The previous formation of this adduct seems to be necessary for the reaction, and thus analogous reactions with $Ni(S_2COEt)_2(bpy)$ (bpy = 2,2′-bipyridine) give the dicarbonyl only as traces whereas with $Ni(S_2CNEt_2)_2$ no reaction is observed, in accordance with the lower tendency of these complexes to interact with a Lewis base.[9] The same tendency is observed for the $Ni(S_2COR')_2$ complexes, where it decreases in the order Et > Cy,[8] as shown for the lower yields obtained for the latter compound.

The abstraction of sulfur as $SPPh_3$ leaves a [Ni(SCOEt)] moiety that can undergo an ethyl migration to give the carbonyl and the SEt group. Dimerization of this group to EtSSEt or, alternatively, coupling to a SCOEt fragment to give EtOCSSEt would account for the observed organic products.

The formation of all the secondary products of this reaction has been well established in thermal decompositions of $Ni(S_2COR)_2$ to NiS, OCS, and ROCSSR[10] or in reactions between palladium or platinum bis(xanthates) and tertiary phosphines with formation of $Pt(S_2CO)(PR_3)_2$, EtOCSSEt, and EtSSEt.[11] The formation of EtSSEt is also possible by partial decomposition of EtOCSSEt.[12] In this case the overall stoichiometry would be

$$2Ni(S_2COEt)_2 + 5PPh_3 \rightarrow Ni(CO)_2(PPh_3)_2 + NiS + 3SPPh_3 + 2EtOC(S)SEt$$

Minor products, like EtSEt, have also been found in palladium xanthate thermolysis, and their appearance has been interpreted as being due to secondary reactions with elimination of COS and formation of PdS.[13] The use of phosphines other than PPh_3 gives lower yields as a consequence of the stronger reducing character of the latter phosphine. Bidentate phosphines do not react under these conditions.

Experimental Section

As a general procedure, the reaction of $Ni(S_2COEt)_2$[14] with PPh_3 is described. A 300-mL Schlenk flask was charged with 0.30 g (1 mmol) of $Ni(S_2COEt)_2$ and 1.57 g (6 mmol) of PPh_3 and evacuated. The closed flask was heated at 140–150 °C for 1 h, giving a black fused mixture, which was slowly cooled to room temperature, yielding a solid. The organic products that condensed on the glass walls were collected, chromatographed on alumina, and identified from their spectral data. The black solid that formed was stirred in Et_2O (150 mL) for 20 h, the mixture was then filtered and the solvent removed in vacuo. After addition of EtOH (50 mL), the mixture was stirred for another 1 h, leaving a gray solid that could be recrystallized from acetone with addition of charcoal to give $Ni(CO)_2(PPh_3)_2$, identified by its correct analysis, spectral data, and melting point. $SPPh_3$ was obtained from the solution by addition of water. The black residue from the Et_2O extraction was washed with acetone (3 × 30 mL), and the amorphous solid was identified as nickel sulfide. All the identified products gave correct analytical and spectral data.

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Registry No. $Ni(S_2COEt)_2$, 3269-24-7; $Ni(S_2COCy)_2$, 53566-81-7; $Ni(CO)_2(PPh_3)_2$, 13007-90-4; $Ni(CO)_2(P(p\text{-}CH_3C_6H_4)_3)_2$, 133551-21-0; $SPPh_3$, 3878-45-3; EtSEt, 352-93-2; EtSSEt, 110-81-6; EtOCSSEt, 623-79-0; nickel sulfide, 11113-75-0.

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Convenient Syntheses of Unsymmetrically B-Substituted Borazines

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Literally hundreds of borazines, $(RBNR')_3$, are known, but only relatively few unsymmetrically substituted derivatives of the six-membered B_3N_3 heterocycle have been characterized and their chemistry has hardly been explored.[1] The most readily available unsymmetrically B-substituted borazine of the type $XR_2B_3N_3R'_3$ is the monochloro compound $Cl(CH_3)_2B_3N_3(CH_3)_3$, which can be prepared from $(ClBNCH_3)_3$ by a Grignard reaction. However, the purification of the product is fairly laborious, due to the presence of substantial amounts of byproducts.[2] It has now been found that a very convenient access to unsymmetrically B-substituted borazines is available by the reaction of a *B,B′,B″*-triorganylborazine with boron tribromide.

