The absorption spectra of 1- and 2-nitronaphthalene anions shown in F and G of Figure 10 provide a particularly interesting comparison with their PD spectra. The absorption spectrum of each of these is unique and relatively complex. Nevertheless, their essential features are apparent in the PD spectra of these two anions shown most clearly in B and C of Figure 7.

Conclusions

We have described and demonstrated a means for measuring the electron photodetachment spectra of polyatomic negative ions at atmospheric pressure. Several significant advantages have been demonstrated to accompany the use of the PDM-ECD for PD measurements. Stable molecular radical anions can be easily generated by resonance electron capture. The internal energy of the ions being studied is under good experimental control since they are in thermal equilibrium with the buffer gas. Absolute PD cross sections are readily determined by the PDM-ECD. While in this study absolute σ_d measurements were made using a reference negative ion whose σ_d was known at a specific wavelength, we have previously shown[8] that absolute PD cross sections can also be accurately determined by the PDM-ECD method without use of a calibration standard. Although these PD spectra were obtained with a low-resolution light system, the PDM-ECD should be equally applicable to the measurement of high-resolution PD spectra with lasers. The most apparent disadvantage of the PDM-ECD method for PD measurements is that the identities of the ions are not indicated by the instrument and must be determined by other means. In the present study this complementary information was readily provided by an atmospheric pressure ionization mass spectrometer.

Both the direct PD and resonance PD mechanisms have been shown to be operative in the PD spectra of 31 different nitroaromatic anions studied here. From measurements involving direct PD, the first detectable onset for photodetachment was determined for 30 molecular anions and 24 of these were compared with known adiabatic electron affinities of the molecules which had been previously determined through measurements of gas-phase electron transfer equilibria.[7,18,19] This comparison of spectroscopic and thermodynamic measurements was found to be consistent with a simple model of direct PD for the nitroaromatic hydrocarbons in which the structures of some of the anions were envisioned to be different and more constrained than those of the molecules. Additional evidence concerning the unusually large geometry change which has been previously suggested[19] to accompany the negative ionization of *p*-dinitrobenzene has been provided here. A systematic tendency for ortho-substituted nitrobenzenes to undergo significant geometry change upon negative ionization was also noted.

A comparison of the gas-phase PD spectra measured here at 200 °C with UV-vis absorption spectra of several of the nitroaromatic anions previously measured[20] in frozen glassy matrices at 77 K indicate that resonance PD is operative and efficient for many of the nitroaromatic anions. Since the peaks and resonances observed are initiated by electronic transitions of the molecular anions, the PD spectra provide a wealth of information concerning the molecular orbitals of the numerous substituted nitroaromatic anions studied here. The resonance PD mechanism accounts for the very high PD cross sections which were frequently observed. The largest PD cross section measured was for 9-nitroanthracene anion, where $\sigma_d = 0.42$ Å^2 at 600 nm. It was concluded that structural differences between the molecule and anion have a strong influence on the facility of the resonance PD mechanism and significantly decrease the magnitude of σ_d at peak maxima whenever poor Franck-Condon factors are suspected.

In our initial report of the PDM-ECD,[8] its application to the sensitive and specific analysis of trace quantities of organic iodides and bromides in the presence of organic chlorides was demonstrated. The discovery here of large and varied PD cross sections for nitroaromatic anions suggests that the PDM-ECD, when used in combination with gas chromatography, also possesses high potential for the selective and sensitive analysis of these molecules. It seems likely that this potential for trace organic analysis might also extend to other classes of compounds of environmental or biomedical interest which can be made to undergo electron capture and photodetachment rapidly under the influence of a specific bandwidth of light.

Acknowledgment. We thank Douglas Zook and David Theiste of MSU for providing the APIMS measurements and the computer-generated figures reported here. This work was supported by the Chemical Analysis Division of the National Science Foundation under Grant No. CHE-8711618.

Selective, Zirconium-Mediated Cross-Coupling of Alkynes: Synthesis of Isomerically Pure 1,3-Dienes and 1,4-Diiodo 1,3-Dienes

Stephen L. Buchwald* and Ralph B. Nielsen

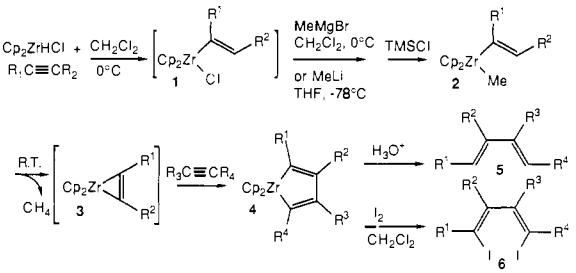
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received July 12, 1988*

Abstract: The coupling reaction of zirconocene alkyne complexes with a second alkyne provides a general method for the preparation of asymmetrically substituted zirconacyclopentadienes. The overall transformation is the chemoselective and regioselective *intermolecular* cross-coupling of two alkynes, a goal that has not been achieved with other methodology. Isomerically pure 1,3-dienes or 1,4-diiodo 1,3-dienes are obtained upon treatment of the metallacyclopentadienes with aqueous acid or iodine. Because this synthesis can be carried out as a one-pot procedure starting from the alkynes and Schwartz's reagent (Cp_2ZrHCl), it is an attractive alternative to other transition-metal-based methods for the synthesis of dienes from vinyl halides and isolated vinylmetal starting materials.

