photolysis.[12] Combination of these results with the literature values for the heats of formation of t-BuOH,[13] t-BuOOBu-t,[14] and H$^\bullet$[13] led to the bond dissociation energies in the silanes (eq 1 and 7).

$$\mathrm{BDE}(\mathrm{R_3Si{-}H}) = \Delta H_\mathrm{R}/2 + 86.1\ \mathrm{kcal\ mol^{-1}} \qquad (7)$$

To prove that the system correctly conformed to the kinetic constraints described above, we demonstrated the ΔH_obsd was independent of the laser light intensity which was attenuated by the use of neutral density filters. In addition, we obtained data in a range where ΔH_obsd was independent of the silane concentration.

In this study, small corrections had to be applied because attack at the Si–H bonds of the silanes by *tert*-butoxyl was the dominant but not unique mode of reaction. In fact, there was generally a small amount of attack at the methyl or methylene groups of the silanes, eq 8. The corrections were calculated by using the ratio

$$t\text{-BuO}^\bullet + \mathrm{R_3SiH} \rightarrow t\text{-BuOH} + \mathrm{R(-H)R_2SiH} \qquad (8)$$

of rate constants k_4/k_8 and the appropriate C–H bond strengths.[15,16] In all cases the corrections were small, $\leq$1 kcal mol^{-1}, so that any imprecision in these data was of little consequence. The results are summarized in Table I. The relative errors of ±1 kcal mol^{-1} on the bond dissociation energies reflect random errors in the photoacoustic experiment. The absolute error of ±2 kcal mol^{-1} takes into account experimental errors in the heats of formation of *tert*-butyl alcohol[13] and di-*tert*-butyl peroxide[14] that were used in the calculations, eq 6 and 7. The value obtained for BDE($\mathrm{Et_3Si{-}H}$) of 90.1 kcal mol^{-1} was in excellent agreement with that of 90.3 kcal mol^{-1} reported for trimethylsilane and lends weight to the accuracy of the photoacoustic approach.

The silicon–hydrogen bond in tris(trimethylsilyl)silane is so weak that the compound serves as an excellent free radical reducing agent that rivals tributyltin hydride (BDE(Sn–H) = 74 ± 2 kcal mol^{-1})[9] in its efficiency, eq 9 and 10. For example, alkyl bromides can be reduced quantitatively by the use of this reagent in monoglyme as solvent.[17]

$$\mathrm{(Me_3Si)_3Si{-}H} + \mathrm{R}^\bullet \rightarrow \mathrm{(Me_3Si)_3Si}^\bullet + \mathrm{RH} \qquad (9)$$

$$\mathrm{(Me_3Si)_3Si}^\bullet + \mathrm{R{-}X} \rightarrow \mathrm{(Me_3Si)Si{-}X} + \mathrm{R}^\bullet \qquad (10)$$

Taken as a whole, the results demonstrate that silicon–hydrogen bonds can be dramatically weakened by successive substitution of silyl groups at the Si–H function, although the origin of the effect is unclear. It is possible that steric compression in $\mathrm{(Me_3Si)_3SiH}$ is relieved on radical formation thus making the Si–H bond quite weak.[17] In addition, the radical may be stabilized by interactions between the unpaired electron and the silicon d-orbitals.[19] However, simple electronic effects do not account for the phenomenon since Si–H bond dissociation energies do not correlate with the group electronegativities of the ligands.

Registry No. $\mathrm{Et_3SiH}$, 617-86-7; $\mathrm{Me_3Si(Me)_2SiH}$, 812-15-7; $\mathrm{(Me_3Si)_3SiH}$, 1873-77-4.

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[12] Φ = 0.89 in isooctane at 25 °C. Burkey, T. J.; Monaghan, R.; Griller, D., unpublished results. See also: Kiefer, H.; Traylor, T. G. *J. Am. Chem. Soc.* **1967**, *89*, 6667.

[13] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970.

[14] Batt, L.; Christie, K.; Milne, R. T.; Summers, A. J. *Int. J. Chem. Kinet.* **1974**, *6*, 877.

