the solvent gave 0.721 g of cyclic sulfite as a colorless oil, which showed two spots by TLC, for the cis and trans isomers, with respect to the oxygen on the sulfur and the carbon substituents. The oil was dissolved in 5 mL of acetonitrile and cooled to 0 °C, and 1.5 g of $NaIO_4$ was added, followed by 2.5 mL of water and 5 mg of $RuCl_3$; the cooling bath was removed, and stirring was continued at rt for 3.5 h. The reaction mixture was worked up as above to give 0.656 g (91% overall yield) of **13** as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.84 (s, 6 H), 0.88 (t, 3 H, $J = 7$), 0.88 (d, 6 H, $J = 7$), 1.10–1.40 (m, 20 H), 1.52–1.66 (m, 3 H), 1.87 (m, 2 H), 3.76 (m, 2 H), 4.95 (ddd, 1 H, $J = 3.5, 5.3, 5.3$), 5.12 (ddd, 1 H, $J = 3.5, 5.3, 5.3$); ^{13}C NMR ($CDCl_3$) δ −3.63, −3.60, 14.09, 18.46, 20.27, 22.67, 25.19, 28.67, 29.09, 29.29, 29.32, 29.43, 29.55, 29.61, 31.23, 31.90, 34.14, 57.84, 83.35, 86.27; IR 1466, 1384, 1210, 1100, 831 cm^{-1}; MS (NH_3 DCI) m/z 479 ($M + H^+$), 496 ($M + NH_4^+$); $[\alpha]_D$ +18.7°; $[\alpha]_{365}$ +57.93° ($CHCl_3$, c 0.84); enantiomer: $[\alpha]_D$ −19.52°; $[\alpha]_{365}$ −58.18° ($CHCl_3$, c 0.82).

2-[2′(*R*)-Dodecyl-3′-methylenecyclopropan-1′(*S*)-yl]ethanol (14). To a well-stirred solution of 0.777 g (3.21 mmol) of the sulfone **4** in 5 mL of THF cooled in a dry ice/acetone slush bath was added 2 mL of 1.6 M (3.2 mmol) of *n*-BuLi, and the resulting golden yellow solution was stirred at −78 °C for 2 h. A solution of 0.62 g (1.30 mmol) of **13** in 2 mL of THF was added over 1 min. Stirring was continued over the next 3.75 h, allowing the reaction mixture to warm up to rt. The reaction mixture was cooled to −78 °C, and an additional 2 mL of 1.6 M (3.2 mmol) *n*-BuLi was added; stirring was continued over the next 18 h, allowing the reaction mixture to warm to rt. Tetra-*n*-butylammonium fluoride trihydrate (1.5 g) was added, and the mixture was refluxed for 1.5 h. The reaction mixture was cooled, diluted with 50 mL of hexane, washed with 2 × 5 mL of water and 5 mL of 2 M HCl, and concentrated in vacuo. The residual oil was flash chromatographed on a 30-g column of SiO_2 using up to 25% of ethyl acetate in hexane to give 0.124 g (36% yield) of **14**: MS (NH_3 DCI) m/z 284 ($M + NH_4^+$); ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, $J = 7$), 1.17–1.62 (m, 26 H), 1.78 (m, 1 H), 3.73 (m, 2 H), 5.31 (m, 1 H), 5.33 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.13, 16.28, 19.56, 22.71, 27.58, 29.37, 29.51, 29.63, 29.67, 29.95, 30.58, 31.94, 63.27, 101.63, 141.85; IR 3600–3150, 883 cm^{-1}; $[\alpha]_D$ −5.90°; $[\alpha]_{365}$ −25.1° ($CHCl_3$, c 0.9); enantiomer $[\alpha]_D$ +6.0°; $[\alpha]_{365}$ +24.9° ($CHCl_3$, c 1.05).

2-[2′(*R*)-Dodecyl-3′-methylenecyclopropan-1′(*S*)-yl]acetic Acid (15). To a well-stirred mixture of 70 mg of pyridinium chlorochromate, 70 mg of Celite, and 40 mg of activated, powdered 4A molecular sieves in 2.5 mL of CH_2Cl_2 was added a solution of 26 mg (0.1 mmol) of **14** in 0.5 mL of CH_2Cl_2, and the reaction mixture was stirred for 18 h; it was diluted with 10 mL of ether and filtered through a 1-g pad of SiO_2; the solvent was evaporated, and the residue was dissolved in 1 mL of acetone and oxidized with 0.5 mL of 6 M Jones reagent at rt for 6 h; excess of the reagent was reduced with the addition of 2-propanol, and the reaction mixture was diluted with 20 mL of a 1:1 hexane and ether mixture, washed several times with water, and concentrated. The residue, upon chromatography on a 5-g column of SiO_2 using 20–100% ethyl acetate in hexane gave 17 mg (65% yield, colorless oil) of **15**: MS (NH_3 DCI) m/z 298 ($M + NH_4^+$); ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, $J = 7$), 1.20–1.50 (m, 22 H), 1.61 (m, 1 H), 1.82 (m, 1 H), 2.40 (dd, 1 H, $J = 8.4, 16.8$), 2.46 (dd, 1 H, $J = 7.4, 16.8$), 5.37 (m, 1 H), 5.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.10, 14.69, 19.60, 22.69, 27.64, 29.36, 29.42, 29.60, 29.67, 31.93, 32.37, 102.72, 139.88, 179.44; IR 3500–2550, 1713, 889 cm^{-1}; $[\alpha]_D$ −10.28°; $[\alpha]_{365}$ −44.86° ($CHCl_3$, c 0.7); enantiomer: $[\alpha]_D$ +10.36°; $[\alpha]_{365}$ +45.12° ($CHCl_3$, c 0.8).

Acknowledgment. The authors thank Professor K. B. Sharpless and Drs. R. Simpson and J. Nadelson for helpful discussions, Drs. M. Shapiro and E. Fu for spectroscopic measurements, and Dr. R. Underwood for preliminary work on **8** and **9**.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **6**–**15** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Selective Hydrosilylation of Alkenes Catalyzed by an Organoyttrium Complex

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Received June 16, 1992

Metal-catalyzed hydrosilylation procedures provide perhaps the most efficient and economical route to organosilanes, and a variety of catalysts have been developed for this reaction.[3] Curiously, relatively little effort has been made to develop general, synthetically useful procedures for hydrosilylation of polyolefins and functionalized alkenes.[3] In this context we have found that $(\eta^5\text{-}C_5Me_5)_2YCH(SiMe_3)_2$ serves as an efficient and selective precatalyst for the hydrosilylation of monosubstituted and 1,1-disubstituted olefins.

