Preparation of Dioxolane 9. The lactone **7** (25 mg) with 2 equiv of 2,2-dimethoxypropane and a catalytic amount of *p*-toluenesulfonic acid in dry *N*,*N*-dimethylformamide (2 mL) was allowed to stand under a nitrogen atmosphere at room temperature for 48 h. After the mixture was neutralized with aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (2 × 5 mL), the combined organic layers were concentrated to dryness (temperature below 40 °C) in vacuo and chromatographed (reversed-phase HPLC; 10-μm ODS column; solvent, MeOH–H_2O, 45:55), 24% of the starting material **7** and 41% of the ketal **9** were afforded. $[\alpha]^{20}D$ = −5.5° (*c* 0.0061, MeOH). IR (neat): 3600–3200, 1770 cm^{-1}. NMR ($CDCl_3$) shifts (δ) from Me_4Si [[atom number], ^{13}C δ's at 75 MHz, ^1H δ's at 300 MHz (*J*'s (hertz at 300 MHz)]: [1] 18.3, 1.34 (d, *J* = 6.0); [2] 74.6, 3.88 (dq, *J* = 8.4, 6.0); [3] 82.6, 3.72 (dd, *J* = 8.4, 4.5); [4] 76.6, 4.54 (ddd, *J* = 8.7, 4.5, 2.4); [5] 31.6, 2.62 (ddd, *J* = 15.3, 8.7, 2.4), 2.31 (ddd, *J* = 15.3, 8.7, 8.4); [6] 67.0, 4.63 (dd, *J* = 8.7, 8.4); [7] 177.2; [8] 109.6; [9] 27.3, 1.40 (s); [10] 26.9, 1.30 (s). $C_{10}H_{16}O_5$ LREIMS *m/z* (rel intens): 216 [M^+ (7)].

Acknowledgment. Partial research support was from NOAA, National Sea Grant College Program, Department of Commerce, University of California Project No. R/MP-41. The U.S. Government is authorized to produce and distribute reprints for governmental purposes. Other grant support was from Syntex Inc. and the University Research Expeditions Program supported field work in Fiji. We are grateful for the cooperation of the Fiji Government. We thank Jim Loo (UCSC) for assistance with NMR measurements, Dr. Tom Matthews (Syntex) for bioactivity data, Professor Mark Midland (UCR) for advice with PCMODEL, and Cal Ponzini and Lisa Hunter for valuable assistance in sponge collection.

2-[(Trimethylsilyl)methyl]-1-(trimethylsilyl)propen-3-yl Carboxylates in Cycloaddition. A Novel Approach for Substitutive Cyclopentannulation

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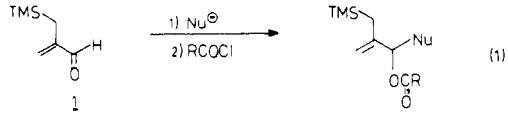
Abstract: Twofold sequential metalation–silylation of methallyl alcohol followed by acid hydrolysis provides 2-[(trimethylsilyl)methyl]-1-(trimethylsilyl)-1-propen-3-ol from which the corresponding acetate and carbonate are readily available. The acetate participates in palladium-catalyzed cycloadditions to give the trimethylsilyl-substituted methylenecyclopentanes. Unlike other substituted trimethylenemethane cycloadditions via their palladium complexes, the regioselectivity of the cycloaddition is dependent upon ligand. With triphenylphosphine as ligand, the cycloadduct that places the trimethylsilyl substituent on the carbon of the trimethylenemethane unit that becomes bonded to the β-carbon of the acceptor is preferentially formed. In complete contrast to the acetate, the corresponding carbonate gives the cycloadducts possessing a carboxylic acid function in lieu of the trimethylsilyl substituent. The in situ carboxylation–cycloaddition is a highly general reaction as demonstrated by α,β-unsaturated esters, ketones, and sulfones participating as acceptors. Excellent diastereoselectivity may accompany this cycloaddition. The facts that olefin geometry is faithfully translated into ring geometry and that β-methoxyenones react without β-elimination suggest that it may be a concerted process. In some cases, cycloaddition proceeds more smoothly than with the parent system; 2-cyclohexenone is a notable case. Thus, a single substrate can provide cycloadducts bearing either a trimethylsilyl or carboxyl substituent by the simple expedient of choice of leaving group. This is the first case of carboxylation accompanying use of carbonates in palladium-catalyzed reactions.

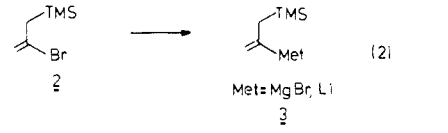
The success of (trimethylenemethane)palladium–L_2 in cycloadditions with a wide variety of acceptors[1,2] led us to seek the ability to incorporate substituents in the TMM unit. We have developed the use of 2-[(trimethylsilyl)methyl]acrolein (**1**) as a convenient general precursor whereby the substituent is introduced in the form of a nucleophile.[3] To expand the scope and ease of



(1)

1

introduction of substituents, we chose to inverse the electronic sense by using the silicon-containing fragment as a nucleophile to condense with an electrophilic partner. 2-Bromo-3-(trimethylsilyl)-1-propene (**2**) is one such reagent.[4] Conceptually, 1-(trimethylsilyl)-2-(trimethylsilyl)methallyl alcohol esters represented by **4** could be a very useful alternative as illustrated in eq 3.[5] A



(2)

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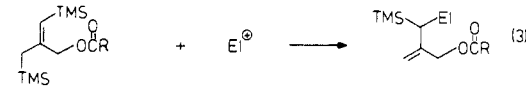

(3)

4

slight varient invokes telescoping the electrophilic substitution with the cycloaddition step in which we can envision a novel pathway as outlined in eq 4. In this concept, the initial trimethylsilyl-

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(1) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315, 2326. For a review, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

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(4) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733. Trost, B. M.; Coppola, B. P. *Ibid.* **1982**, *104*, 6879. For an independent study, see: Nishigawa, H.; Yokoyama, H.; Narimatsu, S.; Itoh, K. *Tetrahedron Lett.* **1982**, *23*, 1267.

(5) For reviews, see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. Fleming, I. *Compr. Org. Chem.* **1979**, *3*, 541. Magnus, P. D.; Sarkar, T.; Djuric, S. *Compr. Organomet. Chem.* **1982**, *7*, 515.

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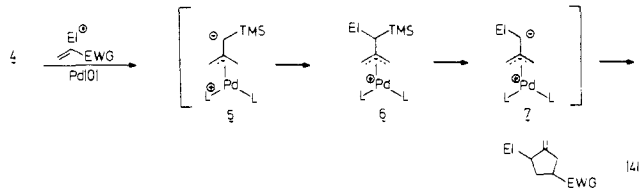
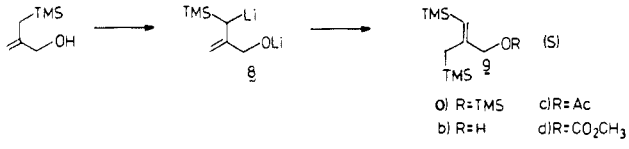


substituted species **5** may be intercepted by an electrophile (El^+) to give **6** faster than it undergoes cycloaddition with a normal electron-deficient olefin. The presence of a silicon allows easy regeneration of a substituted TMM–Pd complex **7**, which then undergoes cycloaddition. A successful electrophile (1) must be more reactive toward **5** than a normal acceptor and (2) must either be less reactive toward the substituted TMM–PdL_2 than the normal acceptor or, at least, react reversibly with **7**. The attractiveness of being able to functionalize and cycloadd simultaneously led us to explore this possibility.

