagents. When a solution of (*tert*-butylethynyl)lithium ((3,3-dimethylbut-1-ynyl)lithium) in THF was added at room temperature to a THF solution of an equimolar quantity of $Fe_3(CO)_{12}$, a color change from green to dark red was observed. To the solution thus formed was added, at −78 °C, an equimolar quantity of *t*-BuSCl. From the reaction mixture one product could be isolated, (μ-σ,π-*t*-BuC≡C)(μ-*t*-BuS)$Fe_2(CO)_6$, a red solid, in 40% yield. This compound had been prepared earlier by the reaction of *t*-BuC≡CBr with [Et_3NH][(μ-CO)(μ-*t*-BuS)$Fe_2(CO)_6$].[7] A similar reaction in which EtSCl was the reactive electrophile gave (μ-σ,π-*t*-BuC≡C)(μ-EtS)$Fe_2(CO)_6$ in 40% yield. Also prepared in 36% yield from PhC≡CLi was (μ-σ,π-PhC≡C)(μ-*t*-BuS)$Fe_2(CO)_6$. These products most likely were formed by the reaction sequence shown in Scheme I, so the general process of eq

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