[15] Estimated by using BDE($\mathrm{Me_4Si}$) = 99 kcal mol^{-1}.[8] A correction of −3 kcal mol^{-1} was allowed for the bond-weakening effect due to a β-silyl group,[16] and one of −4 kcal mol^{-1} was used to account for the change from methyl to methylene.[2]

[16] Auner, N.; Walsh, R.; Westrup, J. *Chem. Commun.* **1986**, 207.

[17] Chatgilialoglu, C.; Griller, D.; Lesage, M., patent application in progress.

[18] Reference deleted in press.

[19] For a related example, see: Bassindale, A. R.; Bowles, A. J.; Cook, M. A.; Eaborn, C.; Hudson, A.; Jackson, R. A.; Jukes, A. E. *Chem. Commun.* **1970**, 559.

[20] Chatgilialoglu, C., unpublished results.

[21] Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* **1982**, *1*, 466.

[22] Average value for $\mathrm{Et_4Si}$ weighted by a factor of $^3/_4$. Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208. See also ref 18.

[23] Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Org. Chem.* **1986**, *51*, 2457.

[24] Value for $\mathrm{Me_3SiSiMe_3}$, (1.7 ± 0.5) × 10^6 M^{-1} s^{-1},[17] weighted by a factor of $^5/_6$.

[25] Value for $\mathrm{(Me_3Si)_4Si}$, (7.8 ± 2.7) × 10^6 M^{-1} s^{-1},[17] weighted by a factor of $^3/_4$.

A Novel Nickel–Chromium Catalyst System for Cyclization via Intramolecular Carbametalation

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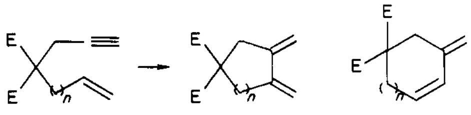
Received March 25, 1987

Intramolecular carbametalations promise to be an exciting approach for ring construction under very mild conditions.[1] In seeking catalytic rather than stoichiometric metal reactions, we have been exploring the palladium(2+)-catalyzed cyclization of enynes.[2] To expand the utility of this palladium-based methodology, we sought alternative catalysts. In this communication, we report the development of a nickel–chromium system[3] which requires attachment to a polymer for adequate catalytic activity.[4]

The enyne **1** was taken as a test substrate. Treatment with a variety of Ni(2+) salts led only to recovered starting material in stark contrast to the Pd system. With the notion that a catalytic system based upon a Ni(1+) – Ni(3+) cycle might be more active,[5] we treated $\mathrm{(Ph_3P)_2NiCl_2}$ (**2**) with 1 equiv of sodium naphthalenide in THF and then added enyne **1**. After 15 min at room temperature, a 2.5:1 mixture of five- and six-membered ring products, **3** and **4**, respectively, was formed in 38% yield in a stoichiometric nickel reaction. Replacing sodium naphthalenide with chromous chloride, also a one-electron reducing agent, and keeping everything else the same gave similar results.



1, n = 1 **3**, n = 1 **4**, n = 1
5, n = 2 **6**, n = 2 **7**, n = 2

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[1] For stoichiometric intramolecular carbametalations of enynes, see: Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. For intramolecular carbalkylation–carbonylation using stoichiometric cobalt complexes, see: Billington, D. C.; Pauson, P. L. *Organometallics* **1982**, *1*, 1560. Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851.

[2] Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. Trost, B. M.; Lautens, M. *Tetrahedron Lett.* **1985**, *26*, 4887.

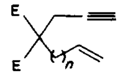
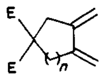
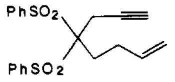
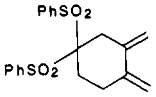
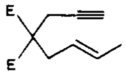
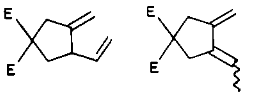
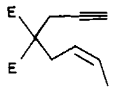
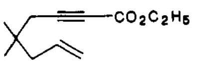
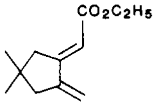
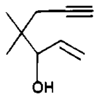
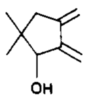
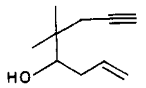
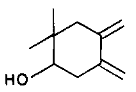
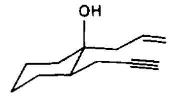
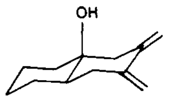
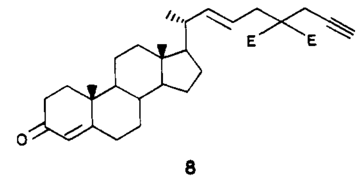
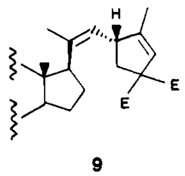
[3] Chromous salts activated by nickel have been reported to effect Barbier type reactions. See: Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 6048. Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1986**, *108*, 5644.

