standard. Analysis after 5 h showed an 87% yield of benzyl mercaptan; extending the reaction time to 19 h increased the yield to 92%.

Hydroformylation of 1-Pentene.[9] A 75-mL stainless steel reaction vessel (Hoke bomb, Whitey, OH), equipped with a $^1/_8 \times ^1/_2$ in. Teflon-coated magnetic stirring bar, was charged with 0.13 g (0.145 mmol of cobalt) of the polymeric cobalt catalyst, 0.085 g (0.4 mmol) of *n*-pentadecane (internal standard), 10 mL of *n*-octane, and 0.63 g (9.0 mmol) of 1-pentene under a nitrogen atmosphere. After the vessel was sealed, a mixture of hydrogen and carbon monoxide (2/1) was introduced. The system was then heated to 180 °C by placing the vessel in an oil bath, and the mixture was stirred magnetically, using an external magnetic stirrer. The maximum pressure (480–510 psi at 180 °C) and equilibrium temperature were obtained in ca. 5 min. After 14 h, the pressure dropped a total of 110 psi, and the vessel was then cooled (0 °C) and vented and an aliquot analyzed by GLC. The product mixture consisted of 1-hexanal (13%), 1-hexanol (33%), 2-methylpentanal (13%), 2-methylpentanol (21%), pentane (7%), and pentenes (2%). Reuse of the catalyst gave identical results.

Benzenethiol Acetate.[10] To a mixture of 0.866 g (1.1 mmol of phosphine) of 3 and acetic acid (0.06 g, 1.0 mmol) in 7 mL of dry methylene chloride was added 0.135 g (1.0 mmol) of phenyl thiocyanate. The mixture was stirred under nitrogen for 5 h at 40 °C; analysis by GLC indicated an 84% yield of benzenethiol acetate.

Registry No. $(EtO)_2POH$, 762-04-9; BuMgBr, 693-03-8; $CH_3CH(NO_2)CH_3$, 79-46-9; $EtOCOCH{=}CH_2$, 140-88-5; $PhCH_2SSCH_2Ph$, 150-60-7; $(CH_3)_2C(NO_2)CH_2CH_2CO_2Et$, 23102-02-5; $PhCH_2SH$, 100-53-8; $CH_2{=}CHCH_2CH_2CH_3$, 109-67-1; $OHC(CH_2)_4CH_3$, 66-25-1; $HO(CH_2)_5CH_3$, 111-27-3; $OHCCH(CH_3)CH_2CH_2CH_3$, 123-15-9; $HOCH_2CH(CH_3)CH_2CH_2CH_3$, 105-30-6; CH_3CO_2H, 64-19-7; PhSCN, 5285-87-0; AcSPh, 934-87-2.

Trialkyl(2-nitro-1-alkenyl)silanes. Synthesis and Diels–Alder Reaction

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With the explosive development of organosilicon chemistry during the past 15 years, (1-alkenyl)trialkylsilanes **1**, or more commonly vinylsilanes, have become increasingly important in selective organic synthesis.[1] Whereas most of them react as nucleophiles, a few reports have appeared recently on electrophilic vinylsilanes possessing an electron-withdrawing group at the β-position.[2] Among these, trialkyl(2-nitro-1-alkenyl)silanes ((nitrovinyl)silanes) **2** are interesting in view of recent attention to the chemistry of nitroalkenes.[3]

In a previous report, we reported the synthesis of the simplest (nitrovinyl)silane **2a** via nitroselenenylation of vinylsilane **1a** and its reaction with organometallic compounds.[4] Recently Padwa has reported the cycloaddition reactions of **2a** prepared by an independent procedure.[5]

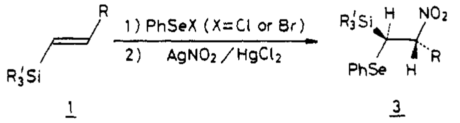
Table I. Synthesis of 2 and 3 via Nitroselenenylation of 1

	1		2	3
	R	R′	yield, %	yield,[c] %
a	H	Me	66[a]	89
b	C_4H_9	Et	37[b]	93
c	C_6H_{13}	Me	42[b]	94
d	C_6H_{13}	Et	40[b]	96
e	C_8H_{17}	Et	43[b]	96

[a] Benzeneselenenyl bromide was used. [b] Benzeneselenenyl chloride was used. [c] Isolated yield based upon 2.

