Bimane Acetylenes and Diacetylenes. Bimanes. 33

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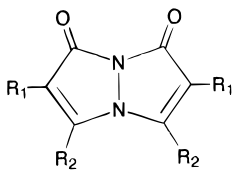
Two series (4,6-dihydro and 4,6-dimethyl) of *syn*-bimanes [1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-diones] have been converted to acetylene and diacetylene derivatives. Their chemical and photophysical properties are reported. The 3-(and 6-)iodo (diiodo) derivatives are the best choices for Stille or Heck condensations with acetylenes or acrylates. Desilylation of (trimethylsilyl)-acetylenes is best carried out with silver nitrate followed by lithium bromide. The acetylenes and diacetylenes are quite stable and highly fluorescent and represent candidate units for incorporation into polymers.

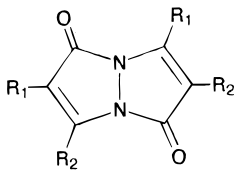
Introduction

The macroscopic properties of polymers are related to the microscopic characteristics of the monomers from which they are made. However, the packing, the strength of intermolecular interactions, and the flexibility of the chains are not simple functions of monomer structure. New monomers should be prepared and evaluated to probe the influence of the new structure on polymer properties. A polymer class of particular interest is that of rodlike polymers. These can be of high strength, high thermal, and thermooxidative stability and have unusual resistance to most solvents. Such properties make them very attractive scientifically and commercially. Monomers for rodlike polymers should have two exocyclic bonds which are positionally and angularly well defined. Typical monomer units include 1,4-phenylene groups and benzene rings to which are fused two apposed heterocyclic five-membered rings.

Bimanes are a class of bicyclic heterocyclic molecules that are readily synthesized.[1] There are two isomers, *syn* (**1**) and *anti* (**2**). A "short form" nomenclature, (R_2,R_1)B, describes the substituents on the ring and is particularly convenient for description and discussion, whereas the systematic name, 1,5-diazabicyclo[3.3.0]octadienedione, is appropriate as a formal name. The symmetrical shape of the bimane ring makes the system suitable for the construction of linear polymeric molecules, and rodlike polymers, using two exocyclic links through the R_1 position ("α position"). In addition to a favorable geometry, bimanes possess other attractive properties for polymer construction. These are high thermal stability,[1] flexibility of the bimane systems[2] **1** and **2** (interconversion between "bent" and "less-bent" conformers,[3] a property that should decrease polymer brittleness), and strong interaction between bimane units in the crystal. The latter leads to interlayer stacking arrangements[4] that should favor crystallite formation in polymers with a concomitant increase in toughness and resistance to solvents.



1
syn-(R_2,R_1)B

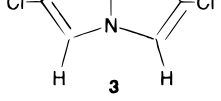


2
anti-(R_2,R_1)B

The molecular design of a bimane monomer suitable for rodlike polymers should include (a) two reactive α-groups in the monomer through which a polymer can be formed and (b) planar α-groups to give good packing and strong intermolecular interactions.

We describe now the preparation and properties of bimane monomers with α-ethynyl groups, R_1 and/or R_1' = C≡CR_3, in which R_3 = H, Si(CH_3)$_3$, or C_6H_5. We also show that oligomers can be formed and that α-ethynyl bimanes can be oxidized to diacetylenes, RC≡CC≡CR, an additional class of potential monomers. Diacetylenes which undergo the unique "diacetylene polymerization" normally have the structure $RCH_2C{\equiv}CC{\equiv}CCH_2R'$, and bimane diacetylenes do not undergo this type of polymerization.

Two series of ethynylbimanes have been prepared, one having R_2 = CH_3 and a second having R_2= H. The first series is more accessible, while the second is expected to have superior thermooxidative stability and stronger packing and stronger intermolecular interactions, according to crystal structure and thin-film studies on *syn*-(H,Cl)B (**3**)[5,6] and confirmed by the crystal structure of *syn*-(H,HC≡C)B (**4**), as we have reported in a communication.[7] The factors responsible for the packing might lead to good crystallite formation in polymers, especially for β-hydrobimane acetylenes. The bond distances and bond angles shown in the bonding scheme are



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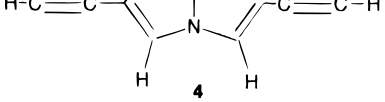

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(2) Kosower, E. M.; Giniger, R.; Radkowsky, A. E.; Hebel, D.; Shusterman, A. *J. Phys. Chem.* **1986**, *90*, 5552−5557.

(3) Conformational isomers of bimanes were previously referred to as "bent" and quasi-planar" (ref 2). Other aspects of the conformational isomerism of the bimanes will be reported in subsequent articles.

(4) Goldberg, I.; Bernstein, J.; Kosower, E. M.; Goldstein, E.; Pazhenchevsky, B. *J. Heterocycl. Chem.* **1983**, *20*, 903−912.

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(6) Goldberg, I.; Kosower, E. M. *J. Phys. Chem.* **1982**, *86*, 332.

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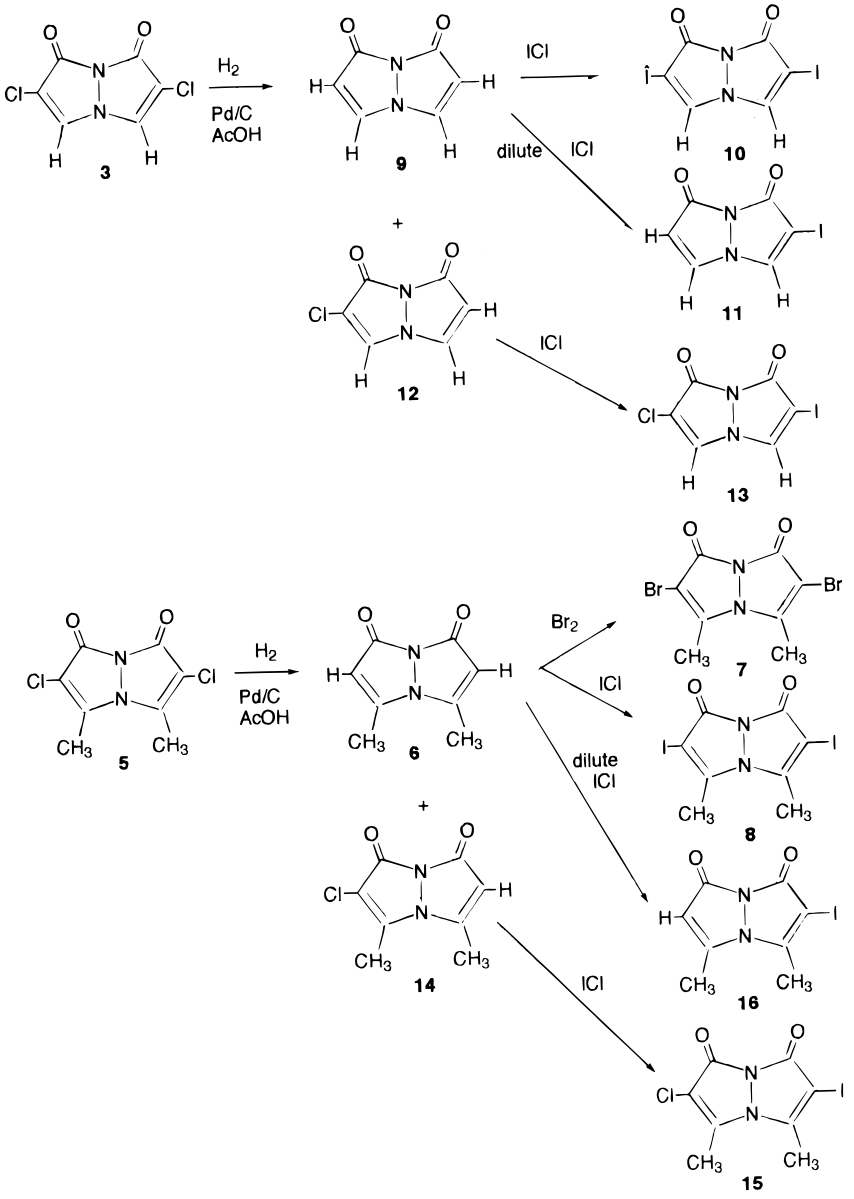
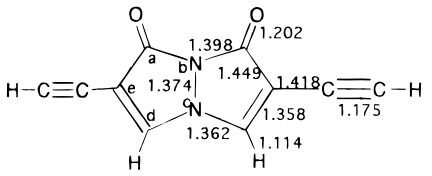
Scheme 1



similar to those observed previously in a number of bimanes. The molecular packing is tight, and the density of 1.537 g cm^{-3} is quite high for a CHNO compound.



bond angles (deg), a, 104.9; b, 108.5; c, 109.6; d, 108.6; e, 108.3; f, 129.7; g, 125.1; h, 121; i, 142.9; j, 140.8

Results

Two general routes can be envisaged for the introduction of an ethynyl group at the R_1 position (α position) of the bimane system. The first approach involves the use of an α-C_2 group that can be converted to an acetylene.[8,9] In an attempt to generate an α,α′-divinylbimane (an interesting goal in itself), the requisite β-(hydroxyethyl)-chloropyrazolinone was prepared easily from the commercially available α-acetyl-γ-butyrolactone. However, the "bimane synthesis[1]" failed, but succeeds with the closely related β-(acetoxyethyl)chloropyrazolinone to give *syn*-(CH_3,$CH_2CH_2OCOCH_3$)B.[10]

The second general approach depends on direct introduction of an ethynyl group[11,12] by a palladium-catalyzed reaction[13] of an appropriate reagent with an α-halobimane derivative.[1] *syn*-(Methyl,chloro)bimane (**5**) is prepared via the "bimane synthesis", hydrogenated to the *syn*-(methyl,hydro)bimane (**6**), and converted to either *syn*-(methyl,bromo)bimane (**7**) with bromine or *syn*-(methyl,iodo)bimane (**8**) with ICl.[1] *syn*-(Hydro,chloro)-bimane (**3**) has been synthesized somewhat more indirectly via the "bimane synthesis" of *syn*-(methoxycar-

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(9) Collier, W. L.; Macomber, R. S. *J. Org. Chem.* **1973**, *38*, 1367.
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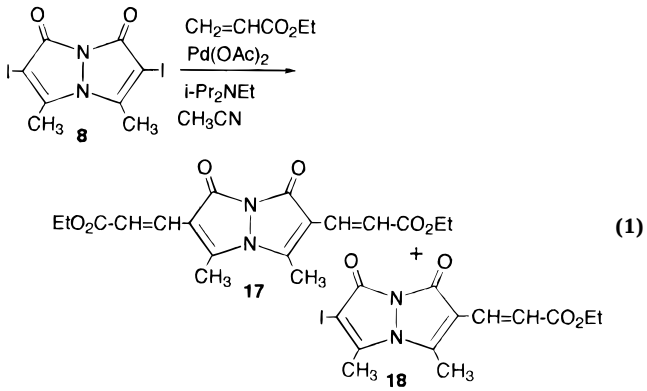
bonyl,chloro)bimane, removal of the ester methyl group, and decarboxylation.[14] An unusual procedure for the "bimane synthesis" of *syn*-(hydro,chloro)bimane from dichloropyrazolinone will be reported elsewhere.[15] *syn*-(H,Cl)B (**3**) was reduced to *syn*-(H,H)B (**9**) via the previously reported method of hydrogenation.[1] The *syn*-(hydro,hydro)bimane was converted into *syn*-(H,I) (**10**) by treatment with ICl; iodine was not sufficiently reactive to form the desired product. The monoiodo derivative, *syn*-(H,I)(H,H)B (**11**), was produced in 60% yield only by reaction of **9** with ICl in very dilute solution but was easily separated from *syn*-(H,I)B. The monochloro derivative, *syn*-(H,Cl)(H,H)B (**12**), produced *syn*-(H,Cl)-(H,I)B (**13**) by reaction with ICl. The methyl monochloro derivative *syn*-(methyl,chloro)(methyl,hydro) bimane (**14**) led to *syn*-(methyl,chloro)(methyl,iodo)bimane (**15**) through reaction with ICl and **6** leads to *syn*-(methyl,hydro)-(methyl,iodo)bimane (**16**) by treatment with dilute ICl. These conversions are summarized in the formulas of Scheme 1.

Ethynyl groups might be produced via an (alkoxycarboxy)vinyl group through addition of halogen, hydrolysis, and halodecarboxylation. One variation of the Heck reaction[16,17] involves coupling of aryl halides with acrylate esters. Both mono- and bis(ethoxycarbonyl)bimanes were produced from *syn*-(CH_3,I)B (**8**) and 2 equiv of ethyl acrylate in CH_3CN under nitrogen in the presence of diisopropylethylamine and $Pd(OAc)_2$. The bis(carbethoxyvinyl) derivative *syn*-(CH_3,HC=CHCO$_2$CH$_2$CH$_3$)B (**17**) was obtained in 40% yield together with 20% yield of the monosubstituted, "mixed" bimane *syn*-(CH_3,I)(CH_3,HC=CHCO$_2$CH$_2$CH$_3$)B (**18**) and *syn*-(CH_3,H)B (**6**) in 3% yield (eq 1). The chloro and bromo analogues, *syn*-(CH_3,-Cl or Br)B (**5**) or (**7**), did not react under the same conditions, but *syn*-(CH_3,Cl)(CH_3,I)B (**15**) gave *syn*-(CH_3,Cl)(CH_3,HC=CHCO$_2$CH$_2$CH$_3$)B (**19**) in 50% yield.

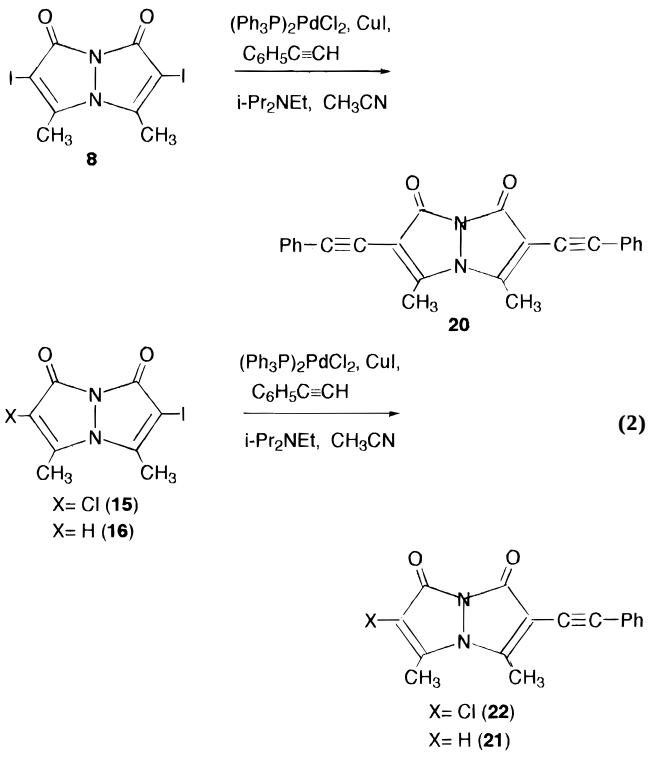


(1)

The carbethoxyvinyl derivatives *syn*-(CH_3,CH=CH-CO$_2$C$_2$H$_5$)B (**17**), *syn*-(CH_3,I)(CH_3,CH=CHCO$_2$C$_2$H$_5$)B (**18**), and *syn*-(CH_3,Cl)(CH_3,CH=CHCO$_2$C$_2$H$_5$)B (**19**) melt between 170 to 215 °C with decomposition to materials of lower chromatographic mobility.

