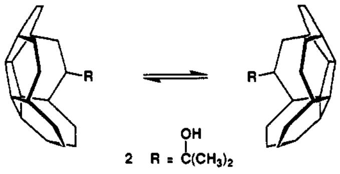
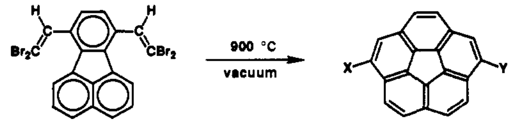
ponent, the corannulene ring system must invert more than 200 000 times per second at room temperature!


2 $R = C(OH)(CH_3)_2$

$\Delta G^\ddagger$ (-64 °C) = 10.2 kcal/mol

The inversion barrier for **2** stands remarkably close in energy to that for inversion of cyclohexane from one chair conformation to another ($\Delta G^\ddagger$ = 10.3 kcal/mol at −67 °C);[4] it lies lower in energy than the barrier for inversion of cyclooctatetraene from one tub conformation to another ($\Delta G^\ddagger$ = 14.7 kcal/mol at −2 °C),[5] but exceeds the barrier for pyramidal inversion of ammonia ($\Delta G^\ddagger$ = 6.0 kcal/mol)[6] by a significant amount. Corannulene shares with ammonia the structural requirement that each nonplanar trigonal atom must pass through a planar configuration (pure sp^2 hybridization) during the inversion process; however, the planarizations need not necessarily all occur contemporaneously during the bowl-to-bowl inversion of corannulene.[7] Calculations on the difference in energy between the bowl and the planar conformations of corannulene have ranged over the years from 0.8[8a] to 70.9 kcal/mol.[8b] The most recent ab initio calculations, however, peg it at 8.8 (STO-3G and 6-31G*),[9] 10.3 (3-21G),[9] and 11.0 kcal/mol (LDF).[10]

Painless access to substituted corannulenes was made possible by our fortuitous discovery that 7,10-bis(2,2-dibromovinyl)fluoranthene (**3**), which gives corannulene (**1**) upon flash vacuum pyrolysis at 1000 °C/10^{-4} Torr,[1] also gives bromocorannulene (**4**) and 1,6-dibromocorannulene (**5**) when the pyrolysis is conducted under only modest vacuum (mechanical pump) with a slow bleed of N_2 admitted through the head of the sample chamber as a carrier gas.[11] At this early stage in the project, the yields of **1**, **4**, and **5** still vary unpredictably from one pyrolysis to the next, but in one run at 900 °C, 50 mg of **3** gave 5.1 mg of **1** (23%), 10.3 mg of **4** (29%), and 1.2 mg of **5** (2.4%). These three compounds were separated and purified by preparative TLC (silica gel/cyclohexane) and characterized by 300-MHz ^{1}H NMR and high-resolution mass spectroscopy.[12]

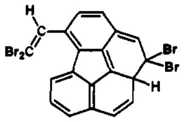


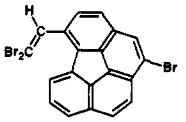
3

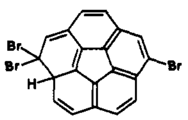
1: X = Y = H
4: X = H, Y = Br
5: X = Y = Br

We suspect that 1,6-dibromocorannulene (**5**) constitutes the primary product in this reaction and that **1** and **4** represent secondary products formed by pyrolytic loss of bromine atoms from **5**. Consistent with this hypothesis is our observation that other brominated aromatics, e.g., 1-bromonaphthalene, do indeed suffer reductive debromination to a major extent under the pyrolysis conditions employed here, although the origin of the hydrogen atom that replaces the bromine remains obscure.

The initial formation of **5** can reasonably be explained by electrocyclic ring closure of **3** to give the pentacyclic intermediate **6**, which should spontaneously aromatize to **7** by loss of HBr. Repetition of these steps on the other side of the molecule would lead via **8** to 1,6-dibromocorannulene (**5**). An alternative mechanism involving cyclization reactions of vinyl radicals, generated by homolysis of C–Br bonds, can also be envisaged; however, no direct evidence is presently available on the mechanisms of these transformations.