While this work was in progress, a related study utilizing an organoneodymium catalyst was reported.[3d] In that effort, unfunctionalized olefins (decene and styrene) were hydrosilylated in modest (GC) yields. Nearly all of the reactions described required 2 days at 80 °C for complete reaction. Left open was the question of whether any type of functionality could be tolerated in this process. This is a critical point owing to the extreme Lewis acidity of organolanthanides and group 3 organometallics which renders them incompatible with many functional groups.[4] For example, even ethers have been found to inhibit the catalytic activity of these organometallics because such Lewis bases complex irreversibly with the metal or are readily cleaved by the complexes, either of which destroy the activity of the catalyst.

From the outset our focus was on the development of a convenient, synthetically useful procedure which would take place at ambient temperatures. As illustrated in Table I, the organoyttrium-catalyzed hydrosilylation procedure fulfills all of these requirements. The process works extremely well for a variety of unhindered alkenes, and reactions can be performed in benzene or toluene utilizing 3 mol % catalyst at ambient temperatures. Furthermore, 1,1-disubstituted alkenes (entries 4, 7, and 9) are much less reactive than monosubstituted olefins, leading to considerable selectivity in hydrosilylation of dienes possessing both types of olefins (entry 7). With the exception of the highly reactive norbornylene (entry 2), more highly hindered alkenes (e.g., cyclohexene and *cis*-1,3-dimethyl-2-methylenecyclohexane) are virtually inert at ambient temperature.[5] Consequently, excellent chemoselectivity can be achieved in hydrosilylation of dienes containing a terminal olefin and any internal olefin (entries 5–9).

The extreme sensitivity of this particular catalyst to steric effects led us to examine the selective hydrosilylation of α,ω-dienes in which the two olefins were differentiated only by allylic substitution of one of the alkenes (entry 12).

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[1] Alfred P. Sloan Foundation Fellow, 1987–1991.

[2] Postdoctoral Research Associate supported by the Deutscher Akademischer Austauschdienst (DAAD).

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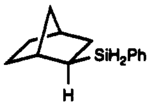
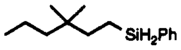
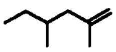
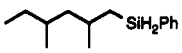
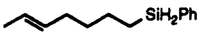
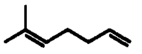
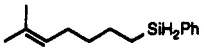
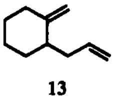
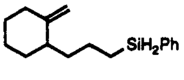
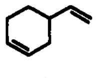
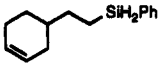
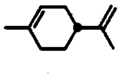
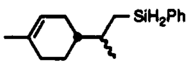
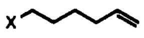
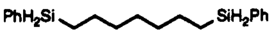
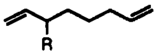
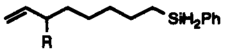
[5] At 60 °C over 42 h, *trans*-3-hexene reacts to provide a mixture of products in which the terminal organosilane predominates.

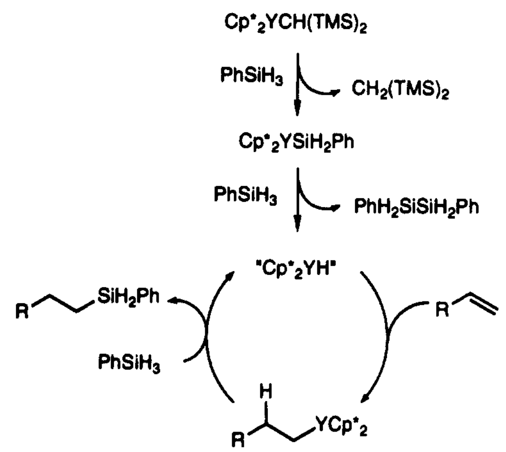
0022-3263/92/1957-6347$03.00/0

Table I. Selective Hydrosilylation of Alkenes Utilizing Catalytic $Cp*_2YCH(TMS)_2$

entry	substrate	product	reaction time[a] (h)	% isoltd yield[b]
1	1-decene 1	 2	14	95
2	norbornylene 3	 4	3.5	85
3	 5	 6	28	94
4	 7	 8	52	56[c]
5	 9	 10	48	96
6	 11	 12	40	94
7	 13	 14	92	91[d]
8	 15	 16	18	97[e]
9	 17	 18	96	61[c]
10				
	19a X = Cl	20a	23	85
	19b X = OBn	20b	26[f]	90
	19c X = OTBDMS	20c	29	83
	19d X = OTHP	20d	21	96
11	 21	 22	26	96
12				
	23a R = OTBDMS	24a	24[g]	54
	23b R = Ph	24b	24[g]	31

[a] Reactions were performed at ambient temperatures in benzene unless indicated otherwise. [b] Refers to yields of purified materials. All of the compounds have been fully characterized spectroscopically (^1H NMR, ^{13}C NMR, IR), and elemental composition has been established by high-resolution mass spectrometry and/or combustion analysis. [c] Isolated as a 2:1 mixture of diastereomers. [d] Isolated as a 96:4 ratio of mono hydrosilylated products. [e] The reaction was performed in toluene. [f] The reaction was performed at 60 °C. [g] Reactions were performed at 34–38 °C.

Scheme I



Although modest yields of the desired products could be isolated, further development of more highly selective catalysts will be required. Finally, despite the extreme Lewis acidity of the organoyttrium catalyst the process is tolerant of a variety of functional groups including halides, ethers, and acetals (entries 10 and 12).

Of two feasible catalytic cycles outlined by Watson and Marks for the hydrosilylation of alkenes by organolanthanides, organoactinides, and related group 3 organometallics,[6] perhaps the most viable is the one depicted in Scheme I.

σ-Bond metathesis[6,7] of $Cp*_2YCH(TMS)_2$[8] with $PhSiH_3$ initially produces a silylyttrium complex, which reacts further with $PhSiH_3$ to generate a disilane and the catalyst for the reaction, "$Cp*_2YH$".[6,7g] Olefin insertion ensues,[4b,c,8b,9] providing an organometallic complex that undergoes σ-bond metathesis with $PhSiH_3$ to release the organosilane,[6,7g] regenerating the active catalyst in the process.