We now disclose our own results on the general synthesis of (nitrovinyl)silanes **2** and the Diels–Alder reaction of **2a** as a dienophile.[5]

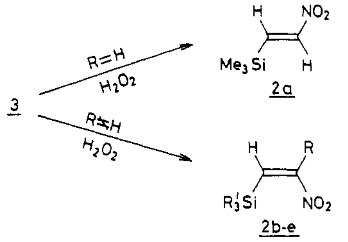
Synthesis of **2** began with nitroselenenylation of vinylsilanes **1**, which involves treatment of **1**[6] with benzeneselenenyl halide (halogen = Cl or Br) followed by addition of silver nitrite in the presence of mercury(II) chloride (eq 1). Nitroselenides **3** were obtained in 37–66% isolated



(1)

yield as shown in Table I. After a number of attempts, the best yields of **3** were obtained by using bezeneselenenyl chloride, except for the case of **1a**, where the use of benzeneselenenyl bromide afforded a significantly improved yield. Although the yields of nitroselenenylation were by no means excellent, both regio- and stereoselectivity are completely controlled: In each case there was obtained a single isomer. The regiochemistry is consistent with the intervention of a β-silyl cation generated by initial reaction of **1** with benzeneselenenyl halide.[7] The stereochemistry of addition across the C=C bond is most probably trans in light of the previous cases involving simple alkenes, where exclusive trans addition has been observed.[4]

Such a stereochemical assignment of **3** is in complete agreement with the stereochemical consequence of subsequent oxidation step which proceeds via syn elimination of benzeneselenenic acid (eq 2).[8] While oxidation of **3a**



(2)

with an excess of hydrogen peroxide provided *E* isomer **2a**, a thermodynamically more stable isomer, **3b–e** upon oxidation under similar conditions afforded *Z* isomers **2b–e** in excellent yields (Table I). Stereochemical assignment of **2** was unequivocally established by considering the anisotropic deshielding effect of the NO_2 group.[9] The

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(4) Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1983**, *24*, 2795.

(5) Padwa, A; MacDonald J. G. *J. Org. Chem.* **1983**, *48*, 3189.

(6) Vinylsilane (**1a**) was purchased from Chisso Co., a Petrarch Chem. Co. Agent in Tokyo. Other vinylsilanes **1b–e** were prepared by hydrosilylation of the corresponding alkynes using chloroplatinic acid as a catalyst: Stork, G.; Colvin, E. W. *J. Am. Chem. Soc.* **1971**, *93*, 2080.

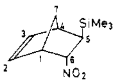
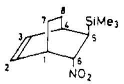
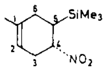
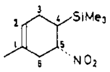
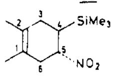
(7) Reference 1a, p 62.

(8) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, 1979.

(9) The strong deshielding anisotropic effect of the nitro group has been discussed in (a) Yamaguchi, I. *Can. J. Chem.* **1962**, *40*, 105. (b) Fraser, R. R. *Ibid.* **1960**, *38*, 2226. We have observed substantial anisotropic effect of the nitro group on the chemical shifts of H-5 of 4-nitro-4-octenes (**4**): δ 5.67 for the *Z* isomer and δ 7.11 for the *E* isomer: Hayama, T; Tomoda, S; Takeuchi, Y; Nomura, Y, *Tetrahedron Lett.* **1982**, *23*, 4733.

0022-3263/84/1949-3235$01.50/0

Table II. Diels–Alder Reaction of 2a

entry	dienes	conditions	adducts	yield,[a] %
1	cyclopentadiene	benzene, reflux, 3 h	 4	94
2	cyclohexadiene	110 °C, 8 h, in sealed tube	 5	61
3	isoprene	110 °C, 8 h, in sealed tube	 6a  6b	94
4	2,3-dimethyl-1,3-butadiene	110 °C, 2.5 h, in sealed tube	 7	87

[a] Isolated unoptimized yield.

chemical shifts of H-1 of compounds **2b–e**, the orientation of which is trans to the NO_2 group, fall in the range δ 5.83–5.93, whereas the corresponding proton (cis to the NO_2) of **2a** shows up at appreciably low field δ 6.96 (d, J = 16.2 Hz.[10] The overall stereochemical outcome from **1** to **2** is therefore retention of configuration about the C=C bond in **1**.