6


7


8

We are continuing to explore the potentially fascinating chemistry of corannulene and its derivatives, especially the π-complexing ability of these substances, both with metals and with organic partners, e.g., C_{60} and other corannulenes inter alia.

Acknowledgment. We thank the Department of Energy for financial support of this work and Lewis Cary for conducting the low-temperature NMR measurements. The open exchange of data, advice, and manuscripts with Jay Siegel has been especially valuable and enjoyable. Helpful discussions with Dieter Wege and John H. Nelson are also gratefully acknowledged.

Registry No. 1, 5821-51-2; **2**, 138816-08-7; **3**, 135584-70-2; **4**, 138816-09-8; **5**, 138816-10-1.

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(3) Repetition of the NMR experiment in a 1:1 mixture of acetone-d_6–CD_2Cl_2 gave the same value for $\Delta G^\ddagger$. The ±0.2 kcal/mol error range we attach to this number reflects our conservative estimates of the possible errors in determining the true coalescence temperature and the maximum peak separation at the low-temperature limit. This variable-temperature NMR experiment is closely patterned after the classic work of Anet et al.,[5] who likewise measured the coalescence temperature of NMR signals from diastereotopic methyl groups on a dimethylcarbinol side chain to determine the barrier for tub-to-tub inversion in the cyclooctatetraene ring system.

(4) Anet, F. A. L.; Ahmad, M.; Hall, L. D. *Proc. Chem. Soc.* **1964**, 145–146 and references cited therein.

(5) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576–3577.

(6) Dennison, D. M.; Uhlenbeck, G. E. *Phys. Rev.* **1932**, *41*, 313.

(7) Wynberg, H.; Nieuwpoort, W. C.; Jonkman, H. T. *Tetrahedron Lett.* **1973**, 4623–4628.

(8) (a) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 3817–3829. See also the earlier work of Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975–986. (b) Gleicher, G. J. *Tetrahedron* **1967**, *23*, 4257–4263.

(9) Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5675–5680. Schulman, J. M. Private communication.

(10) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.*, following paper in this issue.

(11) Flash vacuum pyrolyses were conducted in a commercially available Trahanovsky pyrolysis apparatus purchased from Kontes, Inc., Vineland, NJ 08360. The sample head was modified to allow a slow bleed of nitrogen gas to pass over the sample from a capillary inlet.

(12) Bromocorannulene (**4**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 1 H, H-2), 7.93 (d, 1 H, *J* = 8.6 Hz, H-10), 7.87 (d, 1 H, *J* = 8.6 Hz, H-9), 7.82–7.78 (m, 5 H, H-4,5,6,7,8), 7.71 (d, 1 H, *J* = 8.6 Hz, H-3); high-resolution mass spectrum calcd for $C_{20}H_9Br$ 327.9887, found 327.9873. 1,6-Dibromocorannulene (**5**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 2 H, H-2,5), 7.97 (d, 2 H, *J* = 8.7 Hz, H-7,10), 7.90 (d, 2 H, *J* = 8.7 Hz, H-8,9), 7.72 (s, 2 H, H-3,4); high-resolution mass spectrum calcd for $C_{20}H_8Br_2$ 405.8992, found 405.8982.

Synthesis and Dynamics of the Corannulene Nucleus

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Corannulene (**1**), first synthesized by Lawton and Barth,[2] has presented a formidable synthetic challenge to several groups in-

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(1) (a) University of California at San Diego. (b) San Diego Supercomputer Center.

(2) (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380. (b) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730.