Initially, $(C_2H_5BNCH_3)_3$ and BBr_3 were reacted in a 3:1 molar ratio, in anticipation that all of the bromine of BBr_3 would exchange with the ethyl groups of the borazine to give $(C_2H_5)_3B$ and $Br(C_2H_5)_2B_3N_3(CH_3)_3$. However, even when a mixture of the two neat reagents was heated to reflux, the sole products of any significance were $Br(C_2H_5)_2B_3N_3(CH_3)_3$ and $C_2H_5BBr_2$ (besides unreacted $(C_2H_5BNCH_3)_3$). This result indicated that the Br/C_2H_5 exchange stops with the generation of $C_2H_5BBr_2$ rather than proceeding with the formation of $(C_2H_5)_3B$. Consequently, when equimolar amounts of the two reagents were reacted for several hours, and even at room temperature, $Br(C_2H_5)_2B_3N_3(CH_3)_3$ was formed in excellent yield according to eq 1; only $C_2H_5BBr_2$ and traces of $Br_2(C_2H_5)B_3N_3(CH_3)_3$ were obtained as byproducts.

$$(C_2H_5BNCH_3)_3 + BBr_3 \rightarrow Br(C_2H_5)_2B_3N_3(CH_3)_3 + C_2H_5BBr_2 \quad (1)$$

$Br(C_2H_5)_2B_3N_3(CH_3)_3$ was subsequently converted to $(CH_3S)(C_2H_5)_2B_3N_3(CH_3)_3$ by the reaction with $Pb(SCH_3)_2$ and to $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ by the reaction with anhydrous NH_3, as is shown in the following equations ($R = C_2H_5$, $R' = CH_3$):

$$2BrR_2B_3N_3R'_3 + Pb(SCH_3)_2 \rightarrow 2(CH_3S)R_2B_3N_3R'_3 + PbBr_2 \quad (2)$$

$$BrR_2B_3N_3R'_3 + 2NH_3 \rightarrow (H_2N)R_2B_3N_3R'_3 + NH_4Br \quad (3)$$

Similarly, when $(C_2H_5BNCH_3)_3$ was reacted with 2 molar equiv of BBr_3, the desired $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was readily obtained. Formation of a precipitate was observed when the reaction was performed at room temperature or below, but the latter disappeared on gentle heating of the reaction mixture. In this case, the only byproduct, besides $C_2H_5BBr_2$, was some $(BrBNCH_3)_3$.

Subsequently, $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was converted to $(H_2N)_2(C_2H_5)B_3N_3(CH_3)_3$ and $(CH_3S)_2(C_2H_5)B_3N_3(CH_3)_3$, as additional representatives of unsymmetrically B-substituted borazines.

All of the compounds were obtained in excellent purity and were characterized by their ^1H, ^{11}B, and ^{13}C NMR data. As yet, it is still uncertain if simple Br/C_2H_5 exchange occurs or if a BBr moiety is exchanged with a BC_2H_5 unit. The exclusive formation of $C_2H_5BBr_2$ as byproduct tends to support the latter assumption.

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ on a Varian VXR-400 or XL-200 (^{11}B) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR). Abbreviations are as follows: s = singlet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants *J* are given in hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. Electron impact (EI) mass spectral data were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to m/z 30 for 5% or greater relative abundances (in parentheses) only.

Nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. All preparations were performed in an anhydrous atmosphere under argon cover; solvents were dried by standard procedures.

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2-Bromo-4,6-diethyl-1,3,5-trimethylborazine. A few grains of $NaBH_4$ were added to 60.7 g (0.294 mol) of $(C_2H_5BNCH_3)_3$,[3] and then 73.5 g (0.294 mol) of BBr_3 was added slowly with stirring. An exothermic reaction occurred, and a small amount of an initial precipitate dissolved with time. The mixture was stirred at ambient temperature for 3 h, $C_2H_5BBr_2$ was removed under reduced pressure, and the residue was distilled under vacuum to give 64.5 g (85%) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$, bp 90–92 °C (0.5 Torr). Anal. Calcd for $C_7H_{19}B_3BrN_3$ (M_r = 257.59): C, 32.64; H, 7.44; B, 12.59; Br, 31.02; N, 16.31. Found: C, 32.21; H, 7.49; B, 12.51; Br, 30.96; N, 16.26.