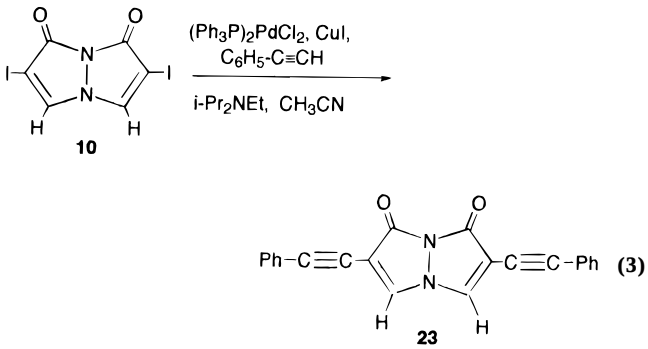
Neither *syn*-(CH_3,H)(CH_3,I)B (**16**) nor *syn*-(CH_3,I)B (**8**) gave a new bimane on treatment with acetylene (cf. refs 18 and 19) in the presence of bis(triphenylphosphine)-palladium(II)chloride, cuprous iodide, and an equivalent of diisopropylethylamine.

(Phenylethynyl)bimanes. In most cases, only α-iodobimanes could be coupled to acetylenes with palladium catalysts in reasonable yields. For example, phenylacetylene was reacted with several α-iodobimanes, *syn*-(CH_3,I)B (**8**), *syn*-(CH_3,H)(CH_3,I)B (**16**), and *syn*-(CH_3,I)-(CH_3,Cl)B (**15**), in the presence of diisopropylethylamine, cuprous iodide, and bis(triphenylphosphine)palladium-(II) chloride to produce 72−80% yield of the corresponding α-(phenylethynyl)bimanes, *syn*-(CH_3,C≡CC_6H_5)B (**20**), *syn*-(CH_3,H)(CH_3,C≡CC_6H_5)B (**21**), and *syn*-(CH_3,Cl)-(CH_3,C≡CC_6H_5)B (**22**). Only the α-iodo groups were replaced (eq 2).



(2)

syn-(H,I)B (**10**) was reacted with phenylacetylene in boiling CH_3CN under nitrogen in the presence of cuprous iodide, bis(triphenylphosphine)palladium(II) chloride, and diisopropylethylamine. *syn*-(Hydro,phenylethynyl)bimane, *syn*-(H,C≡CC_6H_5)B (**23**), was obtained in 85% yield (eq 3).



(3)

Exceptionally, the α-chloro derivative *syn*-(H,Cl)(H,H)B (**12**) reacted under the same conditions to give the mixed bimane *syn*-(H,H)(H,C≡CC_6H_5)B (**24**) in 15% yield (eq 4).

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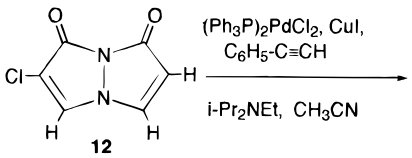

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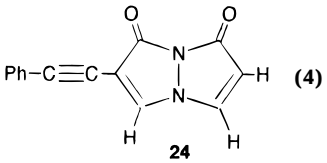
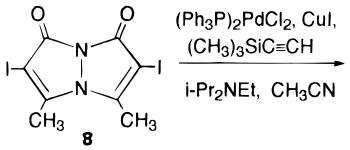


24 (4)

The compounds *syn*-(CH_3,C≡CC_6H_5)B (**20**), *syn*-(CH_3,Cl)(CH_3,C≡CC_6H_5)B (**22**), and *syn*-(CH_3,H)(CH_3,C≡C-C_6H_5)B (**21**) do not change on melting (260−285 °C) even after several minutes at the melt temperature. Thus, (phenylethynyl)bimanes have considerable thermal stability and are also stable to air and water.

((Trimethylsilyl)ethynyl)bimanes. In analogy with the coupling of aryl halides with (trimethylsilyl)acetylene (TMSA),[20,21] the α-iodobimanes *syn*-(CH_3,I)B (**8**), *syn*-(CH_3,I)(CH_3,Cl)B (**15**), and *syn*-(CH_3,I)(CH_3,H)B (**16**) were reacted with TMSA in CH_3CN under nitrogen, in the presence of bis(triphenylphosphine)palladium(II) chloride, cuprous iodide, and diisopropylethylamine, to give 50−60% yields of ((trimethylsilyl)ethynyl)bimanes *syn*-(CH_3,(CH_3)$_3$SiC≡C)B (**25**) accompanied by a 10% yield of *syn*-(CH_3,I)(CH_3,(CH_3)$_3$SiC≡C)B (**26**), *syn*-(CH_3,Cl)-(CH_3,(CH_3)$_3$SiC≡C)B (**27**), and *syn*-(CH_3,H)(CH_3,(CH_3)$_3$-SiC≡C)B (**28**) (eqs 5 and 6).



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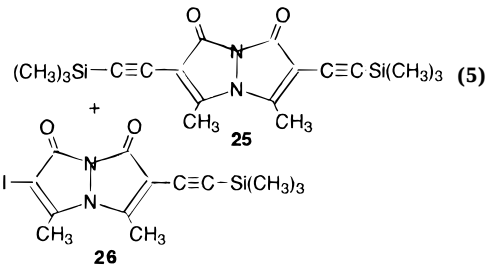
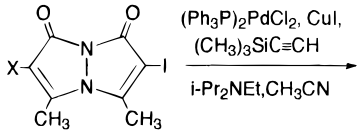
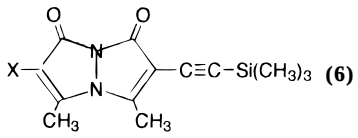


25 + **26** (5)

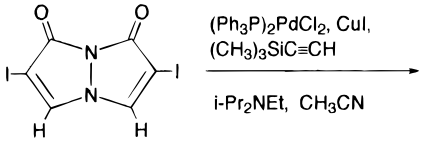


X= Cl (**15**)
X= H (**16**)



X= Cl (**27**)
X= H (**28**) (6)

Reaction of *syn*-(H,I)B (**10**) [but not *syn*-(H,Cl)(H,H)B (**12**) or *syn*-(H,Cl)B (**3**)] with TMSA in CH_3CN under nitrogen in the presence of bis(triphenylphosphine)-palladium(II) chloride, cuprous iodide, and diisopropylethylamine gave *syn*-(hydro,(trimethylsilyl)ethynyl)-bimane, *syn*-(H,C≡C$Si(CH_3)_3$)B (**29**), in 68% yield, the mixed bimane *syn*-(H,I)(H,C≡C$Si(CH_3)_3$)B (**30**) in 3.8% yield, and the partially reduced mixed bimane *syn*-(H,H)-(H,C≡C$Si(CH_3)_3$B (**31**) in 1.2% yield, together with a trace of *syn*-(H,H)B (**9**) (eq 7).



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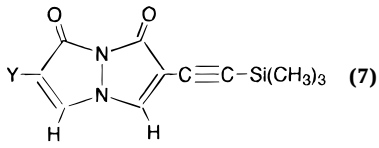

Y= (CH_3)$_3$SiC≡C (**29**)
Y= I (**30**)
Y= H (**31**) (7)

The α-(trimethylsilyl)ethynyl derivatives *syn*-(CH_3,C≡C-$Si(CH_3)_3$)(CH_3,X)B [X = C≡C$Si(CH_3)_3$ (**25**), X = I (**26**), X = Cl (**27**), X = H (**28**)] and the *β*-hydro derivatives *syn*-(H,C≡C$Si(CH_3)_3$)(H,X)B [X = C≡C$Si(CH_3)_3$ (**29**), X = I (**30**), X = H (**31**)], like the α-(phenylethynyl)bimanes, are stable to air and moisture. Although the *β*-methyl compounds are thermally stable (no change on on melting), the *β*-hydro derivatives are decomposed on melting. The α-((trimethylsilyl)ethynyl)bimanes *syn*-(H,C≡C$Si(CH_3)_3$)-(H,X)B [X = C≡C$Si(CH_3)_3$ (**29**), X = I (**30**), X = H (**31**)] are all yellow solids melting between 240 and 320 °C.

Desilylation. Mild base treatment,[22] usually used for removing the trimethylsilyl (TMS) group, is unsuitable for the base-sensitive bimanes. Treatment of α-((trimethylsilyl)ethynyl)bimane derivatives *syn*-(CH_3,X)(CH_3,C≡C-$Si(CH_3)_3$)B [X = C≡C$Si(CH_3)_3$ (**25**), X = I (**26**), X = Cl (**27**), X = H (**28**)] in CH_3CN with aqueous 48% HF at room temperature[23] for 15 h leads to formation of the ethynylbimanes *syn*-(CH_3,C≡CH)(CH_3,Y)B [Y = C≡CH (**32**), Y = I (**33**), Y = Cl (**34**)), Y = H (**35**)] in 15−25% yields (eq 8, path a).

A more effective procedure involves reaction of α-((trimethylsilyl)ethynyl)bimane derivatives *syn*-(CH_3,C≡C$Si(CH_3)_3$)(CH_3,X)B [X = C≡C$Si(CH_3)_3$ (**25**), X = I (**26**), X = Cl (**27**), X = H (**28**)] in ethanol with aqueous silver nitrate[24] at room temperature. The silver acetylides precipitate and are decomposed with either aqueous lithium bromide or potassium cyanide to yield the acetylenes *syn*-(CH_3,C≡CH)(CH_3,Y)B [Y = C≡CH (**32**), Y = I (**33**), Y = Cl (**34**), Y = H (**35**)] in reasonable yields (54−65%) (eq 8, path b).

The silver nitrate procedure was used for the desilylation of the *β*-hydro,((trimethylsilyl)ethynyl)bimanes *syn*-(H,C≡C$Si(CH_3)_3$)(H,X)B [X = C≡C$Si(CH_3)_3$ (**29**), X = I (**30**), X = H (**31**)]. Treatment of the silver acetylides with lithium bromide gave the desilylated products *syn*-

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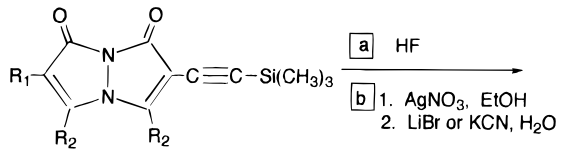
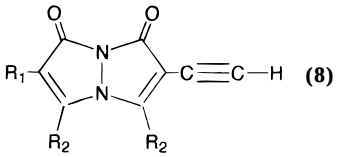


$R_1 = (CH_3)_3SiC{\equiv}C$, $R_2 = H$ (**29**)
$R_1 = (CH_3)_3SiC{\equiv}C$, $R_2 = CH_3$ (**25**)
$R_1 = I$, $R_2 = H$ (**30**)
$R_1 = I$, $R_2 = CH_3$ (**26**)
$R_1 = Cl$, $R_2 = CH_3$ (**27**)
$R_1 = H$, $R_2 = CH_3$ (**28**)
X= H (**31**)



(8)

$R_1 = C{\equiv}C\text{-}H$, $R_2 = H$ (**4**)
$R_1 = HC{\equiv}C$, $R_2 = CH_3$ (**32**)
$R_1 = (CH_3)_3SiC{\equiv}C$, $R_2 = H$ (**36**)
$R_1 = I$, $R_2 = CH_3$ (**33**)
$R_1 = Cl$, $R_2 = CH_3$ (**34**)
$R_1 = I$, $R_2 = CH_3$ (**35**)
Y= I (**37**)
Y= H (**38**)

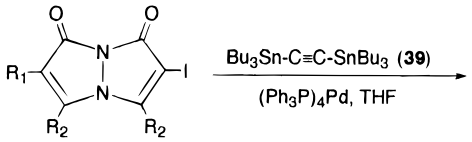
(H,C≡CH)(H,Y)B [Y = C≡CH (**4**), Y = C≡CSi$(CH_3)_3$ (**36**), Y = I (**37**), Y = H (**38**)] in reasonably good yields (eq 8, path b).

The α-ethynylbimanes *syn*-(H,C≡CH)(H,X)B [X = C≡CH (**4**), X = I (**37**), X = H (**38**), X = C≡C-Si$(CH_3)_3$ (**36**)] are, like the methyl homologues, yellow solids with melting points ranging from 205 to 300 °C and, unlike the methyl homologues, decompose on melting. *syn*-(H,C≡CH)B (**4**) shows some changes at room temperature on standing, darkening in color and forming insoluble materials.

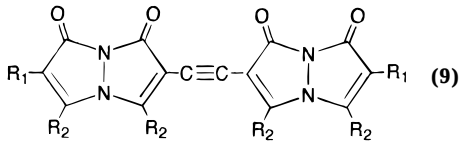
The *syn*-(H,X)B [X = C≡CH (**4**), X = C≡CC_6H_5 (**23**)] are isolated as yellow powders that give red orange crystals after recrystallization. The appearance of *syn*-(H,C≡CC_6H_5)B (**23**) on silica changes from yellow to orange as the solvent evaporates.

Bis(bimane)acetylenes. The cross-coupling of organotin reagents with a variety of organic electrophiles, catalyzed by palladium, provides a novel method[25] for generating a carbon−carbon bond. The palladium-catalyzed coupling of aryl iodides with alkynylstannanes takes place under mild conditions. Bis(tributylstannyl)-acetylene[26] (**39**) reacts with 2 equiv of α-iodobimane, *syn*-(CH_3,I)(CH_3,X)B [X = Cl (**15**), X = H (**16**)], in the presence of catalytic amounts of tetrakis(triphenylphosphine)-palladium(0) in tetrahydrofuran under nitrogen, yielding *syn*,*syn*-(CH_3,X)(CH_3,C≡C−)B(CH_3,X)(CH_3,−)B] [X = Cl (**40**), X = H (**41**)] in 20% yield (eq 9). A blue-green fluorescent intermediate (R_f 0.8, CH_2Cl_2) detected by TLC is probably the ((tributylstannyl)ethynyl)bimane, *syn*-(CH_3,X)(CH_3,C≡CSnBu_3)B [X = Cl (**42**), X = H (**43**)] in agreement with a mechanism involving an organometallic intermediate.[25]

The palladium-catalyzed coupling of bis(tributylstannyl)acetylene (**39**) with 2 equiv of the α-iodo-β-hydrobimane *syn*-(H,I)(H,H)B (**11**) in the presence of tetrakis-(triphenylphosphine)palladium(0) in tetrahydrofuran under nitrogen yielded *syn*,*syn*-[(H,H)(H,C≡C−)B(H,H)-(H,−)B] (**44**) in 21% yield (eq 9). The bis(bimane)-acetylene is a red orange solid which exhibits color changes like those of *syn*-(H,C≡CC_6H_5)B (**23**) on silica. The acetylene **44** has a very high melting point, >320 °C; all three bis(bimane)acetylenes **40**, **41**, and **44** could be heated up to 400 °C in a capillary tube under vacuum without decomposition.