[4] For reviews, see: Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1977**, *15*, 189. *Polymer-Supported Reactions in Organic Synthesis*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980. Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109. Pittman, C. V., Jr. *Compr. Organomet. Chem.* **1982**, *8*, 553–611. For a few cases of "site isolation" see: Haag, W. O.; Whitehurst, D. D. In *Catalysis*; Hightower, J. W., Ed.; 1973; Vol. 1, p 465. Grubbs, R. H.; Lau, C. P.; Cukier, R.; Brubaker, C., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4517. Pittman, C. V., Jr.; Ng, Q. *J. Organomet. Chem.* **1978**, *153*, 85.

[5] Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547. Tsou, T. T.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 1930.

0002-7863/87/1509-5268$01.50/0

Table I. Enyne Cyclizations Catalyzed by Polymer Supported Nickel[a]

entry	substrate[b]	time (h)	product	yield GC	yield isolated
1[c]	 $n = 1$	18	 $n = 1$		82
2	$n = 2$	2.5	$n = 2$	70	60
3		4.5			80
4		6.5	 3:1[d]		75
5		6	13:1[e]		74
6		3			79
7		4		90	53
8		3		80	59
9		3			47
10	 **8**	18	 **9**		77

[a] All reactions were performed under the standard conditions reported in the text unless otherwise noted. [b] E = CO_2CH_3. [c] This reaction was performed in THF alone. [d] The GC shows only one peak for the diene. The NMR spectrum shows predominantly one isomer but a small doublet at δ 1.6 may correspond to a minor amount of the geometrical isomer. [e] The GC shows only one peak. Too little of the minor product is present to allow an accurate determination of its homogeneity by NMR spectroscopy.

Because of the great difference in efficiency between five- and six-membered ring formation in the Pd-catalyzed reaction, we simultaneously examined the cyclization of enyne **5**. In contrast to the experience with Pd in five-membered ring formation compared to six, the nickel–chromium system gave even better results with formation of only the 1,2-dimethylenecyclohexane **6**[6] in 58% yield. The efficacy of this process depended on the nature of the reducing agent. Sodium naphthalenide, DIBAL-H, samarium iodide, and even chromous acetate proved inferior to chromous chloride. Addition of excess triphenylphosphine to the Ni–Cr system allowed the cyclization of **5** to become catalytic whereby 10 mol% of the nickel complex **1** and 20 mol% of triphenylphosphine gave a 55% yield of **6**. In this catalytic system, nickel acetate or nickel acetylacetonoate could substitute for nickel chloride, but chromous chloride is superior to chromous acetate. In addition to THF, acetonitrile and even ethanol are quite suitable solvents. However, a limitation arose with more highly substituted systems wherein the sluggishness of the cyclization led to premature cessation of catalytic activity.

Providing site isolation of the unstable nickel species by coordinating it to a polymer[4] could resolve this problem. A catalyst prepared by effecting ligand exchange between complex **2** and a phosphinylated 2% cross-linked polystyrene[7] (0.78 mequiv Ni/g polymer) effected cyclization of enyne **1** in THF at room temperature catalytically to give an 82% yield of only the 1,2-dimethylenecyclopentane **3**. Thus, the polymeric catalyst not only increased the yield of the cyclization from 38% to 82% but also increased the regioselectivity from a ~3:1 ratio of **3**:**4** to >99:1 ratio (determined by capillary GC analysis). The best conditions for cyclization proved to be use of 10 mol% of the polymeric catalyst and 30 mol% of chromous chloride in 4:1 THF–ethanol at room temperature. After completion of reaction, the beads were removed by filtration and washed thoroughly with ether. The combined organic fractions were evaporated in vacuo, and the product was purified chromatographically.