In support of this mechanism is the observed regiochemistry of the hydrosilylation process. Regioselective olefin insertion placing the metal at the terminal carbon is both electronically and sterically favorable in this and related electrophilically driven reactions like the hydro-

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(8) The precatalyst is readily prepared from $(\eta^5\text{-}C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ by treatment with $LiCH(TMS)_2$ in toluene in a procedure similar to that utilized for the analogous lanthanum complex. (a) Den Haan, K. H.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *322*, 321. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

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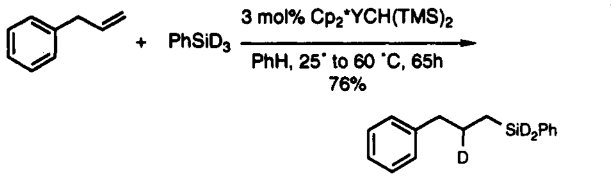
boration reaction. Furthermore, we note that hydrosilylation of 3-phenylpropene with PhSiD$_3$ produces a single product as determined by mass spectrometry, ^{13}C NMR, and ^{2}H NMR (eq 1). Although this result lends credence to the general features of the proposed mechanism outlined in Scheme I, it by no means distinguishes between the two mechanisms mentioned above.[6] This point is currently being addressed in continuing studies.



(1)

In summary, organoyttrium complexes serve as efficient catalysts for the selective hydrosilylation of olefins. Research continues on these and other processes catalyzed by organolanthanides and group 3 organometallics in an effort to bring their unique reactivity and selectivity patterns to bear on problems in selective organic synthesis.[9h,i]

Experimental Section

Materials and Methods. All operations were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on an Ar line connected to a vacuum system (0.04 Torr) or in a nitrogen-filled, Vacuum Atmospheres glovebox.

Benzene, toluene, pentane, THF, and diethyl ether were distilled from Na/K alloy/benzophenone under Ar. These solvents were either freshly distilled prior to use or were stored after drying in the glovebox. Benzene-d_6 was stirred at least 12 h over Na/K alloy and then distilled or vacuum-transferred and stored in the glovebox.

The olefins 1-decene, 6-methyl-1,5-heptadiene, 1,5-heptadiene, 4-vinyl-1-cyclohexene, (+)-limonene, 1,6-heptadiene, 3,3-dimethyl-1-hexene, and 2,4-dimethyl-1-hexene were commercial samples stirred at least 4 h over Na/K alloy and then distilled under Ar. Norbornylene (99%) was degassed on a vacuum line. 6-Chloro-1-hexene was stirred for 3 h over freshly activated (~300 °C, 0.04 Torr) molecular sieves (4 Å) and then distilled onto freshly activated 4-Å molecular sieves under Ar.

Phenylsilane (Aldrich, 99%) was saturated with nitrogen and used as purchased. Anhydrous YCl$_3$ was purchased from Cerac. Pentamethylcyclopentadienyllithium was prepared according to the literature.[10] Bis(trimethylsilyl)methyllithium was prepared by the literature procedure.[11] The complex Cp*$_2$Y(μ-Cl)$_2$Li(OEt$_2$)$_2$ was prepared according to published procedures.[12] All compounds were stored in the glovebox after purification.

Physical and Analytical Measurements. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in CDCl$_3$ using CHCl$_3$ as the reference for ^{1}H NMR and CDCl$_3$ as the reference for ^{13}C NMR unless specified otherwise. FT-IR spectra were recorded neat on NaCl plates. Low-resolution and exact mass spectra were recorded at 70 eV using electron-impact ionization with perfluorokerosene as internal standard. Analytical GC was performed using a 25-m × 320-μm 5% phenyl SE-54 fused silica capillary column.

General Procedure for Catalytic Hydrosilylation. In the glovebox a round-bottomed Schlenk flask equipped with a magnetic stirring bar was loaded with 109 mg (0.21 mmol) of Cp*$_2$YCH(SiMe$_3$)$_2$. Then 8 mL of benzene was added to provide a clear solution of the precatalyst. After the addition of 7.0 mmol (864 μL) of phenylsilane and 7.0 mmol of the olefin the flask was tightly closed and the reaction mixture was stirred at rt in the glovebox. After complete reaction the reaction mixture was taken out of the glovebox and diluted with 300 mL of diethyl ether. The reaction mixture was poured into 100 mL of saturated aq NH$_4$Cl solution. The resulting mixture was shaken, and the organic layer was separated. The aqueous phase was extracted three times with 30 mL of diethyl ether, and the combined organic layers were dried over MgSO$_4$. The solvents were removed, and the product was purified by filtration over SiO$_2$ or flash chromatographed with hexane as eluant and Kugelrohr distilled.

1-(Phenylsilyl)decane (2). Yield: 1.660 g (95%, 99% pure by GC) of 2 as a colorless liquid. For combustion analysis a sample was distilled: bp 93–94 °C/0.04 mmHg. R_f: 0.79 (hexanes). ^{1}H NMR: δ 0.85–1.00 (m, 5 H), 1.22–1.55 (m, 16 H), 4.33 (t, J = 3.7 Hz, $^1J_{29\mathrm{Si,H}}$ = 192 Hz, 2 H), 7.35–7.43 (m, 3 H), 7.55–7.65 (m, 2 H). ^{13}C NMR (APT): δ 9.98 (CH$_2$), 14.10 (CH$_3$), 22.68 (CH$_2$), 25.05 (CH$_2$), 29.25 (CH$_2$), 29.33 (CH$_2$), 29.53 (CH$_2$), 29.62 (CH$_2$), 31.91 (CH$_2$), 32.85 (CH$_2$), 127.97, 129.48 (C$_{\mathrm{para}}$), 132.84 (C$_{\mathrm{ipso}}$), 135.23. IR (thin film): 3052 (w), 2922 (s), 2852 (s), 2126 (s), 1465 (m), 1117 (m), 940 (s), 847 (s), 701 (s), 564 (m) cm^{-1}. LRMS [CI$^+$ (CH$_4$)] m/z (relative intensity): 248 (2), 247 (4), 170 (54), 113 (82), 107 (100), 105 (39), 99 (100), 85 (36), 78 (41), 43 (42). Anal. Calcd for C$_{16}$H$_{28}$Si (248.49): C, 77.34; H, 11.36. Found: C, 77.24; H, 11.57.