Recent advances in organopalladium and organonickel chemistry have led to the development of several preparatively useful methods for the synthesis of isomerically pure 1,3-dienes.[1] Although these methods have the advantage that they are often

0002-7863/89/1511-2870$01.50/0

Scheme I



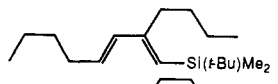
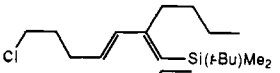
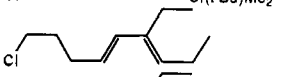
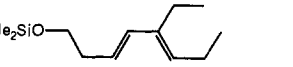
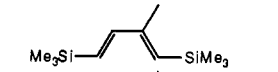
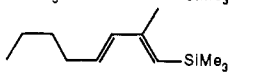
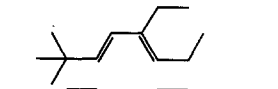
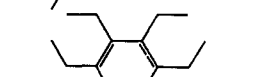
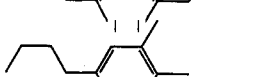
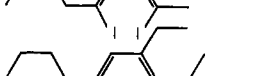
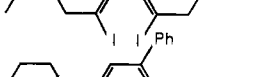
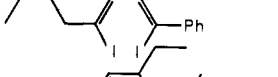
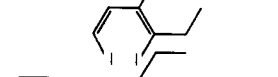
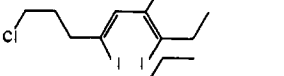
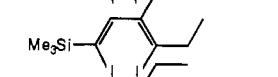
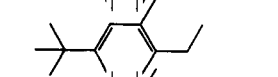
catalytic in palladium or nickel, a major drawback to this route is the need for the preparation and isolation of geometrically pure vinyl halides.[1] Oftentimes this is best accomplished with stoichiometric organometallic reagents, such as the hydrozirconation of an alkyne with $Cp_2Zr(H)Cl$ followed by treatment of the vinylzirconocene derivative with iodine.[1c] We now report a general and selective route to directly form stereodefined 1,3-dienes, based on a stoichiometric, zirconium-mediated reductive coupling of two different alkyne substrates.

For some time it has been known that a free group 4 metallocene or its equivalent (i.e., Cp_2M (M = Ti, Zr, Hf)) can reductively couple two alkynes to give symmetrically tetrasubstituted metallacyclopentadiene products. A number of examples of this reaction type using diphenylacetylene have been reported,[2] and there are a few examples where similar chemistry has been extended to other symmetric internal alkynes.[3] There is one report of the coupling of terminal alkynes with $Cp_2Ti(PMe_3)_2$.[4] Recently, Nugent and Fagan[5] and Negishi[6] have developed the intramolecular coupling of diynes and enynes using a "Cp_2M" reagent. The intermediate metallacycles have been converted into a variety of other compounds, including exocyclic olefins,[5a-c] bicyclic cyclopentenones,[6] and main-group heterocycles.[5d]

Although the synthetic utility of intramolecular cross-coupling has been demonstrated, the corresponding intermolecular reaction has held little promise as a useful synthetic tool. First, the generation of free Cp_2M or its equivalent in the presence of two different alkynes usually leads to a nearly statistical mixture of cross- and self-coupled products. The single reported example of selective intermolecular coupling, other than from our laboratory (vide infra), is the coupling of diphenylacetylene with 5-decyne reported in Negishi.[7] Although useful, this approach does not generally allow for selective cross-coupling of two alkynes and it requires that one of the coupling partners be diphenylacetylene. A second problem is that the factors that control the regiochemical outcome of intermolecular cross-coupling reactions are not understood. Even if chemoselective cross-coupling of two unsymmetrically substituted alkynes can be achieved, up to four regioisomeric products could conceivably result. In contrast, only one isomer results in the intramolecular reaction because of simple geometric constraints of the diyne molecule. A third problem is that sensitive functional groups such as silyl ethers, alkyl halides, and terminal alkynes are incompatible with the relatively harsh, highly reducing conditions that are frequently used to generate Cp_2M. Recent work of Negishi[6] and Nugent[5] has shown that milder reagents such as $Cp_2Zr(n\text{-}Bu)_2$ are compatible with some functionalized enynes, but terminal alkynes appear to be incompatible with this reagent.

We recently reported a method for the preparation of trimethylphosphine-stabilized zirconocene complexes of 1-hexyne and 3-hexyne, and we briefly investigated their reactivity.[8] This

Table I. Dienes **5** and Diiodo Dienes **6**

Entry		Yield	Isomeric Purity	Chemical Purity
5a		66%	>98%	>97%
5b		67%	>98%	≈90%*
		*1-(TBDMS)-1-hexyne impurity		
5c		70%	>96%	>98%
5d		52%	>97%	>98%
5e		45%	>98%	>98%
5f		74%	>98%	>98%
5g		69%	>98%	>98%
6a		73%	>98%	>98%
6b		84%	>98%	>98%
6c		86%	>98%	>98%
6d		80%	>98%	>98%
6e		53%	>98%	>93%*
			*Contaminated with **6a**	
6f		68%	>98%	>98%
6g		87%	>98%	≈96%
6h		86%	>98%	>98%
6i		74%	≈95%	>98%

(1) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813 and references therein. (c) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138. (d) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393 and references therein. (e) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (f) Tellier, F.; Sauvêtre, R.; Normant, J. F. *J. Organomet. Chem.* **1986**, *303*, 309. (g) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47. (h) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. (i) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178.

(2) (a) Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15. (b) Shur, V. B.; Berkovich, E. G.; Vol'pin, M. E.; Lorenz, B.; Wahren, M. *J. Organomet. Chem.* **1982**, *228*, C36. (c) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. (d) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299. (e) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936. (f) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 66. (g) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398. (h) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5079. (i) Watt, G. W.; Drummond, F. O., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 826. (j) Lau, C. P.; Chang, B. H.; Grubbs, R. H.; Brubaker, C. H. *J. Organomet. Chem.* **1981**, *214*, 325.

