absence of a stretching mode of vibration and a resonance near −2 ppm, respectively, arising from B–H–B bridge bonds.

The IR, NMR, and mass spectroscopic data for I are all consistent with its X-ray crystal structure[22] that shows two distorted pentagonal bipyramids joined by a germanium atom at the commo-apical position. A side view of the molecular structure of I is shown in Figure 1. Table I, where selected bond lengths are presented, shows that the Ge–C distances of 2.38 (2) and 2.39 (2) Å are substantially longer than the Ge–B distances [2.14 (3), 2.08 (3), and 2.15 (2) Å] as found previously in stannacarborane–bipyridine complexes.[8,9] The η^5-bonding (ca. 2.1–2.4 Å) of the germanium atom to each of the pentagonal faces of carborane ligands in I is comparable to that found in germanocene and its derivatives. This type of slippage from η^5 to η^3 has been observed in many of the stannocene,[3-5] stannacarborane complex,[8,9] germanocene,[14-17] silicocene,[23] and other metallacarborane[24] derivatives.

We believe that the compound I, along with $[C_2B_9H_{11}]_2Si^{IV}$ [25] and $[(Me_3Si)_2C_2B_4H_4]_2Si^{IV}$,[26] the only examples reported to date in which a group 4 atom is sandwiched by two carborane cages. In these compounds, the group 4 atom is 10-coordinated, indicating the use of d-orbitals by the germanium atom and the silicon atom in bonding to the carborane cages. It is clear that in I the germanium atom interacts only weakly with the cage carbon atoms. However, the germanium in I is in its +4 oxidation state. With the exception of this difference in oxidation state, the title compound I can be regarded as a carborane analogue germanocene.

Studies on the reactivities of $[(Me_3Si)(R)C_2B_4H_4]^{2-}$ ions with MX_4 (R = Me_3Si, Me, H; M = Si, Sn, Pb; X = Cl, Br) are now in progress. The characterization and the chemistry of III will be reported later.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-84-18874, the Robert A. Welch Foundation under Grants N-1016 and N-495, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Professor John A. Maguire for helpful suggestions concerning this work. We are indebted to Professor Edward R. Biehl for obtaining the mass spectra.

Supplementary Material Available: Tables of positional and thermal parameters (Table I), bond distances and angles (Table II), and mass spectrometric data (Table IV) (3 pages); listing of observed and calculated structure factors (Table III) (6 pages). Ordering information is given on any current masthead page.

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(21) FT NMR Data of I: ^1H NMR ($CDCl_3$, relative to external Me_4Si) δ 4.07 [q br (overlapping), 6 H, basal H_t, $^1J(^1H-^{11}B)$ = 110 Hz], 0.62 [br q, 2 H, apical H_t, $^1J(^1H-^{11}B)$ = 171 Hz], 0.35 [br s, 36 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3 \cdot OEt_2$) δ 17.87 [d, 4 B, basal BH, $^1J(^{11}B-^1H)$ = 112 Hz], 4.20 [d, 2 B, basal BH, $^1J(^{11}B-^1H)$ = 108 Hz], −39.14 [d, 2 B, apical BH, $^1J(^{11}B-^1H)$ = 172 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 132.27 [br s, cage carbons], 1.67 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H)$ = 119 Hz]; ^{29}Si NMR ($CDCl_3$, relative to Me_4Si) δ −1.47 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H)$ = 6.5 Hz].

