Synthesis and Chemistry of Alkylpalladium Compounds Prepared via Vinylpalladation of Bicyclic Alkenes[1]

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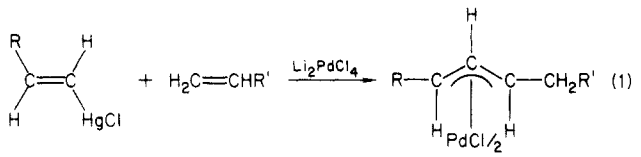
Vinylmercuric chlorides, Li_2PdCl_4, and bicyclic alkenes react to form stable, isolable adducts (**1–9**) in which the vinyl and PdCl groups have been added in a cis, exo fashion across the carbon–carbon double bond. Norbornadiene under the same conditions affords an endo nortricyclyl adduct **10**. These compounds have been fully characterized and undergo reactions with $CO–CH_3OH–Et_3N$, $NaBH_4$, $NaOCH_3–CH_3OH$, H_2, RLi, CuCN, and $Pb(OAc)_4$ to give methyl esters, reduced alkanes and alkenes, cross-coupled hydrocarbons, nitriles, and acetates.

The addition of π-allyl,[3-8] aryl,[10-13] heterocyclic,[14] and benzylic[15] organopalladium compounds to bicyclic alkenes is a well-known reaction. The vinylpalladation of olefins has received less attention. Acyclic[16] and monocyclic[1] olefins have been observed to afford π-allylpalladium compounds in such reactions (eq 1). Prior to our preliminary communication,[1] there was only one example of the vinylpalladation of a bicyclic olefin and that involved norbornadiene, which was observed to form a nortricyclyl derivative (eq 2).[17] Recently, Chiusoli and co-workers



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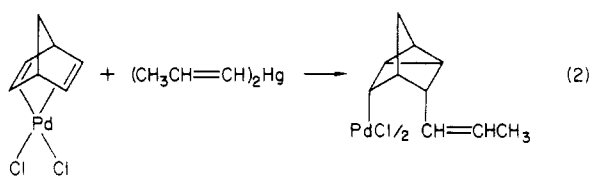
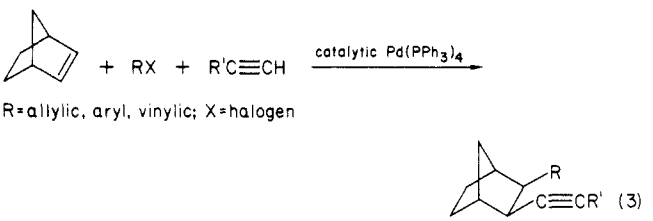


(2)

reported a palladium-catalyzed allyl-, aryl-, or vinylpalladation approach to bicyclic alkynes (eq 3).[18,19] We have observed that the reaction of vinylmercuric chlorides, Li_2PdCl_4, and bicyclic olefins affords stable, cis, exo alkylpalladium adducts.[1] We wish now to report full details on the preparation and chemistry of these bicyclic alkylpalladium compounds.



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Results and Discussion

Preparation. Using a procedure essentially identical with that used earlier for the reaction of vinylmercurials, Li_2PdCl_4, and acyclic[16] or monocyclic[1] alkenes, we have been able to isolate alkylpalladium compounds from a variety of bicyclic olefins. The results are summarized in Table I.

The reaction has proven to be quite general. Norbornene reacts with Li_2PdCl_4 and a wide variety of vinylmercurials to afford the corresponding cis, exo norbornylpalladium compounds in high crude yield. Recrystallization, usually from methylene chloride, resulted in significant losses of material, but modest yields of purified product could be obtained. In general, 10 equiv of olefin proved superior to equivalent amounts (see entry 3, Table I), but with higher boiling olefins, purification of the organopalladium product became difficult and it was desirable to use only 1–1.2 equiv of olefin (entries 7, 8, 10). Introducing the diaza function into norbornene (entry 7) did not seem to significantly lower the yield, but due to purification problems, it was desirable to use only 1.1 equiv of olefin. However, less strained olefins than norbornene afforded sharply reduced yields (entries 8, 9). Norbornadiene was observed to give the corresponding nortricyclylpalladium compound in high yield even when only 1.1 equiv of diene was employed (entry 10).

Characterization. The organopalladium compounds reported in Table I have been fully characterized by ^1H NMR and IR spectral analysis, as well as elemental analysis, and have been shown to be consistent with the structures reported in Table I.

The infrared spectral data provides interesting information on the bonding in these organopalladium compounds. The usual strong absorption found between 960

(1) For a preliminary communication, see: Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, *22*, 5231.
(2) Present address: College of Liberal Arts and Sciences, Okayama University, Tsushima, Okayama 700, Japan.
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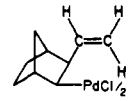
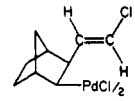
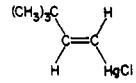
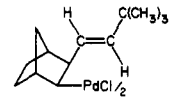
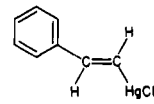
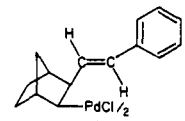
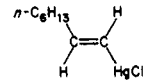
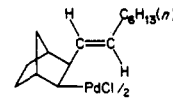
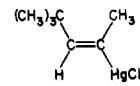
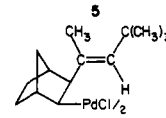
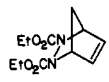
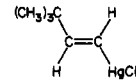
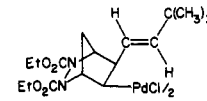
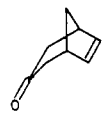
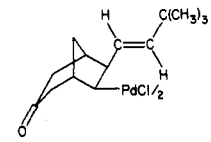
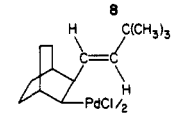
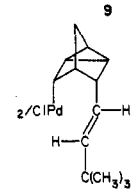
Table I. Vinylpalladation of Bicyclic Olefins

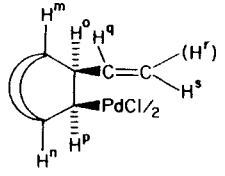
entry	olefin[a]	vinylmercurial	product	% yield[b]
1		$H_2C{=}CHHgCl$	 **1**	63 (46), 70 (40)
2			 **2**	77 (40)
3			 **3**	89 (39), 89 (45), 50 (29)[c]
4			 **4**	58 (22), (38)
5			 **5**	85 (46)
6			 **6**	88 (58)
7			 **7**	45 (15)[c]
8			 **8**	16 (10)[c]
9			 **9**	15 (8)
10			 **10**	84 (44)[c]

[a] 10 equiv of olefin was employed except where indicated. [b] Crude yield (recrystallized yield); multiple entries indicate multiple runs. [c] 1.0–1.2 equiv of bicyclic olefin was employed.

and 980 cm^{-1} in simple *trans*-olefins is not always observed in organopalladium compounds such as compounds **3** and **5–10**. However, a weak olefinic absorption consistently appears near 1540 cm^{-1} instead of 1670 cm^{-1}, as expected for trans disubstituted olefins. Coordination of the olefin to palladium perhaps accounts for this shift. Analogous shifts are observed when comparing norbornadiene (1640, 1535, and 1445 cm^{-1}) and norbornadiene palladium dichloride (1460, 1410, 1305 cm^{-1}). Other functionalized derivatives displayed absorptions corresponding to the appropriate functionality in addition to the usual alkyl absorptions.