***exo*-2-(Phenylsilyl)bicyclo[2.2.1]heptane (4).** Yield: 1.210 g (85%, 99% pure by GC) of 4 as a colorless liquid (>99% one diastereomer by GC analysis). For combustion analysis a sample was distilled: ot 79–80 °C/0.04 mmHg. R_f: 0.85 (hexanes). ^{1}H NMR: δ 1.05–1.15 (m, 1 H), 1.19–1.45 (m, 4 H), 1.50–1.64 (m, 4 H), 2.32 (s (br), 2 H), 4.20 and 4.28 (ABX-system, J_{AB} = 5.9 Hz, J_{AX} = 4.3 Hz, J_{BX} = 3.8 Hz, $^1J_{29\mathrm{Si,H}}$ = 191 Hz, 2 H), 7.36–7.45 (m, 3 H), 7.60–7.66 (m, 2 H). ^{13}C NMR (APT): δ 24.09 (CH), 29.07 (CH$_2$), 33.49 (CH$_2$), 33.66 (CH$_2$), 37.21 (CH), 37.27 (CH$_2$), 38.72 (CH), 127.94, 129.47 (C$_{\mathrm{para}}$), 132.76 (C$_{\mathrm{ipso}}$), 135.45. IR (thin film): 3067 (w), 2948 (s), 2868 (m), 2127 (s), 1118 (m), 933 (s), 876 (m), 848 (s), 828 (s), 731 (m), 698 (m) cm^{-1}. LRMS (EI) m/z (relative intensity): 202 (24), 124 (41), 107 (100), 105 (76). Anal. Calcd for C$_{13}$H$_{18}$Si (202.37): C, 77.16; H, 8.97. Found: C, 76.94; H, 9.17.

3,3-Dimethyl-1-(phenylsilyl)hexane (6). Kugelrohr distillation afforded the pure silane as a colorless liquid. Yield: 1.337 g (87%, >99% pure by GC); ot 90 °C/0.04 mmHg. R_f 0.79 (hexanes). ^{1}H NMR: δ 0.81–0.93 (m, 5 H), 0.85 (s, 6 H), 1.14–1.37 (m, 6 H), 4.31 (t, J = 3.6 Hz, $^1J_{29\mathrm{Si,H}}$ = 192 Hz, 2 H), 7.34–7.45 (m, 3 H), 7.55–7.63 (m, 2 H). ^{13}C NMR (APT): δ 3.87 (CH$_2$), 15.02 (CH$_3$), 17.14 (CH$_2$), 26.59 (C*Me*$_2$), 33.64 (*C*Me$_2$), 36.95 (CH$_2$), 43.75 (CH$_2$), 127.99, 129.52 (C$_{\mathrm{para}}$), 132.79 (C$_{\mathrm{ipso}}$), 135.22. IR (thin film): 3068 (w), 2956 (s), 2928 (s), 2895 (m), 2870 (m), 2132 (s), 1117 (m), 937 (s), 902 (m), 838 (s), 700 (m), cm^{-1}. HRMS: calcd for (M – H)$^+$ = C$_{14}$H$_{23}$Si 219.1569, found 219.1552. LRMS (EI) m/z (relative intensity): 220 (0.6), 219 (1), 142 (39), 135 (37), 107 (100), 85 (63), 84 (27), 43 (44). Anal. Calcd for C$_{14}$H$_{24}$Si: C, 76.28; H, 10.98. Found: C, 75.68; H, 10.66.

2,4-Dimethyl-1-(phenylsilyl)hexane (8). Yield after chromatography: 0.620 g (56%, >99% pure by GC) of silane 8 as a colorless liquid (2:1 mixture of diastereomers by ^{13}C NMR; same ratio as in the crude product). R_f: 0.78 (hexanes). ^{1}H NMR: δ 0.78–1.55 (m, 16 H), 1.76–1.91 (m, 1 H), 4.39 (m, $^1J_{29\mathrm{Si,H}}$ = 192 Hz, 2 H), 7.36–7.47 (m, 3 H), 7.58–7.67 (m, 2 H). ^{13}C NMR (APT): major diastereomer, δ 11.18 (CH$_3$), 17.99 (CH$_2$), 19.36 (CH$_3$), 22.90 (CH$_3$), 27.52 (CH), 29.33 (CH$_2$), 31.69 (CH), 47.31 (CH$_2$), 127.97, 129.45 (C$_{\mathrm{para}}$), 133.14 (C$_{\mathrm{ipso}}$), 135.25, minor diastereomer; δ 11.32 (CH$_3$), 18.96 (CH$_3$), 19.22 (CH$_2$), 22.17 (CH$_3$), 30.04 (CH$_2$), 31.88 (CH), 47.21 (CH$_2$). IR (thin film): 3069 (w), 2954 (s), 2907 (s), 2874 (m), 2130 (s), 1461 (m), 1429 (m), 1377 (m), 1117 (s), 940 (s), 852 (s), 700 (s) cm^{-1}. HRMS: calcd for (M – H)$^+$ = C$_{14}$H$_{23}$Si 219.1569, found 219.1569. LRMS [CI$^+$ (i-C$_4$H$_{10}$)] m/z (relative intensity): 220 (27), 219 (100), 149 (50), 143 (37), 142 (47), 107 (36), 101 (21). Anal. Calcd for C$_{14}$H$_{24}$Si: C, 76.29; H, 10.98. Found: C, 76.09; H, 10.72.

7-(Phenylsilyl)hept-2-ene (10). Yield: 1.380 g (96%, 98% pure by GC) of 10 as a colorless liquid (9:1 mixture of trans/cis isomers). For combustion analysis a sample was distilled: bp 64 °C/0.04 mmHg. R_f: 0.60 (hexanes). ^{1}H NMR: δ 0.94–1.05 (m, 2 H), 1.30–1.60 (m, 4 H), 1.62–2.14 (m, 5 H), 4.35 (t, J = 3.7 Hz, $^1J_{29\mathrm{Si,H}}$ = 192 Hz, 2 H), 5.46 (m, 2 H), 7.37–7.48 (m, 3 H), 7.58–7.67 (m, 2 H). ^{13}C NMR (APT): (trans-isomer) δ 9.82 (CH$_2$), 17.88

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(CH_3), 24.52 (CH_2), 32.15 (CH_2), 32.66 (CH_2), 124.80 (=CH), 127.97, 129.49, 131.29 (=CH), 132.72 (C_{ipso}), 135.22; (cis-isomer) δ 9.89, 12.69 (CH_3), 24.67 (CH_2), 26.42 (CH_2), 123.84 (=CH), 130.49 (=CH). IR (thin film): 3065 (w), 3016 (m), 2922 (s), 2853 (m), 2132 (s), 1432 (m), 1116 (m), 939 (s), 839 (s), 700 (m) cm^{-1}. HRMS: calcd for $(M - H)^+ = C_{13}H_{19}Si$ 203.1256, found 203.1258. LRMS (EI) m/z (relative intensity): 204 (17), 203 (84), 127 (43), 126 (90), 107 (100), 105 (44), 98 (68), 55 (23). Anal. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86. Found: C, 75.84; H, 9.70.