(22) Crystal and experimental data for I. $C_{16}H_{44}B_8Si_4Ge$, mol wt 507.95, monoclinic, space group $P2_1/n$, a = 9.905 (4) Å, b = 11.649 (3) Å, c = 13.793 (3) Å, β = 91.00 (3)°, U = 1591.2 (9) Å^3, Z = 2, d_{calcd} = 1.060 g/cm^3, μ(Mo Kα) = 11.00 cm^{-1}. Data were collected on a Syntex P2_1 diffractometer with a crystal coated in an epoxy resin. A total of 1280 independent reflections was measured in the range $3 < 2\theta < 38°$ ($\theta/2\theta$ scan type, graphite monochromatized MoKα radiation). The data were corrected for decay (ca. 16%) and for Lp effects but not for absorption. Only the 808 observed reflections with $I > 3\sigma(I)$ were used subsequently. The structure was solved by standard Patterson and difference Fourier methods. All non-H atoms were refined anisotropically. The four cage hydrogen atoms were located and included in the refinement with U's set at 0.06 Å^2 but not refined. Full-matrix least squares were used (SHELX76, Sheldrick, G. M., 1976. Program for crystal structure determination, Cambridge, U.K.), the function minimized being $\sum w(|F_0| - |F_c|)^2$. One reflection $\bar{1}01$, possibly affected by extinction, was taken out during the final refinement which converged [$(\Delta/\sigma)_{max}$ = 0.05] to R = 0.079 and R_w = 0.084, the weight used being $w^{-1} = \sigma_F^2 + 0.000816F^2$. $\Delta\rho_{max}$ = 0.45 e/Å^3. Scattering factors for C, H, B, and Si used were those stored in SHELX76. Scattering factors and $\Delta f'$ and $\Delta f''$ for Ge were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(23) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

(24) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* **1972**, *94*, 1865.

(25) Hawthorne, M. F.; Rees, W. S.; Schubert, D. M.; Knobler, C. B. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York, NY, American Chemical Society: Washington, DC, 1986; ORGN 142. Rees, W. S.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367 and 5369.

(26) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Chem. Soc., Chem. Commun.*, in press.

Carboxylative Trimethylenemethane Cycloadditions Catalyzed by Palladium

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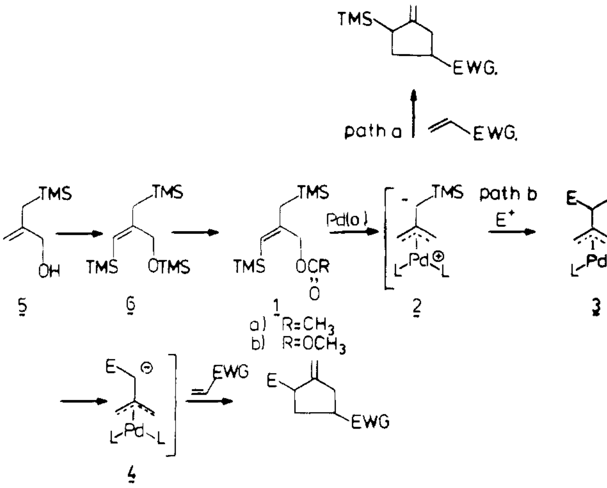
Received March 24, 1986

In developing a cycloaddition strategy to the synthesis of cyclopentanoids,[1,2] we designed the silyl-substituted trimethylenemethane precursor **1** as a dual-purpose conjunctive reagent. The notion was to create a silyl-substituted TMM–Pd complex **2** as a reactive intermediate which could directly cycloadd to give silyl-substituted methylenecyclopentanes (path a) or could be intercepted by an electrophile that is more reactive than the normal TMM–Pd acceptors (path b, i.e., **2** → **3**). The product, still bearing a silicon substituent, could regenerate a substituted TMM–Pd complex **4** for subsequent cycloaddition (eq 1). We wish to report the achievement of this goal and an unusual dichotomy in the reactions of **1** as a function of leaving group.



(1)

The silyl-substituted TMM precursor **1** was prepared by metallation–silylation of **5**[3] (n-C_4H_9Li, TMEDA, THF, −30 °C, then TMS–Cl, −60 °C, 91% yield), chemoselective aqueous sulfuric acid hydrolysis of the *O*-silyl ether **6** (H_2SO_4, H_2O, THF, room temperature), and acylation (AcCl, C_5H_5N, CH_2Cl_2, 0 °C, 77% yield for two steps to **1a**[4] or nC_4H_9Li, THF, $CH_3OC(=O)Cl$, −6 °C, 80% yield for two steps to **1b**[4]). Performing cycloadditions

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(1) For a recent review: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