The ^1H NMR spectral data for all new organopalladium compounds except the nortricyclyl compound **10**, as measured on a 100-MHz instrument, are tabulated in Table II. The terminal vinyl hydrogen (the vinyl hydrogen which is furthest from the bicyclic skeleton) possesses a typical to slightly downfield chemical shift, while the internal vinyl hydrogen (the vinyl hydrogen closest to the bicyclic skeleton) appears appreciably upfield. The shielding effect of an exo palladium adjacent to an exo vinyl moiety is one possible explanation for these observed chemical shifts, since the exo–exo geometry may place the internal vinyl hydrogen closer to the palladium atom. The observed coupling constants between the two vinyl hydrogens present in most of our compounds are approximately 14 Hz, which is consistent with the presence of trans vinyl hydrogens. The reason for the low coupling

Table II. ^{1}H NMR Spectral Data of the Bicyclic Organopalladium Compounds[a]



	δ (mult, J/Hz)							
compd	H^m	H^n	H^o	H^p	H^q	H^r	H^s	other H
1	2.34 (m)	2.55 (m)	2.65 (d, J = 9)	2.82 (dd, J = 3, 9)	4.0–4.5 (2 H, m)		4.82 (dd, J = 2, 14)	0.9–1.7 (6 H, m norbornyl)
2	2.4 (m)	2.6 (m)	3.2 (m)	2.7 (m)	4.2 (dd, J = 5, 5)[b]		5.8 (dd, J = 1.5, 5)	1.1–1.7 (6 H, m, norbornyl)
3	2.30 (m)	2.68 (m)	2.78 (d, J = 11)	2.98 (d, J = 11)	3.98 (dd, J = 3, 14)		5.80 (d, J = 14)	0.9–1.6 (6 H, m, norbornyl), 1.12 (9 H, s, t-Bu)
4[c]	2.26 (m)	2.50[d] (m)	2.80 (m)	3.30–3.40[d] (m)	5.24 (dd, J = 3, 14)		6.97 (d, J = 14)	0.85–1.4 (6 H, m, norbornyl), 7.55–7.95 (5 H, m, aryl)
5	2.65 (2 H, m)		2.80 (2 H, m)		3.97 (dd, J = 3, 14)		5.60 (m)	0.9–1.17 (17 H, m, aliphatic), 2.28 (2 H, m, allylic)
6	2.38 (m)	2.64 (m)	2.80 (d, J = 10)	2.88 (d, J = 10)			5.13 (s)	0.9–1.6 (6 H, m, norbornyl), 1.25 (9 H, s, t-Bu), 1.84 (3 H, s, Me)
7	2.94 (2 H, m)		3.38 (m)	3.50 (d, J = 12)	4.77 (m)		5.88 (d, J = 14)	1.10–1.20 (2 H, m, bridge), 1.20 (9 H, s, t-Bu), 1.28 (6 H, t, J = 7 Hz, Me's), 4.2 (4 H, q, J = 7 Hz, OCH_2's)
8	2.56 (m)	2.88 (m)	3.10 (m)	3.20 (m)	3.97 (dd, J = 3, 14)		4.78 (dd, J = 1, 14)	0.9–2.0 (2 H, m, bridge), 1.18 (9 H, s, t-Bu), 2.20 (1 H, d, J = 4, CHCO), 2.30 (2 H, m, CH_2CO), 2.38 (1 H, d, J = 4, CHCO)
9	2.0 (2 H, m)		2.95 (2 H, m)		4.23 (dd, J = 3, 14)		6.03 (d, J = 14)	0.9–1.7 (8 H, m, bicyclic), 1.2 (9 H, s, t-Bu)

[a] Measured on a Varian HA-100 in $CDCl_3$ unless otherwise indicated. [b] Apparent triplet. [c] Measured in d_6-DMSO. [d] Partially obscured by d_6-DMSO.

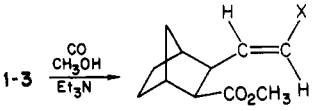
constant of 5 Hz observed in compound **2** is unclear. Carbonylation of compound **2**, as described later, supports the *E* stereochemistry assigned to this compound. The transmetalation and olefin insertion must therefore proceed with retention of the stereochemistry present in the vinylmercurial. The internal vinyl hydrogen is also coupled more strongly to the adjacent allylic hydrogen (as demonstrated by coupling constants of approximately 3 Hz) than the terminal vinyl hydrogen, which is only weakly coupled as demonstrated by coupling constants of 0–1.5 Hz. Of the remaining protons on the bicyclic skeleton, the peak furthest downfield appears as a broad doublet or doublet of multiplets. Since the doublet is not visibly coupled further to the internal vinyl hydrogen, this signal may be tentatively assigned to the hydrogen on the carbon bearing the palladium chloride moiety. The observed coupling constants of approximately 9–12 Hz are consistent with cis, endo hydrogens observed in other norbornyl systems.[20-23] No coupling between endo hydrogens and the bridgehead hydrogens or the bridge hydrogens is discernible. Signals due to the hydrogen on the carbon bearing the vinyl group are partially visible approximately 0.15 to 0.2 ppm upfield of the previously described doublet. Unfortunately, coupling of this hydrogen to the internal vinyl hydrogen (J = 3 Hz) is not clearly discernible here, although the cis, endo coupling (J = 9–11 Hz) is just visible. Multiplets or broad singlets which may be assigned to the bridgehead hydrogens usually appear just upfield of the cis, endo hydrogens. Since the hydrogen adjacent to palladium is tentatively assigned to the furthest downfield endo doublet, the broad singlet furthest downfield is tentatively assigned to the bridgehead hydrogen nearest to palladium. The other norbornyl hydrogens were not assigned, but appear as a multiplet from δ 0.9 to 1.9. Superimposed on these multiplets are the singlet for the *tert*-butyl hydrogens or signals for other appropriate alkyl hydrogens. The functionalized examples also display the expected signals appropriate for the hydrogens of the added functionality.