Preparation of Disilyl Conjunctive Reagent. The monosilyl alcohol **8**, which we have prepared from methallyl alcohol,[6] was metalated with *n*-butyllithium freed of hexane in ether containing 1.1 equiv of TMEDA at −30 °C to room temperature to give a quite soluble dianion **8** (eq 5). The solubility of **8** stands in



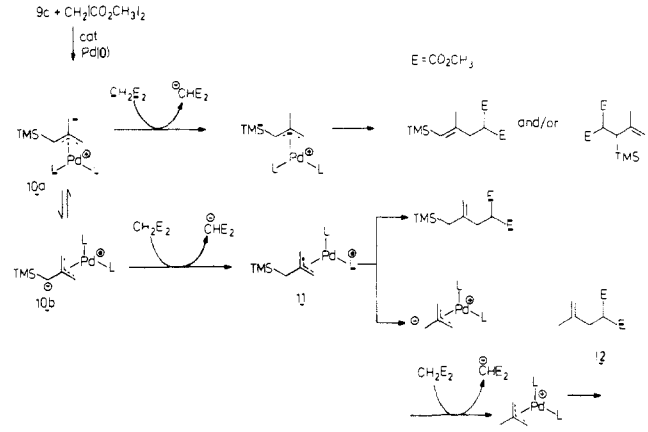
contrast to the dianion of methallyl alcohol, which forms a thick paste. Quenching with trimethylsilyl chloride gives the tris-silylated product **9a** in 91% yield as an approximately 95:5 ratio of geometric isomers. Aqueous sulfuric acid hydrolysis to the alcohol **9b**[7] allows acylation with either acetyl chloride to give **9c** (77% overall for two steps) or methyl chlorocarbonate to give **9d** (80% overall for two steps).

Assignment of olefin geometry is not obvious. Comparison of the spectral properties of **9b** with those of an authentic sample of the *Z* isomer, whose synthesis has been recorded subsequent to our work,[7] suggests the former is also the *Z* isomer.

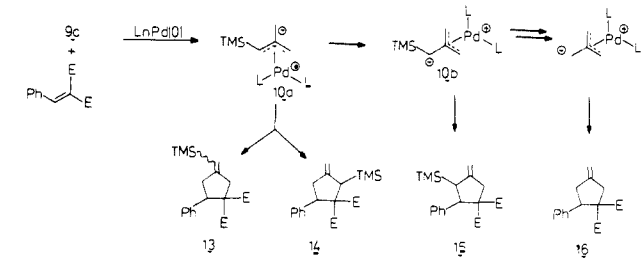
Neutral Alkylation of 9 with Dimethyl Malonate. In order to probe the reactivity of the bis(silyl) conjunctive reagent **9c** toward Pd(0) catalysts, we treated it with a Pd(0) catalyst generated in situ from palladium acetate, triisopropyl phosphite, and *n*-butyllithium (ratio 1:6:2)[8] and excess dimethyl malonate in dioxane at 88 °C. Scheme I reveals the complexity that may befall the process. Surprisingly, a single alkylation product **12** results. The lack of any silylated alkylation products reflects the partitioning between the two initial TMS–TMM–PdL_2 complexes **10a** and **10b** and, most interestingly, between nucleophilic attack on versus desilylation of **11**. The fact that desilylation totally dominates over nucleophilic attack demonstrates how strongly the π-allylpalladium cationic unit activates the C–Si bond toward cleavage.

Cycloadditions of 1-(Trimethylsilyl)-2-[(trimethylsilyl)methyl]allyl Acetate. Using the above reaction conditions but replacing dimethyl malonate with dimethyl benzylidenemalonate gave three regioisomeric products **13–15** as well as protodesilylated product **16**, which were separated by flash chromatography, as shown in Scheme II. The vinylsilane regioisomer **13**, which formed as an *E,Z* mixture, is characterized by a single vinyl proton (δ 4.99 and 4.93) and somewhat downfield trimethylsilyl peaks (δ 0.14 and 0.11). Allylsilane **14**, which is characterized by the exocyclic methylene group (δ 4.79 and 4.58 (1 H each)), the benzylic proton as the X part of an ABX (δ 3.85 (dd, J = 10, 5 Hz)), the methine proton on the carbon bearing silicon (δ 3.00), as well as the TMS group (δ 0.04), appears to be stereohomogeneous. The alternative allylsilane **15**, which formed as a stereoisomeric mixture, is characterized by the terminal methylene group (δ 5.01 (s, 0.5 H), 4.97 (br s, 1 H), 4.79 (br s, 0.5 H)), the benzylic proton as part of an AB pattern (δ 4.12 (d, J = 8.8 Hz, 0.5 H), 4.08 (d, J = 7.4 Hz, 0.5 H)), an isolated methylene group with the two hydrogens appearing as two AB patterns (δ 3.60 and 3.04 (J = 16.8 Hz), 3.20 and 2.84 (J = 13.5 Hz)), as well as the TMS signals (δ −0.06 and −0.14). The final cycloadduct **16** was identical with that derived from the cycloaddition of 2-[(trimethylsilyl)methyl]allyl acetate with dimethyl benzylidenemalonate.[1]

Scheme I. Alkylation with Dimethyl Malonate



Scheme II. Cycloaddition with Dimethyl Benzylidenemalonate Using Triisopropyl Phosphite as Ligand



Since all of our earlier experiments with substituted TMM–PdL_2 complexes gave high regioselectivity for products analogous to **15**,[3,9] it is curious that the TMS analogue showed so little regioselectivity. To test whether the kinetically formed complex **10a** was being trapped faster than equilibration, we varied both the concentration of the trap and the temperature of the reaction. Neither factor changed the ratio of products.

On the other hand, ligands had a dramatic effect, as summarized in Table I. By switching from triisopropyl phosphite (cone angle of 130°) to the sterically more demanding triphenylphosphine (cone angle of 145°),[10] the ratio of **15** to **13** + **14** changed from 1.4 to 4.

While the question of regioselectivity appeared resolved, the problem of protodesilylation to give **16** remained. Since the mechanism of reduction of palladium acetate by *n*-butyllithium is unknown, we examined the effect of the ratio of these two reagents on the product distribution as summarized in Table I. When *n*-butyllithium was added to palladium acetate in the presence of triphenylmethane, a color change was noted at exactly the calculated 2-equiv level, but protodesilylation remained a major problem. Increasing the ratio of *n*-butyllithium to palladium acetate to 6 dramatically decreased the amount of protodesilylated cycloadduct. An increase in this ratio beyond 6 became detrimental due to the formation of additional byproducts. A similar reduction in the protodesilylation occurred upon using DIBAL-H as the reductant or employing preformed tetrakis(triphenylphosphine)palladium.[11]

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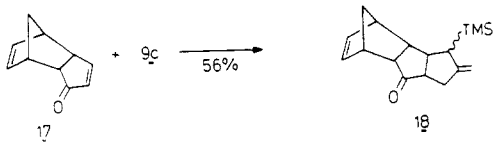
(7) For an independent alternative synthesis, see: Foulon, J. P.; Bourgain-Commercon, M.; Normant, J. F. *Tetrahedron* **1986**, *42*, 1389.
(8) Trost, B. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1985**, *107*, 1293.
(9) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5972.
(10) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

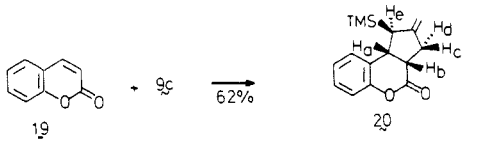
Table I. Product Distribution in Cycloaddition with Dimethyl Benzylidenemalonates[a]

ligand	reductant (reductant:Pd)	trap, M	13	14	15	16	yield, %
$(i\text{-}C_3H_7O)_3P$	$n\text{-}C_4H_9Li$ (2.0)	0.5	0.7		1.0	1.0	62
$(i\text{-}C_3H_7O)_3P$	$n\text{-}C_4H_9Li$ (2.0)	0.1	0.7		1.0	1.0	62
Ph_3P	$n\text{-}C_4H_9Li$ (1.6)	0.2	0.2	0.05	1.0	1.0	62
Ph_3P	DIBAL-H (2.5)	0.2	0.2	0.05	1.0	0.2	
Ph_3P	$n\text{-}C_4H_9Li$ (6.0)	0.2	0.2	0.05	1.0	0.15	65
PH_3P[b]	$n\text{-}C_4H_9Li$ (6.0)	0.2	0.2	0.05	1.0	1.0	
Ph_3P	$n\text{-}C_4H_9Li$ (8.0)	0.2	0.2	0.05	1.0	0.1	
Ph_3P		0.2	0.2	0.05	1.0	0.2	

[a] All reactions performed at 100 °C in dioxane unless otherwise noted. [b] This reaction performed at 65 °C with **9d** in THF.