2-Methyl-7-(phenylsilyl)hept-2-ene (12). Yield: 1.440 g (94%, 99% pure by GC) of **12** as a colorless liquid which was distilled; bp 78–80 °C/0.04 mmHg. R_f: 0.66 (hexanes). ^{1}H NMR: δ 0.92–1.02 (m, 2 H), 1.36–1.55 (m, 4 H), 1.62 (s, 3 H), 1.71 (s, 3 H), 1.95–2.05 (m, 2 H), 4.32 (t, J = 3.7 Hz, $^1J_{^{29}Si,H}$ = 192 Hz, 2 H), 5.13 (t (br), J = 7.2 Hz, 1 H), 7.35–7.46 (m, 3 H), 7.57–7.64 (m, 2 H). ^{13}C NMR (APT): δ 9.89 (CH_2), 17.60 (CH_3), 24.68 (CH_2), 25.68 (CH_3), 27.61 (CH_2), 32.97 (CH_2), 124.58 (=CH), 127.97, 129.49 (C_{para}), 131.37, 132.76, 135.23. IR (thin film): 3064 (w), 2966 (m), 2921 (s), 2855 (m), 2133 (s), 1432 (m), 1117 (m), 938 (m), 842 (s), 700 (m), cm^{-1}. HRMS: calcd for $(M - H)^+ = C_{14}H_{21}Si$, 217.1413, found 217.1423. LRMS (EI) m/z (relative intensity): 218 (4), 217 (10), 175 (51), 140 (71), 134 (46), 107 (100), 105 (62), 84 (96), 69 (50), 41 (70).

1-Methylene-2-[3-(phenylsilyl)propyl]cyclohexane (14). Yield: 222.4 mg (91%, >98% pure by GC) of the silanes as a colorless liquid (96:4 ratio by GC). For combustion analysis a sample was Kugelrohr distilled: ot 90–95 °C/0.04 mmHg. R_f: 0.50 (hexanes). ^{1}H NMR: δ 0.79–0.91 (m, 2 H), 1.06–1.68 (m, 10 H), 1.78–1.99 (m, 2 H), 2.05–2.21 (m, 1 H), 4.21 (m, $^1J_{^{29}Si,H}$ = 192 Hz, 2 H), 4.45 (s (br), 1 H), 4.54 (s (br), 1 H), 7.20–7.31 (m, 3 H), 7.43–7.50 (m, 2 H). ^{13}C NMR (APT): δ 10.13 (CH_2), 22.89 (CH_2), 24.18 (CH_2), 28.78 (CH_2), 33.73 (CH_2), 34.69 (CH_2), 35.26 (CH_2), 42.74 (CH), 105.51 ($C{=}CH_2$), 127.95, 129.47 (C_{para}), 132.72 (C_{ipso}), 135.20, 152.81 ($C{=}CH_2$). IR (thin film): 3068 (m), 3051 (w), 2926 (s), 2853 (s), 2127 (s), 1644 (m), 1445 (m), 1429 (m), 1117 (m), 939 (s), 888 (m), 858 (s), 735 (m), 700 (s), 662 (m) cm^{-1}. HRMS: calcd for $C_{16}H_{24}Si$, 244.1647, found 244.1656. LRMS (EI) m/z (relative intensity): 244 (3), 107 (100), 105 (36), 96 (66), 81 (55). Anal. Calcd for $C_{16}H_{24}Si$: C, 78.62; H, 9.90. Found: C, 78.75; H, 10.02.

4-[2-(Phenylsilyl)ethyl]cyclohex-1-ene (16). Yield (benzene as solvent): 1.440 g (95%, >99% pure by GC) of **16** as a colorless liquid. For combustion analysis a sample was distilled: bp 94–95 °C/0.04 mmHg. R_f: 0.59 (hexanes). ^{1}H NMR: δ 0.97–1.08 (m, 2 H), 1.17–1.32 (m, 1 H), 1.42–1.89 (m, 5 H), 2.04–2.24 (m, 3 H), 4.36 (t, J = 3.7 Hz, $^1J_{^{29}Si,H}$ = 192 Hz, 2 H), 5.67–5.76 (m, 2 H), 7.37–7.48 (m, 3 H), 7.59–7.66 (m, 2 H). ^{13}C NMR (APT): δ 7.10 (CH_2), 25.21 (CH_2), 28.37 (CH_2), 31.45 (CH_2), 31.75 (CH_2), 36.04 (CH), 126.52 (=CH), 127.05 (=CH), 127.97, 129.51 (C_{para}), 132.63 (C_{ipso}), 135.20. IR (thin film): 3063 (w), 3019 (m), 2913 (s), 2840 (m), 2132 (s), 1430 (m), 1117 (m), 938 (s), 883 (m), 840 (s), 700 (m), 658 (m) cm^{-1}. HRMS: calcd for $(M - H)^+ = C_{14}H_{19}Si$ 215.1256, found 215.1260. LRMS [Cl^+ (i-C_4H_{10})] m/z (relative intensity): 216 (20), 215 (100), 139 (63), 138 (55), 57 (89), 43 (82). Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 77.40; H, 9.71.

4-[2-(Phenylsilyl)ethyl]cyclohex-1-ene (16). Yield (toluene as solvent): 0.4200 g (97%, >99% pure by GC) of silane **16**.