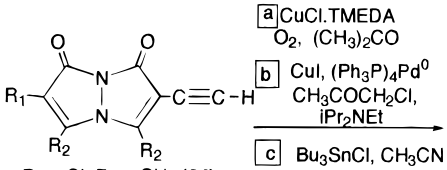
$R_1 = Cl$, $R_2 = CH_3$ (**15**)
$R_1 = H$, $R_2 = CH_3$ (**16**)
$R_1 = H$, $R_2 = H$ (**11**)



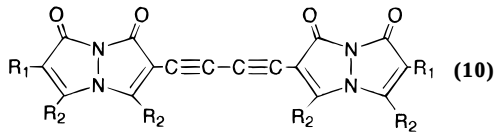
(9)

$R_1 = Cl$, $R_2 = CH_3$ (**40**)
$R_1 = H$, $R_2 = CH_3$ (**41**)
$R_1 = H$, $R_2 = H$ (**44**)

Bimanediacetylenes. The oxidative dimerization of terminal acetylenes to symmetrical diynes (often by the Glaser[27] and Eglinton[28] reactions) gives better yields by the Hay[29] procedure. New methods using Pd catalysts have been developed.[30] From *syn*-(CH_3,X)(CH_3,C≡CH)B [X = Cl (**34**), X = H (**35**)], the Hay method (treatment with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) complex of copper(I) chloride in acetone in the presence of oxygen) gave low yields (8−10%) of diacetylenes (eq 10, path a).



$R_1 = Cl$, $R_2 = CH_3$ (**34**)
$R_1 = H$, $R_2 = CH_3$ (**35**)
$R_1 = H$, $R_2 = H$ (**38**)



(10)

$R_1 = Cl$, $R_2 = CH_3$ (**45**)
$R_1 = H$, $R_2 = CH_3$ (**46**)
$R_1 = H$, $R_2 = H$ (**47**)

Palladium-catalyzed coupling[30] of the α-ethynylbimanes **34** and **35** with chloroacetone and diisopropylethylamine in toluene under nitrogen in the presence of

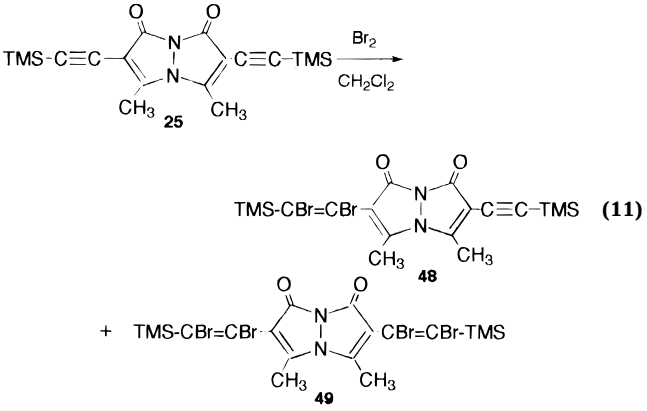
(25) (a) Stille, J. K. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. (c) Stille, J. K.; Labadie, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6129.
(26) Heck, R. F.; Nolley, J. P., Jr. *J. Org. Chem.* **1972**, *37*, 2320.
(27) (a) Glaser, C. *Ber.* **1869**, *2*, 422. (b) Glaser, C. *Justus Liebigs Ann. Chem.* **1870**, *137*, 154.
(28) (a) Eglinton, G.; Galbraith, A. R. *Chem. Ind. (London)* **1956**, 737. (b) Eglinton, G.; McGrae, W. *Adv. Org. Chem.* **1963**, *4*, 252.
(29) (a) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320. (b) Jones, G. E.; Kendrick, D. A.; Holmes, A. B. *Org. Synth.* **1987**, *65*, 52.
(30) Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett.* **1985**, 523.

tetrakis(triphenylphosphine)palladium and cuprous iodide yielded diacetylenes *syn,syn*-[(CH_3,X)(CH_3,C≡C−)B]$_2$ [X = Cl (**45**), X = H (**46**)] in 25−36%, higher than that in older procedures (eq 10, path b). More effective reagents (40% yield) for the formation of **45** and **46** were tributyltin chloride and bis(triphenylphosphine)palladium(II) chloride in CH_3CN, a better solvent for bimanes (eq 10, path c).

syn-(H,H)(H,C≡CH)B (**38**) was dimerized by the Hay method) (eq 10, path a) to *syn,syn*-[(H,H)(H,C≡C−)B]$_2$ (**47**) in 5% yield and with tetrakis(triphenylphosphine)-palladium(0), cuprous iodide,[30] chloroacetone, and diisopropylethylamine in toluene under nitrogen (eq 10, path b) to **47** in 30% yield. A 40% yield of **47** was obtained from **38** with bis(triphenylphosphine)palladium(II) chloride and cuprous iodide in the presence of tributyltin chloride and diisopropylethylamine in CH_3CN [eq 10, path c].

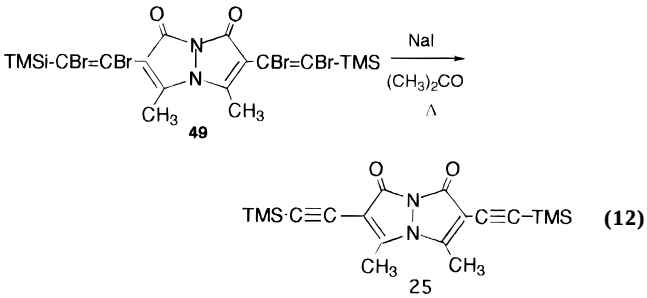
syn,syn-[(CH_3,X)(CH_3,C≡C−)B]$_2$ [X = Cl (**45**), X = H (**46**)] are thermally stable compounds, which were recovered unchanged after heating to 400 °C in a capillary tube under vacuum. Potassium bromide pellets containing diacetylenes exhibited metallic reflection. The diacetylene *syn,syn*-[(H,H)(H,C≡C−)B]$_2$ (**47**), a red powder with a very high melting point (>320 °C), was recovered unchanged after being heated to 420 °C in a capillary tube under vacuum, and exhibits a metallic reflection in a KBr pellet.

Halogenation−Dehalogenation. Bromination and Debromination of *syn*-(CH_3,C≡CSi(CH_3)$_3$)B. Bromine reacts at room temperature with *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) in CH_2Cl_2 to form a monoadduct, *syn*-(CH_3,C≡CSi(CH_3)$_3$)(CH_3,(Br)C=CBrSi(CH_3)$_3$)B (**48**) (1 equiv of bromine), or a bis-adduct, *syn*-(CH_3,BrC=CBrSi(CH_3)$_3$)B (**49**) (2 equiv of bromine), in 80% and 90% yields, respectively (eq 11).



(11)

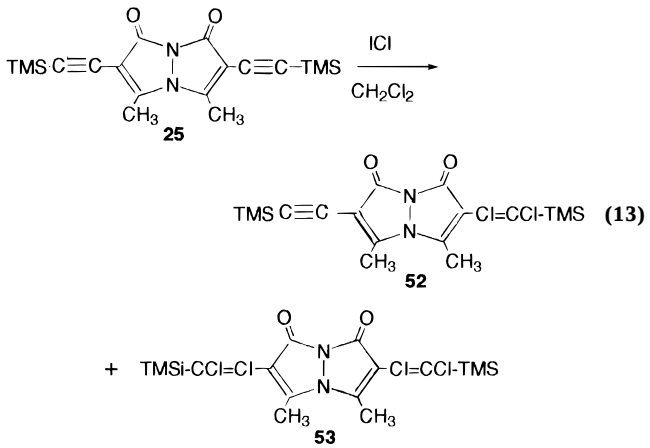
Reaction of *syn*-(CH_3,BrC=C(Br)Si(CH_3)$_3$)B (**49**) with sodium iodide in boiling acetone leads to the elimination of bromine and formation of *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) in 85% yield (eq 12).



(12)

***syn*-(Methyl,(2-carbethoxyethyl)vinyl)bimanes.** Bromine reacts at room temperature with *syn*-(CH_3,-CH=$CHCO_2C_2H_5$)B (**17**) in CH_2Cl_2. One equivalent of bromine yields the dibromo derivative *syn*-(CH_3,$CHBrCHBrCO_2C_2H_5$)(CH_3,CH=$CHCO_2C_2H_5$)B (**50**); 2 equiv of bromine give rise to the tetrabromo derivative *syn*-(CH_3,-$CHBrCHBrCO_2C_2H_5$)B (**51**).

Reaction with ICl. *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) reacts with ICl[31] in CH_2Cl_2 to yield the mono and bis ICl adducts *syn*-(CH_3,C≡CSi(CH_3)$_3$)(CH_3,IC=C(Cl)Si(CH_3)$_3$)B (**52**) and *syn*-(CH_3,IC=C(Cl)Si(CH_3)$_3$)B (**53**), respectively (eq 13).



(13)

Spectroscopic Properties of Bimaneacetylenes and -diacetylenes. Ultraviolet−Visible Absorption Maxima. The ultraviolet−visible absorption maxima of bimaneacetylenes vary with substitution in ways that are striking with respect to (a) the trimethylsilyl effect, (b) the β-hydrogen effect, and (c) the "lack" of diacetylene effect on the position of the maxima.

(**a**) The maxima for the α-(trimethylsilyl)ethynyl derivatives *syn*-(H,C≡CSi(CH_3)$_3$)(H,X)B [X = C≡CSi(CH_3)$_3$ (**29**), X = I (**30**), X = H (**31**)] occur at longer wavelengths than those for the corresponding desilylated derivatives *syn*-(H,C≡CH)(H,X)B [X = C≡CH (**4**), X = I (**37**), X = H (**38**)]. For example, *syn*-(H,C≡CSi(CH_3)$_3$)B (**29**) has a maximum at 445 nm as compared to a maximum at 410 nm (sh 430 nm) for *syn*-(H,C≡CH)B (**4**) in CH_3CN. The mixed bimane *syn*-(H,C≡CH)(H,C≡CSi(CH_3)$_3$)B (**36**) absorbs at 412 nm, a position much closer to that for *syn*-(H,C≡CH)B (**4**) than to the maximum for *syn*-(H,C≡CSi-(CH_3)$_3$)B (**29**).

(**b**) The absorption maxima for α-ethynyl-β-hydrobimanes occur at longer wavelengths than those for the corresponding α-ethynyl-β-methylbimanes. The absorption maximum for *syn*-(H,C≡CC_6H_5)B (**23**) is at 440 nm, 20 nm longer than the 420 nm found for *syn*-(CH_3,C≡C-C_6H_5)B (**20**). Results are summarized in Table 1.

(**c**) The "β-methyl effect" is lacking in the diacetylenes. *syn,syn*-[(H,H)(H,C≡C−)B]$_2$ (**47**) in CH_3CN shows maxima at 425 nm (ϵ 11 200), 305 nm (sh), 280 nm (ϵ 5380), and 250 nm (ϵ 6500); the β-methyl diacetylenes *syn,syn*-[(CH_3,X)(CH_3,C≡C−)B]$_2$ [X = Cl (**45**), X = H (**46**)] in CH_3CN have maxima at 425 nm (ϵ 27 200), 285 nm (ϵ 22 200), and 275 nm (ϵ 27 100) (**45**), and at 415 nm (ϵ 15 000) (**46**).

The bis(bimane)acetylenes *syn,syn*-[[(CH_3,X)(CH_3,-C≡C−)B(CH_3,X)(CH_3,−)B] [X = Cl (**40**), X = H (**41**)] show maxima at 410 nm (ϵ 13 100) and 405 nm (ϵ 19 090) with

(31) Walton, D. R. M.; Welb, M. J. *J. Organomet. Chem.* **1972**, *37*, 41.