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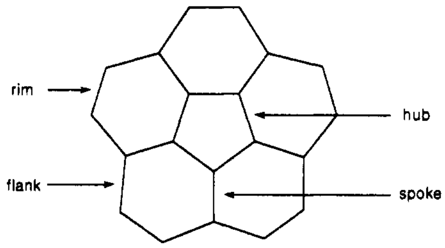
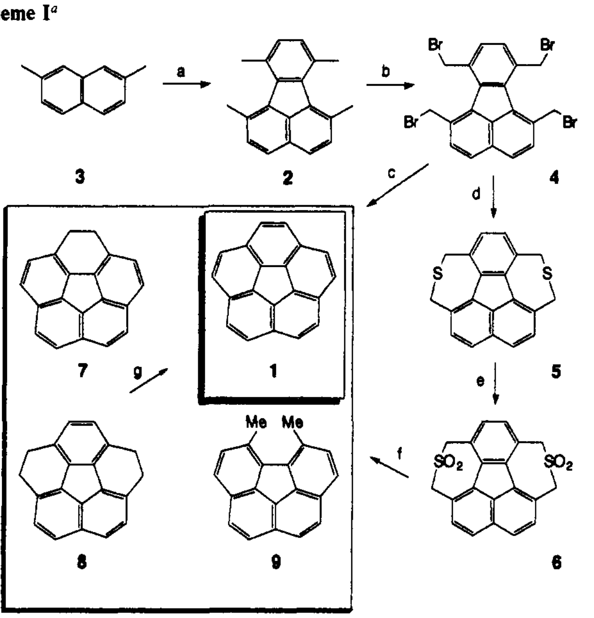
Table I. Inversion Barrier and Selected Geometries for **1**, **7**, **8**, and Coronene[a]



	1			7			8			coronene
	exp[c,d]	LDF	AM1	exp[d]	LDF	AM1	exp[d]	LDF	AM1	exp[c]
bowl depth[b]	0.89	0.91	0.94		0.88	0.91		0.86	0.88	0.00
sp^3 torsion					12	12		8	8	
C–C rim sp^3–sp^3					1.56	1.55		1.58	1.55	
C–C rim sp^2–sp^2	1.39	1.38	1.38		1.39	1.38		1.39	1.39	1.34
C–C flank sp^2–sp^3					1.50	1.49		1.51	1.49	
C–C flank sp^2–sp^2	1.44	1.44	1.44		1.43	1.44		1.42	1.43	1.41
C–C spoke	1.38	1.38	1.38		1.38	1.38		1.38	1.38	1.43
C–C hub	1.42	1.41	1.44		1.41	1.44		1.42	1.44	1.42
barrier to ring inversion	10.2	11.4	16.9	8.5	9.0	13.8	7	7.0	12.0	

[a] All distances are in angstroms, torsions in degrees, and energies in kilocalories/mole. [b] Distance from best plane of hub atoms to best plane of rim atoms. [c] X-ray. [d] Variable-temperature NMR spectroscopy.

Scheme I[a]



[a] (a) Reference 9. (b) NBS, CCl_4, *hν*, 24 h, 80%. (c) Flash vacuum pyrolysis, 1000 °C, 18%. (d) Na_2S, acetone, 75%. (e) H_2O_2, acetic acid, 70%. (f) 400 °C, 7%. (g) Pd/C, xylenes.

terested in strained aromatic hydrocarbons.[3] Its bowl shape resulting from the puckering of the annulus of five six-membered rings has stimulated comparisons between **1** and buckminsterfullerene.[4] Few investigations into the chemistry of **1** and derivatives have appeared.[5]

The C_{5v} symmetry of **1** offered many retrosynthetic dissections.[6] We chose a path that retained the bilateral symmetry of the precursors, descending through 1,6,7,10-tetramethylfluoranthene (**2**) to 2,7-dimethylnaphthalene (**3**).