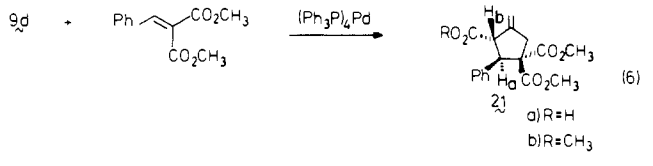
The use of 6 equiv of *n*-butyllithium to palladium acetate was limited to dimethyl benzylidenemalonate as the acceptor. On the other hand, the use of 6 equiv of DIBAL-H as the reducing agent was more compatible with less reactive acceptors. With this modification, the enone **17** and the lactone **19** give the cycloadducts **18** and **20** in 65% and 55% yields, respectively.





No diastereoselectivity was observed in the cycloaddition to enone **17**. On the other hand, the coumarin cycloadduct **20** was a 9:1 mixture of products. On the basis of an analysis of the NMR spectrum, we tentatively assign the major isomer as exo as depicted in **20** (H_e, δ 2.28 (J = 4.8 Hz, J_{de} = 2.0 Hz). The high-field shift of the protons of the TMS group in the minor (δ −0.31) versus the major isomer (δ 0.12) is consistent with a shielding of this group in the minor isomer by its lying in the shielding cone of the benzene ring.

Cycloadditions of 1-(Trimethylsilyl)-2-[(trimethylsilyl)-methyl]allyl Methyl Carbonate. The effect of the leaving group on the efficacy of the cycloaddition led us to explore the reaction of the carbonate **9d**. Only low yields of cycloaddition products resulted when in situ prepared Pd(0) catalyst was used. Switching to tetrakis(triphenylphosphine)palladium as the catalyst led to none of the silylated cycloadducts **13–15**. Elemental composition and spectroscopic data suggest that the product is a carboxylic acid **21** (eq 6). Chemical support for the presence of the free

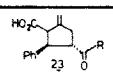
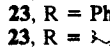
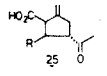
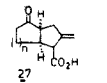
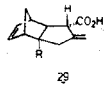
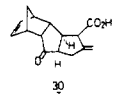
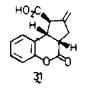
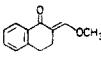
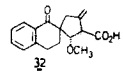
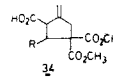
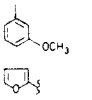
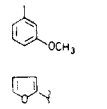
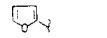
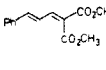
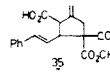
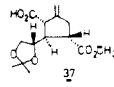
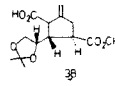
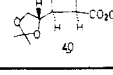


(6)

carboxylic acid arises upon treatment with diazomethane, which gives the tris(methyl ester) **21b** (IR 1722 cm^{-1}; ^{1}H NMR δ 3.72, 3.65, and 3.35 (s, 3 H each)). The regiochemistry is established by the appearance as two methine protons as an AB pattern at δ 4.36 and 3.99 with J = 11.3 Hz.

The facility of this process led us to explore its generality. Table II summarizes the examples. The methylenecyclopentanes are readily characterized by the absorptions for the terminal methylene group in the ^{1}H NMR spectrum at δ 4.8–5.1 and 5.2–5.3 and in the ^{13}C NMR spectrum at δ 137–148 and 109–111 (cf. methylenecyclopentane at δ 152.9 and 104.3).[1,12] The presence of the carboxylic acid is indicated by the ^{13}C NMR spectrum (δ 176–178) and infrared absorptions (3400–2700, 1710–1690 cm^{-1}).

Table II. Carboxylative Cycloaddition of 1-(Trimethylsilyl)-2-[(trimethylsilyl)methyl]allyl Methyl Carbonate[a]

entry	acceptor	adduct	CO_2H,[b] *E*:*Z*	yield,[c] %
	 22	 23		
1	**22**, R = CH_3	**23**, R = CH_3	73:27[d]	61
2	**22**, R = Ph	**23**, R = Ph	80:20[d]	77
3	**22**, R = 	**23**, R = 	70:30[e]	62
	 24	 25		
4	**24**, R = H	**25**, R = H	86:14[e]	37
5	**24**, R = OCH_3	**25**, R = OCH_3	24:76[d]	40
	 26	 27		
6	**26**, n = 1	**27**, n = 1	50:50[d]	41
7	**26**, n = 2	**27**, n = 2	50:50[d]	49
	 28	 29		
8	**28**, R = COPh	**29**, R = COPh	100:0[e]	70
9	**28**, R = SO_2Ph	**29**, R = SO_2Ph	100:0[e]	66
10		 30	31:69[e]	68
11		 31	100:0[e]	81
12		 32	33:67[d]	51
	 33	 34		
13	**33**, R = Ph	**34**, R = Ph	100:0	61
14			66:34[e]	59
15			59:41[d]	70
16	**32**, R = $i\text{-}C_3H_7$	**34**, R = $i\text{-}C_3H_7$	73:27[d]	57
17		 35	75:25[d]	60
18	 36	 37	100:0[e]	54
		 38	50:50[d,e]	13
19	 39	 40	100:0[e]	66

[a] All reactions performed by heating a 1:1 ratio of **9d** and acceptor with 2 mol % $(Ph_3P)_4Pd$ in toluene at 80 °C unless otherwise stated. [b] Stereochemistry of the carboxylic acid with respect to the vincinal substitutent. [c] Isolated yield after chromatographic purification. [d] Ratio was determined by ^{1}H NMR spectroscopy at 270 or 500 MHz with a 5% error limit. [e] Ratio of isolated product. [f] Reaction performed by heating 1:1 ratio of **9d** and acceptor with 2 mol % $Pd(OAc)_2$ and 14 mol % triisopropyl phosphite in toluene at 80 °C. [g] See ref 27.

(11) Coulson, D. R. *Inorg. Synth.* **1972**, *121*, 13.

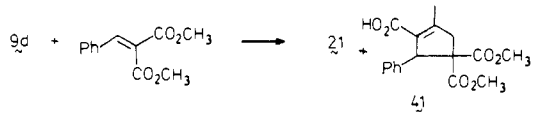
(12) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972; p 71.

The *E* or *Z* geometry of the carboxylic acid group with respect to its vicinal substituent is readily discerned by the coupling constant of J = 10–11 Hz for the *E* and J = 8–9 Hz for the *Z* isomer.

The stereochemistry of the C(3)–C(4) positions as trans for entries 1–5 and 18 is indicated by the 9–10 Hz coupling. In the case of entry 19, the cis coupling constant is only slightly smaller (J = 8.5 Hz). Single-crystal X-ray crystallography[13] unambiguously establishes the relative stereochemistry of **40**.

The regioselectivity of the cycloaddition with the dienylidene malonate of entry 17 is easily discerned by examination of the NMR spectrum of the product. The spectrum of cycloadduct **35** shows two vinyl protons as the AB part of an ABX pattern (δ 6.65 (d, J = 15.4 Hz), 6.52 (dd, J = 15.4, 7.1 Hz)). In contrast to this result, methylenecyclopropane[14] and 2-[(trimethylsilyl)-methyl]allyl acetate[15] undergo cycloadditions with simple dienoates predominantly to exclusively at the C(4)–C(5) double bond.