Decoupling of the NMR spectrum of organopalladium compound **6** also supports the previous assignments. Irradiation at δ 2.88 produces a singlet at δ 2.80 and also sharpens the appearance of the multiplet at δ 2.64, but does not change the appearance of the multiplet at δ 2.38.

Since decoupling did not completely clarify the NMR assignments of these compounds, the effect of $Eu(fod)_3$ on the ^1H NMR spectrum of compound **3** was examined. While the lanthanide of an NMR shift reagent usually exerts its effect through coordination to an appropriate functional group, usually containing oxygen or nitrogen, and compound **3** contains no such functionality, a reversal of the typical coordination mode seemed possible. That is, the palladium might partially coordinate to the ligand of the shift reagent. Through the ligand, the lanthanide would therefore be closer to palladium to induce a shift enabling the cis, endo stereochemistry of the hydrogens to be verified. In fact, with increasing additions of $Eu(fod)_3$, one of the cis, endo hydrogen peaks and one bridgehead multiplet are shifted downfield more than the other endo hydrogen peak or bridgehead multiplet. Since the peak which is shifted most appears as a simple doublet, rather than a doublet of doublets, as expected for the hydrogen coupled to the internal vinyl hydrogen, the most shifted doublet is assigned to the endo hydrogen on the carbon bearing palladium. During this NMR shift experiment the cis, endo coupling constant of 11 Hz becomes clearly visible, confirming the presence of cis, endo hydrogens and the cis, exo addition of the vinylpalladium species to norbornene.

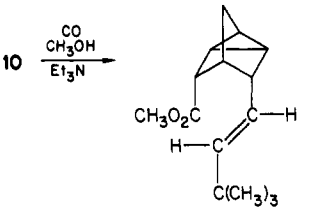
As anticipated from previous work by Vedejs and Weeks[17] with dipropenylmercury, the reaction of norbornadiene, Li_2PdCl_4, and (*E*)-(3,3-dimethyl-1-butenyl)-mercuric chloride affords the nortricyclyl compound **10**. Strongest support for the nortricyclyl structure comes from the NMR data. The ^1H NMR spectrum contains only two vinyl protons at δ 5.25 and 5.35 with a typical trans coupling constant of 14 Hz. A multiplet corresponding to the hydrogen on the carbon bearing palladium or the vinyl moiety occurs at δ 2.8. The remaining nortricyclyl hydrogens appear from δ 1.45 to 2.20. Apparently the cyclopropyl hydrogens are shifted downfield by the palladium and vinyl substituents. Our ^1H NMR spectrum is very similar to one kindly supplied to us by Vedejs for the analogous *cis*-propenyl derivative. The addition of 1 equiv of triphenylphosphine changes the ^1H NMR spectrum quite significantly. The vinyl hydrogens are shifted downfield to δ 6.05 and 6.35. The nortricyclyl hydrogens are shifted upfield. The hydrogen on the carbon bearing palladium or the vinyl moiety shifts from δ 2.8 to 2.25, and the other skeletal hydrogens shift from δ 1.45–2.20 to 0.70–2.00. The *tert*-butyl singlet, however, is shifted only slightly downfield from δ 1.24 to 1.30. The ^1H NMR spectrum of the palladium compound after triphenylphosphine addition and the observation of only two olefinic resonances in both spectra clearly rule out a norbornenyl structure.

Chemistry. We have briefly examined some of the chemistry of these new organopalladium compounds. The carbonylation of organopalladium compounds has been observed to proceed with retention of configuration.[24,25] Carbonylation therefore provides a valuable means of characterizing organopalladium compounds, as well as a useful method of synthesizing the corresponding esters. The carbonylation of compounds **1–3** and **10** in the presence of methanol and triethylamine was observed to afford high yields of the corresponding methyl esters (eq 4 and 5).



(4)

11, X = H, 78%
12, X = Cl, 94%
13, X = *t*-Bu, 78%



(5)

14, 89%

All ^1H NMR and IR spectral data for these esters were consistent with the assigned structures, thus confirming our assignment of structure for the corresponding organopalladium compounds. For ester **12**, we were also able to observe vinyl hydrogen coupling (J = 15 Hz) indicative

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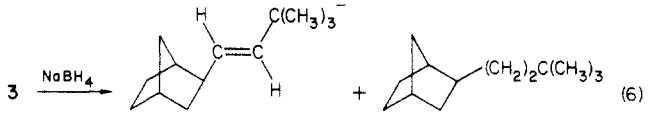
(22) Laszlo, P.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1964**, *86*, 1171.
(23) Subramanian, P. M.; Emerson, M. T.; LeBel, N. A. *J. Org. Chem.* **1965**, *30*, 2624.
(24) Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 485.
(25) Larock, R. C. *J. Org. Chem.* **1975**, *40*, 3237.

of a *trans*-alkene. The stereochemistry of ester **13** was not as obvious. However, successive additions of $Eu(fod)_3$ to this ester eventually separated the vinyl hydrogens in the ^1H NMR spectrum, enabling us to discern the olefinic coupling constant (J = 15 Hz) and the allylic coupling constant (J = 7 Hz). The internal vinyl hydrogen is shifted more than the external vinyl hydrogen in accord with a cis, exo arrangement of the ester and vinyl groups. The hydrogen on the carbon bearing the ester is also shifted faster and further downfield than the other norbornyl skeletal hydrogens. This hydrogen appears as a doublet of doublets with one coupling constant of 10 Hz, which agrees with other observed cis, endo coupling constants.[20-23] Carbonylation of the nortricyclylpalladium compound **10** also confirms its structure assignment.

We have also examined the reduction of these new organopalladium compounds. Reduction of **3** with $NaBH_4$ yielded two major products **15** and **16** (eq 6). In THF,

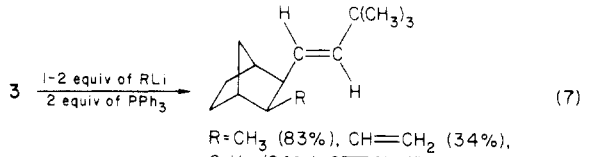


(6)

15 16

alkene **15** predominated (2:1); while in isopropyl alcohol, the hydrocarbon **16** was the major product (4:1). Hydrogen was observed to afford only compound **16**, while sodium methoxide in methanol yielded only compound **15**. Arylpalladium species have previously been reduced by sodium methoxide, presumably via palladium hydride intermediates.[26,27]