(3) (a) Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65. (b) Sabade, M. B.; Farona, M. F. *J. Organomet. Chem.* **1986**, *310*, 311. (c) Demerseman, B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1981**, 665. (d) Yoshifuji, M.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *153*, C15.

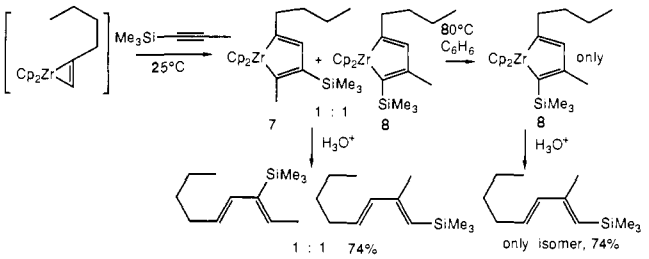
(4) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 3717.

(5) (a) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. (b) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (c) Parshall, G. W.; Nugent, W. A.; Chan, D. M. T.; Tam, W. *Pure Appl. Chem.* **1985**, *57*, 1809. (d) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(6) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (c) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. (d) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(7) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623.

Scheme II



procedure is generally applicable for the preparation of complexes of a variety of alkyne complexes, *including complexes of terminal alkynes*. We now report that ligand-free alkyne complexes can be generated in an in situ manner and selectively trapped with a second alkyne to form asymmetrically substituted zirconacyclopentadienes (Scheme I). Hydrozirconation of the first alkyne with Schwartz's reagent[9] yields the chlorovinylzirconocene **1**, which is converted to the methylvinylzirconocene **2** with either methyllithium in tetrahydrofuran or methylmagnesium bromide in CH_2Cl_2. Compound **2** loses methane at room temperature to form an intermediate alkyne complex **3**, which couples with the second alkyne to form the metallacyclopentadiene **4**. The metallacycle **4** is converted to the diene **5** after treatment with aqueous acid, or to the diiodide **6** upon treatment with ~2.5 equiv of solid I_2 in CH_2Cl_2 at 0 °C (Table I). In most cases this sequence can be carried out as a one-pot procedure, requiring no isolation or purification of any organometallic intermediates, using CH_2Cl_2 as solvent. In many cases only a single regioisomer is observed. In some cases where mixtures are initially formed, equilibration of the mixture to one isomer can be accomplished by heating the reaction mixture to 80 °C. The metallacycles are cleaved with essentially *complete retention of configuration* by protonolysis to give 1,3-dienes or by iodinolysis to give stereodefined 1,4-diiodo 1,3-dienes, which are notoriously difficult to prepare by other means.[10] The latter should be useful as both 1,4-dianion equivalents through halogen–metal exchange[10] and 1,4-dication equivalents through palladium-catalyzed coupling with other vinylmetal species.[1] No evidence is seen for any double-bond isomerization of the diiodo dienes, even after exposure to excess iodine at room temperature for several days.

We have also carried out the first detailed study[11] of the regiochemical outcome of the intermolecular coupling reactions of two alkynes. The regioselectivity of the coupling reactions is, in most cases, predictable based on the nature of the four substituents. If the first alkyne is terminal ($R^2 = H$), coupling occurs such that the hydrogen substituent is in the β-position of the metallacyclopentadiene intermediate. If the second alkyne is an asymmetric internal alkyne ($R^1 \neq R^2$, $R^3 \neq R^4$), a mixture of regioisomers usually results.[12] A notable exception to this is the case where the second alkyne has a silyl substituent (**5a,b,e,f,6i**). The initial coupling reaction at room temperature gives a mixture of regioisomers (**7** and **8**, as shown in Scheme II for the coupling of 1-hexyne with 1-(trimethylsilyl)-1-propyne). Heating the mixture to 80 °C in benzene leads to complete isomerization to the isomer in which the proton on the first alkyne is in the β-position and the silyl substituent of the second alkyne is in the α-position.[13] We believe that both electronic (trialkylsilyl groups are known to stabilize α-carbanions[14]) and steric factors (the α-position is probably less hindered than the β-position[5b]) are responsible for the regiochemical outcome of these equilibrations.

Attempts to use a terminal alkyne as the second coupling partner lead to a mixture of products as has been previously seen by other workers.[5,6] We note that high yields are not obtained when propargyl halides or propargyl ethers are employed. The fact that both 5-chloro-1-pentyne and silyl-protected 3-butyn-1-ol couple smoothly suggests that the difficulties are not due to the inherent reactivity of a primary alkyl halide or a protected alcohol.

In conclusion, we have developed an efficient and selective synthesis of dienes and dihalo dienes from alkyne precursors. This methodology allows for the ready synthesis of a number of 1,3-dienes that are difficult to prepare by other available procedures. The use of alkynes, and not vinyl halides, as the organic starting materials greatly enhances the generality of this method. This coupling strategy is certainly not limited to the synthesis of the two types of organic products reported in this paper. In particular, the "metallacycle transfer" reactions recently reported by Nugent and Fagan[5d] combined with the selective intermolecular couplings reported here should allow for the preparation of a wide spectrum of interesting molecules. Our results in utilizing this and related methodology for the synthesis of a variety of heterocyclic compounds will be the subject of future reports.