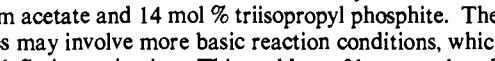
The propensity of the exocyclic double bond to migrate to an endocyclic position was dependent upon the catalyst system.[16] In the cycloaddition of dimethyl benzylidenemalonate with **9d**, use of preformed tetrakis(triphenylphosphine)palladium or generating a (triphenylphosphine)palladium(0) catalyst in situ from 1 mol % $(dba)_3Pd_2{\cdot}CHCl_3$ and 3 mol % triphenylphosphine produces only nonisomerized cycloadduct **21**. On the other hand, generating the (triphenylphosphine)palladium(0) catalyst in situ from 2 mol % palladium acetate, 10 mol % triphenylphosphine, and 4 mol % *n*-butyllithium gave 62.5% *trans*-**21** and 37.5% isomerized product **41** in a combined isolated yield of 71%. A 1:1 mixture of **21** and **41** is obtained in 65% isolated yield from 2 mol % palladium acetate and 14 mol % triisopropyl phosphite. The latter two cases may involve more basic reaction conditions, which then initiate olefin isomerization. This problem of base-catalyzed olefin isomerization also plagued the palladium-catalyzed cycloaddition of 2-(cyanomethyl)allyl methyl carbonate, which relies on a base-promoted deprotonation to generate the reactive (trimethylenemethane)palladium complex.[17] The neutrality associated with the preformed tetrakis(triphenylphosphine)palladium led us to use it as the preferred catalyst in almost all of the cases in Table II.

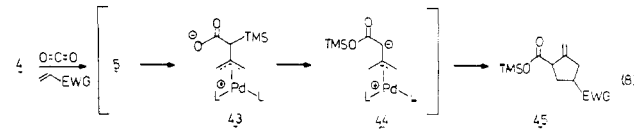


As Table II demonstrates, under these neutral cycloaddition conditions, the exocyclic double bond normally has no tendency to isomerize to the thermodynamically more stable endocyclic position. On the other hand, the stereochemistry of the carboxylic acid did change upon chromatographic purification. We believe that the differing stereoselectivity for the various examples is reflective of the sensitivity of the product toward epimerization.

Discussion

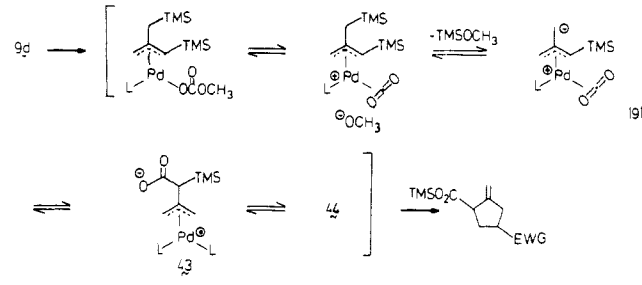
The totally different behavior observed in the cycloaddition of **4** as a function of the ester leaving group is quite striking and unexpected. What could be the source of the carboxylation? At first glance, the difference in the silicon byproduct may offer an explanation. Trimethylsilyl acetate, the byproduct in the cycloaddition of **9c**, is quite innocuous and simply is lost during workup. Trimethylsilyl methyl carbonate (**42**), the byproduct in the cycloadditions of **9d**, may be unstable relative to trimethylsilyl methyl ether and carbon dioxide (see eq 7). Carbon dioxide is quite a reactive electrophile. It could be envisioned to participate in the chemistry of eq 4 as depicted in eq 8. In this scheme, the initial carboxylated TMM–PdL_2 **43** may simply undergo a C to O silicon migration to regenerate a substituted TMM–PdL_2 **44**, which then undergoes cycloaddition. The expected trimethylsilyl esters simply hydrolyze during workup to produce the free acids as the isolated products.



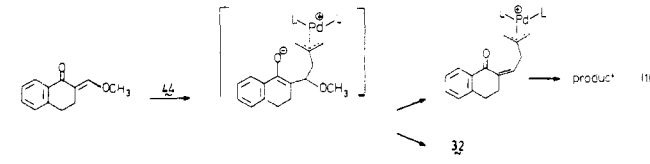


To test this scheme, the reaction of **9c** with dimethyl benzylidenemalonate was performed under an atmosphere of carbon dioxide. An approximate 10% yield of the carboxylated product was obtained even though a large excess of carbon dioxide was present. Considering that, under our normal carboxylation–cycloaddition reaction conditions, (1) an extremely small amount of carbon dioxide could be present at any given moment in time and (2) loss of carbon dioxide from the reaction medium would be expected to occur rather readily at 100 °C in dioxane or 80 °C in toluene, a simple carboxylation by carbon dioxide seems unlikely.

An alternative explanation invokes direct coordination of the carbonate to palladium followed by internal delivery of carbon dioxide to the TMM unit as outlined in eq 9. By having only bound carbon dioxide, as depicted in eq 9, we nicely account for the efficacy of the carboxylation under conditions where free carbon dioxide would be expected to be lost. The ability of palladium catalysts to effect carboxylation lends some credence to this proposal.[18]



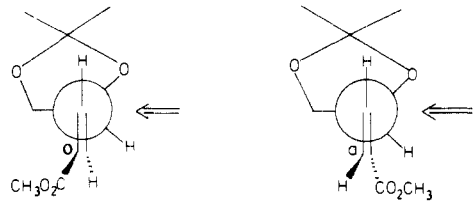
Several features of the cycloaddition of the carboxylated TMM are noteworthy. Comparing the *E*–*Z* olefin pair **36** and **39**, we see the olefin geometry of the starting material is faithfully reflected in the geometry of the product. This result is characteristic of a concerted cycloaddition. The reactions of the β-methoxyenones (Table II, entries 5 and 12) also support such a conclusion. In a stepwise reaction, the β-methoxyenone might have been anticipated to suffer substantial β-elimination from the initial adduct in competition with cyclization (eq 10).



The regioselectivity of the reaction of the dienoate (Table II, entry 17) also is accommodated by a concerted cycloaddition mechanism. The propensity for a dienoate to undergo conjugate addition at a terminus of the polyunsaturated system to create the more highly delocalized dienolate would have led to the preferred cycloaddition to the 4,5-position. On the other hand, LUMO coefficients indicate better overlap occurs at the 2,3-positions in a concerted cycloaddition.

(13) Mignani, S.; Haller, K. J., unpublished work performed in these laboratories.
(14) Buch, H. M.; Schroth, G.; Mynott, R.; Binger, P. *J. Organomet. Chem.* **1983**, *247*, C63.
(15) Raffaelli, A., unpublished work in these laboratories.
(16) Cf.: Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325. Binger, P.; Schuchardt, U. *Chem. Ber.* **1981**, *114*, 3313; **1980**, *113*, 3334.
(17) Schimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183.
(18) Cf.: Sasaki, Y.; Inone, Y.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2375. Musco, A.; Perego, C.; Tartiari, V. *Inorg. Chim. Acta* **1978**, *28*, L 147.

The carboxylated TMM shows a dependence of facial diastereoselectivity on olefin geometry as did the parent TMM.[19,20] Thus, the Z olefin **39** gave a single cycloadduct **40** in contrast to the Z olefin **36**. Reactions through the conformers depicted in **36**-*N* and **39**-*N* correctly predict the major and exclusive diastereomeric cycloadducts. In each of these conformers, the



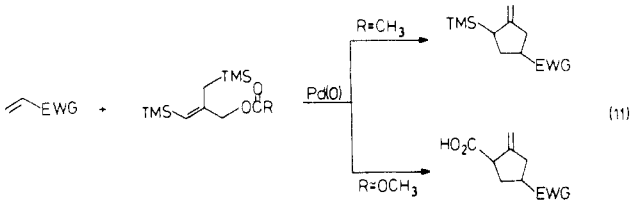
36-N 39-N

substituent at C(a) that projects back eclipses the smallest of the three substituents on C(4). Thus, the bias to react through these conformers should increase as the size of the substituent that projects back increases. Indeed, by going from the *E* olefin to the *Z* olefin we dramatically increase the size of this substituent by changing it from hydrogen (in the *E* olefin) to carbomethoxy (in the *Z* olefin).