(4*R*)-1-Methyl-4-[(1*R*,*S*)-1-methyl-2-(phenylsilyl)ethyl]cyclohex-1-ene (18). Distillation afforded 1.050 g (61%, >99% pure by GC) of silane **18** as a colorless liquid (2:1 mixture of diastereomers by ^{13}C NMR; same ratio as in the crude product): bp 112–118 °C/0.04 mmHg. R_f: 0.55 (hexanes). ^{1}H NMR: δ 0.79–1.00 (m, 4 H), 1.08–1.51 (m, 3 H), 1.56–2.09 (m, 9 H), 4.30–4.39 (m, $^1J_{^{29}Si,H}$ = 193 Hz, 2 H), 5.40 (m, 1 H), 7.33–7.44 (m, 3 H), 7.55–7.63 (m, 2 H). ^{13}C NMR (APT): major diastereomer, δ 15.34 (CH_2), 18.47 (CH_3), 23.42 (CH_3), 26.70 (CH_2), 27.85 (CH_2), 30.81 (CH_2), 34.49 (CH), 40.59 (CH), 120.87 (=CH), 127.97, 129.47 (C_{para}), 133.00, 133.99, 135.21; minor diastereomer, δ 14.94 (CH_2), 18.83 (CH_3), 25.45 (CH_2), 28.91 (CH_2), 30.75 (CH_2), 34.37 (CH), 40.63 (CH), 120.91 (=CH). IR (thin film): 3068 (w), 3051 (w), 3008 (w), 2959 (s), 2911 (s), 2883 (s), 2132 (s), 1429 (m), 1116 (m), 941 (s), 857 (s), 701 (s) cm^{-1}. LRMS (EI) m/z (relative intensity): 244 (23), 243 (84), 167 (58), 166 (100), 107 (70). Anal. Calcd for $C_{16}H_{24}Si$ (244.45): C, 78.62; H, 9.90. Found: C, 78.44; H, 9.90.

1-Chloro-6-(phenylsilyl)hexane (20a). Yield: 1.356 g (85%, 99% pure by GC) of silane **20a** as a colorless liquid. For combustion analysis a sample was distilled. R_f: 0.45 (hexanes). ^{1}H NMR: δ 0.90–1.00 (m, 2 H), 1.34–1.55 (m, 6 H), 1.69–1.80 (m, 2 H), 3.51 (t, J = 6.7 Hz, 2 H), 4.29 (t, J = 3.7 Hz, $^1J_{^{29}Si,H}$ = 193 Hz, 2 H), 7.32–7.42 (m, 3 H), 7.54–7.60 (m, 2 H). ^{13}C NMR (APT): δ 9.86 (CH_2), 24.85 (CH_2), 26.41 (CH_2), 31.94 (CH_2), 32.42 (CH_2), 45.05 (CH_2), 127.99, 129.55 (C_{para}), 132.59 (C_{ipso}), 135.20. IR (thin film): 3068 (w), 2925 (s), 2855 (m), 2132 (s), 1428 (m), 1117 (m), 938 (s), 839 (s), 735 (m), 701 (s), 660 (m) cm^{-1}. LRMS (EI) m/z (relative intensity): 227 (0.1), 226 (0.1), 225 (0.3), 141 (37), 120 (43), 107 (100), 106 (32), 105 (53), 92 (56), 78 (100). Anal. Calcd for $C_{12}H_{19}ClSi$ (226.82): C, 63.54; H, 8.44. Found: C, 63.50; H, 8.35.

6-(Benzyloxy)-1-(phenylsilyl)hexane (20b). Flash chromatography (hexanes/ether = 25/1 as eluent) gave 0.938 g (90%, >99% pure by GC) of **20b** as a colorless liquid. R_f: 0.50 (hexanes/ether = 20/1). ^{1}H NMR: δ 0.92–1.10 (m, 2 H), 1.36–1.69 (m, 8 H), 3.48 (t, J = 6.6 Hz, 2 H), 4.32 (t, J = 3.7 Hz, $^1J_{^{29}Si,H}$ = 193 Hz, 2 H), 4.52 (s, 2 H), 7.28–7.44 (m, 8 H), 7.57–7.62 (m, 2 H). ^{13}C NMR (APT): δ 9.88 (CH_2), 24.94 (CH_2), 25.73 (CH_2), 29.55 (CH_2), 32.55 (CH_2), 70.37 (CH_2), 72.81 (CH_2), 127.46, 127.60, 127.95, 128.33, 129.48, 132.69 (C_{ipso}), 135.19, 138.69 (C_{ipso}). IR (thin film): 3066 (w), 3028 (w), 2926 (s), 2854 (s), 2130 (s), 1454 (m), 1428 (m), 1116 (s), 939 (s), 867 (m), 839 (s), 735 (s), 699 (s) cm^{-1}. LRMS (EI) m/z (relative intensity): 298 (3), 123 (70), 107 (34), 92 (42), 91 (100). Anal. Calcd for $C_{19}H_{26}OSi$ (298.50): C, 76.45; H, 8.78. Found: C, 76.25; H, 8.72.

1-(Phenylsilyl)-6-[(*tert*-butyldimethylsilyl)oxy]hexane (20c). Yield: 0.800 g (83%, 99% pure by GC) of silane **20c** as a colorless liquid. For combustion analysis a sample was Kugelrohr distilled: ot 115–120 °C/0.04 mmHg. R_f: 0.20 (hexanes). ^{1}H NMR: δ 0.07 (s, 6 H), 0.92 (s, 9 H), 0.92–1.00 (m, 2 H), 1.27–1.57 (m, 8 H), 3.61 (t, J = 6.5 Hz, 2 H), 4.31 (t, J = 3.7 Hz, $^1J_{^{29}Si,H}$ = 193 Hz, 2 H), 7.32–7.44 (m, 3 H), 7.56–7.63 (m, 2 H). ^{13}C NMR (APT): δ −5.32 ($SiMe_2$), 9.92 (CH_2), 18.32 (CMe_3), 25.02 (CH_2), 25.38 (CH_2), 25.95 (CMe_3), 32.57 (CH_2), 32.69 (CH_2), 63.23 (CH_2), 127.97, 129.49 (C_{para}), 132.76 (C_{ipso}), 135.22. IR (thin film): 2928 (s), 2856 (s), 2133 (s), 1255 (m), 1102 (s), 939 (m), 836 (s), 775 (m), 700 (m) cm^{-1}. HRMS: calcd for $(M - H)^+ = C_{18}H_{33}OSi_2$, 321.2070, found 321.2074. LRMS [Cl^+ (i-C_4H_{10})] m/z (relative intensity): 323 (2.7), 322 (0.5), 321 (1.6), 181 (100), 43 (53). Anal. Calcd for $C_{18}H_{34}OSi_2$: C, 67.01; H, 10.62. Found: C, 67.31; H, 10.59.