Experimental Section

General. All manipulations, unless otherwise noted, were conducted under a nitrogen or argon atmosphere by using standard Schlenk techniques. NMR spectra were recorded on Bruker WM-250, Varian XL-300, or Varian VXR-500 Fourier transform spectrometers. IR spectra were recorded on a Mattson Instruments Cygnus 100 Fourier transform spectrometer. Gas chromatography analyses were performed on a Hewlett-Packard Model 5890 GC with a flame ionization detector using a 25-m capillary column with cross-linked SE-30 as stationary phase. Gas chromatography/mass spectrum analyses were obtained with a Hewlett-Packard System 5990A GCMS. Electron impact mass spectra and high-resolution mass determinations (HRMS) were recorded on a Finnigan MAT System 8200.

Tetrahydrofuran and benzene-d_6 were distilled or vacuum transferred from sodium/benzophenone ketyl, and CH_2Cl_2 was distilled from CaH_2. Cp_2ZrHCl was prepared according to our published procedure.[9b] Silyl-protected alcohols and alkynes were prepared by conventional procedures. All other reagents were available from commercial sources and were used as received.

General Procedure A for the Preparation of Dienes 5. Cp_2ZrHCl (2.58 g, 10 mmol) was slurried in 30 mL of CH_2Cl_2 at 0 °C under an argon atmosphere, and the first alkyne was added via syringe. The mixture was allowed to stir at 0 °C for 15–60 min, depending on the alkyne, until hydrozirconation was complete, as evidenced by the disappearance of the insoluble hydride and the formation of a clear solution. (In the cases that utilized volatile alkynes, the solvent and any excess of the alkyne were removed under vacuum, and the residue was redissolved in 30 mL of CH_2Cl_2). The second alkyne was added to the 0 °C mixture, and a solution of methylmagnesium bromide (5.38 mL, 1.9 M in ether, 10.5 mmol, Aldrich) was added dropwise over 60 s. The mixture was stirred 60 s at 0 °C, and chlorotrimethylsilane (0.25 mL, 1 mmol) was then added. The mixture was allowed to stir at room temperature until evolution of methane ceased (typically 16–24 h). (If the second alkyne had a single silyl substituent, the solvent was replaced with benzene (30 mL) and the mixture was heated to 80 °C for 24 h.) The resulting solution of **4** with suspended magnesium salts was opened to air and immediately poured into a separatory funnel containing 200 mL of 5% acetic acid and 100 mL of pentane. The mixture was shaken vigorously for 4 min, and the organic layer was separated and washed sequentially with 100 mL of 5% acetic acid and 100 mL of saturated NaCl. The combined organic layer was dried over K_2CO_3 and evaporated to yield the diene, which was purified by radial plate chromatography (Chromatotron, 4-mm silica plate, pentane eluent).

General Procedure B for the Preparation of Dienes 5. Hydrozirconation was carried out as in procedure A, and the solvent was re-

(8) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544.

(9) (a) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (b) For an improved preparation of Schwartz's reagent, cf.: Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

(10) (a) Ashe, A. J.; Drone, F. J. *Organometallics* **1985**, *4*, 1478 and references therein. (b) Reich, I. L.; Haile, C. L.; Reich, H. J. *J. Org. Chem.* **1978**, *43*, 2402 and references therein.

(11) Alt, Rausch, and co-workers have described the selective formation of the α,α'-diphenyltitanacyclopentadiene and a mixture of the regioisomeric dimethyltitanacyclopentadienes in the reaction of $Cp_2Ti(PMe_3)_2$ with, respectively, phenylacetylene and propyne. No discussion of the factors that influence the regiochemical outcome of these coupling reactions is given in this communication.[4]

(12) For example, coupling of the in situ generated 1-hexyne complex with 2-pentyne gives a 1:1 mixture of regioisomers even after heating at 105 °C for 24 h.

(13) Mattia, J.; Humphrey, M. B.; Rogers, R. D.; Atwood, J. L.; Rausch, M. D. *Inorg. Chem.* **1978**, *17*, 3257.

(14) Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, p 520.

moved under vacuum. The product was redissolved in 30 mL of THF, and the solution was cooled to −78 °C. A solution of methyllithium (7.34 mL, 1.43 M in ether, 10.5 mmol, Aldrich) was added. After 5 min of reaction time, chlorotrimethylsilane (0.25 mmol, 1 mmol) was added, followed by the second alkyne. The mixture was allowed to stir at room temperature until methane evolution ceased (16–24 h). (If the second alkyne had a single silyl substituent, the solvent was replaced with benzene (30 mL) and the mixture was heated to 80 °C for 24 h.) The solvent was removed under vacuum, and 30 mL of CH_2Cl_2 was added. The resulting solution of **4** with suspended lithium salts was then subjected to aqueous workup as in procedure A.

General Procedure C for the Preparation of Diiodides 6. A solution of **4** in CH_2Cl_2 was prepared as in procedure A. The stirred solution was cooled to 0 °C, and solid I_2 (Mallinckrodt, 5.1–7.6 g, 20–30 mmol) was added over ~10 min until the dark iodine color persisted. The mixture was stirred for 1 h at room temperature, opened to air, and poured into a separatory funnel containing 200 mL of 5% acetic acid and 100 mL of pentane. The mixture was shaken for 5 min, and the organic layer was washed with 100 mL of 5% acetic acid, 100 mL of water, 100 mL of 5% $NaHCO_3$, and 100 mL of 5% $NaHSO_3$. The aqueous layers were separately back-extracted with pentane. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. (The mixture frequently contains small amounts of thermally unstable impurities, and further purification is usually simplified by allowing a solution of the crude product in 10 mL of pentane to stand overnight at room temperature, followed by filtration to remove the dark precipitate that forms.) The product was purified by radial plate chromatography (Chromatotron, 4-mm silica plate, pentane eluent).

General Procedure D for the Preparation of Diiodides 6. A solution of **4** in CH_2Cl_2 was prepared as in procedure B. The mixture was subjected to iodinolysis, aqueous workup, and chromatography as in procedure C.