The electrophilic property of the (nitrovinyl)silanes **2** is exemplified by the Diels–Alder reaction of **2a** with a variety of dienes (Table II). The structures of the adducts were assigned on the basis of spectral data (IR, ^1H and ^{13}C NMR) and combustion analyses. The stereochemistry of the adduct **4**[5] between **2a** and cyclopentadiene (entry 1) was deduced on the basis of its ^1H NMR spectrum, the fixed dihedral angle relationship giving rise to diagnostic coupling constant.[11] Exclusive formation of the endo adduct is not surprising if one considers a similar trend observed for the Diels–Alder reaction of nitroethylene with cyclopentadiene,[12] which is much more reactive than **2a** as a dienophile. The reaction of **2a** with cyclohexadiene (entry 2) was carried out without solvent to afford again a single stereoisomer **5**,[5] the stereochemistry of which was assigned on the basis of the Karplus relationship.[13] Acyclic dienes (entries 3 and 4) also react with **2a** to give the Diels–Alder adducts **6** and **7**, respectively, in excellent yield. The regiochemical assignment of **6a** and **6b** was made as an inseparable mixture on the basis of the following considerations: (a) the results of empirical calculation of the ^{13}C NMR chemical shifts of the olefinic carbons in **6a** and **6b** using the data of **7**[14] and (b) substituent effect of NO_2 on the ^{13}C chemical shifts of both allylic (β-effect) and olefinic (γ-effect) carbons.[15] The regioisomer ratio (3:1) determined by the ^1H NMR spectrum is as high as that of the Diels–Alder reaction of isoprene with other dienophiles.[16] This indicates that the trimethylsilyl group of **2a** has a negligible steric and electronic effect on the regioselectivity of the addition.

In summary, we have demonstrated that (nitrovinyl)silanes **2** can be prepared by a reaction sequence involving nitroselenenylation and oxidation and that the simplest (nitrovinyl)silane **2a** behaves as a quite normal dienophile, which, however, is less reactive than nitroethylene in the Diels–Alder reaction.

Experimental Section

General Methods. All glassware, syringes, needles, and stirring bars were oven-dried before use. All reactions were performed under dry argon. NMR spectra were obtained by a JEOL FX-90Q spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in δ scale relative to internal tetramethylsilane. IR spectra were recorded on a JASCO A-102 spectrometer and the frequencies are given in reciprocal centimeters.

Materials. Benzeneselenenyl chloride was used as received from Aldrich Chemical Co., NJ. Benzeneselenenyl bromide was prepared by the reaction of diphenyl diselenide and bromine.[17] Tetrahydrofuran (THF) was freshly distilled over sodium benzophenone ketyl under argon. Dichloromethane was distilled over calcium hydride. Acetonitrile was distilled from phosphorus pentoxide. Silver nitrite and mercury(II) chloride were dried at 70 °C under vacuum.

Preparation of 2a. To a stirred solution of benzeneselenenyl bromide (7.56 g, 32 mmol) in THF (40 mL) was added vinylsilane **1a** (4.6 mL, d = 0.690, 32 mmol) at −78 °C under argon. After stirring at this temperature for 10 min, finely powdered mercury(II) chloride (13.0 g, 48 mmol) was added all at once. To the suspension was then added dropwise a solution of silver nitrite (5.12 g, 33 mmol) in dry acetonitrile (40 mL) over 0.5 h at −78 °C. After being stirred for 8 h, the reaction mixture was allowed to warm to room temperature. The resulting white precipitates of silver chloride were removed by filtration, and the filtrate was concentrated in vacuo. The residue was then subjected to silica gel column chromatography to provide the corresponding nitroselenide **3a** (6.34 g, 66% yield): ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H, SiMe), 2.94 (dd, J = 6.2 and 8.3 Hz, 1 H, CHSe), 4.46 (dd, J = 8.3 and 13.0 Hz, 1 H, $CHNO_2$), 4.66 (dd, J = 6.2 and 13.0 Hz, $CHNO_2$), 7.22 (m, 3 H, Ph), 7.52 (m, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ −2.4 (q, SiMe), 27.7 (d, CHSe) 77.8 (t, $CHNO_2$), 128.0 (d, Ph), 128.7 (s, Ph), 129.1 (d, Ph), 134.2 (d, Ph); IR (neat) 2960, 1555, 1480, 1440, 1375, 1250, 1020, 840, 740, 690 cm^{-1}.