Starting from **3**,[7] we modified a synthetic path to 3,8-dimethylacenaphthen-1-one[8] and then developed a route to **2**.[9] Bromination of **2** with NBS in carbon tetrachloride yields the tetrabromo compound, **4**. From **4**, many paths to the ring closures are possible. For example, direct flash vacuum thermolysis of **4** at 1000 °C produces **1** in ca. 18% yield.[10]

A more conventional approach to **1** proceeded through the displacement of the bromines by sodium sulfide in acetone to give the bis-sulfide **5**, which was oxidized to the sulfone **6** by treatment with peroxide in acetic acid. Extrusion of SO_2 by pyrolysis of **5** at 400 °C under static vacuum produced a mixture of **1**, its dihydro and tetrahydro derivatives **7** and **8**, and 5,6-dimethylbenzo[*ghi*]fluoranthene (**9**).[11] Heating the hydrocarbon mixture with palladium on carbon resulted in the formation of additional **1** (Scheme I). Column chromatography with cyclohexane on silica gel gave pure **1** plus fractions enriched in **7**, **8**, and **9**.[12]

The structures of **1**, **7**, and **8** were calculated by semi-empirical techniques using the AM1 Hamiltonian[13] and by ab initio local density functional theory (LDF).[14] Stationary points were found for both the flat and the bowl structure of each. Frequency analysis at the semi-empirical level showed that the bowl structure for each compound was a minimum (positive definite), and the flat structure was a transition state (one negative eigenvalue). The calculated $\Delta E_{(\text{flat-bowl})}$ values for **1**, **7**, and **8** were 16.8, 13.8, and 12.0 kcal/mol (AM1) and 11.4, 9.0, and 7.0 kcal/mol (LDF), respectively.[15]

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(3) (a) Craig, J. T.; Robins, M. D. W. *Aust. J. Chem.* **1968**, *21*, 2237. (b) Davy, J. R.; Iskander, M. N.; Reiss, J. A. *Aust. J. Chem.* **1979**, *32*, 1067. (c) Chapman, O. Personal communication.

(4) (a) Curl, R. F.; Smalley, R. *Sci. Am.* **1991**, *265*, 54. (b) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213. (c) Haymet, A. D. J. *J. Am. Chem. Soc.* **1986**, *108*, 319.

(5) One important study, however, was the electrochemistry of **1**: Janata, J.; Gendell, J.; Ling, C.-H.; Barth, W. E.; Backes, L.; Mark, H. B., Jr.; Lawton, R. G. *J. Am. Chem. Soc.* **1967**, *87*, 3056.

(6) Recently, **1** has been prepared elegantly by flash vacuum pyrolysis of 7,10-diethynylfluoranthene: Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082.

(7) Wolinska-Mocydlarz, J.; Canonne, P.; Leitch, L. C. *Synthesis* **1974**, 566.

(8) Buu-Hoi; Cagniant, P. *Rev. Sci.* **1942**, *80*, 130.

(9) Borchardt, A.; Hardcastle, K.; Siegel, J. S. Submitted for publication.

(10) FVP of 60 mg of **4** gave ca. 5 mg of **1**. The flash vacuum pyrolysis was done by Pei-Chao Cheng using Professor L. T. Scott's apparatus. A great many thanks are in order.

(11) Chromatographic analysis of the hydrocarbon products over a series of pyrolyses showed that the mixture of **1**, **7**, **8**, and **9** was formed with a product ratio of 5:5:1:5. A total of 650 mg of **6** was pyrolyzed to give ca. 25 mg of hydrocarbon mixture.

(12) All isolated compounds were fully characterized. Details are provided in the supplementary material.