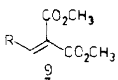
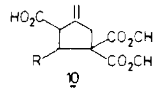
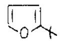
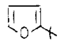
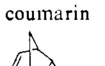
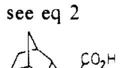
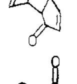
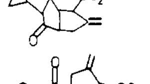
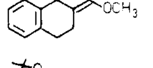
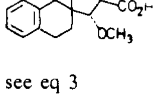
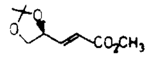
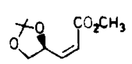
(2) For some recent related work, see: (a) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183. (b) *Tetrahedron Lett.* **1985**, *26*, 3825. (c) Binger, P.; Lu, Q.-H.; Wedemann, P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 316. (d) Trost, B. M.; Bonk, P. *J. Am. Chem. Soc.* **1985**, *107*, 8277.

(3) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58. As in the original procedure, the hexane solution of n-butyllithium is concentrated to remove as much of the hexane as possible. It was subsequently found that the yield could be increased to 98% by leaving the hexane and not adding the THF.

(4) This compound has been fully characterized spectrally and elemental composition determined by high-resolution mass spectroscopy and/or combustion analysis.

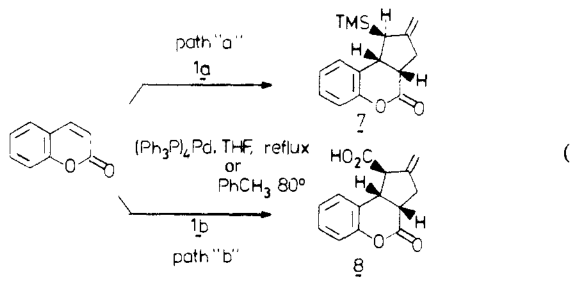
0002-7863/86/1508-6051$01.50/0

Table I. Carboxylative Cycloaddition of Methyl 1-(Trimethylsilyl)-2-[(trimethylsilyl)methyl]prop-1-en-3-yl Carbonate[a]

entry	acceptor	adduct[b]	*E*/*Z*-CO_2H[c]	isolated yield[b]
	 9	 10		
1	**9**, R = Ph	**10**, R = Ph	62/38	61%
2			59/41	70%
3	**9**, R = *i*-C_3H_7	**10**, R = *i*-C_3H_7	73/27	57%
4			80/20	77%
5	coumarin	see eq 2		81%
6			30/70	68
7			67/33	51%
8		see eq 3		66%
9		see eq 4		54%

[a] All reactions performed by heating 1:1 ratios of **1b** and acceptor with 2 mol % $(Ph_3P)_4Pd$ in $PhCH_3$ at 80 °C unless otherwise stated. [b] See ref 4. [c] Stereochemistry of carboxylic acid function with respect to vicinal substituent. [d] All yields are after chromatographic purification. In most cases, the yields of the crude products, which are rather clean, are substantially higher with larger than normal losses occurring on chromatography due to the polarity of the carboxylic acids.

of **1** with a variety of acceptors can be illustrated by their reactions with coumarin (eq 2). By use of the acetate **1a**, the cycloaddition

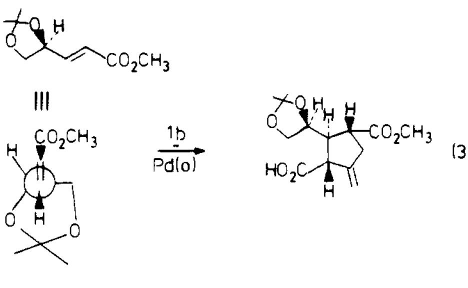


(2)

using $Pd(PPh_3)_4$ proceeds regioselectively to give **7**[4] (eq 2, path a, 62% yield) as a 9:1 ratio of diastereomers. The high field shifts of the Me_3Si group in the minor isomer (δ −0.31) compared to the major isomer (δ +0.12) due to shielding by the benzo ring in the minor isomer leads to the stereochemical assignment depicted in **7** for the major product. Remarkably, performing the same reaction with **1b** leads to none of the silylylated product **7** but produces the carboxylic acid **8**[4] as a single diastereomer (eq 2, path b, 81% yield).