By using these standard conditions, the cyclizations summarized in Table I were performed. Several features are noteworthy. Five- and six-membered rings form with equal facility. High chemo-

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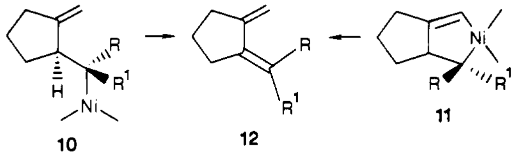
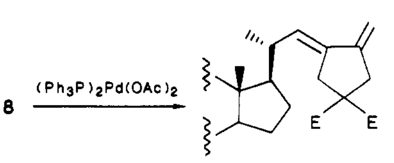
[6] All new compounds have been fully characterized spectroscopically, and elemental composition has been established by high resolution mass spectroscopy and/or combustion analysis.

[7] For the polymer nickel bromide system, see: Pittman, C. V., Jr.; Smith, L. R. *J. Am. Chem. Soc.* **1975**, *97*, 341. For the polymer nickel chloride, see: Allum, K. G.; Hancock, R. D.; Howell, I. V.; Pitkethly, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1975**, *87*, 189.

selectivity exists. For example, esters, ketones, sulfones, and free hydroxyl groups are all tolerated. Whereas, a carboethoxy group on the acetylene appears to promote reaction (entry 6), such a group on the olefin hinders reaction. Olefin geometry plays a role in terms of 1,3- vs. 1,4-diene formation in comparing entries 4 and 5. Unfortunately, without a defined mechanism, it is difficult to rationalize this observation. If we propose either an acyclic **10** or cyclic **11** intermediate which arises by a cis addition to the olefin and propose that elimination proceeds by a cis elimination of nickel hydride, kinetically a trans olefin would lead to **12** R = H, $R^1 = CH_3$ and a cis olefin to **12** R = CH_3, R^1 = H. The steric congestion of placing the methyl group syn with respect to the diene in the case of the *Z* olefin, then, disfavors 1,3-diene formation. Finally, cyclization of enyne **8** in entry 10 led only to the cyclopentene **9**[8] with no other double bond isomers detectable. Furthermore, analysis by 500-MHz ^{1}H and 125-MHz ^{13}C NMR spectroscopy reveals a high diastereoselectivity (88:12). Upon the basis of the ^{13}C chemical shift of C (21) (δ 18.5) and mechanistic considerations, we tentatively assign the stereochemistry depicted for the major isomer. While we cannot rule out isomerization of an exocyclic double bond, such an isomerization has not been observed in any other case even when the products were exposed to an active catalyst system for prolonged periods. This example also differs substantially from the Pd(2+)-catalyzed reaction in terms of the regioselectivity of the hydrogen migration as shown in the diene **13**.[2]



10 **12** **11**



13

The definition of the actual catalyst remains unclear. Neither tetrakis(triphenylphosphine)nickel nor tris(triphenylphosphine)nickel(1+) chloride[9] are active catalysts. On the other hand, addition of chromous chloride to either generates a catalyst, but one which is less active than treating the nickel(2+) complex **2** with chromous chloride. A mixed metal complex like $(Ph_3P)_3NiCrCl_4$ or $(Ph_3P)_3NiCrCl_3$ would account for the special role of chromium chloride salts in generating active catalysts.[10]

Acknowledgment. We thank the National Science Foundation for their generous support of our programs.

Supplementary Material Available: Experimental procedures for preparation of the polymeric catalyst and of 4,4-dicarbomethoxy-1,2-dimethylenecyclohexane; spectral data for products of entries 7, 8, and 9 of Table I (3 pages). Ordering information is given on any current masthead page.