The replacement of the palladium moiety with carbanion species, such as organolithium compounds, has also been briefly investigated. Gas chromatographic analysis indicated that the reaction of compound **3** with an equivalent of either methyllithium, vinyllithium, or *n*-butyllithium in HMPA also forms the reduced hydrocarbon **15** and none of the expected alkylated products. Following a report by Murahashi and co-workers that the addition of triphenylphosphine improves the coupling of vinyllithium and arylpalladium compounds,[28] we have observed that employing 1–2 equiv of an organolithium compound and 2 equiv of triphenylphosphine produces cross-coupled product (eq 7). The stereochemistry of the

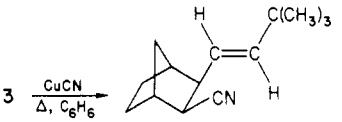


(7)

R = CH_3 (83%), $CH{=}CH_2$ (34%), C_6H_5 (24%), $C{\equiv}CH$ (54%)

methyl derivative was established as cis, exo by oxidation ($KMnO_4$, dicyclohexyl-18-crown-6)[29] of the olefin to the corresponding carboxylic acid and examination of its ^{13}C NMR spectrum.[30] Thus, substitution, at least in the methyl case, proceeds with retention. We have previously taken advantage of this acetylide displacement process to prepare prostaglandin endoperoxide analogues.[9,14,15] The use of *n*-butyllithium in this reaction resulted in none of the desired cross-coupled product, but a 40% yield of olefin **15** was isolated instead. Clearly, alkyllithium reagents containing β-hydrogens cannot be utilized in this process.

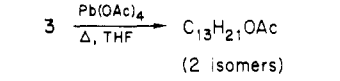
Treatment of organopalladium compound **3** with cuprous cyanide provided the corresponding nitrile in 91% yield (eq 8). The cis, exo stereochemistry was established by ^1H NMR spectral analysis using $Eu(fod)_3$. The peak



(8)

originally located at δ 2.8 was shifted most and appeared as a doublet with a coupling constant of J = 9 Hz, indicative of cis, endo coupling. To our knowledge, cyanation of organopalladium compounds has not been effected in this manner previously.

The reaction of compound **3** with lead tetraacetate afforded a mixture of two isomeric acetates in a ratio of 7.5 to 1 (eq 9). Unfortunately, we were unable to ascertain the exact structure of either of these isomers (see Experimental Section for ^1H NMR and IR spectral data).



(9)

Finally, we have examined possible olefin-insertion reactions of compound **3** with vinyl isobutyl ether, vinyl acetate, methyl acrylate, and allyl chloride, but no recognizable products could be isolated from any of these reactions. It appears that the organopalladium compounds decompose before they undergo olefin substitution.

The chemistry developed on these simple model systems has more recently been applied to the synthesis of prostaglandin endoperoxide analogues. We intend to report on this chemistry shortly.

Experimental Section

Equipment. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were obtained on a Varian Associates HA-100 NMR spectrometer, while the infrared spectra were recorded on a Beckman IR-4250 spectrophotometer. Exact masses were measured on an AEI MS-902 high-resolution mass spectrometer. A Finnegan 4000 gas chromatograph–mass spectrometer was employed for GC–MS molecular weight determinations. Gas chromatographic yields were determined by using hydrocarbon internal standards on a Varian Model 920 or Series 2700 or 3700 gas chromatograph. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Chemicals. Norbornene, norbornadiene, and bicyclo[2.2.2]-oct-2-ene were utilized as obtained from Aldrich. *N,N*-Bis(carboethoxy)-5,6-diazabicyclo[2.2.1]hept-2-ene[31] and bicyclo-[3.2.1]oct-6-en-3-one[32] were prepared according to the literature procedures. Unusual difficulty was experienced with reproducing the bicyclo[3.2.1]oct-6-en-3-one literature synthesis. By rigorously degassing all materials and performing the reaction under argon, a reduced yield of bicyclo[3.2.1]oct-6-en-3-one was isolated. Vinylmercuric chloride was obtained from Orgmet. *trans*-(β-Chlorovinyl)mercuric chloride was prepared by the literature procedure,[33] while all other vinylmercurials used were prepared via hydroboration and subsequent mercuration of the appropriate alkyne.[34,35] Palladium chloride was generously loaned to us by Engelhard and Johnson Matthey. $Eu(fod)_3$ was obtained from Norell.

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Synthesis of the Alkylpalladium Compounds. The following synthesis of the *trans*-1-octenylnorbornylpalladium compound **5** (Table I, entry 5) is representative of that used to prepare compounds **1–9** in Table I. Lithium chloride (0.85 g, 20 mmol), palladium chloride (1.77 g, 10 mmol), and norbornene (9.49 g, 100 mmol) were weighed into a 250-mL round-bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 100 mL of THF was added by syringe. After the mixture was cooled to 0 °C, *trans*-1-octenylmercuric chloride (3.39 g, 10 mmol) was added all at once while backflushing with nitrogen. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Ether and charcoal were then added to the reaction mixture, which was filtered and washed twice with saturated aqueous ammonium chloride. The combined washings were reextracted with ether and the combined ether extractions dried over Na_2SO_4. Removal of the solvent afforded 2.94 g (85% yield) of a pale yellow solid, which was recrystallized from dichloromethane, giving 1.56 g (46% recrystallized yield). In some cases, washing the chloroform or dichloromethane solution with saturated ammonium chloride solution prior to concentrating and cooling the solution provides slightly higher recrystallized yields and reduces some decomposition which is evidenced by the formation of palladium black. Although extensive decomposition occurs upon melting, the observed melting points are different enough to be characteristic. Compound **5**: mp 112–115 °C; IR (KBr) 3040, 2960, 2930, 2880, 2860, 1540, 1470, 1380, 1340, 1310, 1295, 1260, 1215, 1200, 1190, 1160, 1130, 1110, 1080, 1030, 1010, 980, 950, 935, 920, 880, 860, 845, 800, 770 cm^{-1}. Anal. Calcd for $C_{15}H_{22}ClPd$: C, 51.88; H, 7.26. Found: C, 51.99; H, 7.09.

The ^1H NMR spectral data for compounds **1–9** are summarized in Table II. The following compounds were prepared in a similar fashion.

Compound **1**: recrystallized from dichloromethane, mp 194–195 °C; IR (KBr) 3040, 2995, 2950, 2910, 2875, 1530, 1465, 1455, 1400, 1315, 1305, 1290, 1265, 1220, 1200, 1190, 1165, 1140, 1100, 1040, 1020, 985, 975, 960, 940, 900, 850, 800, 770 cm^{-1}. Anal. Calcd for $C_9H_{13}ClPd$: C, 41.09; H, 4.98. Found: C, 41.02; H, 5.08.