(13) AM1/MOPAC: (a) Stewart, J. J. P. *QCPE* **1985**, *5*, 126, 133. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(14) For further information on LDF theory, see: (A) DMOL: BIOSYM Technologies, Inc., 10065 Barnes Canyon Rd., Suite A, San Diego, CA 92121. (b) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B 864. (c) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133. (d) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symposium Series 353; American Chemical Society: Washington, DC, 1987; Chapter 4. (e) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

The calculated geometries of **1** agree well with the X-ray structure (Table I).[19] The relative bowl depths from LDF (C hub plane to C rim plane) for **1**, **7**, and **8** are 0.91 (0.89 Å X-ray), 0.88, and 0.86 Å, respectively. LDF predicts the eclipsed conformation about the C_{sp^3}–C_{sp^3} bonds in **7** and **8** with average H–C–C–H torsion angles of ca. 12° and 8°. Unlike coronene, which shows distinct bond shortening solely in the rim bonds,[20] **1** shows bond alternation within each ring; the spoke and rim bonds are shorter than the hub and flank bonds.

In the ground-state bowl conformation of **7** and **8**, the geminal hydrogens are diastereotopic with an exo/endo relationship; bowl inversion renders these sites equivalent. Thus, variable-temperature NMR studies on mixtures enriched in **7** and **8** allow us to probe the bowl inversion process and assign approximate free energies of activation to the inversion in **7** (8.5 ± 0.5 kcal/mol) and **8** (6–7 kcal/mol).[21,22] This demonstrates the flexible nature of these bowls, a property one can relate to the analogous carbon fragments leading up to buckminsterfullerene.[4]

Acknowledgment. We thank the National Science Foundation Presidential Young Investigator Award Program (CHE-8857812) and the American Cancer Society Junior Faculty Fellowship Program (C-58024) for support of this work. We greatly appreciate additional support of our program from the Exxon Educational Fund, Hoffman-La Roche, Rohm+Haas, Monsanto, Eli Lilly, Zambon (Italia), and Sterling Drug. We thank the San Diego Supercomputer Center for a grant of computer time. We thank Professor Larry T. Scott for many scholarly exchanges and helpful discussions which made the friendly co-pursuit of this chemistry possible.

Supplementary Material Available: Listings of spectral data for compounds **2–15** (6 pages). Ordering information is given on any current masthead page.

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(15) Calculations on the barrier to inversion in **1** have been reported using empirical force field,[16] SCF-MO,[17] and ab initio[18] methods.

(16) Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975.

(17) Gleicher, G. J. *Tetrahedron* **1967**, *23*, 4257.

(18) Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5675.

(19) Hanson, J. C.; Nordman, C. E. *Acta Crystallogr.* **1976**, *B32*, 1147.

(20) Fawcett, J. K.; Trotter, J. *Proc. R. Soc.* **1966**, *A289*, 366.

(21) (a) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 97. (b) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(22) The barrier to inversion for a derivative of corannulene has been measured to be 10.2 ± 0.2 kcal/mol. See: Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

Palladium-Catalyzed Alkylative Cyclization of 1,6- and 1,7-Enynes

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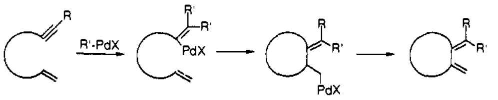
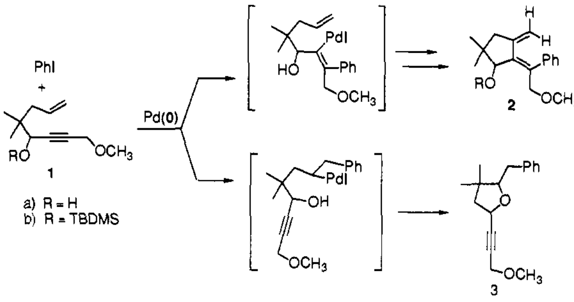
1,2-Bis(alkylidene)cycloalkanes are valuable building blocks for further structural elaboration as well as interesting substances in their own right. The discovery that Pd(0) in the presence of acetic acid catalyzes the cycloisomerization outlined in eq 1 (R′ = H)[1] with generation of the *E* dienes suggested the feasibility of an alkylative cycloaddition which would provide an unprecedented entry to substituted bis(alkylidene)cycloalkanes possessing the R′ stereospecifically *Z* as depicted in **1**, a stereochemical outcome that is of great interest for further cyclization if R′ is an unsaturated group or for itself as in the case of vitamin D.[2] A key unanswered question for the success of an alkylative cyclization concerns the chemoselectivity of carbapalladation of an olefin versus an acetylene.[3-5]