5a: Using procedure B with first alkyne = 1-hexyne (1.38 mL, 12 mmol, Wiley), second alkyne = 1-(*tert*-butyldimethylsilyl)-1-hexyne (1.97 g, 10 mmol). The metallacycle was heated to 80 °C for 12 h in benzene solvent before hydrolysis. Yield 1.840 g (66%), >97% pure by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 6 H), 0.80–1.00 (m, 15 H), 1.20–1.50 (m, 8 H), 2.09 (m, 2 H), 2.27 (m, 2 H), 5.37 (s, 1 H), 6.68 (dt, J = 15, 6.5 Hz, 1 H), 6.00 (d, J = 15 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ −4.153, 13.99, 14.01, 16.94, 22.32, 23.31, 26.53 (large), 31.59, 32.37, 32.51, 32.63, 125.44, 130.11, 135.43, 156.23. IR (neat, NaCl) 3017, 2956, 2929, 2858, 1572, 1470, 1464, 1389, 1378, 1362, 1254, 1248, 1007, 966, 938, 861, 835, 826, 809, 779, 717, 683, 656 cm^{-1}. MS (EI) showed M^+ = 280. HRMS calcd for $C_{18}H_{36}Si$, 280.2586: found, 280.2586 ± 0.0004.

5b: Using procedure B with first alkyne = 5-chloro-1-pentyne (1.06 mL, 10 mmol, Farchan), second alkyne = 1-(*tert*-butyldimethylsilyl)-1-hexyne (1.97 g, 10 mmol). The metallacycle was heated to 80 °C for 12 h in benzene solvent before hydrolysis. Yield 2.25 g containing 10% of the starting 1-(*tert*-butyldimethylsilyl)-1-hexyne (67% yield of **5b**). ^1H NMR (500 MHz, $CDCl_3$) δ 0.095 (s, 6 H), 0.892 (s, 9 H), 0.926 (t, J = 7 Hz, 3 H), 1.40–1.53 (m, 4 H), 1.893 (5 lines, 2 H), 2.20–2.30 (m, 4 H), 3.549 (t, J = 6.6 Hz, 2 H), 5.407 (s, 1 H), 5.628 (dt, J = 15, 7 Hz, 1 H), 6.048 (d, J = 15 Hz, 1 H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ −4.16, 14.03, 16.95, 23.31, 26.53 (large), 29.90, 32.22, 32.32, 32.59, 44.40, 126.56, 127.44, 136.88, 155.72. IR (neat, NaCl) 3019, 2956, 2929, 2857, 1573, 1470, 1463, 1255, 1248, 1007, 968, 836, 825, 810, 778, 657 cm^{-1}. MS (EI) showed M^+ = 300. HRMS calcd for $C_{17}H_{33}ClSi$, 300.2040; found, 300.2040 ± 0.0010.

5c: Using procedure B with first alkyne = 5-chloro-1-pentyne (1.06 mL, 10 mmol, Farchan), second alkyne = 3-hexyne (1.25 mL, 11 mmol). Yield 1.302 g (70%), >96% isomeric purity and >98% chemical purity by GC. ^1H NMR (500 MHz, $CDCl_3$) δ 0.992 (t, J = 6.7 Hz, 2 H), 1.87 (m, 2 H), 2.11 (m, 2 H), 2.23 (m, 4 H), 3.54 (t, J = 6.7 Hz, 2 H), 5.33 (t, J = 7.3 Hz, 1 H), 5.52 (dt, J = 15.6, 7.1 Hz, 1 H), 5.97 (d, J = 15.6 Hz, 1 H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 13.80, 14.32, 19.85, 21.12, 29.97, 32.47, 44.43, 124.69, 132.43, 134.56, 139.05. IR (neat, NaCl) 3022, 2966, 2963, 2934, 2875, 1677, 1673, 1621, 1455, 1444, 1375, 1298, 1280, 1059, 966, 906, 866, 808, 727, 655 cm^{-1}. GCMS showed M^+ = 186. HRMS calcd for $C_{11}H_{19}Cl$, 186.1175; found, 186.1174 ± 0.0006.

5d: Using procedure A with first alkyne = 4-(*tert*-butyldimethylsiloxy)-1-butyne (1.84 g, 10 mmol), second alkyne = 3-hexyne (1.25 mL, 11 mmol, Wiley). Yield 1.387 g (52%), >97% isomeric purity and >98% chemical purity by GC. ^1H NMR (500 MHz, $CDCl_3$) δ 0.052 (s, 6 H), 0.895 (s, 9 H), 0.986 (t, J = 7.5 Hz, 3 H), 0.993 (t, J = 7.5 Hz, 3 H), 2.107 (5 lines, 2 H), 2.210, (q, J = 7.5 Hz, 2 H), 2.310 (4 lines, 2 H), 3.644 (t, J = 7.0 Hz, 2 H), 5.312 (t, J = 7.3 Hz, 1 H), 5.578 (dt, J = 15.7, 7.3 Hz, 1 H), 5.973 (d, J = 15.7 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ −5.26 (q), 13.78 (q), 14.33 (q), 18.36 (s), 19.81 (t), 21.12 (t), 25.99 (q), 36.58 (t), 63.34 (t), 123.03 (d), 132.20 (d), 134.98 (d), 139.26 (s). IR (neat, NaCl) 3022, 2962, 2932, 2858, 1472, 1463, 1384, 1361, 1256, 1104, 1006, 965, 938, 836, 812, 775, 664 cm^{-1}. GCMS showed a small peak at M^+ = 268 and a large peak at $M^+ - 57$ ($M^+ - t$-Bu) = 211. HRMS calcd for $C_{16}H_{32}OSi$, 268.2222; found, 268.2222 ± 0.0005.