Compound **2**: recrystallized from dichloromethane, mp 173–176 °C; IR (KBr) 3035, 3000, 2950, 2930, 2900, 2860, 1470–1460, 1450, 1440, 1400, 1320, 1305, 1290, 1260, 1240, 1210, 1190, 1185, 1170, 1145, 1120, 1115, 1065, 1025, 1000, 970, 960, 945, 935, 920, 875, 855, 810, 790, 775, 730, 710 cm^{-1}. Anal. Calcd for $C_9H_{12}Cl_2Pd$: C, 36.34; H, 4.07; Cl, 23.83. Found: C, 36.45; H, 4.15; Cl, 24.02.

Compound **3**: recrystallized from chloroform, mp 165–166 °C; IR (KBr) 3030, 2940, 2900, 2860, 1535, 1470, 1450, 1390, 1365, 1325, 1305, 1295, 1240, 1210, 1200, 1180, 1125, 1110, 1075, 1035, 1020, 1000, 980, 930, 900, 850, 800, 750 cm^{-1}. Anal. Calcd for $C_{13}H_{21}ClPd$: C, 48.92; H, 6.63. Found: C, 48.80; H, 6.65. M_r 516 (319 × 1.6).

Compound **4**: recrystallized from dichloromethane, mp 230–232 °C; IR (KBr) 3030, 3015, 3005, 2980, 2960, 2930, 2880, 2870, 1540, 1490, 1470, 1450, 1305, 1250, 1210, 1190, 1150, 1125, 1075, 1030, 1105, 975, 935, 875, 865, 750, 690 cm^{-1}. Anal. Calcd for $C_{15}H_{17}ClPd$: C, 53.12; H, 5.05. Found: C, 53.34; H, 5.16.

Compound **6**: recrystallized from chloroform, mp 210–213 °C; IR (KBr) 3050, 2995, 2960, 2870, 1520, 1480, 1450, 1395, 1380, 1365, 1320, 1310, 1295, 1280, 1265, 1215, 1200, 1185, 1160, 1125, 1100, 1060, 1020, 980, 975, 950, 940, 920, 895, 870, 860, 800, 750 cm^{-1}. Anal. Calcd for $C_{14}H_{23}ClPd$: C, 50.47; H, 6.96. Found: C, 49.84; H, 7.02.

Compound **7**: only 1.1 equiv of olefin was employed; recrystallized from dichloromethane, mp 132–135 °C; IR (KBr) 3020, 2995, 2985, 2950, 2920, 2880, 1755–1715, 1540, 1485, 1475, 1450, 1405, 1380, 1320–1295, 1255, 1175, 1130, 1110, 1055, 1030, 910, 875, 860, 770 cm^{-1}. Anal. Calcd for $C_{17}H_{27}ClN_2O_4Pd$: C, 43.89; H, 5.85. Found: C, 44.15; H, 5.98.

Compound **8**: only 1.1 equiv of olefin was employed; recrystallized from dichloromethane, mp 199–200 °C; IR (KBr) 3005, 2960, 2940, 2910, 2870, 1720, 1540, 1480, 1460, 1410, 1395, 1370, 1355, 1340, 1310, 1260, 1240, 1220, 1190, 1175, 1150, 1080, 1030, 1000, 940, 905, 870, 800 cm^{-1}. Anal. Calcd for $C_{14}H_{21}ClOPd$: C, 48.44; H, 6.10. Found: C, 48.70; H, 6.39.

Compound **9**: recrystallized from dichloromethane, mp 159–162 °C; IR (KBr) 3010, 2970, 2940, 2910, 2870, 1540, 1480, 1460, 1395, 1370, 1265, 1235, 1200, 1100, 1025, 910, 850, 800 cm^{-1}. Anal. Calcd for $C_{14}H_{23}ClPd$: C, 50.47; H, 6.96. Found: C, 50.26; H, 7.23.

Compound **10** was prepared by the following modified procedure. Lithium chloride (1.02 g, 24 mmol) and palladium chloride (1.77 g, 10 mmol) were weighed into a 250-mL round-bottom flask equipped with a septum inlet, gas inlet tube, and magnetic stirring bar under nitrogen. THF (120 mL) and norbornadiene (1.1 mL, 11 mmol) were added by syringe, and the mixture was stirred until the palladium chloride dissolved completely (~10 h). After cooling to 0 °C, *trans*-(3,3-dimethyl-1-butenyl)mercuric chloride (3.19 g, 10 mmol) was added to the yellow suspension while backflushing with nitrogen. The mixture was allowed to slowly warm to room temperature and stirred overnight. Ether and dichloromethane (4:3, 700 mL) were added to the reaction mixture, which was then filtered, washed with saturated aqueous ammonium chloride, and dried over Na_2SO_4. Removal of the solvent afforded 2.66 g (84% yield) of a yellow solid, which was recrystallized from dichloromethane, giving 1.41 g (44% yield): mp 187–189 °C; ^1H NMR ($CDCl_3$) δ 1.24 (9 H, s, *t*-Bu), 1.45–2.20 (7 H, m, nortricyclyl), 2.8 (1 H, m), 5.25 (1 H, d, J = 14 Hz, vinyl), 5.35 (1 H, d, J = 14 Hz, vinyl); after the addition of triphenylphosphine, the ^1H NMR spectrum changed to δ 0.7–2.0 (7 H, m, nortricyclyl), 1.30 (9 H, s, *t*-Bu), 2.25 (1 H, m), 6.05 (1 H, d, J = 14 Hz, vinyl), 6.35 (1 H, d, J = 14 Hz, vinyl), 7.2–7.8 (15 H, m, PPh_3); IR (KBr) 3045, 3035, 3020, 3005, 2980, 2950, 2920, 2880, 1585, 1530, 1560, 1500, 1475, 1465, 1450, 1410, 1395, 1380, 1370, 1330, 1195, 1175, 1130, 1100, 1065, 1050, 1040, 1030, 1000, 970, 965, 940, 900, 890, 860, 820, 810, 795, 760, 705, 660 cm^{-1}. Anal. Calcd for $C_{13}H_{19}ClPd$: C, 49.23; H, 6.04. Found: C, 49.23; H, 6.04. M_r 528 (317 × 1.7).

Carbonylation of Compounds 1–3 and 10. The following general procedure was employed. The organopalladium compound (1 mmol) was weighed into a round-bottom flask equipped with a septum inlet, magnetic stirring bar, and gas inlet tube. After the flask was flushed with nitrogen, 10 mL of methanol was added by syringe, and the mixture was cooled to −78 °C. Then, 1.4 mL (10 mmol) of triethylamine was added by syringe. After the mixture was flushed with carbon monoxide, a balloon containing carbon monoxide was attached to the gas inlet tube, and the reaction mixture was allowed to slowly warm to room temperature with stirring. The stirring was continued overnight. Ether and activated carbon were added to the reaction mixture, which was then filtered, washed with 2 N hydrochloric acid and aqueous sodium chloride, and then dried over Na_2SO_4. Removal of the solvent gave almost pure esters **11–14** as determined by ^1H NMR spectral analysis and thin-layer chromatography.