2-[[(6-Phenylsilyl)hexyl]oxy]oxacyclohexane (20d). Yield: 0.843 g (96%, >99% pure by GC) of silane **20d** as a colorless liquid. For combustion analysis a sample was Kugelrohr distilled: ot 150 °C/0.04 mmHg. R_f: 0.41 (hexanes/Et_2O = 9/1). ^{1}H NMR: δ 0.89–0.98 (m, 2 H), 1.32–1.90 (m, 14 H), 3.32–3.41 (dt, J = 9.5, 6.7 Hz, 1 H), 3.45–3.53 (m, 1 H), 3.67–3.77 (dt, J = 9.5, 6.8 Hz, 1 H), 3.81–3.91 (m, 1 H), 4.29 (t, J = 3.7 Hz, $^1J_{^{29}Si,H}$ = 192 Hz, 2 H), 4.54–4.58 (m, 1 H), 7.30–7.41 (m, 3 H), 7.52–7.59 (m, 2 H). ^{13}C NMR (APT): δ 9.85 (CH_2), 19.58 (CH_2), 24.91 (CH_2), 25.41 (CH_2), 25.77 (CH_2), 29.52 (CH_2), 30.67 (CH_2), 32.55 (CH_2), 62.21 (CH_2), 67.51 (CH_2), 98.76 (CH), 127.91, 129.44 (C_{para}), 132.66 (C_{ipso}), 135.15. IR (thin film): 3068 (w), 2934 (s), 2854 (s), 2130 (s), 1429 (m), 1352 (m), 1200 (m), 1135 (m), 1117 (m), 1078 (m), 1034 (s), 939 (s), 839 (s), 701 (m) cm^{-1}. HRMS: calcd for $C_{17}H_{28}O_2Si$: 292.1859, found 292.1833. LRMS (EI) m/z (relative intensity): 292 (3), 107 (39), 85 (100). Anal. Calcd for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.65. Found: C, 69.96; H, 9.97.

1,7-Bis(phenylsilyl)heptane (22). Kugelrohr distillation yielded 0.875 g (80%, 93% pure by GC) of silane **22** as a colorless liquid. Impurities were 4% of an isomer (almost the same mass spectrum by GC–MS) and <2% of 7-(phenylsilyl)hept-1-ene (by GC–MS, M^+ = 204); ot ~140 °C/0.04 mmHg. R_f: 0.64 (hexanes). ^{1}H NMR: δ 0.90–1.00 (m, 4 H), 1.22–1.58 (m, 10 H), 4.31 (t, J = 3.7 Hz, $^1J_{^{29}Si,H}$ = 193 Hz, 4 H), 7.33–7.45 (m, 6 H), 7.56–7.63 (m, 4 H). ^{13}C NMR (APT): δ 9.93 (2 CH_2), 24.99 (2 CH_2), 28.77 (CH_2), 32.61 (2 CH_2), 127.97, 129.49 (C_{para}), 132.79 (C_{ipso}), 135.23. IR (thin film): 3068 (w), 3051 (w), 3018 (w), 2922 (s), 2852 (m), 2132 (s), 1428 (m), 1116 (m), 938 (s), 844 (s), 736 (m), 700 (s) cm^{-1}. HRMS: calcd for $C_{19}H_{28}Si_2$, 312.1730, found 312.1732. LRMS (EI) m/z (relative intensity): 312 (0.3), 156 (40), 126 (55), 107 (100), 105 (35), 98 (36). Anal. Calcd for $C_{19}H_{28}Si_2$: C, 73.00; H, 9.03. Found: C, 73.40; H, 9.38.

8-(Phenylsilyl)-3-[(*tert*-butyldimethylsilyl)oxy]oct-1-ene (24a). Yield: 281.4 mg (54%, 96% pure by GC) of **24a** as a colorless liquid. For combustion analysis a sample was Kugelrohr distilled; ot ~125 °C/0.04 mmHg. R_f: 0.10 (hexanes). ^{1}H NMR: δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.89 (s, 9 H), 0.88–0.97 (m, 2 H), 1.26–1.50 (m, 8 H), 4.05 (m, 1 H), 4.27 (t, J = 3.7 Hz, $^1J_{29\mathrm{Si,H}}$ = 192 Hz, 2 H), 5.00 (d (br), J = 10.9 Hz, 1 H), 5.11 (d (br), J = 17.3 Hz, 1 H), 5.71–5.84 [ddd (not resolved), J = 6.0, 10.3, and 16.8 Hz, 1 H], 7.30–7.42 (m, 3 H), 7.51–7.59 (m, 2 H). ^{13}C NMR (APT): δ −4.87 (SiMe), −4.43 (SiMe), 9.90 (CH_2), 18.22 (CMe_3), 24.72 (CH_2), 24.98 (CH_2), 25.86 ($C\mathit{Me}_3$), 32.75 (CH_2), 37.90 (CH_2), 73.83 (CH), 113.45 ($=CH_2$), 127.97, 129.49 (C_{para}), 132.76 (C_{ipso}), 135.22, 141.90 ($=CH$). IR (thin film): 2928 (s), 2856 (m), 2133 (s), 938 (m), 837 (s), 775 (m), 700 (m) cm^{-1}. LRMS [CI$^+$ (CH_4)] *m/z* (relative intensity): 347 (0.8), 181 (100). Anal. Calcd for $C_{20}H_{36}OSi_2$ (348.68): C, 68.90; H, 10.41. Found: C, 69.17; H, 10.54.