To a vigorously stirred solution of **2a** (2.40 g, 8 mmol) in dichloromethane was injected 30% aqueous hydrogen peroxide (1.8 mL, 16 mmol) at 0 °C and the mixture was stirred for 30 min. The usual ethereal workup provided an oil, which was passed through a silica gel column to give **2** (1.03 g, 89% yield): ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H, MeSi), 6.96 (d, J = 16.2 Hz, 1 H), 7.36 (d, J = 16.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.0 (q, MeSi), 137.9 (d), 147.3 (d); IR (neat) 2960, 1530, 1350, 1250, 1085, 965, 920, 845 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NO_2Si$: C, 41.35; H, 7.63; N, 9.64. Found: C, 41.13; H, 7.83; N, 9.46.

Spectroscopic and analytical data of other (nitrovinyl)silanes **2b–e**, prepared by using benzeneselenenyl chloride according to the procedure described above, follow.

2b: ^1H NMR ($CDCl_3$) δ 0.53–1.59 (m, 22 H, $SiEt_3$ and aliphatic H), 2.64 (t, J = 6.5 Hz, allylic CH_2), 5.86 (s, 1 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 3.9 (t), 7.6 (q), 13.7 (q), 22.1 (t), 29.9 (t), 33.7 (t), 130.1 (d), 163.7 (s); IR (neat) 2960, 1530, 1465, 1345, 1240, 1020, 735 cm^{-1}. Anal. Calcd for $C_{12}H_{25}NO_2Si$: C, 59.21; H, 10.35; N, 5.75. Found: C, 59.39; H, 10.50; N, 5.72.

2c: ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H, SiMe), 0.78–1.64 (m, 11 H, aliphatic H), 2.59 (t, J = 7.2 Hz, allylic H), 5.93 (s, 1 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ −1.0 (q), 14.0 (q), 22.5 (t), 27.7 (t), 28.6 (t), 31.5 (t), 33.6 (t), 133.1 (d), 162.6 (s); IR (neat) 2950, 1535, 1470, 1345, 1250, 860, 740, 695 cm^{-1}. Anal. Calcd for $C_{11}H_{23}NO_2Si$: C, 57.60; H, 10.11; N, 6.11. Found: C, 57.34; H, 9.80; N, 5.91.

2d: ^1H NMR ($CDCl_3$) δ 0.57 (m, 26 H, aliphatic H), 2.61 (t, J = 7.2 Hz, 2 H, allylic H), 5.83 (s, 1 H, olefinic H); ^{13}C NMR

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(10) The large coupling constant between H-1 and H-2 (J = 16.2 Hz) clearly indicates the trans stereochemical relationship. We could not detect any sign for the formation of the cis isomer, which would be thermodynamically less stable than the trans isomer.

(11) The proton coupling constant between H-5 and H-6 is 0.5 Hz, suggesting that these protons are in the trans configuration.[13] The assignment of the orientation of the nitro group was based on Alder's endo rule.[16]

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($CDCl_3$) δ 3.9 (t), 7.6 (q), 14.0 (q), 22.7 (t), 27.8 (t), 28.6 (t), 31.6 (t), 34.0 (t), 130.1 (d), 163.7 (s); IR (neat) 2960, 1535, 1465, 1345, 1240, 1020, 860, 730 cm^{-1}. Anal. Calcd for $C_{14}H_{29}NO_2Si$: C, 61.94; H, 10.77; N, 5.16. Found: C, 61.77; 11.04; N, 5.09.