5e: Using procedure A with first alkyne = (trimethylsilyl)acetylene (1.60 mL, 11 mmol), second alkyne = 1-(trimethylsilyl)-1-propyne (1.48 mL, 10 mmol, Wiley). The metallacycle was heated to 80 °C for 24 h in benzene solvent before hydrolysis. Yield 0.962 g (45%), >98% purity by GC. ^1H NMR (300 MHz, $CDCl_3$) δ 0.091 (s, 6 H), 0.142 (s, 6 H), 1.906 (s, 3 H), 5.609 (s, 1 H), 5.850 (d, J = 18.7 Hz, 1 H), 6.570 (d, J = 18.7 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ −1.23 (q), 0.09 (q), 16.92 (q), 128.52 (d), 132.87 (d), 150.17 (d), 151.09 (s). IR (neat, NaCl) 2955, 1564, 1249, 1203, 986, 862, 840, 787, 770, 696 cm^{-1}. GCMS showed M^+ = 212. HRMS calcd for $C_{11}H_{24}Si_2$, 212.1417; found, 212.1417 ± 0.0006.

5f: Using procedure A with first alkyne = 1-hexyne (1.25 mL, 11 mmol), second alkyne = 1-(trimethylsilyl)-1-propyne (1.48 mL, 10 mmol, Wiley). The metallacycle was heated to 80 °C for 24 h in benzene solvent before hydrolysis. Yield 1.468 g (74%), >98% purity by GC. ^1H NMR (300 MHz, $CDCl_3$) δ −0.01 (s, 9 H), 0.76 (t, J = 7 Hz, 3 H), 1.10–1.30 (m, 4 H), 1.75 (s, 3 H), 1.96 (m, 4 lines, 2 H), 5.27 (s, 1 H), 5.55 (dt, J = 15.5, 7 Hz, 1 H), 5.96 (d, J = 15.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 0.07, 13.94, 17.70, 22.29, 31.63, 32.40, 129.14, 130.47, 136.67, 150.20. IR (neat, NaCl) 3013, 2957, 2927, 2874, 2860, 1580, 1466, 1458, 1442, 1379, 1260, 1248, 965, 869, 837, 770, 710, 690 cm^{-1}. GCMS showed M^+ = 196. HRMS calcd for $C_{12}H_{24}Si$, 196.1647; found, 196.1647 ± 0.0006.

5g: Using procedure A with first alkyne = 3,3-dimethyl-1-butyne (1.30 mL, 10.5 mmol), second alkyne = 3-hexyne (1.25 mL, 11 mmol, Wiley). Yield 1.146 g (69%), >98% purity by GC. ^1H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J = 7 Hz, 6 H), 1.04 (s, 9 H), 2.12 (5 lines, 2 H), 2.23 (q, J = 7 Hz, 2 H), 5.34 (t, J = 7 Hz, 1 H), 5.62 (d, J = 16 Hz, 1 H), 5.86 (d, J = 16 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 13.82, 14.38, 19.85, 21.17, 29.79, 32.93, 127.48, 131.74, 138.17, 139.36. IR (neat, NaCl) 3023, 2961, 2904, 2874, 1473, 1462, 1362, 1296, 1260, 1060, 968, 905, 870, 822, 748 cm^{-1}. GCMS showed M^+ = 166. HRMS calcd for $C_{12}H_{22}$, 166.1721; found, 166.1719 ± 0.0003.

6a: Using procedure D with first alkyne = 3-hexyne (1.38 mL, 12 mmol, Wiley), second alkyne = 3-hexyne (1.38 mL, 12 mmol, Wiley), and iodine (7.58 g, 30 mmol). Yield 3.095 g (73%), >98% pure by GC. ^1H NMR (500 MHz, $CDCl_3$) δ 1.116 (t, J = 7 Hz, 6 H, overlapped), 1.120 (t, J = 7 Hz, 6 H, overlapped), 2.250, 2.386 (ab of multiplets, 4 H), 2.546, 2.657 (ab of multiplets, 4 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ 13.32 (q), 13.77 (q), 25.46 (t), 34.51 (t), 108.66 (s), 149.18 (s). IR (neat, NaCl) 2969, 2932, 2872, 1629, 1605, 1459, 1451, 1429, 1375, 1314, 1276, 1257, 1216, 1124, 1107, 1091, 1058, 939, 853, 810, 779 cm^{-1}. GCMS showed no M^+ = 418, but $M^+ - 127$ (I^-) = 291. HRMS calcd for $C_{12}H_{20}I$, 291.0610; found, 291.0612 ± 0.0010.

6b: Using procedure D with first alkyne = 1-hexyne (1.38 mL, 12 mmol, Wiley), second alkyne = 2-butyne (0.94 mL, 12 mmol, Wiley), and iodine (6.00 g, 24 mmol). Yield 3.30 g (84%), >98% pure by GC. ^1H NMR (500 MHz, $CDCl_3$) δ 0.930 (t, J = 7.3 Hz, 3 H), 1.370 (m, 2 H), 1.542 (m, 2 H), 1.898 (s, 3 H), 2.520 (m, 5 H), 6.238 (s, 1 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ 13.87 (q), 18.09 (q), 21.41 (q), 29.58 (q), 31.40 (t), 44.45 (t), 96.90 (s), 110.88 (s), 139.64 (s), 141.20 (d). IR (neat, NaCl) 2957, 2929, 2871, 2858, 1617, 1464, 1457, 1429, 1378, 1294, 1265, 1208, 1112, 1056, 978, 813, 741, 655, 639 cm^{-1}. MS showed a small M^+ = 390 and a large $M^+ - 127$ (I^-) = 263. HRMS calcd for $C_{10}H_{16}I_2$, 389.9341; found, 389.9342 ± 0.0013.