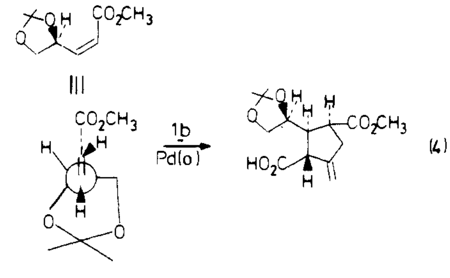
This carboxylative cycloaddition appears to be general as summarized in Table I. The highly reactive arylidene malonate acceptors **9** successfully participate to give the cycloadducts **10**[4] (entries 1–3) even though it might have been thought to intercept **2** competitive with carboxylation. The spiro example (entry 7) is interesting both not only because of the ability to form spiro fused rings but also because a β-methoxy group can be tolerated. Such a group normally deactivates the Michael acceptor ability of electron-deficient olefins and may participate in addition–elimination reactions rather than cycloaddition. This acceptor appears to be at least as reactive as non-methoxy bearing acceptors and does not create complications of addition–elimination reactions in the Pd(0)-catalyzed carboxylative cycloaddition.[5]

Most interesting observations arise in the cycloadditions of the *E*,*Z* pair **11** and **12**. In each case, the carbon bearing the free carboxylic acid function is a single epimer assigned as the thermodynamically more stable *E* isomer. Most interesting is the facial selectivity with respect to the acceptor. The *E* isomer **11** gives as the major adduct **13**[4] in analogy to the parent TMM–Pd species (10:1). The *Z* isomer **12** dramatically increases the facial selectivity so that only a single diastereomeric product **14**,[4] whose



(3)

11 13

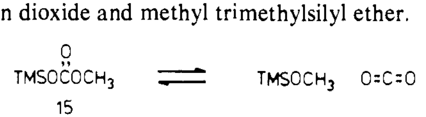


(4)

12 14

stereochemistry has been established by X-ray crystallography, results. If the reactive conformers are as depicted in the Newman projections as in **11** and **12**, the somewhat higher diastereoselectivity of the *Z* isomer **12** is readily understood. All other conformations dramatically increase nonbonded interactions between the *Z*-carbomethoxy group and the dioxolane while maintaining an open face to approach of the attacking TMM–Pd species. Contrary to our earlier observations,[5] this cycloaddition is stereospecific. Furthermore, these trends directly parallel the recently described Diels–Alder reactions of the same *E*,*Z* pair.[6]

The rationalization of this carboxylative cycloaddition derives from understanding the nature of the silyl carboxylate products.[7] Whereas the trimethylsilyl acetate derived from **1a** is relatively inert, methyl trimethylsilyl carbonate **15** may be in equilibrium with carbon dioxide and methyl trimethylsilyl ether. Indeed, **15**



$$\underset{15}{\mathrm{TMSO\overset{O}{\overset{\|}{C}}OCH_3}} \rightleftharpoons \mathrm{TMSOCH_3}\quad \mathrm{O{=}C{=}O} \tag{5}$$

may be considered to be a convenient carrier of carbon dioxide. The high reactivity of carbon dioxide toward **2** permits it to preferentially capture the latter even in the presence of reactive TMM–Pd acceptors. The relative rates of these two competing processes must be dependent upon the nature of the initial TMM–Pd species, since in other work,[8] where we have employed carbonate as a leaving group, no carboxylation concomitant with cycloaddition occurred. The carboxylate anion created in **3** (E

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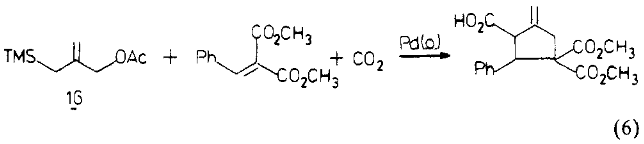
[5] Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315, 2326.