The efficacy of this cycloaddition with cyclohexenone stands in contrast to the rather low yields obtained when the parent TMM cycloaddition is performed with this acceptor.[1,21] The sluggishness of cyclohexenone as an acceptor in concerted cycloadditions is well documented.[22] With the parent system, a side reaction that begins to occur arises from the basicity of the TMM–PdL_2 species. In the carboxylated TMM–PdL_2 intermediate, the basicity of the carbanion center is dramatically decreased by the presence of the anion stabilizing group. By minimizing the competing basic reaction pathway with the carboxy substituent, the simple cycloaddition proceeds with fewer complications and thus higher isolated yields.

Summary

While our main attention has focused on the in situ carboxylation–cycloaddition, we should not lose sight of the ability to effect a cycloaddition of the silyl-substituted TMM. As outlined in eq 11, simple switching of the leaving group generates two quite

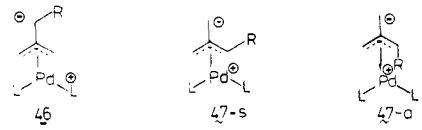


(11)

differently substituted cycloadducts, the silyl- or carboxyl-substituted methylenecyclopentenes.

The regioselectivity of the silyl-substituted TMM intermediate with triisopropyl phosphite as a ligand is quite unusual. The facts that all previous substituents showed a high selectivity and that silicon stabilizes an adjacent carbanion center[5] led to the expectation that the silicon substituent should also have shown high regioselectivity. The 0.7:1 selectivity observed with a (triisopropyl phosphite)palladium(0) catalyst is thus unexpected.

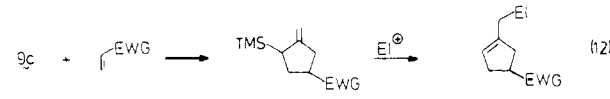
Using Fenske–Hall calculations,[23] we noted that the TMM–PdL_2 complex **46** is the more stable complex regardless of the electronic nature of R (R = CH_3, OH, CN).[24,25] Indeed, reaction



46 47-s 47-a

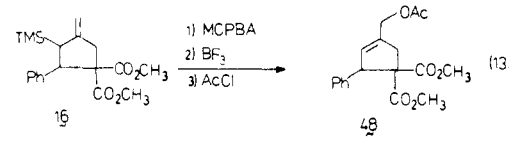
via this intermediate accounts for the regioselectivity of the cycloadducts. For R = SiH_3, these calculations suggest that **47a** is the most stable form.[25] Thus, theory predicts that the silyl-substituted TMM should indeed lead to products like **13** and **14** (Scheme II) observed experimentally. The fact that substantial amount of product still derived from **46** may derive from the unfavorable nonbonded steric interactions between the silicon substituent and the palladium template in **47a**. Experimental support for this conjecture derives from the observation that increasing the effective steric bulk of the ligands on palladium dramatically increased the amount of the product derived from **46**. Indeed, using triphenylphosphine ligands on palladium and the trimethylsilyl substituent, very good regioselectivity via **46** was observed for a number of acceptors. *Thus, it appears that the regioselectivity preference for formation of cycloadducts via* **46** *may arise due to both electronic and steric factors.*

The regiocontrolled formation of allylsilanes in the cycloaddition provides a quite versatile synthetic intermediate. As shown in eq 12, subsequent reactions with electrophiles can provide regio-



(12)

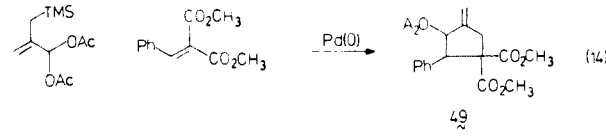
controlled electrophilic substitution.[5] As a simple illustration, the allylsilane **16** is converted regioselectively into the allyl acetate **48** as depicted in eq 13. By using the direct cycloaddition of the



(13)

16 48

acetoxy TMM intermediate, the regioisomeric allyl acetate **49** is available (eq 14).[3]



(14)

49

The carboxylation–cycloaddition is the first reported instance of carboxylation accompanying use of carbonates as leaving groups in palladium-catalyzed reactions.[26] Its potential for further applications remains an exciting challenge.

Experimental Section

Preparation of 1-(Trimethylsiloxy)-2-[(trimethylsilyl)methyl]-3-(trimethylsilyl)prop-2-ene (9a). A 500-mL three-neck flask equipped with

(19) Trost, B. M.; Mignani, S. M. *Tetrahedron Lett.* **1986**, *27*, 4137. Trost, B. M.; Lynch, J.; Renaut, P. *Tetrahedron Lett.* **1985**, *26*, 6313.

(20) Cf. Diels–Alder reactions, see: Mulzer, J.; Kappert, M.; Huttner, G.; Jibul, I. *Tetrahedron Lett.* **1985**, *26*, 1631.

(21) Also, codimerization of methylenecyclopropane with cyclohexenone fails. See: Balavoine, G.; Eskenazi, C.; Guillemot, M. *J. Chem. Soc., Chem. Commun.* **1979**, 1109.

(22) However, for Lewis acid catalyzed reactions, see: Angell, E. C.; Fringuelli, F.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1985**, *50*, 4696 and earlier references cited therein.

(23) Fenske, R. F.; Hall, M. B. *Inorg. Chem.* **1972**, *11*, 768.

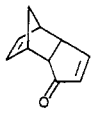
(24) Gordon, D. J.; Fenske, R. F.; Nanninga, T. N.; Trost, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 5974.

(25) Gordon, D. J. Ph.D. Thesis, University of Wisconsin, 1982.

(26) For the first use of carbonates in Pd(0)-catalyzed reactions, 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: Amsterdam, 1981; pp 75–93. For extensive development of this leaving group, see: Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.

(27) We synthesized the *Z* enoate **39** by performing the Emmons–Wadsworth–Horner reaction with trimethyl phosphonoacetate with LDA in THF and the acetonide of (*R*)-glyceraldehyde containing some acetic acid (Renaut, P., unpublished work in these laboratories): $]\alpha]^{25}_D$ +98.54° (*c* 5.48, $CHCl_3$); IR ($CDCl_3$) 1705 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.35 (dd, *J* = 12.0, 6.8 Hz, 1 H), 5.82 (dd, *J* = 12.0, 1.5 Hz, 1 H), 5.45 (dq, *J* = 7.2, 1.5 Hz, 1 H), 4.35 (dd, *J* = 9.0, 7.2 Hz, 1 H), 3.69 (s, 3 H), 3.60 (dd, *J* = 9.0, 7.2 Hz, 1 H), 1.43 (s, 3 H), 1.37 (s, 3 H); calcd for $C_9H_{14}O_4$ 186.0656, found 186.0658.