6c: Using procedure D with first alkyne = 1-hexyne (1.38 mL, 12 mmol, Wiley), second alkyne = 3-hexyne (1.38 mL, 12 mmol, Wiley), and iodine (7.58 g, 30 mmol). Yield 3.659 g (86%), >98% pure by GC. ^1H NMR (500 MHz, $CDCl_3$) δ 0.933 (t, J = 7.5 Hz, 3 H), 0.999 (t, J = 7.6 Hz, 3 H), 1.105 (t, J = 7.5 Hz, 3 H), 1.380 (6 lines, 2 H), 1.555 (5 lines, 2 H), 2.365 (q, J = 7.5 Hz, 2 H), 2.541 (t, J = 7.0 Hz, 2 H), 2.602 (q, J = 7.5 Hz, 2 H), 6.189 (s, 1 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ 13.22 (q), 13.87 (q), 14.34 (q), 21.46 (t), 25.77 (t), 31.41 (t), 34.28 (t), 44.47 (t), 108.32 (s), 112.01 (s), 139.55 (d), 145.03 (s). IR (neat, NaCl) 2965, 2931, 2871, 1644, 1610, 1459, 1427, 1374, 1314, 1295, 1255, 1199, 1112, 1091, 1065, 1024, 975, 734, 921, 831, 797, 739, 730 cm^{-1}. GCMS showed no M^+ = 418, but $M^+ - 127$ (I^-) = 291. HRMS calcd for $C_{12}H_{20}I$, 291.0610; found, 291.0610 ± 0.0008.

6d: Using procedure D with first alkyne = 1-hexyne (1.38 mL, 12 mmol, Wiley), second alkyne = diphenylacetylene (1.79 g, 10 mmol, Aldrich), and iodine (6.68 g, 26 mmol). Yield 4.112 g (80%), >98% pure

by NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.960 (t, J = 7.3 Hz, 3 H), 1.422 (6 lines, 2 H), 1.615 (5 lines, 2 H), 2.663 (t, J = 7.3 Hz, 3 H), 6.691 (s, 1 H), 7.00–7.23 (m, 9 H), 7.28–7.45 (m, 1 H). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ 13.91 (q), 21.56 (t), 31.52 (t), 45.18 (t), 103.90 (s), 114.70 (s), 127.10 (d), 127.68 (d), 127.71 (d), 127.86 (d), 130.00 (d), 130.45 (d), 137.82 (s), 140.39, 143.67 (s), 146.58 (s). IR (neat, NaCl) 3078, 3054, 3027, 3019, 2956, 2929, 2870, 2858, 1947, 1877, 1801, 1749, 1632, 1597, 1574, 1491, 1464, 1442, 1378, 1264, 1084, 1071, 1029, 830, 755, 697, 638 cm^{-1}. MS showed a small M^+ = 514 and a large $M^+ - 127$ (I^-) = 387. HRMS calcd for $C_{20}H_{20}I_2$, 513.9654; found, 513.9655 ± 0.0023.

6e: Using procedure D with first alkyne = acetylene (15 psig for ca. 30 min), second alkyne = 3-hexyne (1.38 mL, 12 mmol, Wiley), and iodine (5.58 g, 22 mmol). Yield 1.929 g (53%), ~93% pure by GC, with ~7% **6a** as a contaminant. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.107 (t, J = 7.5 Hz, 3 H), 1.123 (t, J = 7.6 Hz, 3 H), 2.415 (q, J = 7.5 Hz, 2 H), 2.637 (q, J = 7.5 Hz, 2 H), 6.398 (d, J = 8.0 Hz, 1 H), 6.877 (d, J = 8.0 Hz, 1 H). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ 13.31 (q), 14.46 (q), 25.06 (t), 34.45 (t), 83.81 (d), 108.72 (s), 143.63 (s), 145.21 (d). IR (neat, NaCl) 3060, 2968, 2930, 2871, 1632, 1586, 1452, 1429, 1375, 1292, 1258, 1190, 1142, 1088, 1057, 924, 823, 793, 710, 687 cm^{-1}. GCMS showed a small M^+ = 362 and a large $M^+ - 127$ (I^-) = 235. HRMS calcd for $C_8H_{12}I_2$, 361.9028; found, 361.9031 ± 0.0011.

6f: Using procedure D with first alkyne = 5-chloro-1-pentyne (1.06 mL, 10 mmol, Farchan), second alkyne = 3-hexyne (1.38 mL, 12 mmol, Wiley), and iodine (6.1 g, 24 mmol). Yield 2.98 g (68%), >98% pure by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.010 (t, J = 7.6 Hz, 3 H), 1.108 (t, J = 7.3 Hz, 3 H), 2.066 (5 lines, 2 H), 2.362 (q, J = 7.6 Hz, 2 H), 2.604 (q, J = 7.3 Hz, 2 H), 2.733 (td, J = 6.9, 1.2 Hz, 2 H), 3.638 (t, J = 6.4 Hz, 2 H), 6.312 (s, 1 H). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ 13.20, 14.32, 25.79, 31.61, 34.27, 41.37, 43.49, 108.48, 109.28, 141.47, 144.83. IR (neat, NaCl) 2968, 2932, 2871, 1456, 1451, 1442, 1429, 1374, 1311, 1290, 1262, 1250, 1199, 1091, 1057, 926, 866, 829 cm^{-1}. GCMS showed no M^+ = 438, but a large $M^+ - 127$ (I^-) = 311. HRMS calcd for $H_{11}H_{17}ClI$, 311.0064; found, 311.0065 ± 0.0006.