2e: ^1H NMR ($CDCl_3$) δ 0.57–1.46 (m, 30 H, aliphatic H), 2.62 (t, J = 7.2 Hz, 2 H), 5.86 (s, 1 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 3.9 (t), 7.6 (q), 14.1 (q), 22.8 (t), 27.8 (t), 28.9 (t), 29.3 (t), 29.3 (t), 31.9 (t), 34.0 (t), 130.0 (d), 163.7 (s); IR (neat) 2950, 1530, 1465, 1340, 1235, 1025, 860, 730 cm^{-1}. Anal. Calcd for $C_{16}H_{33}NO_2Si$: C, 64.16; H, 11.10; N, 4.68. Found: C, 64.41; H, 11.13; N, 4.67.

Diels–Alder Reaction of 2a. The reactions were performed under the conditions indicated in Table II by using an excess of diene without solvent except for the case of cyclopentadiene. Spectral and analytical data of the adducts are described below.

4:[5] ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H, SiMe), 1.12–1.86 (m, 3 H, H-5 and 7), 2.84 (br m, 1 H, H-4), 3.52 (br m, 1H, H-1), 4.83 (dd, J = 3.9, 5.0 Hz, 1 H, H-6), 5.78 (dd, J = 3.0, 5.6 Hz, H-3 or 2), 6.48 (dd, J = 3.0, 5.6 Hz, H-2 or 3); ^{13}C NMR ($CDCl_3$) δ –2.2 (q), 32.0 (d), 44.3 (d), 47.3 (t), 48.8 (d), 87.8 (d), 129.5 (d), 142.2 (d); IR (neat) 3080, 2960, 1640, 1545, 1370, 1250, 875, 833, 715 cm^{-1}. Anal. Calcd for $C_{10}H_{17}NO_2Si$: C, 56.83; H, 8.11; N, 6.63. Found: C, 56.92; H, 8.13; N, 6.51.

5:[5] ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H, SiMe), 1.11–1.69 (m, 5 H, H-5, 7, and 8), 2.67 (br m, 1 H, H-4), 3.28 (br m, 1 H, H-1), 4.47 (dd, J = 2.8, 5.6 Hz, 1 H, H-6), 5.93 (t, J = 7.6 Hz, 1 H, H-3 or 2), 6.52 (t, J = 7.6 Hz, 1 H, H-2); ^{13}C NMR ($CDCl_3$) δ –2.0 (q), 21.9 (t), 22.8 (t), 30.5 (d), 30.9 (d), 36.1 (d), 87.6 (d), 127.4 (d), 139.2 (d); IR (neat) 3050, 2950, 1610, 1545, 1365, 1250, 855, 835, 750, 685 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NO_2Si$: C, 58.63; H, 8.50; N, 6.22. Found: C, 58.34; H, 8.33; N, 6.48.

6a and **6b**: ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H, SiMe), 1.67 (br s, 3 H, Me), 1.74–2.94 (m, 5 H, allylic H and CHSi–), 4.42–4.74 (m, 1 H, $CHNO_2$), 5.19–5.49 (m, 1H, olefinic H); ^{13}C NMR ($CDCl_3$) δ –3.1 (q, SiMe), 23.0 (q, Me), 23.1 (q, Me), 24.1 (d), 25.1 (d), 25.6 (d), 28.8 (t), 29.7 (t), 33.8 (t), 84.0 (d), 84.6 (d), 116.8 (d, C-2, major), 120.7 (d, C-2, minor), 129.8 (s, C-1, minor), 133.9 (s, C-1, major); IR (neat) 2960, 1630, 1545, 1370, 1250, 840 cm^{-1}. Anal. Calcd for $C_{10}H_{19}NO_2Si$: C, 56.30; H, 8.98; N, 6.57. Found: C, 56.50; H, 8.69; N, 6.72.