Table 1. Ultraviolet−Visible Absorption Maxima of α-Substituted Bimanes in Acetonitrile

	absorption	
	λ_{max}, nm (ϵ_{max})	
syn-(R_2,R_1)B (R_2,R_1)		
(CH_3,C≡CC_6H_5) (**20**)	430 (8700)	280 (13200)
(H,C≡CC_6H_5) (**23**)	440 (3000)	280 (4750)
(CH_3,C≡$CSi(CH_3)_3$) (**25**)	408 (7500)	258 (11250)
(H,C≡$CSi(CH_3)_3$) (**29**)	430 (3300), 445 sh	250 (3950)
(CH_3,C≡CH) (**32**)	400 (6600)	240 (9460), 260 sh (4100)
(H,C≡CH) (**4**)	410 (10000), 430 sh	240 (10800)
syn-(R_2,R_1)(R_2,$R_{1'}$)B (R_2,R_1)(R_2,$R_{1'}$)		
(CH_3,I)(CH_3,C≡$CSi(CH_3)_3$) (**26**)	405 (5000)	238 (7500)
(H,I)(H,C≡$CSi(CH_3)_3$) (**30**)	410 (13600)	245 (11900), 230 (13240)
(CH_3,H)(CH_3,C≡$CSi(CH_3)_3$) (**28**)	382 (5430)	245 (8690)
(H,H)(H,C≡$CSi(CH_3)_3$) (**31**)	395 (6700)	240 (7280)
(CH_3,C≡CH)(CH_3,C≡$CSi(CH_3)_3$) (**54**)	405 (7800)	245 (11400), 280 sh (5000)
(H,C≡CH)(H,C≡$CSi(CH_3)_3$) (**36**)	412 (14000)	260 (17300)
(CH_3,H)(CH_3,C≡CH) (**35**)	375 (5500)	220 (8400)
(H,H)(H,C≡CH) (**38**)	385 (7900)	230 (8300)
(CH_3,Cl)(CH_3,C≡CC_6H_5) (**22**)	402 (14700)	278 (20900), 225 (19800)
(CH_3,Cl)(CH_3,C≡$CSi(CH_3)_3$) (**27**)	395 (12900)	242 (28800)
(CH_3,Cl)(CH_3,C≡CH) (**34**)	388 (7550)	240 (10600), 255 sh (7200)
(CH_3,H)(CH_3,C≡CC_6H_5) (**21**)	398 (9110)	268 (11900), 225 (10800)
(CH_3,I)(CH_3,C≡CH) (**33**)	393 (5500)	270 (4200), 230 (6700)
α-((2-Ethoxycarbonyl)ethenyl)bimanes		
syn-(CH_3,R_1)(CH_3,$R_{1'}$)B		
(CH_3,CH=$CHCO_2C_2H_5$) (**17**)	382 (13600)	295 (10100)
(CH_3,I)(CH_3,CH=$CHCO_2C_2H_5$) (**18**)	400 (9670)	300 sh (6440), 275 (10960)
(CH_3,Cl)(CH_3,CH=$CHCO_2C_2H_5$) (**19**)	385 (13300)	285 (15200), 275 (16200)
(CH_3,H)(CH_3,CH=$CHCO_2C_2H_5$) (**55**)	372 (9000)	287 (7660)

Table 2. Fluorescence Excitation Maxima of α-Substituted Bimanes

	solution[a] λ_{max}, nm	solid λ_{max}, nm
syn-(R_2,R_1)B (R_2,R_1)		
(CH_3,C≡CC_6H_5) (**20**)	435	400, 415, 425, 480
(H,C≡CC_6H_5) (**23**)	450	400, 470, 485
(CH_3,C≡$CSi(CH_3)_3$) (**25**)	400, 448, 464	
(H,C≡$CSi(CH_3)_3$) (**29**)	433, 450	370, 400, 436, 445, 470
(CH_3,C≡CH) (**32**)	405	384, 420, 450
(H,C≡CH) (**4**)	400	418, 437, 458
syn-(R_2,R_1)(R_2,$R_{1'}$)B (R_2,R_1)(R_2,$R_{1'}$)		
(CH_3,I)(CH_3,C≡$CSi(CH_3)_3$) (**26**)	402	
(H,I)(H,C≡$CSi(CH_3)_3$) (**30**)	400, 411, 420, 430	400, 490, 510
(CH_3,H)(CH_3,C≡$CSi(CH_3)_3$) (**28**)	400	
(H,H)(H,C≡$CSi(CH_3)_3$) (**31**)	390	395, 407, 420, 434, 464, 480, 490, 515
(CH_3,C≡CH)(CH_3,C≡$CSi(CH_3)_3$) (**54**)	410	395, 470
(H,C≡CH)(H,C≡$CSi(CH_3)_3$) (**36**)	370, 400, 420	
(CH_3,H)(CH_3,C≡CH) (**35**)	395	384, 410
(H,H)(H,C≡CH) (**38**)	385	400, 470, 490, 500
(CH_3,Cl)(CH_3,C≡CC_6H_5) (**22**)	400, 410	378, 424, 440, 452
(CH_3,Cl)(CH_3,C≡$CSi(CH_3)_3$) (**27**)	400	400, 418, 435
(CH_3,Cl)(CH_3,C≡CH) (**34**)	400	340, 396, 450, 470, 480
(CH_3,H)(CH_3,C≡CC_6H_5) (**21**)	400	
(CH_3,I)(CH_3,C≡CH) (**33**)	405	

[a] Measured with acetonitrile solutions at λ_{max} of fluorescence emission (Table 3).

another maximum at 260 nm (ϵ 22 100) (**40**) and 240 nm (ϵ 23 600) (**41**).

Fluorescence Excitation Spectra. The excitation spectra should be similar to the absorption spectra, but those of bimanes have some unusual characteristics. The excitation maxima usually show a small red shift in comparison to the absorption maxima in solution, about 5−10 nm for the α-conjugated, *β*-methyl compounds and 3−5 nm for the α-ethynyl-*β*-hydrobimane derivatives. The excitation maxima for the solid state emissions of all of the α-ethynyl derivatives show a large red shift in comparison to the absorption maxima of the compounds in solution. Table 2 summarizes the excitation maxima for bimanes in solution and in the solid state.

The excitation maxima for the bis(bimane)acetylenes BAB (B = bimane, A = acetylene), **40** and **41**, show a red shift of 3−5 nm with respect to the absorption maxima. For the diacetylenes BAAB, **45** and **46**, the excitation maxima (400, 415, 433, 442 nm) show 10−15 nm red shifts with respect to the absorption maxima for solutions and 50−60 nm red shifts for solids.

Fluorescence Emission Spectra. The most striking and useful characteristic of many bimanes is their strong fluorescence. The α-ethynylbimanes exhibit strong fluo-

Table 3. Fluorescence Emission Maxima of α-Substituted Bimanes

	emission (ϕ_F) (CH_3CN) λ_{max}, nm	emission (solid) λ_{max}, nm
syn-(CH_3,R_1)(CH_3,$R_{1'}$)B (R_1,$R_{1'}$)		
(CH_3,C≡CC_6H_5) (**20**)	490 (0.60)	550, 590
(H,C≡CC_6H_5) (**23**)	505, 540 (1.0)	590
(CH_3,C≡$CSi(CH_3)_3$) (**25**)	463, 480 sh (0.30)	508
(H,C≡$CSi(CH_3)_3$) (**29**)	473, 500 sh (0.95)	510, 550 sh
(CH_3,C≡CH) (**32**)	445, 467, 482 sh (0.50)	460, 488, 550
(H,C≡CH) (**4**)	460, 467, 480 (0.82)	535, 580
syn-(R_2,R_1)(R_2,$R_{1'}$)B (R_2,R_1)(R_2,$R_{1'}$)		
(CH_3,I)(CH_3,C≡$CSi(CH_3)_3$) (**26**)	460, 481 sh (0.35)	492
(H,I)(H,C≡$CSi(CH_3)_3$) (**30**)	457, 478 sh (0.52)	520, 565 sh
(CH_3,H)(CH_3,C≡$CSi(CH_3)_3$) (**28**)	435, 470 sh (0.40)	470
(H,H)(H,C≡$CSi(CH_3)_3$) (**31**)	434, 470 sh (0.60)	490, 525 sh
(CH_3,C≡CH)(CH_3,C≡$CSi(CH_3)_3$) (**54**)	455, 476 (0.87)	510, 565
(H,C≡CH)(H,C≡$CSi(CH_3)_3$) (**36**)	454, 470 sh (0.60)	527, 580
(CH_3,H)(CH_3,C≡CH) (**35**)	428, 465 sh (0.84)	450, 490
(H,H)(H,C≡CH) (**38**)	425, 455 sh (0.72)	570
(CH_3,Cl)(CH_3,C≡CC_6H_5) (**22**)	488 (0.64)	538
(CH_3,Cl)(CH_3,C≡$CSi(CH_3)_3$) (**27**)	458, 480 sh (0.58)	488
(CH_3,Cl)(CH_3,C≡CH) (**34**)	437, 470, 485 sh (0.82)	
(CH_3,H)(CH_3,C≡CC_6H_5) (**21**)	478 (0.60)	530
(CH_3,I)(CH_3,C≡CH) (**33**)	443, 464, 476 sh (0.34)	
CH=$CHCO_2C_2H_5$ (**17**)	425 sh, 448 (0.42)	
I,CH=$CHCO_2C_2H_5$ (**18**)	450, 475 sh (0.30)	
Cl,CH=$CHCO_2C_2H_5$ (**19**)	461, 480 sh (0.70)	
H,CH=$CHCO_2C_2H_5$ (**56**)	433 (0.40)	

rescence in CH_3CN solutions with quantum yields ranging from 0.3 to 1.0. The emission maxima occur at shorter wavelengths (mono(ethynyl)bimanes) or at somewhat shorter wavelengths (bis(ethynyl)bimanes) than for the unconjugated *syn*-(CH_3,CH_3)B. A phenyl group shifts the emission maxima to longer wavelengths (Table 3). The α-((carboxyethyl)vinyl)bimanes are also strongly fluorescent.

Solid State Fluorescence. Emission maxima from solid α-ethynylbimane show a red shift from that found in solution, with the shift for *syn*-(H,C≡$CSi(CH_3)_3$)(H,X)B [X = C≡$CSi(CH_3)_3$) (**29**), X = I (**30**), X = H (**31**)] quite a bit smaller than that for the *syn*-(H,C≡CH)(H,X)B [X = C≡CH (**4**), X = I (**37**), X = H (**38**)]. *syn*-(H,C≡$CSi(CH_3)_3$)B (**29**) shows a difference of 37 nm between the solid and solution emission, whereas for *syn*-(H,C≡CC_6H_5)B (**23**) the difference is 75 nm.

The fluorescence emission maxima for the bis(bimane)acetylenes *syn*,*syn*-[(CH_3,X)(CH_3,C≡C−)B(CH_3,X)(CH_3,−)B] [X = Cl (**40**), X = H (**41**)] in CH_3CN are at 500 nm (ϕ_F 0.2) (**40**), 491 nm (shoulder, 464 nm) (ϕ_F 0.9) (**41**), with red shifts for the solids to 565 nm (**40**), 555 nm (**41**), respectively. There is little difference between the bis(bimane)acetylenes and the diacetylenes in fluorescence properties. The fluorescence emission maxima for the diacetylenes *syn*,*syn*-[(CH_3,X)(CH_3,C≡C−)B]$_2$ [X = Cl (**45**), X = H (**46**)] and *syn*,*syn*-[(H,H)(H,C≡C−)B]$_2$ (**47**) in CH_3CN have maxima at 500 nm (ϕ_F 0.77), 490 nm (ϕ_F 0.45), and 480 nm and 500 nm (ϕ_F 0.2) (**47**) with fluorescence maxima at 565 nm (**45**), 550 nm (**46**), 535 nm and 565 nm (**47**) for the solids.

Infrared Absorption Spectra. The infrared absorption bands due to the ring carbonyl stretching vibration of α-ethynylbimanes are found between 1730 and 1760 cm^{-1}. The −C≡C− stretching vibration for the α-(trimethylsilyl)ethynyl derivatives, *syn*-(H,C≡$CSi(CH_3)_3$)(H,X)B [X = C≡$CSi(CH_3)_3$) (**29**), X = I (**30**), X = H (**31**)] is found at 2160 cm^{-1} with an intensity almost equal to that of the C−H stretching band for the β-hydrogen. The C≡C− stretching vibration is observable for β-methyl derivatives but not for the β-hydro-α-ethynyl derivatives *syn*-(H,C≡CH)(H,X)B [X = C≡CH (**4**) and X = H (**38**)]. The C≡C band could also not be detected in the case of *syn*-(H,C≡CC_6H_5)B (**23**). The ≡C−H stretching vibration in *syn*-(H,C≡CH)(H,X)B [X = C≡$CSi(CH_3)_3$) (**54**) and X = H (**38**)] is found at 3250 cm^{-1} and at 3260 cm^{-1} for *syn*-(H,C≡CH)B (**4**). The ≡C−H bending vibrations are found at 660−670 cm^{-1}. The infrared absorption data for these derivatives in KBr are summarized in Table 4.

The intensity of the C≡C stretching vibration of disubstituted acetylenes is usually weak.[32] In the case of the α-phenylethynyl derivatives, the band could not be detected. The α-(trimethylsilyl)ethynyl derivatives did show a weak band in the 2140−2160 cm^{-1} region. The C≡C stretching bands for terminal acetylenes are more intense and are found in the region of 2110−2100 cm^{-1} for the α-ethynylbimanes.

The C≡C stretching vibration could not be detected in the infrared spectra in KBr matrix of bisbimanes linked either by an acetylene group (**40** and **41**) or by a diacetylene group (**45**, **46**, and **47**).

The infrared spectrum of the diacetylene *syn*,*syn*-[(H,H)(H,C≡C−)B]$_2$ (**47**) in a KBr pellet has a carbonyl stretching vibration at 1750 cm^{-1} and an absorption at 3100 cm^{-1} for the C−H stretching vibration. No −C≡C− stretching vibration could be observed.

^{1}H NMR Spectra. α-Ethynyl Derivatives. The chemical shifts for the β-methyl groups in α-ethynylbimane derivatives move to lower fields as the ethynyl group becomes more electron withdrawing. For the α-phenylethynyl derivatives in $CDCl_3$ solution, *syn*-(CH_3,C≡CC_6H_5)B (**20**), the chemical shift is at 2.58, in comparison to 2.53 for *syn*-(CH_3,C≡CH)B (**32**) and 2.48 for *syn*-(CH_3,C≡$CSi(CH_3)_3$)B (**25**).

(32) Bellamy, L. J. *Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975.

Table 4. Infrared Absorption of α-Ethynylbimanes[a]

	ν, cm^{-1}			
	CO	C≡C	ring C−H	≡C−H
syn-(R_2,R_1)B (R_2,R_1)				
(CH_3,C≡CC_6H_5) (**20**)	1750, 1680			
(H,C≡CC_6H_5) (**23**)	1740		3100	
(CH_3,C≡CSi(CH_3)$_3$) (**25**)	1750, 1680	2160		
(H,C≡CSi(CH_3)$_3$) (**29**)	1750	2160	3160, 3120, 3080	
(CH_3,C≡CH) (**32**)	1780, 1680	2110	3280	670, 640
(H,C≡C-H) (**4**)	1760		3160, 3120, 3070, 3060	3260, 660
syn-(R_2,R_1)(R_2,$R_{1'}$)B (R_2,R_1)(R_2,$R_{1'}$)				
(CH_3,I)(CH_3,C≡CSi(CH_3)$_3$) (**26**)	1740, 1670	2140		
(H,I)(H,C≡CSi(CH_3)$_3$) (**30**)	1740	2160	3160, 3100	
(CH_3,H)(CH_3,C≡CSi(CH_3)$_3$) (**28**)	1740, 1670	2150		
(H,H)(H,C≡CSi(CH_3)$_3$) (**31**)	1740	2160	3140, 3100	
(CH_3,C≡C-H)(CH_3,C≡CSi(CH_3)$_3$) (**54**)	1780, 1680	2110		3280, 670, 640
(H,C≡CH)(H,C≡CSi(CH_3)$_3$) (**36**)	1740	2160	3150, 3130, 3090	3250, 670
(CH_3,H)(CH_3,C≡CH) (**35**)	1740, 1680	2105		3240, 670
(H,H)(H,C≡CH) (**38**)	1730		3150, 3130, 3090, 3060	3250, 670
(CH_3,Cl)(CH_3,C≡C-C_6H_5) (**22**)	1750, 1680			
(CH_3,Cl)(CH_3,C≡CSi(CH_3)$_3$) (**27**)	1760, 1680	2150		
(CH_3,Cl)(CH_3,C≡CH) (**34**)	1760, 1670	2110		3260, 650
(CH_3,H)(CH_3,C≡C-C_6H_5) (**21**)	1750, 1670			
(CH_3,I)(CH_3,C≡CH) (**33**)	1760, 1675	2100		3270, 660

[a] KBr matrix.