Table IV. Experimental Details for Carboxylation–Cycloaddition

entry	acceptor: mg, mmol	**9d**, mg, mmol	catalyst, mg	solvent, mL	time, h	product:mg, % yield (*E*:*Z*)
1	**22** (R = CH_3): 80, 0.55	150, 0.55	12	3	10	**23** (R = CH_3): 81, 61 (73:27)
2	**22** (R = Ph): 75, 0.36	100, 0.36	8.3	2	5	**23** (R = Ph): 85, 77 (80:20)
3	**22** (R = CH=CHPh): 130, 0.55	150, 0.55	12	2	36	**23** (R = CH=CHPh): 110, 62 (70:30)
4	**24** (R = H): 38, 0.55	150, 0.55	12	1.5	37	**25** (R = H): 34, 37 (85:15)
5	**24** (R = OCH_3): 36, 0.36	100, 0.36	8.3	2	40	**25** (R = OCH_3): 28, 40 (23:77)
6	**26** (*n* = 1): 30, 0.36	100, 0.36	*a*	2	41	**27** (*n* = 1): 27, 41 (50:50)
7	**26** (*n* = 2): 70, 0.73	200, 0.73	*b*	2	49	**27** (*n* = 2): 70, 49 (50:50)
8	**28** (R = COPh): 100, 0.55	150, 0.54	12	2.5	6	**29** (R = COPh): 77, 70 (100:0)
9	**28** (R = SO_2Ph): 170, 0.73	200, 0.72	16	3	7	**29** (R = SO_2Ph): 150, 66 (100:0)
						
10	80, 0.54	150, 0.54	12	3	5	**30**: 90, 68 (31:69)
11	coumarin: 100, 0.73	200, 0.73	16	3.5	7	**31**: 140, 81 (100:0)
12	2-(methoxymethylene)-1-tetralone: 67, 0.36	100, 0.36	8.3	2	5	**32**: 53, 51 (33:67)
13	**33** (R = Ph): 80, 0.36	100, 0.36	8.3	2	6	**34** (R = Ph): 70, 61 (100:0)
14	**33** (R = 3-$CH_3OC_6H_4$): 90, 0.36	100, 0.36	8.3	2.5	8	**34** (R = 3-$CH_3OC_6H_4$): 89, 59 (66:34)
15	**33**: 77, 0.36	100, 0.36	8.3	2.0	6	34: 78, 70 (59:41)
16	**33** (R = *i*-C_3H_7): 68, 0.36	100, 0.36	8.3	2.0	9	**34** (R = *i*-C_3H_7): 60, 57 (73:27)
17	**33** (R = PhCH=CH): 130, 0.54	150, 0.54	12	3.5	10	**35**: 110, 60 (75:25)
18	**36**: 100, 0.54	150, 0.54	12	1	6	**37**: 82, 54 (100:0) **38**: 20, 13 (50:50)
19	**39**:[c] 100, 0.54	150, 0.54	12	1	6	**40**: 100, 66 (100:0)

[a] Catalyst consisted of 1.6 mg of palladium acetate and 0.012 mL of triisopropyl phosphite. [b] Catalyst consisted of 3.2 mg of palladium acetate and 0.024 mL of triisopropyl phosphite. [c] Reference 27.

a mechanical stirrer was charged with *n*-butyllithium (1.5 M in hexane, 110 mL, 200 mmol), the bulk of the hexane was removed in vacuo, and 60 mL of anhydrous ether and TMEDA (35 mL, 232 mmol) were added. 2-[(Trimethylsilyl)methyl]-2-propen-1-ol (11.0 g, 76.4 mmol) was added dropwise over 15 min at −30 °C. THF (30 mL) was then added. The reaction was allowed to warm to room temperature and then stirred mechanically for 2 h. The reaction was quenched with trimethylchlorosilane (35 mL, 275 mmol) at −60 °C, and the dark reaction mixture was allowed to stir for 10 min before diluting with 20 mL of ether. The cloudy mixture was then washed with saturated sodium bicarbonate (1 × 100 mL), water (1 × 100 mL), saturated copper sulfate (2 × 100 mL), water (1 × 100 mL), and saturated sodium chloride (1 × 100 mL), dried over anhydrous potassium carbonate, concentrated by atmospheric distillation, and then distilled (Kugelrohr, 1 mmHg, 50 °C) to give a colorless oil (20.4 g, 91%) of greater than 90% purity: TLC R_f 0.77 (1:10, ether/pentane); IR ($CDCl_3$) 1605, 1445, 1405, 1370, 840 cm^{-1}; ^1H NMR (100 MHz) δ 5.25 (s, 1 H), 3.90 (s, 2 H), 1.66 (s, 2 H), 0.04 (s, 9 H), 0.02 (s, 9 H), 0.01 (s, 9 H); ^{13}C NMR (15.01 MHz) δ 154.0, 117.0, 68.4, 23.7, 0.39, −0.49, −0.61; calcd for $C_{13}H_{32}OSi_3$ 288.1761, found 288.1761.

Preparation of 2-[(Trimethylsilyl)methyl]-3-(trimethylsilyl)prop-2-en-1-ol (9b). To a solution of 1-(trimethylsiloxy)-2-[(trimethylsilyl)-methyl]-3-(trimethylsilyl)propene (2.0 g, 6.9 mmol) in 12 mL of THF was added 3.1 mL of 1 N sulfuric acid. The mixture was then stirred for 90 min, after which potassium carbonate was added until bubbling ceased. The organic layer was then separated, the aqueous layer was extracted with ether (10 mL), and the combined organic layers were dried over magnesium sulfate. The solvent was distilled at atmospheric pressure to yield a colorless oil, which was carried onto the next step without further purification: TLC R_f 0.22, (1:10, ether/pentane); IR ($CDCl_3$) 3605, 3444, 1725, 1605, 1410, 830 cm^{-1}; ^1H NMR (100 MHz) δ 5.28 (s, 1 H), 3.90 (s, 2 H), 3.60 (br s, 1 H), 1.68 (s, 2 H), 0.08 (s, 9 H), 0.02 (s, 9 H); ^{13}C NMR (15.04 MHz) δ 155.4, 117.2, 68.4, 24.4, 0.6, −0.4; calcd for $C_{10}H_{24}OSi_2$ 216.1365, found 216.1345.

Preparation of 1-Acetoxy-2-[(trimethylsilyl)methyl]-3-(trimethylsilyl)prop-2-ene (9c). To a solution of 2-[(trimethylsilyl)methyl]-3-(trimethylsilyl)propen-1-ol (1.5 g, 6.9 mmol) in pyridine (2.0 mL, 25 mmol) and CH_2Cl_2 (30 mL) at 0 °C was added acetyl chloride (1.1 mL, 16 mmol) dropwise via syringe over a period of 10 min. The white cloudy mixture was then stirred for a further 30 min and then diluted with 100 mL of ether. The ether solution was washed with saturated sodium carbonate (2 × 30 mL), saturated copper sulfate (2 × 20 mL), and water (1 × 20 mL), dried over anhydrous potassium carbonate, and then distilled (Kugelrohr, 0.03 mmHg, 50 °C) to give 1.4 g (5.4 mmol, 77% for both steps) of a colorless liquid: TLC R_f 0.44 (1:10, ether/pentane); IR ($CDCl_3$) 1735, 1608, 1370, 840 cm^{-1}; ^1H NMR (100 MHz) δ 5.22 (s, 1 H), 4.37 (s, 2 H), 2.02 (s, 3 H), 1.70 (s, 2 H), 0.02 (s, 9 H), 0.00 (s, 9 H); ^{13}C NMR (15.4 MHz) δ 170.1, 150.1, 121.5, 69.8, 24.5, 20.1, 0.27, −0.72; calcd for $C_{12}H_{26}O_2Si_2$ 258.1464, found 258.1344.

Preparation of 2-[(Trimethylsilyl)methyl]-3-(trimethylsilyl)prop-2-en-1-yl Methyl Carbonate (9d). To a −78 °C solution of 2-[(trimethylsilyl)methyl]-3-(trimethylsilyl)propen-1-ol (5.0 g, 23 mmol) in 40 mL of THF was added *n*-butyllithium (1.5 M in hexane, 15.4 mL, 23 mmol). After the mixture was stirred for 15 min, methyl chloroformate (3.55 mL, 46 mmol) was added over 15 min, and the reaction was allowed to stand for 12 h at −6 °C. Addition of 100 mL of water and 200 mL of ether, separation of the organic layer, washing of the latter with 50 mL of saturated sodium bicarbonate, drying over anhydrous potassium carbonate, and concentration in vacuo gave material that was directly chromatographed (5% EtOAc in hexane) to yield 5.4 g (85%) of pure material. It was distilled directly prior to use: bp 80 °C (~0.5 mmHg); TLC R_f 0.67 (4:1, hexane/EtOAc); IR ($CDCl_3$) 1745, 1610, 1445, 860 cm^{-1}; ^1H NMR (270 MHz) δ 5.29 (s, 1 H), 4.46 (s, 2 H), 3.77 (s, 3 H), 1.73 (s, 2 H), 0.08 (s, 9 H), 0.04 (s, 9 H); ^{13}C NMR (15.04 MHz) δ 155.3, 149.2, 121.9, 73.1, 54.8, 24.5, 0.5, −0.5; calcd for $C_{12}H_{26}O_3Si_2$ 274.1413, found 274.1420.