Ester **11**: 78% yield; ^1H NMR ($CDCl_3$) δ 1.1–2.6 (10 H, m, norbornyl), 3.6 (3 H, s, OCH_3), 4.8–5.9 (3 H, m, vinyl); IR (CCl_4) 3040 (=CH), 2980, 2970, 2960, 2890, 1740 (C=O), 1640 (C=CH_2), 1510, 1460, 1440, 1420 (=CH_2), 1360 (OCH_3), 1300, 1280, 1240, 1220, 1190, 1170, 1150, 1115, 1040, 1000, 950, 910 (=CH_2), 870 cm^{-1}; MS, m/z 180.11516 (calcd for $C_{11}H_{16}O_2$, 180.11503).

Ester **12**: 94% yield; ^1H NMR ($CDCl_3$) δ 1.1–2.2 (7 H, m, norbornyl), 2.3–2.7 (3 H, m, norbornyl), 3.6 (3 H, s, OCH_3), 5.78 (1 H, dd, J = 7 Hz, J = 15 Hz, =CH), 6.0 (1 H, d, J = 15 Hz, CHCl); IR ($CHCl_3$) 3020 (=CH), 2970, 2880, 1760 (C=O), 1620 (C=CCl), 1450, 1435, 1365, 1300, 1190 (O=CO), 1150, 1110, 1030, 935 (trans HC=CH), 825 (CCl) cm^{-1}; MS, m/z 214.07475 (calcd for $C_{11}H_{15}ClO_2$, 214.07404).

Ester **13**: 78% yield; ^1H NMR ($CDCl_3$) δ 0.95 (9 H, s, *t*-Bu), 1.0–1.75 (6 H, m, norbornyl), 1.85–2.10 (2 H, m, bridgehead), 2.5 (2 H, m, endo norbornyl near the vinyl and ester moieties), 3.55 (3 H, s, OCH_3), 5.05 (1 H, ddd, J = 15 Hz, J = 7 Hz, J = 1 Hz, internal vinyl), 5.45 (1 H, d, J = 15 Hz, external vinyl); the gradual addition of $Eu(fod)_3$ enabled observation of the coupling constant of the endo, cis hydrogens (J = 10 Hz) and clarified the appearance of the trans vinyl hydrogens; IR (CCl_4) 3030 (=CH), 2980, 2950, 2910, 2890, 1740 (C=O), 1480, 1465, 1440, 1400, 1375, 1355, 1310, 1290, 1250, 1220, 1185, 1175, 1155, 1125, 1045, 975, 945, 915, 810 cm^{-1}; MS, m/z 236.17967 (calcd for $C_{15}H_{24}O_2$, 236.17764).

Ester **14**: 89% yield; mp 42.5–43.0 °C; ^1H NMR ($CDCl_3$) δ 0.9 (9 H, s, *t*-Bu), 1.1–1.7 (5 H, m, nortricyclyl), 2.1–2.4 (3 H, m, allylic, H α to carbonyl, bridgehead H β to carbonyl), 3.6 (3 H, s, OCH_3), 5.2 (1 H, dd, J = 5.7 Hz, J = 15.8 Hz, CHC*H*=), 5.6 (1 H, d, J = 15.8 Hz, =CH-*t*-Bu); IR (CCl_4) 3080, 3040, 2970, 2880, 1750 (C=O), 1480, 1465, 1440, 1360, 1290, 1240, 1210, 1170, 1070, 1040, 970 (CH=CH) cm^{-1}; MS, m/z 234.14190 (calcd for $C_{15}H_{22}O_2$, 234.14198).

Reduction of Compound 3. The reduction of compound **3** with $NaBH_4$ was carried out as follows. Compound **3** (0.319 g, 1.0 mmol) was weighed into a 25-mL round-bottom flask equipped with a septum inlet, gas inlet tube, and magnetic stirring bar. After the mixture was flushed with nitrogen, 10 mL of 2-propanol was added by syringe and the flask subsequently cooled in an ice bath. While the mixture was backflushed with nitrogen, 0.037 g (1.0 mmol) of $NaBH_4$ was added all at once and the reaction mixture immediately turned black. It was slowly warmed to room temperature and stirred overnight. Gas chromatographic analysis indicated two large peaks with the first peak approximately one-fourth the size of the second peak.

The same reaction with THF as the solvent in place of 2-propanol turned black a little slower (within 15 min). Gas chromatographic analysis indicated the same two large peaks, but the first peak was now approximately twice the size of the second. These two compounds were found to be identical with the compounds **15** and **16** reported below.

The reaction of compound **3** and hydrogen was effected as follows. Compound **3** (0.319 g, 1 mmol) was weighed into a 25-mL round-bottom flask equipped with a septum inlet, magnetic stirring bar, and gas inlet tube. After the mixture was flushed with nitrogen, 10 mL of methanol was added by syringe, and the mixture was cooled to −78 °C. After the mixture was flushed with hydrogen, a balloon containing hydrogen was attached to the gas inlet tube, and the reaction mixture was warmed to room temperature slowly. The stirring was continued overnight. Ether and activated carbon were added to the reaction mixture, which was then filtered. Removal of the solvent afforded 118 mg (65% yield) of compound **16** which proved to be more than 90% pure by gas chromatographic and NMR spectral analysis: ^1H NMR ($CDCl_3$) δ 0.9 (9 H, s, *t*-Bu), 1.0–2.3 (15 H, m); IR (CCl_4) 2960, 2870, 1470, 1450, 1390, 1365 cm^{-1}; MS, *m/z* 180.18765 (calcd for $C_{13}H_{24}$, 180.18781).

The reduction of compound **3** to olefin **15** using sodium methoxide follows. Sodium methoxide (108 mg, 2 mmol) was weighed into a 25-mL round-bottom flask equipped with a septum inlet, gas inlet tube, and magnetic stirring bar. After the mixture was flushed with nitrogen, 10 mL of methanol was added via syringe, and the mixture was stirred for 15 min. After the flask was cooled in an ice bath, 319 mg (1 mmol) of organopalladium compound **3** was added at once to the solution while it was backflushed with nitrogen. The mixture was slowly warmed to room temperature and stirred overnight. Ether and activated carbon were added to the mixture, which was then filtered, washed successively with 2 N hydrochloric acid and aqueous sodium chloride, and dried over sodium carbonate. Removal of the solvent afforded 115 mg (65% yield) of olefin **15** which proved to be more than 90% pure by gas chromatographic and NMR spectral analysis: ^1H NMR ($CDCl_3$) δ 1.0 (9 H, s, *t*-Bu), 1.0–2.4 (11 H, m, norbornyl), 4.9–5.5 (2 H, m, CH=CH); IR ($CDCl_3$) 3000 (=CH), 2960, 2880, 1480, 1460, 1390, 1375, 1310, 1270, 965 (CH=CH) cm^{-1}; MS, *m/z* 178.17184 (calcd for $C_{13}H_{22}$, 178.17215); R_f 0.65 (hexane).