The chemical shift for the hydrogen of the acetylene was found at 3.43, considerably downfield compared to chemical shifts noted for terminal acetylene hydrogens at ∼2.0.[33]

The chemical shifts for the β-hydrogen in α-ethynylbimane derivatives move to lower fields as the ethynyl group becomes more electron withdrawing. The chemical shift for the β-hydrogen in *syn*-(H,C≡CC_6H_5)B (**23**) is 7.661 and 7.577 for *syn*-(H,C≡CSi(CH_3)$_3$)B (**29**) in $CDCl_3$ solution. *syn*-(H,C≡CH)B (**4**) was not soluble in $CDCl_3$; in CD_3CN, the chemical shift for the β-hydrogen is 8.02.

The chemical shifts for the terminal acetylenes are found between 3.40 and 3.36.

α-Carbethoxyvinyl Derivatives. The chemical shifts in $CDCl_3$ for the vinyl hydrogens of the derivatives *syn*-(CH_3,HC=$CHCO_2C_2H_5$)B (**17**), 7.08−7.30, *syn*-(CH_3,I)-(CH_3,HC=$CCO_2C_2H_5$)B (**18**), 7.05−7.28, *syn*-(CH_3,H)-(CH_3,HC=$CCO_2C_2H_5$)B (**34**), 7.04−7.28, and *syn*-(CH_3,Cl)-(CH_3,HC=$CCO_2C_2H_5$)B (**19**), 7.04−7.28, appear at quite low field as compared with unconjugated vinyl protons. The chemical shifts for the β-methyl group of the α-(carbethoxyvinyl)bimanes range from 2.55 for the symmetrical **17** to 2.52 for the unsymmetrical *syn*-(CH_3,I)-(CH_3,HC=$CHCO_2C_2H_5$)B (**18**). The chemical shift is very similar to those found for the β-methyl groups in α-ethynylbimanes.

Discussion

Certain salient points concerning the synthesis and photophysical properties of the bimaneacetylenes will be discussed.

Palladium-Catalyzed Coupling of *syn*-(CH_3,I)-(CH_3,X)B. Hagihara[13] developed the bis(triphenylphosphine)palladium(II) chloride−cuprous iodide−amine system that readily catalyzes the reaction of iodobimanes with acetylenes under mild conditions. A similar catalytic system developed by Heck[34] and Cassar[35] required more drastic conditions and gave lower product yield. We chose the Hagihara route for the preparation of α-ethynylbimanes because of the ready availability of the catalyst, the simplicity of the procedure, the mildness of the reaction conditions, and the high product yields.

The very low solubility of *syn*-(CH_3,I)B (**8**) caused the reaction with acetylene itself to fail. The reaction with phenylacetylene was carried out at 80 °C to increase the solubility of the *syn*-(CH_3,I)B (**8**) in CH_3CN. We suppose that reaction proceeds via the mechanism proposed by Hagihara.[13] In agreement with the mechanism, the formation of a strongly yellow fluorescent bimane−palladium complex was noted during the reaction (by TLC). Its chromatographic mobility and color were very similar to that of a bimane−palladium complex isolated from another reaction.[36] The product, *syn*-(CH_3,C≡CC_6H_5)B (**20**), was obtained in 80% yield accompanied by a minor amount of the reduced bimane *syn*-(CH_3,H)B (**6**). The successful reactions of phenylacetylene with other α-iodo derivatives, *syn*-(CH_3,X)(CH_3,I)B [X = Cl (**15**), X = H (**16**)], yielding the corresponding acetylenes *syn*-(CH_3,X)-(CH_3,C≡CC_6H_5)B [X = Cl (**22**), X = H (**21**)] show that an unreactive halogen substituent or a potentially reactive hydrogen do not interfere.

Reaction with TMSA. Reaction of the α-iodobimane derivatives *syn*-(CH_3,X)(CH_3,I)B [X = I (**8**), X = Cl (**15**), X = H (**16**)] with (trimethylsilyl)acetylene (TMSA) was carried out at temperatures between 30 and 40 °C because of the volatility of the TMSA. Excess TMSA (∼5.0%) was used to correct for loss of the reagent. A larger excess of the reagent led to formation of (CH_3)$_3$-SiC≡CC≡CSi(CH_3)$_3$ consistent with the proposed reaction mechanism in which the activation of the catalyst is via formation of a diacetylene. A bimane−palladium complex could be observed by TLC. Replacement of the α-iodo group by hydrogen also occurred. One limitation is the high cost of the TMSA; an inexpensive synthesis

(33) Tendil, J.; Verney, M. *Tetrahedron Lett.* **1972**, 4023.
(34) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259.
(35) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253.
(36) Hershkovits, E. Ph.D. Thesis, Tel-Aviv University, 1990.

has now been described *in Organic Syntheses*.[37] *syn*-(CH_3,X)B derivatives [X = Cl (**5**), X = Br (**7**)] were found to be unreactive.

Alkyne−Alkene versus Bimane Reactivity toward Halogen. In view of the high reactivity of alkyl-substituted bimanes toward bromine, the reaction of *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) with bromine and ICl was examined. Both bromine and ICl reacted with the ethynyl group. The bromine adduct *syn*-(CH_3,BrC=CBrSi(CH_3)$_3$)B (**49**) eliminated bromine on treatment with NaI in boiling acetone to yield *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**). Bromine also added to the double bond of *syn*-(CH_3,CH=CHCO$_2$C$_2$H$_5$)B (**17**). In neither the vinyl nor the ethynyl derivatives was any *β*-bromomethyl derivative formed even in the presence of excess bromine.

Ultraviolet−Visible Absorption and Excitation Spectra. The ultraviolet and visible absorption maxima of bimanes are shifted to longer wavelengths if α-vinyl or α-ethynyl groups are conjugated to the ring. The effect of the vinyl group on the bimane ring is apparently smaller than that of ethynyl groups in view of the longer wavelength absorption found for the α-ethynyl derivatives. The α-phenylethynyl derivative *syn*-(CH_3,C≡C-C_6H_5)B (**20**) has an absorption maximum at 430 nm, showing that conjugation is increased by the phenyl ring.

The α-ethynyl derivatives *syn*-(CH_3,C≡CH)(CH_3,X)B [X = C≡CH (**32**), X = I (**33**), X = Cl (**34**), X = H (**35**)] absorb at shorter wavelengths than the α-(trimethylsilyl)ethynyl derivatives *syn*-(CH_3,C≡CSi(CH_3)$_3$)(CH_3,X)B [X = C≡CSi(Me)$_3$ (**25**), X = I (**26**), X = Cl (**27**), X = H (**28**)]. This might be explained by the greater polarizability of silicon. The excitation maxima for many bimanes in solutions are at wavelengths 10−15 nm longer than the corresponding absorption maxima. In the case of the α-vinyl- and α-ethynylbimanes, the excitation maxima are 5−10 nm longer than the absorption maxima. The α-phenylethynyl derivative *syn*-(CH_3,C≡CC_6H_5)B (**20**) and the α-ethynylbimane, *syn*-(CH_3,C≡CH)B (**32**) show very large red shifts in the excitation spectra of the crystals as compared to spectra in solution, suggesting that the bimanes are more planar in crystals. Since the photophysics of bimanes is the subject of ongoing studies, we emphasize here the phenomenological aspects of the behavior of the bimaneacetylenes.

Fluorescence Emission Spectra. Like most *syn*-bimanes, the α-vinyl and α-ethynyl derivatives are fluorescent. The emission maxima are about 50−60 nm longer in wavelength than the absorption maxima. The complexity of the emission spectra, two or three overlapping curves, at 430 and 490 nm, may be due to the coexistence of a few excited state conformers, including bent and quasiplanar conformers.[2] The rate constant for conformer interconversion is 10^{11} s^{-1} in 1-propanol.[38]

^{1}H NMR Spectra. The chemical shift for the acetylenic proton in terminal acetylenes is at about 2.0 and is quite sensitive to the medium. In nonpolar solvents such as CCl_4, the peak shifts upfield whereas in hydrogen-bonding solvents the peak shifts downfield.[16] The chemical shift found for the acetylenic protons in α-ethynylbimanes in $CDCl_3$ is around 3.45, indicating strong hydrogen bonding.

(37) Jones, C. E.; Kendrick, D. A.; Holmes, A. B.; Sporikov, C. N. *Org. Synth.* **1987**, *65*, 61. The reagent has recently become available from Farchan at a more economical price.

(38) Giniger, R.; Huppert, D.; Kosower, E. M. *Chem. Phys. Lett.* **1985**, *118*, 240−245.

Conclusions

We have established a firm basis for using bimanes combined with acetylene and diacetylene groups as building blocks for more complex materials, such as rodlike polymers. The strong and colorful fluorescence of the bimaneacetylenes coupled to their stability may also be useful.

Experimental Section

Instrumentation. Infrared spectra: dispersive and FT-IR spectrometers. ^{1}H NMR spectra: 90, 360, and 200 MHz FT-NMR spectrometers. Fluorescence spectra: spectrofluorimeter with a corrected spectra attachment and a digital integrator.

Quantum yields: quinine sulfate in 0.1 N H_2SO_4 as reference. Quantum yields were calculated according to the equation

$$\phi_F = \frac{F_s[\epsilon_q C_q(0.55)]}{F_q(\epsilon_s C_s)}$$

using excitation of sample and quinine sulfate at the same wavelength. Symbols: *F*, integrated area under fluorescence curve; s, sample; q, quinine sulfate; *C*, concentration; *ϵ*, absorption coefficient.

***syn*-(Methyl,iodo)bimane, *syn*-(CH_3,I)B (8).** ICl (3.0 g, 18.5 mmol) in CH_2Cl_2 (20 mL) was added to a solution of *syn*-(CH_3,H)B (**6**) (1.0 g, 6.1 mmol) in CH_2Cl_2 (200 mL), and the reaction mixture was stirred for 0.5 h. After removal of most of the CH_2Cl_2, the *syn*-(CH_3,I)B (**8**) was filtered off (2.7 g, 90% yield): yellow crystals (CH_3CN), mp 220 °C (dec); IR (KBr) 1760, 1675, 1575, 730 cm^{-1}; ^{1}H NMR (CD_3CN) *δ* 2.54 (s, 6H); UV (CH_3CN) λ_{max} 384 (*ϵ* 7600), 268 (4500), 232 (5200); fluorescence (CH_3CN) λ_{max} 440 nm, 460 sh (ϕ_F 0.21); mass spectrum *m*/*z* 416 (M^+).

***syn*-(Methyl,chloro)(methyl,iodo)bimane, *syn*-(CH_3,Cl)(CH_3,I)B (15).** ICl (1.1 g, 7.0 mmol) in CH_2Cl_2 (10 mL) was added to a solution of *syn*-(CH_3,H)(CH_3,Cl)B (**14**) (1.0 g, 5.0 mmol) in CH_2Cl_2 (100 mL). After 0.5 h, the solvent was evaporated, CCl_4 (100 mL) was added, and the *syn*-(CH_3,Cl)(CH_3,I)B (**15**) was filtered off (1.6 g, 95% yield): yellow crystals (CH_3CN), mp 215 °C; IR (KBr) 2960, 2920, 1760, 1680, 1600, 1565, 810, 730, 600 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.47 (s, 3H), 2.49 (s, 3H); UV (CH_3CN) λ_{max} 378 nm (*ϵ* 3360), 252 sh (7600), 228 (11400); fluorescence (CH_3CN) λ_{max} 432 nm, 450 sh (ϕ_F 0.43); mass spectrum *m*/*z* 320, 322 (M^+) (fits 1 Cl with *m*/*z* 320 = 100%).

***syn*-(Methyl,hydro)(methyl,iodo)bimane, *syn*-(CH_3,I)(CH_3,H)B (16).** A solution of ICl (250 mg, 1.65 mmol) in CH_2Cl_2 (20 mL) was added dropwise via a Soxhlet apparatus carrying an efficient condenser to a solution of *syn*-(CH_3,H)B (**6**) (200 mg, 1.25 mmol) in CH_2Cl_2 (250 mL) under reflux. The rate of ICl addition is kept low enough to ensure the introduction of a very highly dilute ICl solution. Addition was completed in about 3 h, after which the solvent was evaporated and the residue flash chromatographed on silica gel [eluant, CH_2Cl_2:EtOAc (1:5)], yielding *syn*-(CH_3,I)B (**8**) (50.0 mg, 10% yield), *syn*-(CH_3,I)(CH_3,H)B (**16**) (190 mg, 55% yield), and *syn*-(CH_3,H)B (**6**) (45 mg, 23% recovery).

***syn*-(CH_3,I)(CH_3,H)B (16):** yellow crystals (CH_3CN), mp 205 °C; IR (KBr) 3105, 2920, 1750, 1746, 1670, 1590, 780, 730, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$) *δ* 2.40 (s, 3H), 2.47 (s, 3H), 5.49 (s, 1H); UV (CH_3CN) λ_{max} 376 nm (*ϵ* 10000), 238 sh (12140), 222 (15700); fluorescence (CH_3CN) λ_{max} 424 nm, 452 sh (ϕ_F 0.53); mass spectrum *m*/*z* 286 (M^+).

***syn*-(Methyl,2-carbethoxyvinyl)bimane, *syn*-(CH_3,HC=CHCO$_2$CH$_2$CH$_3$)B (17).** Diisopropylethylamine (65 mg, 0.5 mmol) and ethyl acrylate (60 mg, 0.6 mmol) were added to a suspension of *syn*-(CH_3,I)B[3] (**8**) (104 mg, 0.25 mmol) in CH_3CN (50 mL). $Pd(OAc)_2$ (1.0 mg) was added under nitrogen, and the mixture was refluxed for 36 h. The solvent was evaporated and the residue flash chromatographed on silica gel (eluant, CH_2Cl_2−EtOAc (1:1)). The major fluorescent

products were *syn*-(CH_3,HC=$CHCO_2C_2H_5$)B (**17**) (45 mg, 50% yield) and *syn*-(CH_3,H)B (**16**) (2.0 mg, 5% yield).

***syn*-(CH_3,HC=$CHCO_2C_2H_5$)B (17):** yellow crystals (CH_3CN−2-propanol (3:1)), mp 185 °C; IR (KBr) 2920, 2840, 1740, 1710, 1660, 1620, 1550, 970, 860, 780, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.319 (t, 6H), 2.55 (s, 6H), 4.25 (q, 4H), 7.08 (d, J = 18 Hz, 1H), 7.30 (d, J = 18 Hz, 1H) ppm; UV (CH_3CN) λ_{max} 382 nm (ϵ 13 600), 295 (10 100); fluorescence (CH_3CN) λ_{max} 425 sh, 448 nm (ϕ_F 0.42); mass spectrum *m*/*z* 288 ($M^+ - CO_2CH_2CH_3$).