Cycloadditions of 9c. General Procedure. Palladium acetate (2–4 mol %) and ligand (5–7 equiv with respect to palladium) were added to the reaction flask in a glovebag. The flask was fitted with a septum and solvent added. After a homogeneous solution was obtained (warming may be necessary), the reductant was added at room temperature. After the resultant mixture was stirred at room temperature for 10 min, the acceptor and the substrate were added, and the reaction was heated at the specified temperature until completion as determined by TLC monitoring. The reaction was concentrated by distillation and the residue purified by flash chromatography with 10:1 pentane/ether. Table III summarizes the details for the cycloaddition to dimethyl benzylidenemalonate and appears in the supplementary material.

4,4-Dicarbomethoxy-3-phenyl-1-[(trimethylsilyl)methylene]cyclopentane (13). These data correspond to a 57:43 ratio of diastereomers: IR ($CDCl_3$) 1732, 1645, 1632, 1609, 1502, 1460, 1430, 842 cm^{-1}; ^1H NMR (270 MHz) δ 7.24 (m, 5 H), 5.5 (s, H), 4.99 (s, 0.43 H), 4.93 (s, 0.57 H), 4.01 (m, 1 H), 3.74 (s, 1.3 H), 3.70 (s, 1.7 H), 3.34 (s, 1.3 H), 3.31 (s, 1.7 H), 3.3–2.7 (m, 4 H), 0.14 (s, 3.9 H), 0.11 (s, 5.1 H); ^{13}C NMR (15.4 MHz) δ 171.7, 170.2, 169.6, 156.2, 151.0, 140.8, 140.5, 128.3, 128.1, 127.7, 126.8, 121.3, 105.5, 68.5, 65.8, 52.7, 52.1, 51.9, 51.7, 50.4, 49.0, 42.6, 41.2, 40.1, 39.7, −0.2, −0.8; calcd for $C_{19}H_{26}O_4Si$ 346:1598, found 346.1600.

4,4-Dicarbomethoxy-3-phenyl-5-(trimethylsilyl)-1-methylenecyclopentane (14): ^1H NMR (270 MHz) δ 7.25–7.15 (m, 5 H), 4.79 (s, 1 H), 4.58 (s, 1 H), 3.85 (dd, *J* = 10.0, 5.0 Hz, 1 H), 3.63 (s, 3 H), 3.07 (s, 3 H), 3.00 (br s, 1 H), 2.38 (m, 2 H), 0.04 (s, 9 H); calcd for $C_{19}H_{26}O_4Si$ 346.1598, found 346.1600.

4,4-Dicarbomethoxy-3-phenyl-2-(trimethylsilyl)-1-methylenecyclopentane (15). These data correspond to a 50:50 ratio of diastereomers: IR ($CDCl_3$) 1728, 1645, 1494, 1451, 1435, 850 cm^{-1}; ^1H NMR (270

MHz) δ 7.3–7.1 (m, 5 H), 5.01 (br s, 0.5 H), 4.97 (br s, 1 H), 4.79 (br s, 0.5 H), 4.12 (s, J = 8.8 Hz, 0.5 H), 4.08 (d, J = 7.4 Hz, 0.5 H), 3.75 (s, 1.5 H), 3.70 (s, 1.5 H), 3.60 (d, J = 16.8 Hz, 0.5 H), 3.25 (s, 1.5 H), 3.23 (s, 1.5 H), 3.20 (d, J = 13.5 Hz, 0.5 H), 3.04 (d, J = 16.8 Hz, 0.5 H), 2.84 (m, 1 H), 2.48 (d, J = 8.8 Hz, 0.5 H), −0.06 (s, 4.5 H), −0.14 (s, 4.5 H); ^{13}C NMR (15.4 MHz) δ 172.4, 172.1, 170.0, 169.6, 151.0, 141.1, 139.6, 129.4, 128.5, 127.5, 127.3, 126.2, 126.0, 105.9, 103.9, 66.1, 65.6, 54.5, 53.2, 52.9, 52.5, 52.3, 52.0, 44.6, 40.6, 40.1, 39.3, −0.8, −2.7; calcd for $C_{19}H_{26}O_4Si$ 346.1598, found 346.1600.

Cycloaddition of 9c with 17. Preparation of 18. According to the above general procedure, 106 mg (0.73 mmol) of **17**, 164 mg (0.64 mmol) of **9c**, 5 mg (3.5 mol %) of palladium acetate, 29 mg (5 mol %) of triisopropyl phosphite, and 0.15 mL of a 1.5 M solution of DIBAL-H in hexane (6 mol %) in 2 mL of dioxane at 100 °C for 16 h gave 82 mg (56% yield) of **18**: TLC R_f 0.67 (4:1, hexane/EtOAc); IR ($CDCl_3$) 1722, 1618, 1442, 845 cm^{-1}; ^{1}H NMR (270 MHz) δ 6.21 (m, 1 H), 6.13 (br s, 2 H), 6.03 (m, 1 H), 4.80 (s, 1 H), 4.75 (s, 1 H), 4.65 (s, 1 H), 4.50 (s, 1 H), 3.15 (m, 2 H), 3.03 (m, 2 H), 2.90 (m, 1 H), 2.70–2.25 (m, 10 H), 1.95 (m, 1 H), 1.68 (m, 2 H), 1.50 (m, 2 H), 1.36 (m, 2 H), 0.15 (s, 9 H), 0.01 (s, 9 H); ^{13}C NMR (15.4 MHz) δ 149.6, 137.2, 136.4, 136.2, 135.6, 134.9, 134.5, 56.3, 55.2, 54.9, 54.0, 53.1, 52.3, 51.9, 50.6, 49.6, 48.6, 47.5, 46.8, 45.8, 45.5, 44.7, 44.5; calcd for $C_{17}H_{24}OSi$ 272.1590, found 272.1596.

Cycloaddition of 9c with Coumarin. Preparation of 20. According to the above general procedure, 105 mg (0.74 mmol) of coumarin, 150 mg (0.58 mmol) of **9c**, 5.0 mg (3.5 mol %) of palladium acetate, 29 mg (5 mol %) of triisopropyl phosphite, and 0.15 mL of a 1.5 M solution of DIBAL-H in hexane (6 mol %) in 2 mL of dioxane at 100 °C for 16 h gave 107 mg (62% yield) of **20**: TLC R_f 0.62 (4:1, hexane/EtOAc); IR ($CDCl_3$) 1755, 1476, 1450, 840 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.20 (m, 2 H), 7 11 (m, 1 H), 7.00 (m, 1 H), 4.84 (br s, 1 H), 4.69 (br s, 1 H), 3.49 (dd, J = 7.7, 4.8 Hz, 1 H), 3.10 (q, J = 7.7 Hz, 1 H), 2.74 (dd, J = 15.0, 7.7 Hz, 1 H), 2.69 (ddd, J = 15.0, 7.7, 2.0 Hz, 1 H), 2.28 (dd, J = 4.8, 2.0 Hz, 1 H), 0.12 (s, 9 H); Irrad. δ 3.10 (3.49 (d, J = 4.8 Hz), 2.74 (d, J = 15.0 Hz), 2.69 (dd, J = 15.0, 2.0 Hz)); Irrad. δ 2.28 (3.49 (d, J = 4.8 Hz), 2.65 (dd, J = 15.0, 7.7 Hz)); ^{13}C NMR (15.04 MHz) δ 169.2, 156.2, 150.5, 148.6, 140.0, 128.1, 124.3, 116.9, 105.5, 43.5, 41.1, 38.2, −1.9; calcd for $C_{16}H_{20}O_2Si$ 272.1227, found 272.1231.