NMR data: $\delta(^1H)$ 3.08 (6 H, s), 2.96 (3 H, s), 1.1–0.9 (10 H, m); $\delta(^{11}B)$ 37.2 (2 B, s, $h_{1/2}$ = 250 Hz), 31.6 (1 B, s, $h_{1/2}$ = 160 Hz); $\delta(^{13}C)$ 36.4, 33.2, 7.5, 7.2*. EI mass spectrum (9 eV): *m/z* 260 (16), 259 (80), 258 (76), 257 (100), 256 (56), 255 (16), 207 (16), 206 (12), 178 (8).

2-Amino-4,6-diethyl-1,3,5-trimethylborazine. A solution of 23.7 g (92.0 mmol) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$ in 100 mL of ether was added slowly with stirring to a mixture of 100 mL of ether and ca. 20 mL of anhydrous liquid ammonia cooled in a dry ice bath. The mixture was allowed to warm to room temperature and was stirred for 12 h. It was filtered and volatiles were evaporated off the clear filtrate under reduced pressure. The remaining colorless liquid was distilled under vacuum to give 14.8 g (83%) of product, bp 85–86 °C (0.5 Torr). Anal. Calcd for $C_7H_{21}B_3N_4$ (M_r = 193.71): C, 43.40; H, 10.93; B, 16.74; N, 28.92. Found: C, 43.26; H, 10.97; B, 16.66; N, 28.91.

NMR data: $\delta(^1H)$ 2.89 (3 H, s), 2.76 (6 H, s), 2.33* (2 H, s), 0.99–0.95 (10 H, m); $\delta(^{11}B)$ 36.4 (2 B, s, $h_{1/2}$ = 230 Hz), 26.2 (1 B, s, $h_{1/2}$ = 160 Hz); $\delta(^{13}C)$ 33.0, 31.0, 8.0, 6.6*. EI mass spectrum (11 eV): *m/z* 195 (23), 194 (100), 193 (70), 192 (19), 191 (6), 181 (6), 180 (6), 179 (8), 178 (7), 165 (8), 164 (8).

2-(Methylthio)-4,6-diethyl-1,3,5-trimethylborazine. A stirred mixture of 4.70 g (18.2 mmol) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$, 7.7 g (26 mmol) of $Pb(SCH_3)_2$, and 20 mL of hexane was heated to reflux for 24 h. The mixture was cooled to room temperature and filtered, and hexane was evaporated from the clear filtrate. The remaining colorless liquid was distilled under reduced pressure to give 2.2 g (54%) of product, bp 124–127 °C (0.5 Torr). Anal. Calcd for $C_8H_{22}B_3N_3S$ (M_r = 224.78): C, 42.75; H, 9.86; B, 14.43; N, 18.69; S, 14.26. Found: C, 42.73; H, 9.81; B, 14.29; N, 18.56; S, 14.18.

NMR data: $\delta(^1H)$ 3.03 (6 H, s), 2.94 (3 H, s), 2.17 (3 H, s), 1.10–0.90 (10 H, m); $\delta(^{11}B)$ 36.5 (s, $h_{1/2}$ = 260 Hz); $\delta(^{13}C)$ 34.8, 33.0, 11.8, 7.6, 6.9*. EI mass spectrum (15 eV): *m/z* 227 (6), 225 (72), 224 (59), 223 (19), 215 (6), 214 (6), 213 (12), 212 (13), 211 (9), 210 (25), 209 (16), 208 (8), 198 (6), 197 (7), 196 (31), 195 (32), 194 (16), 193 (10), 184 (9), 183 (8), 182 (16), 181 (11), 180 (8), 179 (10), 178 (38), 177 (28), 176 (9), 150 (16), 149 (9), 119 (12), 117 (12), 114 (12), 68 (20), 50 (12), 49 (13), 48 (100), 47 (50), 46 (11).