***syn*-(Methyl,iodo)(methyl,2-carbethoxyvinyl)bimane, *syn*-(CH_3,I)(CH_3,HC=$CHCO_2CH_2CH_3$)B (18).** *syn*-(CH_3,I)B (**8**) (52 mg, 0.12 mmol) was mixed with ethyl acrylate (10 mg, 0.10 mmol) and diisopropylethylamine (16 mg, 0.12 mmol) in CH_3CN (20 mL). Under nitrogen, $Pd(OAc)_2$ (1.0 mg) was added and the mixture was refluxed for 20 h. After removal of the solvent, the residue was chromatographed to yield *syn*-(CH_3,I)B (**8**) (5 mg, 10%), *syn*-(CH_3,I)(CH_3,HC=$CHCO_2CH_2CH_3$)B (**18**) (23 mg, 50%), and *syn*-(CH_3,H)B (**6**) (0.9 mg, 5%).

***syn*-(CH_3,I)(CH_3,HC=$CCO_2C_2H_5$)B (18):** yellow crystals from 2-propanol−CH_3CN (1:3), mp 215 °C (dec); IR (KBr) 2990, 2900, 2840, 1740, 1710, 1670, 1620, 1540, 970, 950, 870, 720, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, 3H), 2.52 (s, 3H), 2.52 (s, 3H), 4.25 (q, 2H), 7.05 (d, J = 15.8 Hz, 1H), 7.28 (d, J = 15.8 Hz, 1H); UV (CH_3CN) λ_{max} 400 nm (ϵ 9670), 300 sh (6440), 275 (10 960); fluorescence (CH_3CN) λ_{max} 450 nm, 475 sh (ϕ_F 0.30); mass spectrum *m*/*z* 388 (M^+).

***syn*-(Methyl,hydro)(methyl,2-carbethoxyvinyl)bimane, *syn*-(CH_3,H)(CH_3,HC=$CHCO_2CH_2CH_3$)B (55).** *syn*-(CH_3,H)(CH_3,I)B (**16**) (29 mg, 0.1 mmol) was stirred with ethyl acrylate (12 mg, 0.12 mmol), diisopropylethylamine (13 mg, 0.1 mmol), and $Pd(OAc)_2$ (1.0 mg) in CH_3CN (10 mL) for 20 h under nitrogen. Chromatography gave, in order of elution, *syn*-(CH_3,H)(CH_3,HC=$CHCO_2CH_2CH_3$)B (**55**) (7.8 mg, 30% yield) and *syn*-(CH_3,H)B (**6**) (2.4 mg, 15% yield).

***syn*-(CH_3,H)(CH_3,HC=$CHCO_2C_2H_5$)B (55):** yellow crystals (CH_3CN), mp 170 °C; IR (KBr) 3160, 2980, 1750, 1710, 1680, 1630, 1560, 970, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, 3H), 2.40 (s, 3H), 2.53 (s, 3H), 4.25 (q, 2H) 5.56 (s, 1H), 7.04 (d, 1H), 7.28 (d, 1H); UV (CH_3CN) λ_{max} 372 nm (ϵ 9000), 287 (7660); fluorescence (CH_3CN) λ_{max} 445 nm (ϕ_F 0.40); mass spectrum *m*/*z* 262 (M^+).

***syn*-(Methyl,chloro)(methyl,2-carbethoxyvinyl)bimane, *syn*-(CH_3,Cl)(CH_3, HC=$CHCO_2CH_2CH_3$)B (19).** A mixture of *syn*-(CH_3,Cl)(CH_3,I)B (**15**) (33 mg, 0.1 mmol), ethyl acrylate (12 mg, 0.1 mmol), diisopropylethylamine (13.0 g, 0.1 mmol), and $Pd(OAc)_2$ (1.0 mg) in CH_3CN (10 mL) under nitrogen was refluxed for 24 h. After removal of the solvent, chromatography gave, in order of elution, *syn*-(CH_3,Cl)(CH_3,-HC=$CHCO_2CH_2CH_3$)B (**19**) (10.5 mg, 35% yield) and *syn*-(CH_3,Cl)(CH_3,H)B (**14**) (3.0 mg, 15% yield).

***syn*-(CH_3,Cl)(CH_3,HC=$CCO_2C_2H_5$)B (19):** yellow crystals (2-propanol), mp 190 °C; IR (KBr) 2920, 2840, 1740, 1710, 1670, 1620, 970, 860, 720 cm^{-1}; ^1H NMR ($CDCl_3$) 1.32 (t, 3H), 2.44 (s, 3H), 2.54 (s, 3H), 4.25 (q, 2H), 7.04 (d, 1H), 7.28 (d, 1H); UV (CH_3CN) λ_{max} 385 nm (ϵ 13 300), 285 sh (15 200), 275 (16 200); fluorescence (CH_3CN) λ_{max} 461 nm, 480 (ϕ_F 0.70); mass spectrum *m*/*z* 296 (M^+).

***syn*-(Methyl,phenylethynyl)bimane, *syn*-(CH_3,C≡C-C_6H_5)B (20).** Bis(triphenylphosphine)palladium(II) chloride (5.0 mg) and cuprous iodide (2.0 mg) were added to a mixture of phenylacetylene (63 mg, 0.62 mmol), diisopropyl ethylamine (65.5 mg, 0.5 mmol), and a suspension of *syn*-(CH_3,I)B (**8**) (104 mg, 0.25 mmol) in CH_3CN (100 mL). The reaction mixture was stirred for 3 h at 80 °C under nitrogen. After evaporation of the solvent, the residue was flash chromatographed on silica gel [eluant, CH_2Cl_2−ethyl acetate (1:1)]. The major bright green fluorescent fractions yielded *syn*-(CH_3,C≡CC_6H_5)B (**20**) (740 mg, 80% yield): orange crystals (CH_3CN), mp 285 °C; IR (KBr) 1750, 1680, 1560, 770, 755, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.58 (s, 6H), 7.36 (m, 4H), 7.54 (m, 6H); UV (CH_3CN) λ_{max} 430 nm (ϵ 4200), 282 (6060); fluorescence (CH_3CN) λ_{max} 490 nm (ϕ_F 0.60); fluorescence (solid) λ_{max} 550 nm, 590; fluorescence excitation (solid) λ_{max} 280 nm, 335, 400, 412, 425, 440, 454, 475, 480; mass spectrum *m*/*z* 362 (M^+).

***syn*-(Methyl,chloro)(methyl,phenylethynyl)bimane, *syn*-(CH_3,Cl)(CH_3,C≡CC_6H_5)B (22).** Bis(triphenylphosphine)-palladium(II) chloride (5.0 mg) and cuprous iodide (5.0 mg) were added to a mixture of *syn*-(CH_3,Cl)(CH_3,I)B (**15**) (162 mg, 0.5 mmol), diisopropylethylamine (65.5 mg, 0.5 mmol), and phenylacetylene (56.1 mg, 0.55 mmol) in CH_3CN (150 mL). The reaction mixture was stirred for 3 h at 80 °C under nitrogen, the solvent evaporated, and the residue flash chromatographed on silica gel [eluant, CH_2Cl_2−ethyl acetate (1:2)]. The bright green fluorescent fractions gave *syn*-(CH_3,Cl)(CH_3,C≡CC_6H_5)B (**22**) (110 mg, 75% yield): yellow crystals (CH_3CN), mp 260 °C; IR (KBr) 1750, 1680, 760, 740, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$) 2.49 (s, 3H), 2.57 (s, 3H), 7.36 (m, 2H), 7.53 (m, 3H); UV λ_{max} 402 nm (ϵ 14 700), 278 (20 900), 225 (19 800); fluorescence (CH_3CN) λ_{max} 488 nm (ϕ_F 0.64); mass spectrum *m*/*z* 298 (100%), 300 (34%) (M^+) (fits a molecule with 1 Cl).

***syn*-(Methyl,hydro)(methyl,phenylethynyl)bimane, *syn*-(CH_3,H) (CH_3,C≡CC_6H_5)B (21).** Bis(triphenylphosphine)-palladium(II) chloride (5.0 mg) and cuprous iodide (5.0 mg) were added to a mixture of *syn*-(CH_3,H)(CH_3,I)B (**16**) (143 mg, 0.5 mmol), diisopropylethylamine (65.5 mg, 0.5 mmol), and phenylacetylene (56.1 mg, 0.55 mmol) in CH_3CN (150 mL). The reaction mixture was stirred for 3 h at 80 °C under nitrogen, the solvent evaporated, and the residue flash chromatographed on silica gel [eluant, CH_2Cl_2−ethyl acetate (1:2)]. The bright green fluorescent fractions gave *syn*-(CH_3,H)(CH_3,C≡CC_6H_5)B (**21**) (72 mg, 70% yield): yellow crystals (CH_3CN), mp 268 °C; IR (KBr) 3105, 1750, 1680, 760, 740, 730, cm^{-1}; ^1H NMR ($CDCl_3$) 2.42 (s, 3H), 2.54 (s, 3H), 7.33 (m, 2H), 7.51 (m, 3H); UV (CH_3CN) λ_{max} 398 nm (ϵ 9110), 268 (11 900), 225 (10 800); fluorescence (CH_3CN) λ_{max} 478 nm (ϕ_F 0.64); mass spectrum *m*/*z* 264 (100%) (M^+).

Reaction of α-Iodobimanes with TMSA. Bis(triphenylphosphine)palladium(II) dichloride (5−10 mg) and cuprous iodide (5.0 mg) were added under nitrogen to a mixture of α-iodobimane (ca. 1.0 mmol), TMSA (1.2 equiv), and diisopropylethylamine (1.0 equiv) in CH_3CN. On TLC, the blue fluorescence of the starting materials gradually changed to the yellow-green fluorescence of products with different chromatographic mobilities. The solvent-free residue was flash chromatographed on silica gel.

***syn*-(Hydro,(trimethylsilyl)ethynyl)bimane, *syn*-(H,-C≡$CSi(CH_3)_3$)B (29).** Bis(triphenylphosphine)palladium(II) chloride (5.0 mg) and cuprous iodide (2.0 mg) were added to TMSA (300 mg, 3.0 mmol), diisopropylethylamine (364 mg, 2.8 mmol), and *syn*-(H,I)B (**10**) (540 mg, 1.46 mmol) in CH_3CN (500 mL). The mixture was stirred for 16 h under nitrogen, the solvent evaporated, and the residue flash chromatographed on silica gel [eluant, EtAc−CH_2Cl_2], yielding, in order of elution, *syn*-(H,C≡$CSi(CH_3)_3$)B (**29**) (320 mg, 67% yield), *syn*-(H,I)(H,C≡$CSi(CH_3)_3$)B (**30**) (20 mg, 4% yield), and *syn*-(H,H)-(H,C≡$CSi(CH_3)_3$)B (**31**) (4 mg, 1% yield).

***syn*-(H,C≡$CSi(CH_3)_3$)B (29):** yellow crystals (CH_3CN), mp 320 °C (dec); IR (KBr) 3160, 3120, 3080, 2160, 1750, 1550, 870, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.232 (s, 18H), 7.578 (s, 2H); UV (CH_3CN) λ_{max} 445 nm (1500 sh), 430 (ϵ 3330), 250 (3950); fluorescence (CH_3CN) λ_{max} 473 nm, 500 sh (ϕ_F 0.95); fluorescence (solid state) λ_{max} 510 nm, 550 sh; fluorescence excitation (solid state) λ_{max} 370 nm, 400, 436, 445, 470; mass spectrum *m*/*z* 328, 329, 330 (M^+).

***syn*-(H,I)(H,C≡$CSi(CH_3)_3$)B (30):** yellow crystals (CH_3CN), mp 240 °C; IR (KBr) 3160, 3100, 2960, 2950, 2160, 1740, 1680, 1510, 840, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.235 (s, 9H), 7.593 (s, 1H), 7.626 (s, 1H); UV (CH_3CN) λ_{max} 410 nm (ϵ 13 660), 245 sh (11 900), 230 (13 240); fluorescence (CH_3CN) λ_{max} 457 nm, 478 sh (ϕ_F 0.52); mass spectrum *m*/*z* 358, 359 (M^+).

***syn*-(H,H)(H,C≡$CSi(CH_3)_3$)B (31):** yellow crystals (CH_3-CN), mp 250 °C; IR (KBr) 3140, 3100, 2950, 2160, 1740, 1670, 1540, 1440, 1310, 1280, 1240, 1050, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$) 0.236 (s, 9H), 5.852 (d, J = 3.6 Hz, 1H), 7.512 (d, J = 3.6 Hz, 1H), 7.591 (s, 1H); UV (CH_3CN) λ_{max} 395 nm (ϵ 6700), 240 (7280); fluorescence (CH_3CN) λ_{max} 434 nm, 470 sh (ϕ_F 0.6); fluorescence emission (solid state) λ_{max} 525 nm, 565; fluorescence excitation (solid state) λ_{max} 395 nm, 490, 515; mass spectrum *m*/*z* 231, 232 (M^+).

***syn*-(Methyl,(trimethylsilyl)ethynyl)bimane, *syn*-(CH_3,-C≡CSi(CH_3)$_3$)B (25).** According to the general procedure, TMSA (240 mg, 2.4 mmol), diisopropylethylamine (262 mg, 2.0 mmol), and the catalysts were added to *syn*-(CH_3,I)B (**8**) (416 mg, 1.0 mmol) in CH_3CN (500 mL). The reaction mixture was stirred for 20 h at 40 °C. After workup, chromatography gave, in order of elution [eluants, CH_2Cl_2−EtOAc], *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) (178 mg, 50% yield), *syn*-(CH_3,I)(CH_3,C≡CSi(CH_3)$_3$)B (**26**) (38.0 mg, 10% yield), *syn*-(CH_3,H)(CH_3,C≡CSi(CH_3)$_3$)B (**28**) (1.3 mg, 25% yield), and *syn*-(CH_3,H)B (**6**) (2.0 mg, 0.12% yield).

***syn*-(CH_3,C≡CSi(CH_3)$_3$)B (25):** yellow crystals (2-propanol), mp 187 °C; IR (KBr) 2950, 2160, 1750, 1680, 1550, 870, 760, 750 cm^{-1}; ^1H NMR ($CDCl_3$) 0.24 (s, 18H), 2.48 (s, 6H); UV (CH_3CN) λ_{max} 408 nm (ϵ 7500), 258 (11 250); fluorescence (CH_3CN) λ_{max} 463 nm, 481 sh (ϕ_F 0.30); mass spectrum *m*/*z* 356 (M^+).