7: ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H, SiMe), 1.61 (s, 6 H, Me), 1.70–2.86 (m, 5 H, allylic H and CHSi), 4.57 (m, 1 H, $CHNO_2$), ^{13}C NMR ($CDCl_3$) δ –3.1 (q, SiMe), 18.5 (q, 2 × Me), 26.1 (d, C-4), 30.5 (t, C-3), 35.5 (t, C-6), 84.9 (d, C-5), 121.7 (s, C-2), 125.6 (s, C-1); IR (neat) 2960, 1630, 1545, 1370, 1255, 840, 695 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NO_2Si$: C, 58.11; H, 9.31; N, 6.16. Found: C, 57.87; H, 9.52; N, 6.28.

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Registry No. **1a**, 754-05-2; **1b**, 42067-72-1; **1c**, 57365-47-6; **1d**, 31930-43-5; **1e**, 90584-19-3; **2a**, 91201-28-4; **2b**, 91190-96-4; **2c**, 91190-97-5; **2d**, 91190-98-6; **2e**, 91190-99-7; **3a**, 91191-00-3; **3b**, 91191-01-4; **3c**, 91191-02-5; **3d**, 91191-03-6; **3e**, 91191-04-7; **4**, 91237-30-8; **5**, 91237-31-9; **6a**, 91190-93-1; **6b**, 91190-94-2; **7**, 91190-95-3; cyclopentadiene, 542-92-7; cyclohexadiene, 29797-09-9; isoprene, 78-79-5; 2,3–dimethyl-1,3-butadiene, 513-81-5.

Reactions of Phenylytterbium Iodide with Organic Halides in the Presence of Transition-Metal Catalysts

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Although numerous compounds with lanthanoid metals (Ln) have been prepared and characterized,[1] their applications to organic synthesis are still rare. Luche et al. reported that trichlorolanthanoid catalyzed selective 1,2-reduction of α,β-unsaturated ketones with sodium borohydride and alcohols.[2] Kagan et al. described unique SmI_2-mediated reactions such as reduction, alkylation, and coupling,[3] and Imamoto et al. utilized cerium compounds to organic synthesis.[4]

Table I. Copper-Catalyzed Coupling of PhYbI with *n*-BuI[a]

	product and yield, %	
catalyst (mol %)	*n*-BuPh[b]	PhPh[c]
none	trace	3
CuI (0.05)	21 (190)	13
CuBr (0.05)	38 (380)	6[d]
CuCl (0.06)	31 (240)	3
$CuCl_2$ (0.04)	8 (100)	1
$Cu(OAc)_2$ (0.05)	11 (120)	4

[a] PhYbI was prepared from Yb (0.5 mmol) and PhI (0.75 mmol) in THF (3 mL) at –30 °C, and the coupling reactions were carried out at room temperature with stirring overnight by using *n*-BuI (0.75 mmol) and copper catalysts. [b] GC yields based on Yb and numbers in parentheses are yields based on the copper catalyst. [c] GC yields based on PhI. [d] A 0.7% yield (based on Yb) of *n*-octane was also formed.

The first divalent organolanthanoid σ complexes of type RLnI were prepared from lanthanoid metals and organic iodides (RI) in tetrahydrofuran (THF) by Evans et al.[5] We reported some reactions of organolanthanoids, RLnI, with ketones, aldehyde, esters, nitriles, and acid chlorides[6] and showed that the reaction with esters gives ketones as main products rather than tertiary alcohols[6a] and that the addition reaction to α,β-unsaturated carbonyl compounds proceeds regioselectively at the 1,2-positions.[6c] It has also been found that the type of the reaction caused by RLnI differs depending upon Ln: addition reaction being caused by Eu and Yb, Tishchenko condensation by Pr, Nd, and Dy, and coupling by Sm.[7] As part of our interest in utilizing organolanthanoid complexes for organic synthesis, we have investigated the reactions of PhYbI with organic halides (RX). We describe the coupling reactions of PhYbI with RX in the presence of transition-metal catalysts.

Results and Discussion

Coupling Reactions of PhYbI with Butyl Halides. PhYbI, prepared in situ from Yb metal and iodobenzene (PhI) in THF at –30 °C, was allowed to react with *n*-butyl iodide (*n*-BuI) in the presence of cuprous bromide (CuBr) to give the cross-coupled product *n*-butylbenzene (*n*-BuPh)

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