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(8) IR ($CDCl_3$) 1725, 1660, 1615 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (s, 1 H), 5.46 (s, 1 H), 4.95 (d, J = 9.8 Hz, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 2.79 (dd, J = 13.9, 7.9 Hz, 1 H), 2.44–2.23 (m, 4 H), 2.08–1.98 (m, 3 H), 1.85–1.77 (m, 3 H), 1.70–1.25 (m with methyl, s at δ 1.67 and 1.65, 12 H), 1.23–0.91 (m with methyl, s at 1.19, 9 H), 0.56 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.2, 172.2, 171.8, 171.2, 149.0, 136.0, 127.6 (CH), 123.7 (CH), 122.5 (CH), 65.2, 58.6 (CH), 55.4 (CH), 53.9 (CH_3), 52.5 (CH_3), 46.6 (CH), 43.5, 39.8 (CH_2), 38.6 (CH_2), 35.9 (CH), 35.7 (CH_2), 33.9 (CH_2), 32.8 (CH_2), 31.9 (CH_2), 24.7 (CH_2), 24.1 (CH_2), 21.0 (CH_2), 18.5 (CH_3), 17.3 (CH_3), 15.2 (CH_3), 13.1 (CH_3).

(9) (a) D'Aniello, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1978**, *100*, 1474. (b) Kanai, H.; Kushi, K.; Sakanoue, K.; Kishimoto, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2711.

(10) A mixed metal complex between Ni(1+) and stannous chloride is known. See ref 9a.

The Conrotatory Electrocycloreversion of the *cis*-3,4-Diarylcyclobutene Cation Radical[1]

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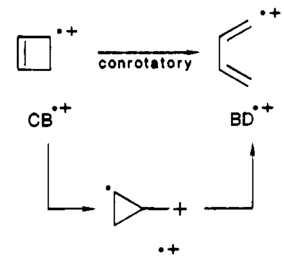
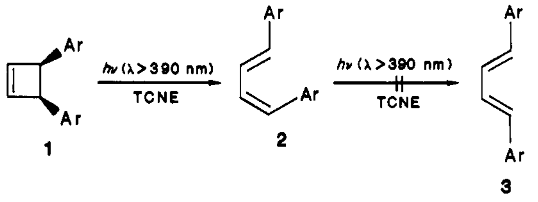
Received February 17, 1987

Theoretical analyses[2] predicted that the ground-state electrocycloreversion of a cyclobutene radical cation ($CB^{\bullet+}$) to a 1,3-butadiene radical cation ($BD^{\bullet+}$) would occur preferably in a conrotatory manner[2b] if the cycloreversion is a direct pathway or would occur in a two-step process passing through a cyclopropylcarbinyl ($CPC^{\bullet+}$) radical cation intermediate[2c] independent of symmetry constraints. There is, however, no experimental investigation that tested those theoretical predictions in terms of stereochemistry.[3-6] We examined this, and for the first time, report the stereospecific conrotatory electrocycloreversions of *cis*-3,4-diarylcyclobutene radical cations $\mathbf{1}^{\bullet+}$ to *cis,trans*-1,4-diaryl-1,3-butadienes **2**. The process occurred either by the photoexcitation of the electron donor–acceptor (EDA) complexes of **1** and tetracyanoethylene (TCNE) or under photoinduced electron-transfer conditions. **1a**[7,8a] and **1b**[8b,9] exhibited the charge-





a; Ar = C_6H_5, **b**; Ar = *p*-ClC_6H_4

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(1) Organic Photochemical Reaction no. 81. For no. 80, see: Yamashita, Y.; Ikeda, H.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, in press.

(2) (a) Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577. (b) Dunkin, I. R.; Andrews, L. *Tetrahedron* **1985**, *41*, 145. (c) Bellville, D. J.; Chelsky, R.; Bauld, N. L. *J. Comput. Chem.* **1982**, *3*, 548. Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(3) Although there are many experimental investigations of the reactions of cyclobutene radical cations, most of them are of the gas-phase reactions by using mass spectroscopic techniques[4] or of reaction in frozen media.[5] However, a putative electrocycloreversion of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene radical cation in solution was recently reported.[6]

(4) (a) Hoffman, M. K.; Bursey, M. M.; Winter, R. E. K. *J. Am. Chem. Soc.* **1970**, *92*, 727. (b) Mandelbaum, A.; Weinstein, S.; Gil-Av, E.; Leffin, J. H. *Org. Mass. Spec.* **1975**, *10*, 842. (c) Gross, M. L.; Russel, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 2082. (d) Dass, C.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5724. (e) Dass, C.; Sack, T. M.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 5780.

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