(1)

The reaction of iodobenzene with enyne **1** was chosen to test the feasibility of the process. Enyne **1a** followed by iodobenzene is added to a suspension consisting of 2 mol % $Pd(OAc)_2$, 4 mol % Ph_3P (TPP), and 1 equiv of silver carbonate (method A). Heating eventually to 75 °C led to the desired alkylated cycloadduct **2a**.[7] The stereochemistry is assigned as depicted on the basis of a positive NOE between one of the vinyl protons and the aromatic ring protons. Decomposition accompanying isolation of **2a** led to preparative cyclization of the silyl ether **1b** to give diene **2b**[7] in 60% yield after purification. Switching the catalyst to 2 mol % $(dba)_3Pd_2{\cdot}CHCl_3$ and 4 mol % tri-*o*-tolylphosphine (TOT) (method B) gives the furan **3** as a major product in addition to the diene **2a**.[6] The two products appear to derive from the selectivity of the initial carbapalladation as illustrated in eq 2.



(2)

The use of vinyl bromides proves most interesting. Reacting enyne **1b** with β-bromostyrene using method A but replacing silver carbonate with triethylamine leads to the bicyclic product **5**[7] as a single diastereomer, as determined by both chromatographic and spectroscopic analysis (eq 3), apparently as a result of electrocyclic cyclization of the initial hexatriene **4**. The unusual

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(1) Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636. Trost, B. M. *Janssen Chim. Acta* **1991**, *9*, 3. Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34.

(2) For two excellent recent leading references, see: Posner, G. H.; Nelson, T. D. *J. Org. Chem.* **1991**, *113*, 6958. For some reviews, see: Georghiou, P. E. *Chem. Soc. Rev.* **1977**, *6*, 83. Lythgoe, B. *Chem. Soc. Rev.* **1990**, *9*, 449. Kametani, T.; Furayama, H. *Med. Res. Rev.* **1987**, *7*, 147.

(3) For a review of the Heck reaction, see: Heck, R. F. *Org. React.* (*N.Y.*) **1982**, *27*, 345. For examples of polycyclizations, see: Zhang, Y.; Wu, G.; Agnel, G. Negishi, E. *J. Am. Chem. Soc.* **1990**, *112*, 8590. Grigg, R.; Dorrity, M. J.; Malone, J. F.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1990**, *31*, 1343. Kucera, D. J.; Overman, L. E. *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1990; ORGN 128. Carpenter, N. E.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5864. Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328. Zhang, Y.; Negishi, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 3454.

(4) For some examples of Heck reactions involving acetylenes, see: Fournet, G.; Balme, G.; Van Hemelryck, B.; Gore, J. *Tetrahedron Lett.* **1990**, *31*, 5147. Negishi, E.; Noda, Y.; Lamaty, F.; Vawter, E. J. *Tetrahedron Lett.* **1990**, *31*, 4393. Grigg, R.; Dorrity, M. J.; Malone, J. F.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1990**, *31*. 1343. Lee, G. C. M.; Tobias, B.; Holmes, J. M.; Harcourt, D. A.; Garst, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9330. Silverberg, L. J.; Heck, R. F. *J. Organomet. Chem.* **1991**, *409*, 411.

(5) Cf.: Trost, B. M.; Burgess, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1084. Grigg, R.; Sukirthalingam, S.; Sridharan, V. *Tetrahedron Lett.* **1991**, *32*, 2545.

(6) Cf.: Fournet, G.; Balme, G.; Gore, J. *Tetrahedron* **1990**, *46*, 7763.

(7) New compounds have been characterized spectrally and their elemental compositions established by combustion analysis and/or high-resolution mass spectrometry. All yields are for isolated pure product unless otherwise indicated.

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