[6] Mulzer, J.; Kappert, M.; Huttner, G.; Jibul, I. *Tetrahedron Lett.* **1985**, *26*, 1631. For a review, see: Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447.

[7] For use of carbonates in Pd-catalyzed allyl alkylations, see: Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550. Trost, B. M. In *New Synthetic Methodology and Biologically Active Substances*; Yoshida, Z., Ed.; Elsevier Scientific: Amsterdam, 1981. Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523.

[8] Trost, B. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1985**, *107*, 1075.

= CO_2^-) may accept the second trimethylsilyl group to generate the substituted TMM–Pd species **4** E = CO_2SiMe_3. Desilylation of the silyl esters anticipated as the initial products during workup accounts for the ultimate products. The regioselectivity of the cycloaddition is anticipated based upon our earlier observations[9] as well as the recent work of Tsuji.[2a] Since Tsuji has shown that the carbomethoxy-substituted TMM–Pd species could be generated by deprotonation compared to desilylation,[2a] we briefly examined the reaction of the parent acetate **16** in the presence of carbon dioxide. However, yields of carboxylated cycloadduct according to eq 6 were only 10% or less. Apparently, the silyl-substituted TMM–Pd precursor **1** favorably balances the reactivity of **2** toward carbon dioxide vis-ã-vis electron-deficient olefins. The stereospecificity of this reaction reopens the question of the concertedness of this Pd-catalyzed cycloaddition. Synthetically, the opportunity to functionalize the TMM–Pd intermediate in concert with the cycloaddition expands the scope of this approach to cyclopentanoids.[10]



(6)

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health, and Rhone-Poulenc for their generous support of our programs.

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[9] Trost, B. M.; Nanninga, T. N.; Satoh, T. *J. Am. Chem. Soc.* **1985**, *107*, 721.

[10] For a recent overview, see: Paquette, L. A. *Recent Synthetic Developments in Polyquinane Chemistry*; Springer-Verlag: Berlin, 1984. Ramaiah, M. *Synthesis* **1984**, 529.

A Synthesis of Substituted Pyrrolidines via a Palladium(2+)-Catalyzed Cyclization. An Unusual Approach to a Carbapenem

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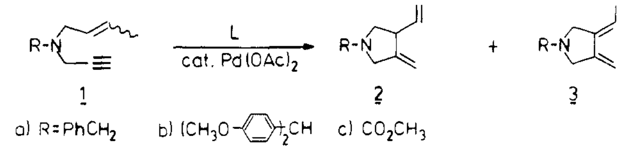
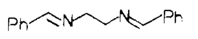
Five-member ring nitrogen heterocycles represent a highly common structural unit of many natural products including such diverse types as the pyrrolizidine alkaloids[1] and the carbapenems[2] (e.g., thienamycin[3]). While the presence of a basic nitrogen frequently inhibits reactions catalyzed by higher oxidation states of transition metals, we wish to report that palladium acetate efficiently cyclizes nitrogen-substituted 1,6-enynes to form substituted pyrrolidines including the very sensitive carbapenem nucleus.[4]

In order to explore the feasibility of the reaction as a function of the substituent on nitrogen, we reacted the crotyl propargyl amine derivatives **1a–c** with 5 mol % of palladium acetate and 10 mol % of triphenylphosphine in benzene-d_6 (~0.5 M) at 65 °C for approximately 1 h. The initial substrate **1a** gave a 75% yield of a mixture of **2a**[5] and **3a**[5] in a 2:1 ratio which is invarient with reaction time, indicating no interconversion by isomerization.



The formation of the 1,3-diene stands in contradistinction to our earlier observations[4a] in the carbocyclic case which led us to predict formation of only the 1,4-diene **2a**. Increasing the effective steric bulk (i.e., **1b**) or planarizing nitrogen (i.e., **1c**) has no effect on this ratio (1b gave 2b/3b in 2.8:1 ratio; **1c** gave **2c**/**3c** in 2:1 ratio). Variation of phosphine ligands among tri-*o*-tolyphosphine, triphenylphosphine, and dppb[6] gave a slight increase in **2a** vs. **3a** from 1.6:1 to 2.5:1. A major improvement arose in switching to the nitrogen ligand **4**[7] which produces a 9:1 ratio of **2a**/**3a**. Trisubstituted olefin **5a** gave only the 1,4-diene **6**[5] even with the phosphine ligands.