8-(Phenylsilyl)-3-phenyloct-1-ene (24b). Yield: 90.0 mg (31%, 95% pure by GC) of **24b** as a colorless oil. Kugelrohr distillation gave 82.0 mg (28%, 96% pure by GC); ot ~130 °C/0.04 mmHg. R_f: 0.30 (hexanes). ^{1}H NMR: δ 0.87–0.97 (m, 2 H), 1.14–1.50 (m, 6 H), 1.63–1.74 (m, 2 H), 3.18–3.27 (m, 1 H), 4.29 (t, J = 3.7 Hz, $^1J_{29\mathrm{Si,H}}$ = 191 Hz, 2 H), 4.97–5.06 (m, 2 H), 5.88–6.02 (m, 1 H), 7.16–7.43 (m, 8 H), 7.54–7.59 (m, 2 H). ^{13}C NMR (APT): δ 9.92 (CH_2), 24.89 (CH_2), 27.06 (CH_2), 32.68 (CH_2), 35.23 (CH_2), 49.86 (CH), 113.88 ($=CH_2$), 126.09 (C_{para}), 127.58, 127.97, 128.42, 129.49 (C_{para}), 132.73 (C_{ipso}), 135.22, 142.49, 144.61 (C_{ipso}). IR (thin film): 3067 (w), 3026 (w), 2924 (s), 2854 (m), 2131 (s), 1116 (m), 937 (s), 847 (s), 737 (m), 699 (s) cm^{-1}. HRMS: calcd for $C_{20}H_{26}Si$, 294.1804, found 294.1802. LRMS (EI) *m/z* (relative intensity): 294 (1), 118 (46), 117 (100), 107 (45). Anal. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 8.90. Found: C, 81.76; H, 9.01.

2-Deuterio-3-phenyl-1-(phenyldideuteriosilyl)propane. Yield: 122.6 mg (0.53 mmol, 76%, >99% pure by GC); ot ~100 °C/0.04 mmHg. R_f: 0.33 (hexanes). ^{1}H NMR: δ 0.97 (d, J = 8.3 Hz, 2 H), 1.77 [[quint, t (not resolved)], $^3J_{\mathrm{H,H}}$ = 8.0 Hz, $^2J_{\mathrm{H,D}}$ = 1.8 Hz, 1 H], 2.67 (d, J = 7.6 Hz, 2 H), 7.13–7.43 (m, 8 H), 7.53–7.59 (m, 2 H). ^{13}C NMR (APT): δ 9.42 (CH_2Si), 26.52 [t, $^1J_{\mathrm{C,D}}$ = 19.8 Hz (CHD)], 38.82 (CH_2Ph), 125.76 (C_{para}), 127.99, 128.27, 128.51, 129.57 (C_{para}), 132.37 (C_{ipso}), 135.23, 142.10 (C_{ipso}). IR (thin film): 3065 (m), 3025 (m), 2917 (s), 1557 (s), 1495 (m), 1453 (m), 1428 (m), 1115 (m), 738 (s), 697 (s), 640 (m), 624 (m), 595 (m) cm^{-1}. HRMS: calcd for $C_{15}H_{15}D_3Si$, 229.1366, found 229.1363. LRMS (EI) *m/z* (relative intensity): 229 (1.1), 228 (1.2), 109 (100), 91 (79). Anal. Calcd for $C_{15}H_{15}D_3Si$ (229.41): C, 78.53; H, 7.91 (H plus D as H). Found: C, 78.30; H, 7.94 (H plus D as H).

Acknowledgment. We thank the National Institutes of Health and the German Academic Exchange Service (DAAD) for their generous support of this research and Dr. Kevin Bobbitt for performing the ^{2}H NMR spectra.

Supplementary Material Available: Experimental and spectroscopic data for starting materials phenyltrideuteriosilane, **13**, **19b**, **19c**, **19d**, and $Cp_2{}^*YCH(SiMe_3)_2$ (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

2-Arylbenzoxazole Formation through *o*-Fluoro Displacement Reactions

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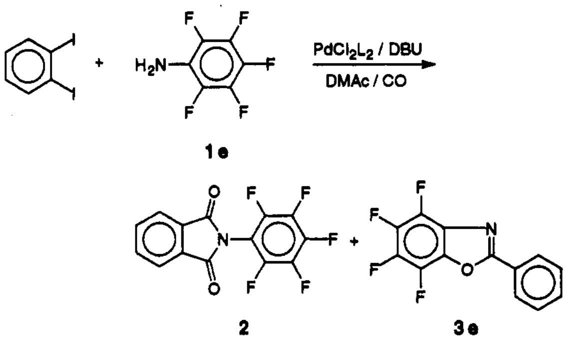
Received March 30, 1992 (Revised Manuscript Received July 28, 1992)

Recently, a novel method for the formation of N-substituted phthalimides via the palladium-catalyzed carbonylation and condensation of aryl diiodides and primary amines was reported.[1] The method was a general one and provided easy access to phthalimides with common electron-donating and -withdrawing substituents. The general scope of this reaction suggested that the use of highly deactivated amines might also give the desired phthalimides. Interest has been generated over polymeric materials containing fluorine, which have been shown to possess good thermooxidative stability as well as increased solubility and processability.[2] Perfluorinated aromatic amines are poor nucleophiles and as such have found limited utility in the preparation of high-performance materials such as polyimides and aramids.[3] Described herein are the results of an investigation into the palladium-catalyzed carbonylation and condensation of iodoaromatics and fluorinated anilines.

A reaction was run in which a DMAc solution containing *o*-diiodobenzene, pentafluoroaniline (**1e**), 1.2 equiv of DBU, and 3% $PdCl_2L_2$ (where L = PPh_3) were allowed to react under 95 psig of carbon monoxide (CO) at 115 °C (eq 1).



(1)

After 22 h, the reaction mixture showed the presence of a small amount of the desired *N*-(pentafluorophenyl)phthalimide **2** but also a number of other products. The major constituent of the reaction mixture was determined to be 2-phenyl-4,5,6,7-tetrafluorobenzoxazole (**3e**).

A probable route for the formation of **3e** is shown in Scheme I. In this reaction, palladium(0) oxidatively adds to the aryl iodide and then inserts CO to give the acylpalladium complex **4** (ligands on Pd are omitted for clarity). Complex **4** is attacked by pentafluoroaniline to give iodoamide intermediate **5**. The amide nitrogen in **5** is relatively non-nucleophilic, and when the other aryl–iodide bond is activated by palladium, only a small portion undergoes CO insertion and subsequent attack by the amide nitrogen producing the imide **2** (path a). A majority of **5** undergoes reduction and amide **6e** is formed. With heating, and in the presence of base, **6e** slowly cyclized with displacement of fluoride to give the observed benzoxazole **3e** (path b). Alternately, cyclization of the benzoxazole may precede reduction of the aryliodide bond, although no 2-(2′-iodophenyl)-4,5,6,7-tetrafluorobenzoxazole was observed.

If **6e** were an intermediate, then an alternate method for making **3e** would be to start with iodobenzene and

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