Reaction of Compound 3 with Organolithium Compounds. These reactions were carried out by using the following general procedure. Compound **3** (319 mg, 1 mmol) and 525 mg (2 mmol) of triphenylphosphine were weighed into a 25-mL round-bottom flask equipped with a septum inlet, gas inlet tube, and magnetic stirring bar. After the mixture was flushed with nitrogen, 10 mL of THF was added, and the reaction mixture was stirred at room temperature for 15 min. After the flask was cooled in an ice bath, 1.2–2.0 mmol of organolithium compound was added by syringe and the mixture was allowed to slowly warm to room temperature and stirred overnight. The mixture was then quenched with a small amount of methanol. Ether and Celite were added to the mixture, which was then filtered to remove palladium. After removal of the solvent, hexane and Celite were added to the brown solid, which was again filtered and evaporated. The resultant oil was chromatographed on a silica gel column with hexane as the eluant.

Reaction with methyllithium: 83% yield; R_f 0.59 (hexane); ^1H NMR ($CDCl_3$) δ 0.9 (3 H, d, J = 7.5 Hz, Me), 1.0 (9 H, s, *t*-Bu), 1.0–2.3 (10 H, m, norbornyl), 4.9–5.5 (2 H, m, CH=CH); IR (CCl_4) 3030 (=CH), 2970, 2880, 1480, 1465, 1370, 980 (CH=CH) cm^{-1}; MS, *m/z* 192.18757 (calcd for $C_{14}H_{24}$, 192.18781). Oxidation with $KMnO_4$ and dicyclohexyl-18-crown-6 in benzene at 25 °C for 5 days[29] afforded the corresponding carboxylic acid in 40% yield. ^{13}C NMR spectral analysis[30] indicated that the acid is the 2-exo,3-exo isomer.

Reaction with vinyllithium: 34% yield; R_f 0.56 (hexane); ^1H NMR ($CDCl_3$) δ 1.0 (9 H, s, *t*-Bu), 1.0–2.4 (10 H, m, norbornyl), 4.6–5.7 (5 H, m, vinyl); IR (CCl_4) 3040, 3000 (=CH), 2960, 2870, 1635 (=CH_2), 1475, 1455, 1420 (=CH_2), 1360, 980 (CH=CH), 905 (CH=CH_2) cm^{-1}; MS, *m/z* 204.18715 (calcd for $C_{15}H_{24}$, 204.18781).

Reaction with phenyllithium: 24% yield; R_f 0.46 (hexane); ^1H NMR ($CDCl_3$) δ 0.7 (9 H, s, *t*-Bu), 1.1–2.7 (9 H, m, norbornyl), 2.9 (1 H, d, J = 9 Hz, CHPh), 4.5 (1 H, dd, J = 9 Hz, J = 15 Hz, CHC*H*=C), 5.1 (1 H, d, J = 15 Hz, C=CH-*t*-Bu), 7.1 (5 H, s, Ph); IR (CCl_4) 3040 (ArH), 2970, 2880, 1600, 1490, 1470, 1450, 1360, 965 (CH=CH), 720, 695 (Ar) cm^{-1}; MS, *m/z* 254.20294 (calcd for $C_{19}H_{26}$, 254.20346).

Reaction with lithium acetylide: 54% yield; R_f 0.37 (hexane); ^1H NMR ($CDCl_3$) δ 1.0 (9 H, s, *t*-Bu), 1.0–2.4 (9 H, m, norbornyl), 2.0 (1 H, d, J = 2 Hz, C≡CH), 2.5 (1 H, dt, J = 2 Hz, J = 8 Hz, CHC≡C), 5.1–5.6 (2 H, m, CH=CH); IR (CCl_4) 3340 (≡CH), 3050 (=CH), 2990, 2900, 2120 (C≡C), 1485, 1470, 1405, 1375, 975 (CH=CH), 630 (≡CH) cm^{-1}; MS, *m/z* 187.14895 [calcd for $C_{14}H_{19}$ (P − CH_3), 187.14867].

Reaction of Compound 3 and CuCN. The reaction of compound **3** and CuCN was carried out as follows. Compound **3** (319 mg, 1 mmol) and 448 (5 mmol) of cuprous cyanide were weighed into a 25-mL round-bottom flask equipped with a septum inlet, reflux condenser, and magnetic stirring bar. After the mixture was flushed with nitrogen, 10 mL of THF was added by syringe, and the mixture was refluxed for 12 h. Ether and activated carbon were added to the mixture, which was then filtered. After removal of the solvent, the resultant oil was chromatographed on a silica gel column with 4:1 hexane ether as the eluant, which afforded 85 mg (42% yield) of the corresponding nitrile. The following yields were obtained by gas chromatographic analysis after refluxing for 1 h in the indicated solvent: benzene (91%), THF (81%), acetonitrile (68%); R_f 0.47 (4:1 hexane/ether); ^1H NMR ($CDCl_3$) δ 1.0 (9 H, s, *t*-Bu), 1.0–2.8 (10 H, m, norbornyl), 5.1–5.7 (2 H, m, CH=CH); IR (CCl_4) 3040 (=CH), 2970, 2880, 2250 (CN), 1480, 1460, 1400, 1370, 1300, 975 (CH=CH) cm^{-1}; MS, *m/z* 203.16695 (calcd for $C_{14}H_{21}N$, 203.16740). The addition of $Eu(fod)_3$ during ^1H NMR spectral analysis of this compound resulted in the shift of one hydrogen originally located at δ 2.8. This was observed to be a doublet with J = 9 Hz, indicating that the cyano and vinyl groups are located cis, exo to one another on the norbornyl skeleton.