6g: Using procedure C with first alkyne = (trimethylsilyl)acetylene (1.42 mL, 10 mmol, Farchan), second alkyne = 3-hexyne (1.25 mL, 11 mmol, Wiley), and iodine (5.58 g, 22 mmol). Yield 3.784 g (87%), >98% isomeric purity and ~96% chemical purity by GC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.227 (s, 9 H), 1.005 (t, J = 7.5 Hz, 3 H), 1.117 (t, J = 7.5 Hz, 3 H), 2.40 (q, J = 7.5 Hz, 2 H), 2.61 (q, J = 7.5 Hz, 2 H), 6.805 (s, 1 H). ^{13}C{^{1}H} (75.4 MHz, $CDCl_3$) δ −1.52, 13.31, 14.44, 25.15, 34.11, 107.16, 114.53, 146.17, 151.19. IR (neat, NaCl) 2968, 2932, 2898, 2873, 1582, 1453, 1374, 1248, 1196, 1089, 925, 893, 840, 753, 695 cm^{-1}. GCMS showed no M^+ = 434, but a large $M^+ - 127$ (I^-) = 307. HRMS calcd for $C_{11}H_{20}ISi$, 307.0379; found, 307.0379 ± 0.0008.

6h: Using procedure C with first alkyne = 3,3-dimethyl-1-butyne (1.30 mL, 10.5 mmol, Farchan), second alkyne = 3-hexyne (1.25 mL, 12 mmol, Wiley), and iodine (5.4 g, 21 mmol). Yield 3.606 g (86%), >98% pure by GC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.998 (t, J = 7.5 Hz, 3 H), 1.107 (t, J = 7.5 Hz, 3 H), 1.236 (s, 9 H), 2.369 (q, J = 7.5 Hz, 2 H), 2.695 (q, J = 7.5 Hz, 2 H), 6.191 (s, 1 H). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) (multiplicity from gated decoupling) δ 13.17 (q), 14.18 (q), 25.65 (t), 30.23 (large, q), 34.15 (t), 40.13 (s), 107.97 (s), 128.25 (s), 136.98 (d), 145.77 (s). IR (neat, NaCl) 2972, 2932, 2905, 2871, 1631, 1478, 1458, 1390, 1374, 1362, 1254, 1233, 1191, 1090, 1040, 942, 831, 803 cm^{-1}. GCMS showed no M^+ = 418, but a large $M^+ - 127$ (I^-) = 291. HRMS calcd for $C_{12}H_{20}I$, 291.0610; found, 291.0610 ± 0.0003.

6i: Using procedure D with first alkyne = 1-hexyne (1.25 mL, 11 mmol), second alkyne = 1-(trimethylsilyl)-1-propyne (1.48 mL, 10 mmol, Wiley). The metallacycle was heated to 80 °C for 24 h in benzene solvent before hydrolysis. Iodinolysis with 5.5 g of solid I_2 was carried out in CH_2Cl_2 solvent at −78 °C. Yield 3.311 g (74%), ~95% isomeric purity by GC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 9 H), 0.89 (t, J = 7 Hz, 3 H), 1.34 (m, 6 lines, 2 H), 1.53 (m, 2 H), 1.98 (s, 3 H), 2.50 (m, 3 lines, 2 H), 6.18 (s, 1 H). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 1.52, 13.89, 21.48, 22.22, 31.46, 44.26, 108.48, 109.35, 142.93, 153.85. IR (neat, NaCl) 2956, 2930, 2871, 2859, 1635, 1576, 1457, 1437, 1250, 1110, 891, 842, 757, 690 cm^{-1}. GCMS showed no M^+ = 448, but a large $M^+ - 127$ (I^-) = 321. HRMS calcd for $C_{12}H_{22}SiI$, 321.0536; found, 321.0535 ± 0.0010.

Acknowledgment. We gratefully acknowledge financial support for our work from Dr. Alfred Bader, Firmenich SA, and the National Institutes of Health (Grant GM 34917). S.L.B. is the recipient of a Distinguished New Faculty Grant from the Camille & Henry Dreyfus Foundation, Inc., a Junior Faculty Research Award from the American Cancer Society, and an Innovation Recognition Award from Union Carbide and is a Lilly Grantee. R.B.N. thanks the National Science Foundation and A. D. Little Inc. for graduate fellowships. We thank Mr. Qun Fang for preliminary experiments.

Registry No. 5a, 119244-75-6; **5b**, 119244-77-8; **5c**, 119244-78-9; **5d**, 119244-79-0; **5e**, 119244-80-3; **5f**, 119244-81-4; **5g**, 119244-82-5; **6a**, 119244-76-7; **6b**, 119244-83-6; **6c**, 119244-84-7; **6d**, 119244-85-8; **6e**, 119244-86-9; **6f**, 119244-87-0; **6g**, 119244-88-1; **6h**, 119244-89-2; **6i**, 119244-90-5; Cp_2ZrHCl, 37342-97-5; 1-hexyne, 693-02-7; 5-chloro-1-pentyne, 14267-92-6; 1-(*tert*-butyldimethylsilyl)-1-hexyne, 96475-79-5; 3-hexyne, 928-49-4; 4-(*tert*-butyldimethylsiloxy)-1-butyne, 78592-82-2; (trimethylsilyl)acetylene, 1066-54-2; 1-(trimethylsilyl)-1-propyne, 6224-91-5; 3,3-dimethyl-1-butyne, 917-92-0; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; acetylene, 74-86-2.