***syn*-(Methyl,iodo)(methyl,(trimethylsilyl)ethynyl)bimane, *syn*-(CH_3,I)(C≡CSi(CH_3)$_3$)B (26).** According to the general procedure, TMSA (49 mg, 0.5 mmol), diisopropylethylamine (65 mg, 0.5 mmol), and the catalysts were added to *syn*-(CH_3,I)B (**8**) (208 mg, 0.5 mmol) in CH_3CN (200 mL). The mixture was stirred for 20 h at room temperature under nitrogen. After workup, chromatography gave, in order of elution [eluant, CH_2Cl_2−EtOAc], *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) (18 mg, 10% yield), *syn*-(CH_3,I)(CH_3,C≡CSi(CH_3)$_3$)B (**26**) (68 mg, 35% yield), and *syn*-(CH_3,I)B (**8**) (20 mg, 10% yield).

***syn*-(CH_3,I)(CH_3,C≡CSi(CH_3)$_3$)B (26):** yellow crystals (2-propanol), mp 180 °C; IR (KBr) 2950, 2140, 1740, 1670, 840, 750, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 0.24 (s, 9H), 2.46 (s, 3H), 2.48 (s, 3H); UV (CH_3CN) λ_{max} 405 nm (ϵ 5000), 238 (7500); fluorescence (CH_3CN) λ_{max} 460 nm, 478 sh (ϕ_F 0.28); mass spectrum *m*/*z* 386 (M^+).

***syn*-(Methyl,chloro)(methyl,(trimethylsilyl)ethynyl)bimane, *syn*-(CH_3,Cl)(CH_3,C≡CSi(CH_3)$_3$)B (27).** According to the general procedure, TMSA (55.0 mg, 0.56 mmol), diisopropylethylamine (65 mg, 0.5 mmol), and the catalysts were added to *syn*-(CH_3,Cl)(CH_3,I)B (**15**) (162 mg, 0.5 mmol) in CH_3CN (150 mL). After 20 h of stirring at room temperature under nitrogen, workup and chromatography gave, in order of elution, *syn*-(CH_3,Cl)(CH_3,C≡CSi(CH_3)$_3$)B (**27**) (85 mg, 58% yield) and *syn*-(CH_3,Cl)(CH_3,H)B (**14**) (9.0 mg, 5% yield).

***syn*-(CH_3,Cl)(CH_3,C≡CSi(CH_3)$_3$)B (27):** yellow crystals (2-propanol), mp 290 °C; IR (KBr) 2980, 2150, 1760, 1680, 1590, 1570, 860, 840, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9H), 2.46 (s, 3H), 2.49 (s, 3H); UV (CH_3CN) λ_{max} 395 nm (ϵ 12 900), 242 (28 800); fluorescence (CH_3CN) λ_{max} 458 nm, 480 sh (ϕ_F 0.58); mass spectrum *m*/*z* 294 (M^+).

***syn*-(Methyl,hydro)(methyl,(trimethylsilyl)ethynyl)bimane, *syn*-(CH_3,H)(CH_3,C≡CSi(CH_3)$_3$)B (28).** According to the general procedure, TMSA (107 mg, 1.2 mmol), diisopropylethylamine (131 mg, 1.0 mmol), and the catalysts were added to *syn*-(CH_3,I)(CH_3,H)B (**16**) (290 mg, 1.0 mmol) in CH_3CN (200 mL), and the mixture was stirred for 24 h at room temperature under nitrogen. After workup, chromatography yielded, in order of elution, of *syn*-(CH_3,H)(CH_3,C≡CSi(CH_3)$_3$)B (**28**) (150 mg, 60% yield) and *syn*-(CH_3,H)B (**6**) (8.0 mg, 5% yield).

***syn*-(CH_3,H)(CH_3,C≡CSi(CH_3)$_3$)B (28):** yellow crystals (2-propanol−CH_3CN), mp 210 °C; IR (KBr) 3100, 2950, 2150, 1740, 1670, 840, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9H), 2.40 (d, 3H), 2.47 (s, 3H), 5.54 (s, 1H); UV (CH_3,CN) λ_{max} 382 nm (ϵ 5430), 245 (8690); fluorescence (CH_3CN) λ_{max} 435 nm, 470 sh (ϕ_F 0.40); mass spectrum *m*/*z* 260 (M^+).

Desilylation Procedures. Procedure A (HF). To a solution of a bimane, *syn*-(CH_3,X)(CH_3,C≡CSi(CH_3)$_3$)B [X = C≡CSi(CH_3)$_3$) (**25**), I (**26**), H (**28**), Cl (**27**)] (0.1 mmol) in CH_3CN (10 mL), was added 48% HF (2 mL). After the solution was stirred for 15 h, CH_2Cl_2 (50 mL) was added and the reaction mixture neutralized with $NaHCO_3$. The organic phase was washed with water, dried over $MgSO_4$, and evaporated to yield *syn*-(CH_3,X)(CH_3,C≡CH)B [X = C≡CH (**32**), I (**33**), H (**35**), Cl (**34**)], which were purified by flash chromatography on silica gel [eluants, CH_2Cl_2, EtOAc].

Procedure B ($AgNO_3$/LiBr). *syn*-(CH_3,X)(CH_3,C≡CSi(CH_3)$_3$)B [X = C≡CSi(CH_3)$_3$ (**25**), I (**26**), H (**28**), Cl (**27**)] (0.1 mmol) was dissolved in hot ethanol (15 mL). After cooling, a solution of silver nitrate (1.2 equiv) in water (1.0 mL) was added, producing a silver acetylide precipitate (TLC test for starting material). Lithium bromide (1.4 equiv) was then added, and stirring was continued for ca 0.5 h. CH_2Cl_2 (50 mL) was added, the silver bromide filtered off through Celite, the filtrate evaporated, and the residue flash chromatographed on silica gel [eluant, CH_2Cl_2−EtOAc] to give the product, *syn*-(CH_3,X)(CH_3,C≡CH)B [X = C≡CH (**32**), I (**33**), H (**35**), Cl (**34**)].

Procedure C ($AgNO_3$/KCN). A solution of silver nitrate (1.2 equiv) in water (1.0 mL) was mixed with a solution of *syn*-(CH_3,X)(CH_3,C≡CSi(CH_3)$_3$)B [X = C≡CSi(CH_3)$_3$ (**25**), I (**26**), H (**28**), Cl (**27**)] (0.1 mmol) in ethanol (15 mL) (TLC test for starting material). Potassium cyanide (4.8 equiv) in water (2 mL) was added. After the silver acetylide precipitate dissolved, CH_2Cl_2 (50 mL) was added, the extract washed with water (2 × 20 mL), the organic phase dried ($MgSO_4$), and the solvent evaporated. The products were separated by flash chromatography.

***syn*-(Hydro,ethynyl)bimane, *syn*-(H,C≡CH)B (4).** A solution of silver nitrate (600 mg, 2.6 mmol) in water (4 mL) was added to a warm solution of *syn*-(H,C≡CSi(CH_3)$_3$)B (**29**) (400 mg, 1.2 mmol) in ethanol (100 mL). The reaction mixture was stirred for 0.5 h (or until there were no fluorescent spots on TLC). A solution of lithium bromide (225 mg, 2.6 mmol) in water (2 mL) was added, the silver bromide filtered off through Celite, the solvent evaporated, and the residue flash chromatographed on silica gel [eluant, CH_2Cl_2−EtOAc (1:1)]. The main fluorescent product was *syn*-(H,C≡CH)B (**4**) (145 mg, 66% yield) together with *syn*-(H,C≡CH)(H,C≡CSi(CH_3)$_3$)B (**36**) (39 mg, 11% yield).

***syn*-(H,C≡CH)B (4)** was isolated as a yellow powder, red-orange crystals (CH_3CN): mp 310 °C; IR (KBr) 3260, 3160, 3120, 3070, 1760, 1670, 1550, 770, 740, 710, 660 cm^{-1}; ^1H NMR (CD_3CN) δ 3.74 (s, 2H), 8.02 (s, 2H); UV (CH_3CN) λ_{max} 410 nm (ϵ 10 000), 430 sh (7600), 240 (10 800); fluorescence (CH_3-CN) λ_{max} 460 nm, 467 sh, 480 (ϕ_F 0.87); fluorescence (solid state) λ_{max} 535, 580 nm; fluorescence excitation (solid state) λ_{max} 375, 435, 480, 516 nm; mass spectrum *m*/*z* 182, 183 (M^+).

***syn*-(H,C≡CH)(H,C≡CSi(CH_3)$_3$B (36):** yellow crystals (CH_3-CN), mp 205 °C; IR (KBr) 3250, 3160, 3120, 3080, 2960, 1740, 1670, 910, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9H), 3.40 (s, 1H), 7.59 (s, 1H), 7.62 (s, 1H); UV (CH_3CN) λ_{max} 412 nm (ϵ 14 000), 260 (17 300); fluorescence (CH_3CN) λ_{max} 454 nm, 470 sh (ϕ_F 0.10); mass spectrum *m*/*z* 257 (M^+).

***syn*-(Methyl,ethynyl)bimane, *syn*-(CH_3,C≡CH)B (32).** *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) was converted to *syn*-(CH_3,-C≡CH)B (**32**) by procedures A (15% yield) or B or C (45% yield). ***syn*-(CH_3,C≡CH)B (32):** orange crystals CH_3CN, mp 170 °C; IR (KBr) 3280, 2980, 2940, 2110, 1780, 1760, 1680, 1595, 1560, 759, 670, 640 cm^{-1}; ^1H NMR ($CDCl_3$) 2.53 (s, 6H), 3.45 (s, 2H); UV (CH_3CN) λ_{max} 400 nm (ϵ 6600), 260 sh (4100), 240 (9460); fluorescence (CH_3CN) λ_{max} 445 nm, 467, 482 sh (ϕ_F 0.50); fluorescence excitation (solid state) λ_{max} 395 nm, 435; mass spectrum *m*/*z* 212 (M^+).

***syn*-(Methyl,(trimethylsilyl)ethynyl)(methyl,ethynyl)bimane, *syn*-(CH_3,C≡CSi(CH_3)$_3$)(CH_3,C≡C-H)B (54).** *syn*-(CH_3,C≡CSi(CH_3)$_3$)B (**25**) was converted to *syn*-(CH_3,C≡CSi-(CH_3)$_3$)(CH_3,C≡CH)B (**54**) by procedure A. TLC verified the presence of **54**. Workup and chromatography gave *syn*-(CH_3,C≡CSi(CH_3)$_3$)(CH_3,C≡CH)B (**54**) (3.0 mg, 10% yield) and *syn*-(CH_3,C≡CH)B (**32**) (2.0 mg, 10% yield).

***syn*-(CH_3,C≡CSi(CH_3)$_3$)(CH_3,C≡CH)B (54):** yellow crystals (CH_3CN), mp 165 °C; IR (KBr) 3280, 2980, 2940, 2110, 1780, 1760, 1680, 1590, 750, 670, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9H), 2.52 (s, 3H), 2.61 (s, 3H), 3.45 (s, 1H); UV (CH_3-CN) λ_{max}405 nm (ϵ 7800), 280 sh (5000), 245 (11 400); fluorescence (CH_3CN) λ_{max} 455 nm, 476 (ϕ_F 0.87); mass spectrum *m*/*z* 284 (M^+).

***syn*-(Methyl,iodo)(methyl,ethynyl)bimane, *syn*-(CH_3,I)-(CH_3,C≡C-H)B (33).** *syn*-(CH_3,I)(CH_3,C≡CSi(CH_3)$_3$)B (**26**) was converted to *syn*-(CH_3,I)(CH_3,C≡CH)B (**33**) by procedure A (20% yield) or B or C (48% yield). *syn*-(CH_3,I)(CH_3,C≡CH)B (**33**): yellow crystals (CH_3CN), mp 218 °C; IR (KBr) 3270, 2980, 2960, 2920, 2100, 1760, 1675, 1580, 1540, 740, 725, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (s, 3H), 2.52 (s, 3H), 3.45 (s, 1H); UV

(CH_3CN) λ_{max} 393 nm (ϵ 5500), 270 (4200), 230 (6700); fluorescence (CH_3CN) λ_{max} 443 nm, 464, 476 sh (ϕ_F 0.34); mass spectrum *m/z* 314 (M^+).

***syn*-(Methyl,chloro)(methyl,ethynyl)bimane, *syn*-(CH_3,Cl)(CH_3,C≡CH)B (34).** *syn*-(CH_3,Cl)(CH_3,C≡CSi(CH_3)$_3$)B (**27**) was converted to *syn*-(CH_3,Cl)(CH_3,C≡CH)B (**34**) in 24% yield by procedure A. Procedures B and C gave higher yields (65%).

***syn*-(CH_3,Cl)(CH_3,C≡CH)B (34):** yellow crystals (CH_3CN), mp 210 °C (dec); IR (KBr) 3260, 2980, 2930, 2100, 1760, 1730, 1670, 1590, 1550, 1440, 1400, 1300, 1260, 1200, 1150, 1060, 1030, 940, 730, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.475 (s, 3H), 2.531 (s, 3H), 3.427 (s, 1H); UV (CH_3CN) λ_{max} 388 nm (ϵ 7550), 255 sh (7200), 240 (10 600); fluorescence (CH_3CN) λ_{max} 437 nm, 470, 485 sh (ϕ_F 0.82); mass spectrum *m/z* 222 (100%), 224 (30%) (M^+).

***syn*-(Methyl,hydro)(methyl,ethynyl)bimane, *syn*-(CH_3,H)(CH_3,C≡CH)B (35).** *syn*-(CH_3,H)(CH_3,C≡CSi(CH_3)$_3$)B (**28**) was converted to *syn*-(CH_3,H)(CH_3,C≡CH)B (**35**) by procedure A (25% yield) or B or C (62% yield). ***syn*-(CH_3,H)(CH_3,C≡CH)B (35):** yellow crystals (CH_3CN), mp 210 °C; IR (KBr) 3240, 3060, 2100, 1740, 1680, 770, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H), 2.50 (s, 3H), 3.39 (s, 1H), 5.57 (s, 1H); UV (CH_3CN) λ_{max} 375 nm (ϵ 5500), 220 (8400); fluorescence (CH_3CN) λ_{max} 428 nm, 465 sh (ϕ_F 0.84); mass spectrum *m/z* 188 (M^+).

Bis(tributylstannyl)acetylene,[4] $Bu_3SnC{\equiv}C\text{-}SnBu_3$ (39). Tributyltin chloride (50 g, 15 mmol) was added to a suspension of lithium acetylide:ethylene diamine complex (2.1 g, 7.0 mmol) in dry THF (30 mL). The reaction mixture was refluxed for 24 h. Water (50 mL) was added, the solvent was evaporated, diethyl ether (15 mL) was added, and the solids were filtered off through Celite. The filtrate was evaporated and the residue distilled to afford bis(tributylstannyl)acetylene (**39**) (3.4 g, 80% yield): bp 160 °C (0.3 mm); ^1H NMR (CCl_4) 0.88 (t, J = 7.2 Hz, 6H), 0.99 (t, J = 7.8 Hz, 4H), 1.32 (m, 4H), 1.50 (m, 4H).