The reaction of compound **3** and lead tetraacetate was effected as follows. Compound **3** (319 mg, 1.0 mmol) and lead tetraacetate (510 mg, 1.15 mmol) were weighed into a 25-mL round-bottom flask equipped with a septum inlet, reflux condenser, and magnetic stirring bar. After the mixture was flushed with nitrogen, 10 mL of THF was added by syringe, and the mixture was refluxed for 4 h. Ether and Celite were added to the mixture, which was then filtered. After removal of the solvent, the resultant oil was chromatographed on a silica gel column with 5:1 hexane/ether as the eluant. Gas chromatographic analysis indicated that the product (155 mg, 66% yield) was a 7.5:1 mixture of two isomers of unknown structure: 300-MHz ^1H NMR δ 0.99 (9 H, s), 1.06–1.19 (2 or 3 H, m), 1.50–1.60 (2 or 3 H, m), 1.81 (2 H, d, J = 5.4 Hz), 1.99 (3 H, s), 2.14 (1 H, s), 2.20 (1 H, d, J = 4.4 Hz), 2.23 (1 H, d, J = 7.3 Hz), 4.63 (1 H, t, J = 5.4 Hz), 5.48 (1 H, d, J = 15.8 Hz), 5.59 (1 H, dd, J = 7.3 Hz, J = 15.8 Hz); IR (CCl_4) 3070, 2980, 2880, 1740 (C=O), 1460, 1360, 1240, 1215, 1080, 1040, 1020, 975 cm^{-1}; MS, *m/z* 236.17798 (calcd for $C_{15}H_{24}O_2$, 236.17764).

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82352-99-6; **9**, 82328-07-2; **10**, 101953-38-2; **11**, 101933-76-0; **12**, 101933-77-1; **13**, 82316-15-2; **14**, 101933-78-2; **15**, 82316-14-1; **16**, 82316-13-0; H_2C=CHHgCl, 762-55-0; ClHC=CHHgCl, 1190-78-9; $(CH_3)_3CCH$=CHHgCl, 36525-02-7; PhCH=CHHgCl, 36525-03-8; n-$C_6H_{13}CH$=CHHgCl, 36627-23-3; $(CH_3)_3CCH$=$C(CH_3)$HgCl, 38010-69-4; bicyclo[2.2.1]hept-2-ene, 498-66-8; diethyl 2,3-diazabicyclo[2.2.1]-5-ene-2,3-dicarboxylate, 14011-60-0; bicyclo[3.2.1]oct-2-en-6-one, 31444-29-8; bicyclo[2.2.2]oct-2-ene, 931-64-6; bicyclo[2.2.1]hepta-2,5-diene, 121-46-0; 2-(3,3-dimethyl-1-butenyl)-3-methylbicyclo[2.2.1]heptane, 82316-17-4; 2-(3,3-dimethyl-1-butenyl)-3-vinylbicyclo[2.2.1]heptane, 82316-18-5; 2-(3,3-dimethyl-1-butenyl)-3-phenylbicyclo[2.2.1]heptane, 82316-20-9; 2-(3,3-dimethyl-1-butenyl)-3-ethynylbicyclo[2.2.1]heptane, 82316-19-6; 3-cyano-2-(3,3-dimethyl-1-butenyl)bicyclo[2.2.1]-heptane, 82316-16-3; lithium chloride, 7447-41-8; palladium chloride, 7647-10-1.

Pentamethyldisilyl Radical: Absolute Rate Constants for Its Formation and for Some Halogen Abstraction and Addition Reactions[1]

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Pentamethyldisilane is a better hydrogen donor than Et_3SiH toward *tert*-butoxyl (k's for the overall reaction are 17 and 5.7×10^6 M^{-1} s^{-1}, respectively, at ca. 27 °C) and toward primary alkyl radicals (k's for Si–H bond cleavage are ca. 10 and 1.0×10^4 M^{-1} s^{-1}, respectively, at 120 °C). Absolute rate constants for various reactions of the $Me_3SiSiMe_2$· radical have been measured by laser flash photolysis at room temperature. In halogen atom abstractions, for example, the $Me_3SiSiMe_2$· radical is slightly less reactive than Et_3Si·, but it is more reactive than n-Bu_3Ge· and n-Bu_3Sn·. Pentamethyldisilane would appear to offer an attractive alternative to n-Bu_3SnH and n-Bu_3GeH in radical chain reactions in which the desired product is formed by a hydrogen transfer not to the organic radical formed initially but to a second radical formed by a slow β-scission or rearrangement of the initial radical.

Tri-*n*-butyltin hydride has become an extremely popular reagent in organic synthesis by free-radical chain reactions. It is frequently employed in systems in which the initially formed organic radical must first undergo a unimolecular reaction such as a β-scission,[3]

$$n\text{-}Bu_3Sn\cdot + R_1X \rightarrow R_1\dot{X}SnBu_3 \xrightarrow{\beta} R_1\cdot \xrightarrow{n\text{-}Bu_3SnH} R_1H$$

or a rearrangement,[4]

$$n\text{-}Bu_3Sn\cdot + R_2X \rightarrow R_2\cdot \xrightarrow{\rho} R_3\cdot \xrightarrow{n\text{-}Bu_3SnH} R_3H$$

if the desired product is to be obtained. In certain cases, the scission or rearrangement of the intermediate radical ($R_1\dot{X}SnBu_3$ or R_2·) is slow relative to its reduction by tin hydride to form unwanted products ($R_1XHSnBu_3$ or R_2H). Under such conditions, a less active hydrogen donor that can nevertheless fulfill the other requirements of these chain processes can provide a very useful alternative to the usual tin hydride method. We have previously shown that tri-*n*-butylgermanium hydride has the necessary chemical properties to fulfill these requirements. That is, n-Bu_3Ge· adds to multiple bonds and abstracts halogen atoms with rates similar to those of the n-Bu_3Sn· radical[5] while n-Bu_3GeH is only ca. $^1/_{20}$ as good as n-Bu_3SnH as an H atom donor to primary alkyl radicals.[6] These properties of n-Bu_3GeH/n-Bu_3Ge· have already been demonstrated to be useful in some synthetic procedures.[7]

Table I. Rate Constants for the Reaction of *tert*-Butoxyl Radicals with Some Silanes[a]

silane	k, M^{-1} s^{-1}	ref
$Me_3SiSiMe_2H$	1.7×10^7	this work
$Me_3SiSiMe_2D$	9.9×10^6	this work
$PhSiH_3$	7.5×10^6	14
$PhSiMe_2H$	6.6×10^6	14
Et_3SiH	5.7×10^6	14

[a] Temperatures: 294 ± 1 K for $Me_5Si_2H(D)$ and ca. 300 for the other three silanes.

Trialkylsilyl radicals are more reactive in additions to multiple bonds[8,9] and in halogen atom abstractions[10] than n-Bu_3Sn· and n-Bu_3Ge·, but they are rather poor H atom donors toward alkyl radicals and tend therefore not to support chain reactions except at elevated temperatures.[11,12] However, disilanes have been shown by com-

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