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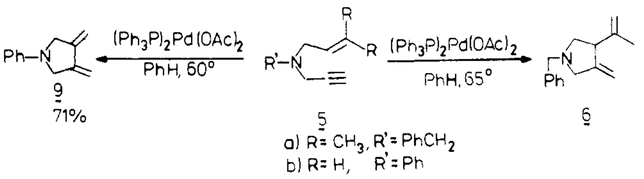
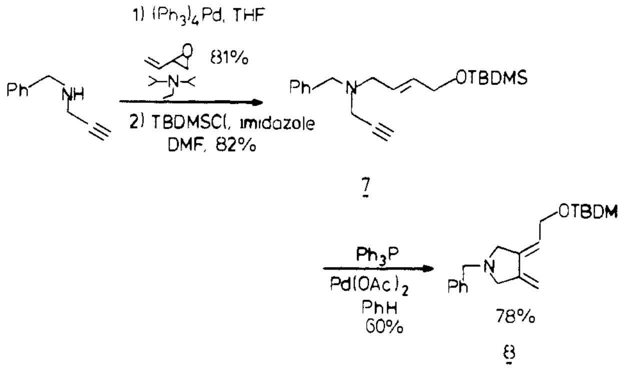


Allylic oxygen substituents have a strong directive effect. A Pd(0)-catalyzed alkylation readily provided the enyne **7**. Its cyclization produced exclusively the 1,3-diene **8**.[5] We tentatively attribute this regioselectivity to the electron-withdrawing inductive effect of oxygen which inhibits the β-H insertion by an extremely electrophilic palladium.[8] The parent 2,3-dimethylenepyrrolidine (**9**)[5] was also readily available by a similar cyclization of **5b**.



The ease of availability of the requisite enyne combined with the ability to generate both 1,3- and 1,4-dienes as products enhances the utility of this process. Equations 1–4 (Scheme I) illustrate the ability to annulate a pyrrolidine ring onto either a carbocyclic or heterocyclic ring. In these examples, many of the ring systems created have relevance to alkaloids. For example,

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[1] Warren, F. L. *Fortschr. Chem. Org. Naturst.* **1966**, *24*, 239. Robins, D. J. *Ibid.* **1982**, *41*, 115.

[2] Southgate, R.; Elson, S. *Progr. Chem. Org. Nat. Prod.* **1985**, *47*, 1.

[3] Albers-Schonberg, G.; Arison, B. H.; Hensens, O. D.; Hirshfield, J.; Hoogsteen, K.; Kaczka, E. A.; Rhodes, R. E. Kahan, J. S.; Kahan, F. M.; Ratcliffe, R. W.; Walton, E.; Ruswinkle, L. J.; Morin, R. B.; Christensen, B. G. *J. Am. Chem. Soc.* **1978**, *100*, 6491.

[4] For carbocycle formation by cyclization of 1,6-enynes, see: (a) Pd: Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. (b) Zr: Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *Ibid.* **1985**, *107*, 2568. (c) For cyclopentenone formation in reactions of enynes and cobalt, see: Billington, D. C.; Pauson, P. L. *Organometallics* **1982**, *1*, 1560.

[5] Full spectral characterization has been obtained on all new compounds. Unless otherwise noted elemental composition has been determined by high-resolution mass spectroscopy or combustion analysis.

[6] dppb = 1,4-bis(diphenylphosphino)butane.

[7] The efficacy of this ligand in these reactions has been established by Mr. David Jebaratnam in these laboratories and will be discussed in a future publication.

[8] Trost, B. M.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1985**, *107*, 4586. For the effect of phosphines on β-hydrogen insertion in the Heck reaction, see: Chalk, A. J.; Magennis, S. A. *Catal. Org. Synth.* **1977**, *6th*, 139.