2,4-Dibromo-6-ethyl-1,3,5-trimethylborazine. A few grains of $NaBH_4$ were added to 20.6 g (99.7 mmol) of $(C_2H_5BNCH_3)_3$, and then 50.0 g (199 mmol) of BBr_3 was added slowly with stirring. An exothermic reaction occurred, and a small amount of precipitate appeared. The mixture was stirred at ambient temperature for 2 h and subsequently heated to 85 °C (bath temperature) for 16 h to give a clear solution. $C_2H_5BBr_2$ was removed under reduced pressure, and the residue was distilled under vacuum to give 27.5 g (89%) of product: bp 105–108 °C (0.5 Torr), mp 27–28 °C. Anal. Calcd for $C_5H_{14}B_3Br_2N_3$ (M_r = 308.44): C, 19.47; H, 4.58; B, 10.52; Br, 51.81; N, 13.62. Found: C, 19.31; H, 4.52; B, 10.39; Br, 51.79; N, 13.70.

NMR data: $\delta(^1H)$ 3.23 (3 H, s), 3.11 (6 H, s), 1.12 (2 H, unsym q, *J* = 7), 0.97 (3 H, unsym t, *J* = 7); $\delta(^{11}B)$ 37.6 (1 B, s, $h_{1/2}$ = 270 Hz), 31.7 (2 B, s, $h_{1/2}$ = 160 Hz); $\delta(^{13}C)$ 40.0, 36.6, 7.2, 7.1*. EI mass spectrum (10 eV): *m/z* 311 (35), 310 (30), 309 (100), 308 (79), 307 (60), 306 (30).

2,4-Bis(methylthio)-6-ethyl-1,3,5-trimethylborazine. This compound was prepared in a fashion analogous to that for $(CH_3S)(C_2H_5)_2B_3N_3(CH_3)_3$ from 19 g (63 mmol) of $Pb(SCH_3)_2$ and 9.73 g (31.6 mmol) of $Br_2(C_2H_5)_2B_3N_3(CH_3)_3$ (30 mL of hexane, 24-h reflux). After filtration and solvent evaporation, the residue was distilled under reduced pressure to give 5.2 g (68%) of product, bp 128–132 °C (0.5 Torr). Anal. Calcd for $C_7H_{20}B_3N_3S_2$ (M_r = 242.82): C, 34.62; H, 8.30; B, 13.36; N, 17.30; S, 26.41. Found: C, 34.55; H, 8.29; B, 13.21; N, 17.26; S, 26.40.

NMR data: $\delta(^1H)$ 3.13 (3 H, s), 3.00 (6 H, s), 2.18 (6 H, s), 1.1–0.9 (5 H, m); $\delta(^{11}B)$ 36.8 (s, $h_{1/2}$ = 200 Hz); $\delta(^{13}C)$ 37.0, 34.6, 11.7, 7.5, 6.8*. The 12-eV mass spectrum exhibited only an ion cluster at *m/z* 243.

2,4-Diamino-6-ethyl-1,3,5-trimethylborazine. This compound was prepared in a fashion analogous to that for $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$. From 9.07 g (29.4 mmol) of $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was obtained 2.43 g (46%) of product, bp 95–98 °C (0.5 Torr). Anal. Calcd for $C_5H_{13}B_3N_5$ (M_r = 180.67): C, 33.24; H, 10.04; B, 17.95; N, 38.76. Found: C, 33.17; H, 9.98; B, 17.21; N, 38.58.

NMR data: $\delta(^1H)$ 2.72 (6 H, s), 2.57 (3 H, s), 2.24* (4 H, s), 0.98–0.92 (5 H, m); $\delta(^{11}B)$ 36.2 (1 B, s, $h_{1/2}$ = 220 Hz), 26.2 (2 B, s, $h_{1/2}$ = 150 Hz); $\delta(^{13}C)$ 31.1, 29.2, 8.1, 6.1*. EI mass spectrum (10 eV): *m/z* 182 (11), 181 (100), 180 (65).

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