Palladium-Catalyzed Reaction of α-Iodo-*β*-methylbimanes with Bis(tributylstannyl)acetylene. Tetrakis(triphenylphosphine)palladium(0) (1.0 mg) and then bis(tributylstannyl)acetylene (**39**) (0.05 mmol) were added to a solution of *syn*-(CH_3,X)(CH_3,I)B (X = Cl or H) (0.1 mmol) in dry THF under nitrogen, the mixture was refluxed for 20 h, the solvent was evaporated, and the residue was flash chromatographed on silica gel [eluant, CH_3CN].

***syn,syn*-[(CH_3,Cl)(CH_3,C≡C−)B(CH_3,Cl)(CH_3,−)B] (40).** According to the general procedure, *syn*-(CH_3,Cl)(CH_3,I)B (**15**) (32.0 mg, 0.1 mmol), bis(tributylstannyl)acetylene (**39**) (30 mg, 0.05 mmol), and catalyst in THF (30 mL) were reacted to yield *syn,syn*-[(CH_3,Cl)(CH_3,C≡C−)B(CH_3,Cl)(CH_3,−)B] (**40**) (11 mg, 5.2% yield).

***syn,syn*-[(CH_3,Cl)(CH_3,C≡C−)(CH_3,Cl)(CH_3,−)B] (40):** orange powder, mp >310 °C; IR (KBr) 2920, 1760, 1680, 1610, 1580, 980, 740, 725 cm^{-1}; ^1H NMR (CD_3CN) 2.49 (s, 6H), 2.56 (s, 6H); UV (CH_3CN) λ_{max} 410 nm (ϵ 13 100), 260 (22 100); fluorescence (CH_3CN) λ_{max} 500 nm, (ϕ_F 0.20); fluorescence (solid) λ_{max} 565 nm.

***syn,syn*-[(CH_3,H)(CH_3,C≡C−)B(CH_3,H)(CH_3,−)B] (52).** According to the general procedure, *syn*-(CH_3,H)(CH_3,C≡C−)B (**30**) (29.0 mg, 0.1 mmol), bis(tributylstannyl)acetylene (**39**) (30 mg, 0.05 mmol), and catalyst in THF (50 mL) were reacted to yield *syn,syn*-[(CH_3,H)(C≡C−)B(CH_3,H)(CH_3,−)B] (**52**) (8.7 mg, 50% yield) marked by its distinctive orange fluorescence.

***syn,syn*-[(CH_3,H)(CH_3,C≡C−)B(CH_3,H)(CH_3,−)B] (52):** yellow crystals (CH_3CN), mp >310 °C; IR (KBr) 3080, 1740, 1670, 1570, 940, 780, 740 cm^{-1}; ^1H NMR (CD_3CN) 2.44 (s, 6H), 2.53 (s, 6H), 5.61 (s, 2H); UV (CH_3CN) λ_{max} 405 nm (ϵ 19 090), 240 (23 600); fluorescence (CH_3CN) λ_{max} 491 nm (ϕ_F 0.90); fluorescence (solid state) λ_{max} 555 nm; fluorescence excitation (solid state) λ_{max} 400 nm, 460.

Oxidative Coupling of 3-Ethynylbimanes. Method A. Cuprous chloride−*N*,*N*,*N*′,*N*′-tetramethylethylenediamine complex was added to *syn*-(CH_3,X)(CH_3,C≡CH)B (0.1 mmol) dissolved in acetone (2 mL). A slow stream of oxygen was passed in over 2 h. The acetone was evaporated and the residue flash chromatographed on silica gel [eluant, CH_3CN].

Method B. Diisopropylethylamine (27 mg, 0.2 mmol), tetrakis(triphenylphosphine)palladium(0) (5.0 mg), and cuprous iodide (5.0 mg) were mixed with dry toluene (30 mL) under nitrogen. Chloroacetone (9.3 mg, 0.1 mmol) and *syn*-(CH_3,X)(CH_3,C≡CH)B (0.1 mmol) were then added successively, the mixture was stirred for 20 h, the solvent was evaporated, and the residue was flash chromatographed on silica gel [eluant, CH_3CN].

Method C. Tributyltin chloride (33 mg, 0.1 mmol) and diisopropylethylamine (13.0 mg, 0.1 mmol) were mixed with a solution of *syn*-(CH_3,X)(CH_3,C≡CH)B (0.1 mmol) in CH_3CN (30 mL). Bis(triphenylphosphine)palladium(II) chloride (5.0 mg) and cuprous iodide (5.0 mg) were added, the mixture was refluxed for 15 h under nitrogen, the solvent was evaporated, and the residue was flash chromatographed on silica gel [eluant, CH_3CN].

***syn,syn*-[(CH_3,Cl)(CH_3,C≡C−)B]$_2$ (45).** According to the general procedures, *syn*-(CH_3,Cl)(CH_3,C≡CH)B (**27**) (22.0 mg, 0.1 mmol) afforded 1.6 mg (method A, 8.0% yield) or 6.2 mg (method B, 30% yield) or 8.7 mg (method C, 40% yield) of *syn,syn*-[(CH_3,Cl)(CH_3,C≡C−)B]$_2$ (**45**).

***syn,syn*-[(CH_3,Cl)(CH_3,C≡C−)B]$_2$ (45):** red powder (CH_3CN); mp >320 °C; IR (KBr) 2910, 2140, 1750, 1680, 1590, 1540, 940, 740, 730, 650 cm^{-1}; ^1H NMR (CD_3CN) 2.485 (s, 6H), 2.569 (s, 6H); UV (CH_3CN) λ_{max} 425 nm (ϵ 27 200), 305 (6600), 285 sh (22 200), 272 sh (27 100), 257 (36 600); fluorescence (CH_3CN) λ_{max} 500 nm (ϕ_F 0.77); fluorescence (solid state) λ_{max} 550 nm, 565; fluorescence excitation (solid state) 390 nm, 480.

***syn,syn*-[(CH_3,H)(CH_3,C≡C−)B]$_2$ (46).** According to the general procedures, *syn*-(CH_3,H)(CH_3,C≡CH)B (**28**) (18.0 mg, 0.1 mmol) afforded 2.0 mg (method A, 10% yield) or 5.0 mg (method B, 25% yield) or 7.6 mg (method C, 40% yield) of *syn,syn*-[(CH_3,H)(CH_3,C≡C−)B]$_2$ (**46**).

***syn,syn*-[(CH_3,H)(CH_3,C≡C−)B]$_2$ (46):** orange solid (CH_3CN); mp >320 °C; IR (KBr) 3080, 2960, 2920, 1740, 1720, 1680, 1570, 720, 690 cm^{-1}; ^1H NMR (CD_3CN) 2.48 (s, 6H), 2.57 (s, 6H), 5.61 (s, 2H); UV (CH_3CN) λ_{max} 415 nm (ϵ 15 000), 280 sh (12 300), 268 (14 900), 250 (17 500); fluorescence (CH_3CN) λ_{max} 485 nm, 500 (ϕ_F 0.35); fluorescence (solid state) λ_{max} 550 nm.

***syn*-(Hydro,hydro)bimane, *syn*-(H,H)B (9).** Potassium carbonate (0.8 g, 5.8 mmol), AcOH (50 mL), and Ac_2O (2.5 mL) were heated until evolution of CO_2 had ceased. *syn*-(Hydro,chloro)B (**3**) (0.55 g, 2.7 mmol) was added to the KOAc solution, followed by 10% Pd/C (5 mg). Hydrogen was bubbled into the reaction mixture at 70−80 °C. After 3 h, TLC showed that all of the *syn*-(H,Cl)B (**3**) had reacted and that very little *syn*-(H,H)(H,Cl)B (**12**) remained. The reaction mixture was filtered hot, the AcOH removed under reduced pressure, and the residue flash chromatographed on silica gel [eluant, EtOAc−CH_3CN (1:2)]. Deep violet fluorescent fractions contained 170 mg of *syn*-(H,H)B (**9**) (55% yield): white crystals (CH_3CN), mp 302 °C; IR (KBr) 3180, 3100, 1750, 1735, 1670, 980 cm^{-1}; ^1H NMR ($CDCl_3$) 5.79 (d, J = 4 Hz, 1H), 7.51 (d, J = 4 Hz, 1H); UV (CH_3CN) λ_{max} 385 nm (ϵ 5000 sh), 368 (6200), 240 sh (3300), 218 (7600); fluorescence (CH_3CN) 398 nm, 415 sh (ϕ_F 1.0); mass spectrum *m/z* 136 (M^+).

***syn*-(Hydro,iodo)bimane, *syn*-(H,I)B (10).** A solution of ICl (500 mg, 3.3 mmol) in CH_2Cl_2 (10 mL) was added to a solution of *syn*-(H,H)B (**9**) (170 mg, 1.25 mmol) in CH_2Cl_2 (300 mL), and the mixture was stirred for 0.5 h. After removal of most of the CH_2Cl_2, 380 mg of *syn*-(H,I)B (**10**) was filtered off (80% yield): yellow crystals (CH_3CN), mp 270 °C; IR (KBr) 3120, 3090, 3060, 1740, 1630, 1510, 1470, 1400, 1250, 1190, 1090, 920, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.647 (s); UV (CH_3CN) λ_{max} 385 nm (ϵ 8300), 260 sh (8000), 228 (14 800); fluorescence (CH_3CN) λ_{max} 445 nm, 457 (ϕ_F 0.45); fluorescence (solid state) λ_{max} 470 nm, 535, 556, mass spectrum *m/z* 388 (M^+).

Glossary. The large number of fairly similar structures in the paper suggests that a compact list of all structures using short-form bimane formulas would make it easier to follow the text. (**1**) *syn*-(R_2,R_1)B, (**2**) *anti*-(R_2,R_1)B, (**3**) *syn*-(H,Cl)B, (**4**) *syn*-(H,HC≡C)B, (**5**) *syn*-(CH_3,Cl)B, (**6**) *syn*-(CH_3,H)B, (**7**) *syn*-(CH_3,Br)B, (**8**) *syn*-(CH_3,I)B, (**9**) *syn*-(H,H)B, (**10**) *syn*-(H,I), (**11**) *syn*-(H,I)(H,H)B, (**12**) *syn*-(H,Cl)(H,H)B, (**13**) *syn*-(H,Cl)(H,I)B, (**14**) *syn*-(CH_3,Cl)(CH_3,H)B, (**15**) *syn*-(CH_3,Cl)(CH_3,I)B, (**16**) *syn*-(CH_3,H)(CH_3,I)B, (**17**) *syn*-(CH_3,HC=CHCO$_2$CH$_2$CH$_3$)B, (**18**) *syn*-(CH_3,I)(CH_3,HC=CHCO$_2$CH$_2$CH$_3$)B, (**19**) *syn*-(CH_3,Cl)(CH_3,HC=CHCO$_2$CH$_2$CH$_3$)B, (**20**) *syn*-(CH_3,C≡CC_6H_5)B, (**21**)

syn-(CH_3,H)(CH_3,C≡CC_6H_5)B, (**22**) *syn*-(CH_3,Cl)(CH_3,C≡C-C_6H_5)B, (**23**) *syn*-(H,C≡CC_6H_5)B, (**24**) *syn*-(H,H)(H,C≡CC_6H_5)B, (**25**) *syn*-(CH_3,$(CH_3)_3$SiC≡C)B, (**26**) *syn*-(CH_3,I)(CH_3,$(CH_3)_3$-SiC≡C)B, (**27**) *syn*-(CH_3,Cl)(CH_3,$(CH_3)_3$SiC≡C)B, (**28**) *syn*-(CH_3,H)(CH_3,$(CH_3)_3$SiC≡C)B, (**29**) *syn*-(H,C≡C-Si$(CH_3)_3$)B, (**30**) *syn*-(H,I)(H,C≡CSi$(CH_3)_3$)B, (**31**) *syn*-(H,H)(H,C≡CSi$(CH_3)_3$B, (**32**) *syn*-(CH_3,C≡CH)B, (**33**) *syn*-(CH_3,C≡CH)(CH_3,I)B, (**34**) *syn*-(CH_3,C≡CH)(CH_3,Cl)B, (**35**) *syn*-(CH_3,C≡CH)(CH_3,H)B, (**36**) *syn*-(H,C≡CH)(H,C≡CSi$(CH_3)_3$)B, (**37**) *syn*-(H,C≡CH)-(H,I)B, (**38**) *syn*-(H,C≡CH)(H,H)B, (**39**) $Bu_3SnC{\equiv}CSnBu_3$, (**40**)-*syn*,*syn*-(CH_3,Cl)(CH_3,C≡C−)B(CH_3,Cl)(CH_3,−)B], (**41**) *syn*,*syn*-(CH_3,H)(CH_3,C≡C−)B(CH_3,H)(CH_3,−)B], (**42**) *syn*-(CH_3,Cl)-(CH_3,C≡$CSnBu_3$)B, (**43**) *syn*-(CH_3,H)(CH_3,C≡$CSnBu_3$)B, (**44**) *syn*,*syn*-[(H,H)(H,C≡C−)B(H,H)(H,−)B], (**45**) *syn*,*syn*-[(CH_3,-Cl)(CH_3,C≡C−)B]$_2$, (**46**) *syn*,*syn*-[(CH_3,H)(CH_3,C≡C−)B]$_2$, (**47**) *syn*,*syn*-[(H,H)(H,C≡C−)B]$_2$, (**48**) *syn*-(CH_3,C≡CSi$(CH_3)_3$)(CH_3,-BrC═CBrSi$(CH_3)_3$)B, (**49**) *syn*-(CH_3,BrC═CBrSi$(CH_3)_3$)B, (**50**)-*syn*-(CH_3,CHBrCHBr$CO_2C_2H_5$)(CH_3,CH═$CHCO_2C_2H_5$)B, (**51**) *syn*-(CH_3,CHBrCHBr$CO_2C_2H_5$)B, (**52**) *syn*-(CH_3,C≡CSi$(CH_3)_3$)-(CH_3,IC═C(Cl)Si$(CH_3)_3$)B, (**53**) *syn*-(CH_3,IC═C(Cl)Si$(CH_3)_3$)B, (**54**) *syn*-(CH_3,C≡CH)(CH_3,C≡CSi$(CH_3)_3$)B, (**55**) *syn*-(CH_3,H)-(CH_3,CH═$CHCO_2C_2H_5$)B, (**56**) *syn*-(H,CH═$CHCO_2C_2H_5$)B.

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Supporting Information Available: ^{1}H NMR spectra of **15**, **16**, **19**−**22**, **25**, **27**, **30** and **34** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

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