Cycloaddition Reactions of 9d. General Procedures. Method 1. Into the reaction flask in a glovebag under nitrogen was placed 2 mol % of tetrakis(triphenylphosphine)palladium. Subsequently, 1 equiv of 2-[(trimethylsilyl)methyl]-1-(trimethylsilyl)propen-3-yl methyl carbonate, 1 equiv of the acceptor, and enough toluene to form a 0.35–0.75 M solution was added and the reaction heated at 80 °C for the stated time. Upon cooling the reaction was diluted with 20 mL of an aqueous buffer solution and 20 mL of chloroform. The layers were separated, the organic layer was dried over magnesium sulfate, and the solvents were removed in vacuo. Flash chromatography on silica gel, to which was added 5% water, and elution with 4:1 chloroform/methanol gave the pure adducts. Table IV summarizes the details. Characterization data appears as supplementary material.

Method 2. To 2 mol % palladium acetate was added 14 mol % triisopropyl phosphite in 1 mL of toluene or dioxane. Sequentially, 1 equiv of the bis(silyl) carbonate **9d**, 1 equiv of the acceptor, and enough additional solvent to form a 0.35–0.75 M solution was added. The reaction was heated at 80 °C for the stated time and worked up as above.

Specific Example (23, R = Ph). To a yellow solution of 8.3 mg (2 mol %) of tetrakis(triphenylphosphine)palladium in 1 mL of toluene was added 100 mg (0.36 mmol) of **9d** and 75 mg (0.36 mmol) of (*E*)-benzylideneacetophenone in 1 mL of toluene. The resulting solution was heated at 80 °C for 5 h, at which time TLC showed disappearance of starting materials. After workup according to the general procedure, 85 mg (77%) of an 80:20 trans to cis mixture of pure cycloadducts was obtained as a colorless oil, which solidified upon standing: mp 170–171 °C, TLC R_f 0.60 (4:1, chloroform/methanol); IR (C_6H_6) 3400–2500, 1700, 1680, 850 cm^{-1}; ^{1}H NMR (270 MHz, DMSO) δ 12.0 (s, 1 H), 7.8–8.0 (m, 2 H), 7.4–7.7 (m, 4 H), 7.0–7.3 (m, 4 H), 5.0 and 5.1 (two s, 2 H), 4.75 (q, J = 9 Hz) and 4.25 (dt, J = 10.5, 8.1 Hz) (total 1 H), 3.95 (dd, J = 9.0, 7.5 Hz) and 3.55 (dd, J = 10.5, 2.5 Hz) (total 1 H), 3.80 (d, J = 7.5, Hz 1 H), 3.12 (dd, J = 15.8, 9.0 Hz) and 2.90 (dd, J = 16.5, 7.4 Hz) (total 1 H), 2.35 (dd, J = 15.8, 9.0 Hz, 1 H); ^{13}C NMR (50.3 MHz, DMSO; *E* only) δ 200.4, 172.8, 147.8, 139.0, 136.1, 134.1, 128.9, 128.1, 127.9, 127.6, 126.3, 109.3, 55.6, 49.3, 47.5, 37.2; calcd for $C_{20}H_{18}O_3$ 306.1256, found 306.1261.

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Registry No. (*E*)-**9a**, 112373-90-7; (*Z*)-**9a**, 112374-24-0; (*Z*)-**9b**, 112373-91-8; (*Z*)-**9c**, 112373-92-9; (*Z*)-**9d**, 112373-93-0; (±)-(*E*)-**13**, 112373-94-1; (±)-(*Z*)-**13**, 112373-95-2; **14**, 112373-96-3; (±)-*cis*-**15**, 112373-97-4; (±)-*trans*-**15**, 112373-98-5; (±)-**16**, 112374-00-2; **17**, 112374-03-5; **18**, 112373-99-6; **19**, 91-64-5; (±)-**20**, 112455-91-1; (*E*)-**22** (R = CH_3), 1896-62-4; (*E*)-**22** (R = Ph), 614-47-1; (*E*)-**22** (R = *E*-CH=CHPh), 35225-79-7; (±)-*trans*-**23** (R = CH_3), 112374-04-6; (±)-*cis*-**23** (R = CH_3), 112455-94-4; (±)-*trans*-**23** (R = Ph), 112455-92-2; (±)-*cis*-**23** (R = Ph), 112455-93-3; (±)-*trans*-**23** (R = *E*-CH=CHPh), 112374-05-7; (±)-*cis*-**23** (R = *E*-CH=CHPh), 112455-95-5; **24** (R = H), 78-94-4; (*E*)-**24** (R = OCH_3), 51731-17-0; (±)-*trans*-**25** (R = H), 112374-06-8; (±)-*cis*-**25** (R = H), 112374-07-9; (±)-*trans*-**25** (R = OCH_3), 112374-08-0; (±)-*cis*-**25** (R = OCH_3), 112455-96-6; **26** (*n* = 1), 930-30-3; **26** (*n* = 2), 930-68-7; (±)-*trans*-**27** (*n* = 1), 112374-09-1; (±)-*cis*-**27** (*n* = 1), 112374-10-4; (±)-*trans*-**27** (*n* = 2), 112374-11-5; (±)-*cis*-**27** (*n* = 2), 112374-12-6; (±)-**28** (R = COPh), 112374-01-3; (±)-**28** (R = SO_2Ph), 112374-02-4; (±)-**29** (R = COPh), 112374-13-7; (±)-**29** (R = SO_2Ph), 112374-14-8; (±)-*trans*-**30**, 112374-15-9; (±)-*cis*-**30**, 112458-27-2; (±)-**31**, 112455-97-7; (±)-*trans*-**32**, 112455-98-8; (±)-*cis*-**32**, 112455-99-9; **33** (R = Ph), 6626-84-2; **33** (R = C_6H_4-3-OCH_3), 22621-56-3; **33** (R = 2-furyl), 74299-84-6; **33** (R = *i*-C_3H_7), 36825-11-3; **33** (R = *E*-CH=CHPh), 66684-74-0; (±)-*trans*-**34** (R = Ph), 112374-16-0; (±)-*trans*-**34** (R = C_6H_4-3-OCH_3), 112374-17-1; (±)-*cis*-34 (R = C_6H_4-3-OCH_3), 112374-18-2; (±)-*trans*-**34** (R = 2-furyl), 112374-19-3; (±)-*cis*-**34** (R = 2-furyl), 112374-20-6; (±)-*trans*-**34** (R = *i*-C_3H_7), 112374-21-7; (±)-*cis*-**34** (R = *i*-C_3H_7), 112374-22-8; (±)-*trans*-**35**, 112374-23-9; (±)-*cis*-**35**, 112456-00-5; (*S*)-(*E*)-**36**, 81703-93-7; **37**, 112456-01-6; *trans*-**38**, 112456-02-7; *cis*-**38**, 112456-03-8; (*S*)-(*Z*)-**39**, 81703-94-8; **40**, 112456-04-9; $(Ph_3P)_4Pd$, 14221-01-3; $Pd(OAc)_2$, 3375-31-3; $(i\text{-}C_3H_7O)_3P$, 116-17-6; Ph_3P, 603-35-0; CH_2=C(CH_2OH)CH_2TMS, 81302-80-9; $(CH_3O)_2P(O)CH_2CO_2CH_3$, 5927-18-4; (*Z*)-2-(methoxymethylene)-1-tetralone, 40685-29-8; (*R*)-glyceraldehyde acetonide, 15186-48-8.

Supplementary Material Available: General methods, variations in the cycloaddition of **9c** with dimethyl benzylidenemalonate (Table III), and cycloadduct characterization for all adducts of Table IV (7 pages). Ordering information is given in any current masthead page.